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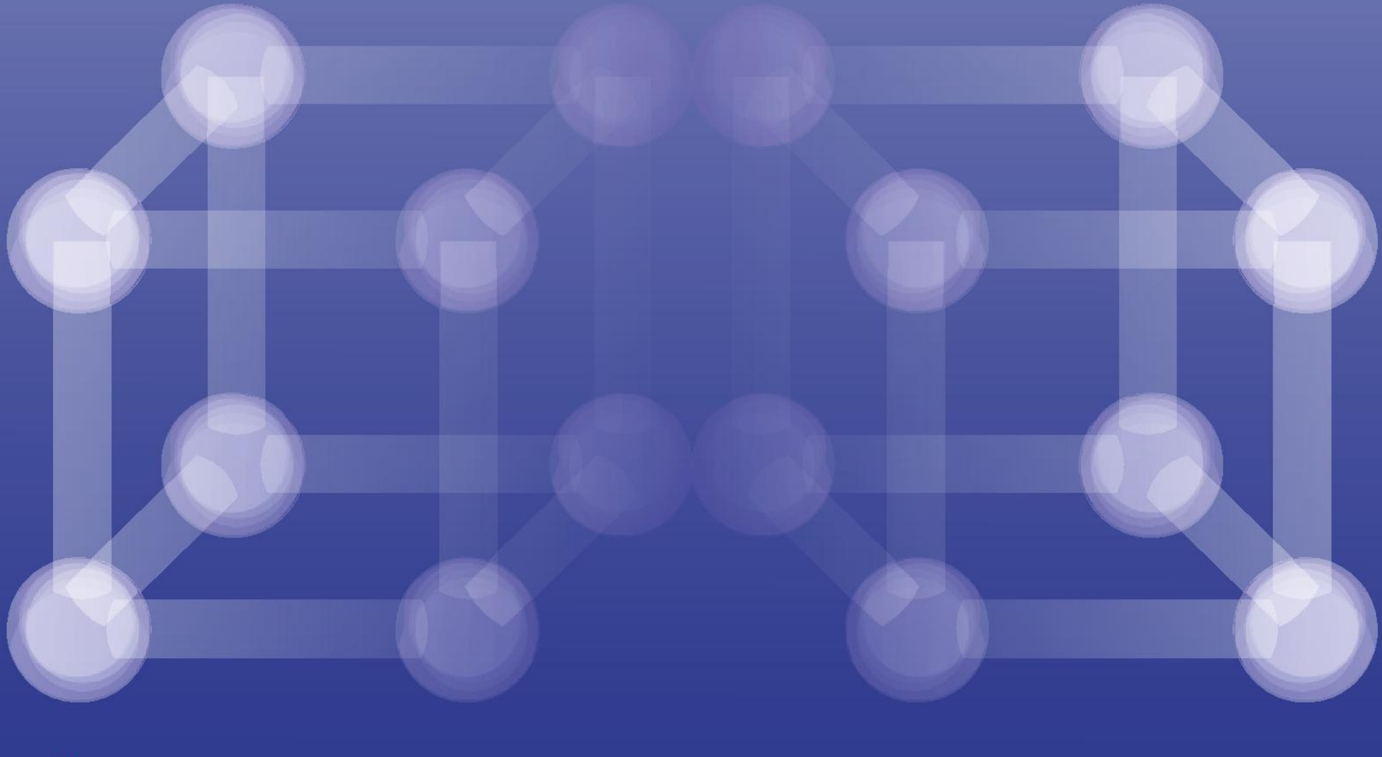
BOOK OF ABSTRACTS



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PLENARY LECTURES

The rise of silylenes in homogeneous catalysis

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Selective activation of small molecules by using non- and semi-metals instead of expensive and toxic precious metals is a contemporary challenge in catalysis. Recently, we developed the zwitterionic silylene **1** which shows an unprecedented reactivity pattern with respect to small molecule activation based on divalent silicon. Silylene **1** is a stronger sigma-donor ligand towards transition-metals than N-heterocyclic carbenes (NHCs) and phosphines and enables unique catalytic transformations involving cooperative ligand-metal effects. Likewise, the chelate silylene-carbene ligand **2**, which is accessible by the reaction of **1** with the corresponding NHC, exhibits superior catalytic performance in various metal-mediated catalytic transformations. Furthermore, the remarkably rich reactivity pattern of **1** and the first bis(silylene)-based pincer arene ligands **4**-**7** can be used as a new generation of powerful steering ligands in homogeneous catalysis. I wish to discuss a few unique features of these N-heterocyclic silylenes in metal-free and non-precious metal-mediated stoichiometric and catalytic transformations.

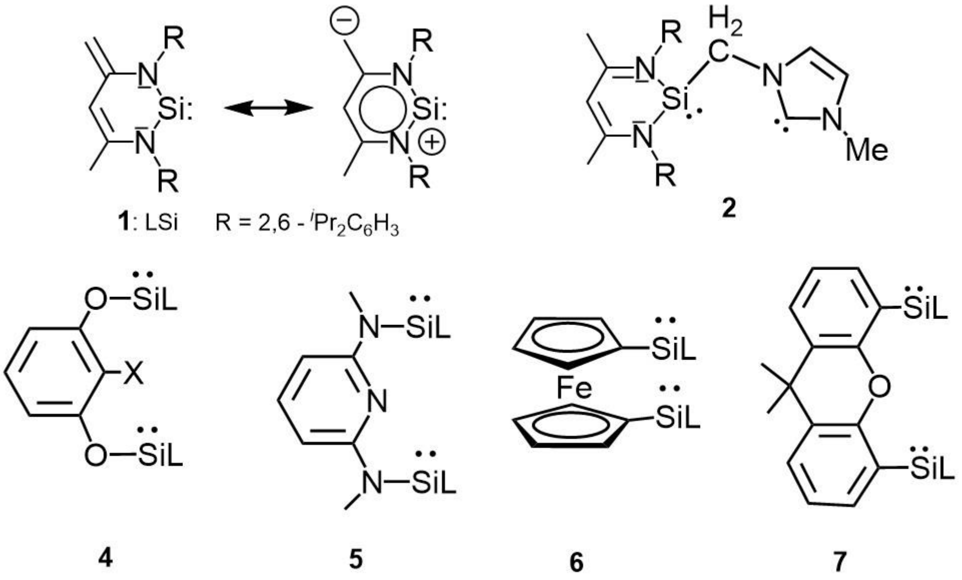

Figure 1. Isolable silylenes as steering ligands in metal-mediated catalysis.

Acknowlegment

I thank the Deutsche Forschungsgemeinschaft (Cluster of Excellence UniCat, UniSysCat) and the Einstein Foundation Berlin for financial support.

Polyphosphorus complexes as building blocks in supramolecular chemistry

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Polyphosphorus complexes are an important class of compounds, useful for many applications. Because of the lone pairs at the phosphorus atoms, they are able to self-assemble with Lewis-acidic transition metal moieties. Especially the five-fold symmetric P_5 ring of pentaphosphaferrocene $[Cp^RFe(\eta^5\text{-}P_5)]$ enables these complexes for unique supramolecular aggregations to form spherical molecules. By the coordination to Cu(I) and Ag(I) units, respectively, (i) novel organomometallic-organic coordination networks[1] or (ii) unprecedented giant spheres are formed with the latter usually exhibiting a fullerene-like topology constructed by non-carbon atoms (Figure 1a).[2] The aggregations to spheres are usually template-controlled to encapsulate an appropriately sized molecule, however, novel strategies lead to large spheres also in the absence of appropriate templates.[3] Furthermore, (ii) under certain conditions, giant superspheres are constructed revealing a topology beyond the Fullerene-design (Figure 1b).[4-6] The largest sphere so far (4 x 5 nm) comes close to the size of small or medium-sized proteins as for instance hemoglobin (Figure 1c).[4] Moreover, first results for the alignment of spherical balls by bidentate linkers will be presented leading to three-dimensional extended networks.

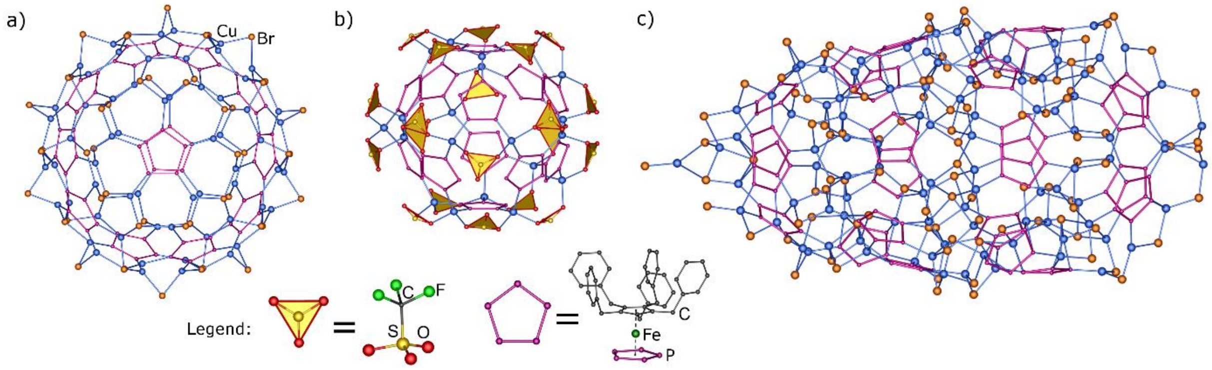

Figure 1. Molecular structure of the cores of superspheres a) $[(Cp^{Bn}FeP_5)_{12}Cu_{70}Br_{83}]$ with I-C_{140} topology of the outer shell, b) D_2 isomer of $[(Cp^{Bn}FeP_5)_{12}(CuOTf)_{20}]$ and c) rugby-ball $[(Cp^{Bn}FeP_5)_{24}(CuBr)_{96}]$.

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Half-sandwich rare-earth and group 4 metal complexes for novel chemical transformations and functional polymer synthesis

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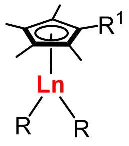
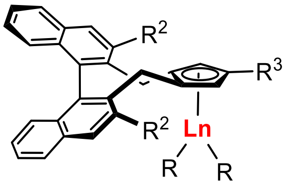
Half-sandwich rare-earth and group 4 metal complexes serve as unique platforms for various chemical transformations.[1,2] The half-sandwich rare-earth dialkyl complexes such as **1** in combination with a cocatalyst such as $[Ph_3C][B(C_6F_5)_4]$ showed unprecedented catalytic activity and selectivity for the polymerization and copolymerization of various functional □-olefins[3] as well as for the C−H bond activation and transformation[4] of heteroatom-containing organic substrates with the assistance of the unique rare-earth metal−heteroatom interaction. The half-sandwich rare-earth metal complexes bearing chiral Cp ligands (**2**) demonstrated excellent enantioselectivity in a wide range of asymmetric transformations.[5] Mono-Cp-ligated titanium hydride clusters such as **3** and **4** exhibited unprecedented reactivity toward inactive molecules, such as the activation and functionalization of dinitrogen[6a,b,e] C−C bond cleavage and rearrangement of benzene[6c] and hydrodenitrogenation of pyridines and quinolines[6d] under mild conditions.

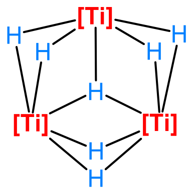


1



2

(Ln = Sc, Y, La, Sm, Gd)



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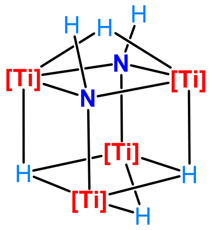

4

[Ti] = $Ti(C_5Me_4SiMe_3)$

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Periodic table as a playground for new electrode battery materials design

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Ninety percent of the energy produced today come from fossil fuels. Rapid consumption of these energy sources makes dramatically negative impact on our future due to ecological damage and climate change. In this sense the development of the environmentally benign renewable energy sources capable to replace fossil fuels and concurrently efficient large energy storage devices requires no justification.

Li-ion batteries (LIBs) have been originally developed for portable electronic devices, but nowadays new application niches are envisaged in electric vehicles and stationary grid-scale energy storages. However, LIBs may be not fully adopted for these applications. The geographical scarcity and excessive demand for Li resources intensifies the development of alternative sustainable technologies based on vastly accessible materials, namely Na- and K- ion batteries (NIBs and KIBs, respectively).

The battery performance is critically governed by the properties of the electrode materials. The first generation of cathode materials for the Li-ion batteries based on the mixed oxides has already been widely commercialized. However, the potential to further improve the performance of these materials is almost exhausted. The compounds, containing alkali and transition metal cations together with different polyanions $(X_mO_n)^{p-}$ (X=B, P, S, Si), are now considered as the most promising cathode materials for the next generation of the Me-ion batteries. Covalently-bonded structural frameworks in these compounds offer long-term structural stability, which is essential for good cyclability and safety. Further advantages are expected from combining different anions (such as $(XO_4)^{p-}$ and F^-) in the anion sublattice, with the hope to enhance the specific energy and power of the batteries. Moreover, following the periodic law principle and playing with ionic radii and crystallochemical properties of both alkali and transition metals enable tuning the crystal structure to design novel electrode materials with unique and advanced electrochemical characteristics.

An overview of the research on fluoride-phosphates with the general formula of A_xMPO_4F (A = Li, Na, K; M = V, Fe, Co) adopting various structure types depending on the A and M metals and various vanadium-based phosphates as prospective electrode materials for the Me-ion batteries will be presented with a special emphasis on the interrelation between chemical composition, synthesis conditions, crystal structure peculiarities and electrochemical properties of the materials important for practical applications.

Acknowledgements

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Chemical design and multifunctional properties of porous coordination polymers

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Metal-organic frameworks (MOFs) are among the most fascinating families of solid-state materials, because of their highly tunable compositions, structures, and functional properties. Lying on the crossing of fundamental inorganic/organic chemistry and development of novel materials, MOFs have become one of the most attractive research fields during the past two decades. Here we describe some of the work on chemical design, synthesis, structural characterization and investigation of multifunctional materials based on MOFs carried out at Novosibirsk during last years.

Substitution of ligands in [$Li_2Zn_2(piv)_6(py)_2$] with bpy and terephthalate bridges results in a series of isoreticular porous frameworks [$Li_2Zn_2(R\text{-}bdc)_3(bpy)$]. The introduction of different substituents R onto the terephthalate linkers affects the free volume of the porous compounds and the N_2 adsorption behavior. The CH_4 and CO_2 adsorption and relative selectivities have been investigated in detail, and interestingly, a fascinating interplay of luminescence properties with wavelength of excitation and nature of the host aromatic guest molecules has been observed. Moreover, such compounds demonstrate very high selectivity in the processes of separation of benzene and cyclohexane.

For the first time we report synthesis of MOFs based on Re_6 octahedral chalcogenide clusters. The frameworks demonstrate excellent CO_2/N_2 and CO_2/CH_4 selectivity, red luminescence, paramagnetic behavior and an ability to react with oxidizing agents due to the presence of redox-active cluster fragment. The oxidation of cluster nodes changed dramatically properties of the framework, and this process if fully reversible.

We report isostructural series of zinc(II) – thiophene-2,5-dicarboxylate (tdc) based on novel polynuclear building blocks such as Zn_{12} carboxylate wheels [$Zn_{12}(tdc)_6(glycolSate)_6(dabco)_3$], where glycolate is a deprotonated polyatomic alcohol. The obtained MOFs demonstrated excellent adsorption selectivity for CO_2/N_2 gas mixture, and in separation of benzene/cyclohexane mixtures both in gas and liquid phases. Most interestingly, the affinity of the porous MOF towards either benzene or cyclohexane could be rationally switched by the nature of the polyatomic alcohol. Particularly, the channels of the compound with glycerol are lined with polar $-CH_2-OH$ pendant groups, capable of adsorption of alkaline metal cations from solutions with marked size-selectivity in order $Li^+ > Na^+ > K^+ > Cs^+$. Strong luminescence quenching in the presence of cesium(I) ions suggests potential sensing applications of these multifunctional MOFs.

Acknowledgements

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From white to black phosphorus: a journey into the chemistry of a bewitching element

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In this lecture some of the most recent achievements in the field of elemental phosphorus' reactivity, originating from the author's own research in Florence (Italy) during the last two decades, will be presented and discussed.

The selected arguments that will be outlined during the lecture will encompass the different allotropes of elemental phosphorus with particular emphasis to the extremely reactive and toxic white allotropic form and, on the opposite end, to the incredibly inert black allotrope. More in details the lecture will include:

i) the activation of **white phosphorus** mediated by organoruthenium fragments and other late-transition metal complexes pointing out the unusual and fascinating hydrolytic degradation of the P_4 molecule which follows its η^1-coordination to the metal. This reaction results in a variety of unusual P_x fragments ($x \leq 4$), such as P-oxyacids, mono-, di-, and triphosphanes and hydroxyphosphanes, stabilised by coordination to one or two ruthenium centers;[1]

ii) our most recent results in the chemistry of the less reactive allotrope of the element, *i.e.* **black phosphorus**, which may be easily exfoliated providing access to 2D-flakes of **phosphorene** (the all-P analogue of graphene).[2] The latter continues the fascinating tradition of the element phosphorus, which behaves as a perfectly tailored platform to host transition-metal nanoparticles[3] and, likely, to coordinate different transition metal fragments.[4,5]

Acknowledgements

MP thanks all the coworkers listed in the references for their unvaluable help in developing this chemistry. Thanks are also expressed to the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant Agreement No. 670173) for funding the project PHOSFUN "Phosphorene functionalization: a new platform for advanced multifunctional materials" through an ERC Advanced Grant. Finally,the Italian Ministry for Education and Research (MIUR) is kindly acknowledged for financial support through Project PRIN 2015 (grant number 20154X9ATP).

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Small molecule activation by multimetallic complexes of f-elements

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In the current energetic context, the search for renewable alternatives to fossil fuels is attracting increasing attention toward the chemical low energy conversion of cheap and largely available C_1 sources such as CO_2 and CO or N sources such as N_2 into higher value organic molecules. Multimetallic complexes of f-elements were found to promote the facile transformation of largely available small molecules such as CO, CO_2 and N_2. *Tert*-butoxysiloxides proved effective ligands in supporting the reactivity of low valent *f* elements with small molecules because of their polynucleating nature and multiple binding modes. Moreover, these ligands provided a facile access to multimetallic nitride bridged uranium complexes.[1] Uranium nitrides are attractive candidates for stoichiometric and catalytic small molecule transformation and for N-transfer reactions that are key steps in the construction of value-added chemical compounds. The multimetallic nitride bridged diuranium(IV) complex **1**, easily reacts with CO_2, CS_2 and cleaves CO and H_2,[2] promoting the formation of N-C and N-H bonds affording diverse N-functionalized products (Figure 1). Furthermore, the metal centers in **1** can be further reduced leading to a multimetallic K_3UNU nitride bridged diuranium(III) complex, which present extraordinary reactivity towards dinitrogen.[3] An overview of small molecule activation and transformation by multimetallic complexes of f-elements will be presented.

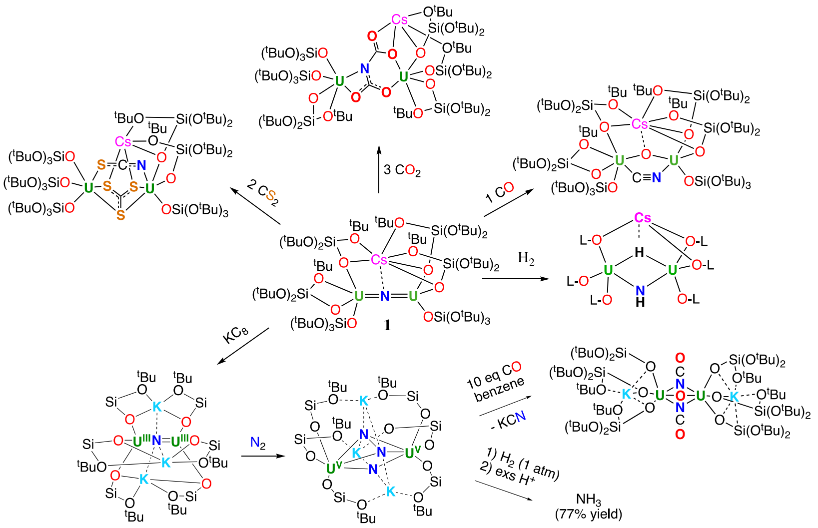

Figure 1. Reactivity of Multimetallic Nitride-bridged Uranium Complexes

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From simple discrete metal complexes to supramolecular assembly and nanostructures

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Recent works in our laboratory have shown that novel classes of chromophoric and luminescent metal-containing molecular materials could be assembled through the use of various metal-ligand chromophoric building blocks. In this presentation, various design and synthetic strategies will be described. A number of these simple discrete metal complexes are found to undergo supramolecular assembly to give a variety of nanostructures and morphologies. Subtle changes in the microenvironment and nanostructured morphologies have led to drastic changes in both the electronic absorption and emission properties of these supramolecular assemblies. Explorations into the underlying factors that determine their spectroscopic properties and morphologies as well as their assembly mechanisms have provided new insights into the understanding of the interplay of the various intermolecular forces and interactions for the directed assembly of novel classes of metal-containing soft materials and hybrids. The exploration into the potential applications and functions of these discrete metal complexes and their supramolecular assemblies and polymers will also be described.

Acknowledgements

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Self-assembling luminescent complexes: from understanding to artificial virus

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Luminescent molecules that can undergo self-assembly are of great interest for the development of new materials, sensors, biolabels…. The talk will illustrate some of the recent results on soft structures based on metal complexes able to aggregate in fibers, gels and soft mechanochromic materials [1]. The emission of the compounds can be tuned by an appropriate choice of the coordinated ligands as well as of their aggregation in different structures. The formation of soft assemblies allows the tuning of the emission color, by pressure and temperature leading to a new class of materials possessing reversible properties. The monitoring of the different emission properties, used as fingerprint for each of the assembled species, allowed an unprecedented real-time visualization of the evolving self-assemblies [2]. The assemblies can be employed as very sensitive labels for the detection of toxins and drugs [3]. Indeed even though sensing based on fluorescent and luminescent probes are commonly used, the use of aggregates in water allows to distinguish between analytes possessing very similar electronic properties. Sensing can also be done using electrochemiluminescence, ECL. We have recently achieved the first example of aggregation induced ECL showing that assemblies in solution and in the solid state (deposited on the electrode) can generate bright emission [4].

Finally I wish to close my talk showing novel capsules that can be realized using a unique approach to template virus proteins to reconstruct virus-like particles. We use luminescent Pt(II)-complex amphiphiles, able to form supramolecular structures in water solutions, that can act as templates of viruses capsid proteins. The platinum assemblies can have different morphologies and extremely high emission of which the color depends on the assembly. Interestingly we are able to change the size and shape of the particles even though we use the same natural proteins. The obtained virus-like particles can be visualized by their intense emission at room temperature, generated by the self-assembly of the Pt(II)-complexes inside the capside [5].

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KEYNOTE LECTURES

Donor-flexible ligands for efficient redox catalysis

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While catalytic reductions (hydrogenation, hydroelement functionalizations) is very well understood mechanistically and high activity catalysts are available, oxidation catalysis is much less developed. This is due in parts to the mechanistic complexity of oxidation reactions (substrate recognition, multistep multi-electron transformations), and in other parts due to the harsh conditions for oxidation reactions, requiring catalysts with a specific set of properties that impart high activity and high robustness. In the search of suitable ligands that meet these criteria, we have become particularly intrigued by ligands that can formally adopt either a neutral or a zwitterionic form (see Figure). Through their different bonding modes, these ligands provide opportunities to (transiently) store protons and electrons, which is an excellent prerequisite for mediating oxidation reactions. We will briefly discuss fundamental aspects[1] and will demonstrate the potential of these donor-flexible ligands to induce challenging bond activation catalysis, such as water oxidation, transfer hydrogenation, and olefin oxidation to provide an efficient route to carbonyl compounds.[2]

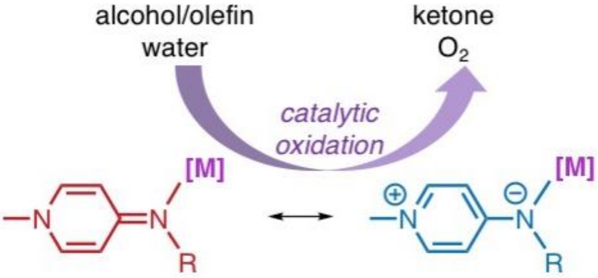

Figure 1.

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Molecular Turnstiles

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Molecular translational or rotational motors are architecture for which movements between a fixed and a mobile portion may be induced by external stimuli.[1] As a first step towards molecular motors, a series of molecular turnstiles have been designed and synthesized. The first category is based on Sn(IV)porphyrins as stators bearing at the meso positions interactions sites and equipped with different handles as rotors. The connection between stators and rotors is achieved through Sn-O (Fig. 1).[2-7] The second design principle is based on the covalent attachment of the rotor to the stator using two opposite meso positions on the porphyrin backbone (strapped porphyrins) (Fig. 2).[8,9] Finally, the tired approach is based on organometallic Pt complexes as rotors and coordinating handles as stators (Fig. 3).[10-15] The design, synthesis and structural characterizations, both in solution by multidimensional ^{1}H-NMR techniques and in the solid state by X-ray diffraction on single crystals, of a series of molecular gates and turnstiles will be presented and discussed.

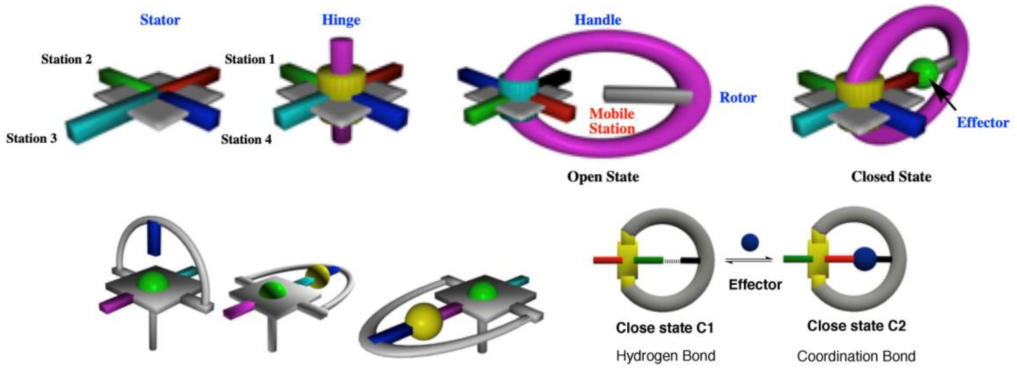

Figure 1. Design principle of molecular turnstiles

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Single ion magnets based on Co(II) Kramer's ion. Prospects for the development of new magnetic materials

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In the lecture, the structure and magnetic properties of single ion magnets (SIM) related to Co(II) complexes have been considered.

Particular attention has been paid to the results of experiments and theoretical modeling of hexacoordinated complexes of Co(II) with negative and positive magnetic anisotropy, which we have obtained recently[1,2]. To analyze magnetic anisotropy of these complexes, additional experimental techniques, such as SQUID magnetometry and EPR spectroscopy have been used, as well as theoretical modeling using parametrized Griffith's Hamiltonian with parameters obtained from ab initio calculations. As follows from the analysis, magnetic anisotropy of these complexes is mainly triaxial, with different signs of axial components. Independently on the sign of the axial anisotropy, Co(II) complexes exhibit a slow paramagnetic relaxation in the constant magnetic (DC) field, i.e., belong to the class of field induced non-monoaxial single ion magnets (FI-SIMs). Such type of SIM behavior is due to Kramer's character of Co(II) ion[1,2]. Possibility to produce new magnetic materials based on these compounds is being discussed.

Acknowledgements

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Actinide oxide nanoparticles: formation, structure and properties

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Actinides and mainly plutonium are of the primary importance in nuclear waste technologies. Plutonium is considered as an element of surprise as it has seven redox states among which four oxidation states could be present and even co-exist under environment relevant conditions (III-VI). In the dominant tetravalent form Pu is extremely insoluble and earlier was found to form nanoparticles at the mineral/water interface. However the knowledge gap remains concerning the routes of formation of such oxide nanoparticles, their crystallinity, presence of other oxidation states ($PuO_{2\pm x}$) and properties.

This contribution will show the results of plutonium nanoparticles studies as well as its chemical analogs – Ce^{3+}/Ce^{4+} and Th^{4+}. Initially Pu was taken in various redox forms from III to VI and the kinetics of redox transformations and nanoparticle formation was traced at various pH/Eh values. HR-TEM, SAED, XRD, atomic pair distribution function analysis (PDF), several types of spectroscopies: high energy resolution fluorescence detection (HERFD) at L_3 and M_5-edges, X-ray emission spectroscopy (XES) and EXAFS spectroscopy were applied to characterize the precipitates.

It was established that crystalline 2-3 nm PuO_2-like nanoparticles are formed under the steady state conditions independently on the initial oxidation state. However in case of Pu(VI) the formation of such nanoparticles proceed through slow formation of Pu(V)-containing nanoparticles that result in significant solubility increase.

The behavior of cerium oxide nanoparticles of different sizes have been explored at different temperatures and electronic structure changes by state-of-the-art soft and hard X-ray experiments combined with computational methods have been traced. We confirm the absence of the Ce(III) oxidation state at the surface of CeO_2 even for particles as small as 2 nm. The solubility of CeO_{2-x} was interpreted at various pH/Eh values and thermodynamic constants (solubility products) have been calculated that may give a clue concerning the oxidant/antioxidant activity of CeO_{2-x}.

The facile chemical precipitation method and subsequent thermal treatment were shown to be suitable for preparation of crystalline ThO_2 nanoparticles in a wide range of particle sizes (from 2.5 to 34.3 nm). The lattice parameter of ThO_2 was found to increase by up to 1.1 %, in comparison with the bulk material whose particle size decreased to 2.5 nm. The decrease in the particle size was also accompanied by a significant decrease in the Th-Th coordination number.

Photoactive Cr(0) and Mo(0) complexes with chelating isocyanide ligands

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The most popular photoactive metal complexes are based on precious metals such as ruthenium or iridium, but interest in alternatives made from earth-abundant metal elements is growing.[1] We discovered that chelating isocyanide ligands can be used to obtain robust Cr(0) and Mo(0) complexes with a similar electronic structure as the well-known Ru(2,2'-bipyridine)$_3^{2+}$ parent compound.[2] The Cr(0) and Mo(0) complexes emit MLCT luminescence with lifetimes ranging from 2 ns to 2000 ns in fluid solution at room temperature, and emission quantum yields up to ca. 20% can be obtained.[3,4] In their long-lived excited states, these complexes are very strong reductants, and this can be exploited for photoredox catalysis. The Cr(0) complex was employed for sensitized triplet-triplet annihilation upconversion with anthracene.[5]

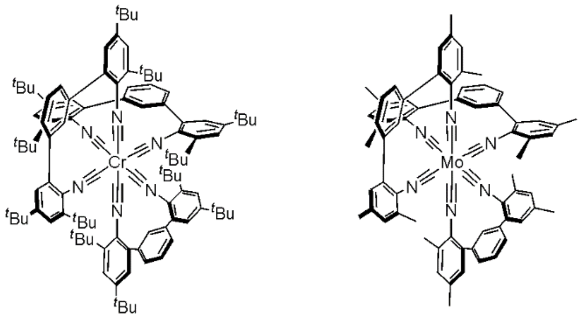

Figure 1. Luminescent Cr(0) and Mo(0) complexes with diisocyanide ligands.

Acknowledgements

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Multifunctional nanomaterials based on Prussian blue

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From 1704, year of the discovery of the oldest coordination polymer, Prussian blue, to now, many cyano-bridged coordination polymers were synthesised and extensively studied.

Significant parts of the current research activity on these materials is devoted to the synthesis and study of size and shape controlled cyano-bridged coordination polymer materials at the nanoscale.[1] These nanomaterials have the same advantages as the corresponding bulk materials and their ease of synthesis under mild conditions allows control of their size, shape and organization, and thus control over their properties. Further, they can be combined with many other organic or inorganic molecules/materials at the nanoscale to afford nanohybrids.

In this presentation, we will illustrate synthetic methodologies that we developed for the preparation of such nano-objects and their combination with optically active materials through their controlled deposition on gold surface,[2] the adsorption of organic luminophores[3] or their core-shell combination with gold nanoparticles.[4]

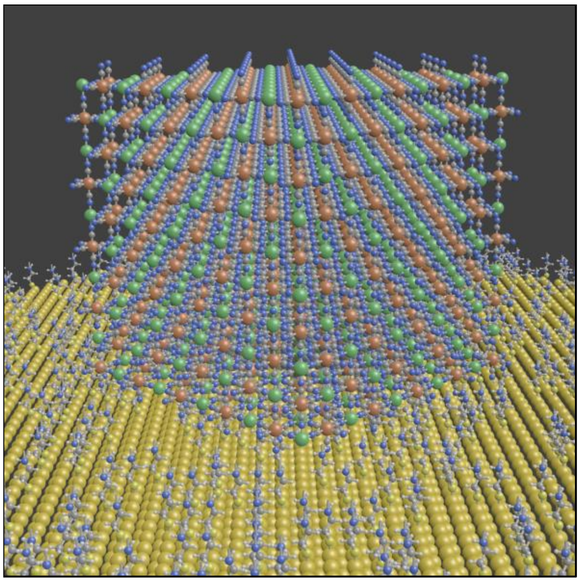

Figure 1. Schematic representation of a Prussian blue analogue nanoparticle on a cysteamine-functionalized gold surface

Acknowledgements

This work was supported by the French National Research Agency as part of the “Investissement d’Avenir” Program (LabEx CheMISyst ANR-10-LABX-05-01) and “AAP Générique” Program (ANR-18-CE09-0012-01). N. G. thanks the Vietnam International Cooperation Department of the Ministry of Education and Training.

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Pincer Complexes Bearing Multifunctional Ligands

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Repulsive steric ligand-substrate interactions are largely responsible for stereocontrol and often for chemoselectivity over the course of transition metal-catalyzed reactions. This generally accepted paradigm of small-molecule catalysis involves the sterically induced destabilization of a certain transition state that shifts the reaction to a kinetically viable path. However, chemo- and stereoselectivity in enzyme-like catalysis stem from an opposite phenomenon: attractive substrate-“ligand” interactions.

In this lecture, I wish to communicate on the catalysis by some new carbometalated PC(sp3)P-based complexes bearing secondary interacting site.[1-3]

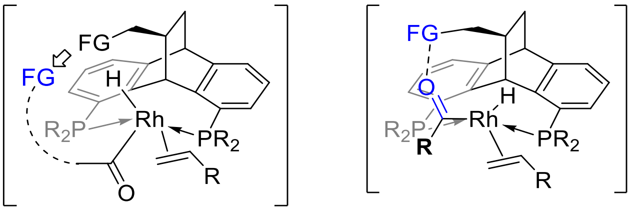

Figure 1.

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High-Temperature Lanthanide Single-Molecule Magnets

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Single-molecule magnets (SMMs) are coordination compounds that display magnetic memory effects.[1] We have a particular interest in metallocene SMMs based on dysprosium, and, over the years, we have reported a few examples of such materials.[2] Our work has shown that the $[Cp]^-$ ligands provide a strong axial crystal field that enhances the magnetic anisotropy of Dy^{3+}, leading us to propose that a cation of the type $[Cp_2Dy]^+$ should be an interesting synthetic target.[3] Recently, we described the properties of $[(\eta^5\text{-}Cp^*)Dy(\eta^5\text{-}C_5{}^iPr_5)][B(C_6F_5)_4]$ ([**1**][B(C$_6$F$_5$)$_4$]), the first SMM to show magnetic hysteresis above the boiling point of liquid nitrogen (Figure 1).[4]

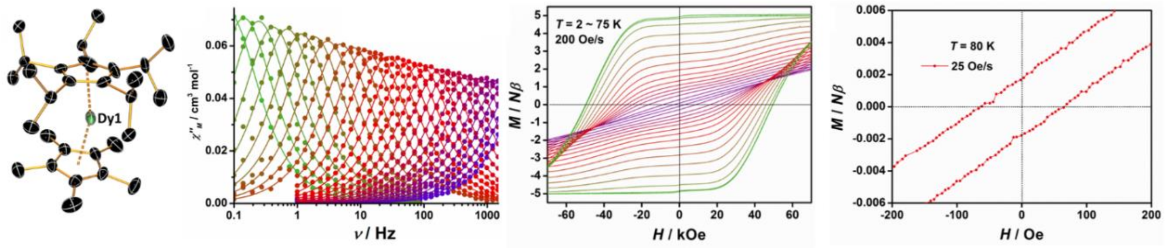

Figure. 1 Molecular structure of **1**, and frequency-dependence of the out-of-phase susceptibility, magnetic hysteresis at 2-75 K (sweep rate of 200 Oe s^{-1}) and at 80 K (sweep rate of 25 Oe s^{-1}) for [**1**][B(C$_6$F$_5$)$_4$]

Having established the design principles required to optimize the SMM properties of dysprosium sandwich complexes, we now turn our attention to the cyclobutadienyl ligand, $[Cb]^{2-}$. There were, hitherto, no lanthanide complexes of $[Cb]^{2-}$ ligands, hence investigations of such materials furnish an opportunity for fundamental advances in lanthanide organometallic chemistry. In addition, the greater formal charge and the four-fold symmetry provided by the $[Cb]^{2-}$ ligand provide a strategy for the development of SMMs. Our initial results on such systems will be described.[5]

Acknowledgements

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Luminescent probes based of phosphorescent metal complexes; “design on demand”.

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Phosphorescent metal complexes attract extensive interest due to their unique photophysical characteristics, which pave the way to diverse applications of these compounds, e.g. as probes in luminescent microscopy and sensors for molecules and ions of biological importance.[1-3] These areas of research is rapidly developing because phosphorescent complexes provide some important advantages in investigation of structure and physiological properties of the biological objects as compared to commonly used fluorescent organic dyes. Large Stokes shift (150 - 400 nm) and lifetime in micro- and millisecond range allow avoiding the signal self-quenching and minimize interference of background fluorescence that essentially increase sensitivity and resolution of imaging in luminescent microscopy. Additionally, major parameters of the phosphorescent emission, such as intensity and lifetime, display strong response onto variations in the characteristics of the probe environment (O_2, pH and metal ions concentration in the objects under study), thus providing powerful tools for analysis of physiological status of biomedical samples using either phosphorescent intensity measurements or lifetime imaging mode.[2,3]

To exploit in full these useful features of the phosphorescent emitters it is necessary to match the requirements of bioimaging, such as solubility and stability in physiological media, excitation and emission wavelengths in the window of biological tissue transparency (*in vivo* experiments), the presence of active functions used for the probe vectorization and targeting to certain organelles and strong response onto media parameter to be measured. These, often incompatible, requirements can be satisfied by modification of the ligand environment in the luminescent complexes and their conjugation with suitable bio-carriers to tune the photophysical and physico-chemical characteristics of the final products. It is worth noting that ”building-blocks” structure of transition metal complexes makes possible relatively independent tuning of various targeted properties through step-by-step insertion of purpose ligands and functional moieties into metal ion environment using the chemistry, which is substantially easier compared to modification of organic chromophores. In this lecture major synthetic approaches, which can be used for the design and preparation of the phosphorescent probes with predetermined properties suitable for application in bioimaging will be described and critically analyzed.

Acknowledgements

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Solid-gas reactions in synthetic chemistry - what can we learn from reaction pathways?

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Solid-gas reactions play an important role in the synthesis, use and wear of many functional materials and in technologically relevant processes. Like in most chemical reactions involving solids little is known about their mechanisms, which impedes synthesis planning as well as knowledge-based reaction and process control. The study of such reactions *in situ* is demanding due to the oftentimes harsh conditions and therefore, progress is intimately coupled to instrumental developments at radiation sources, such as synchrotron and neutron, including sample environment.[1-4]

The above mentioned issues are especially relevant for metastable compounds, which are at local minima in the thermodynamic energy landscape and as such a real challenge for solid-state chemical synthesis. *In situ* studies are an efficient way of probing their formation and decomposition and may help in effectively screening the multi-parameter space in view of an optimized synthesis. Revealing reaction pathways can thus help looking into the black box of solid-gas reactions, which sometimes enable improved synthesis and control of technologically relevant reactions.

Examples are given for a variety of solids, e. g. metal hydrides and intermetallics (hydrogen storage, HDDR, heterogeneous catalysis), metal nitrides and oxides (magnetic materials, photocatalysts, proton conductors). Many new metastable compounds with intriguing properties were discovered by such *in situ* studies. Several instrumental methods for *in situ* measurements in flowing or static gas atmosphere (H_2, Ar, NH_3, air) at elevated pressures and temperatures will be described, including X-ray and neutron powder diffraction, Raman spectroscopy and thermal analysis.

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New advances in gold chemistry: from hydrides to OLEDs

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Hydride complexes of gold have often been inferred in catalytic cycles but as a class of compounds have only been known for 10 years.

This talk will discuss the synthesis of several new classes of gold(III) hydrides, including the first anionic hydrides, hydrido(aryl) and (hydrido)phosphine complexes. The compounds show unexpected mechanistic diversity, with odd-electron pathways involving Au(II) leading to highly stereo- and regioselective alkyne hydroaurations.

Ligands trans to Au-H exert an overriding influence and dictate the nature of the gold frontier orbitals. They thereby control the NMR chemical shift, the Au-H hydricity, the Au-H bond distance, and the overall chemical reactivity. It turns out there are two distinctly different types of gold hydrides. The NMR shift can be used to distinguish between them, and to estimate the Au-H bond length.

This work has also led to the first examples of detectable gold borane (Au-HB) and silane (Au-HSi) sigma complexes and has provided evidence for gold hydride formation by heterolytic H-H and remarkably fast C-H activation.

While searching for ligands that might stabilise gold hydrides, we discovered that cyclic (alkyl)(amino)carbenes (CAAC) form Cu(I), Ag(I) and Au(I) adducts which show strong photoluminescence. These compounds are now being developed as a new type of photoemitters in organic light-emitting diodes (OLEDs) and will be the subject of a separate talk at this conference by Dr. Alexander Romanov.

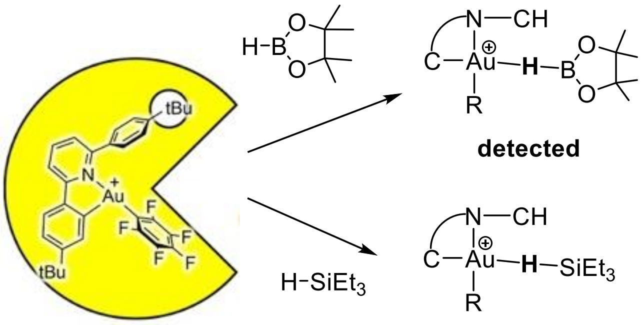

Figure 1. Formation of Au(III) H-B and H-Si complexes based on “Pacman”-type ligand structures

Acknowledgements

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Complexation of $SiCl_2$ with weak Lewis bases: matrix isolation and quantum chemical studies

S. E. Boganov, V. M. Promyslov, S. S. Rynin, I. V. Krylova, M. P. Egorov

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Complexation of $SiCl_2$ with weak Lewis bases (AllX (X = Cl, Br), butadiene-1,3, acetylene, HCL, N_2) was studied by matrix isolation technique and quantum chemical calculations. Key role of weak interactions in reactivity of dichlorosilylene will be discussed.

Highly Sensitive Heterospin Pressure Sensors

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An active search for molecular magnetic materials of new types whose structure and functional properties can change with temperature, pressure, and magnetic field or under irradiation has been stimulated by the development of fundamental science and high potential for their application. The effect of the external pressure on the physicochemical characteristics of multispin compounds remains a promising but least studied field of research. Along with growth of interest in materials whose physical characteristics are sensitive to the external pressure, manometers and stress memory detectors of various types formerly having no analogs have increased in number. A new promising class of objects of this type may be heterospin crystals based on Cu(II) complexes with nitroxides, which exhibit the spin-crossover-like phenomenon. The increase of pressure provokes a transition from high-spin to low-spin state, which again transforms into the high-spin state when the external load is removed. The solids are elastic and show reversible phase transformation which accompanied by a reversible contrastive change of color. Thus, the results of the study suggest that transition metal complexes with kinetically stable nitroxides are promising compounds that can serve as a basis for creating sensors expected to be highly sensitive to the external pressure.[1,2] Moreover the study of pressure influence on magnetic properties and crystal structure could give valuable information for estimation the so-called “chemical pressure” or scale of potential change in initial crystal structure (e.g. modification of substituents in organic ligands, solvents molecules and other spacers) for development of chemical ways to control physical properties.

Acknowledgements

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Zintl ions as ligands towards lanthanide organometallics

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Solid phases containing lanthanide (Ln) cations and main-group element Zintl type anions are well known. They are considered as appealing materials for different energy conversion devices. However, their molecular analogues are really uncommon. The report is focused on an overview of the recent results of the long-term collaboration between research groups of the author, Prof. Dr. M. Scheer and Prof. Dr. P.W. Roesky in the field of molecular Ln polypnictides.

During the last decade using the reactions between appropriate pnictogen containing substrates and Sm(II) (Ln = Sm, Yb) species we succeeded in the synthesis of a variety of homolanthanide and mixed *d*-metal/Ln complexes containing such Zintl anions as P_{10}^{4-}, E_8^{4-}, E_4^{2-}, E_3^{2-}, etc. (E = P, As, Sb).[1-11]

For instance, the first molecular Ln polyphosphide, $[(Cp^*_2Sm)_4P_8]$ was obtained via reduction of P_4 by $[Cp^*_2Sm]$.[1] To access its heavier analogues $[(Cp^*_2Sm)_4E_8]$ (E =As, Sb) incorporating the Realgar-type E_8^{4-} Zintl ions we have developed original synthetic approaches based on the different routes of preparation of E^0 nano-particles readily reactive towards Sm(II) compounds.[10-11]

The “reductive approach” has been found to be very fruitful for preparation of compounds with uncommon combinations of elements and bonds between them.

Acknowledgements

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Ultrafast electron transfer reactions: charge photoseparation in photosynthetic reaction centers.

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The lecture will give general ideas about the relation between the molecular design of the photosystem I (PS I) reaction center (RC) and ultrafast electron transfer processes in PS I leading to the uniquely high efficiency of charge separation. RC contains 6 chlorophyll (Chl) molecules organized as shown in Figure 1A. PS I contains ~96 Chl molecules of antenna also. We propose new approaches to study fast electron transfer reactions with high temporal resolution and selective excitation of RC Chls by femtosecond laser spectroscopy. Experiments were carried out with PC I complex from *Synechocystis sp. PCC 6803* wild type and with different variants of *Synechocystis sp. PCC 6803*, where amino acid as axial ligands to Mg atom of Chl was varied in RC. The overall properties of the Chls, not only their spectral features, are altered as consequences of chemical modifications on coordination bonds by which the central Mg atom, the Lewis acid, of Chl molecules interacts with amino acid sidechains, as the Lewis base, in proteins. The femtosecond transient spectrum manifests the features of the primary ion-radical pair P700^{+}A0^{-} at time delay <180 fs, followed by formation of the secondary pair P700^{+}A1^{-} with a characteristic time of 26 ps. The obtained data are rationalized in the framework of the adiabatic three-state model that includes the chlorophyll dimer P700 as the primary electron donor, and two symmetrically arranged nearest chlorophyll molecules of the primary acceptor A0 (Figure 1B). A strong electronic coupling between P700 and A0 is governed by a specific arrangement of chlorophylls. Excitation in the maximum of P700 absorption band generates electronic states with the highest contribution from excited state P700*, whereas excitation in the far-red edge of P700 band predominantly generates charge transfer state P700^{+}A0^{-} in both branches of redox-cofactors. The model accounts for the ultrafast formation of P700^{+}A0^{-} and the exponential decline of PS I absorption in accordance with the Urbach rule.

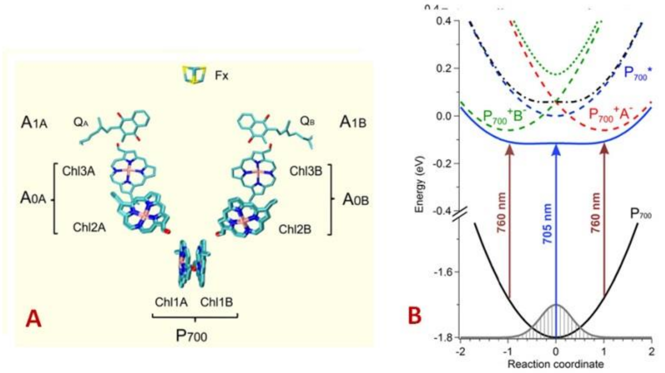

Figure 1. A. Scheme of reaction center in PS **I.**
B. The adiabatic three-state model of the potential energy surface of P700 and A0 system.

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Towards technological development of personalized biomaterials for bone tissue engineering

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The present lecture is targeted to shortening of rehabilitation time and life quality improvement of the patients with bone tissue diseases through implementation of personalized tissue-engineered methodology and technologies.

The first main objective of this work was development and optimization of three-dimensional (3D) printing processes to fabricate novel, innovative composite scaffolds based on calcium phosphates and polymers for bone tissue engineering needs. The ideal scaffold will act as a three-dimensional template which mimics the extracellular matrix of the tissue onto which bone forming cells can attach, multiply, migrate and function.

The second main objective of the present work was to develop the technology for fabrication of osteogenic-based bone repair systems. Hereby, the living cell component or gen constructs is added to the printed scaffold prior to implantation *in vivo*, which increases the cost-to-benefit ratio of the biomedical treatment.

The results of this work provide concrete opportunities to implement scientific innovation and to allow commercialization and clinical application of the innovative biomaterials required in the fields of orthopedics, dentistry, oral and maxillofacial surgery, neurosurgery and oncology.

Acknowledgements

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INVITED LECTURES

Pyramidane: the smallest member of the fenestranes family

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Pyramidanes or [3.3.3.3]fenestranes, the compounds with a square-pyramidal shape, represent a novel highly challenging class of polyhedral clusters featuring an "invertedly" tetrahedral apical atom. They are the smallest possible members of fenestranes family of the highly strained compounds with a central quaternary atom serving as a joint vertex for four fused cycles.

Comprehensively approached on theoretical grounds, pyramidane and its derivatives still eluded their synthetic realization, and only recently first representatives of pyramidanes were described. In this presentation, we report on a series of the group 14 element pyramidanes with all-C-, all-Si- and all-Ge-bases, and Ge-, Sn- and Pb-apexes, their synthesis, structural features, and their particular bonding situations (Figure).[1] Hybrid pyramidanes with the group 14 elements at the base and group 13 or group 15 element at the apex of the square-pyramid will be also presented.[2]

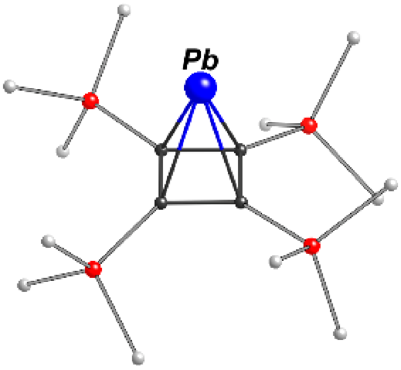

Figure 1. Plumbapyramidane.

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Medicinal Inorganic Chemistry as a Tool for Metal-Based Drug Design

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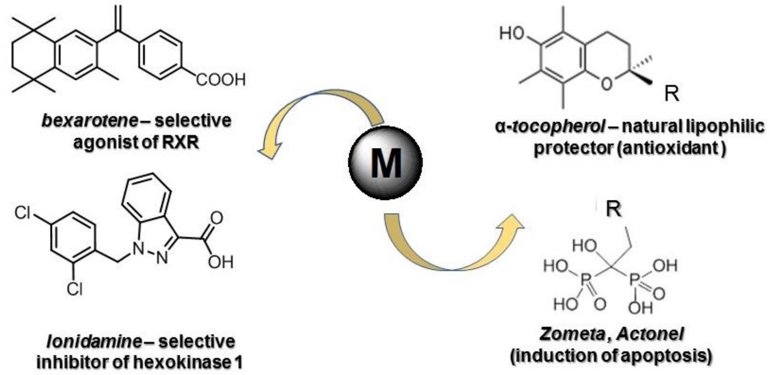
There is an urgent need for the discovery of new drugs with novel modes of biological action, because several diseases develop resistances to known drugs. Metal compounds (metal-based drugs) might offer biological and chemical diversity that is distinct from that of organic substances. Nowadays metal-based drugs are a commercially important sector of the pharmaceutical market. It has become increasingly apparent that metal-based pharmaceuticals can play a crucial role in oncology, treatment of metabolism- and genetic disorders, cardiovascular disease, gene therapy, inflammation, stroke, diabetes, malaria, and neurological disease. The goal of medicinal chemists is to create new inorganic molecules as drug candidates.

We will discuss the need for rationalization of the investigational approaches available to create hybrid metal-based drugs. Our key approaches were (**1**) to maintain the interaction with the target, and (**2**) to keep the balance between the antitumor potency and general toxicity. Scheme illustrates our **two approaches:**



The biological activity has been studied in *in vitro, ex vivo, in vivo* experiments and in enzymatic reactions with targets (*xanthine oxidase*, *lipoxygenase, glutathione reductase, thioredoxin reductase etc.*).

Thus, we can conclude that the combination of two physiologically active moieties in a molecule is a promising approach to find the novel hybrid pharmaceutical agents.

Acknowledgements

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B-N lightweight inorganic hydrides dehydrogenation mediated by transition metal complexes: a combined experimental-theoretical approach

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Lightweight inorganic hydrides are at the forefront of contemporary chemical hydrogen storage research. They are easy-to-handle and thermally stable compounds with relatively high hydrogen content. Among the most studied materials belonging to this class there are ammonia borane ($NH_3{\cdot}BH_3$, AB, 19.3 % H wt.)[1] and borohydrides (BH_4^-, 18.3 % H wt.).[2] In the last decade, homogeneously catalyzed AB and BH_4^- dehydrogenation has become increasingly popular; H_2 evolution is mediated by organometallics of *d*-block elements. In this lecture, a selection of examples will be presented (Figure 1),[3] with a focus on the H_2 generation mechanism as a result of initial dihydrogen bonding (DHB) interaction between hydridic and protonic H atoms present in the reaction environment. The combination of experiment (NMR and IR spectroscopic studies at variable temperature, kinetic rate measurements) and theory (DFT studies of the reaction mechanism and identification of intermediates) is a particularly useful approach to get insights in this field.

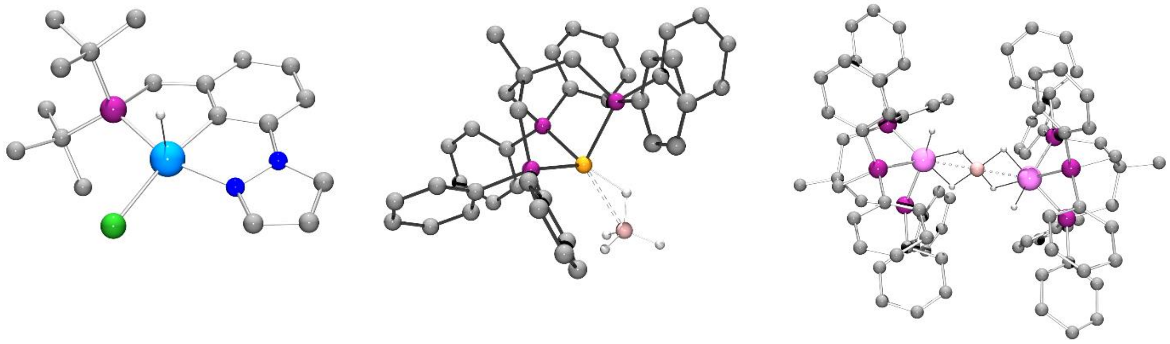

Figure 1. Selected examples of homogeneous catalysts for AB and BH_4^- dehydrogenation.

Acknowledgements

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Immobilized Pd(0) and Pd(II) catalysts for C-C cross-coupling reactions

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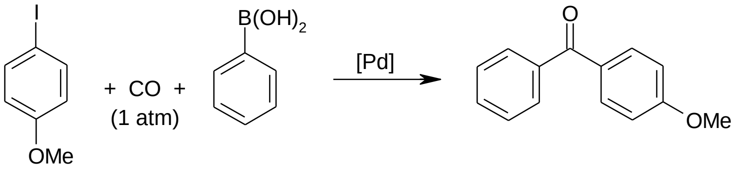
Palladium catalysts have found a broad application in different C-C bond-forming reactions employing aryl halides as substrates. The Heck, Suzuki or Sonogashira reactions present very useful methods leading directly to arylated olefins, biaryls and diarylacetylenes. These compounds are important substrates for pharmaceutical industry and therefore their high purity is a very important issue. In this context, efficient separation of palladium catalysts from reaction products is necessary to avoid traces of metal in the final product. Immobilization of palladium catalyst on the solid support facilitates good separation and, in addition, recycling of the catalyst.

Porous materials, such as MOFs, present a promising class of supports for palladium catalysts. For our studies we used two MOF materials, MIL-101-NH$_2$, (iron MOF) and UiO-66-NH$_2$ (zirconium MOF) as supports for Pd(II) complex, $PdCl_2(CH_3CN)_2$. Next, both materials were carbonized to form PdO&Fe$_2$O$_3$@C and PdO&ZrO$_2$@C composites. The as prepared palladium catalysts were tested in Suzuki-Miyaura and carbonylative Suzuki-Miyaura cross-coupling with good to excellent results.



[Pd] = Pd@MIL-101-NH$_2$, Pd@Fe$_2$O$_3$@C

Pd@UiO-66-NH$_2$, Pd@ZrO$_2$@C

The main aim of these studies is understanding of the role of Pd(II) and Pd(0) in cross-coupling reactions. It is well accepted in the literature that Pd(0), very often in the form of nanoparticles, is responsible for the catalytic activity. Formation of Pd(0) in situ is expected in our systems containing Pd(II) immobilized on MOFs. However, contribution of PdO in these reactions was also mentioned. By selection of MOF-immobilized palladium catalyst we expect to get deeper knowledge about the reaction mechanism. In particular, the role of PdO in the catalytic process could be explained.

Acknowledgements

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Catalytic Silylation of Molecular Nitrogen

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The discovery of a homogeneous catalytic process that utilizes N_2 as a reactant is being actively pursued by numerous research groups.[1] Besides those efforts aimed at discovering new catalysts for the production of ammonia, there is considerable interest in generating tris(trimethylsily)amine ($N(SiMe_3)_3$) by reduction of N_2 in the presence of excess Me_3SiCl, a reducing agent, and a soluble catalyst (Figure 1).[1,2]

Current efforts in our group are focused on optimizing the process by investigation of new catalyst precursors. We attribute the high number of turnovers[2] of $N(SiMe_3)_3$ to the stability of the ligand on cobalt. The tridentate NNP donor set[3] carries a negative charge (**2** is formally Co(I)), provides a sterically hindered environment at the Co center, and is stable to excess reducing agent. For example, changing the isopropyl substituents on phosphorus in **2** to tert-butyl groups maintains high turnovers; however, reducing the bulk on the N-aryl group from o-isopropyls to o-Me's is deleterious to the process.

This presentation will focus on new ligand designs[4] aimed at improving the efficiency of the catalytic silylation of coordinated dinitrogen.

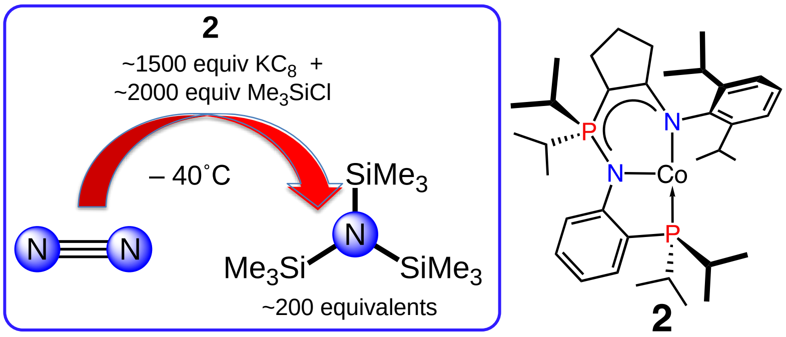

Figure 1. Functionalization of molecular nitrogen using the homogeneous catalyst precursor 2 to efficiently produce $N(SiMe_3)_3$

Acknowledgements

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Hypercoordinate silicon, germanium and tin compounds: unusual structure, dynamic stereochemistry and biological activity

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Hypercoordinate silicon, germanium and tin compounds are the focus of intense research due to the diversity of their structures, chemical properties, stereodynamic behaviour and practical use in stereoselective synthesis and medical diagnostics.[1]
The structures and stereodynamic behavior of the penta- (TBP) and hexacoordinated (Oh) (C,O)-chelate of acetamides, lactams and imides derivatives with different coordination units (OMC_3X, OMC_2F_2, $OMCF_3$ and $O_2MC_2X_2$; M = Si, Ge, Sn; X = Me, MeO, *i*-PrO, F, Cl, Br, I, OTf) were studied by multinuclear (^1H, ^{13}C, ^{15}N, ^{17}O, ^{19}F, ^{29}Si) and ^1H, ^{13}C, ^{19}F dynamic NMR (DNMR) spectroscopy.[2-4]

Ligand permutations in TBP and Oh and fluorine exchange at metal catalysed by acids were detected. The activation parameters ($\Delta G^{\#}_{298}$, $\Delta H^{\#}$, $\Delta S^{\#}$) of all processes were determined by DNMR on various nuclei. The $\Delta S^{\#}$ values for ligand permutation in the series of TBP complexes with the strongest intramolecular coordination (for example X = Br, I, OTf) are negative while a lesser degree of O→M interaction, for example, in some complexes with X = Cl increases the entropy of activation. The influence of solvent, nature of the central atom, nucleofugacity of the X substituent in the different coordination sets and the presence of external nucleophiles on the activation ($\Delta G^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$) parameters of the stereodynamic processes were determined. Possible regular and non-regular mechanisms are discussed on the basis of experimental (DNMR) data and quantum-chemical calculations using a DFT model.

Evaluation of proliferation of U-937 tumor cells was done using a radioisotope method. Proliferation was evaluated by measuring the radioactivity incorporated into DNA of 3H-thymidine, and the result was expressed as a percentage of control.

Acknowledgements

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Design of multichromophore molecular emitters based on combination of transition metal complexes

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Construction of luminescent compounds demonstrating multiply luminescence due to partial or blocked intramolecular energy transfer between different chromophore and emission centers is one of the most interesting and demanded trend in the modern coordination chemistry of transition metals (TMs).

The key point in design of heterometal molecular emitters based on polynuclear molecular ensembles is 'building blocks' strategy where TM complexes/ TM metalloligands are selectively connected together through a suitable linker. Every 'building block' in this kind of molecular aggregates plays its own role in resulting emission and can be involved in intramolecular energy transfer, energy exchange or quenching.

We prepared Au(I), Pt(II), Ir(III) and Ln(III) emissive complexes based on a few heterofunctional polydentate ligands and used the metalloligands obtained to construct multichromophore molecular emitters.

In general, using of TM luminescent complexes as 'building blocks' for design of luminescent polynuclear heterometallic molecular aggregates will be discussed, and some general principles of molecular polychromatic emitters design will be presented in framework of the lecture.

Acknowledgements

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Metal Organic Frameworks on 2D Solid Surfaces

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Fabricating of solid-supported porphyrin-based metal organic networks which are a new class of functional porous materials promising for various applications remains a challenging problem for supramolecular chemistry. Surface-directed assembly of molecules and nanosized objects offers a labile platform for tailoring solid surfaces with well-defined supramolecular and hybrid assemblies presenting various functionalities. Several examples enlightening the application of this concept to the fabrication of stable surface-attached metal organic frameworks (SURMOFs) as films on planar solid supports as well as on dispersed solid particles will be discussed. One of them shows that SURMOFs can be assembled from variously substituted zinc porphyrins or PDI derivatives as linkers on surfaces, decorated with graphene oxide (GO).[1, 2] Because the microscopically flat 2D carbon template initiate the growth of macroscopically uniform SURMOF films (Fig.1a), they exhibited both well-resolved X-ray diffraction and angle dependence of fluorescence making it possible to determine the relation between the structure of linkers and the packing motives in the films (Fig.1b). The surface effect manifests itself as different packing of SURMOFs in bulk and in 2D space due to steric limitations, whereas the coordination motive dictates the morphology of SURMOFs.

Another approach was used to fabricate catalytically active supramolecular hybrids on colloidal templates: (i) the porphyrin-based SURMOF/GO composites obtained in the Pickering emulsions, and (ii) a synergetic catalyst assembled from ZnTCPP and zinc acetate on the particles of layered europium hydroxochloride as anion-exchange 2D template. A combination of methods including MALDI-TOF spectroscopy was exploited for understanding the origin of synergetic effects and the mechanisms of catalysis in these solid-associated supramolecular hybrids.

These strategies provide a basis for new types of self-assembled coordination structures on solid matrices suitable for their integration with modern planar technologies in chemical sensing, optics, molecular electronics and catalysis.

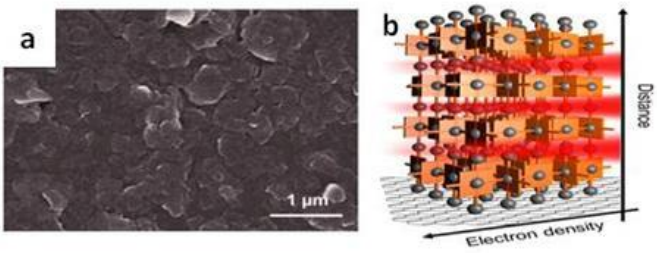

Figure 1. (a) SEM image of the para-ZTCPP/ZnAc2 SURMOF on the GO template and **(b)** the distribution of the electron density within this SURMOF.

Acknowledgements

The work was supported by RFBR (grant 18-29-04026-MK) and the Ministry of Science and High Education RF.

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Strategic advantages of reactive polyiodide melts for scalable perovskite photovoltaics

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The recent meteoric rise of metal halide perovskites as light harvesters for solar cells has stunned the scientific community. Within the last few years their power conversion efficiencies surged from 3% to well over 23 %. While the efficiency race continues, many approaches for perovskite solar cells scale up were proposed, having own advantages and drawbacks, including recently discovered approach based on the usage of a new class of precursors coined as Reactive polyiodide melts (RPM).

RPMs are liquid polyiodides which can be readily prepared by mixing powders of I2 with organic halides (MAI, FAI, GuaI)[1]. The RPM has been recently found to be a highly corrosive decomposition product which forms under sunlight and cause degradation of perovskite solar cells components, including spiro-MeOTAD and gold electrode[2]. On the contrary, an extremely high reactivity of the RPM is an important advantage of such compounds as they easily oxidize metallic Pb and lead compounds (e.g. PbI_2, PbO) thus forming perovskite according to the following reaction: $MAI_3 + Pb \rightarrow MAPbI_3$.

Therefore, the RPM open up a new formation strategy of hybrid lead halide perovskites using the RPM. We present that perovskite crystals and thin films can be easily obtained through the direct reaction between reactive polyiodide melts and metallic lead. Due to its unique composition the RPM acts simultaneously as a liquid medium and a highly reactive precursor that swiftly converts metallic lead into perovskite. This new approach allows fabrication of high quality polycrystalline perovskite films with micron-size grains without use of solvents and heating.

The perovskite solar cells made via this approach yield a solar to electric power conversion efficiency (PCE) of over 17% on 4 mm^2 and over 13% on 3 cm^2 respectively[3]. We demonstrate applicability of this method for the fabrication of highly uniform perovskite films with micron-size grains over large substrates of 10x10 cm^2 and 20x30 cm^2, including flexible supports. The proposed strategy has a high potential for industrial scale mass-production of perovskite modules including roll-to-roll manufacturing on flexible substrates, because the initial lead thin films can be easily deposited in a highly controlled way.

Acknowledgements

A.T. and E.G. acknowledge the financial support from Russian Science Foundation, project number 19-73-30022 and JSC “Krasnoyarskaya HPP”

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A journey from Mn-mediated synthesis of NHC-phosphine ligands to Mn-based catalysts with non-classical H_2 activation mode

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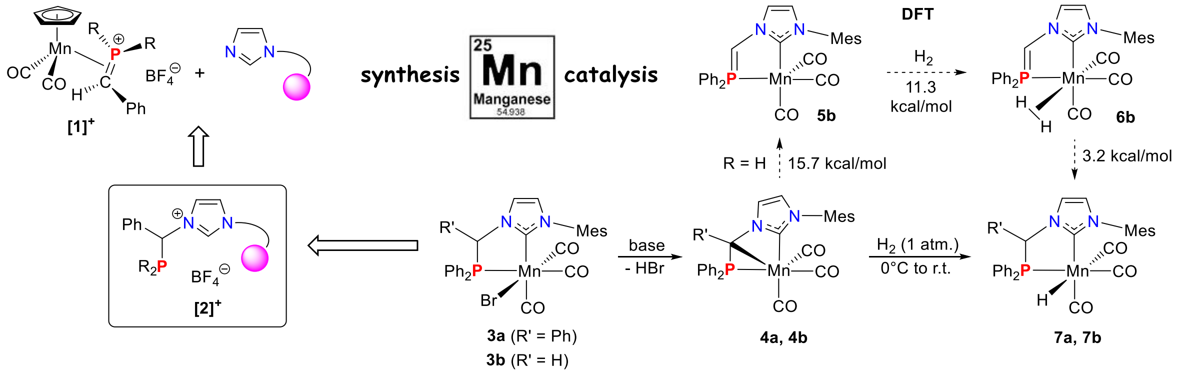
The utilization of organometallic complexes of abundant 3d transition metals in organic synthesis and homogeneous catalysis is one of the major trends in chemistry of this century. In this direction, we have recently shown that Mn(I) methylenephos-phonium complexes [**1**]$^+$ (see Scheme), readily available from industrially produced $CpMn(CO)_3$ and secondary phosphines, can be used for the efficient preparation of a variety of NHC-phosphine pre-ligands [**2**]$^+$ from simple imidazole precursors.[1]

We have also observed that the phenyl group in the link between NHC and phosphine moieties facilitates the deprotonation of this position in Mn(I) complex **3a** to form the NHC-phosphinomethanide product **4a** being more stable than its non-substituted analogue **4b** (see Scheme). Both **4a-b** are able to activate H_2 under mild conditions. DFT calculations show that the preferred reaction pathway for **4b** includes its isomerization into the unconventional NHC-ylide **5b**, coordination of a H_2 molecule and finally heterolytic H–H bond cleavage in the resulting η^2-H_2 intermediate **6b** to form the hydride **7b**.[2] The latter result shows the first evidence for the implication of pentavalent phosphorous species in metal-ligand cooperation. Such H_2 activation is relevant for catalysis as complexes **3a-b** constitute one of the most efficient Mn-based catalytic systems for ketone hydrogenation (TON up to 6200).[2]



Acknowledgements

We thank the joint CNRS/RFBR grant no. 19-53-15014 (PRC2330) and the IUF (France) for the support of this project. Computational studies were performed using HPC resources from CALMIP (Grant no. P18038). R. B. is grateful to the Embassy of Yemen in Paris for a PhD fellowship.

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Inorganic Nanomaterials for Catalytic Energy Technologies

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Metal-oxide nanomaterials permit engineering of potent catalysts for H_2/O_2 production via photocatalytic H_2O splitting or low-temperature dehydrogenation of Formic molecules (HCOOH, $HCOO^-$). Herein we present engineering of catalytic nanomaterials by Flame-Spray-Pyrolysis (FSP) which is a one-step flame-synthesis technology allowing production of high-purity, high crystallinity nanocatalysts at several grams-per-hour rates. Controlled synthesis of metal-oxides, and metal-sub-oxides by FSP allows engineering of their surface-groups & energy-band gap. Herein we will discuss the engineering of novel nano-hetero-structures consisting of [metal oxide]-[metal suboxide]-[metal] nanoparticles and their evaluation for photocatalytic H_2 production & low-temperature dehydrogenation of HCOOH. The underlying electron-transfer mechanisms & thermodynamics will be analysed and discussed. An innovative FSP approach will be discussed in the context of scalable synthesis of inorganic nanocatalysts under precise control of crystal-phase, particle-size and catalytiDc performance

Metal complexes interfaced with inorganic particles: the hybrid technology in catalysis

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Engineering of molecular catalysts grafted on solid supports, is a potent technology to develop well-defined surface species on functionalized inorganic particles. This includes:

[a] tailoring of ligands' motifs, that in turn determine the performance of the metal catalysts,

[b] engineering of the support materials, and

[c] develop/optimize the chemical processes to attach the molecular catalysts on the supports.

We will discuss how the design of single-site catalysts and the textural features of structured support matrices modify the behavior of the hybrid catalysts using examples of interest in epoxidation reactions and hydrogen production from formic acid. The reaction-intermediates and thermodynamic aspects of such systems will be highlighted, with emphasis on the synergistic role of the support with the redox evolution of the catalytic metal center.

The roles of HCO_3^-/CO_3^{2-} in catalytic oxidation processes

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The fact that the redox potential of the couple $CO_3^{\cdot -}/CO_3^{2-}$, 1.57 V, is considerably lower than that of the $OH^{\cdot}/H_2O$ suggests that in many catalytic oxidation processes carbonate might be involved. Indeed results point out that the Fenton reaction in the presence of HCO_3^- proceeds *via*:

$Fe(H_2O)_6^{2+} + HCO_3^- \rightleftharpoons Fe^{II}(CO_3)(H_2O)_3 + H_3O^+ + 2H_2O$

$Fe^{II}(CO_3)(H_2O)_3 + OOH^- \rightleftharpoons (CO_3)Fe^{II}(OOH)(H_2O)_2^- + H_2O$

$(CO_3)Fe^{II}(OOH)(H_2O)_2^- \rightarrow (CO_3)Fe^{IV}(OH)_3(H_2O)^-$

$(CO_3)Fe^{IV}(OH)_3(H_2O)^- \rightarrow Fe^{III}(OH)_3(H_2O) + CO_3^{\cdot -}$

i.e. the active ROS in physiological media and in advanced oxidation processes is $CO_3^{\cdot -}$ and not $OH^{\cdot}$.

Furthermore DFT calculations suggest that $CO_3^{\cdot -}$ is expected as the active species in photo-catalytic oxidation processes.

The observation that $Cu^{II}(CO_3)_n^{(2n-2)-}$ and $Ni^{II}L^{2+}$ in the presence of bicarbonate are good electro-catalysts for water oxidation is due to:

a. The carbonate ligand lowers considerably the redox potential of the central cation.

b. The carbonate ligand is a non-innocent ligand, *i.e.* a considerable charge transfer from the central cation to the carbonate occurs. This charge transfer is involved in the water oxidation.

Acknowledgements

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Thermodynamics and transport properties of promising cathode materials based on the double-perovskite type cobaltites

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The layered cobaltites $LnBaCo_2O_{6-\delta}$, where Ln is a lanthanide metal, have been the subject of extensive research in recent years as materials exhibiting good catalytic activity in electrochemical processes and promising cathodic performance. Among other layered cobaltites $PrBaCo_2O_{6-\delta}$ is distinguished with the highest values of electrical conductivity, oxygen volume diffusion, surface exchange coefficient. The DFT based calculations reveal oxygen diffusion controlled by minority O2 vacancies in CoO_2 planes while majority O3 vacancies in PrO layers maintain geometry of the transport pathway along ⟨101⟩ directions in the crystalline lattice. This finding suggests that the light doping of Pr and Co sites may provide an efficient tool for properties tuning of the cobaltites. The high-temperature electric transport measurements, thermodynamic properties and energy-statistic characteristics of defect formation reactions in $Pr_{1-x}YxBaCo_{1-y}M_yO_{6-\delta}$, where M = Cu, Ni and Al, confirm that independently on the electrical activity of substituting cations the doping may be accompanied with improved thermodynamic stability of the crystalline lattice and enhanced electron and oxygen ion disordering. Particularly advantageous characteristics are attained in dual-phase composite $Pr_{0.9}Y_{0.1}BaCo_{1.8}Ni_{0.2}O_{6-\delta}$/ $Ce_{0.8}Sm_{0.2}O_{1.9}$ where overvoltage for oxygen reduction does not exceed 40 mV at 1073 K and current density 1 $A{\cdot}cm^{-2}$. The combination of good cathodic performance with moderate thermal expansion, good conductivity and high electro-chemical activity distinguish the developed composite as one of the promising cathode materials for intermediate temperature solid oxide fuel cells.

Biomimetics of redox metalloenzymes as a novel class of copper anticancer agents: from discovery to preclinical evaluation

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Metal-based anticancer drugs play an important role in chemotherapy. The discovery of cisplatin resulted in tremendous growth in research associated with inorganic metal complexes for cancer therapy. Therefore, in recent years, there has been a rapid expansion in research and development of novel metal-based anticancer drugs to improve clinical effectiveness, to reduce general toxicity, and to broaden the spectrum of activity. The variety of metal ion functions in biology has stimulated the development of new metallodrugs other than Pt drugs with the aim of obtaining compounds with alternative mechanisms of action. Among non-Pt compounds, copper complexes are potentially attractive. It has been established that the properties of copper-coordinated compounds are largely determined by the nature of ligands and donor atoms bound to the metal ion.

In an attempt to receive more insight and determine the action mechanism and antitumor activity of copper complexes, we have synthesized and characterized new mono and binuclear Cu(I,II) complexes containing substituted 2-alkylthio-5-arylmethylene-4H-imidazolin-4-ones. Copper containing complexes were cytotoxic for a variety of cancer cell lines. In contrast to majority of other known metal-containing drugs, these compounds were shown to be accumulated at the cell nucleus and the presence of copper ions as a complex constituent was essential for both accumulation in the cell nucleus and rapid DNA fragmentation accompanied by DNA 3′-end generation as a result of nuclease cleavage. Copper containing complexes were able to inhibit number of polymerases that allowed us to hypothesize that interaction of copper containing complexes with the proteins in the vicinity of DNA may result in copper ions release that cause DNA damage followed by rapid DNA degradation by cellular nucleases. Experiments with mice models showed that complexes is less toxic than the well-known drug cisplatin and have a pronounced antitumor effect. A novel class of metal complexes, based on a 2-thioxoimidazol-2-one heterocyclic core could be utilized as a smart platform for construction of anticancer chemotherapy agents. Data of preclinical evaluation of copper complexes will also be presented.

Multinuclear 4(5)d-complexes as versatile building blocks for design and synthesis of nanomaterial with bioanalytical and biochemical applicability

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The present report is focused on highlighting multinuclear 4(5)d-complexes exemplified by hexanuclear molybdenum and rhenium clusters, as well as polyoxometalate derivatives as promising building blocks of the nanomaterial for biomedical or bioanalytical applications. It is shown that watersoluble polymers form supramolecular assemblies with the inorganic complexes which, in turn, is the way for tuning their properties. In particular, the enhanced hydrophilicity of the supramolecular assemblies facilitates watersolubility of the complexes along with the enhanced photoluminescence.[1,2] The hydrophilic cluster-based supramolecular assemblies are good basis for the application as cellular contrast agents or as facile building blocks for the bifunctional nanomaterial applicable as therapeutic and contrast agents.[3,4]

The apical ligands of the hexarhenium clusters provide a basis for both ligand exchange and complex formation with lanthanide ions. The apical ligand exchange is highlighted as the reason for sensing of the enzymatic hydrolysis of acethylcholine.[5] The gadolinium complexes of the polyoxometalate derivatives (keplerates) and the hexarhenium clusters bearing specific ligands in the apical positions are represented as very promising bulding blocks in design and synthesis of contrast agents for NMR tomography.[6,7] The structure-property relationships are also discussed.

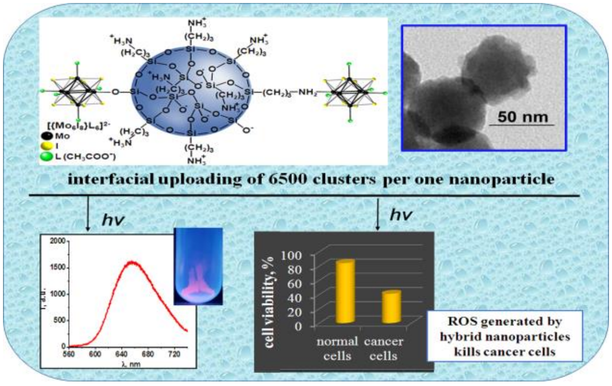

Figure 1. Cartoon image of the design and application of the cluster-based nanomaterial.

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Tailoring Light-Harvesting Materials through Strong and Weak Bonding in Complex Bismuth Iodides and Polyiodides

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Although the efficiency of solar cells based on complex lead iodides has passed the psychological level of 20%, toxicity of lead has raised concerns and now other compounds are scrutinized as potential solar light absorbers to replace their efficient but toxic lead counterparts. So far the photovoltaic efficiency of Bi-based solar cells has reached only 2.1 %,[1] but the search for new materials is gaining interest and new compounds have been recently synthesized and examined for potential photovoltaic properties. The intrinsic drawback of complex bismuth halides is their relatively wide band gap of 2.0-2.2 eV that precludes efficient light harvesting;[2] therefore, band engineering aiming at finding tools for diminishing the gap thus rendering better charge transfer is coming to the fore.

In this report, we present several approaches that have been recently proven to have a reasonable impact on the electronic structure of complex bismuth iodides and indeed lead to narrower band gaps. Firstly, this is condensation of BiI_6^{3-} octahedra into 1D or 2D polymeric anions; secondly, I_2 molecules or I_3^- anions can be used for stitching the Bi/I substructure; finally, multifold hydrogen bonds and secondary I…I interactions also contribute to narrowing the band gap. We will show examples of such crystal structures, discuss synthesis of these compounds, and present their optoelectronic properties.

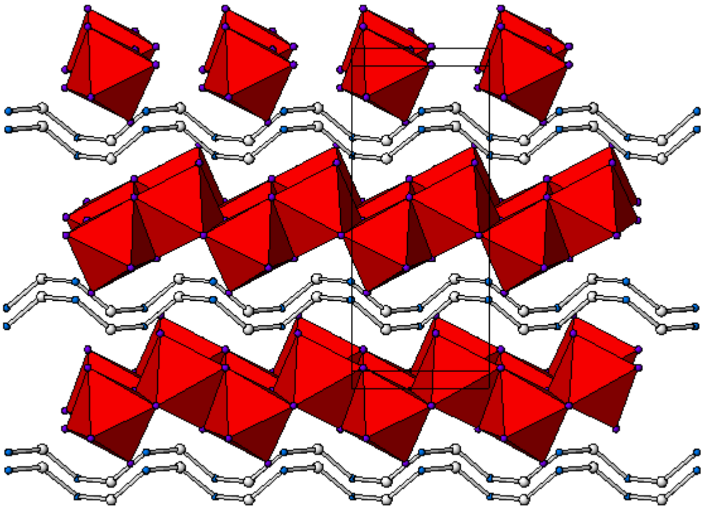

Figure 1. View of the crystal structure of $KBiI_4$□H_2O [3]

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Cluster iodides of early transition metals

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Chemically robust octahedral cluster halide complexes of early transition metals, $[\{M_6(\mu_3\text{-}X)_8\}L_6]$ and $[\{M_6(\mu_3\text{-}X)_{12}\}L_6]$ (M = Nb, Ta, Mo, W; X = Cl, Br or I; *L* = neutral or anionic ligands) are stable, chemically robust and easily available. The iodide clusters of Mo and W exhibit superior emission lifetime and quantum yield values. We are carrying out systematic studies on the influence of terminal ligands *L* on the properties of the $[\{M_6I_8\}L_6]$ clusters, in order to achieve predictable tuning of their potentially useful characteristics such as the redox, spectroscopic and photophysical behaviour, that is intrinsically due to the presence of the $\{M_6I_8\}^{4+}$ cluster core, by the choice of an appropriate *L*. Coordination chemistry, photocatalytic activities on the water reduction reaction and other possible applications of the $[\{M_6I_8\}L_6]$ clusters will be discussed.

Coordination chemistry of Nb and Ta iodide clusters is virtually non-existent. Nevertheless, these iodides merit attention owing to unique combination of properties, offered by the cluster iodides of tantalum: the $[\{Ta_6(\mu_3\text{-}I)_{12}\}L_6]$ clusters will have 18 heavy (i.e., strongly X-ray absorbing) atoms per molecule. This makes them good candidates for new X-ray contrast agents. Additionally, their redox and optical properties makes them a good candidates for hydrogen generation from water using sunlight. In this work we will report preparation, photocatalytic and reactivity studies of some key $[\{Ta_6(\mu_3\text{-}I)_{12}\}L_6]$ clusters.

Related topics on Nb and Re cluster iodides are also included.

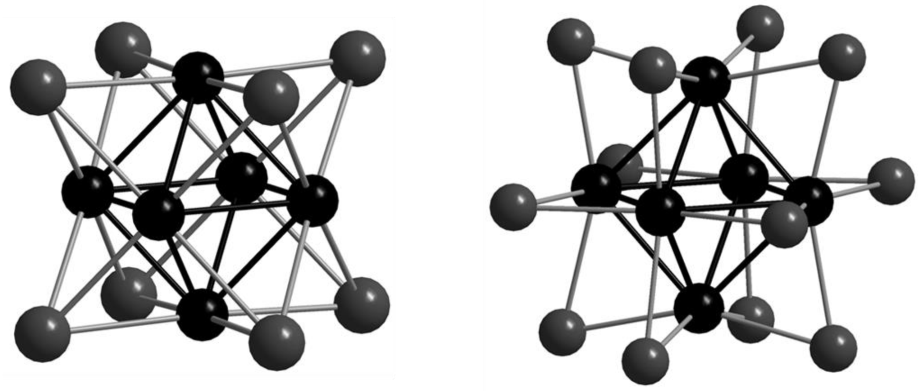

Figure 1. Octahedral cluster cores: $\{M_6I_8\}$ **(left),** $\{M_6I_{12}\}$ **(right)**

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We acknowledge financial support from the Russian Foundation for Basic Research (grant 18–33–20056)

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ORAL PRESENTATIONS

Carbonyl Clusters Containing Osmium and Antimony

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We have been studying the chemistry of organometallic clusters containing osmium and antimony. When we started, there was only one osmium-antimony cluster (besides stibine-substituted derivatives) known.[1] The initial impetus for the study was driven partly by the expectation that the chemistry will parallel that of the much better developed chemistry of the phosphorus analogues. But it quickly became apparent that the antimony-containing clusters often behave very different. For example, the first known cluster of the class, $Os_3(\mu\text{-}SbPh_2)(\mu\text{-}H)(CO)_{10}$, could undergo nucleophilic addition reactions with two-electron donors such as PPh_3 or ^tBuNC via cleavage of an Os-Os bond.

In this talk, I will present our work on this class of compounds – we have observed a diversity of structural types and reactivity. Comparison will also be made with the chemistry of the arsenic and bismuth homologues, as well as with those of the ruthenium homologues.

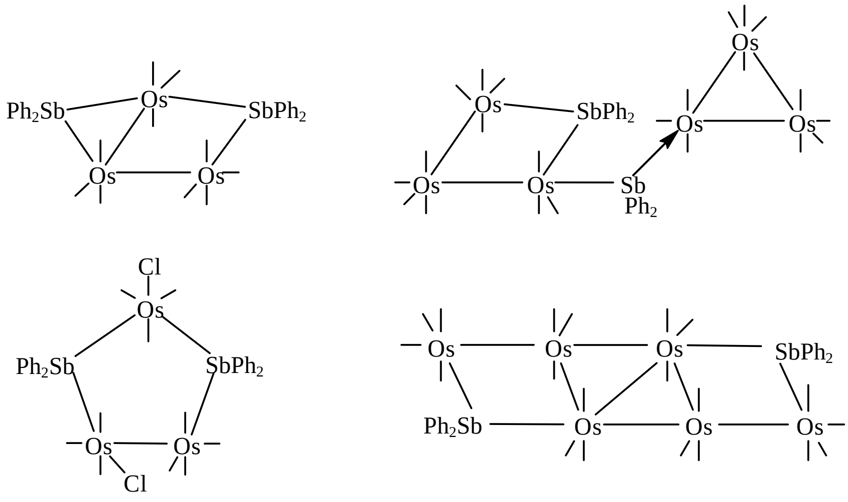

Figure 1. Some osmium-antimony clusters

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Alloy nanoclusters synthesized by one-phase co-reduction methods

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Development of a rational synthesis toward alloy nanoclusters is emerging due to the broad applications of alloys in photoluminescent materials, image, sensing, and catalysis. Along this line, a series of structurally precise dichalcogenolate-protected copper and silver superatomic nanoclusters and their alloys have been prepared via a template galvanic replacement method.[1] Notable examples are two-electron $[MCu_{12}(CCPh)_4(S_2CNR_2)_6]^+$ (M = Cu, Ag, Au) and eight-electron superatoms, $[MAg_{20}\{E_2P(OR)_2\}_{12}]^+$ (M = Ag, Au; E = S, Se) (Figure 1).

While highly successful in building group 11 bimetallic nanoclusters by galvanic exchange, which is particularly useful in controlling the as-synthesized cluster nuclearity and its core geometry, the extension of this methodology in doping group 10 metals such as Pd and Pt appears to no avail. Therefore we shift our attention on a traditional co-reduction synthesis. Luckily several brand new molecules such as $[MAg_{20}\{E_2P(OR)_2\}_{12}]$ (M = Pd, Pt; E = S, Se), $[Pt_2Ag_{33}\{E_2P(OR)_2\}_{17}]$ and $[Pt_3Ag_{44}\{E_2P(OR)_2\}_{22}]$ can be fabricated via this route. All these new alloys have been characterized by single crystal X-ray diffraction as well as ESI-MS, and the synthetic details, structure and boding characteristics, will be thoroughly discussed in this presentation.

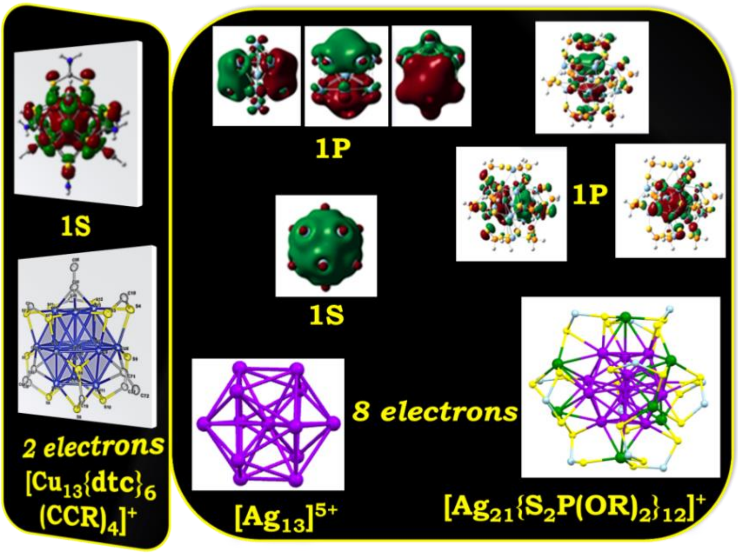

Figure 1. Structural drawings and orbital representations of two- and eight-electron superatoms

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Halogen-rich complexes of Sb, Bi and Te: halogen-bonding assisted formation of extended frameworks

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Halide complexes of p-block elements attract an interest due to their optical properties and possible applications in photovoltaics. During our studies of bromobismuthates (III), we have found that reactions of general scheme "$[BiBr_6]^{3-}$ + Br_2 +(cation)Br_x" in HBr solutions may result in anionic polybromide Bi(III) complexes where $\{Br_2\}$ units are connected with bromide lidands of Bi(III) coordination sphere via halogen bonding, yielding in $\{Br_x\}_y$-type polymeric ligands. In some cases, there also form tribromide $\{Br_3\}^-$ ligands coordinated to bismuth atoms. The structure of anionic part strongly depends on the nature of cation used in reaction. Mixed-halide complexes – polybromide-chlorobismuthates and polyodide-bromobismuthates – may be obtained by similar straightforward synthetic approach. Related polybromide- or polyidodide-bromotellurates (IV) can be obtained as well; in all cases, those consist of mononuclear $[TeBr_6]^{2-}$ and $\{X_2\}$ (X = Br, I) dihalogen building blocks. For antimony, similar reactions in presence of Br_2 proceed in more sophisticated way, usually resulting in formation of bromoantimonates (V), sometimes accompanied by polybromide units (Figure 1).

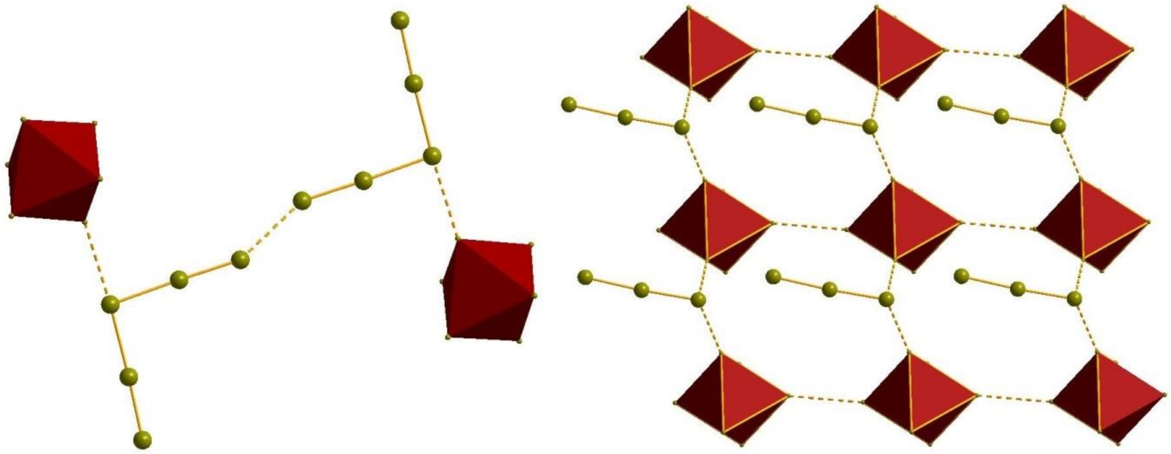

Figure 1. Polybromide-bromoantimonates (V): $\{[SbBr_6]\{Br_{10}\}]^{4-}$ **(left)** and $[SbBr_6]\{Br_3\}]^{2-}$ **(right)**

In presence of I_2, there form polyiodo-bromoantimonates (III), revealing several additional structural types, including those where Sb atom is 5-coordinated (pyramidal environment).

Acknowledgements

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Metal-organic compounds in chemical deposition of thin film materials: design, structure and transformations.

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Application of many kinds of functional materials in a form of thin films is of high interest. The development of simple, cost effective, easy scalable and universal technique of thin films production remains an important task for material sciences. Chemical deposition methods, MOCVD and MOCSD, seems to be most perspective, however their require a special design of compatible metal-organic precursors.

Here, we proposed alkaline (Na, K), alkaline earth (AEE, Ca, Sr, Ba), rare earth element (REE, La-Lu) and transition metal (Cu, Ni, Fe, Co, Mn) aliphatic carboxylates, beta-diketonates and their mixed-ligand complexes with ancillary neutral donor ligands (polyglymes and polyamines) as metal-organic precursors for MOCSD and MOCVD. The aforementioned homo- and mixed-ligand complexes were synthesized via ligand exchange reactions in either aqua or anhydrous conditions.

Reaction of metal carboxylates or beta-diketonates with ancillary donor ligands leads to formation of highly soluble or/and volatile mononuclear mixed ligand complexes. Controlled hydrolysis of mixed-ligand complexes allows us to stabilize the precursor solution in alcohols and carbonic acids. The intermediate products of hydrolysis being polynuclear hydroxoclusters, e.g. $Ln_6(OH)_8(Carb)_n(HCarb)_m$ were isolated in a form of single crystals and powders and were thoroughly studied by XRD and PDF methods (in-lab and synchrotron sources) and DFT simulations.

Designed compounds were successfully used for deposition of large variety of oxide thin films, e. g. LaLuO3, LuFeO3, LaNiO3, LaMnO3, Y2O3, La2O3, etc. Textured thin films of Tl-based superconductors were also prepared by two stage process by ex-situ thallination of polycrystalline (Ca,Ba)xCuO2 and (Ca,Sr)xCuO2 thin films on IBAD-MgO/Hastelloy-based substrate. Perfluorinated metal-organic precursors were applied for fabrication of up-converting NaYF4:Yb,Er thin films and nanoparticles for increasing the efficiency solar cells.

Acknowledgements

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Dioxygen and Copper: Insights from a Supramolecular Perspective

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Metal ions are essential to life for all organisms. More than 30% of the enzymes present one or more metal ions in their active sites. They may have a structuring role vis-à-vis the protein, they may also be key in the recognition of a substrate or of a cofactor, or they may act as catalyst for the activation of substrates and small molecules such as water or dioxygen. The knowledge of these metallic systems is an infinite source of inspiration for chemists. The lack of knowledge of their role makes them a subject of fundamental studies essential to the understanding of life.

The aim of our work is to design supramolecular systems that will mimic both, the coordination core, and the hydrophobic pocket of a metallo-enzyme active site. Our strategy relies on the synthesis of cavity-based ligands that allow the control of the metal ion micro-environment, together with the approach and the binding of guest molecules.

Since many years,[1] we have been developing systems based on the calix[6]arene scaffold, giving rise to the so-called “funnel complexes”. From the four generations of calix[6]arene-based ligands, various aspects of dioxygen activation at a mononuclear Cu(I) center have been tackled.[2] Hence, a focus on supramolecular aspects of the metal/O_2 interaction when confined in cavities will be presented, as well as new perspectives for bio-inspired catalysis.

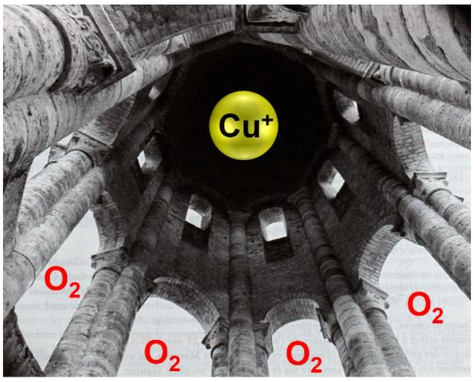

Figure 1. Supramolecular control of a metal ion embedded in a cavity open to the solvent

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Homogeneous catalysis in Ru(edta) mediated oxidation of thio-molecules

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Redox signaling is a process of utmost importance for the detection of damaged cells, as well as repair, and replacement of damaged cells inside of tissue. The Ru^{III}(EDTA) complex (EDTA^{4-} = ethylenediaminetetraacetate) is prospective in many ways and have unique features that are significant for biochemical applications. The progress of Ru^{III}(EDTA) catalyzed bioinorganic transformations in terms of revealing their mechanistic information along with the most recent advances in Ru^{III}(EDTA) chemistry concerning oxidation of redox signaling molecules involving Ru^{III}(EDTA) complexes is the subject of this talk.

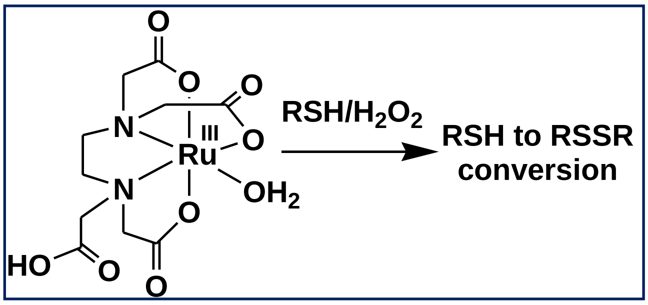

Figure 1. Ru(edta) mediated redox reactions of signaling molecules

This talk mainly covers the application of Ru^{III}(EDTA) complexes in mediating redox reactions of biologically important signaling molecules viz. H_2O_2, NO, H_2S and RSH (thiols) highlighting the our own recent studies[1] on such catalytic systems. Details of the reaction mechanisms that have been elucidated for peroxide activation, thiol oxidation and dioxygen activation involving Ru^{III}(EDTA) complexes would be discussed in this lecture.

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Myths and realities of the oxygenation chemistry of non-redox-active organometallics

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Over the past 150 years of painstaking studies on the oxygenation chemistry of organometallics with non-redox-active metal centres (^{NR}MR), a certain mythology has arisen around the mechanistic pathways of these reactions as well as factors controlling the character of their outcomes. For example, common wisdom states that the oxygenation reactions are extremely fast owing to their radical-chain nature, whilst the formation of occasionally isolated metal alkoxides results from the comproportionation reaction of a metal alkylperoxide ^{NR}MOOR and the parent ^{NR}MR compound.[1] On the contrary, our systematic studies have dispelled widely held myths and shown that despite the highly oxidizing properties of metal alkylperoxides, these species are not smoothly reduced by the parent metal alkyl complexes with the formation of metal alkoxides.[2] In turn, reactions between (L)^{NR}MR complexes and O_2 can be conducted in a highly controllable manner without liberation of an R$^\bullet$ radical and, thus, provide an access to metal alkylperoxides[3] and a vast array of other oxygenated products, *e.g.*, metal peroxides, hydroxides, and even carboxylate species.[4] The results also suggest that the isolation of such variety of products from the reaction of O_2 with (L)^{NR}MR -type complexes likely results from the O-O bond scission affording metal oxyl (L)^{NR}MO$^\bullet$ and $^\bullet$OR radicals. Moreover, our discoveries strongly have contradicted the notion that generally R$^\cdot$ radicals are the initiating species in organic reactions mediated by R_nM/air systems, and simultaneously demonstrated that oxygen-centred radical species resulting from the O-O bond homolysis in ^{NR}MO-OR species are the key intermediates responsible for the initiation process.[5] In their entirety, our results provided a basis for a new mechanism for the oxygenation of organometallics with non-redox-active metal centres, an inner-sphere electron-transfer mechanism (ISET).[6]

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Catalysis with the bidentate oxazoline ligand HEdmoz (E = O, S): high activities and new reactivities in Re and Mo catalysed Oxygen Atom Transfer.

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Oxygen atom transfer (OAT) catalysis is a ubiquitous and important reaction both in biological systems (e.g. enzymes) as well as chemical industry (e.g. epoxidation). With a background in bioinorganic chemistry and an interest in homogeneous catalysis, we are employing oxido Mo and Re complexes in a modular approach for application in both these realms of chemical science. In the last few years we further developed the chemistry of the well-established and easily modifiable bidentate *O,E*-ligand HEdmoz. This thiophenolate ligand HSdmoz enabled a novel type of Mo epoxidation catalyst with high activities, reaching TONs of 100,000 for various olefins.[1] Furthermore, the phenolate ligand HOdmoz allowed for the unusual, Re catalysed reduction of small and environmentally persistent anions (e.g. ClO_4^-) under mild conditions in aqueous solution.[2]

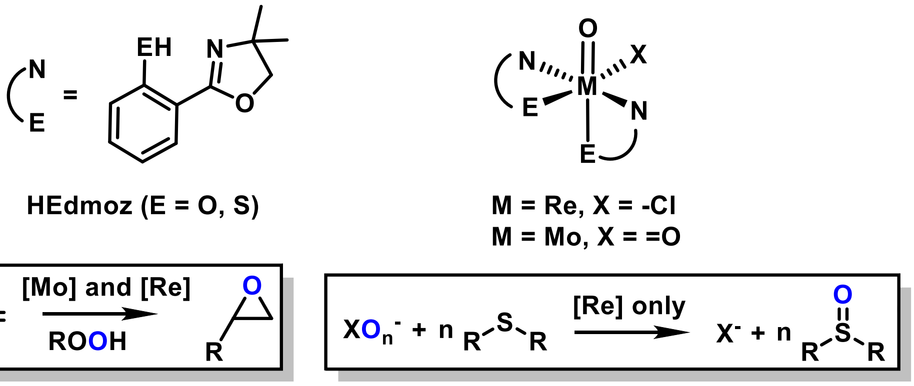

Figure 1. Examples of oxygen atom transfer reactions catalysed by Mo and Re complexes

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The mechanisms of reduction of $M(H_2O)_k^{n+}$ to form M°-nano-particles differs from that commonly assumed: The reduction of $Ag(H_2O)_2^+$ in aqueous solutions by H_2

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The mechanism formation of M°-nanoparticles, M°-NPs, via the reduction of MnLx complexes by a variety of reducing agents occurs in principle via the following steps[1]:

(1) $M_nL_x + ne^- \rightarrow M°(\text{solvated}) \rightarrow$ self-nucleation → formation of a seed → growth

Most studies do not discuss the reduction step, assuming that it involves a common electron transfer, see for example the recently published paper[2] stating that: "Because the redox potential is positive, the oxidation of Au does not occur under normal conditions" and the cited redox potential is the redox potential of $M_n{}^+{}_{aq}/M°_{(solid)}$ and not the redox potential of $Mn^+{}_{aq}/M°_{(solvated)}$, which is quite different. ($M°_{(solid)}$ – is a solid metal and $M°_{(solvated)}$ is a solvated metallic atom). Leaching of a single atom or leaching of a small cluster is suggested as an important step in a catalytic cycle, without checking the thermodynamic plausibility of such a step[3]. However, the difference in the redox potentials of the couples $M_n{}^+{}_{aq}/M°_{(solvated)}$ and $M_n{}^+{}_{aq}/M°_{(solid)}$ equals the evaporation energy of the metal/n. As a result all $M°_{(solvated)}$ are very strong reducing agents. Thus for example the redox potential of the couple $Ag°_{aq}/Ag^+{}_{aq}$ is -1.8 V vs. NHE.

DFT calculations concerning the mechanism of reduction of $Ag(H_2O)_2^+$ by H_2[4] prove that AgH_{aq} is formed as an intermediate. The AgH_{aq} agglomerize to form a variety of $\{(AgH)_n\}_{aq}$ and $\{(AgH)_nAg\}^+{}_{aq}$. H_2 release occurs only from these agglomerates. It is suggested that the first agglomeration step is $\{(AgH)_n\}_{aq} + Ag(H_2O)_2^+ \rightarrow (Ag_2H)^+{}_{aq}$. Thus M°(solvated) are not transients in the formation of M°-NPs except when very strong reducing agents, *e.g.* $e^-{}_{aq}$, are used. As clearly, $Ag°_{aq}$, and other $M°_{aq}$ are not formed as intermediates in the reduction of $Ag^+{}_{aq}$ and $Mn^+{}_{aq}$, the suggested mechanisms of nucleation and seed formation have to be revised. Therefore, one has to re-evaluate the results concerning the mechanisms of formation of M°-NPs.

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Proton-Assisted Air Oxidation Mechanisms of Iron(II) *bis*-Thiosemicarbazone Complexes at Physiological pH: a Kinetico-Mechanistic Study

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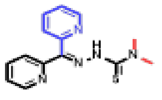
The kinetics of oxidation for different biologically-active Fe^{II} *bis*-thiosemicarbazone complexes in water at varying dioxygen concentration, temperature, pressure, and pH has been monitored. From the data collected, the thermal and pressure activation parameters have been used to interpret the operating reaction mechanisms. The oxidation reactions observed can be resolved as a single-step process, producing the expected ferric complex, with rates increasing on decreasing pH.



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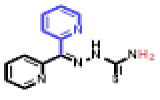

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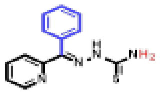

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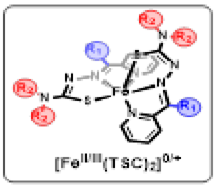

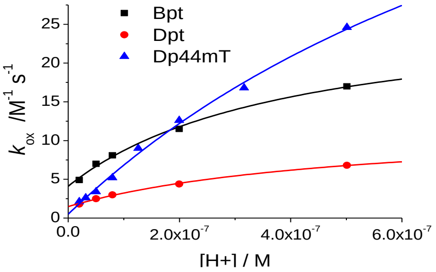

Figure 1. [H^+]-dependence of the second order rate constants (k_{ox}) for the oxidation of the Fe^{II} *bis*-thiosemicarbazone complexes (left) studied at 25 ºC

The complexes bearing terminal, non-coordinated, unsubstituted amines present a less pronounced increase, which could be due to NH···O_2 interactions taking place, as observed in previous methanol solution studies, as well as in other oxidation reactions involving these complexes.[1,2] These interactions disappear for the fully methylated terminal amine ligand, therefore increasing the effect of the pH on the rates.

Acknowledgements

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Hydrogenation and transfer hydrogenation with homogeneous Mn catalysts: the nature and role of off-cycle intermediates

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Catalytic reduction of carbonyl moieties in ketones and esters to their corresponding alcohols are fundamental to the production of high value fine-chemicals.[1] In recent years, traditional Ru and Ir catalysts have been complemented by novel first-row transition metal catalysts due to their favourable sustainability, economics, and reduced toxicity.[2,3] The practical implementation of such hydrogenation catalysts based on e.g. Fe or Mn is often hampered by their limited stability under the catalytic conditions. Understanding the catalytic and deactivation paths for such systems is required key to tailoring their properties towards enhanced and sustained catalytic performance.

Herein we report on preparation, characterisation, and detailed kinetic investigation of the catalytic performance of Mn complexes **1**, **2**, and **3** in transfer hydrogenation of ketones using practical and convenient hydrogen donors. The activity in direct hydrogenation of esters and ketons with H_2 is is also investigated. Under optimised conditions **1** enables quantitative reduction of a series of ketones at catalyst loading below 100 ppm, effectively rivalling catalyst concentrations more commonly utilised for privileged Ru-catalysts. Complexes **2** and **3** are significantly less active. Mn-P,N-complex **2** shows comparable activity to current open literature, while **3** is the least active but can be used for enantioselective preparation of chiral aryl alcohols with 75 – 87 % *ee*. The origin of the divergent reactivity of **1** – **3** was investigated with combination of high-throughput screening, kinetic stoichiometric reactivity studies, ^{1}H-NMR spectroscopy, ESI-MS and DFT calculations. Our detailed mechanistic analysis sheds light on the nature of critical reaction steps leading to catalytic turnover and on the nature and relative importance of off-cycle Mn species. Ultimately our integral studies led to the proposal of an unifying reaction mechanism for the transfer hydrogenation of ketones with the bidentate Mn-catalysts under study.

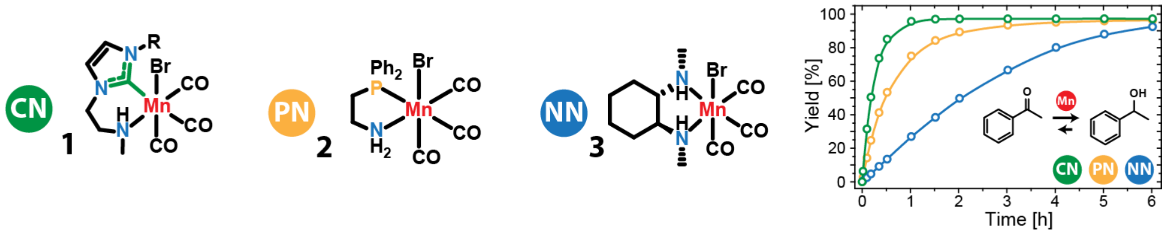

Figure 1. Transfer hydrogenation of acetophenone with isopropanol with Mn-XN catalysts.

Acknowledgements

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Computational study of NO single-site disproportionation on Fe^{II}(MOF-5)

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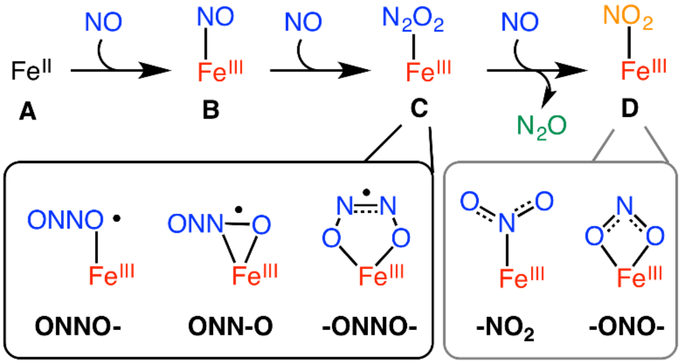
The first single-site heterogeneous catalyst to promote the disproportionation of NO into N_2O and NO_2^- was reported in 2015;[1] this material is an Fe(II)-doped derivative of MOF-5, called Fe^{II}(MOF-5), which allows the reaction to proceed smoothly under mild conditions. The available experimental data, which comprises results derived from a large number of spectroscopic techniques, allowed the identification of some species formed in the reaction course. One of the most striking results consists of the first experimental evidence of a monoanionic hyponitrite radical intermediate. This compound could be directly related to the formation of a new N–N bond between two NO units, and allowed the proposal of a plausible reaction mechanism for the overall disproportionation reaction (Scheme 1). The present work is focused in computationally explore the full reaction mechanism of NO disproportionation on Fe^{II}(MOF-5), including different Fe-bound N_xO_y species. After having determined the most favorable reaction sequence, the features of the computed structures will be compared with the experimental evidences reported in the original communication in order to assess the validity of the calculated reaction mechanism. Additionally, the computed mechanism will be applied to other analogous transition metal doped MOF-5 systems such as Mn^{II}(MOF-5) and Co^{II}(MOF-5) to check whether those materials could be employed in the disproportionation of NO.



Scheme 1. Proposed species in the Fe^{II}(MOF-5) catalyzed NO disproportionation

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Carbene-Metal-Amide Materials for Full Colour OLEDs

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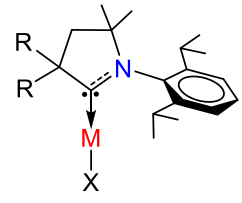
Highly efficiency red and green phosphorescent OLEDs have been succesfully commercialized, but very short operating stability remains a fundamental challenge for blue OLEDs. Phosphorescent iridium complexes retain leading position as materials for OLED technology. Organic thermally activated delayed fluorescencent (TADF) and hyperfluorescent materials are the main competitors which can be also 100% energy efficient and emit light by harvesting all excited states (singlet and "dark" triplet excited states). Here we present our materials design strategy.

We designed a new family of the materials – carbene metal amides (CMA) where donor amide and carbene acceptor moieties are linked by a metal atom.[1,2] CMA materials allow effective tuning of the energy gap between singlet and triplet excited states down to zero via the rotation of donor and acceptor about the metal-amide bond. When the gap is close to zero, facile reversed intersystem crossing process is possible, enabling highly efficient emission. We report an efficient electroluminescence (EL) from a group of mononuclear copper, silver and gold complexes. Surprisingly silver complexes show good light, oxygen/moisture and thermal stability. Silver-based materials display green emission, good photoluminescence quantum yields up to 74% while delayed emission is one of the shortest known to date for silver emitters (200–400 ns).[3] First OLEDs using silver emitting molecules as dopants demonstrate moderate external quantum efficiencies up to 11 and 14% via solution processing or vacuum deposition. Comparison and key differences with analogous champion gold (28% EQE) and copper-based carbene-metal-amides for wide colour range OLEDs will be presented. Our work demonstrates linear coinage metal complexes as a next generation materials for energy efficient OLEDs.[1–3]



M = Cu, Ag, Au
X = amide

Acknowledgements

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Synthesis and functional properties of coordination compounds based on azoles and polycyclic nitrogen heterocycles

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Poly(azolyl)alkanes are flexible neutral nitrogen ligands capable of forming both molecular coordination compounds and coordination polymers. In this contribution we report the synthesis, sorption and luminescence properties of zinc, cadmium and copper coordination polymers with bis(1,2,4-triazol-1-yl)alkanes, bis(imiazol-1-yl)alkanes, bis(pyrazol-1-yl)alkanes, 1,3-bis(1,2,4-triazol-1-yl)adamantane.

Also, the synthesis and crystal structures of new arene-ruthenium complexes with oximes of 11H-indeno[1,2-b]quinoxalin-11-one and indolo[2,1-b]quinazoline-6,12-dione (tryptanthrine), as well as their spectral characteristics and catalytic activity in transfer hydrogenation reaction are discussed.

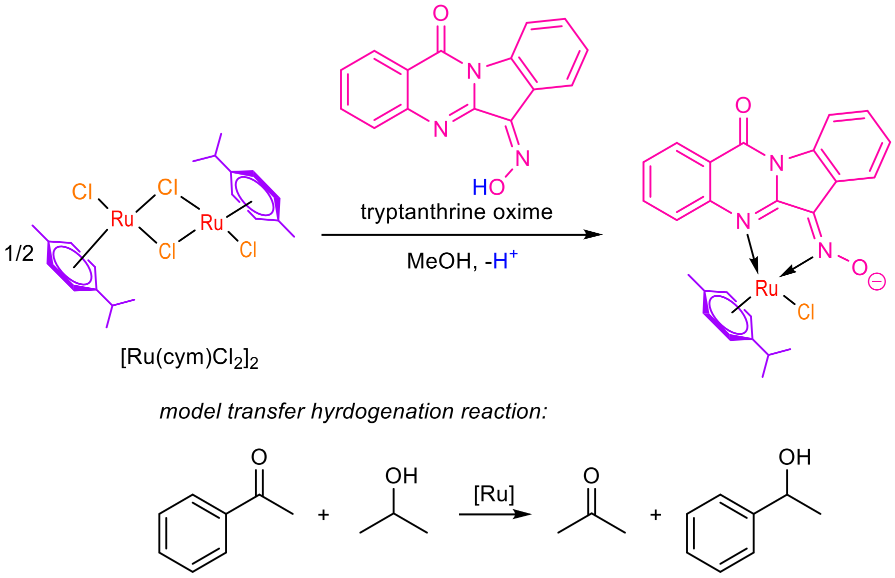

Figure 1. Synthesis and catalytic activity of arene-ruthenium complexes with tetracyclic oximes

Acknowledgements

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Group 11 metal pyrazolates complexes with N, P containing bases: structures and photophysical properties

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Copper(I) and silver(I) pyrazolates represent an important class of coordination compounds used in numerous fundamental areas, such as acid-base chemistry, metallophilic bonding, supramolecular assemblies.[1] Our contribution to the chemistry of the trinuclear macrocyclic copper(I) and silver(I) pyrazolates is the investigation of their intermolecular interactions with bases of different nature in solution and succeeding transition to the solid state.[2]

Here we report the study of complexation of copper(I) and silver(I) pyrazolates with bases of different nature. Addition interactions of the metal pyrazolates with nitrogen (phenanthroline derivatives) and phosphorus (tertiary phosphines) containing donor ligands lead to the formation of complexes of different structures. Mono-, di-, tri- and tetranuclear complexes were obtained(Figure 1).[3] Structures and luminescent properties with theoretical insight of all compounds will be discussed. Variation of ligand structure and metal atoms leads to the compounds possible to emit the light in a wide spectral range.

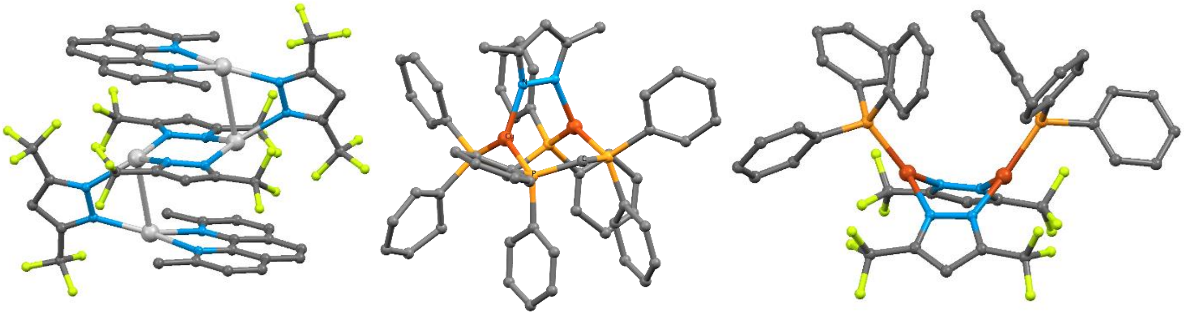

Figure 1. Different types of structures of metal pyrazolates with bases

Acknowledgements

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Bis(pyrazol-1-yl)acetato Ligands – A Toolbox

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During the last two decades bis(pyrazol-1-yl)acetato ligands have emerged to a very useful toolbox for the synthesis of bioinorganic models, organometallics and hybrid materials. Synthetic routes to various of these heteroscorpionate ligands will be reported, that differ in their substituents attached to the pyrazoles. This allows to fine tune the sterical hindrance or solubility of the corresponding complexes.[1] In another concept, additional vinyl groups attached to the pyrazole donors enable the copolymerization of the ligands or complexes with MMA or EGDMA.[2] The obtained copolymers are suitable for catalytic applications such as the Mo(VI)-oxo mediated oxygen atom transfer (OAT).[2]

Moreover, bis(pyrazol-1-yl)acetato complexes offer an organometallic chemistry almost as fruitful as that of Cp or Tp complexes. Exemplary, manganese(I) based CO releasing molecules (CORMs), artificial enzymes based on embedded ruthenium carbonyl complexes and carbon rich ruthenium cumulenylidene complexes will be reported.[3,4,5]

Furthermore, we observed a cation induced self-assembly of [12-MC-3] metallacoronates based on bis(pyrazol-1-yl)acetato ligands that allows access to nano sized complexes.[6] Also p-block metal complexes will be a topic of this talk. Finally, copper complexes bearing bis(pyrazol-1-yl)acetic acids as chelating ligands will be reported.[7] Dioxygen activation by the copper(I) complexes causes either hydroxylation of the ligand or H_2O_2 generation, depending on the substituents of the ligands.

Acknowledgements

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Ammonium peroxogermanate as a waste-free, versatile precursor for germanium compounds and nanomaterials

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High, nearly 100%, yield synthesis of ammonium peroxogermanate (APG), $(NH_4)_6[Ge_6(\mu\text{-}OO)_6(\mu\text{-}O)_6(OH)_6]\cdot 6H2O$, is presented, and its crystal structure is determined by single crystal X-ray study. It comprises centrosymmetric hexanuclear peroxogermanate anions $[Ge_6(\mu\text{-}OO)_6(\mu\text{-}O)_6(OH)_6]^{6-}$ with six μ-oxo- and six μ-peroxo groups forming negatively charged layers. The space between these layers is filled by ammonium cations and water molecules, forming a highly stable structure due to hydrogen bonding. Highly soluble macroporous amorphous germanium oxide (HSGO) is then synthesized by mild treatment of APG. The compound forms highly oversaturated metastable germanium oxide solution with a solubility of 100 g/L, over 20 times higher than the solubility of amorphous germanium oxide. HSGO solution is a versatile reagent that can react with basic and acidic reagents to give a diverse range of salts including, e.g., germanium sulfide, germanium hydrophosphate, and potassium germanate. In the absence of acid or base, the aqueous HSGO solution yields hexagonal germanium oxide under ambient conditions[1].

A peroxogermanate thin film was deposited in high yield at room temperature on graphene oxide (GO) from peroxogermanate sols. The deposition of the peroxo-precursor onto GO and the transformations to amorphous GeO_2, crystalline tetragonal GeO_2, and then to cubic elemental germanium were followed by electron microscopy, XRD, and XPS. All of these transformations are influenced by the GO support. The initial deposition is explained in view of the sol composition and the presence of GO, and the different thermal transformations are explained by reactions with the graphene support acting as a reducing agent. As a test case, the evaluation of the different materials as lithium ion battery anodes was carried out. This is the first demonstration of the peroxide route to produce peroxogermanate thin films and thereby supported germanium and germanium oxide coatings. The advantages of the process over alternative methodologies are discussed.

Acknowledgements

The financial support of Russian Science Foundation (grant 16-13-00110) is acknowledged.

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Functionalization of the surface for tailoring of hybrid nanoadsorbents

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The insight into the molecular aspects of ligand grafting and potential maximal capacity of hybrid organic–inorganic adsorbents bearing ligand monolayers as active functions, allowed to produce adsorbents with high specific affinity towards target cations or specific molecules. Materials with bi- or multifunctional surface layers possess, undoubtedly, certain advantages over the materials with monofunctional coatings. Combining hydrophobic and hydrophilic groups, reveals opportunities for creating, for example, the patchy surface with hydrophobic walls and a hydrophilic center, influencing their sorption capacity [1] or catalytic properties. Introducing aminophosphonic [2] or aminocarboxylic [3] functions on the surface allows to create adsorption materials specific for certain metal cations. The principles for design of functional ligand monolayers have been developed using insight into coordination geometry of relevant molecular compounds [2, 3]. Tailoring of functional ligand layer facilitates further attachment of larger bio-catalyst molecules. Grafting of specific enzymes, hydrolases and oxidases, along with ligands capable to efficiently adsorb metal cations open for creation of multifunctional adsorbents, combining removal of hazardous metal cations with bio-catalytic action, destroying organic pollutants [4-6].

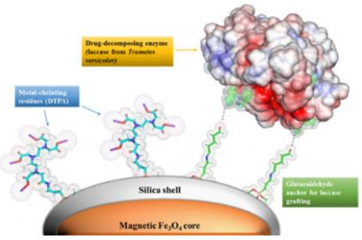

Figure 1. Simultaneous grafting of molecular recognition function and immobilization of a biocatalyst

Acknowledgements

Olle Engqvist Byggmästare Foundation Project “Magnetic nano adsorbents for complex water purification” 2017/175(180) and the FP-7 EU Program grant 309373 “Development of a Sustainable Exploitation Scheme for Europe’s Rare Earth Deposits”(EURARE) are gratefully acknowledged for the support of studies of multifunctional adsorbents.

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Molecular mono- and dichalcogenide (O–Te) complexes of samarium with bulky formamidinate supporting ligands

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Among the large variety of lanthanide complexes possessing direct bonds with a chalcogen atom, the majority are chalcogenolates or derivatives of chalcogen-substituted oxo-acids (such as thiocarbamates; *i. e.* those containing Ln–Q–E moiety, where Q denotes any chalcogen excluding oxygen, E = C or another non-metal). The purely chalcogenide or di-/polychalcogenide complexes, that is, those containing a Q_n^{2-} anion, are very rare. Indeed, this combination of soft and basic anion with strong Lewis acidic cation should be drastically unstable towards solvolysis, thus causing sufficient synthetic problems. It seems that the only reliable method of synthesis of such complexes should involve redox processes because metathesis reactions will not provide sufficient driving force for the formation of Ln–Q_n bonding. On the other hand, the oxygen-bound molecular complexes of lanthanides can be easily formed by (unwanted) hydrolysis or oxidation; *e. g.* well known samarocene oxides $[(SmCp^{x}{}_2)_2(\mu\text{-}O)]$. One of the latter, namely decamethylsamarocene oxide, have been recently found to be a valuable synthetic source of an O^{2-} anion.[1]

We attempted syntheses of molecular chalcogenides by reduction of chalcogen sources with low valent Sm complex, $[Sm(DippForm)_2(THF)_2]$ (DippForm = $HC(NDipp)_2^-$, Dipp = 2,6-diisopropylphenyl). It was shown that the reaction with monoatomic chalcogen donors, Ph_3PQ (for S and Se), or $(n\text{-}Bu)_3PTe$ leads to a mixture of both mono- and dichalcogenide complexes, [**Sm**$_2$(μ-Q)] and [**Sm**$_2$(μ-Q$_2$)] (**Sm** denotes the $Sm(DippForm)_2^+$ moiety). The ratios of mono- and dichalcogenide products can be controlled by reaction conditions, which made it possible to provide a reasonable reaction sequence. It includes the formation of a reactive radical intermediate, [**Sm**Q·], which either dimerizes or reacts with another equivalent of [**Sm**(THF)$_2$] to yield di- or monochalcogenide, respectively. Analogous reaction with Ph_3PO leads only to the coordination of phosphine oxide to the Sm centre; while the μ-oxide complex can be cleanly obtained by oxidation with Me_3NO. Attempted synthesis of the peroxide complex, [**Sm**$_2$(μ-O$_2$)], is also discussed.

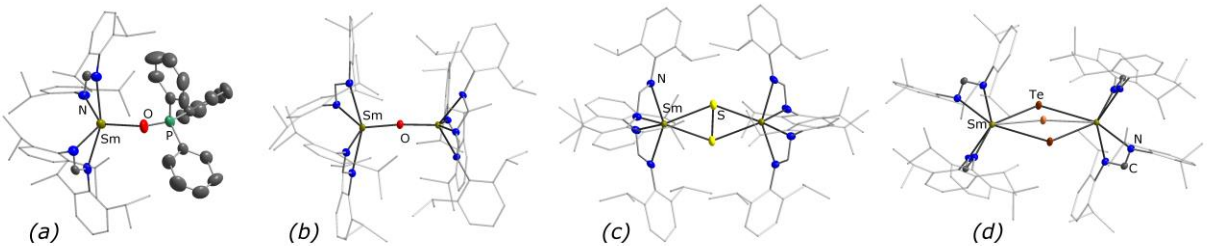

Figure 1. Molecular structures of the complexes *(a)* $[Sm(OPPh_3)]$, *(b)* $[Sm_2(\mu\text{-}O)]$, *(c)* $[Sm_2(\mu\text{-}S_2)]$, and *(d)* co-crystal of $[Sm_2(\mu\text{-}Te)]$ + $[Sm_2(\mu\text{-}Te_2)]$ (organic ligands are simplified)

Acknowledgements

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Dual-targeting Dual-action Platinum(IV) Platform for Enhanced Anticancer Acitivity and Reduced Kidney Toxicity

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In this work, we designed a novel highly efficient Pt(IV) platform to ensure targeted *in vivo* delivery of dual-action Pt(IV) prodrugs. The dual targeting was established by liposomal encapsulation of Pt(IV) complexes, thereby utilizing the enhanced permeability and retention (EPR) effect as the first stage of targeting to attain high accumulation of the drug-loaded liposomes in the tumor. After the release of the Pt(IV) prodrug inside cancer cells, a second stage of targeting directed a portion of the Pt(IV) prodrugs to the mitochondria. Upon intracellular reduction, these Pt(IV) prodrugs released two bioactive molecules, acting both on the mitochondrial and on the nuclear DNA.

Our Pt(IV) system showed excellent activity *in vitro* and *in vivo*, characterized by enhanced mitochondrial damage and complete tumor remission, respectively. Notably, marked *in vivo* activity was accompanied by reduced kidney toxicity, highlighting the unique therapeutic potential of our novel dual-targeting dual-action platform. This study provides an exciting strategy for improving on the clinical success of Pt-based anticancer drugs.

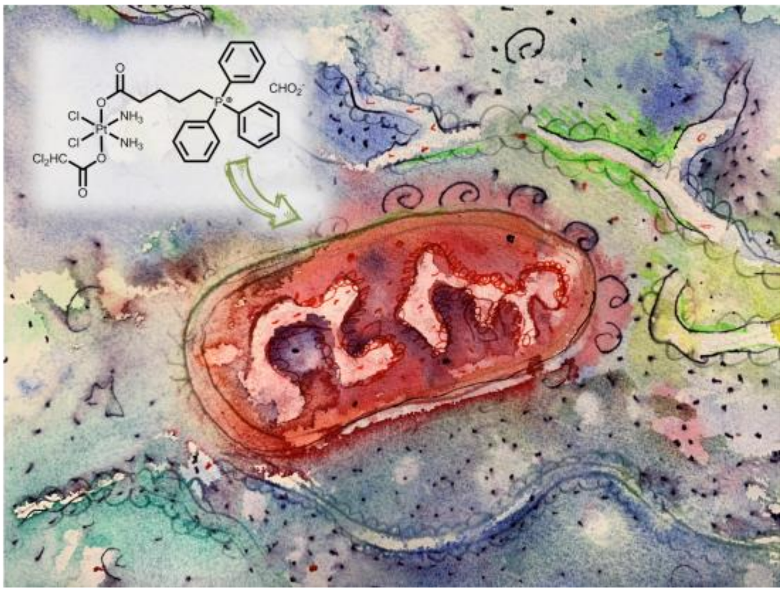

Figure 1. Targeted delivery of Pt(IV) drug to mitochondria

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Design of new nanomaterials based on cluster complexes as cellular contrast and therapeutic agents

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Multifunctional nanomaterials have attracted much attention in recent decades due to their biomedical applicability. The luminescence and therapeutic effect are very important properties of the multifunctional nanomaterials, in particular, as contrast agents for imaging and therapy of cancer. The present work introduces a facile synthetic route to embed phosphorescent cluster complexes onto silica-water interface of amino-decorated silica nanoparticles. The hybrid cluster nanoparticles have high luminescence, which remains stable within three months after their assembly. High uptake capacity of the clusters complexes derives from ionic self-assembly and coordination bonds between the complexes and ionic (amino- and siloxy-) groups at the silica surface. The coordination via amino- or siloxy-groups restricts aquation and hydrolysis of the embedded clusters, in comparison ones in aqueous solution. High potential of the hybrid cluster nanoparticles in the ROS generation was revealed by EPR measurements facilitated by spin trapping. The high positive charge and convenient colloid stability of the assembled hybrid nanoparticles are the prerequisite for their efficient cellular uptake, which is exemplified in the work by MCF-7 cell line. The measured dark and photoinduced cytotoxicity of the hybrid cluster nanoparticles reveals significant photodynamic therapy effect on the MCF-7 cancer cell line versus the normal cells. This effect is entirely due to the embedded clusters and is dependent on the chemical composition of the cluster. Thus, presented hybrid cluster nanoparticle are promising basis for further application as cellular contrast and therapeutic agents.

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Coordination with transition metals as tool for managing of macrocyclic aminomethylphosphines lability

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Macrocyclic polyphosphines exist as mixtures of diastereomers due to the high inversion barrier of phosphorus atoms in phosphines. Separation of these mixtures and isolation of individual isomers in a pure state is a serious obstacle for the use of macrocyclic phosphines in coordination and supramolecular chemistry, as well as in catalysis.[1] We have proposed the stereoselective synthesis of P_4N_2 macrocyclic aminomethylphosphines *via* the covalent self-assembly approach. The main disadvatage of macrocyclic aminomethylphosphines which restricts their further application is lability in solutions, in particular their stereoisomerisation and splitting onto medium cycles. The complexation with transition metals is well known approach to separate the steroisomeric mixtures of polyphosphines. The macrocyclic effect is a well-established tool that coordination chemistry offers to design robust complexes. The “fit” metal-ion allows to isolate the “fit” stereoisomer from isomeric mixture. Another advantage of complexation with “fit” metal-ion is possibility to prevent the stereoisomerisation. We successfully applied this approach to stopping of transformation of various isomers of 14-, 16-, 18-, 20- and 22-membered P_4N_2 aminomethylphosphine ligands in solutions (figure1).[2] It was found that isolation of each stereoisomer by complexation with transition metal strongly depends on coordination polyhedron of metal ion and organization of bonding sites of macrocyclic ligand. Moreover, metal-ion is able to change the configuration of phosphorus atoms in course of complexation to give complex with “fit” stereoisomer. The stability of formed complexes in solution to isomerization is significantly higher than that of free ligand and depends on the solvent and counter-ion.

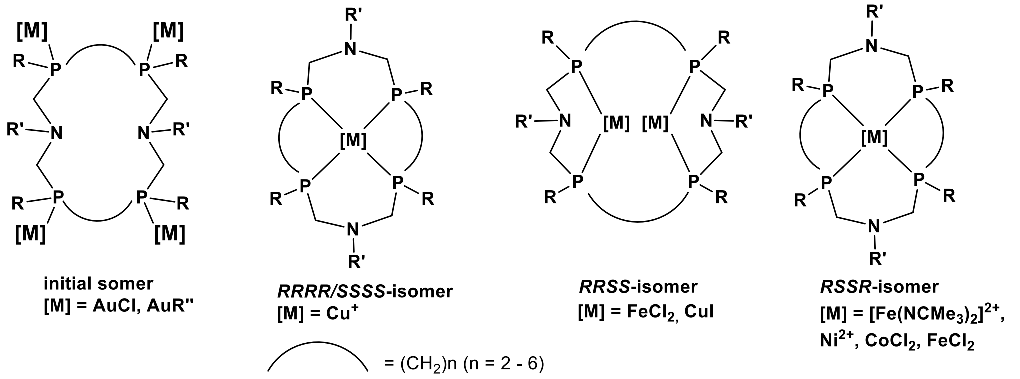

Figure 1. Type of complexes with various stereoisomers of macrocyclic aminomethlphosphine ligands

Acknowledgements

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High-valent diiron phthalocyanines: key intermediates in bio-inspired oxidation of methane and oxidative defluorination of perfluoroaromatics

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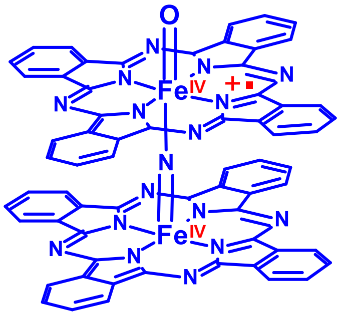
N-bridged diiron phthalocyanine and porphyrin complexes are particularly suitable for stabilization of Fe(IV)Fe(IV) complexes and can be used for generation of bio-inspired oxidizing active species by activation of H_2O_2 and peracids. For the first time, the ultra high-valent diiron oxo species (L)Fe^{IV}-N-Fe^{IV}($L^{+\cdot}$)=O (L = phthalocyanine or porphyrin) have been prepared at low temperatures in our group and characterized by cryospray MS, UV-vis, EPR and Mössbauer techniques.[1]

Ultra high-valent oxidation state



Oxidation of methane and ethane
Oxidation of alkanes
Oxidation of aromatic compounds
Oxidation of alkylaromatic compounds
Dechlorination of chlorinated compounds
Oxidative activation of aromatic C-F bonds

Figure 1. μ-Nitrido high-valent diiron oxo species and their reactivity

The highly electrophilic (L)Fe^{IV}-N-Fe^{IV}($L^{+\cdot}$)=O species exhibit remarkable reactivity.[1] In particular, oxidation of methane[2,3] and oxidative transformation of aromatic C-F bonds[4] can be performed under mild and clean conditions with high conversions and turnover numbers. μ-Nitrido diiron species show the same mechanistic features (e.g., ^{18}O labelling, formation of benzene epoxide and NIH shift in the aromatic oxidation) as the enzymes operating via high-valent iron oxo species.

Particular emphasis will be given on characterization of these species by advanced spectroscopic, labelling and reactivity studies. X-ray absorption and emission spectroscopies assisted with DFT calculations provide an insight into the electronic structure of these complexes which explains the origin of their remarkable catalytic properties.

Acknowledgements

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H_2 oxidation and proton reduction in [FeFe]-hydrogenase biomimetics: looking backwards and forwards for new synthetic mimics. The DFT viewpoint.

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[FeFe]-hydrogenases are surprising homogeneous catalysts for both H_2 uptake and production.[1] The discovery that their active site (the so-called H-cluster) focuses its reactivity in a small and unique organometallic Fe_2S_2 subunit, has triggered the inorganic chemistry community to investigate the key factors responsible for its activity so as to transfer them into the design of functional biomimetics.

Reasonably assuming that diiron compounds, resembling the two-center core of the H-cluster, could behave as active electrocatalysts with [FeFe]-hydrogenases-like reactivity, an ever-increasing number of diiron models have been synthesized in the last few decades.[2,3] Most of these compounds features a Fe_2S_2 scaffold and has been designed by modification of the bridgehead group or by replacing carbonyls and cyanides, present in the natural cofactor, with other ligands. However, despite their similarity to the H-cluster, enzyme efficiency is still far from that of Fe_2S_2 synthetic derivatives (a problem which especially affects the H_2 oxidation reactivity).[4,5]

One strategy to fill this gap could be putting more efforts in disclosing essential molecular determinants to i) ameliorate Fe_2S_2 systems performances and/or ii) reproduce key structural features of the H-cluster (which presumably underpin the high activity of the enzyme) but that are difficultly achieved by synthetic mimics. A completely different strategy, instead, would be going beyond the current structural paradigm of a "dithiolate based" mimicry through significant modifications of the metal coordination sphere, to probe their effects on reactivity and catalysis.[6] A survey on our recent DFT studies regarding the aforementioned strategies will be presented, aiming at providing hints to improve biomimicry efficiency or, at least, to unravel new reaction mechanisms

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Tuning and mechanistic insights of metal chalcogenide molecular catalysts for the hydrogen-evolution reaction

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With increased public awareness of alternative clean energy sources, the requirement for novel materials with excellent electrochemical and/or photochemical performance to meet these needs has never been so crucial. Demand for energy is predicted to double by 2050, and although this soar in demand may still be met by fossil fuels, the associated increase in CO_2 emissions could have calamitous effects on the environment.[1] Utilization of hydrogen as energy source is a viable alternative to fossil fuels and is considered as one of the ideal energy carriers of the future. However, the sustainable electrochemical production of hydrogen presents a great challenge.

Metal chalcogenides have attracted tremendous research interest as they play a fundamental role in a wide range of important energy generation and storage applications.[2] 2D transition metal and molecular chalcogenides (TMCs) present exciting opportunities in sustainable energy applications as they contain earth-abundant elements.[3] In this work we demonstrate the potential of a bottom-up approach by exploiting the well-defined structures of modular molecular progenitors that consist of Mo or W centres linked by chalcogen atoms, where it is possible to use them as transferable building blocks for the generation of supramolecular species with functionalities which can be pre-designed and finely tuned.[4]

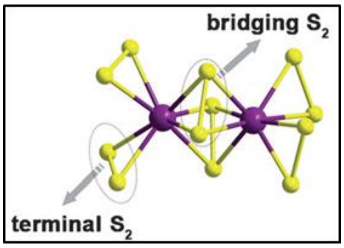

Figure 1. Representation of the $[Mo_2S_{12}]^{2-}$. Mo, purple; S, yellow

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Lanthanide Cyclobutadienyl Sandwich Complexes

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Carboyclic π-conjugated ligands such as cyclopentadienyl and cyclooctatetraene have long been used in rare-earth organometallic chemistry.[1-3] However, rare-earth complexes of dianionic cyclobutadienyl ligands, $[Cb]^{2-}$, have, until recently, remained unexplored. Our group recently reported the first rare-earth Cb complexes,[4] finding that the potassium cyclobutadienyl $[K_2\{\eta^4\text{-}C_4(SiMe_3)_4\}]$ reacted with $[LnCl_3(THF)_{3.5}]$ [Ln = Y, Dy], to yield the bis-Cb sandwich complexes $[Ln\{\eta^4\text{-}C_4(SiMe_3)_4\}\{\eta^4\text{-}C_4(SiMe_3)_3\text{-}\kappa\text{-}(CH_2SiMe_2\}]^{2-}$, with a tuck-in silylmethyl ligand arising from deprotonation of an $SiMe_3$ group (Figure 1). The dysprosium version of this compound is a single-molecule magnet (SMM).

Continuing our work on cyclobutadienyl coordination chemistry, we here present the reactivity of a wider range of rare-earth elements with the alkali metal salts $[K_2\{\eta^4\text{-}C_4(SiMe_3)_4\}]$ (M = Na, K) (Figure 1). Single-crystal X-ray diffraction revealed the reactivity to be dependent on the alkali metal, with formation of a series of iso-structural compounds $[Ln\{\eta^4\text{-}C_4(SiMe_3)_4\}\{\eta^4\text{-}C_4(SiMe_3)_3\text{-}\kappa\text{-}(CH_2SiMe_2\}]^{2-}$ (Ln = Y, La, Pr, Dy and Lu) when M = potassium. In contrast, the new sodium cyclobutadienyl reacts with lanthanide salts to yield $[Ln\{\eta^3\text{-}C_4(SiMe_3)_4(H)\}\{\eta^4\text{-}C_4(SiMe_3)_3\text{-}\kappa\text{-}(CH_2SiMe_2\}]^{2-}$ complex, which features a protonated η^3-cyclobutenyl ligand and a tuck-in silylmethyl group.

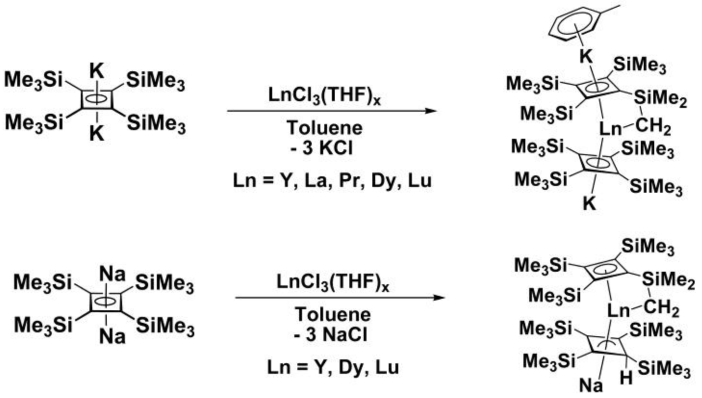

Figure 1. Diverse rare-earth cyclobutadienyl complexes

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Alkyl complexes of Ln^{II} and Ca – universal catalysts for intermolecular C−E (E = N, P, S) bond formation

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Rare earth metal σ-bonded alkyl complexes are widely investigated through last decades due to their unique reactivity in various stoicometric and catalytic reactions. Despite the large amount of known alkyl species of Ln^{III} their divalent analogues (Yb, Sm and Eu) remain scars. Alkyl complexes of heavy alkaline-earth metals (Ca and Sr), which in most cases are isostructural and demonstrate chemistry similar to Yb^{II} and Sm^{II} respectively, are also poorly investigated.

For preparation of Ln^{II} and Ca alkyl complexes the tridentate bis(2-(dimethylamino)-5-methylphenyl)methanido ligand $[2,2'\text{-}(4\text{-}MeC_6H_4NMe_2)_2CH]^-$ was used and bis(alkyl)s $[2,2'\text{-}(4\text{-}MeC_6H_4NMe_2)_2CH]_2M$ (M = Yb^{II}, Sm^{II}, Ca) were synthesized. Presence in *o*-position of the phenyl rings additional NMe$_2$-groups capable for coordination to the M^{2+} ions allows to achieve high stability of such benzhydryl species.

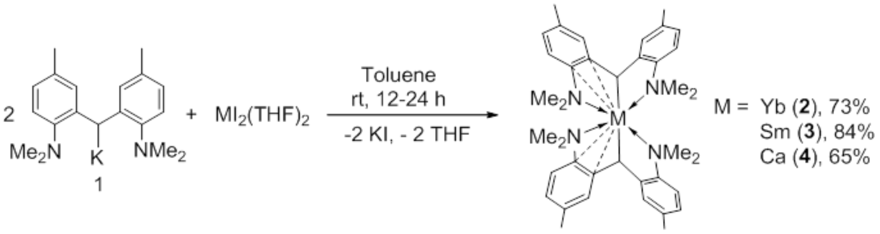

Figure 1. Synthesis of bis(alkyl) complexes $[2,2'\text{-}(4\text{-}MeC_6H_4NMe_2)_2CH]_2M$ (M = Yb^{II}, Sm^{II}, Ca)

It has been shown that $[2,2'\text{-}(4\text{-}MeC_6H_4NMe_2)_2CH]_2M$ complexes are universal catalysts for the intermolecular carbon–element bonds formation. They demonstrated high activity and selectivity in a wide range of intermolecular hydrophosphination, hydrotiolation and hydrosilylation reactions of alkenes and acetylenes.

High activity and selectivity of complexes $[2,2'\text{-}(4\text{-}MeC_6H_4NMe_2)_2CH]_2M$ made it possible to carry out the catalytic synthesis of organophosphorus polymers by double addition of primary phosphine PhPH$_2$ to bis(ethinyl) substituted aromatic substrates. Thin films of the obtained organophosphorus polymers showed photoluminescent and semiconductor properties.

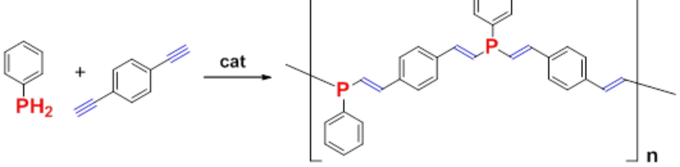

Figure 2. Preparation of conjugated phosphorous containing polymer

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Lanthanide tris- and tetrakis complexes with 4-acyl-pyrazol-5-ones – synthesis and luminescent properties

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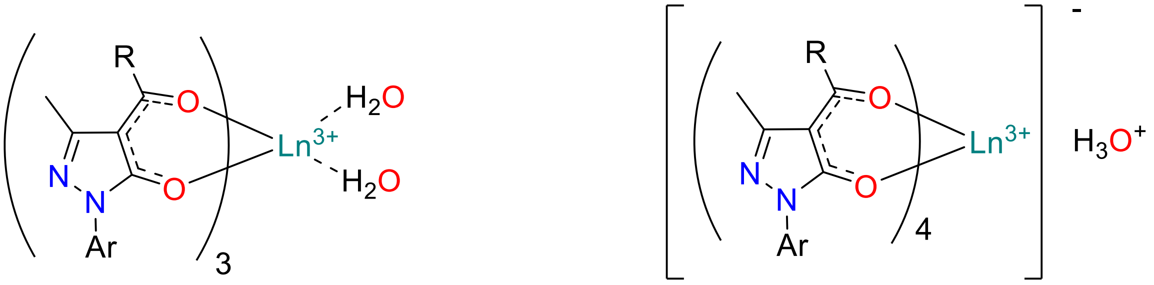
Acylpyrazolonate ligands were extensively used for the preparation of variety of complexes with *d*-elements and selected lanthanides [1]. Two main type of complexes were obtained for these ligands – neutral tris complexes (1) and anionic tetrakis complexes (2), bearing cation on the outer sphere of complex. In some cases free acids with H_3O^+ or $(H_5O_5)^+$ cations were isolated. The coordination polyhedron for Ln^{3+} in tetrakis complexes is represent by perfect square antiprism, and such environment is favorable for manifestation of SMM properties.



I **II**

Figure 1. Chemical structures of lanthanide tris (**1**) and tetrakis (**2**) complexes with acylpyrazolone ligand.

Unfortunately, known synthetic pathways to these complexes are unreliable and often led to unpredictable result. We have investigated complicated temperature-depended equilibrium between tris and tetakis species in solutions and elaborated direct pathways to both types of complexes. Besides, some aspects of crystal structures and luminescent properties of lanthanide complexes with different composition will be discussed in the presentation.

Acknowledgements

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Assembled Complexes of Mixed-Valent $\mathrm{Ru^{II}Ru^{III}}$ Carboxylates and Chrolido or Cyanidometalate Linkers

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Mixed-valent $\mathrm{Ru^{II}Ru^{III}}$ dinuclear ruthenium carboxylates are relatively new compounds among dinuclear metal carboxylates having copper acetate type dinuclear core.[1,2] We have engaged in synthetic works on metal-assembled complexes using $\mathrm{Ru^{II}Ru^{III}}$ mixed-valent complex as building blocks, because this unit generates a paramagnetc $S = 3/2$ spin state as spin source to make molecule-based magnetic materials.[2] In order to perform a systematic study, we introduced long alkyl chains for chlorido-bridged chain compounds of $\mathrm{Ru^{II}Ru^{III}}$ 3,4,5-trialkoxybenzoates, $[\mathrm{Ru_2\{3,4,5\text{-}(}n\text{-}\mathrm{C}_m\mathrm{H}_{2m+1}\mathrm{O)_3C_6H_2CO_2\}_4Cl}]_n$ (m = 2—18) and found a molecular fastener effect in magnetic interaction[3] and liquid crystalline properties.[4] Cyanidometalate ions are also useful linkers to form metal-assembled complexes. When we used diamagnetic cyanidometalates such as dicyanidoargentate(I) $\mathrm{Ag(CN)_2^{-}}$, tetracyanidonickelate(II) $\mathrm{Ni(CN)_4^{2-}}$, teracyanidopalladate(II) $\mathrm{Pd(CN)_4^{2-}}$, tetracyanidoplatinate(II) $\mathrm{Pt(CN)_4^{2-}}$, and hexacyanidocobaltate(III) $\mathrm{Co(CN)_6^{3-}}$, weak antiferromagnetic interaction was observed in the mixed-metal complexes.[2,5] On the other hand, when we used paramagnetic linkers, we found ferrimagnetic interactions in the mixed-metal complexes of $\mathrm{Ru^{II}Ru^{III}}$ carboxylate with hexacyanidoferrate(III) $\mathrm{Fe(CN)_6^{3-}}$ and octacyanidotungstate(V) $\mathrm{W(CN)_8^{3-}}$.[6] The magnetic properties will be discussed based on the crystal structures in addition to the adsorption properties for $\mathrm{N_2}$.

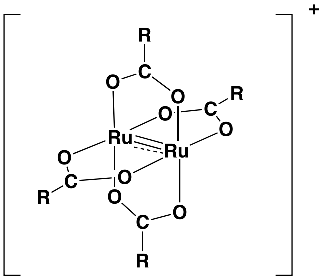

Figure 1. Dinuclear $\mathrm{Ru^{II}Ru^{III}}$ carboxylates

Acknowledgements

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Metal-Metal and Metal-Support Synergy in Heterobimetallic Catalyts Supported on Silica

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«If you look at the diverse chemistry of mononuclear complexes, imagine what the future would hold in polymetallic systems for cooperative reactivity in catalysis».[1] A current frontier area in organometallic catalysis is cooperative activity between two distinct metal centers in order to foster transformations not possible otherwise. Associating early and late transition metals in molecular edifices is thus particularly attractive, yet still underexplored.[2] In particular, most systems developed to date feature bulky ligands in order to stabilize such heterobimetallic edifices, but most of the time prevent substrates to bind across the two metals, which could explain why catalytic applications of these heterobimetallic complexes are limited at the moment.[3] Surface organometallic chemistry allows the isolation of highly unsaturated organometallic species featuring unique reactivity,[4] and is an attractive approach to overcome this limitation. Yet there is no well-established methodology allowing access to early/late heterobimetallic catalysts immobilized at the surface of a solid support to date.

In this presentation we will describe our latest results[5-6] focused on the development of new modular synthetic approaches to yield well-defined early/late heterobimetallic species featuring unsupported metal-metal bonds in solution and supported at the surface of silica materials using a surface organometallic chemistry approach. The mechanistic blueprint, synthesis, advanced characterization, structure and catalytic reactivity of these unique early/late heterobimetallic species will be presented.

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Tandem Catalysis Utilizing Methanol

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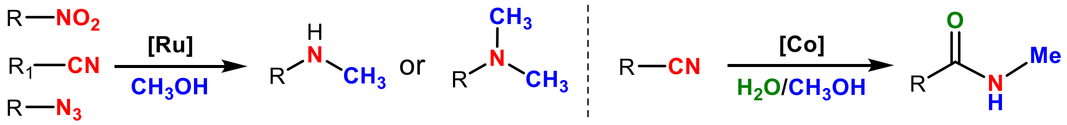
Development of a new strategy to replace multi-pot, stepwise reactions with one-pot sequential process has significant importance. Furthermore, absence of functional group protection-deprotection technique, extensive work-up, isolation and purification of the intermediates reduces the time, cost and waste formation in tandem catalytic processes. Utilization of readily available methanol as a C_1 building block is indisputably atom economical and greener strategy compare to the conventional methods which require toxic methyl halides or other strong reagents which generate stoichiometric amount of salt waste. Utilizing methanol for the first time we reported a simple air and moisture stable Ru(II) catalysed tandem transformation of various nitro compounds and nitriles to the corresponding N-methylated amines.[1,2] Notably, several N,N-dimethyl and N-monomethyl amines were synthesized selectively from organic azides using methanol.[3] This methodology was successfully applied for the one-pot reaction of bromide derivatives and sodium azide. Remarkably, cobalt catalysed tandem conversion of nitrile to N-methylated amide using water/methanol also achieved.[4] Practical application aspects and mechanistic investigation of these catalytic systems will be presented.



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Inverted Ligand Field in Organofluorine Metal Chemistry: from the Concept to C–C Bond Formation Reactions

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Fluorine is the most electronegative element in the periodic table and has therefore unique chemical properties. The formal replacement of C–H by C–F bonds in an organic molecule has a deep impact in its physicochemical properties. Thus, organofluorine compounds have found a wide range of applications as pharmaceuticals, agrochemicals, and materials. In a similar way, trifluoromethyl, CF_3, is probably the most electronegative organyl group. In fact, CF_3 shows unique behavior as a ligand, being also especially suited for stabilizing complexes in high oxidation states.

In this context, coinage metals form a singular series of homoleptic compounds with formula $[M(CF_3)_4]^-$ (M = Cu, Ag, Au) and unusually high stabilities. In particular, the copper derivative $[Cu(CF_3)_4]^-$ has been the subject of intense debate in relation with the assignment of the metal oxidation state and also concerning the role of the fluorinated ligands.[1] The origin of this controversy lies in the particular electronic structure of the complex, which has been recently described as a rare case of "Inverted Ligand Field".[2]

In this communication we will examine the electronic structures of the whole series of $[M(CF_3)_4]^-$ complexes (M = Cu, Ag, Au) and we will thoroughly determine their unimolecular decomposition pathways by the combined use of experimental (MS) and theoretical (DFT) methods. Finally, we will show how this fundamental information can be used to enable photoinduced transfer of trifluoromethyl groups to simple organic substrates.

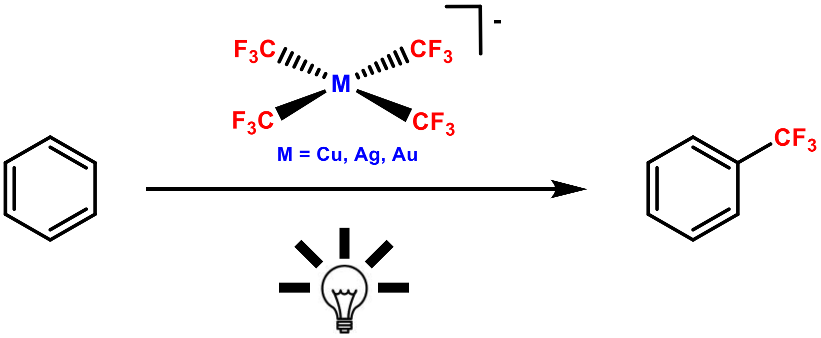

Figure 1. Light-driven trifluoromethyl transfer from coinage-metal compounds to benzene

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Support from the Spanish MINECO/FEDER (Project CTQ2015-67461-P) is acknowledged.

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Expanded ring N-heterocyclic carbenes – versatile ligands for transition metal mediated catalysis

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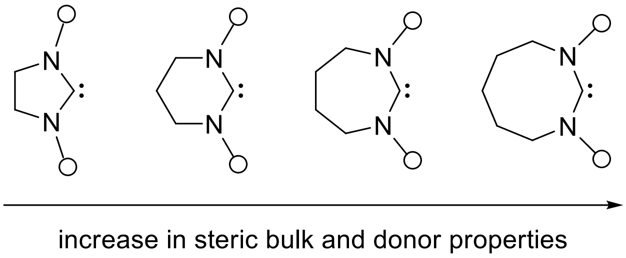
N-heterocyclic carbenes (NHCs) are highly tunable ligands for construction of transition metal complexes. The core of NHC can consist of five-, six-, seven-, and even eight-membered ring heterocycle. By varying the size of the cycle, donor and steric properties can be tuned in a wide range. Expansion of the ring leads to significant increase in electron donating properties, as well as increase in steric hindrance of the carbene. Additionally, steric and electronic properties of NHCs can be varied by changing the nature of the core heterocycle. Complexes of transition metals bearing NHCs based on mono-, di-, tri-, and tetrazoles were obtained.

In this contribution we present an overview of our results in carbene chemistry in last decade:

- Theoretical considerations of electronic structure and properties of various carbenes.
- Methods of synthesis of carbene ligands and their transition metal complexes.
- Design, synthesis and optical properties of iridium-based materials for OLED.
- Applications of Pd, Au, Cu complexes in homogeneous catalysis.



Acknowledgements

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Reactions of Amidoximes with Metal-activated Nitriles

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The chemistry of oxime species and, in particular, amidoximes is a rapidly developing field of science.[1] The increasing number of publications concerning amidoximes is due primarily to the significant properties of polyamidoxime materials with respect to the adsorption of cations of heavy metals in water.[2] In this respect, reactivity studies of the amidoxime group in the presence of a metal center is a challenging task.

In the framework of our project on metal-involving reactions of oximes, we studied coupling reactions of amidoximes with nitrile ligands at boron(III),[3] zinc(II)[4] and platinum(II)[5-7] centers. Depending on reaction conditions, the nature of the nitrile and metal centers, amidoximes can act as HO-nucleophiles (***a***),[3,4,6] HN-nucleophiles (***b***),[5,7] *C*-electrophiles[4] (***c***), and *N*-electrophiles (***d***).[7]

Such reactions lead to a broad spectrum of coordination compounds, such as zinc(II)[4] and platinum(II)[6] imino species and 1,3,5-triazapentadiene platinum complexes,[5,7] and also to organic systems, among which 1,2,4-oxadizazoles[4] (widely used in pharmacology and chemistry of materials) and carboxamides.[4] We found that amidoximes are substantially stronger nucleophiles than ketoximes, due to the significant +*M* effect of the amide group. For most of the studied reactions we established mechanisms and all these results will be presented.

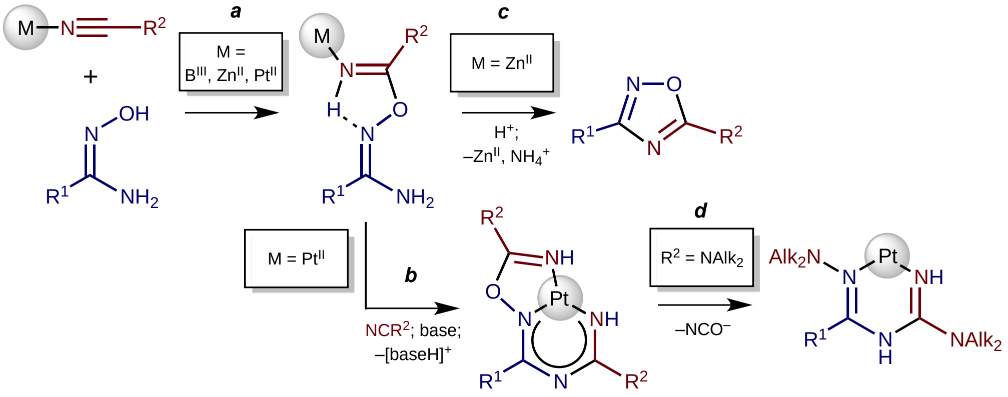

Figure 1. Reactions of amidoximes with nitrile ligands

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Russian Science Foundation is thanked for financial support (grant 17-73-20004).

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Catalytic Oxo/Imido Heterometathesis: A Novel X=N Bond Forming Strategy

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Imido complexes of early transition metals ($L_nM{=}NR$) display a rich spectrum of reactivity patterns.[1] In particular, *heterometathesis* reactions that proceed, similarly to olefin metathesis, via [2+2] cycloaddition of various multiple bonds over M=NR bond followed by cycloreversion of the corresponding metallacycle represent a promising methodology for the transformation of valuable nitrogen-containing substrates.

Our group has been particularly attracted by the synthetic potential of the *oxo/imido heterometathesis* reactions between imido complexes and different organic and inorganic oxo compounds (carbonyl and carboxyl derivatives, isocyanates, nitro and nitroso compounds, CO_2, etc.) that result in the imidation of the oxo substrate and the formation of the corresponding oxo complex. We have shown that *N*-sulfinylamines can be used to transform the oxo complex back to imido, thus rendering the reaction catalytic (Fig. 1). Search for the more active catalysts led us to the use of the Surface Organometallic Chemistry approach and designing the desired catalytic sites on the surface of solid support (Fig. 1), which appeared crucial for preventing the deactivation of the reactive intermediates and reaching high activities.

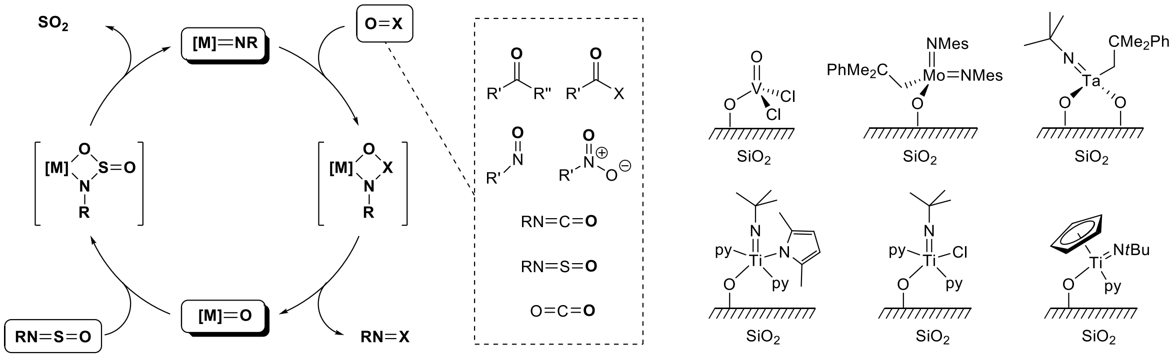

Figure 1. Catalytic cycle and selected examples of oxo/imido heterometathesis catalysts

In this report recent developments in the design of the oxo/imido heterometathesis catalysts and exploring the synthetic potential of this novel X=N bond forming strategy in our group will be discussed, focusing mainly on the most active silica-supported Ti-based systems (Fig. 1).[2]

Acknowledgements

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Centenary of transition-metal sandwich complexes: From intriguing structures to unusual spectroscopic properties

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Transition-metal sandwich compounds represent one of the most interesting and intriguing families of organometallics. Reported firstly in 1919 by F. Hein,[1] they were considered for a long time as metal phenyl □-complexes. In 1950's the sandwich structures of ferrocene and bis(benzene)chromium were discovered.[2-4] Since then, sandwich complexes have played key roles in both pure and applied organometallic chemistry. Metallocenes, bisarene derivatives and mixed sandwiches serve as excellent model molecular systems for studying the nature and properties of the metal-ligand delocalized chemical bonds. On the other hand, intense chemical interest has been focused on these complexes during last decades because of their relevance to organic synthesis, catalysis, biochemistry and material science.

Sandwich systems are of special interest to electron spectroscopy since they form the only class of organometallics revealing clearly defined Rydberg transitions in the gas-phase photoabsorption and photoionization spectra. Rydberg states can be used as intermediate levels in the multiphoton ionization (MPI) processes. The resonance enhanced MPI spectroscopy can give unique information on molecular and electronic structures of excited sandwich systems.[5,6]

Another specific feature of sandwich compounds consists in very low ionization energies making it possible to employ one-photon versions of the modern laser ionization techniques such as zero kinetic energy and mass-analyzed threshold ionization spectroscopy for studying their electronic structures.[7-8] Laser ionization spectroscopy in combination with DFT calculations provides a powerful instrument for analysis of fine ligand effects on the sandwich electronic structures. Recent DFT-supported spectroscopic results concerning the metal and ligand influence on the intramolecular interactions in sandwich complexes are given in the presentation.

Acknowledgements

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Magnetic Bistability in Coordination Nanohoops

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Molecular materials that show magnetic bistability are of interest due to their potential applications as switches, qubits and nanoscale information storage devices.[1,2,3] Single-molecule magnets (SMMs) and spin-crossover (SCO) compounds are materials that provide basic blueprints for targeting magnetic bistability, and we are interested in developing routes to both types using coordination nanohoops, a hugely under-exploited class of cycloparaphenylene ligands.[1,2,4]

In collaboration with the Jasti Group we are exploring the reactivity of a novel family of bipy−embedded polycyclic aromatic ligands, commonly called bipy[*n*]CPPs, in the presence of different metallo−organic precursors.[4,5] Their unique structures provide an array of attractive photophysical and redox properties, making them ideal candidates for our research goals. Here we present the synthesis and physical characterisation of the first reported 3*d* and 4*f* bipy[*n*]CPPs compounds (*n* = 8, 9).

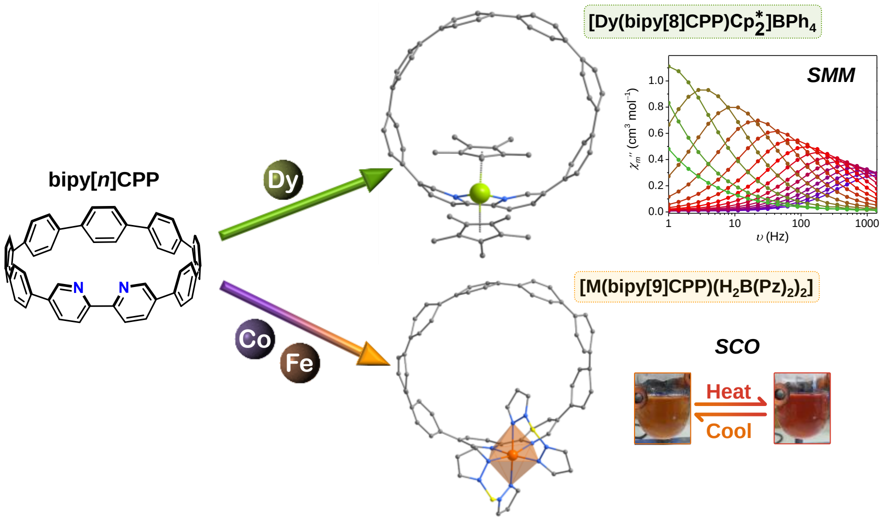

Figure 1. Design and physical properties of 3*d*/4*f*−nanohoop systems

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Trigonal prismatic complexes for molecular spintronics

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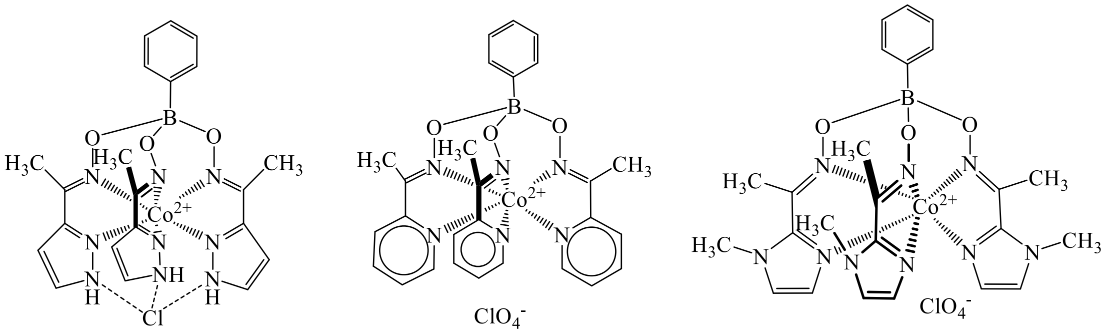
Controlling the magnetic states of individual molecules (so-called single molecule magnets, SMMs) opens wide possibilities for creating new devices for ultrahigh-density information storage. SMMs are paramagnetic *d*- or *f*-metal complexes with a large magnetic anisotropy that results in a slow magnetic relaxation between the lowest energy states with an opposite orientation of the magnetic moment. Among the SMMs based on the first row transition metal ions, cobalt(II) complexes have the largest barrier of magnetization reversal, which in the case of a two-coordinate linear cobalt(II) complex[1] approaches the theoretical limit of 450 cm^{-1}. Those linear cobalt(II) complexes (as well as their cobalt(I), iron(I) and iron(II) analogues) are, however, intrinsically unstable, making any future steps towards possible technological applications extremely challenging.

Among other coordination environments that ensure large magnetic anisotropy of the cobalt(II) ion while keeping the complex chemically stable, a trigonal prism (TP) recently emerged as an ideal geometry for new SMMs[2]. Despite several successful attempts[3] to obtain new SMMs with very large magnetization reversal barriers, these compounds are still rather unusual, as the TP geometry has been so far only provided by rather exotic rigid clathrochelate ligands.

In the talk, possible approaches toward molecular design of effective cobalt(II)-based SMMs will be discussed. Among others, coupling them with porphyrine and phatalocyanin moieties is proposed as a novel pathway to introduce them into a truly molecular spintronic device, which requires combining several magnetic centers in a single molecule with a possibility to fine tune the interaction between them.



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Unprecedented sensitivity of the temperature dependence of the magnetic properties of heterospin complexes to external pressure

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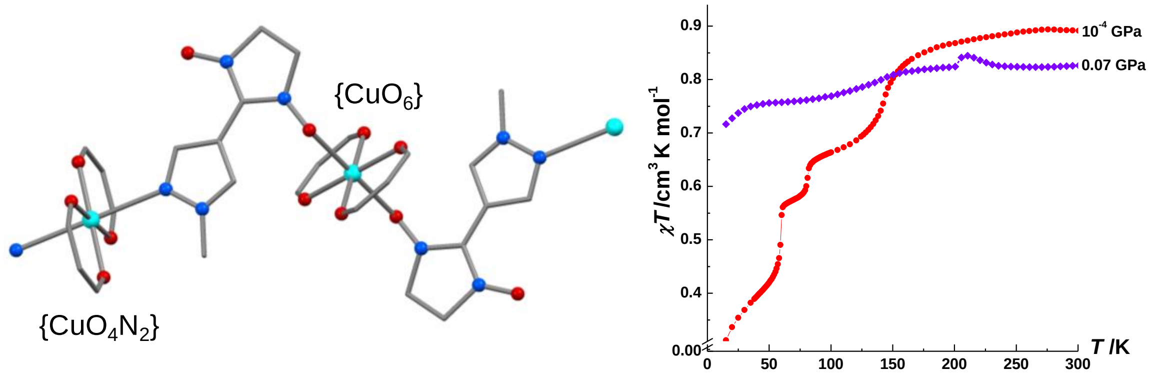
The study of the single-crystal-to-single-crystal transformation induced by external factors for the chain polymer Cu(II) complex with nitronyl nitroxide (Fig. 1a) revealed a substantial difference between the temperature-induced structural transformations at atmospheric pressure and at elevated hydrostatic pressure.

The cooling of crystals under normal conditions causes a rearrangement of the intrachain exchange clusters {>N–•O−Cu(II)–O•−N<} accompanied by a shortening of the distances between the paramagnetic centers. This changes the character of exchange interactions and generates multistage spin transitions.

An increase in the hydrostatic pressure of up to ~0.07 GPa completely changes the intracrystalline displacements of molecules relative to one another and leads to a drastic shortening in the O…O distances between the nitroxyl fragments of adjacent chains. This, in turn, significantly affects the interaction energy of the unpaired electrons of the paramagnetic centers, leads to an increase in the antiferromagnetic exchange between them, and the complete suppression of spin transitions (Fig 1b). Such a change in the intracrystalline dynamics and, as a consequence, in the magnetic behavior of the heterospin complex under elevated external pressure was detected for the first time.

This indicates that heterospin complexes of this type can function as a sensor which are highly sensitive to the variation of the external pressure.



a b

Figure 1. Chains in the structure of [Cu(hfac)$_2$L]-**II** and dependences χ_f(T) at P = 1 atm (red) and 0.07 GPa (violet) for [Cu(hfac)$_2$L]-**II** (d). The H atoms and the geminal CH$_3$ and CF$_3$ groups are omitted

Acknowledgements

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Pulse-EPR technique for studying charge transfer in adducts of lanthanide 3,5-dinitrobenzoates with aminobenzene derivatives

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One of the problems in the development of the magnetic materials on a basis of the lanthanides is the presence of diamagnetic ligands, the “spin ballast” in the complexes. Conversion of the ligands into magnetically active fragments is possible due to formation of a charge transfer complex (CTC)[1] between organic molecules that can serve as efficient electron density donors, and an electron-acceptor ligand. Recently we obtained and studied CT complexes containing binuclear Ln 3,5-dinitrobenzoates and *N,N*-dimethylaniline[2] ($[Ln_2(DNBZ)_6(DMSO)_4]\cdot x$DMA; DMA = Me_2NPh; DNBZ = 3,5-$(NO_2)_2C_6H_3CO_2^-$) or *N,N,N′,N′*-tetramethylphenylenediamine[3] ($[Ln_2(DNBZ)_6(DMSO)_4]\cdot x$TMPD$\cdot y$MeCN; TMPD = 1,4-$(Me_2N)_2C_6H_4$) which represent an original type of hybrid compounds. Supramolecular structures of those complexes are formed due to stacking interactions between donor aromatic amine molecules and acceptor DNBZ fragments. With use of diaminodurene (DAD), and 1,2-phenylenediamine (PDA), two new original series of CT adducts, $[Ln_2(DNBZ)_6(DMSO)_4]\cdot 4$DAD (Ln = Sm, Gd-Er, Y; DAD = 1,4-$(H_2N)_2C_6Me_4$) (Fig., left) and $[Ln_2(DNBZ)_6(DMSO)_2]_2\cdot$PDA$\cdot$4MeCN (Ln = Gd-Er), were obtained.

CT in the complexes was characterized by UV-vis and reflectance spectra. The CW EPR and dc magnetic measurements allowed us to unequivocally confirm paramagnetism of Y compounds with DAD and TMPD due to CT. The ESEEM technique helps to understand and attribute the presence of nonzero electron density on organic fragments involved in CT – DAD/TMPD and DNBZ (Fig., right).

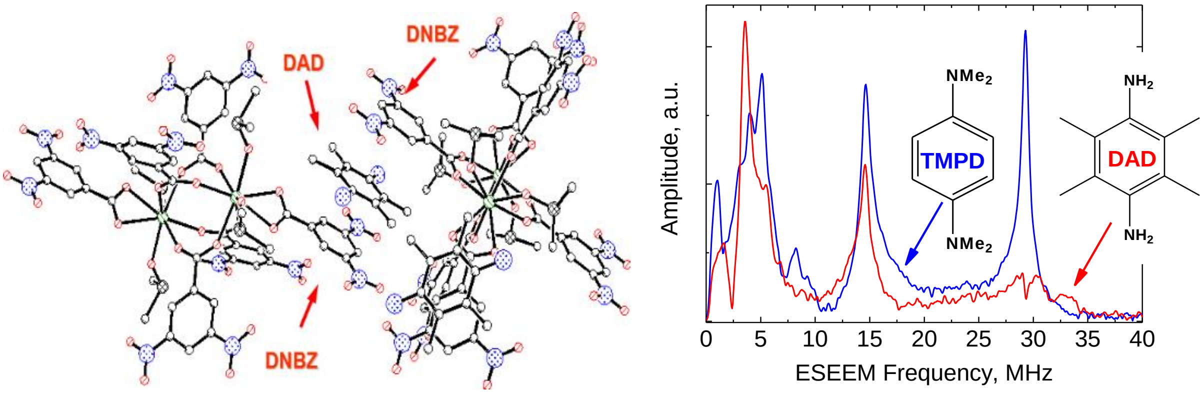

Figure. Fragment of the supramolecular structures of compounds $[Ln_2(DNBZ)_6(DMSO)_4]\cdot 4$DAD (left), and 2-pulse FT-ESEEM (right) of $[Y_2(DNBZ)_6(DMSO)_4]\cdot 4$DAD (red) and $[Y_2(DNBZ)_6(DMSO)_4]\cdot$TMPD$\cdot$2MeCN (blue) at 293K

Acknowledgements

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Porous chitin/MOF808 composite material for metal ion pollutants and dyes removal from aqueous media

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Metal-organic frameworks (MOFs) are crystalline, highly porous and three-dimensional ordered materials with well-defined cages and channels. They have recently been proposed as pollutants adsorbents from aqueous media, being the Zr-based MOFs, such as the MOF808,[1] the most widely used family.

On the other hand, chitin is the second most abundant natural polymer used in various industrial applications.[2] This polymer has a simple design, low operational cost, easy handling, high efficiency and easy regeneration ability that make it an ideal mesoporous support to generate MOF@Chitin membranes for water decontamination.

In the present study, nanoparticles of MOF808 have been synthesized via solvothermal method and different amounts (5, 10 and 15 wt.%) were incorporated into the gel solution chitin composites. The synthesized chitin/MOF808 composites were structurally, morphologically and thermally characterized by means of X-ray diffraction, Raman and IR spectroscopies, TEM and SEM microscopy and by thermogravimetric (TGA/DSC) analysis. The surface area of the composites was also determined by BET method and the potential for the removal of organic (dyes) and inorganic (metals) pollutants from aqueous media was investigated showing an improvement between 30% and 50% comparing with the pristine chitin or MOF material.

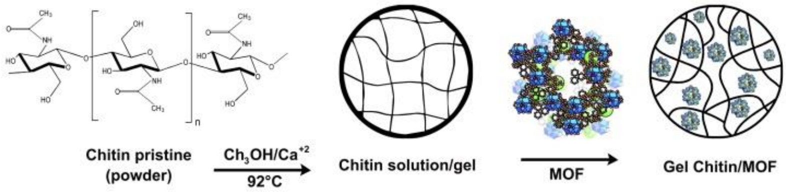

Figure 1. Schematic illustration for the fabrication of the Chitin/MOF808 composite

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Catalytic CO_2 reduction based on earth-abundant metal complexes

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The search for green and economical renewable energy sources is one of the most important challenges facing scientists in the 21st century. One of the most promising sources of carbon neutral and renewable energy comes from the reduction of CO_2 to generate various fuels, including CO, methanol or light hydrocarbons. Since CO_2 is a stable molecule, in order for this process to occur at reasonable rates with low over-potentials, an efficient catalyst is required. Ideally, the energy required for CO_2 reduction should be obtained from solar energy, since more solar energy strikes the earth in one hour than can be consumed by the whole planet in one year. Sunlight can also be first converted to electricity in photovoltaic cells, which can then be used for electrocatalytic CO_2 reduction in the presence of a catalyst.

In this presentation, we will describe our work on the design of highly active and robust homogeneous CO_2 reduction catalysts based on molecular transition metal complexes. In order to be economically viable, the complexes should be made from earth-abundant metals, such as Mn, Fe, Co, Ni and Cu.

We are interested in molecular catalysts because their structures are more well-defined and in general they have higher catalytic activity which can be readily tuned by systematic variation of the ligands.

Acknowledgements

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New chemistry of ammonia and nitrogen at metal-metal bonded diruthenium centers

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Ammonia has arisen as an attractive potential large-scale energy carrier due to its improved storage and transport over hydrogen, provoking calls to explore a potential *Nitrogen Economy*. Two fundamental technologies are needed in order to realize a zero-carbon nitrogen energy economy: (1) Ammonia synthesis from solar electricity, and (2) high-performance direct ammonia fuel cells. Both are mechanistically challenging multi-proton, multi-electron transformations, prompting investigations into the fundamental coordination chemistry and reactivity of ammonia with transition metals. We report unusual reactivity of ammonia with metal-metal bonded compounds that results in the spontaneous metal-centered reduction and oxidation of ammonia to dinitrogen. Mechanistic aspects of this chemistry will be presented as well as results on electrocatalytic oxidation of ammonia to dinitrogen.

Acknowledgements

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Heteroldianions as Precursors for Unusual Silicon and Germanium Compounds

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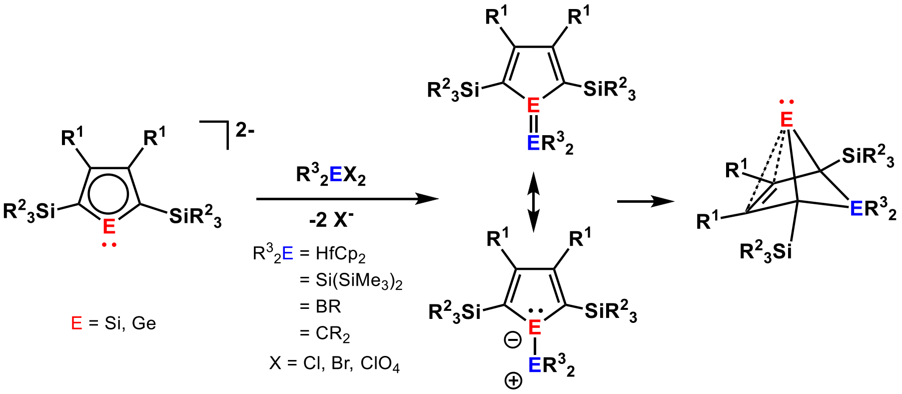
In the past, the interest in heteroldianions, **1**, was mainly driven by the possible occurrence of aromaticity in these compounds.[1] We used germole and silole dianions for the synthesis of fulvene-type heteroalkenes, **2** (Scheme 1). Controlled by the group ER^3_2, these heteroalkenes **2** are stable compounds, or they undergo a rearrangement reaction to form new type of tetrylenes **3**, which are stabilized by homoconjugation.[2-4] We will present the synthesis of compounds of the type **2** and **3** and first studies on their reactivity.[5]



1 **2** **3**

Scheme 1. Synthesis of fulvenes 2 and tetrylenes 3 from dianions 1

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Rediscovering cyclobutadiene rhodium complexes

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Diene rhodium complexes are widely used in organometallic synthesis and catalysis. At the same time, their cyclobutadiene analogs have remained obscured for a long time because there were no convenient methods for preparation of such compounds.[1] We have recently developed the first general method for synthesis of cyclobutadiene rhodium complexes from the commercially available ethylene complex $[(C_2H_4)_2RhCl]_2$ (figure 1).[2,3]

We have also discovered that the cyclobutadiene complexes can act as catalysts for various organic transformations, most notably for the selective reductive amination of aldehydes and ketones in the presence of CO as deoxygenative agent (figure 2). [2,4,5]

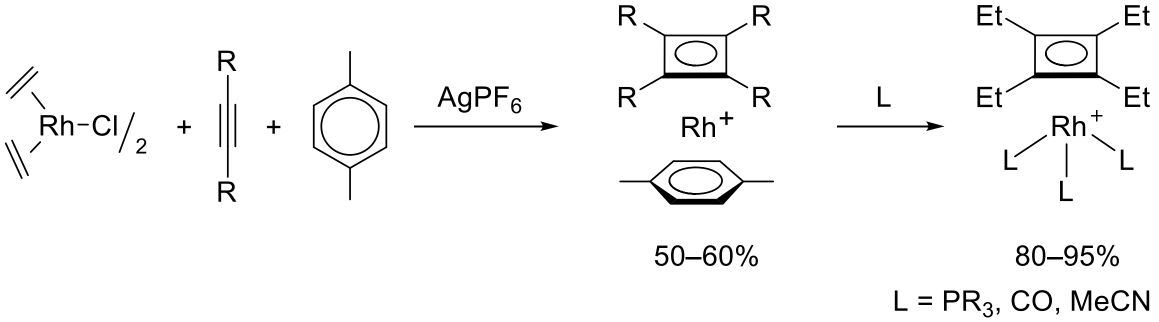

Figure 1. Developed method for synthesis of cyclobutadiene rhodium complexes

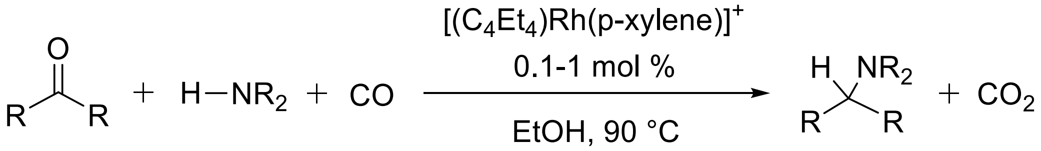

Figure 2. Catalytic application of cyclobutadiene rhodium complexes

Acknowledgements

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Luminescent transition metal carbene complexes – photophysics and photocatalysis

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Inspired by the excellent emission properties of our recently developed isocyano Re(I) diimine complexes, $[Re(CNR)_4(N–N)]^+$, $[Re(CO)(CNR)_3(N–N)]^+$, and $[Re(CO)_2(CNR)_2(N–N)]^+$,[1] we have developed a new series of charge-neutral strongly phosphorescent isocyanoborato complexes for the electroluminescent device application.[1b,1c] As these complexes display two different types of MLCT transitions {[dπ(Re) → π*(N–N)] and [dπ(Re) → π*(CNR)]}, we have also developed a new class of phosphorescent Re(I) isocyanide complexes.[2] Although many of these isocyano complexes can be used as photocatalysts or photosensitizers, their applications are limited by the instability of the isocyanide ligands toward nucleophilic attack. In this context, we have extended our work to develop new classes of luminescent metal carbene (NHC) complexes.[3] Some of these carbene complexes not only display interesting photophysical properties, they also exhibit excellent photocatalytic activity as well as CO_2 capturing properties.[4] To elucidate the electronic structures of these complexes, DFT and TD-DFT calculations have also been performed.

On the other hand, the photoredox catalysis for organic transformations using the ^{3}MLCT excited states of these complexes and the triplet emissive excited state of the cyclometalated Ir(III) complex, $[Ir(ppy)_3]^+$ will also be reported.[5]

Acknowledgements

Financial supports from RGC GRF grants (Project Nos. CityU 1106217 and CityU 11303318) from the Research Grants Council of the Hong Kong are highly acknowledged.

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Photoluminescent studies of Ln(III) complexes on pyridyltriazole basis

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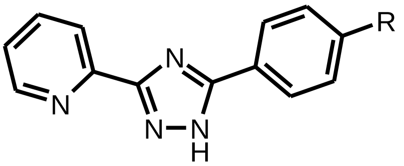
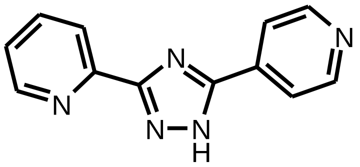
One way of overcoming the problem of faint f−f absorption transitions of the trivalent lanthanide ions to achieve bright luminescence is to surround the lanthanide with organic ligands, which harvest light, transfer the electronic energy to the metal ion, and protect it from nonradiative deactivation. Usually β-diketonates use for producing effective ionic luminescence of Ln(III) cations but quantum yields are rarely reach 50 % in this case. In the last decades several N-donor ligands effectively enchanced ionic luminescence were described. Here we describe the synthesis, structure and photophysical properties of heteroleptic trianionic lanthanide(III) complexes with pyridyltriazoles as a new N-donor sensitizers.





Title complexes were obtained by usual synthesis in solution and mechanochemistry. Coordination compounds were fully characterized by various means including elemental analysis, ESI-MS, UV-Vis, IR-spectroscopy. In the solid state, the lanthanide ions are coordinated by two pyridyltriazole ligands and the nitrate anions, which has been characterized exemplarily by X-ray crystal structure for the terbium complex.

It was found that title triazole are excellent sensitizers of ionic luminescence of Tb(III), Eu(III) and Dy(III) ions (efficiency up to 97 % for Tb, 82 % for Eu, and 23% for Dy), and satisfactory for and Sm(III) ions. The main factor determining the efficiency of luminescence is the matching of the triplet level energy of the ligand and the resonance level of the lanthanide. These results show that the pyridyltriazole ligands provide a very attractive alternative to the well know β-diketonates, carboxylates and tetrazole sensitizers for the assembly of highly luminescent, lanthanide complexes.

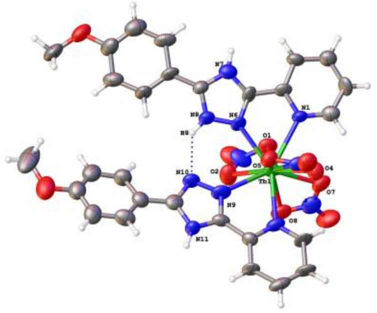


Figure 1. Structure of Tb(III) complex with 5-(4-methoxyphenyl)-3-(pyridine-2-yl)-1,2,4-triazole

Acknowledgements

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Cluster complexes of molybdenum, tungsten and rhenium with pnictogenide inner ligands

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In present study we report the synthesis and investigation of cluster compounds starting from the oxides and iodides of molybdenum, tungsten and rhenium as precursor. In the course of the work, the interaction in the systems metal oxide -X-KCN where X = S, Se, Te, P, As, and also in the system metal iodide -X-KCN where X = P, As were studied. For example, it was shown that in the case of the reaction with KCN, a new six-nuclear cluster complex of tungsten namely $[W_6(\mu_4\text{-}O)_2(\mu_3\text{-}CCN)_4(CN)_{14}]^{10-}$ with the unique ligand $(CCN)^{3-}$ is formed. Also, starting from rhenium iodide, number of Re_4 pnictocyanide rhenium cluster complexes was obtained. (Figure 1)

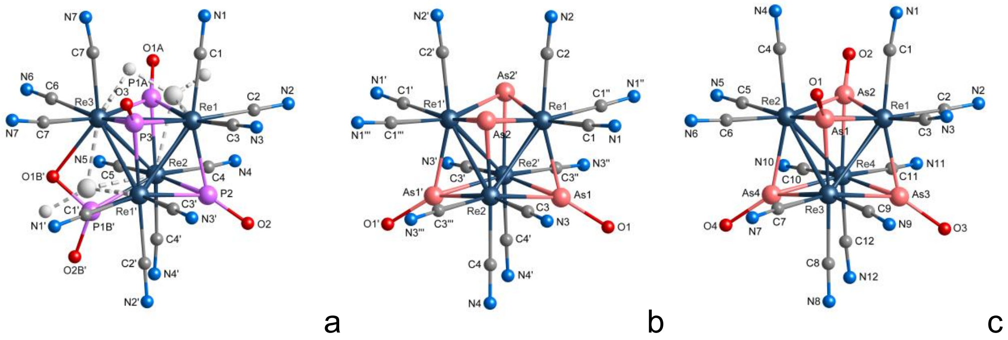

Figure 1. Structures of the cluster anions $[\{Re_4(PO)_3(PO_2)\}(CN)_{12}]^{8-}$. Dashed lines represent the alternative positions of disordered PO^{3-} and PO_2^{3-} groups (a), $[\{Re_4As_2(AsO)_2\}(CN)_{12}]^{8-}$ (b) and $[\{Re_4(AsO)_4\}(CN)_{12}]^{8-}$ (c)

Acknowledgements

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Complexes of Lewis acids and superacids

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Results of comprehensive experimental and computational studies of series of molecular complexes of Lewis acids ($SbCl_5$, $SbCl_3$, $SbBr_3$, $E(C_6F_5)_3$ (E = B, Al, Ga, In)) with Lewis bases (diethyl ether, pyridine (Py) and acetonitrile (AN)) will be presented.

Structural features of the complexes were determined by single crystal X-ray diffraction. In complexes of SbX_3 (X=Cl,Br) with Py, all Sb atoms adopt a pseudo-octahedral coordination geometry which is completed by additional Sb···X contacts shorter than sum of van der Waals radii, with X-Sb···X angles close to 180º.[1] These contacts were analyzed by electrostatic potentials, the orbital interactions and topological analysis, which indicate presence of Sb···X pnictogen bonding.

Volatility and thermal stability of complexes was studied by mass-spectrometry and automatic static tensimetry with membrane null-manometer.[4] Complexes with pyridine of 1:1 composition are generally stable with respect to dissociation of DA bond up to catalytic polymerization of pyridine.

Thermodynamic characteristics of all complexes have been computed using B3LYP and M06-2X functionals with def2-SVP and def2-TZVP basis sets. Analysis of trends in donor-acceptor (DA) bond energies, bond distances, values of charge transfer, HOMO-LUMO energies will be presented.

Complexes of novel Lewis superacid $Al\{OC(C_6F_5)_3\}_3$ with Et_2O, Py and AN were structurally characterized.[2] $Al\{OC(C_6F_5)_3\}_3$ forms weakly coordinating anions (WCA) $[XAl\{OC(C_6F_5)_3\}_3]^-$ (X=F,Cl),[2] which, according to molecular electrostatic potentials, are comparable to the classical Krossing's[3] WCA $[Al(OC(CF_3)_3)_4]^-$ (figure 1) but show more favorable crystallization behavior due to the absence of disorder.

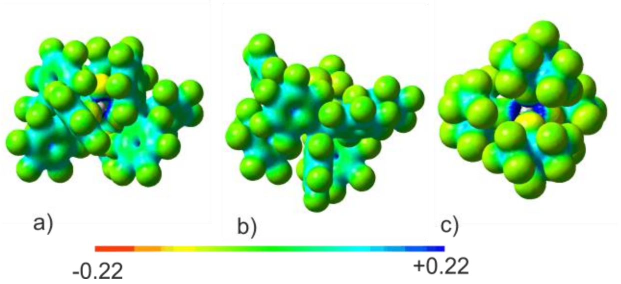

Figure 1. Projection of the calculated electrostatic potential on the 0.025 e^- $Bohr^{-3}$ isodensity surface. a) $[FAl\{OC(C_6F_5)_3\}_3]^-$; b) $[ClAl\{OC(C_6F_5)_3\}_3]^-$; c) $[Al(OC(CF_3)_3)_4]^-$. B3LYP/6-311++G(2d,2p) level of theory

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This work was supported by RSF grant 18-13-00196.

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First complexes of crown compounds with an anticrown

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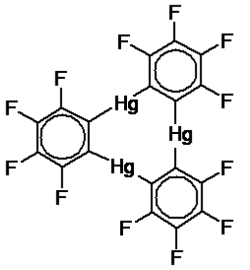

(1)

Anticrowns represent charge-reversed analogues of crown ethers and related species. Therefore, one might suggest that these macroheterocyclic antipodes containing several Lewis acidic and, correspondingly, several Lewis basic centers in the chain would readily react with each other. Indeed, we have found that the three-mercury anticrown (*o*-$C_6F_4Hg)_3$ (**1**)[1] is able to bind crown ethers with the formation of sandwich complexes. In the reaction of **1** with 1,3,5-trioxane the isolated 1:1 adduct has a cage structure. If the reactions of **1** with crown ethers are carried out in the presence of traces of water, novel sandwich adducts additionally containing coordinated molecules of H_2O are formed.[2] It has also been shown that the reactions of **1** with aqueous [18]crown-6 in methanol or acetone lead to self-assembly of unusual supramolecular aggregates in which the crown ether and water guests are sandwiched by two mutually parallel anticrown units while the solvent species are bonded to the Hg centres from the outer sides of the planes of the molecules of **1**.[3]

The interaction of **1** with thiacrowns ([9]thiacrown-3 and 1,3,5-trithiane) in CH_2Cl_2 results in the formation of complexes having sandwich and cage structures, respectively.[4]

Anticrown **1** can also form complexes with azacrowns.[5] One of such complexes, viz., the adduct of **1** with N,N,N-trimethyl-1,3,5-triazacyclohexane, has a unique double-cage structure. Interestingly, if the reaction of **1** with 1,4,8,11-tetraazacyclotetradecane (cyclam) is carried out in CH_2Cl_2, the subtraction of HCl from the solvent occurs and the sandwich complex $\{[(o\text{-}C_6F_4Hg)_3]_2Cl_2\}[(CH_2)_{10}(NH_2)_2(NH)_2]$ containing two chloride anions and the molecule of diprotonated cyclam between the planes of the anticrown species is produced. This supramolecular ensemble is the first example of a complex wherein the anionic species is simultaneously coordinated with two types of anion receptors, namely with an anticrown and protonated azacrown.

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This work was supported by the Russian Foundation for Basic Research (project code 19-03-00875).

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Simulating biological macromolecules with inorganic cations

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Biological macromolecules need to function in a physiological environment that includes not only water but also ions such as Na^+, K^+ and Cl^-. Other ions, such as Ca^{2+}, Mg^{2+} and Zn^{2+} are important for biological regulation, catalysis and for maintaining the protein structure. To understand the biological roles of these inorganic ions, it is important to study their dynamics in the biological context - how they bind proteins, move along the protein or membrane surface, and adopt new configurations during catalysis. Quite often, this is difficult or even impossible to be studied by experiments. The binding of halogens and alkali ions to macromolecules is transient, which makes it difficult to follow these ions by spectroscopic or structural methods; other biologically or environmentally important ions such as Zn^{2+} and Cd^{2+} are spectroscopically silence. Computational methods can be very useful in this regard, but limitations in accuracy or scale may limit their usability.

In this talk, I will describe some simulation studies where the dynamics of ions were followed, or when their binding preferences were estimated in a biological context. In particular, efforts to understand and overcome the limitations of modelling Zn^{2+} binding proteins[1,2] and the specificity of alkali ions to biomolecules[3,4] will be discussed. The use of energy decomposition analysis to understand ion binding and the potential of polarisable force fields will also be described.

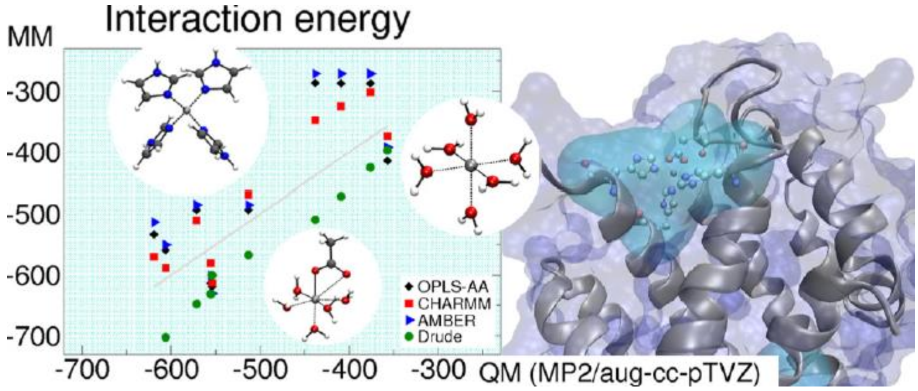

Figure 1. Comparison between interaction energies for complexes including Zn^{2+} calculated with MP2 and molecular mechanics (left) is used to estimate the accuracy of forcefields to simulate biomolecules with inorganic ions (right). Reproduced from [1]

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Lanthanide–polycyanidometallate coordination frameworks for construction of luminescent Single-Molecule Magnets

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Trivalent lanthanide ions are able to combine strong magnetic anisotropy, leading to the effect of slow magnetic relaxation, with strong photoluminescence resulting from their f-f electronic transitions. Therefore, they are great candidates for the preparation of luminescent Single-Molecule Magnets (SMMs) exhibiting magnetic hysteresis of a molecular origin which is combined with emission properties, often correlated with their magnetic nature.[1] One of the promising strategy to induce the SMM behavior consists of the incorporation of lanthanide ions into metal-organic frameworks in which selection of the molecular building blocks controls the coordination sphere of 4f metal ion, governing both photoluminescence and magnetic anisotropy.[2] We present our approach towards luminescent SMMs created within heterometallic coordination frameworks based on lanthanide(3+) ions and polycyanidometallates of transition metal ions.[3-9] In particular, we report a series of Dy(III) complexes of SMM character inserted into coordination systems of various dimensionality with metal cyanide complexes of Co(III), Rh(III), Re(V) and Cu(I), which work as diamagnetic linkers in efficient tuning of magnetic anisotropy and visible luminescence of 4f metal ion.

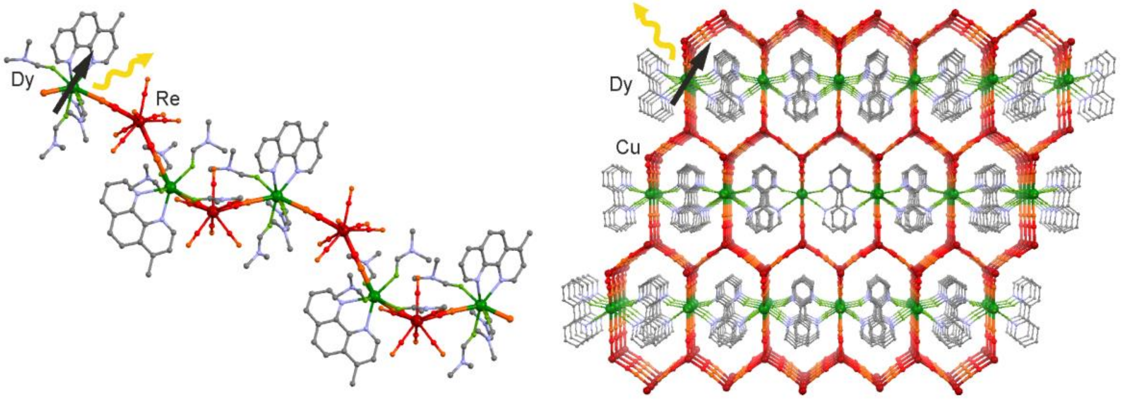

Figure 1. Bimetallic $Dy^{III}[M(CN)_x]^{n-}$ coordination systems incorporating luminescent Dy(III) SMMs

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Polyarylcyclopentadienyl complexes of lanthanides, synthesis, structure and luminescence

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Polyarylsubstituted cyclopentadienyl ligands provide an effective steric control in coordination sphere of 4-f metal cations due to bulky substituents at the cyclopentadienyl rings. Consequently, Lanthanide complexes with aryl substituted cyclopentadienyl ligands form a great variety of structures: from coordination polymers to mononuclear complexes.

We have used 1,3-diphenylcyclopentadienyl, 1,2,4-triphenylcyclopentadienyl, 1,2,3,4-tetraphenylcyclopentadienyl[1] and diphenyl-aryl-cyclopentadienyl (aryl = p-$MeOC_6H_4$-, o-$MeOC_6H_4$-, 9-$C_{14}H_9$-) ligands to design different types of neodymium, gadolinium, terbium and dysprosium complexes with different number of cyclopentadienyl ligands in the metal coordination sphere.

$$LnCl_3(THF)_3 + Cp^{Ph}K \rightarrow [(Cp^{Ph})_nLnCl_{3-n}(KCl)_x(THF)_y]$$

$$Ln = Nd, Gd, Tb, Dy \quad Cp^{Ph}\ (\text{Figure 1})$$

Aryl-substituted cyclopentadienyl ligands readily absorb electromagnetic radiation and efficiently transfer energy to the central ion of the complex Using of polyarylsubstituted cyclopentadienyl ligands (π-type ligands) allowed to develop a new approach to design "antenna-ligands" for Ln^{3+} ions to enhance the photoluminescence of lanthanide complexes. All types of the complexes have been studied by single-crystal X-ray diffraction and optical spectroscopy. All terbium an dysprosium complexes are luminescent at ambient temperature.

In the presentation, we will discuss structures and photophysical properties of different types of polyaryl-substituted cyclopentadienyl complexes of Nd, Gd, Tb, Dy.

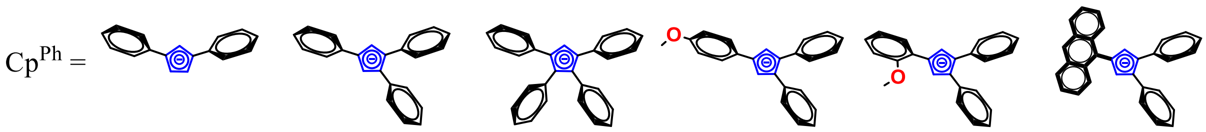

Figure 1. Different type of Cp-ligands used

Acknowledgements

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Rare earth complexes with polyanionic acenaphthene diimine ligands

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Polyanions, molecules with high negative charges and extended π-electron conjugated systems, have attracted considerable interest owing to their unique structures and electronic properties.[1] But to date only some examples of metal polyanionic organic systems, mainly alkali metals salts of carbocyclic or heterocyclic hydrocarbons, are known. Among the known polyanionic metal complexes there are only a few compounds containing the tri- and tetraanion of the redox-active, namely diiminopyridine ligand.[2] Conformational rigid redox-active ligand, 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian), being used in complexation of the main group metals as well as rare earths, gives rise to compounds with unusual structure and exceptional properties. Wherein ligand itself can take part in chemical transformations, i.e. in bonds formation–breaking and electron transfer.[3]

A series of homo- and heterometallic complexes of rare-earth elements (ytterbium, thulium, lanthanum, samarium) and calcium in which the metal atoms are bound to a tri- or tetra-anionic acenaphthenediimine ligands (dpp-bian[4] and 1,2-bis[(2,6-dibenzhydryl-4-methylphenyl)imino]acenaphthene) is obtained and structurally characterized. These compounds can be used as multielectronic reducing agents in organic synthesis, as well as precursors for mixed inorganic phases of a given composition.

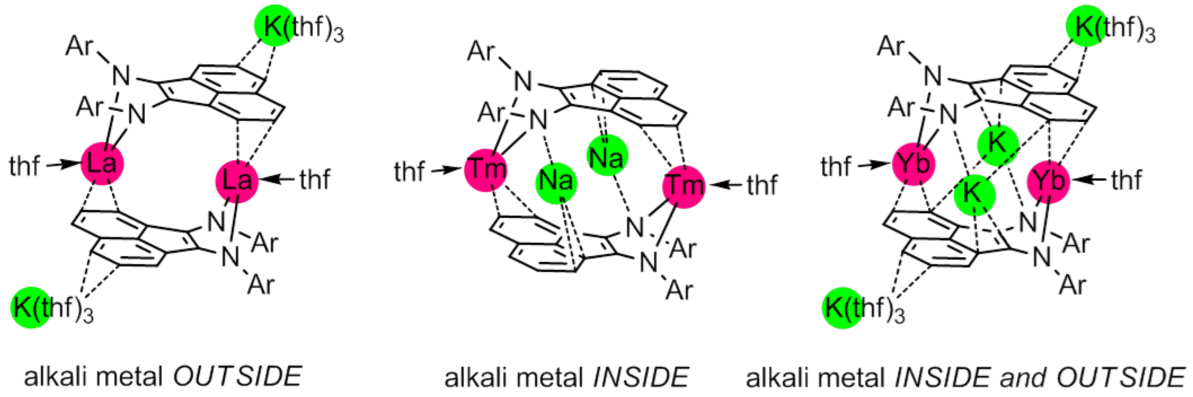

Figure 1. Lanthanide complexes with tetraanion of dpp-bian

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Lanthanide complexes with 2-(tosylamino)-benzylidene-N-(aryloyl)-hydrazones - universal luminescent materials

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D-metal complexes with 2-(tosylamino)-benzylidene-N-(aryloyl)-hydrazones possess sufficient charge mobility for their use in OLED, which makes these ligands promising for the production of electroluminescent complexes. At the same time, the preparation of f-metal complexes with these Schiff bases is a difficult task both due to the complexity of the formation of these compounds and their variable composition. Therefore, the purpose of this work was the synthesis and study of the structure of lanthanide complexes with 2-(tosylamino)-benzylidene-N-(aryloyl)-hydrazones H_2L^n in the form of single crystals and powders, as well as in solution, and their testing as photo- and electroluminescent materials.

It was shown that the composition of the product depends on the local excess of lanthanide or ligand. Thus, when $2KHL\cdot H_2O$ is added to $LnX_3\cdot 6H_2O$ (X = Cl, NO_3), the complex $Ln(HL)_2X$ is formed, containing monodeprotonated ligands HL^-. At the same time, with the addition of $LnX_3\cdot 6H_2O$ to $2KHL\cdot H_2O$, as well as by reaction between $Ln(OH)_3$ and H_2L, the complex Ln(L)(HL) is formed, containing both HL^- and L^{2-}. The interaction of Ln(L)(HL) with KOH leads to the formation of a highly soluble complex of the composition $K[Ln(L)_2](solvent)_x$.

Despite the significantly different composition, the structure of the complexes obtained is similar: according to both single crystal X-ray data and PXRD, all the complexes for which the structure is established are monomers, and the structure of the $[Ln(L)_2]^-$ anion, of the Ln(L)(HL) molecule, and of the $[Ln(HL)_2]^+$ cation is the same and does not depend on the degree of deprotonation of the ligand, nor on the substituent in its composition.

The composition and structure of the complexes in the solution was determined for benzoyl-containing ligand L^1 derivatives according to 1D and 2D ^1H NMR spectroscopy. It was established that $Ln(L^1)(HL^1)$ and $Ln(HL^1)_2Cl$ dissociate in DMSO, while the anion in the composition of $KLn(L^1)_2$ is stable. Comparison of theoretically calculated and experimentally determined pseudocontact shifts made it possible to establish the structure of the $[YbL^1(DMSO)_x]^+$ cation, as well as the orientation of the magnetic susceptibility tensor in the molecule, which can be described by the anisotropy values $\Delta\chi_{ax} = 13.1\cdot10^{-32}$ m^3, $\Delta\chi_{rh} = 1.9\cdot10^{-32}$ m^3.

OLED device based on $K[Yb(L^1)_2]$ demonstrated the record efficiency for the Yb-based OLEDs of 385μW/W. This complex was also sucessfully used for bioimaging. While Eu(L)(HL) were used as materials for luminescent thermometry and demonstrated record sensitivity (up to 17%) in the operating temperature range.

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This work is supported by RScF (17-73-10072) and RFBR (18-33-00250).

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Metal complexes as functional, structure directing building blocks

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The functional group is an immensely successful concept – possibly the defining one in preparative organic chemistry. However, it is largely lacking in inorganic chemistry. While assembly of discrete coordination complexes into more complicated structures of varying dimensionality is commonplace, the versatility of such approaches nowhere matches the synthetic control which is routine in organic synthesis.[1-4]

To some extent this can be traced to larger geometrical diversity and less well developed orthogonal reactivities in coordination chemistry. In this presentation it will be argued that a significant broadening of the palette of orthogonal reactivities available to the preparative coordination chemist can be reached by consideration of metallophilic interactions and by systematic exploitation of ligand-metal preferences as conventionally expressed by the Pearson HSAB principle. Additionally it will be argued that rules for preferred geometries of ligands bridging metal centers can serve as strong predictors for the resulting structures.

Some successes in using functional-inorganic modules in systematic bottom-up synthesis of more complicated inorganic materials will be illustrated. These range from the use of robust fluoride complexes in assembly of mixed transition metal - lanthanide complexes to the targeted synthesis of actinide chains directed by platinum-platinum metallophilc interactions.

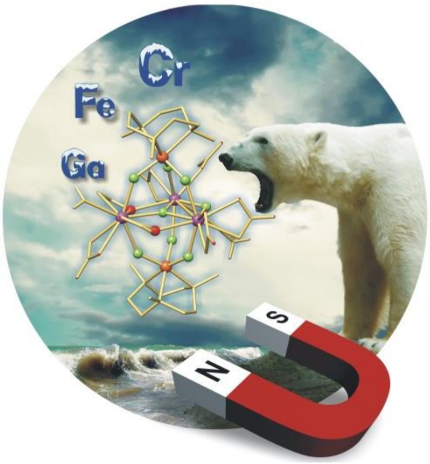

Figure 1. Using fluoride-bridging to direct nuclearity in heretonuclear transition-metal lanthanide complexes

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Exploitation of knowledge databases in the design of d-metal(II) malonates with N,N'-containing linkers

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Metal-organic frameworks (MOFs) have been attracting great interest in the past decades due to their fascinating architectures and potential application in many areas. Recent progress in reticular chemistry and data analysis of coordination polymers and MOFs allows new directions for developing the syntheses of coordination polymers with a desired mutual disposition of ligands. Knowledge databases collecting information about typical coordination modes of ligands, metal environment, occurrences of underlying nets and relations between composition of a complexes, and topology of its' underlying net allow prediction of the most abundant composition, connectivity and periodicity even for multicomponent reaction mixtures in a quantitative manner.

We applied an algorithm of such prediction to M : An^{2-} : L : H_2O mixtures (M = Co^{II}, Cu^{II}, Ni^{II}, Zn^{II}; An^{2-} = derivatives of the malonic acid; L = analogs of 4,4'-bipyridine). We found that novel compounds obtained from such mixtures realize highly probable compositions, M^{II} environment and ligand connectivities.[1] The majority of these complexes also have one of the predicted topologies of underlying nets and only few form novel networks. A series of isoreticular coordination polymers containing malonate derivatives and analogues of 4,4′-bipyridine were isolated. The effects of the precursor, either M(II) nitrate or M(II) acetate, on the composition and dimensionality of the resulting architecture are discussed.

Some of complexes containing 1,2-bis(pyridin-4-yl)ethylene were found to have close packing of ethylene groups (<4.2 Å). We succeeded in carrying out a photoinitiated [2 + 2] cycloaddition reaction for these compounds in a single-crystal-to-single-crystal manner. The 3D→3D (with network change), 3D→3D (with a constant net topology) and 0D→1D transformations of complexes were observed. Among them the first diastereoselective solid-state crossed photocycloaddition of olefins in a 3D Zn(II) coordination polymer was characterized by means of XRD.[2] A racemic mixture of two enantiomers of an unsymmetrical (1*R*,2*S*,3*S*)-substituted cyclobutane derivative was synthesized in high yield (75% based on XRD data, and 80% based on ^{1}H NMR data) without any solvents or catalysts. Overall, potential of reticular chemistry and knowledge databases in the synthesis of coordination polymers with desired disposition of ligands (particularly, photosensitive) was demonstrated.

Acknowledgements

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Energy Framework Approach to the Supramolecular Reactions

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The network of E --- E and E—π (E=Se, Te) chalcogen bonds assemble Ph_2E_2 molecules into quite stable modular 1D chain architectures, which are persistently reproduced in their cocrystals with the halogen bond (XB) donors. These relatively stable 1D Long-range Supramolecular Synthon Aufbau Modules (LSAM [1]) can be visualized and validated using energy framework approach of Crystal Explorer [2]. (see Figure 1).

Accordingly, the supramolecular reaction of Ph_2E_2 with the XB donor (*p*-DITFB) is directed to substitute less strong chalcogen or hydrogen bonded ntermolecular links between the LSAM Ph_2E_2 chains by the stronger Te---I and I---πPh XBs and can be presented as insertion of the XB-donor columnar LSAMs between the columnar XB-acceptor LSAMS, or in terms of energy frameworks – as insertion into the voids of XB-acceptor energy framework [3]. This approach allows a certain degree of cocrystal structure predictability. Persistent packing patterns found in parent and binary crystals may give an insight into the mechanism of crystallization process.

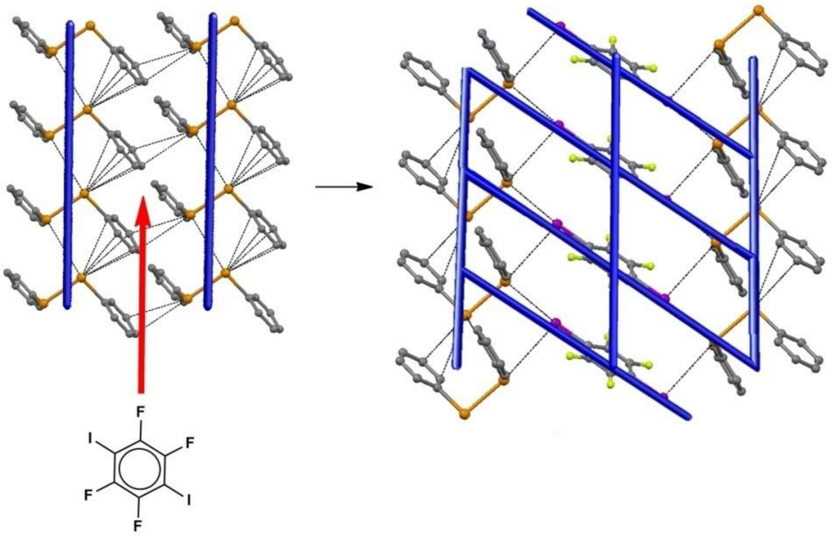

Figure 1. Supramolecular insertion of *p*-DITFB into the voids between the 1D chains in the energy framework of Ph_2Te_2

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Acceleration of the corrosion reaction of magnesium by Fenton reagents

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Magnesium alloys have attracted increased attention in recent years for a variety of applications, chief among which are alternative energy and medical implants. The use of biodegradable implants in the complex system of the human body, in which myriad reactions occur, must consider the potential effects of the body's natural chemical reactions on implant corrosion rates. The aim of this study was to elucidate the synergistic effects of pure Mg and Mg alloys on the Mg corrosion reaction with reagents that participate in the Fenton reaction. We corroborated our results with six different measurement methods (hydrogen evolution rate (HER), gas chromatography (GC), potentiodynamic polarization, inductively coupled plasma (ICP) spectrometry, Auger electron spectroscopy, (AES), and scanning electron microscope (SEM)). The results point out that the corrosion and hydrogen evaluation rates of Mg were elevated by the addition of Fenton reagents, divalent iron and hydrogen peroxide, to a saline solution. In the context of Mg-based alloy medical implant development and use, this observation is significant.

Metal complexation with alkoxyamines: a smart way to control C–ON bond homolysis and nitroxide mediated polymerization

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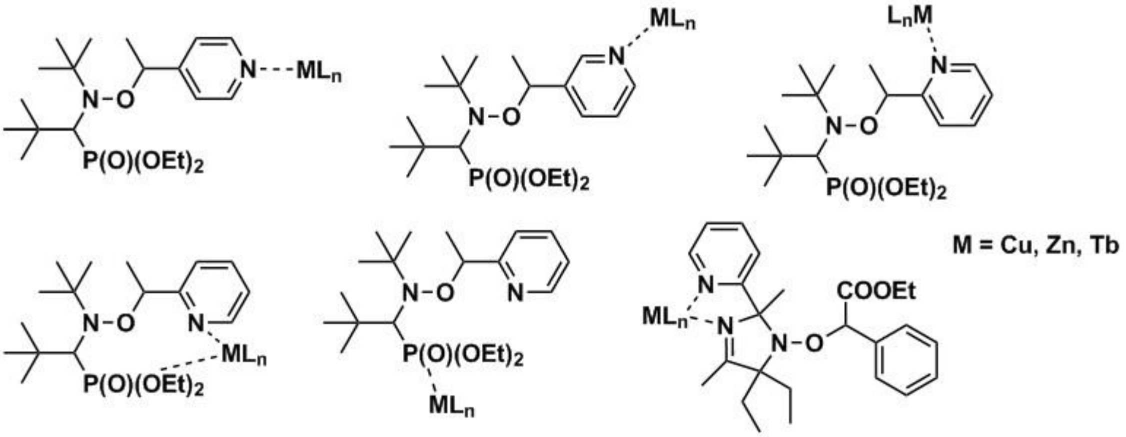
The ability of alkoxyamines to control the radical polymerization, the so-called Nitroxide Mediated Polymerization (NMP) has undergone tremendous advances and has been applied to preparation of various new and smart materials. As C–ON bond homolysis rate constant k_d is an important parameter of alkoxyamine reactivity, it is of particular importance to vary the value of k_d without alteration of the molecule's structure. In this work, we demonstrate that an alkoxyamine's homolysis can be effectively turned by complexation with a metal ions.[1-4] Namely, when complexation involves alkyl part of the alkoxyamine, the value of k_d would increase and vice versa.

Just imagine, a 54-fold decrease in the C—ON bond homolysis rate constant k_d was observed for alkoxyamines coordinated by Tb(III) cation. Such unprecedented suppress of the alkoxyamine homolysis opens new possibility for handling and storage of highly reactive alkoxyamines that could be easily activated in situ upon NMP. An opposite effect, up to 30-fold increase in k_d was revealed for alkoxyamines coordinated by Cu(II) or Zn(II) cations. Moreover, NMP performed using *in situ* generated complexes exhibit the same features as NMP initiated using beforehand prepared complexes that open up new prospects for production of hybrid materials.



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A non-innocent affair in metal-nitroxide coordination brings redox switchability and memory

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Coordination chemistry of nitronyl nitroxide free radicals has played a major role in the development of molecular-based magnetic materials. Even today, the metal-nitroxide bond remains a singular source of very diverse and original bistable magnetic systems based on d-p or f-p hetero-spin frameworks.[1-3]

Thus, with nitronyl nitroxide (NIT) wearing imidazole groups (ImHR), we synthesized lamellar compounds $\{[Mn_2(NITImR)_3]X\}_n$, in which positively charged 2D manganese-radical coordination polymers alternate with layers of anions X^-. Compounds with imidazole (NITImH) as substituents and BF_4^-, ClO_4^- and PF_6^- anions, exhibit a thermo-induced valence tautomerism (VT) by electron transfer between the manganese ions and radicals.[4] The transition is reversible with hysteresis in the room temperature domain which make these systems attractive as novel switchable materials (fig.1). Nevertheless, when adding substituents on the imidazole moiety of the radical (NITImHR; R= methyl or chlorid) we lose the valence tautomerism and the compounds behave as ferrimagnets (fig. 1), with T_C at 50 K.

In this presentation we show how magnetic properties of these systems may be tuned either by anions, substituents on radical or by pressure, and how this may be related with interaction and cooperativity between layers of Mn(II)-radical polymers.

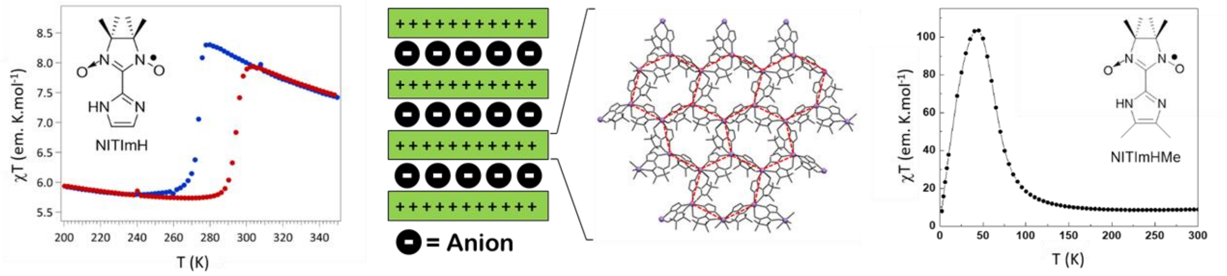

Figure 1: Temperature dependence of □T for $\{[Mn_2(NITIm)_3]ClO_4\}_n$ and $\{[Mn_2(NITImMe)_3]ClO_4\}_n$

Acknowledgements

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Synthesis and properties of nitrosyl sulfur-iron complexes – nitric oxide donors

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The 1998 Nobel Prize was awarded for the discovery of the role of nitric oxide in the body. It has been established that nitric oxide signaling occurs by binding NO to co-enzymes of heme or non-heme proteins. The active centers of non-heme proteins are Fe-S clusters that are structurally and spectroscopically identical to synthetic iron-sulfur-nitrosyl complexes of μ-S type (DNIC).

Theoretical studies have shown the non-trivial electronic structure of DNIC: the node of the DNIC molecule consists of an iron atom, two thiol-containing and two nitrosyl ligands. Despite the simplicity of the geometrical structure of the molecules, their electron structure is extremely complex. J. Enemark and R. Feltham proposed to describe these molecules by the sum of the d-electrons on the iron atom and the unpaired electrons on NO groups, because streaming of electron density from the iron atom to NO groups occurs easily and reversibly. As a result, one unpaired electron is formed on the iron-thiol-nitrosyl site, which gives a signal in the EPR spectrum with the 2.03 g-factor. DNICs can exist in binuclear paramagnetic μ-N-C-S form and diamagnetic μ-S form (Fig.1a-c). The diamagnetism of the latter occurs due to the pairing of the spins of two $Fe(NO)_2$-units along sulfur bridges (antiferromagnetic interactions).

Recently, we synthesized a water-soluble, structurally well-characterized DNIC with an acetylcysteine ligand, $[Fe_2(C_5H_8NO_3S)_2(NO)_4]\cdot 2H_2O$ of the μ-S structure type (Fig.1d). Due to the small distance between the iron atoms, the binuclear complex must be diamagnetic. Unexpectedly for us, it turned out that in the EPR spectra of crystalline samples of this complex, a signal with a 2.010 g-factor is observed, which disappears with the dissolution of the complex in water or alcohol. In this case, the dissolution of the complex in DMSO leads to an increase in the classical signal for DNIC with g-factor of 2.03. We suggested that the appearance of the signal in the EPR spectrum is caused by the crystal packing nature of molecules, in particular, the water sublattice.

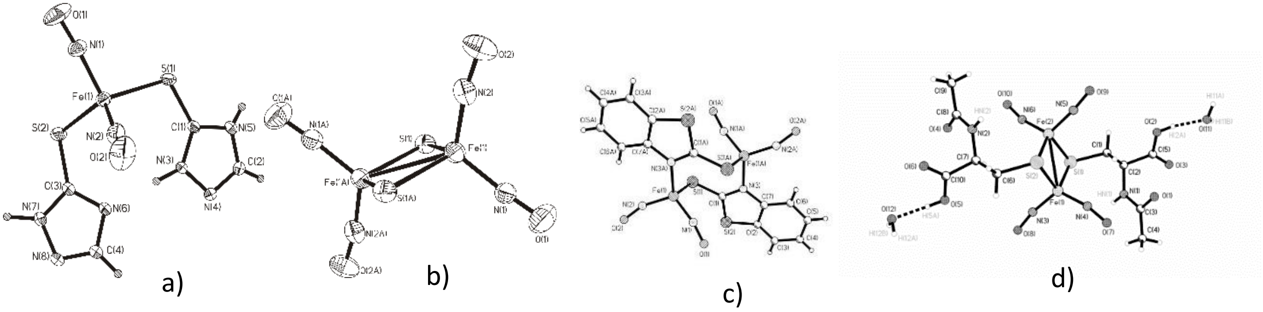

Figure 1. a) mononuclear dinitrosyl DNIC; b) Red Roussin's Solt – DNIC of μ-S structure type; c) DNIC with 2-mercaptobenzthiazole of μ-N-C-S type; d) DNIC with acetylcysteine.

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Visible Light Driven Generation and Reactivity of Stable Bis-Cyclometalated Pt(IV) Hydrides

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Although photophysical studies on Pt(II) complexes with cyclometalated 2-arylpyridines are abundant,[1] the exploitation of their excited-state reactivity has only been marginally addressed. Pioneering works explored photooxidative addition reactions of alkyl halides to complexes of this kind,[2] and more recently they have been used as photocatalysts in fluoroalkylation reactions of alkenes and alkynes.[3] We recently discovered a photoinduced C-H oxidative addition reaction that occurs upon visible light irradiation of methyl complexes of the type *cis-N,N*-[PtMe(C^N)(N^CH)], where N^CH represents an *N*-coordinated 2-arylpyridine and C^N is the corresponding cyclometalated ligand, resulting in unstable Pt(IV) methyl hydride intermediates [PtMe(H)(C^N)$_2$] that reductively eliminate methane to give *cis*-[Pt(C^N)$_2$].[4] This novel photochemical reactivity pattern could open the way to visible light driven C-H activation/functionalization processes mediated by Pt complexes. However, the reported system is not amenable for further developments because the Pt(IV) methyl hydrides are highly unstable, precluding any subsequent reactions with organic substrates.

In search for alternative platforms for photoinduced C-H activations, we have examined the photoreactivity of *cis-* and *trans-N,N* isomers of Pt(II) complexes of the type [PtCl(C^N)(N^CH)]. The *trans-N,N* isomers proved photostable under visible light irradiation in solution, but some derivatives with a *cis-N,N* configuration cleanly gave stable Pt(IV) hydrido complexes [PtH(Cl)(C^N)$_2$], which could be structurally characterized. Insight into the excited-state reactivity of *cis-N,N*-[PtCl(C^N)(N^CH)] complexes has been gained from TDDFT calculations and reactivity studies on [PtCl(H)(C^N)$_2$], including insertion of unsaturated molecules into the Pt-H bond, have been carried out.

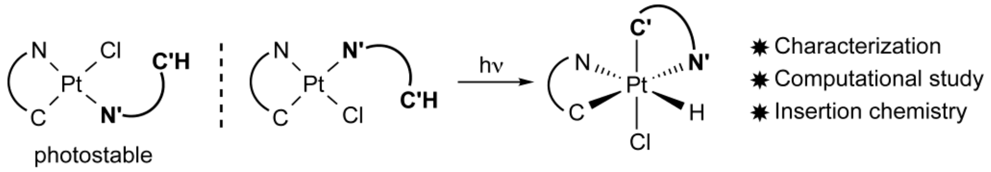

Figure 1. C^N: Cyclometalated 2-arylpyridine.

Acknowledgements

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A highly sensitive ethene sensor based on copper(I) coordination compounds

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Ethene is a highly diffusive and relatively unreactive gas that induces ageing responses in plants in concentrations as low as parts per billion. Monitoring concentrations of ethene is critically important for transport and storage of food crops, necessitating the development of a new generation of ultra-sensitive detectors. In this presentation I will show that simple coordination compounds of copper(I) effectively bind ethene. Functionalization of graphene with these copper complexes creates sensors, with which biologically-relevant concentrations of ethene down to ppb levels can be detected.[1] Chemically-induced dipole fluctuations in the copper compounds cause subtle field effects in graphene as they bind or release ethene. By exploiting these changes in the dipole moments we are able to track the reaction and provide insight in the sensing mechanism.

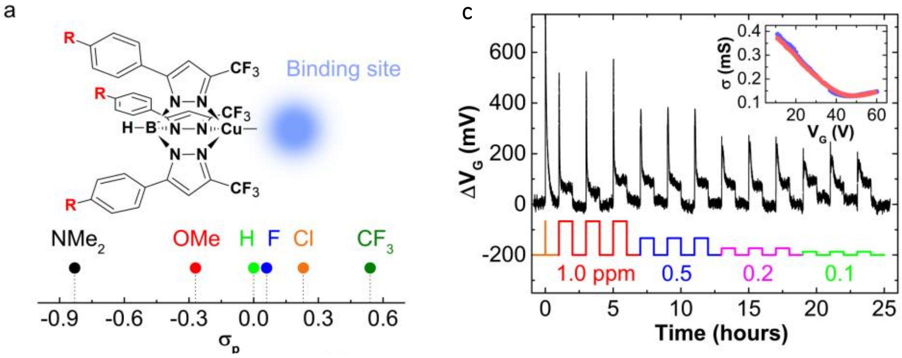

Figure 1. Chemical structure of the sensitizer molecules (left) and baseline-corrected trace of the response of a GFET (*R* = F) exposed to various concentrations of ethene gas (right).

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Materials for light activated metal oxide gas sensors

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Gas sensors based on semiconductor oxides have the necessary sensitivity to detect the main air pollutants at the level of the corresponding threshold values, however, the required working temperatures are quite high. The need for heating significantly increases power consumption (PC), which is the main restriction for coupling gas sensors with portable and mobile devices. To reduce PC, we propose to use the photoactivation by UV or visible light instead of thermal heating.

Metal oxide semiconductors (MOS) absorb UV light, which energy corresponds to the band gap. The influence of UV radiation on the receptor function of wide-gap MOS is determined by the following factors: (i) increasing the concentration of charge carriers in a semiconductor matrix; (ii) change in the type and concentration of surface adsorption centers; (iii) formation of highly active radical particles. The increase in sensor response under UV light is achieved with the use of active photocatalysts (e.g. nanocrystalline TiO_2) which exhibit high activity in the oxidation of various (both organic and inorganic) compounds at room temperature.

A further reduction in sensor PC is possible by using photoactivation with visible light. The main challenge that has been identified for light activated sensors is their low optical response. To increase the optical sensitivity and to shift it towards longer wavelengths, it is necessary to create special defects in the semiconductor matrix or introduce the sensitizers that provide light absorption in the visible region. As such sensitizers, A^2B^6 and A^3B^5 semiconductor quantum dots as well as organic dyes – macrocyclic and heterocyclic transition metal complexes can be used[1-3].

In this work we discuss the possibility of low temperature detection of NO_2, CO, NH_3, HCOH with light activated semiconductor gas sensors. The activation of the sensor signal under light occurs through different mechanisms. Thus, for the oxidizing gas (NO_2), which compete with oxygen for the same adsorption sites, the photogeneration of electron-hole pairs plays a major role in the process of photodesorption. In contrast, to detect reducing gases (CO, NH_3), the presence of chemisorbed oxygen on the surface of MOS is necessary. In this case, the light activation of sensor signal consists in the unpinning of the MOS Fermi level. For volatile organic compounds (HCOH) the photolysis of analyte molecules on the surface of MOS facilitates their subsequent oxidation with chemisorbed oxygen, leading to a change in conductivity of the semiconductor.

Acknowledgements

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Multifunctional silica nanoparticles as efficient contrast agent

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Design of nanoparticles able to generate remote influence on neuronal activity constitutes an important challenge in nanotechnology and bioengineering. The report introduces both synthesis and *in vitro* biological behavior of dual magnetic-fluorescent silica nanoparticles. The amino group-decoration of silica nanoparticles (d=78 nm) provides their efficient internalization into motoneurons, which is visualized by red fluorescence arisen from $[Ru(dipy)_3]^{2+}$ complexes encapsulated into a silica matrix. The internalized nanoparticles are predominantly located in the cell cytoplasm as it is revealed by confocal microscopy imaging. Magnetic function of the nanoparticles resulted from inclusion of 17 nm sized superparamagnetic iron oxide cores into the silica matrix provides their responsivity to magnetic fields. The fluorescent analysis revealed the “on-off” switching of Ca^{2+} influx under the application and further removal of permanent magnetic field. The result for the first time highlights moving of the nanoparticles within the cell cytoplasm in permanent magnetic field as a promising tool to enhance neuronal activity of motoneurons.

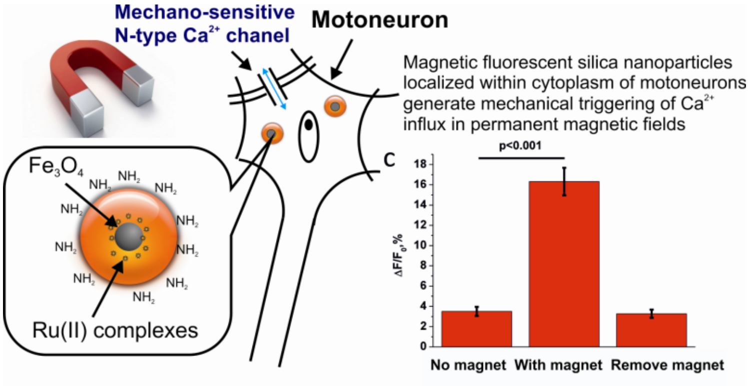

Figure 1.

Acknowledgements

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Supramolecular assembling of sandwich crown-phthalocyaninates of paramagnetic lanthanides studied by NMR spectroscopy

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SMM properties of sandwich Tb(III) phthalocyaninates attract focused attention and many efforts are made to decrease the rates of magnetization relaxation and increase spin-reversal barriers. While the exact characteristic of these properties are found by SQUID magnetometry, first insights into magnetic properties of these complexes can be obtained by routine NMR measurements.[1]

For example, ^{1}H-NMR characterization of heteroleptic Tb(III) trisphthalocyaninate **1** bearing terminal crown-substituted ligand (Figure 1a) evidenced of strong lanthanide-induced shifting of resonance signals associated with large axial magnetic anisotropy. Further assembling of **1** into the cation-induced dimer $\mathbf{1_2{\bullet}4K^+}$ resulted in significant shifts of resonance signals even for protons remote from sites of supramolecular dimerization (Figure 1b). This observation let us expect efficient magnetic interaction between all four Tb^{3+} ions within the supramolecular dimer which in turn might lead to enhancement of its magnetic properties in comparison with the monomeric complex **1**.[2]

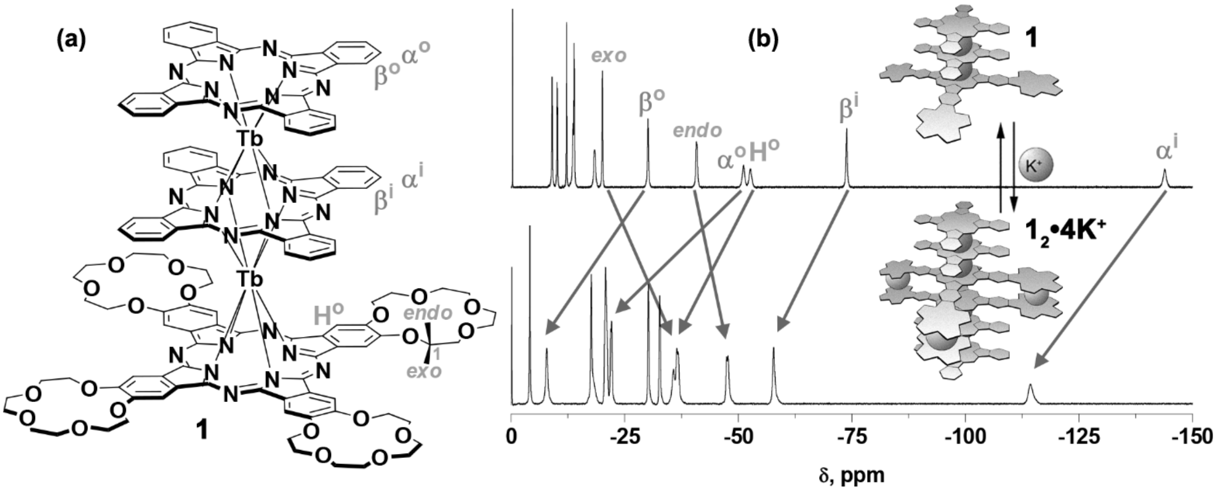

Figure 1. (a) Heteroleptic complex 1, (b) ^{1}H-NMR spectra for complex 1 and supramolecular dimer $1_2{\bullet}4K^+$ in $CDCl_3$ + 20vol.% CD_3OD.

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This work was supported by Russian Science foundation (grant 18-73-10174)

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Novel Mn and Re catalysts for homogeneous and heterogeneous CO_2 electroreduction

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Converting carbon dioxide via electrochemical reduction into useful chemicals and fuels for energy storage by employing renewable energy sources represents an excellent strategy for mitigating the challenges of intermittent renewable energy production and the need to reduce CO_2 emissions. Despite the numerous advantages of heterogeneous electrocatalysis, clever integration with the homogeneous counterpart allows a rational design of the catalysts, by tuning both the metal center and/or the ligand. One of the greatest challenge of the homogeneous approach lies in the search of stability, durability and improved turnover number (TON) efficiencies. Bipyridine transition metal complexes represent one of the most studied classes of molecular electrocatalysts. The role of the substituents on the electrochemical properties and the related overpotentials required for CO_2 transformation have been analyzed on a large series of new 2,2'-bipyridine metal complexes fac-M(bpy-R)$(CO)_3$X (where M = Mn, X = Br or M = Re, X = Cl).[1] Electrochemical behaviors of the complexes in acetonitrile under Ar and their catalytic performances for CO_2 reduction with added water and MeOH have been investigated by cyclic voltammetry and controlled potential electrolysis. The complexes carrying only electron withdrawing groups lose their catalytic activities towards CO_2 reduction, whereas electron donor ligands and push-pull systems display electrocatalytic current enhancement under CO_2 atmosphere. The only detected reduction product by GC analysis is CO: for example, fac-Re (bpy-4,4'-NMe_2)$(CO)_3$Cl gives CO with high faradic efficiency and a TON of 18 and 31, in absence of external proton source and with 5% MeOH, Our research group synthesized a Mn bipyridine derivative in which two pendant phenolic groups act as local proton source capable of reducing CO_2 even in anhydrous acetonitrile. In this case a considerable amount of HCOOH was also detected.[2,3] Impressive results have been obtained by using the organometallic complex (fac-Mn(apbpy)$(CO)_3$Br) (apbpy = 4-(4-aminophenyl)-2,2′-bipyridine) grafted electrochemically onto carbon cloth serves as an electrocatalyst in the aqueous reduction of CO2 to syngas.[4] A faradaic efficiency of around 60% for CO and 40% for H_2 at −1.35 V is achieved together with a productivity rate higher than 870 $\mathrm{Nl_{CO}\ h^{-1}\ g_{Mn}^{-1}}$ at turnover numbers of up to 33 200 during 10 hours of operation.

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Dihydrogen bonding and proton transfer from MH acids to palladium hydride

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Neutral transition metal hydrides are very important participants of various organometallic transformations and can demonstrate different reactivity being formally the sources of hydride ion H^- or proton H^+. The hydride ligands possessing a partly negative charge are proton accepting sites forming a dihydrogen bond, $M–H^{\delta-}\cdots{}^{\delta+}HA$, whereas those serving as a proton source give hydrogen bond of $M–H^{\delta+}\cdots B$ type (B = organic base) [1]. Recently we have established that interaction between the two hydrides with opposite partial charge on hydrogen atom is mediated by a dihydrogen bonded complex ($M–H^{\delta-}\cdots{}^{\delta+}H–M'$) [2]. Intramolecular proton-hydride transfer inside the dihydrogen bonded complex [3] leads to the formation of bimetallic contact ion pair accompanied by H_2 molecule release.

In this talk we report the results of the detailed spectral and quantum chemical studies of the reaction between the stable electron-rich (^{tBu}PCP)PdH hydride (1) and $CpW(CO)_3H$ [4] and its analogue $TpW(CO)_3H$ (Tp = κ^3-N-hydridotris(pyrazolyl)borate). The reaction mechanism was studied by variable temperature IR (ν_{MH}, ν_{CO}, ν_{BH}) and NMR spectroscopy (^1H, ^{31}P, ^{11}B) in a wide temperature range (190-300 K). The reversibility of the hydrogen evolution stage was proved. The peculiarities of products and intermediates structure were assessed by DFT calculations. The influence of the ligands nature on the thermodynamic and kinetic parameters of the various stages of the process will be discussed.

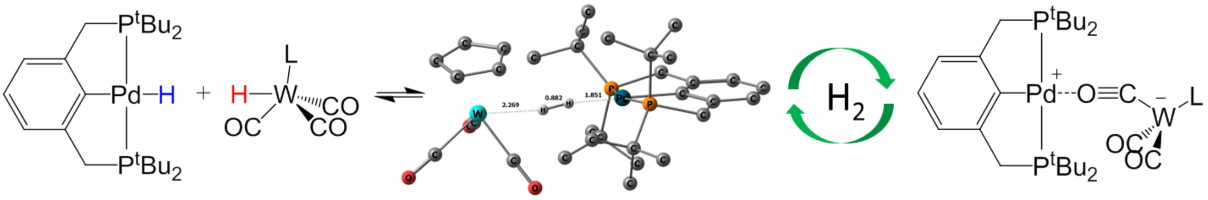

Figure 1.

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Heterometallic Complexes with NHC Ligands

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N-Heterocyclic carbenes (NHC) are known as usefull ligands for coordination compounds. Different catalytic applications of NHC complexes were also reported[1,2]. In this research, we deal with the synthesis of heterometallic complexes with N,N'-dimethylimidazol-2-ylidene.

The dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ is shown to interact with dimethylimidazolium carboxylate ($NHCCO_2$) and CO group substitution product $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(NHC)$ (I) is formed (NHC = N,N'-dimethylimidazol-2-ylidene). Reaction of I with $SnCl_2$ excess in chloride anion presence results in complex $(\eta^5\text{-}C_5H_5)Fe(CO)(NHC)SnCl_3$ (II) formation in low yield. II can be also obtained in reaction $(\eta^5\text{-}C_5H_5)Fe(CO)(NHC)I$ with $SnCl_2$ excess as well as complex $(\eta^5\text{-}C_5H_5)Ni(NHC)SnCl_3$ (III) from $(\eta^5\text{-}C_5H_5)Ni(NHC)I$. Thiolate group substitution in presents of stannous chloride excess was used to prepare new metal-tin bond. Dimers $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SPh]_2$ and $[(\eta^5\text{-}C_5H_5)NiS^nPr]_2$ react with $NHCCO_2$ to form monomeric NHC nickel and iron complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(NHC)SPh$ (IV) and $(\eta^5\text{-}C_5H_5)Ni(NHC)S^nPr$ (V), respectively. Heterometallic complexes II and III are obtained in reaction of IV and V with $SnCl_2$ excess in good yield. For complex II, it can observe one-electron quasi-reversible oxidation wave, but for complex III, one-electron irreversible oxidation wave is observed. The monomeric complex V is rapidly oxidized in air to form the sulfone complex $(\eta^5\text{-}C_5H_5)Ni(NHC)SO_2{}^nPr$ (VI), while its reactions with the adducts $W(CO)_5(THF)$ and $(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)$ afford $(\eta^5\text{-}C_5H_5)Ni(Me_2Im)(\mu\text{-}S^nPr)W(CO)_5$ (VII) and $(\eta^5\text{-}C_5H_5)Ni(Me_2Im)(\mu\text{-}S^nPr)Mn(CO)_2(\eta^5\text{-}C_5H_5)$ (VIII).

Acknowledgements

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Coordination Potential of Alkyne Complexes with Terminal Group 15 Element Donors

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Alkynes with proximate donor substitution are electronically flexible linkers with high conjugation potential. Side-on coordination at the triple bond converts such alkynes into chelate ligands.[1,2] In dinuclear complexes the resulting μ-η²-*C*,*C'*-κ²-*X*,*X'* coordination mode provides a basis for strong intermetallic cooperativity.[1] In this contribution novel systems with group 15 donor centers either in a trigonal planar fashion for X = NR or in a tetrahedral geometry for X = PR_2 will be presented.

Terminal phosphine substituents are introduced into alkyne complexes by electrophilic substitution at coordinated acetylene in order to ensure side-on coordination of bis(phosphino)alkynes.[3] In contrast, respective amino substitution in **3** is accomplished by isocyanide coupling at the metal template.[4] Nucleophilic substitution at diiodoacetylene complexes in turn leads to carbenium carbine complexes **4** with rearranged C_2 moiety.[5] Synthetic strategies to as well as reactivity and coordination behavior of such systems depicted in Figure 1 will be discussed. The metalla-diphos ligands **1** and **2** in particular reveal to be functional ligands in multiple regards. They are characterized by highly reversible redox activity. While the donor strength of the phosphine groups can be adapted by variation of the substituents at phosphorus (R = Ph, *i*Pr), the redox potential is tunable by the co-ligands at tungsten. These studies are motivated by the potential use of such redox-active diphosphines for catalysis.

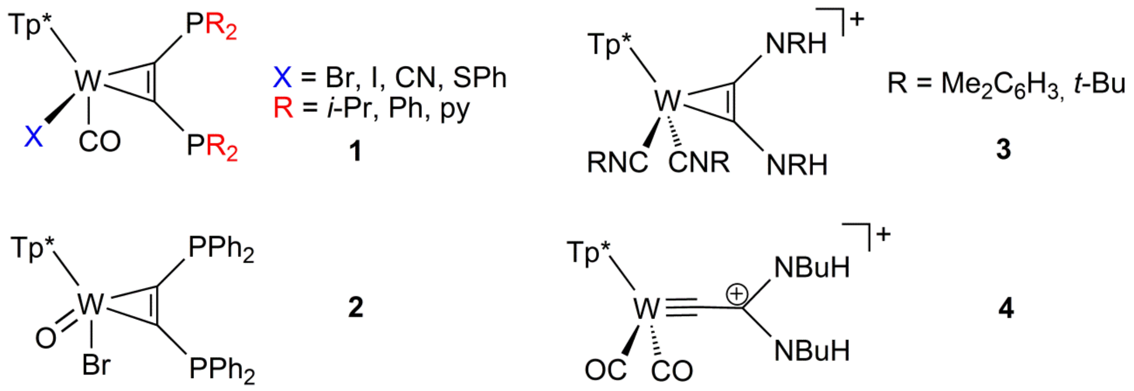

Figure 1. Metalla-alkyne ligand system under study.

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Computational Modeling of Transition Temperatures in Spin-Crossover Systems

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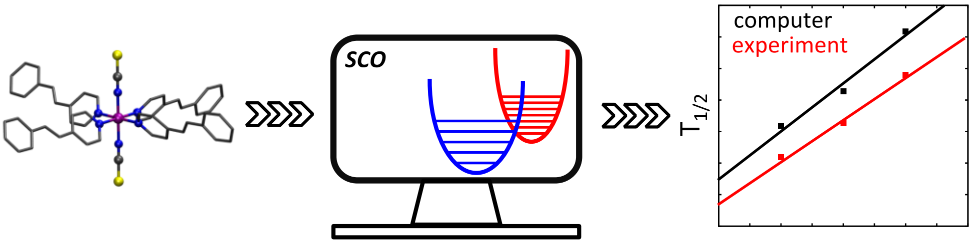
Due to their inherent technological applications as molecular level switches, Spin-Crossover systems (SCO) are the focus of intense research both in chemistry and physics. SCO molecules display two alternative electronic states with similar energies accessible by means of an external stimulus, most commonly the temperature, which grants access to the manipulation of an electronic structure property using a macroscopic perturbation.

In this presentation, the use of electronic structure methods at Density Functional Theory (DFT) level to compute the transition temperature ($T_{1/2}$), will be outlined. After a proper benchmarking of different DFT methods to compute spin-state energies for first row transition metal systems,[1] several families of SCO systems,[2-4] including $[Fe(stpy)_4(NCX)_2]$ (X = S, Se, or BH_3), $[Mn(Cp^R)_2]$ (R = Me, ^{i}Pr or ^{t}Bu), or the unusual $[PhB(MesIm)_3Fe–N=PR_3]$ SCO family will be analyzed using the reported methodology, and the experimental trends observed will be fully rationalized in terms of the underlying electronic structure in terms of the relevant molecular orbitals. The same methodology can be used to study dinuclear SCO systems, and allows us to explain the electronic origin of the two-step *vs*. single-step experimentally observed in such systems.[5] The results allows us to build simple yet accurate models to explain the role of electronic and steric effects (or both combined) over the experimentally observed shifts in $T_{1/2}$. The reported strategy not only allows for an accurate calculation of the $T_{1/2}$ but also allows us to make proper predictions, which in turns enable the use of this computational approach for the rational design of new SCO molecules with tailored properties.



Acknowledgements

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Towards molecular design of spin-crossover complexes based on 2,6-di(pyrazole-3-yl)pyridines

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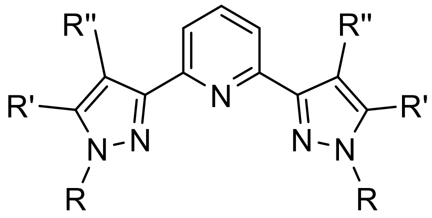
Spin-crossover (SCO) complexes with d^4-d^7 metal ions, which are able to reversibly switch between the two spin states under an applied stimulus (temperature, pressure, light irradiation, electric or magnetic field),[1] offer wide opportunities for their potential applications in high density data storage, switching, sensing and other molecular devices.[2] Most often, they have an iron(II) ion in a (pseudo)octahedral N_6 environment that results in an SCO occurring between diamagnetic low-spin (LS, S = 0) and paramagnetic high-spin (HS, S = 2) states.

2,6-di(pyrazole-1-yl)pyridine (1-bpp) is among the most studied in SCO research owing to its synthetic versatility and possibility to control the spin state of the metal ion by a judicious choice of substituents.[3] Complexes of isomeric 3-bpp are much less understood,[4] as not so many of them were derived from functionalized 3-bpp, and their spin state is extremely sensitive to the environment,[5] thus precluding a 'truly molecular' design[6] of SCO compounds based on 3-bpp.

In a search for new derivatives of 3-bpp that would finally make it possible, we obtained a series of iron(II) complexes $[Fe(3\text{-bpp})_2]^{2+}$ with substituted 3-bpp ligands (Scheme 1) and probed their spin state in solids (by magnetometry and X-ray diffraction) and in solutions (by variable-temperature NMR spectroscopy). Such an extensive study allowed us to get insight into the role of different substituents in 3-bpp (with distinct steric and electronic properties and H-bonding ability) and to propose a new approach in the ligand design to produce SCO complexes of functionalized 3-bpp for many future applications.



Scheme 1. Functionalized 3-bpp ligands.

Acknowledgements

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Light-Induced Spin-Crossover at Room Temperature

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Spin-crossover metal complexes is a highly promising class of molecular magnetic switches for many applications, including molecular electronics, memory devices, molecular sensing, and catalysis. The switching of these species is usually triggered by the change of temperature or irradiation with light *at very low temperatures*. By integrating photoisomerizable ligands into spin-crossover iron(II) complexes, we achieved efficient photoswitching in solution, solid state, and thin films *at room temperature* (Figure 1).[1–5]

Our concept of light-induced switching at room temperature together with our latest results on thin films obtained by physical vapor deposition and on derivatization targeting chemical anchoring to surfaces will be presented.

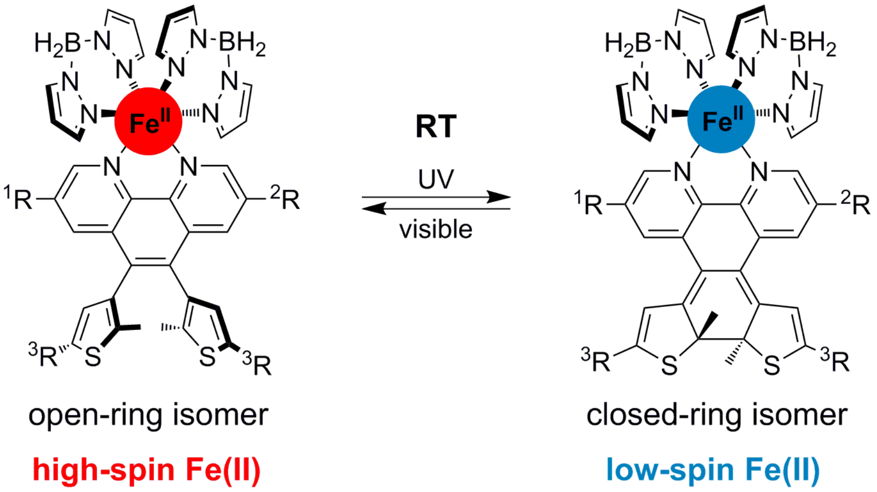

Figure 1.

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Cr(III)-chromophores displaying room temperature millisecond excited-state lifetimes: toward efficient sensitizers for polymetallic energy-converting devices

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Polypyridine-Cr(III) complexes are well known to exhibit interesting photophysical and photochemical properties. For instance, they can be used as luminophores and dyes for solar cells, as sensitizers in up-conversion or downshifting processes and in photoredox catalysis. Such appealing features arise from the remarkable long-lived excited-state displayed by some of these complexes, which can reach several hundreds of microseconds. In this regard, Heinze *et al.*, reported the $[Cr(ddpd)_2]^{3+}$ complex, which displays efficient NIR photoluminescence with a ^2E excited-state lifetime (□(^{2}E)) of 898 □s,[1] much longer than that found in the classic $[Cr(tpy)_2]^{3+}$ chromophore, □ □ 35 □s.[2] This remarkable difference is mainly due to the ability of the 'ddpd' ligand to chelate to Cr(III) with larger N-Cr-N bite angles, thus preventing important non-radiative relaxation pathways and enhancing the ^2E lifetime. In this contribution, we report on the structural and millisecond excited state lifetimes of the heteroleptic $[Cr(ddpd)(tpy\text{-}R)]^{3+}$ (R = H, COOEt) derivatives, which combine the structurally favourable 'ddpd' and the unfavourable 'tpy'[3] binding units (Fig 1. left) . Moreover, we present a novel homoleptic Cr(III) chromophore $[Cr(L)_2]^{3+}$ (emission spectrum fig 1. right) displaying □(^{2}E) of 1.28 ms and an overall quantum yield (ϕ) of 7.3 % at room temperature in aqueous solution.[4] Preliminary results on the chiral resolution of the latter compound will also be presented.

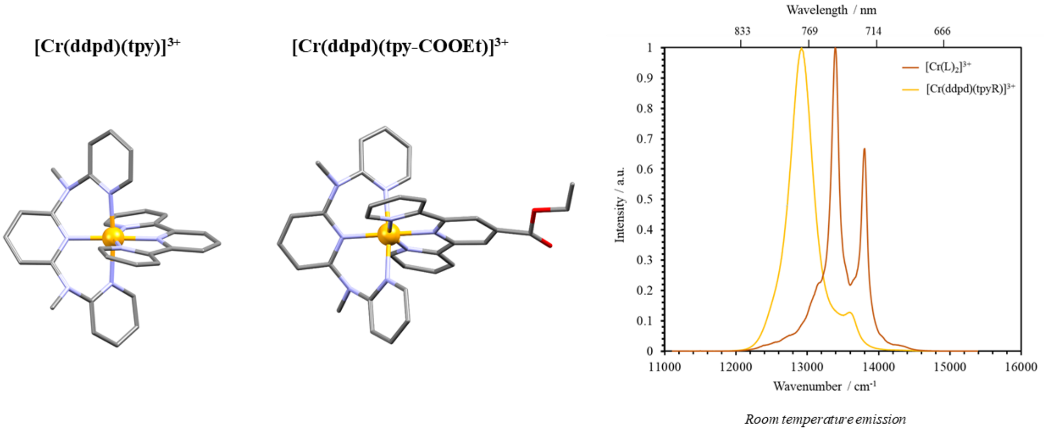

Figure 1

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Assembly of multi-layered mixed-metal W/Mo and mixed-valence W(VI)/Mo(V) molecular metal oxide cages

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The fabrication of redox-active molecular metal oxide (polyoxometalates, POMs) that can switch between multiple states is critical for their application in electronic devices and catalysis;[1-4] yet, a sophisticated synthetic methodology is not well developed for such cluster types. In this contribution we describe a strategy using heteroanion-directed and reduction-driven assembly to produce new multi-layered POM cages templated by multiple redox-active pyramidal heteroanions (Figure 1). The heteroanions greatly affect the self-assembly process of the resultant POM cages, leading to the generation of unprecedented multi-layered structures. The introduction of reduced molybdenum centres is essential for the self-assembly of the compounds and results in mixed-metal (W/Mo) and mixed-valence (WVI/MoV) POM cages, as confirmed by redox titration, spectroscopy and spectrometry studies. Extensive analysis reveals that the mixed metal cages are a statistical mixture of isostructural clusters with variable ratios of W/Mo.

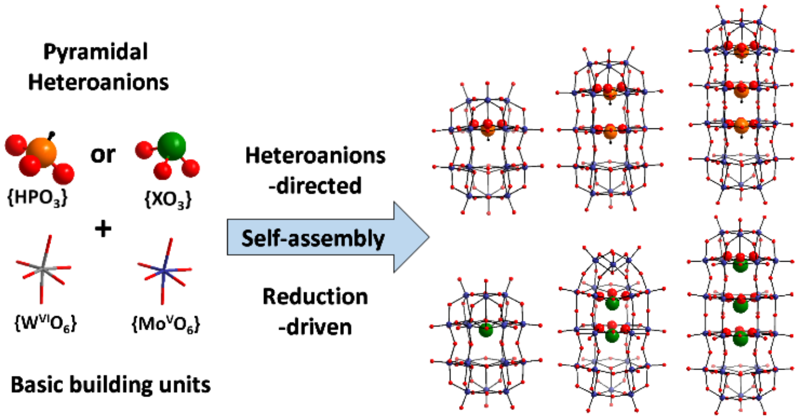

Figure 1. Schematic representation of heteroanion-directed and reduced Mo^V-driven assembly of multi-layered POM cages. Color scheme: P orange; Se green; W/Mo^V indigo; O red; H black.

Acknowledgements

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Vanadium oxide thin film formation on reduced graphene oxide by peroxide route and its application as electrode material

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P-block element peroxocompounds[1-4] are used as precursors to coat clays, graphene oxide and other particulates. The hydrogen peroxide route is very effective for p-block element oxide and sulphide composites preparation. The synthesized composites demonstrate good electrochemical properties as anodes for Li, Na and K-ion batteries.[5-8]

We provide an alternative method for the formation of a thin film of supported vanadium oxide on rGO.[9] We show that thin film formation on rGO can be obtained by deposition of large grains of peroxovanadate on GO and subsequent microexplosive decomposition of the vanadate by thermal treatment of the filtered composite yields the desirable nanocomposite. The fragmented vanadate redistributes as a nanolayer on the graphene oxide by the thermal treatment. The V_3O_7-rGO composite product was tested as a sodium ion battery anode and showed high charge capacity at high rate charge-discharge cycling (150 mAh g^{-1} at 3000 mA g^{-1} vs 300 mAh g^{-1} at 100 mAg^{-1}) due to the nanomorphology of the vanadium oxide.[9]

It is proposed to use vanadium oxide based composite as an efficient electrode material for supercapcitors.[10]

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Molecular Brake Based on the Zn(II) Porphyrin Dimer: Dynamic Behavior in Solution and Ultrathin Films

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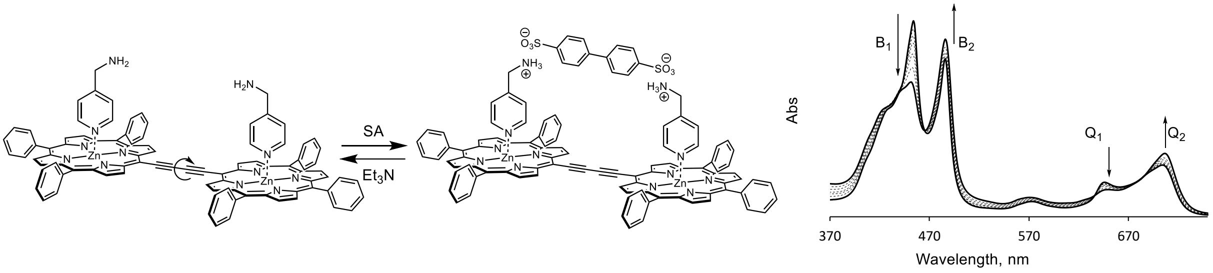
Various types of covalently bonded dimers, trimers and oligomers based on porphyrin backbone are of interest due to their ability to form extremely large π-conjugated systems and, therefore, to display charge, energy and electron transfer properties. Optical properties of such systems usually are different from the corresponding monomers. Interestingly, UV-Vis spectra of the some mentioned systems are sensible to their geometry.[1]

Herein we describe a porphyrin dimer molecule containing two macrocycles interconnected by a butadiyne bridge, that allows them flipping around the axis of the linker. Dimer solution in dichloromethane is a mixture of conformers with different dihedral angles between porphyrin rings and, consequently, different degree of π-conjugation. It has a great influence on a UV-Vis spectrum of the dimer. Adding of a bidentate "handle" molecule or matched sulfonic acid/triethylamine combination hinder flipping process, that can be monitored by UV-Vis spectroscopy (Scheme 1). Surprisingly, it does not influence on luminescence spectra, since only orthogonal and planar conformers emit after excitation.[2] Excited planar form has lower energy, therefore, 'orthogonal emission' was observed at low temperatures or if dimer is chemically locked in this position.[3] However, we found that close packing of Langmuir-Blodgett films, composed of dimer molecules, also hinder the flipping process so, that both types of fluorescence is observed.



Scheme 1. Switching of the dimer with sulfonic acid/triethylamine system (left) monitored by UV-Vis spectra (right) in dichloromethane solution.

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Magnetism of diamagnetic compounds

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NQR experiments on coordination oxy compounds based on Group 15 elements with valence s- and p-electrons evidenced that they exhibit unique magnetic properties, essentially different from those of conventional diamagnetics[1-4]. No long-range magnetic order exists in these compounds, but studies on nuclear quadrupole interactions showed that ordered local magnetic fields H_{loc} of various strength ($3 < H_{loc} < 250$ G) and orientation are present in many of them. These fields, although much weaker than typical internal magnetic fields of magnetics with valence d- and f-electrons, originate from the electron system of the compounds.

Strong increase in the resonance intensities in external Zeeman fields (H_{ext}) (Fig. 1) as well as specific influence of H_{ext} on the nuclear spin-spin relaxation (T_2) were observed for such compounds. We present new experimental results detecting and characterizing these anomalies in $BiSbO_4$ and $Bi_4Si_3O_{12}$ conventionally considered as diamagnetics.

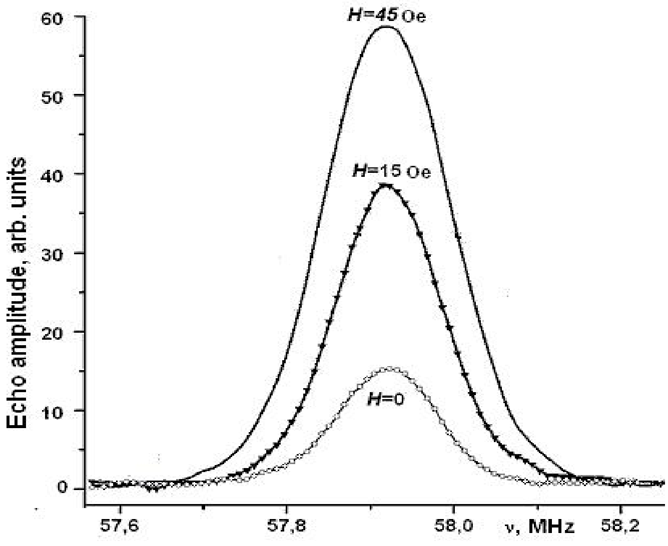

Figure 1. Increase in the intensity of the line in the ^{209}Bi NQR spectrum of the compound Bi_3O_4Br in weak external magnetic fields *H*.

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Paramagnetic NMR spectroscopy – a tool for molecular switches studies

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Nuclear magnetic resonance (NMR) spectroscopy is routinely used for studying diamagnetic chemical compounds, while paramagnetic ones are rarely investigated by NMR due to some data acquisition and analysis difficulties. On the other hand, in some cases paramagnetic NMR spectroscopy allows to obtain detailed structural and electronic information. In this talk the general principles of paramagnetic NMR spectroscopy application to studies of single molecule magnets[1] and spin-crossover compounds[2] will be discussed.

Single molecule magnets (SMMs) are molecules able to retain their magnetization in the absence of an applied magnetic field similarly to a permanent magnet. This unique behavior opens prospects for information storage on a molecular level. To keep molecules magnetized at higher temperatures, an intrinsic energy barrier to magnetization reversal should be enormous. For transition metals-based SMMs the energy barrier to magnetization reversal is proportional to the zero-field splitting (ZFS) of energy levels within the ground term. Energy levels, being eigenvalues of a Hamiltonian, can be estimated if the latter is defined by some experimental methods. In NMR spectra of a paramagnetic compound anisotropy of magnetic susceptibility tensor $\Delta\chi$ causes a pseudocontact chemical shift of each nucleus. Modeling of temperature dependence of $\Delta\chi$ within spin-Hamiltonian formalism can allow to estimate energy levels including ZFS:

$$\chi_a = \frac{N_A kT}{10} \frac{\partial^2}{\partial B_a^2} ln\left(\sum_i e^{-\frac{\langle \psi_i | \hat{\mathcal{H}} | \psi_i \rangle}{kT}}\right)$$

where ψ_i are the eigenvectors of a spin-Hamiltonian; $a = x, y, z$.

The spin-crossover (SCO) is a phenomenon of the spin state changes due to external stimuli such as a variation of temperature, pressure etc. Properties of a molecule in different spin states are also different, that is a core of many developed physical methods for SCO studies. In NMR spectra of a SCO compound chemical shifts take the weighted average values and can serve as a "fingerprint" of spin state.

Acknowledgements

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Simple one- and two-parameter models for calculating atomic charges in molecules

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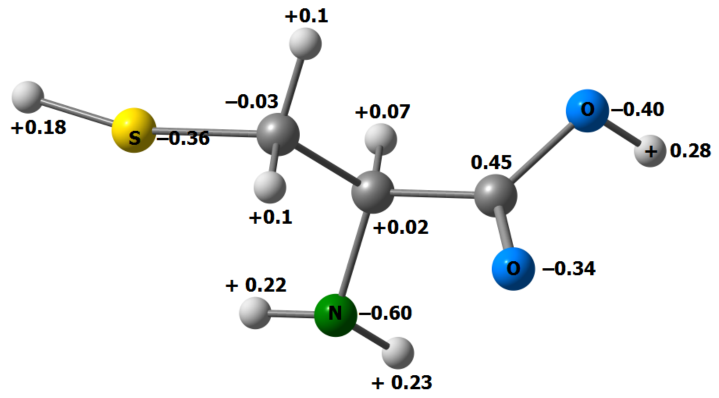
The concept of atomic charges in molecules is widely used by chemists to qualitatively describe molecular properties and reactivity. Nevertheless, there is no unique way to define a charge of an atom in a molecule. Hence, many alternative schemes exist that differ in the way how the molecular electron density is partitioned among the atoms.

We propose two new atomic-charge methods, the *Adjusted Charge Partitioning* (ACP)[1] and its iterative version, *Iterative ACP*.[2] To partition the valence electron density into atomic components, Slater-type weighting factors $c_A r^{2n-2} e^{-\alpha_A r}$ are used. Within the *ACP method*, both c_A and α_A are fixed parameters reflecting atomic electronegativity and atomic size, respectively. The parameters are adjusted to reproduce molecular dipole moments in the best way. In the *Iterative ACP*, only α_A is fixed, while the coefficient c_A is determined iteratively in every calculation.

The advantage of the ACP method is that it is non-iterative, thus fast and reliable. The Iterative ACP is more accurate, flexible and easier to parameterize, but a little bit more computationally demanding.

Extensive numerical tests show that the resulting atomic charges accurately reproduce experimental dipole moments, are insensitive to basis sets used and chemically consistent.



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Cage Metallasesquioxanes: synthesis and properties

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Cagelike metallacomplexes, designed on sesquioxanes of silicon[1] or germanium[2] (cage metallasesquioxanes, CMSs) are in the research focus of scientific teams worldwide due to picturesque molecular architecture and significant potential of CMSs' further application. Synthetic approaches to CMSs include: self-assembly, synthon reactions, transmetalation and recently developed synthesis using different organic (N-, P-, O-) ligands.[3-4] The latter approach was found especially fruitful for copper-based CMSs' isolation, giving rise to numerous products of varied nuclearity and cage shapes. Features of CMSs' synthesis, catalytic/magnetic behavior, as well as methods of CMSs' supramolecular organization will be presented.

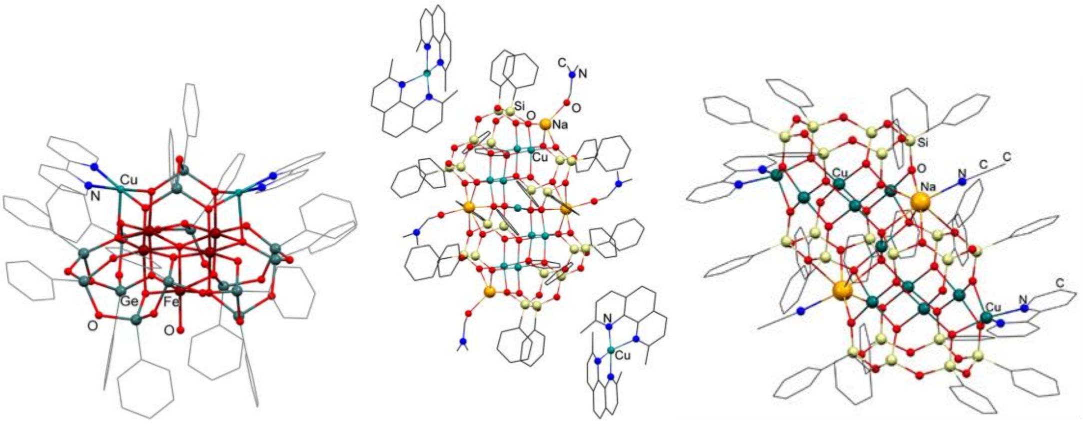

Figure 1. Molecular structures of Cu(II)-based CMSs

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Ru and Pt anticancer compounds with targeting ligands

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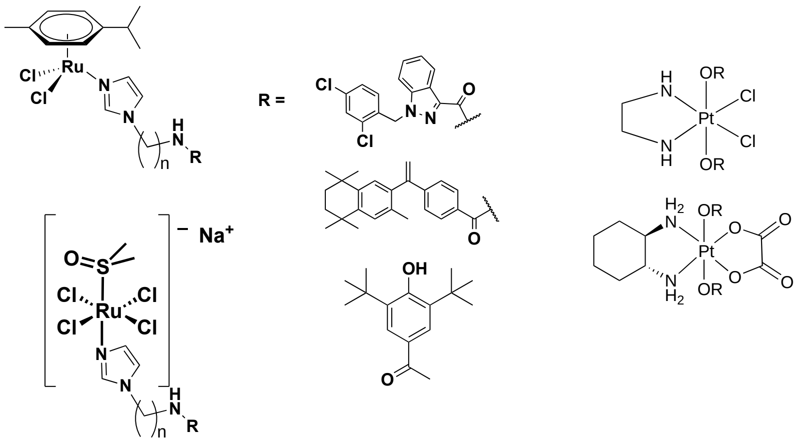
The search for the new metal-based anticancer compounds traditionally based on platinum(II) compounds; however, in the recent years much of interest is shifting towards development of Pt (IV)[1,2] and non-platinum anticancer drugs[3,4] and it was shown that the ruthenium-based compounds could be an excellent alternative of platinum drugs for the number of tumours

The tumour specificity of Pt(IV) and ruthenium compounds can be influenced by ligand sphere around a metal atom. Linking Pt and Ru part to the targeting biologically active organic molecules can improve the anticancer properties.

This presentation will focus on the hybrid complexes of Pt(IV), Ru(II) and Ru(III) bearing biologically active moiety. Several compounds found to be highly cytotoxic against a number of the human cancer cell lines with excellent selectivity towards cancer cells.



Acknowledgements

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Aryl substituted dota derivatives as reagents for radionuclear conjugation to transport biomolecules

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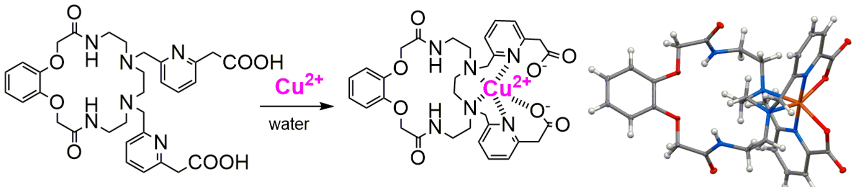
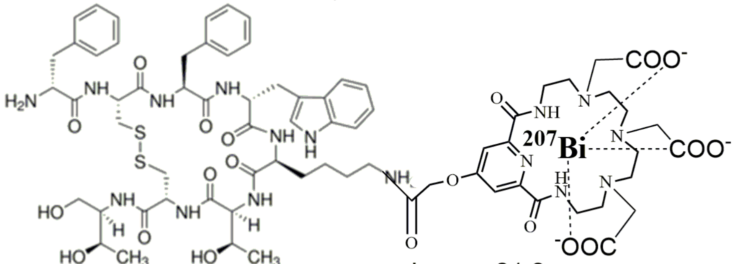
Bifunctional chelating agents have been used widely to derivatize tumor-specific monoclonal antibodies with radiometal ions for cancer imaging and therap. Since most radionuclides are metals, the conjugation of antibodies to radiometal complexes represents one of the most versatile strategies for selective delivery of diagnostic or therapeutic radiation to primary tumors or metastatic disease.

In the present report the synthesis and complex formation analysis of the bifunctional derivatives of the azamacrocyclic chelating agents are presented.



Logβ = 15.7



Logβ = 21.2

Novel generation of produced bifunctional radiometal chelates has improvements with greater thermodynamic, kinetic, and physiological stability, as well as more versatile chemistry for attachment to biomolecules. The developed macrocyclic chelating agents possess relatively rigid, preorganized cavities which enable them to demonstrate the high rate of incorporation of the metal ion into the chelate complex and to bind a wide variety of metal ions with extremely high stability constants.

Acknowledgements

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YOUNG ORAL PRESENTATIONS

Syntheses, crystal structures and the surface properties of perfluorinated MOFs

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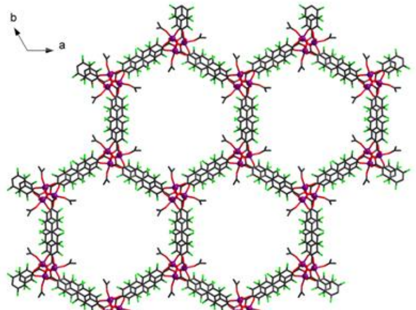
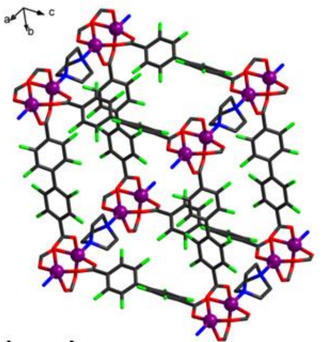
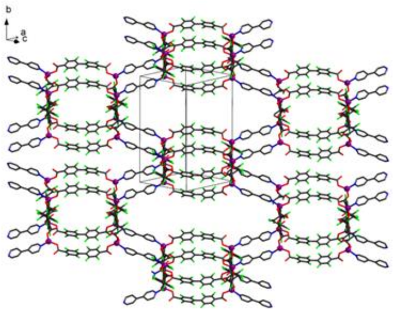
Metal-organic frameworks (MOFs) have attracted much attention due to their high specific surface area, pore volumes and the feasibility of functionalization of the internal surface. An application of perfluorinated carboxylates, *e.g.* octafluorobiphenyl-4,4'-dicarboxylate oFBPDC^{2-}, is a promising approach to get novel MOFs with interesting surface properties, including hydrophobicity and selectivity of adsorption.

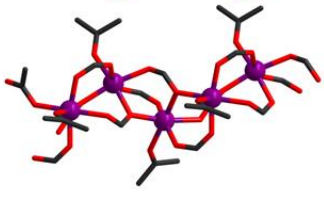
The conditions for the synthesis of perfluorinated MOFs are absolutely different from those for non-fluorinated material. Using weakly coordinating solvents (CH_3CN, alcohols, acetone, THF) together with the decrease of the temperature down to a room temperature appeared to be very productive. This approach allows 1D, 2D and 3D coordination polymers to be obtained, which crystal structures were determined by single crystal X-ray diffraction.[1,2]

One of them, doubly interpenetrated [Zn_2(dabco)(oFBPDC)$_2$], is a permanently porous solid with the BET surface area of 441 m^2/g. In addition, it shows IAST selectivity factors of 11.3 and 4.9 for the separation of gas binary mixtures CO_2/N_2 and CO_2/CH_4, respectively. The value of water contact angle (136 °) and the shapes of water and C_6-hydrocarbon vapour adsorption curves confirm hydrophobic nature of this material.[1]

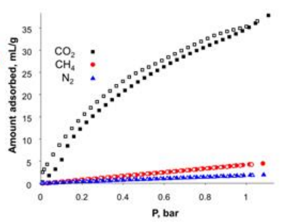




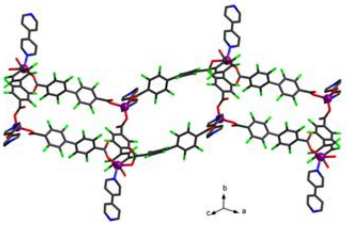




Selective adsorption



Water contact angle > 130 °



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Tetranuclear Cu_4I_4 clusters on pyridylcontaining cyclophosphines

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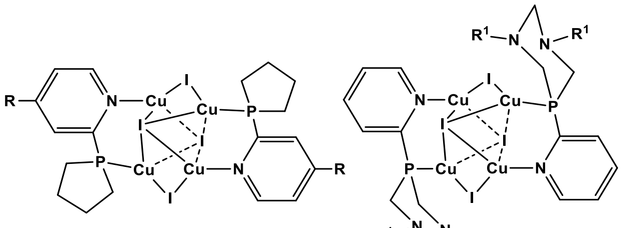
Tetranuclear copper (I) iodide clusters bearing hybrid P,N-ligands, particularly pyridylphosphines, garnered significant attention due to their rich structural topology which reflects on the photophysical properties[1]. Herein we describe a series of luminescent Cu_4I_4 clusters based on pyridylcontaining cyclophosphines with alkyl substituents on phosphorus atom – pyridylphospholanes and 1,3-diaza-5-phosphacyclohexanes (Chart 1).



R = H (*1*), CH_3 (*2*)

R^1 = *p*-Tol (3), Ph_2CH (4)

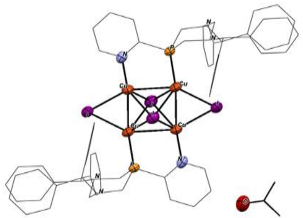


Figure 1. Molecular structure of crystalline solvate of complex $4*CH_3CO$. Hydrogens are omitted

Chart 1. Objects of investigation

Complexes **1** - **4** have octahedral Cu_4I_4 core. Crystallization of complex **4** from different solvents gives corresponding crystalline solvates ($\mathbf{4}*(\mathbf{CH})_2\mathbf{CO}$ (Fig.1), $\mathbf{4}*2\mathbf{CH_3CN}$, or $\mathbf{4}*2\mathbf{CH_2Cl_2}$) with slightly different Cu_4I_4 metal-halide core geometry according to their X-ray data. Notably, that under ambient temperature crystals of $\mathbf{4}*2\mathbf{CH_3CN}$ undergo destruction, which accompanies by losing of molecules of solvent, giving complex **4-*a*** of $L_2Cu_4I_4$ composition. Compounds **1** and **2** demonstrate dual emission with maxima at 490-505 and 600-615 nm at room temperature[2]. Complex **4** demonstrates green luminescence with λ_{em} at 493 nm. By the contrast to complex **4** emission maxima of **4-*a*** registered at 720 nm. Thermochromic behavior of complexes **1**, **2**, **4-*a*** was found for a wide range of temperatures (-175 – 100 °C) that makes them perspective candidates as molecular thermometers. Compound **4-*a*** also demonstrate vapochromism towards dichloromethane, acetone, ethyl acetate, tetrahydrofuran which can be detected by naked eye. The nature of luminescence of obtained compounds was studied using quantum-chemical computations.

Acknowledgements

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Metalla-Silsesquioxanes and Germsesquioxanes: Synthesis, Structure, and Properties

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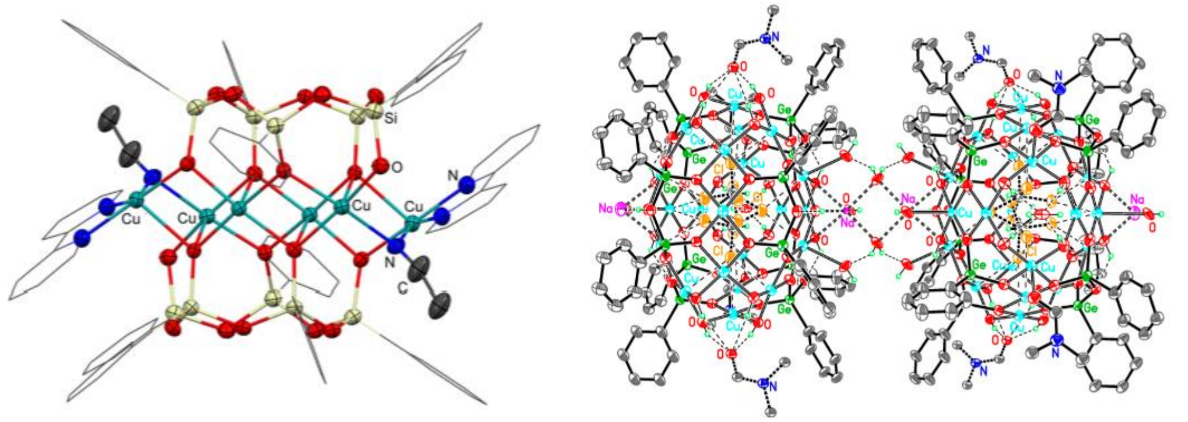
An attractive family of cagelike metallasilsesquioxanes (CLMSs) is known by its members unusual structural, catalytic, and magnetic (spin-glass) properties. The interest to a framework organometallic complexes containing transition metal ions is due to a variety of their structural organizations and topologies, which may be controlled by means of coordination chemistry tools through modulation of various parameters, including the nature and connectivity of building blocks and metal ions, as well as through the nature of organic ligands.

However, the majority of cage-like metal complexes are enabled by branched monosubstituted ($RSiO_{1.5}$) silsesquioxane ligands, but analogous architectures based on germanium instead of silicon are relatively poorly reported in the literature.



$[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{10}H_8N_2)_2]$, [1] $[C_{144}H_{164}Cu_{42}Ge_{24}Na_4O_{102}]$, [2]

Fig.1 The molecular structure of copper sil- and germsesquioxane

Here we present an approach to obtaining sil- and germsesquioxanes containing metal ions (Fig 1), and investigation them on the catalytic activity and magnetic properties.

Aknowledgements

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Thin-film optical sensors based on new amphiphilic (*trans*-A$_2$)BC-type porphyrins

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High values of molar extinction coefficient and luminescence quantum yield of porphyrins provide the possibility of obtaining a response of sufficient intensity from ultrathin films. This forms the basis for the use of porphyrin films as optical sensors for determination of heavy metal ions. The binding of metal ions by free base porphyrin leading to change in the optical characteristics of the ligand can easily be detected by optical spectroscopy or even visually.

In the present work, reusable solid thin film sensors based on Langmuir-Schaefer (LS) multilayer structurs of new series of (*trans*-A$_2$)BC-type porphyrins with acceptor diethoxyphosphoryl and heteroatom-containing donor groups for selective determination of Hg^{2+} in aqueous solutions is reported (Fig. 1). The structural features of amphiphilic (*trans*-A$_2$)BC-type porphyrins (Fig. 1 a) due to bulky diethoxyphosphoryl group as well as alkyl chain prevent the formation of porphyrin aggregates both in monolayers at the air/water interface and in solid films. Interesting that only solid LS films sensors are demonstrated an excellent selectivity for Hg^{2+} in contrast to solutions and Langmuir monolaers of porphyrins at the air/water interface due to the immobilization of molecules on solid substrate fixing a structure that is complementary to Hg^{2+}. It was found that the heteroatom (O, S, N) bound to a porphyrin macrocycle affects the structure of the LS films and binding time of Hg^{2+} by these film sensors.

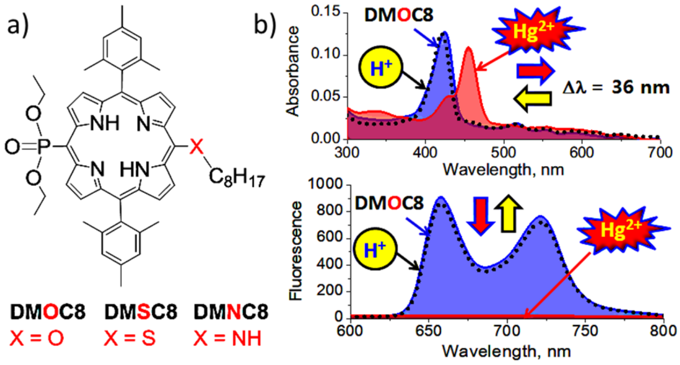

Figure 1. (a) Structure of amphiphilic porphyrins. (b) Absorption and emission spectra of DMOC8 LS film immersed in Hg^{2+} aqueous solution and after regeneration of film in 0.01 M HCl.

Acknowledgements

This work was carried out in the frame of the International Associated French–Russian Laboratory of Macrocycle Systems and Related Materials (LAMREM) of CNRS-RAS. The authors thank Russian Foundation for Basic Research for financial support (project № 18-33-00339 and № 17-53-16018).

Lactone production by Pd-catalyzed cyclocarbonylation of allylic alcohols with ionic liquid as stabilizer

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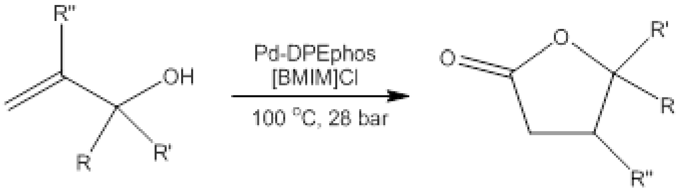
Palladium-catalyzed cyclocarbonylation of unsaturated allylic alcohols and alkynols in presence of hydrogen forms lactones as the main product. The lactonization process may form both five- and six-membered lactone products, which find many important applications in the food, perfume and polymer industry.[1]

Ionic liquids (ILs) have during the last two decades demonstrated to be efficient reaction media for making homogeneously catalyzed processes green.[2] ILs can provide effective immobilization and good stability of transition metal-based catalytic systems, while providing several other solvent advantages such as, e.g. high thermal and chemical stability and negligible low vapor pressures. Moreover, the application of ILs can provide a stabilized catalytic solution, facilitating efficient product separation and catalyst recovery.[3]

In this work, the cyclocarbonylation of 2-methyl-3-buten-2-ol was for the first time studied using a Pd-DPEphos (DPEphos: bis[(2-diphenylphosphino)phenyl] ether) catalyst in presence of the IL [BMIM]Cl (BMIM: 1-butyl-3-methylimidazolium chloride) to selectively produce 4,4-dimethyl-γ-butyro-lactone. The results showed that the presence of IL in the reaction mixture provided stabilization of the catalyst system and prevented formation of Pd-black, allowing the catalytic system to be reused in three consecutive reactions after intermediate extraction of the lactone product.



Scheme 1. Pd-catalyzed cyclocarbonylation of allylic alcohols to lactones with IL

Acknowledgements

The Department of Chemical Engineering, Shiraz University and the Department of Chemistry, Technical University of Denmark are acknowledged for supporting the work.

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Complexes of some transition metals with nitrogen-containing ligands like cytostatics and luminophores: synthesis and characterization

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Nowadays physiologically active substances based on inorganic, organometallic, and coordination compounds are widely used in medicine as diagnostic and antitumor agents. Cisplatin and its derivatives are still one of the most effective drugs, but they have a number of drawbacks that limit their clinical use: dose-dependent side effects (nephrotoxicity, neurotoxicity, etc.) and resistance to therapy. In addition, these drugs have a limited spectrum of action. In this regard, development of new antitumor drugs based on platinum and other metals is continuing to improve clinical efficacy, reduce overall toxicity and extend the spectrum of action.

This work is devoted to the synthesis and characterization of new coordination compounds of copper(II), palladium(II), silver(I), zinc(II), and cadmium(II) with pyridine, triazole, and tetrazole derivatives. All of the complexes were characterized by elemental analysis, powder diffraction analysis, UV-Vis and IR-spectroscopy. The molecular and crystal structures some of the complexes have been determined using single-crystal X-ray diffraction analysis.

The cytotoxic activity of the complexes, ligands and metal salts on the viability of Hep-2 (laryngeal cancer cells) and MCF-7 (breast cancer cells) was investigated at various incubation times and concentrations of tested compounds in ethanol (48 or 72 hours, 1-50 μM). The cytotoxicity studies were carried out by means of IN Cell Analyzer 2200 using dual staining with Hoechst 33342/propidium iodide (PI). The half maximal inhibitory concentration (IC_{50}) was defined as drug concentration that reduces the number of living cells by 50%.

The luminescent properties of the ligands and complexes of zinc(II), and cadmium(II) have been investigated. Absorption and emission are observed at two wavelengths in luminescence spectra of triazole derivatives and most complexes. Quantum yields were also measured and it was shown that in the coordination compounds the quantum yield increases as compared with ligands.

Acknowledgements

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Hybrid supramolecular system based on zinc(II) porphyrin and pyridine end-decorated molybdenum(II) halide cluster

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Gayane Kirakosyan,[a,d] Alexander Martynov,[a] Mikhail Grigoriev,[a] Dmitry Piryazev,[b,c]
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Among the large variety of organic compounds porphyrins are promising candidates for hybrid supramolecular systems due to the rich chemical and photophysical characteristics. Halide Mo(II) clusters also possess remarkable photophysical properties and could be used as inorganic part[1]. Herein we report the design, synthesis and structural features of supramolecular hybrid organic-inorganic cluster-porphyrin systems bonded via metal-ligand coordination[2].

The zinc(II) 5,15-di(tolyl)porphyrinate (**P**) was used as an organic part and the octahedral pyridine end-decorated Mo(II) halide cluster $[(Mo_6I_8)(PyCOO)_6][Bu_4N]_2$ (**C**) as inorganic. The formation of the **CP$_n$** (n=2, 6) systems via N_{Py}**...**Zn axial coordination was investigated both in solid state and in solution. The crystal structures of **CP$_n$** (n=2, 6) were determined by X-ray structural analysis (Figure 1). The supramolecular association in solutions ($CDCl_3$, CH_2Cl_2) was investigated by UV-Vis titration, ^{1}H NMR and DOSY measurements. Our approach may open the way for the creation of a new family of hybrid systems exhibiting interesting photophysical properties.

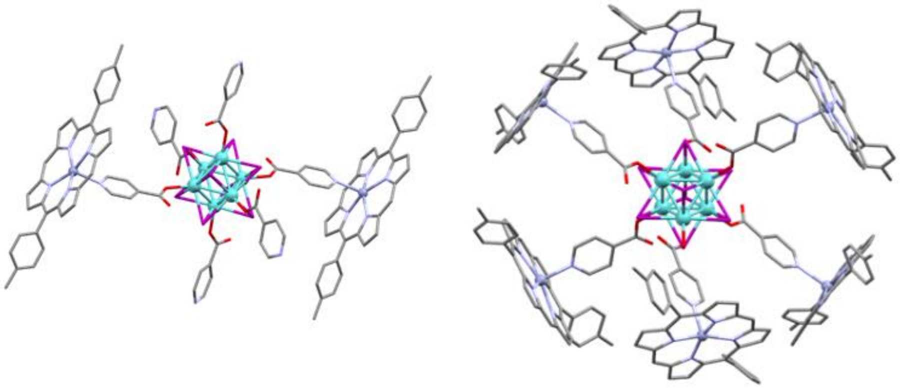

Figure 1. Crystal structures of CP_2 and CP_6

Acknowledgements

This work was supported by the Council for Grants of the President of the Russian Federation for support of leading scientific schools (Grant NSh-3867.2018.3).

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Indenyl rhodium(III) complexes: Synthetic and catalytic chemistry

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The catalytic applications of indenyl metal complexes are well known.[1] Their enhanced catalytic activity in comparison with cyclopentadienyl analogs is attributed to easy slippage of indenyl ligand from η^5 to η^3 coordination mode (the so-called indenyl effect). This structural flexibility of the indenyl ligand facilitates the ligand substitution and catalytic reactions. However, the indenyl complexes of transition metals are still poorly studied in catalysis, that can be explained by their limited commercial availability. In the present work we developed general approaches to indenyl rhodium(III) complexes and used them as catalysts for divers organic transformations, e.g. C-H activation of aromatic compounds.[2-5]

The most significant progress was achieved with the use of indenyl rhodium complexes in reductive amination of aldehydes or ketones in the presence of carbon monoxide as a reducing agent.[2,4] Solvent screening showed that protic solvents (e.g., water and alcohols) are the best choice for the reaction. The methodology enables full compatibility with a range of functional groups prone to reduction (e.g. N-benzyl, PMB, halo-, cyclopropanes).

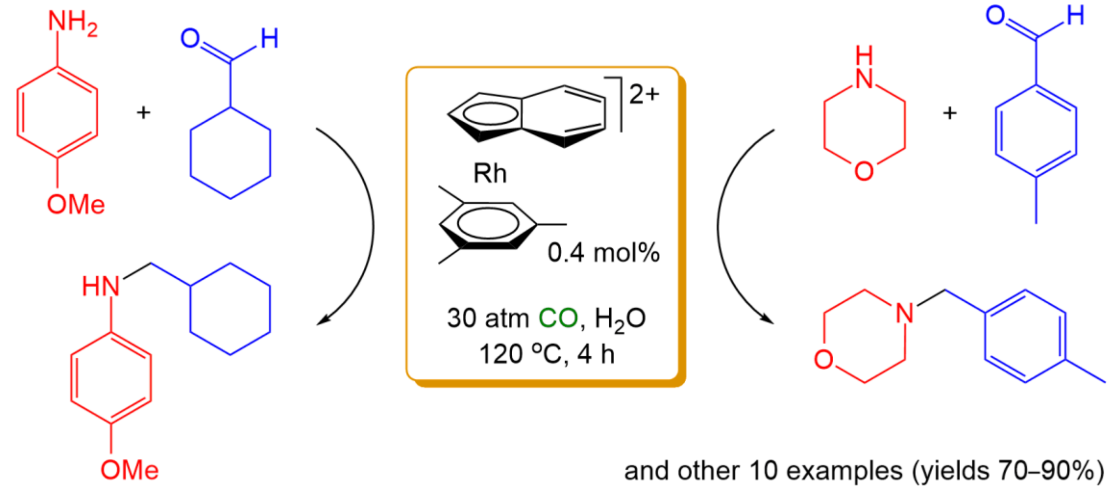

Figure 1. Reductive amination of carbonyl compounds in the presence of carbon monoxide as a reducing agent catalyzed by indenyl rhodium(III) complexes.

Synthesis and structure of the catalysts as well as mechanisms of catalytic reactions will be also discussed.

Acknowledgements

This work was supported by the Russian Science Foundation (Grant No. 17-73-30036).

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Advancing the oxygenation chemistry of magnesium alkyls incorporating β-diketiminate ligands

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Exceptional reactivity of main group metal-carbon bonds towards O_2 has lain at the heart of organometallic chemistry since Frankland's ground-breaking discovery in 1849.[1] Despite decades of extensive studies on the oxygenation of magnesium alkyls, the isolation and structural characterization of discrete products of these reactions still remains a challenge. Although the formation of the most frequently encountered magnesium alkoxides via unstable alkylperoxide intermediates has commonly been accepted, the latter species have been elusive for over 100 years.

Herein we significantly advance the oxygenation chemistry of magnesium alkyls supported by β-diketiminate ligands and demonstrate that the controlled reaction of (L)MgR-type complexes with O_2 leads selectively to the corresponding magnesium alkylperoxide or alkoxide compounds (Figure 1).[2,3] Thus, the longstanding dogma that the formation of magnesium alkoxides results from the comproportionation of MgOOR and Mg-R species seems to be invalid. Moreover, these results paved the way for rational development of very efficient catalytic system based on (L)MgOOR/*t*BuOOH species for the epoxidation of electron-deficient olefins, which will also be presented.

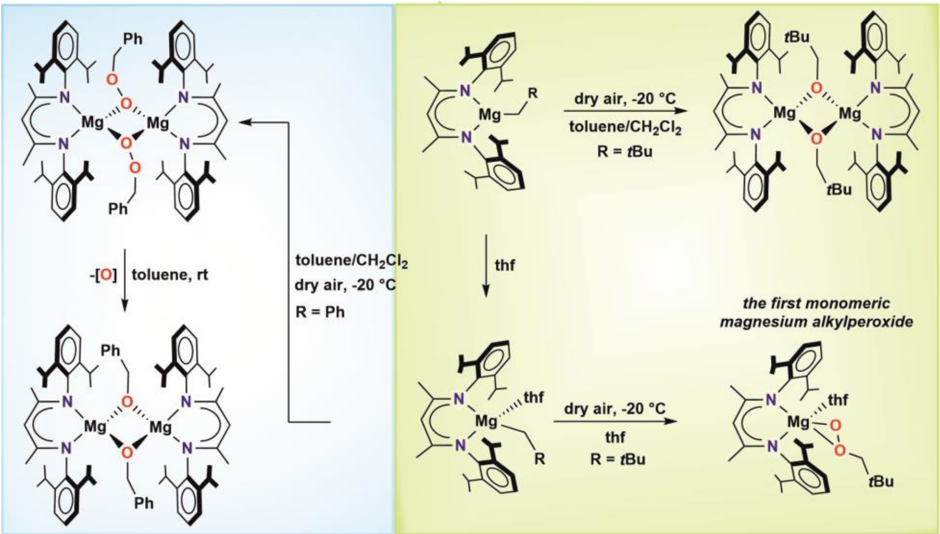

Figure 1. The oxygenation of the alkylmagnesium complexes stabilized by the β-diketiminate ligand.

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Inorganic ligands as the basis for effective contrast agents

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The present work introduces Gd^{3+} complexes with giant keplerate polyanions and hexanuclear cluster anions $[\{Re_6Q_8\}(L)_6]^{4-}$ ($Q = S^{2-}$, Se^{2-} or Te^{2-};$L=CN^-$, SO_3^{2-}), as a promising basis for MRI contrast agents.

The impact of Gd^{3+} binding with different building blocks of keplerates on the magnetic relaxivity of the complexes is revealed by comparative study of the keplerates $[\{Mo_6O_{21}\}_{12}\{Mo_2O_4(OAc)\}_{30}]^{42-}$, $[\{Mo_6O_{21}\}_{12}\{Mo_2O_4(HPO_4)\}_{30}]^{72-}$, and $[\{Mo_6O_{21}\}_{12}\{Mo_2O_2S_2(OAc)\}_{30}]^{42-}$. The transformation of the external pores from Mo_9O_9 to $Mo_9O_6S_3$ in the $\{Mo_2O_2S_2(OAc)\}$-keplerate and an increase in the Gd^{3+}-to-keplerate ratio are the factors that decrease the relaxivity. The rapid degradation of the free keplerates in aqueous solutions restricts the use of the Gd^{3+}-bound keplerates with 1 : 1 stoichiometry as MRI contrast agents. In this work, the optimized stoichiometry of the complexes, their self-assembly into ultra-small nanoparticles and their hydrophilic coating by a triblock copolymer are highlighted as tools for increasing both the colloid and chemical stability of the keplerate complexes. Optimal keplerate compositions have been identified to achieve a compromise of low cytotoxicity and high stability; these Gd^{3+} bound keplerates exhibit longitudinal and transverse relaxivity values (95 and 114 mM^{-1} s^{-1}, respectively), well within the region of interest for MRI techniques.

Interaction of Gd^{3+} with hexarhenium leads to formation colloidal core-shell nanoparticles, where hard cores are the water insoluble $Gd_x[\{Re_6Q_8\}(L)_6]_y$ complexes, hydrophilic shells are built from pluronic F-127. The comparative analysis of TEM, PXRD, luminescence and magnetic data for the dried colloids indicates that the nature of the cluster anions $[\{Re_6Q_8\}(L)_6]^{4-}$ greatly affects the size and crystallinity of the hard cores, which in turn influences both magnetic relaxivity and luminescence of the corresponding aqueous colloids. The analysis of the results revealed hydrophilic colloids based on $Gdx[\{Re_6S_8\}(CN)_6]_y$ as the best ones from the viewpoint of the functional properties, which along with the low cytotoxicity makes them very promising basis for further application as contrast agents in both MRI and luminescent imaging.

Acknowledgements

We thank RSF (grant no. 17-13-01013) for financial support.

Synthesis of carboxylated nanodiamond particles grafted by lanthanides via ion-exchange reaction

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Diamond nanoparticles ranging 4-5 nm produced by explosive method, named detonation nanodiamonds (DND) are an emerging class of carbon nanomaterials, which possess a unique set of chemical, physical properties.[1] Detailed information on the method for preparation stable hydrosol of carboxylated DNDs particularly in physiological media has been recently published [2,3], which important for medical applications. As an example, we also inform that carboxylated DNDs grafted by Gd ions can be an effective contrast agent for magnetic resonance imaging due to reducing of spin−lattice (T1) and spin−spin (T2) relaxation times of water protons.[4]

In this work we report on grafting various lanthanide ions onto surface of DND particles. We used colloidal DND particles covered with carboxylate groups and $Ln(OOCCH_3)_3{\cdot}4H_2O$ or $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = Ce, Pr, Sm, Eu, Gd, Dy, Ho, Tm) as precursors. Using conductometry and ζ-potential measurements we have demonstrated that the grafting has been realized due to ion exchange reaction between protons of three surface carboxylate groups and a lanthanide ion. EDX analysis and FTIR spectroscopy study are in accordance with the titration results. A number of lanthanide ions bound to DND surface is occurred to be dependent on anion component of Ln-containing precursors. Furthermore, powders of DND grafted by Eu ions have been characterized by PL spectroscopy.

Acknowledgements

Fomina I.G. and Yudina E.B. thank the RFBR (project N 18-2919038 mk) for support of their research

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Conversion of Ethyl Levulinate to γ-Valerolactone Using PNP-pincer Complexes

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The depletion of fossil feedstock has urged humanity to seek for alternative energy sources for industry, transportation and households. The field of catalysis is recognized as being an important aspect of the transformation towards a more green production. Here, we present the use of two commercially available PNP-pincer complexes for the homogeneous catalytic transformation of ethyl levulinate into the two high value chemicals namely, ethanol and γ-valerolactone.[1]

The catalytic system does not rely on the use of solvents besides the substrate itself (neat conditions), and full conversion can be reached under mild conditions. Furthermore, the products can easily be isolated in a high yield by simple fractional distillation. A variety of homogeneous hydrogenation catalysts were screened under our reactions conditions. However, the Ru(II) and Ir(III) based complexes, depicted in Figure 1 below, showed superior performance when activated *in situ* by sodium ethoxide.

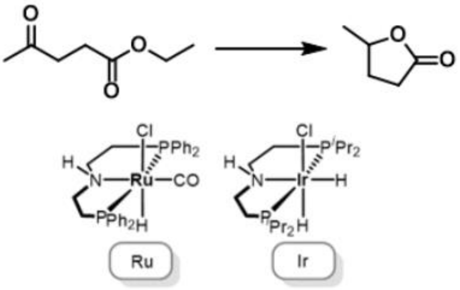

Figure 1. Shows the transformation of ethyl levulinate into the main product γ-valerolactone. By screening of several PNP-pincer complexes, the Ru(II) and Ir(III) complexes depicted in the figure revealed the best performance.

Acknowledgements

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Adsorption and catalytic properties of Salen-modified MIL-101

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Metal-organic frameworks is a perspective class of porous materials for gas storage and separation, catalysis and for many other applications. One of the most important advantages of MOFs is a possibility of properties tuning via directional modification, for example by means of post-synthetic modification (PSM).

Mesoporous chromium(III) aminoterephthalate MIL-101-NH_2 is a coordination polymer with a high hydrolytic and thermal stability. Moreover, side amino-group is opened great opportunities for PSM. There are two different routes to obtain MIL-101-NH_2: reduction of chromium(III) nitroterephthalate MIL-101-NO_2 by tin(II) chloride (MIL-101-NH_2(Sn)) or direct synthesis from aminoterephthalic acid and chromium(III) salt (n-MIL-101-NH_2). We have found that these two structurally identical MOFs possesses rather different adsorption properties as well as precursor is important for further PSM process and influence on properties of modified samples.

A series of Salen-modified n-MIL-101-Sal-M (M = Cr, Zr, Co, Ni) and MIL-101(Sn)-Sal-Cr have been obtained by treatment of n-MIL-101-NH_2 or MIL-101-NH_2(Sn) with salicylaldehyde and metal salt. Formation of salen complexes inside porous structure have been confirmed spectroscopically, by X-Ray diffraction and nitrogen adsorption.

MIL-101-Sal-Cr(Sn) and n-MIL-101-Sal-Cr have been used to demonstrate the precursor influence on adsorption properties. MIL-101-Sal-Cr(Sn) shows better in several times selectivity factors for binary CO_2/CH_4 and CO_2/N_2 gas mixtures separation than n-MIL-101-Sal-Cr: 23 and 646 *vs.* 9 and 108 correspondingly. However, MIL-101-Sal-Cr(Sn) demonstrates much lower sorption capacity and catalytic activity.

Adsorption of carbon dioxide, methane and nitrogen were investigated for all compounds in the series. n-MIL-101-Sal-Ni shows increasing of selectivity factor for CO_2/CH_4 binary mixture in 1.6 times while sorption capacity keeps at the same level. MIL-101-Sal-Zr shows increasing of selectivity factors for CO_2/N_2 binary gas mixture separation in 3 times.

Study of catalytic properties of the modified frameworks was carried out at the reaction of cycloaddition CO_2 to propylene oxide (fig. 1). We observed increasing of yield of the target product after modification of MIL-101-NH_2.

This work was partially supported by Russian Science Foundation (Project No. 19-73-20087).

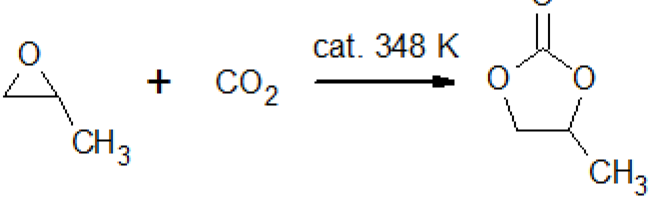

Figure 1.

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BODIIM - a 2π-electron expanded BODIPY fluorescence dye

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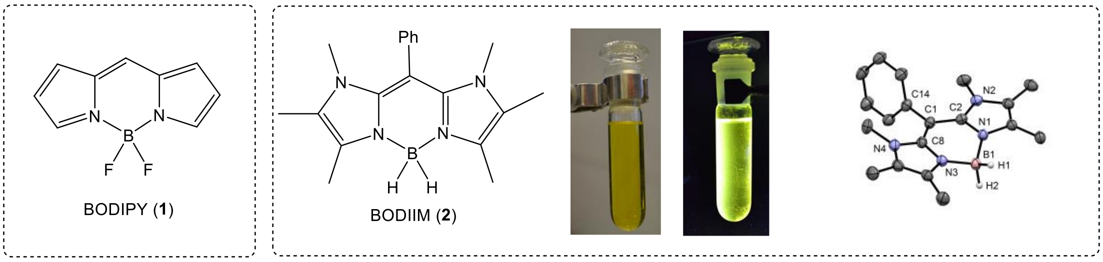
Boron-functionalized dipyrromethenes (**1**, BODIPYs) are fluorescent dyes with important applications as imaging probes and sensors covering the areas from optoelectronic materials to pharmaceuticals. The 12π-electron system displays strong fluorescence (λ_{abs} ~ 500 nm, λ_{em} ~ 530 nm) with low Stokes-shifts.[1] For the variation of the optical properties of BODIPYs the 1,7-CH-positions in the parent BODIPY (**1**) were substituted for N-Me groups to design a novel bisimidazole based system (**2**) termed BODIIM. This compound contains a BH_2-moiety, which is highly sought after for BODIPYs commonly prepared as BF_2-derivatives. The BODIIM-core can be considered as 14π-electron system, which leads to absorptions at 360 nm and 405 nm and emits greenish light at 520 nm giving rise to an intense Stokes-shift.



BODIPY (**1**)

BODIIM (**2**)

Figure 1. Prototype of a BODIPY-compound (1, left) and the novel BODIIM-compound (2, right).

The *meso*-carbon atom in the novel BODIIM system features nucleophilic activity and can be reacted with boranes to give borane adducts showing blue fluorescence. The reversibility of borane complexation can be demonstrated by addition of strong Lewis bases, e.g. N-heterocyclic carbenes, retrieving the starting BODIIM system. This allows for a controlled reversibility of the fluorescent properties as a switchable system.

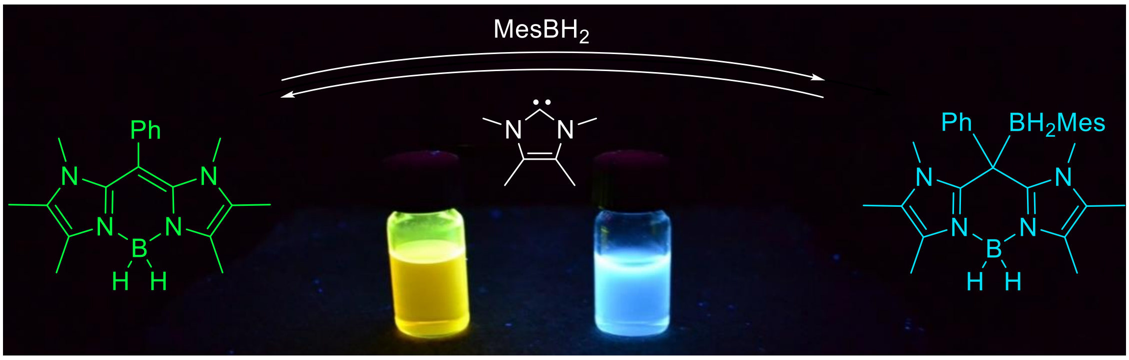


Figure 2. Reversible fluorescent switch of the novel BODIIM system**.**

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New approach in the synthesis of trans-substituted diimine carbonyl rhenium(I) complexes.

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Nowadays phosphorescent carbonyl Re(I) complexes with diimine ligands are widely used in various practical applications such as luminescent sensing, biomolecular imaging, photocatalysis, electroluminescent materials, since their photophysical parameters could be tuned in a wide region.

The light-absorption and emission characteristics of $[Re^{I}(NN)L_4]$ species (NN = diimine, L = ancillary ligands) are generally dominated by excited states with ^{3}MLCT (Re→NN) nature and could be effectively tuned by the modification of the diimine ligand or varying of ancillary ligands. The first approach is more common since Re^{I} compounds are chemically and thermally quite robust and substitution of CO ligand is accompanied by steady-state UV irradiation or presence of decarbonylation agent - trimethylamine N-oxide. Typically, these reactions occur only in presence of ancillary ligand with strong trans influence (PR_3, CN^-),[1,2] that restrict the number of possible ligand combinations.[3]

In our recent research we combined the synergetic effect of Ultraviolet and Microwave irradiation that allow us to synthesize new type of carbonyl diimine rhenium complexes with two trans-coordinated acetonitriles in quantitative yields (Fig. 1). We also studied possible further substitution of coordinated acetonitrile molecules with ligands of other types.

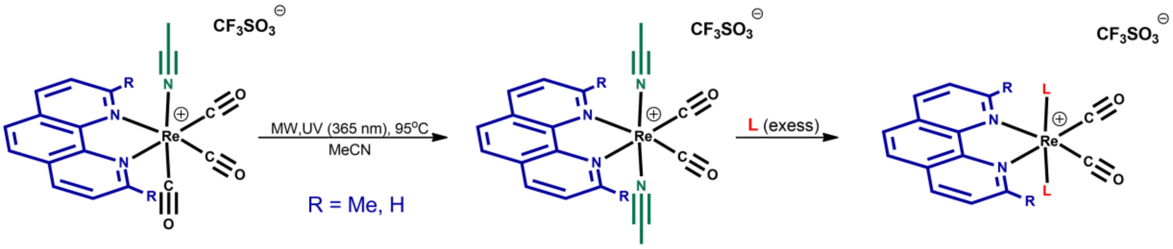

Figure 1. Scheme of synthesis of new trans-substituted rhenium(I) complexes**.**

The final compounds were fully characterized by elemental analysis, X-ray crystallography, ESI-MS, 1D (^{1}H) and 2D (^{1}H-^{1}H-COSY) NMR spectroscopy. Luminescence properties of all complexes have been studied and the interpretation of emissive states has been supported by TD-DFT calculations.

Acknowledgements

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One-Dimensional Organic Semiconductors Assembled from Lutetium Double-Decker Phthalocyanine

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Organic semiconductor nanowires are widely applied components of organic electronic devices such as solar cells, transistors and sensors. Until recently, nanowires have been fabricated from either conjugated copolymers or polycyclic molecules through aromatic stacking. However, both methods yield 1D materials with comparatively poor conductive properties due to the polycrystalline structure of nanowires.

Herein we report a new method of self-assembly of supramolecular wires containing double-decker tetra-15-crown-5-substituted lutetium phthalocyanine (LuL_2), potassium ions and inorganic particles (ceria nanoparticles and micronized mica). The crystalline supramolecular structures were synthesized through a two-step procedure. The certain amount of inorganic particles was introduced into the solutions of LuL_2 from their hydrosols to form a layer of ligands on the particle surface. These modified particles act as crystallization seeds, which promote the formation of the supramolecular aggregates with a high aspect ratio. The growth of supramolecular structure then proceeds through a coordination of crown-ether groups of LuL_2 with potassium ions after the adding of metal salt into the system. The as-formed crystalline structures were deposited onto the solid supports via dip coating. The hybrid assemblies were examined by SEM and X-ray methods showing the formation of 1D crystals with ultra-high aspect ratio and length up to 100 microns (Fig.1). The nanowires exhibited better electrical properties than those of previously reported one-dimensional organic nanostructures.

Our results demonstrate the applicability of the self-assembly strategy towards fabrication of nanowires for organic electronic devices.

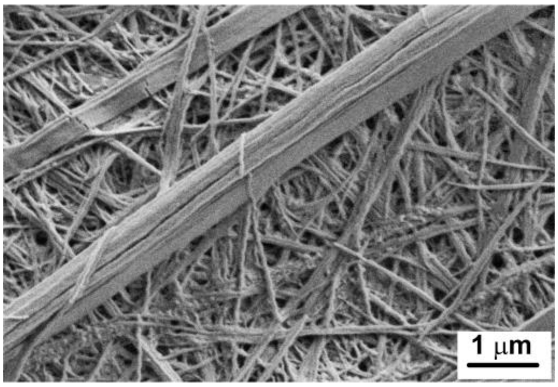

Figure 1. SEM image of phthalocyanine-based wires.

Acknowledgements

The authors wish to thank Russian Foundation for Basic Research (grant mk_18-29-04026), Ministry of Science and High Education RF. X-ray diffraction was performed using the equipment of CKP FMI of IPCE RAS.

Pt(II)-M’ and Pd(II)-M’ complexes (M’ = Ag(I), Au(I)) as frozen models of relevant intermediates in bimetallic catalysis

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The study of heteropolynuclear complexes with metal-metal interactions between closed or pseudo-closed shell transition metals (d^8, d^{10}, $d^{10}s^2$) is attracting attention because of their luminescent properties and their potential use as a tool for crystal engineering.[1] Remarkably, this interest has grown lately because species containing these interactions play an important role in cooperative catalysis.[2] Indeed, some of these processes operate through the participation of heterobimetallic couples formed by a donor basic and an acceptor acidic centre allowing the advance of key transmetalation steps.[3,4]

In this contribution we present a series of heterodinuclear and heterotrinuclear complexes resulting from the interaction between a donor basic centre of a cyclometalated metal complex (Pd(II), Pt(II)) and an acceptor acidic metal centre (Ag(I), Au(I)). Intriguingly these compounds present short interactions between the acidic metal and one of the C_{ipso} of the cyclometalated ligand in the solid state, but rich fluxional behaviors in solution are observed instead. The experimental observations are consistent with the operation of intramolecular “metronome-like” dynamic behaviors in solution. Thus, these complexes can be regarded as snapshots of transmetalation processes which have been arrested at different degrees of the transfer, which strongly depends on the nature of the metals involved (figure 1).

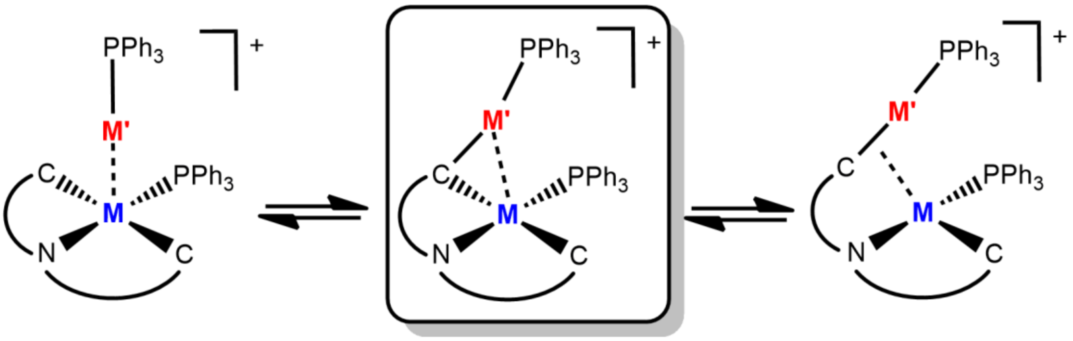

Figure 1. Schematic representation of a transmetalation step subject of discussion

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Rhodium-catalyzed CO-assisted reductive transformations

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Rhodium-catalyzed transformations has attracted much attention in recent years.[1] We present here two reactions catalyzed by rhodium. The rhodium complex **1** $[(\text{cyclooctadiene})\text{Rh}(C_{10}H_4Me_2(OMe)_4)]^+$ (1 mol%) catalyses reductive amination under mild conditions (40–130 °C) and produces a variety of amines in good yields (74–95%) without affecting the functional groups.[2]

In addition, an efficient and highly productive rhodium-catalyzed method for the synthesis of nitriles employing aldehydes or ketones, methyl cyanoacetate, water and carbon monoxide as starting materials has also been developed. Simple rhodium chloride without any ligands can be used. The fine tuning of the substrate can lead to the activity higher than 5000 TON.[3]

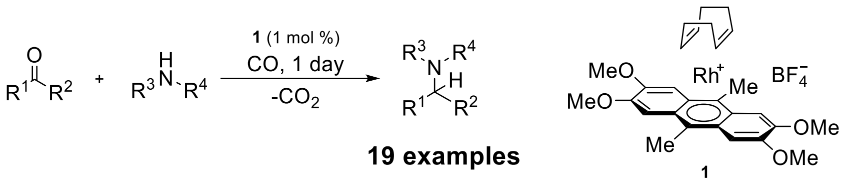

Figure 1. Reductive amination

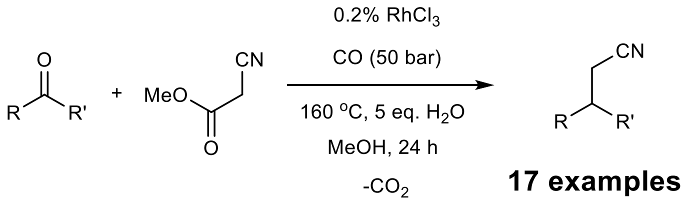

Figure 2. Reductive alkylation

Acknowledgements

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Mn(I) vs Fe(II) Catalysts for the Hydrogenation of Ketones: A Comparison by Experiment and Calculation

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We describe here the first Mn(I) complexes with P-stereogenic PN(H)P pincer ligands (**1**) as catalysts for the asymmetric hydrogenation of ketones. Complex **1b** (1 mol%, 50 bar H_2, toluene, 80 °C) hydrogenates acetophenone to 1-phenylethanol with 99% yield and 55% ee after 16 h reaction time (Figure 1).

Furthermore, we studied **1a** for the sake of comparison with the iron(II) analogue **2a**, which has been previously prepared in our group.[1] The comparison between the isoelectronic manganese(I) and iron(II) hydrogenation catalysts has rapidly grown into a hot topic,[2] but no quantitative analysis has been reported to date.

Kinetic studies show that the Mn(I) catalyst **1a** is ca. 30 times less active than the Fe(II) analogue **2a**. DFT calculations, NMR spectroscopic, and kinetic studies indicate that the lower catalytic activity is due to the large energetic span[3] between the transition state of dihydrogen activation (2) and the alkoxide complex that is formed as resting species (4) (Figure 2).[4] The role of the *trans* ancillary ligand (CO for Mn vs H^- for Fe, respectively) on the energetic span will be discussed.

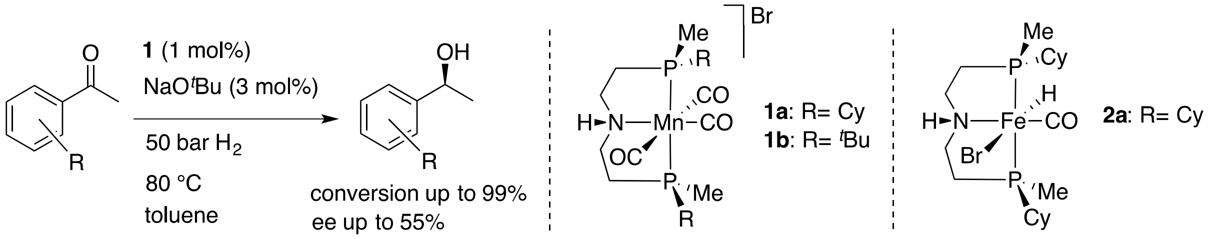

Figure 1. Asymmetric hydrogenation of ketones

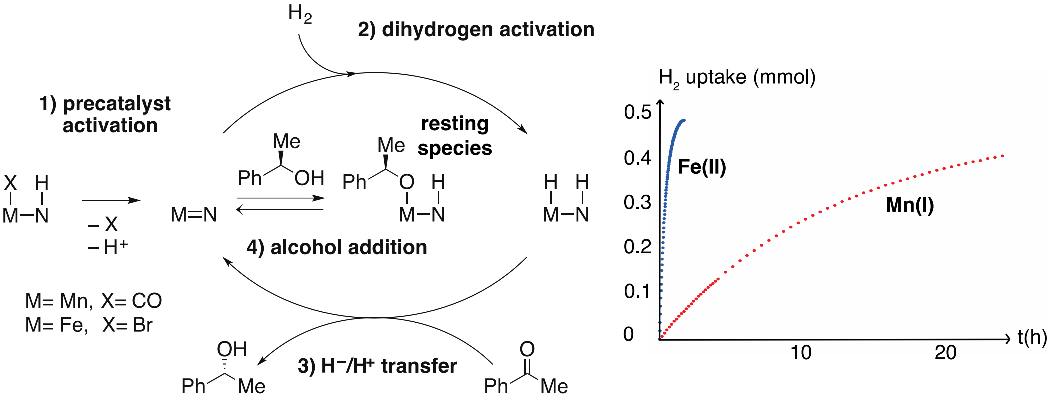

Figure 2. Reaction mechanism and kinetic study for Mn(I) and Fe(II)-catalyzed asymmetric hydrogenation of ketones

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Compounds containing lone pair element cations and structural related properties

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Several p-block elements can form cations with oxidation states where they have a lone electron pair (E) that occupies space. This volume can be compared with the volume of an O^{2-} or a F^{-} anion. Most such cations e.g. Se^{4+}, Te^{4+} or I^{5+} adopt one sided coordination. The heavy cations have a less active E since it is attracted closer to the nucleus and can be highly coordinated e.g. Bi^{3+} or Pb^{2+}.[1]

Some inorganic compounds containing light and heavy lone-pair cations will be presented. The oxides or oxo-fluoride compounds belong to the M-L-O/F system where M is a transition metal, L is a lone pair cation. The compounds $CoBi_2O_2F_4$ [2], $Cu_2SeO_3F_2$ [3], and $K_3Sc(IO_3)_6$ show different structural characteristics so that the M-cations are arranged in layers or in chains. The lone-pairs help to open up the crystal structures. Physical properties of the compounds will also be presented.

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Carbene insertion into N-H bonds of 2-aminothiazole and 2-amino-1,3,4-thiadiazole derivatives catalyzed by iron phthalocyanine.

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Carbene transfer reactions catalyzed by metal complexes are widely used in organic chemistry.[1] Due to the high versatility of this synthetic strategy involving metal carbene complexes, a large range of elaborated compounds can be prepared via carbene insertion into C-H, N-H and O-H bonds.[1] Among metal complexes, metalloporphyrins have been extensively studied as catalysts for carbene transfer reactions.[2] In contrast, their phthalocyanine counterparts have been rarely used.[3]

We present here the first detailed study of application of Iron(III) phthalocyaninate decorated with crown ether substituents, $[(15C5)_4PcFe]Cl$, (*figure 1, d*) in carbene mono- and double N-H insertion (*Figures 1a, 1b*).[4] $[(15C5)_4PcFe]Cl$ efficiently catalyzes the insertion of carbene formed from ethyl diazoacetate precursor into amino group of 2-aminothiazole and 2-amino-1,3,4-thiadiazole derivatives (*Figure 1c*).

Turnover numbers up to 3360 have been achieved. Ethyl glycinate amino acid derivatives bearing heterocyclic moieties were obtained under catalytic conditions for the first time with 36 – 69 % yields in the case of single N-H insertion products and up to 77 % in the case of double N-H insertion products.

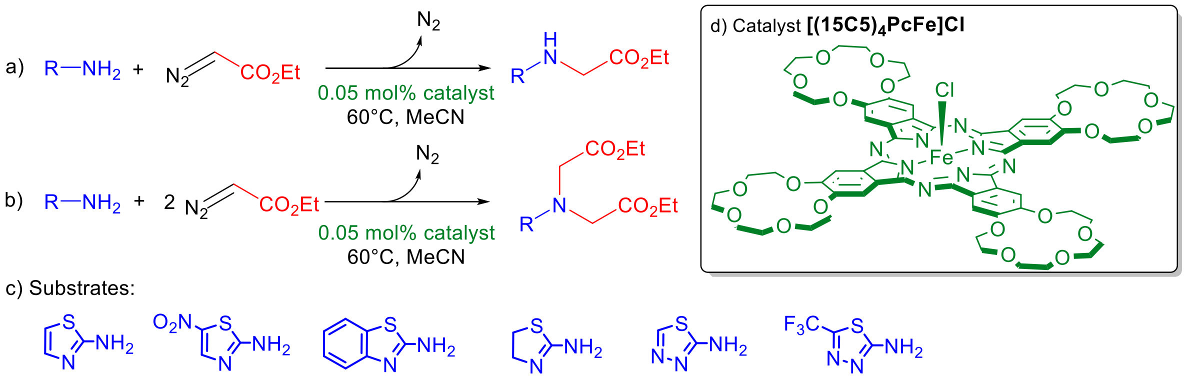

Figure 1. Reactions of single (a) and double (b) carbene insertion in amino group of substrates (c) catalyzed by $[(15C5)_4PcFe]Cl$ (d).

Acknowledgements

This research was supported by Agence National de Recherche (ANR, France, grant ANR-16-CE29-0018-01). LPC is indebted to Ministère de l'Education Nationale, de l'Enseignement Supérieur et de la Recherche, France for the PhD fellowship).

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Molecular structure of palladium and platinum acetates: DFT and QTAIM study

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Two well-known coordination complexes, platinum(II) acetate $Pt_4(\mu\text{-}OOCMe)_8$ and palladium(II) acetate $Pd_3(\mu\text{-}OOCMe)_6$ have quite different molecular structures:[1,2] $Pt_4(\mu\text{-}OOCMe)_8$ has slightly distorted square metal skeleton and very short (2.49 Å) Pt-Pt distances, while $Pd_3(\mu\text{-}OOCMe)_6$ has triangular framework and much longer (3.1-3.2 Å) Pd-Pd distances.

In this work we studied the electronic structure of the Pt(II) and Pd(II) acetates to recognize why platinum(II) forms tetrameric acetate complexes, while palladium(II) has only trimeric structures. For this purpose we employed the hybrid functional PBE0 with scalar-relativistic corrections and QTAIM theory.

Calculations showed that the platinum-platinum bonding in $Pt_4(\mu\text{-}OOCMe)_8$ stabilizes complex by 50.1 kcal/mol. This estimation was obtained as the difference in the total electronic energy between platinum acetate and isoelectronic complex **1b**, in which the shortest Pt-Pt distance is 3.234 Å. In the case of palladium the structure **1a** lies significantly higher in energy (by 22.2 kcal/mol) than structure **1b**.

Topological analysis of the electron density revealed larger delocalization indices for Pt-Pt and Pt-O interactions than those for Pd-Pd and Pd-O.

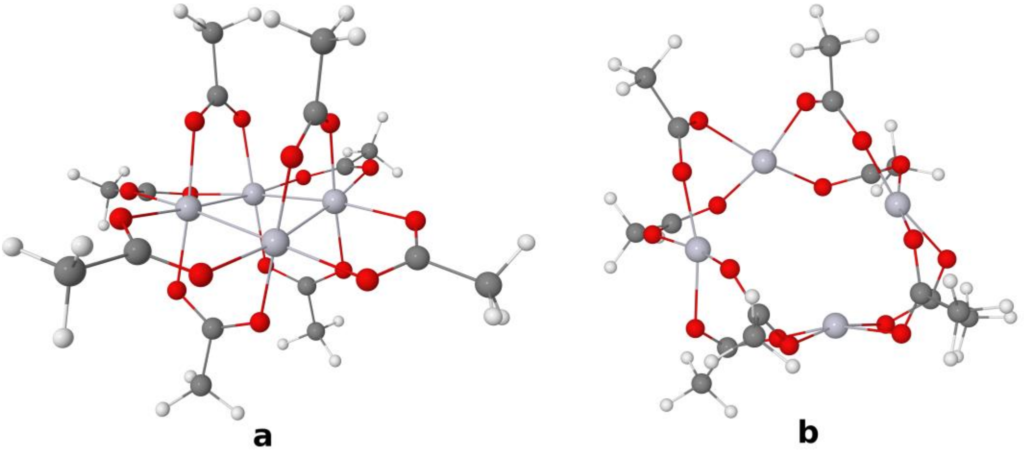

Figure 1. Equilibrium structures of $M_4(\mu\text{-}OOCMe)_8$: with short (a) and long (b) M-M distances. M = Pt, Pd

Acknowledgements

This work is supported by the Russian Science Foundation under grant 18-73-1020.

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Effect of cation size of tetraalkylammonium-based ionic liquids on specific capacitance of N-doped graphene nanoflakes

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Nitrogen doping of sp^2-carbon nanomaterials is an effective way to modify their surface and electrical properties. Moreover, such modification facilitates charge transfer across electrode/electrolyte interface and introduces pseudocapacitance that is especially important for electrochemical applications of graphene-based materials. This work focuses on the synthesis of N-doped graphene nanoflakes (N-GNFs) with high nitrogen doping level (8.5–10.9 at.%) and their application as an electrode material in electrochemical double layer capacitors with ionic liquid electrolyte. N-GNFs were synthesized at 800°C for 0.25, 0.5, 1.0, 1.5 hours by chemical vapor deposition technique using acetonitrile as a precursor and MgO as a mesoporous template. The BET specific surface area of synthesized N-GNFs was 1000, 820, 580 and 440 m^2/g, correspondingly. According to the TEM analysis N-GNFs of 30–70 nm in diameter replicated the shape of MgO template particles (Fig. 1). XPS showed the presence of pyridone, pyridine, pyrrole and graphitic nitrogen species in the synthesized materials. N-GNFs were tested as electrodes of electrochemical double layer capacitor using acetonitrile solutions of bis(trifluoromethylsulfonyl)imides of tetraalkylammonium-based ionic liquids ($N^+Me_4TFSI^-$, $N^+Et_4TFSI^-$,$N^+Bu_4TFSI^-$) as electrolytes. It was found that the specific capacitance of N-GNFs increased with the reduction of the cation size due to the formation of higher charge density on the carbon surface by smaller ions. In addition, the specific capacitance of N-GNFs, as expected, monotonously increased with the increase in the specific surface area (Fig. 2).

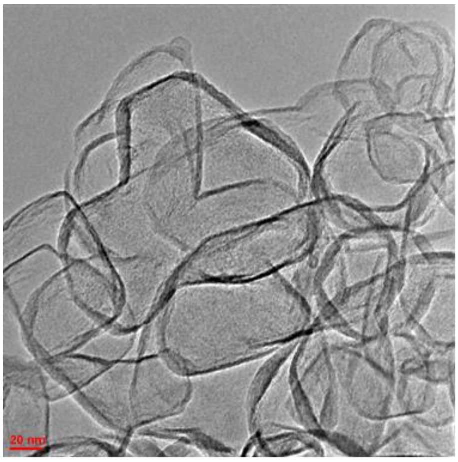

Figure 1. TEM image of N-GNFs

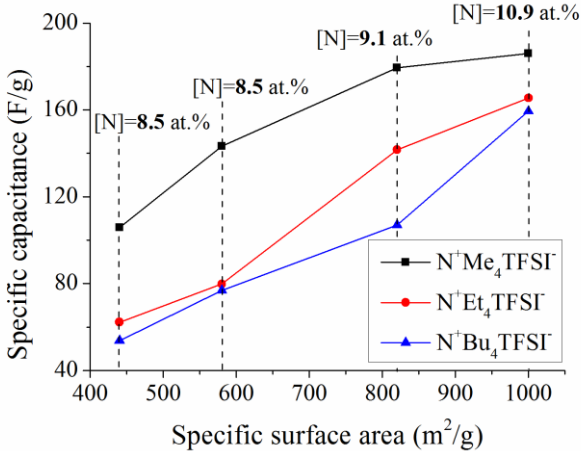

Figure 2. Specific capacitance of N-GNFs versus specific surface area.

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Divalent lanthanides and alkaline-earth metal complexes coordinated by NHC ligands – efficient catalysts for highly regio- and chemoselective hydrophosphinations with PH_3

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The formation of C–P bonds via single-step intermolecular hydrophosphination reactions of unsaturated substrates is a promising, atom-efficient route to a wide range of phosphorus-containing compounds. Despite the progress achieved in this field, a substrate scope of this reaction remains limited and mainly involves activated olefins and ubiquitous phenyl- and diphenylphosphine.[1] Addition of PH_3 to alkenes and alkynes is a progressive and convenient synthetic route to a variety of primary, secondary and tertiary phosphines.

The first example of intermolecular hydrophosphination of styrene, 2-vinylpyridine and phenylacetylene with PH_3 catalyzed by complexes $[(Me_3Si)_2N]_2M(NHC)_n$ (M = Ca, Yb, Sm; n = 1, 2) coordinated by series of NHC ligands is described. The reactions of styrene with PH_3 proceed under mild conditions in quantitative yields to afford exclusively anti-Markovnikov product and allow for the chemoselective synthesis of primary, secondary and tertiary phosphines (Figure 1). Addition of phenylacetylene to PH_3 regardless the initial molar substrates ratio results in the exclusive formation of a tertiary tris-(Z-styryl)-phosphine. Crucial effect of the Lewis base coordinated to the metal center on catalytic activity in styrene hydrophosphination with PH_3 was demonstrated.[2]

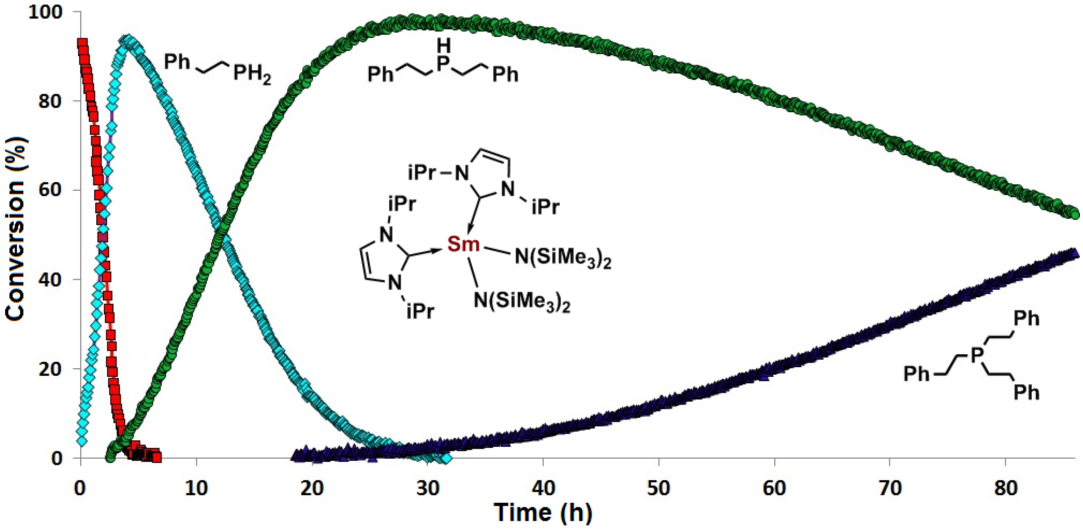

Figure 1. Plot of the reagents conversion vs reaction time for the catalytic hydrophosphination of styrene with PH_3

Acknowledgements

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N-H•••π-Bonding and Guest Entrapment by an Inorganic Macrocycle

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Modern coordination chemistry is overwhelmingly based on supramolecular interactions involving organic architectures, reflecting the earth-abundance and thermodynamic stability of carbon-bonded molecules. However, the question of what happens when you depart from this 'natural' world to the supramolecular chemistry of 'unnatural' structures based on non-carbon frameworks remains largely unanswered, and is an area that potentially provides new directions in molecular activation, host-guest and biomimetic chemistry. Here we explore the unusual host-guest chemistry of a non-carbon macrocyclic framework based on P-N bonds. The polar coordination site of this system promotes new modes of guest encapsulation via hydrogen bonding with the □-systems of unsaturated bonds, and with reactive anionic phosphorus centers. Guests can be kinetically-locked within the structure, with halide anions displaying stronger effective binding than in any classical organic or metal-organic receptor reported to date. Our study underscores the future promise of inorganic host-guest chemistry.

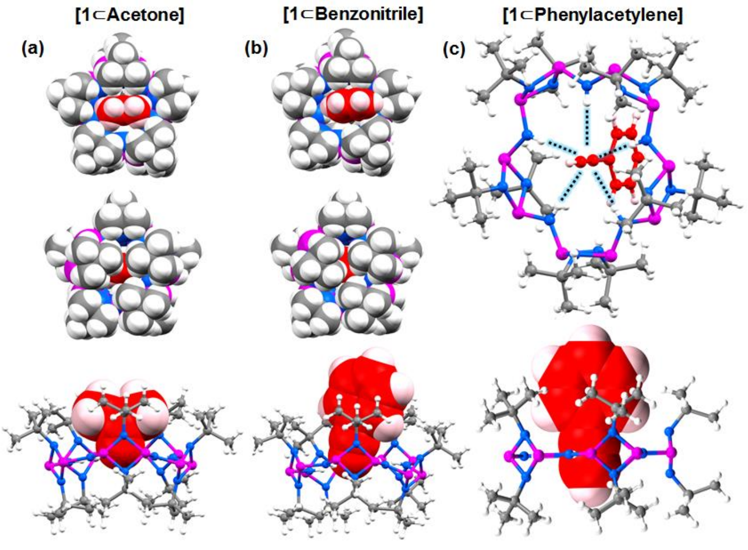

Figure 1 Space-filling diagrams host guest complexes of an inorganic macrocycle **1**

The reaction of dimethylphosphate 1,3-dimethylimidazolium with sulfur

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The investigated of 1,3-dimethylimidazolium dimethylphosphate with elemental sulfur S_8 was established. The reaction was carried out in a benzene medium with intensive mixing, temperature 298 K, and was accompanied by the dissolution of sulfur with a gradual deepening of the brown color. After the mixing was stopped, the stratification of the reaction system was observed, the reaction product accumulated in the lower layer, which made it possible to separate it using separating funnel. The structure of the interaction product of 1,3-dimethylimidazolium dimethylphosphate with elemental sulfur was characterized by ^{1}H and ^{13}C NMR spectroscopy, UV-Vis spectroscopy and high-resolution mass spectrometry. It was found out, while varying the ionic liquids, that the reaction with elemental sulfur is possible only in the presence of dimethyl phosphate-anion and flows through the oxygen atom, carrying a negative charge, with the opening of the S_8 cycle. It was previously shown that the interaction of dimethylphosphate tri-*n*-butylmethylphosphonium with elemental sulfur, occures exclusively on dimethylphosphate-anion and not the cation in this ionic liquid.[1] On the contrary, the 1,3-dimethylimidazolium cation according to ^{13}C NMR spectroscopy is active in the reaction and presumably intercepts the polysulfide-anion formed as a result of the opening of the S_8 cycle due to its nucleophilic attack on the position 2 of the 1,3-dimethylimidazolium cation.

Acknowledgements

The work was supported by Mendeleev University of Chemical Technology of Russia. Project Number 036-2018.

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Designing of the recycling procedure of the model salts containing highly-fluorinated weakly coordinating anions

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Weakly Coordinating Anions (shortly: *WCA*) are large anions with the negative charge dissipated over several electronegative atoms and often shielded by the bulky organic groups. Due to such construction, they have relatively weak interaction with the cations and are extremely resistant chemically, electrochemically and thermally, which can be utilized in the extremely oxidizing environments. Another property of metal salts containing these anions is the solubility of many of them in moderately polar solvents of limited solvating ability, e.g. dichloromethane. This allows for use of these substances as precursors in synthesis of various solvent-free metal ionic compounds, which is often impossible to carry out with other methods. Borohydrides (Fig. 1) or the derivatives of metal amidoboranes are among the compounds prepared utilizing WCAs.[1,2]

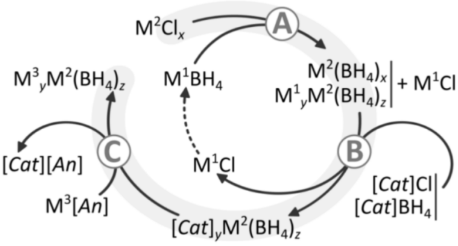

Figure 1. Synthesis of mixed-metal borohydrides, $M_{3y}[M_2(BH_4)_z]$, $z= x+ y$. For the zinc compound prepared this way: M_1=Li, M_2= Zn, M_3=Li, Na, K, [Cat]= [Ph_4P] or [nBu_4N], [An]=[$Al\{OC(CF_3)_3\}_4$] or [$B\{3,5\text{-}(CF_3)_2C_6H_3\}_4$].

The main goal of the current work is to close the loop of the synthetic process and to resynthesize Li[An] salt from the usual by-product – [Cat][An], where [Cat] = [Bu_4N] and [An] = [$Al(O(CF_3)_3)_4$]. For this purpose we carried out a series of experiments to test out a few potential reaction pathways to obtain the desirable product – Li[$Al(O(CF_3)_3)_4$].[3] We aim at development of preferably one-step, high yield method. During the study we use moisture-free environment (Schlenk line and glovebox), wide range of solvents as well as ultrasounds and vibrational mill as the dissipating and facilitating factors. The products are characterized by a variety of methods such as powder and single crystal X-ray diffraction, FTIR and NMR spectroscopies, and thermogravimetric analysis. What is more, we conducted some DFT calculations for the selected crystal structures to explain their electronic properties.

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Heterobimetallic Lanthanide Isocarbonyl Complexes as Single-Molecule Magnets

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4*f*/3*d* isocarbonyl complexes have previously been shown to display single-molecule magnet (SMM) behaviour with large energy barriers to magnetic reversal **(Figure 1)**.[1] Isocarbonyl bridging ligands present an opportunity to explore the structural and electronic effects of bridging systems in relation to SMMs, as polymetallic complexes may provide higher blocking temperatures and energy barriers.

Here, research is focused on utilising the heavier *d*-block metal tungsten, in combination with 4*f* elements to investigate the effect on both the structural and magnetic properties in order to expand on the understanding of isocarbonyl SMMs. (**Figure 2**). [2, 3]. The exhibited physical, electronic and magnetic properties are probed through the characterisation of a number of new CO-bridged 4*f*/5*d* complexes.

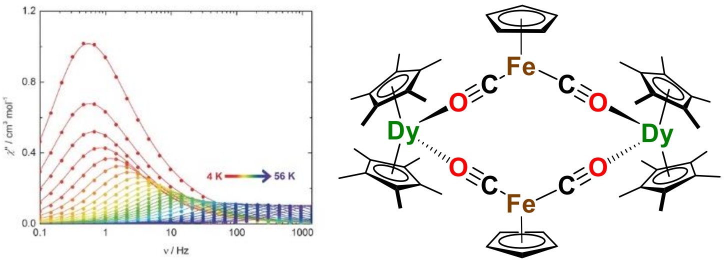

Figure 1: A 4*f*/3*d* carbonyl bridged dimer, **DyFp**, demonstrating SMM behaviour

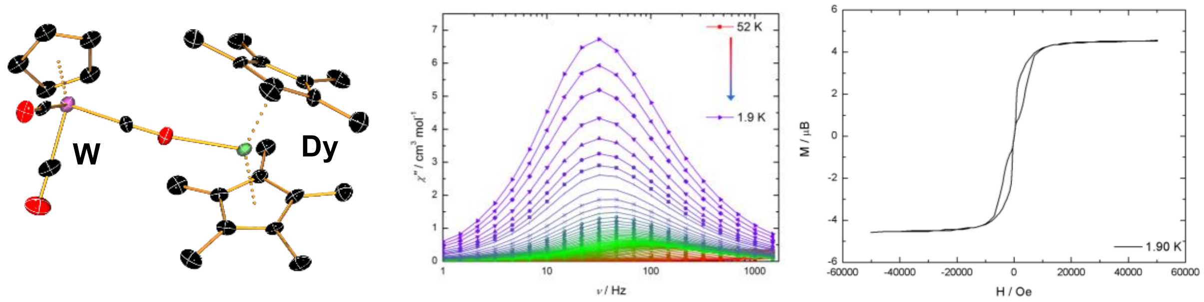

Figure 2: 4f/5d isocarbonyl bridged complexes, crystal structure, out-of-phase susceptibility and magnetic hysteresis of **DyW**

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POSTERS

Synthesis and crystal structures of the first examples of coordination polymers based on 3-(1,2,4-triazol-1-yl)-1-adamantane carboxylic acid

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Adamantane has been long recognized as a perfect platform to support various moieties that are capable of metal coordination for construction of highly ordered metal-organic compounds known as metal-organic frameworks (MOFs). These species find their application in a wide range of different areas – from catalysis to optics and since the first report, the number of publications regarding MOFs rises exponentially.

Amongst the most effective and popular moieties being used for the formation of coordination bonds are the carboxylic group and nitrogen-containing heterocycles – diazoles, triazoles, tetrazole. In this work, 1,2,4-triazole and tetrazole fragments were successfully combined with 1-adamantane carboxylic acid, effectively creating a versatile MOF building block of a mixed azole/carboxylate character. New ligands were used for the synthesis of several polymers with a number of transition metals, such as copper, zinc, cadmium, nickel and cobalt. Their crystal structures were determined by single crystal X-Ray analysis. A curious observation considering influence of substituents on a resulting MOF geometry has been made.

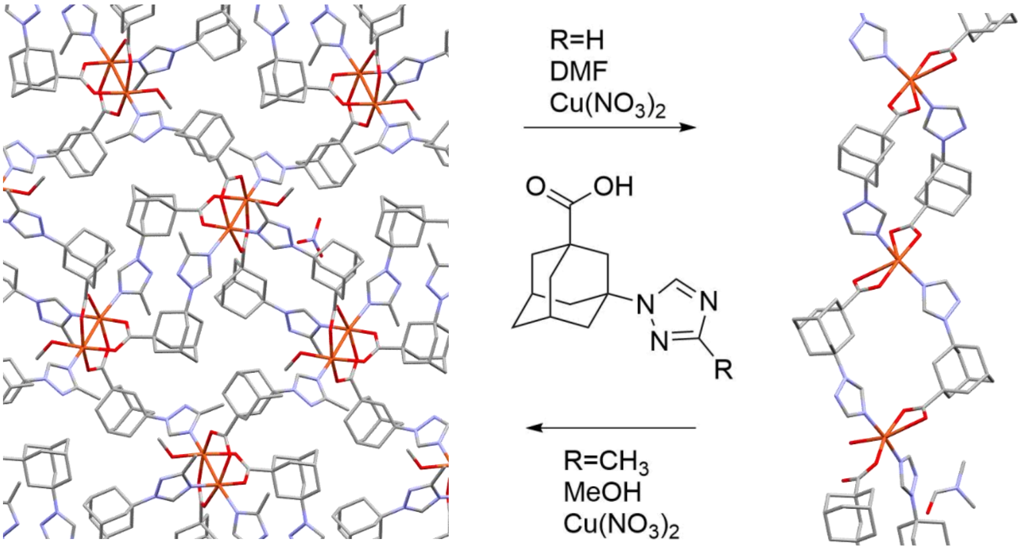

Figure 1. An example of substituent and reaction conditions affecting MOF geometry. Hydrogen atoms are omitted for clarity.

Acknowledgements

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Ruthenium (II) Complexes of 2-substituted Imidazo-1,10-phenanthrolines: Physicochemical and Gas Sensory Properties

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In this work, a series of imidazo[4,5-f][1,10]phenanthroline-containing ligands and their complexes with ruthenium (II) cation was synthesized (**Fig. 1**). Polypyridine imidazophenanthroline-containing Ru(II) complexes are capable of photo-induced electron transfer, including to the conduction band of some semiconductor materials.[1,2] Such photosensitization process will reduce the operating temperature of semiconductor gas sensors and thus reduce their energy consumption.

Energies of HOMO and LUMO of the complexes were suitable for electron transfer from excited state of photosensitizer to the conduction band of semiconductor oxides SnO_2 and In_2O_3 (**Fig. 2**). By means of time-resolved fluorescent spectroscopy, it was shown that the excited states of synthesized complexes have a triplet nature with a high lifetime sufficient for electron transfer to the conduction band of semiconductor.

Hybrid organic-inorganic materials with synthesized complexes based on SnO_2 and In_2O_3 were obtained and studied as sensitive elements of gas sensors in relation to NO_2 and NO gases. Measurements showed that modification of the surface of semiconductor oxides with organic dyes leads to photosensitivity and the appearance of a reproducible sensory signal in the presence of analyte gases at room temperature under periodic illumination with visible light LEDs. Hybrid materials with metal complexes **3** and **5** demonstrated the best results. They were able to determine NO_2 and NO within 0.25–2 ppm at room temperature under periodic illumination with the longest wavelength red LED. For instance, the MPC of NO is 2.6 ppm.

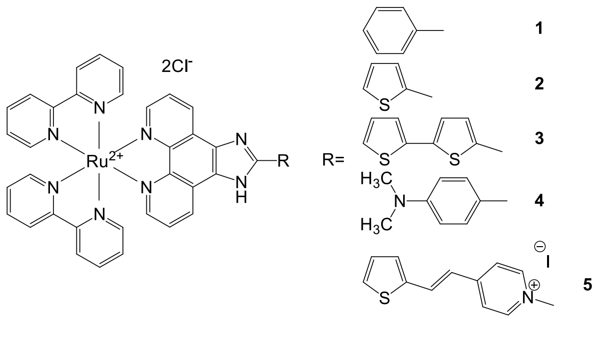

Figure 1. Structures of synthesized complexes

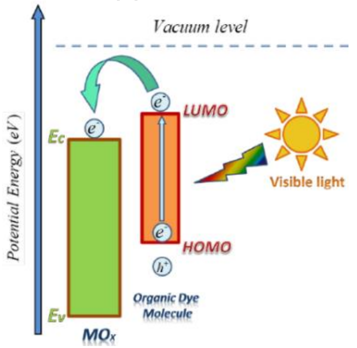

Figure 2. Photoinduced sensitization in a hybrid semiconductor-dye material

Acknowledgements

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Synthesis and properties of the complexes with 4-amino-2,1,3-benzothiadiazole and its derivatives

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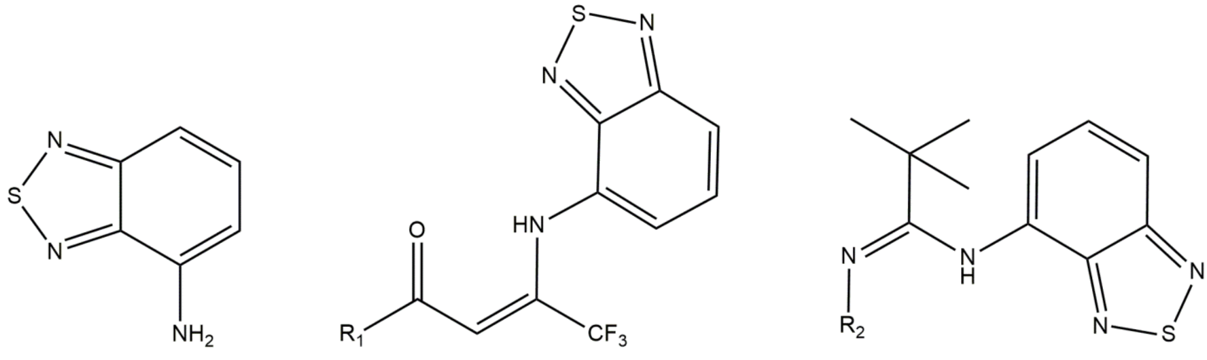
The chemistry of 2,1,3-benzothiadiazole (btd) and its derivatives are actively explored in recent years. Due to photophysical and electron-withdrawing properties, btd derivatives can be used as components of organic light-emitting diodes, solar cells, dyes and as fluorescent markers in biological research.[1,2] Also, these compounds are perspective as ligands in the coordination chemistry. The introduction of additional donor substituents in the carbon ring enhances the coordination ability of btd unit. From this point of view, the 4-amino-2,1,3-benzothiadiazol (NH_2-btd) is interesting. It can be used as a ligand; furthermore, the presence of the amino group gives the possibility for further functionalization of NH_2-btd.

In this work, new complexes $[ZnHal_2(NH_2\text{-btd})_n]$ (Hal = Br, I; n = 1, 2) were obtained with different Zn-to-ligand ratio. Several coordination types of NH_2-btd are observed: 1) *via* N atom of NH_2-group; 2) N atom of the heterocyclic fragment; 3) bridging type *via* both N atoms. Depending on the coordination type, the complexes show polymeric or molecular structure.

We functionalized NH_2-btd using two ways: 1) reactions with β-diketones gave new ketoimines (HK^{R1}-btd); 2) reactions with N-arylpivalimidoyl chlorides gave amidines (HA^{R2}-btd). Treatment of zinc chloride with these btd derivatives in the presence of a base afforded $[Zn(K^{R1}\text{-btd})_2]$ and $[Zn(A^{R2}\text{-btd})Cl]_2$ respectively.

The structures of new compounds were established by single-crystal X-ray diffraction, and their photophysical properties were studied.



NH_2-btd

HK^{R1}-btd, R_1= CF_3-, 2-C_4H_3S-

HA^{R2}-btd, R_2= Mes-, Dipp-

Figure 1. NH_2-btd and its derivatives

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Tetra-24-crown-8-phthalocyanines as a platform for new supramolecular ensembles

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Development of molecular machines and switches is on the foremost edge of the nowadays science. Crown-phthalocyanines attract the attention of the researchers as the very promising platform for formation of molecular machines because of their intensive absorbance in visible range and its high sensitivity to external influence as well as their ability to form different supramolecular ensembles.

In this work we present synthesis and investigation of supramolecular aggregation of 24-crown-8-substituted phthalocyanine and ist metal complexes (Mg(II), Zn(II), Cu(II), Ni(II)) with viologens as the first step towards creation of new electrochemically-driven molecular machines. It was shown that addition of viologen to MgPc and ZnPc solution leads to slight bathochromic shift of the Q-band in UV-Vis spectra (Fig. 1) which can evidence the formation of J-aggregates. However, in the same conditions for H_2Pc, CuPc and NiPc significant hypsochromic shift of the Q-band occurred (Fig. 2) that can testify the formation of cofacial dimers. The difference can be explained by the presence of axial ligands in the molecules of MgPc and ZnPc which prevent the formation of cofacial dimers as it was earlier shown on similar compounds[1]. Also it was shown that supramolecular aggregation strongly depends on the solvents and concentration of the solutions. The most prominent results were shown in the mixture of CH_2Cl_2 with acetone at the concentrations of 10^{-4}.

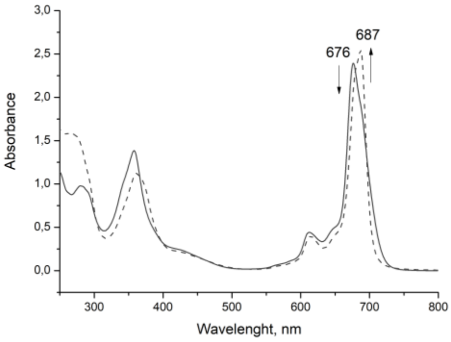

Figure 1. UV-Vis spectrum of ZnPc in CH_2Cl_2 ($C=10^{-4}$) by addition of 2 eq. of viologen

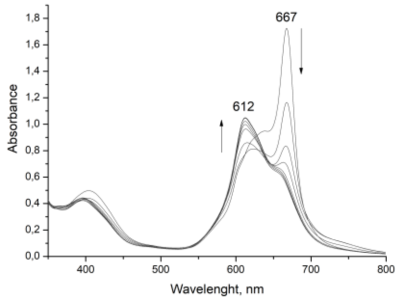

Figure 2. UV-Vis spectrum of NiPc in CH_2Cl_2 ($C=10^{-4}$) by addition of 2 eq. of viologen

Acknowledgements

This work was supported by the Russian Science Foundation (Grant 18-73-00249).

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Rutenium (II) mixed-ligand complexes with 2-arylbenzimidazoles and some N^N-donor ligands: synthesis, optical and electrochemical properties

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Polypyridyl ruthenium (II) complexes are used as sensitizers in DSSC. Such complexes contain two types of ligands: "donor" C^N ligands, that absorb the light effectively, and "anchoring" N^N ligands, that are covalently bonded to the surface of mesoporous titania and responsible for electron transfer to semiconductor`s conduction band. Cyclometalation increases stability of complexes due to formation of five-membered metalocycle containing covalent metal-carbon bond. Introduction of various substitutes into C^N ligand affect electron structure of molecule, and, consequently, photophysical and electrochemical properties.

In this work we introduce Ru (II) complexes with various 2-arylbenzimidazoles, dimethyl (dmdcbpy) and dioctyl (dodcbpy) esters of 4,4`-dicarboxy-2,2`-bipyridine and some auxiliary N^N ligands. All the complexes are characterized by NMR, UV-vis and luminescence spectroscopy, and cyclic voltammetry (CV). For some complexes crystals for X-ray structural analysis are obtained.

A series of complexes with general formula $[Ru(dmdcbpy)_2L]PF_6$ is obtained, where L = 1-phenyl-2-aryl-benzimidazole with -Cl, $-NO_2$, -OMe, -NMe2 and -H substitutes in 2-aryl ring. An increase in the electron-donor properties of substituents in 2-arylbenzimidazole from $-NO_2$ to -OMe leads to a decrease in the redox potential (Ru^{3+}/Ru^{2+}), and to a red-shift of absorption and luminescence bands, except for nitro-substituted one: the bands are not shifted to the short-wave region, comparing to the other complexes, and its` luminescence is not very intense.

Tris-heteroleptic complexes have more electron transitions due to the lower symmetry. However, during the synthesis of mixed-ligand complexes, the problem of separation of three formed complexes arises. The complexes are separated by column chromatography, but, because of similar structure, their eluotropic properties differ slightly from each other. To solve this problem, long alkyl substituents were introduced into one of the ligands. Such substituents also isolate the complexes from each other on the semiconductor`s surface in the cell; the density of adsorbed dye and the size of cations are important to avoid undesired interfacial charge transfers. A series of complexes was obtained, where cyclometalated ligand is 1-phenyl-2-(4-chlorophenyl)benzimidazole, dmdcbpy and dodcbpy are used as anchoring ligands, and 1,10-phenanthroline, 4,4'-diocthoxy-2,2'-bipyridine, 5,5'-dimethyl-2,2'-bipyridine – as auxiliary ligands.

Novel reactivities of NHC-stabilized benzylboranes

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Benzylboranes / benzylborates have been known for decades and are nowa-days typically used in radical or anionic benzyl transfer reactions to electrophilic substrates with scission of the B–C bond between the boron atom and the benzyl entity.[1,2] Reactions with retention of the mentioned B–C bond are very rare but include the addition of alkynes to form hydroboranaphthalenides.[3,4] The currently limited chemistry of benzyl boranes is surprising despite various reactive sites in parent benzylboranes of type $PhCH_2BH_2$, which includes a broad scope for reactions at B–H bonds, benzylic CH_2 moieties and the aromatic system in the phenyl ring.

In order to improve the stability of the parent benzyl borane $PhCH_2BH_2$, I*i*Pr (I*i*Pr = :C{N(*i*Pr)CH}$_2$) was introduced to form the respective carbene-borane adduct, (I*i*Pr)-BH_2Bn. Reactions with BCl_3 and BBr_3 afforded complete halogenation at the parent boron atom in the carbene adduct, whereas BI_3 led to partial iodination at boron with concomitant borylation of the phenyl moiety, Figure 1.

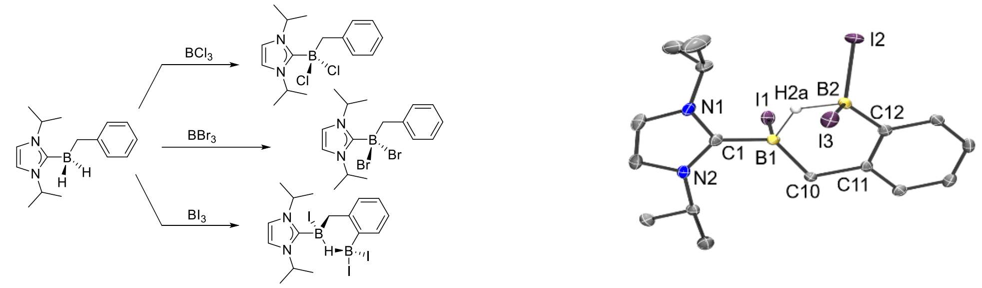

Figure 2. I*i*Pr-benzylborane and its reactivity towards borontrihalides (left), cristal structure of bisborylated product (right)

The functionalization of the benzylic CH_2 entity in I*i*Pr-BBr_2Bn could be achieved by the radical bromination with introduction of one or two bromine atoms at carbon, respectively. The product I*i*Pr-$BBr_2CHBrPh$ showed remarkable behaviour towards BI_3 with formation of a zwitterionic species, Figure 2.

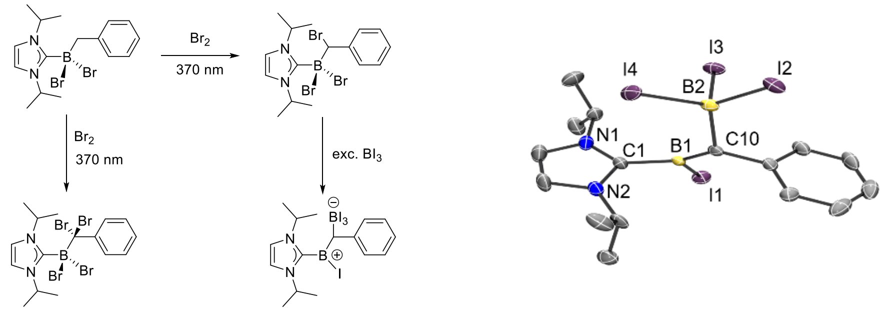

Figure 3. UV induced radical bromination of I*i*Pr-BBr_2Bn and subsequent reaction with BI_3 (left), crystal structure of zwitterionic species (right)

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Modulation of reactivity and geometry of cyclometalated Ir(III) complexes with 2-arylphenanthroimidazoles

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Cyclometalated iridium(III) complexes are widely used in various fields of chemistry because of their unique photophysical and electrochemical properties as well as their exceptional stability. Still, for some purposes the rare labile Ir(III) complexes are needed. It is supposed that sterically hindered ligands could destabilize the inert octahedral geometry of Ir^{3+} increasing lability of the complexes. We studied[1] two bis-cyclometalated complexes of Ir(III) with 1,2-diphenanthroimidazole (**1**) and 1-phenyl-2-(3,4-dimethoxyphenyl)-phenanthroimidazole (**2**). Single-crystal X-ray analysis showed that the first complex crystallizes in a monomeric form with a rare trigonal-bipyramidal geometry, while the second has the common octahedral dimeric structure. The reactivity of complex **1** was demonstrated in a gas-solid reaction with iodine. The ligand exchange was monitored by X-ray diffraction as the initial single-crystal retained during the process. An exceptional steroselectivity caused by the crystal packing peculiarities was revealed (Fig. 1).

In summary, a way to control the reactivity of cyclometalated iridium(III) complexes by influencing their geometry has been proposed. A stereoselective ligand exchange reaction in a pentacoordinated Ir(III) complex with single-crystal retention has been characterized by X-ray analysis.

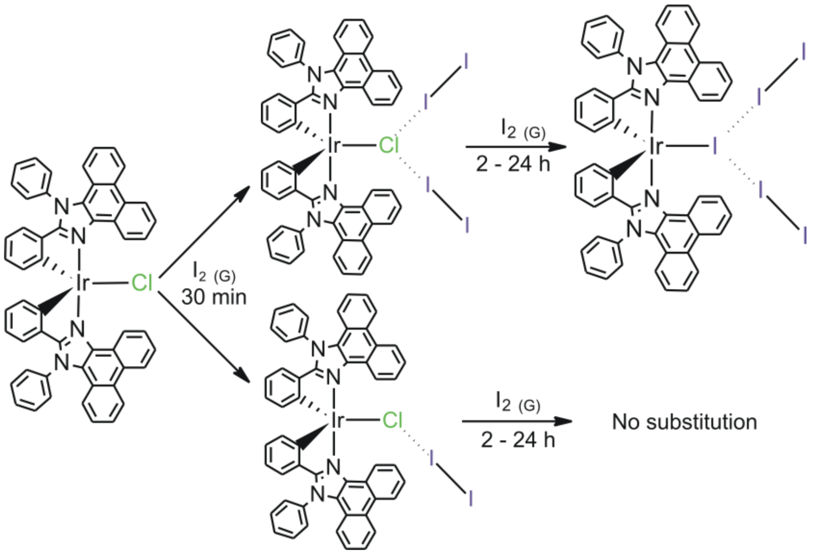

Figure 1. Ligand substitution in complex 1

Acknowledgements

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Counterion effects on the formation of isopropyl-bis(2-picolyl)amine (*i*Pr-bpa) complexes with Zn(II) and Cu(II)

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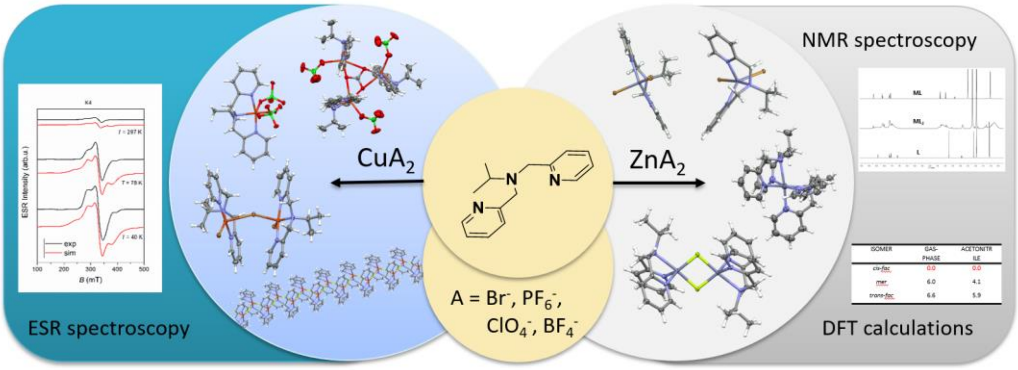
Bis(2-picolyl)amine (**bpa**) ligands are tridentate ligands, with flexible linking arms that allow both meridional (*mer*) and facial (*fac*) coordination geometry. The formation of geometrical isomers, as well as the formation of complexes of different stoichiometry and coordination number, can be influenced by a number of effects, for example the coordinating ability of the counterion.[1] Counterions of strong coordinating ability, due to their localized charge, compete with the ligands for binding the metal, and often lead to formation of **ML** or bridged complexes. In literature, similar complexes were studied as models for multinuclear zinc enzymes[2] for capturing CO_2. Large counterions of dispersed charge, such as perchlorate do not interfere with binding of the ligand, enabling formation of **ML₂** complexes. A similar system was described as a fluorescent Zn(II) indicator.[3]

In this work, we studied how different counterions effect the stoichiometry, coordination number and geometry of complexes. Crystal structures of four Zn(II) and four Cu(II) complexes were determined, revealing complexes of a large structural variety: monomeric **ML** and **ML₂**, bridged dimers, a coordination polymer and a cyclic trimer that binds atmospheric CO_2. For Cu(II) complexes, the local magnetic properties were studied by ESR spectroscopy, while NMR spectroscopy was used to study the solution structure of Zn(II) complexes. For the **ML₂** complex obtained with the perchlorate anion, DFT calculations were used to determine the relative stability of isomers.



ISOMER	GAS-PHASE	ACETONITRILE
cis-fac	0.0	0.0
mer	6.0	4.1
trans-fac	6.6	5.9

Figure 1. Crystal structures and methods of characterization of *i*Pr-bpa complexes with Zn(II) and Cu(II)

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Dehydrocoupling of Silanes and Alcohols under General Base Catalysis

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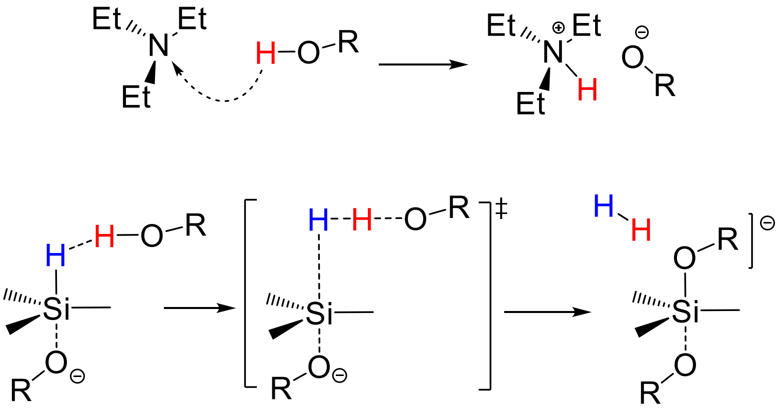
Recently we have reported on the formation of the SiH···HO dihydrogen bonds (DHB) between silanes and fluorinated alcohols in solution.[1] DHB complexes are well known as intermediates of the reactions involving hydride-proton transfer.[2] However, the reaction between silanes and alcohols doesn't proceed in the absence of catalysts (such as Lewis acids[3] or Brønsted bases[4]).

Current work aimed to reveal the reaction mechanism and identify possible intermediates of dehydrocoupling of silanes ($PhSiH_3$, Ph_2SiH_2) and proton donors [$(CF_3)_2CHOH$, *p*-NO_2PhOH] in the presence of Et_3N. The reaction was studied by combination of molecular spectroscopy methods (NMR, IR and UV) with *ab initio* DFT calculations.

The ion pair $[Et_3NH]^+[RO]^-$ formation was shown spectroscopically. According to DFT calculations alkoxide anion $[RO]^-$ is able to coordinate Si atom yielding 5-coordinate species $[L_3Si(OR)H]^-$. This leads to Si–H bond activation and concomitant increase of silicon hydride basicity. In turn, the increase of DHB complex strength promotes hydride-proton transfer and H_2 evolution. On the base of experimental data and DFT calculations the optimal reaction mechanism for dehydrocoupling is suggested (Scheme 1).



Scheme 1.

Acknowledgements

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The comparison of the low-spin and high-spin intermediates Fe(V)=O in the selective oxidation of organic substrates

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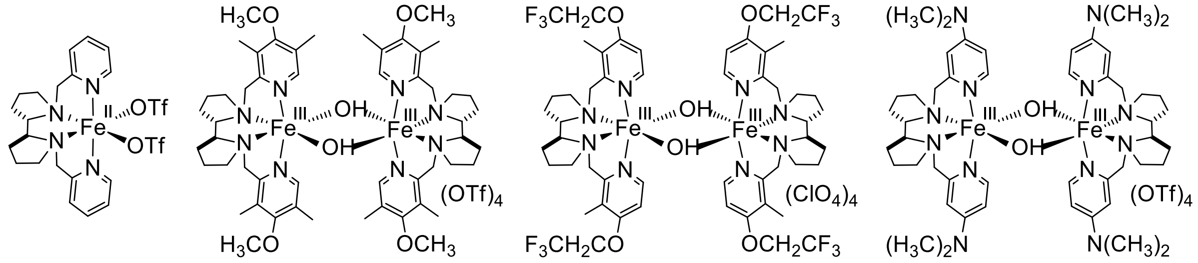
The ability of the enzymatic systems to conduct chemo-, regio- and stereoselective oxidation of organic substrates under mild conditions has inspired the search for synthetic iron based catalyst systems capable of conducting similar transformations. The significant progress in the search of the chemical systems capable of oxidizing C-H and C=C bonds with preparative activity and selectivity has been achieved by the synthesis of complex 1 (Figure 1).[1] It is generally accepted that the active species of the catalyst systems based on non-heme iron complexes and hydrogen peroxide as an oxidant are oxoiron(V) intermediates. However, electronic and steric factors that determine the activity and selectivity of these intermediates are unclear.



1 **2** **3** **4**

Figure 1. Structures of complexes used in this work

It is very interesting to compare the activity and selectivity of the low-spin (S = 1/2) and high-spin (S = 3/2) Fe(V)=O species in regio- and stereoselective oxidation of organic substrates, because for the related Fe(IV)=O intermediates, the spin-state is considered as one of the key factors determining its chemical reactivity.[2] Thus, catalyst systems **1-4**/$H_2O_2(CH_3CO_3H)/RCOOH$ have been compared in the enantioselective epoxidation of chalcone, hydroxylation of cyclohexane, menthyl acetate, dihydrocitronellol acetate, and (−)-ambroxide. The systems, exhibiting the high-spin (S = 3/2) intermediates, demonstrate higher enantioselectivity (*ee*) in the epoxidation of chalcone and higher regioselectivity in the hydroxylation of alkanes. High-spin intermediates are less reactive toward cyclohexene than low-spin intermediates. These reduced reactivity is consistent with their higher enantioselectivity and regioselectivity.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, grant 18-33-20078.

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Iridium(III) complexes based on phenanthro[9,10-d]imidazole: luminescence tuning through N^C ligand design

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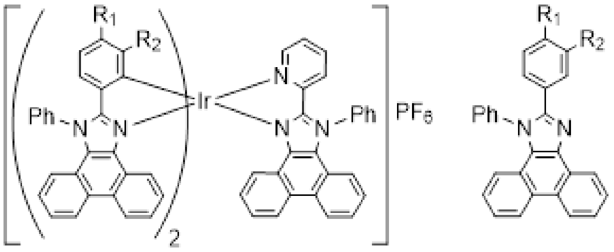
Nowadays, researchers worldwide carrying out investigation of cyclometalated complexes of platinum group elements. In particular, iridium (III) complexes are intensively studied because of their high emission efficiency and long lifetime of the excited state. These complexes are used in OLED technologies, in luminescent microscopy, and bioimaging as efficient phosphor.[1]

Novel iridium(III) complexes with ligands based on phenanthro[9,10-d]imidazole were obtained (Figure 1). The complexes and ligands were characterized by using NMR spectroscopy, mass spectrometry, X-ray diffraction analysis. The photophysical properties of the ligands and complexes were carefully investigated. These complexes obtained possess efficient triplet emission in solution. Variation of the ligand structure enabled to shift the emission band in the red region. Thus, it gives us an opportunity to use the compounds to visualize tissues or organs of macro-objects through the first therapeutic transparency window.[2]



1: R_1=R_2=H
2: R_1=H, R_2=Br
3: R_1=NO_2, R_2=H
4: R_1=OH, R_2=H

Figure 1. Structures of the complexes and ligands under study

Acknowledgements

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Fabrication of Uniform Surface Coatings of Graphene Oxide on Solid Substrates

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Graphene oxide (GO) is a chemical derivative of graphene, a ground breaking material for many applications such as electronics, chemical sensing, catalysis etc. This functionalized 2D carbon can be packed into monolayers on solid surfaces there by serving as perfectly flat templates for bottom-up self-assembly or as a precursor of conductive films on glasses. However, the methods for the deposition of the GO layers with controlled packing density remain to be developed. Herein we describe a strategy for the formation of uniform films of GO on solid surfaces depending on the applied experimental parameters.

The GO surface films were formed by a vertical transferring of the self-assembled GO monolayers from the oil/GO hydrosol interfaces onto the silicon wafers. The quality of the resulting films was evaluated by SEM examination in combination with the measurements of the contact angles of the silicon substrate before and after the transferring of GO monolayer onto the solid support (Figure 1). The contact angle steadily decreased with the increase of the packing density of GO on the surface. The increase of the hydrosol concentration also led to the increase of the packing density. The chemistry of non-polar solvent did not have a significant effect on the morphology of the GO films. However, the morphology of the films significantly depended on temperature. Based on these observations, we suggested a procedure for the increase of packing density of GO in films via subsequent reduction and deposition protocol.

We believe that our method provides feasible and simple “soft matter” approach to the formation of functionalized films of 2D carbons and it can be extended to the large-scale fabrication of the GO films.

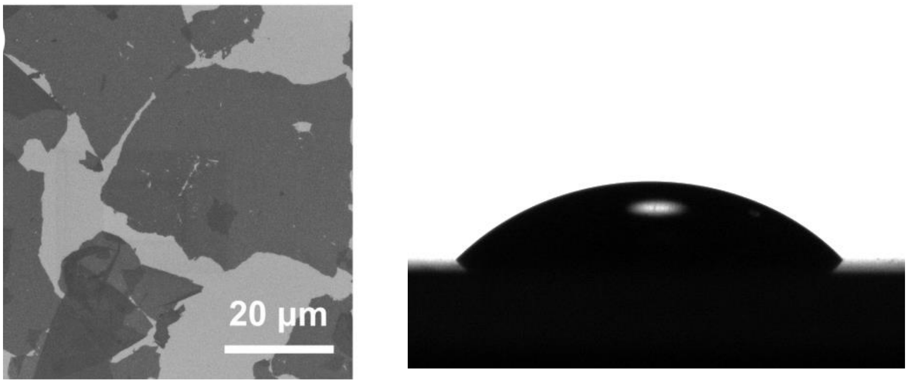

Figure 1. SEM-image and the contact angle of the GO monolayer transferred from the oil/water interface onto the silicon wafer

Acknowledgements

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Study of oligoelementosilazanes interaction with the carbon materials surfaces

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We have conducted a comparative study of oligoelementosilazanes solutions interaction with the of carbon materials surfaces, which is required for choosing effective impregnating compositions in the development of ceramic-matrix composite materials. The investigated oligoementosilazanes (OMGS -M) involving fragments of Si-N-M, where M = Ta, Ti, Zr, Hf and Y in various combinations, ensure the formation of oxidation resistant ceramic nitride-, carbonitridesilicon matrices in the process of pyrolysis. The nature of the impregnating composition interaction with the surface depends on the surface properties (lyophilic or lyophobic ones). Moreover, the impregnating capacity, and, consequently, their wetting of the surface is determined by the limiting wetting angle (LWA), which is measured by the Young-Laplace method.

It was found that all oligoelementosilazanes are featured by good wettability, except for zirconium-containing oligosilazane for which LWA is above 124,0 °. However, the addition of yttrium to it therewith significantly reduces the LWA to 24,1°. The best values were obtained for the impregnating composition based on OMGS -TaHf. Depending on the LWA value in the range from 0°(fig.1, a) to 124°(fig.1, b), all the studied oligoelementosilazanes can be distributed in the following sequence:

OMGS -TaHf >OMGS -TaY > OMGS -ZrY >OMGS -TiY > OMGS -Zr.

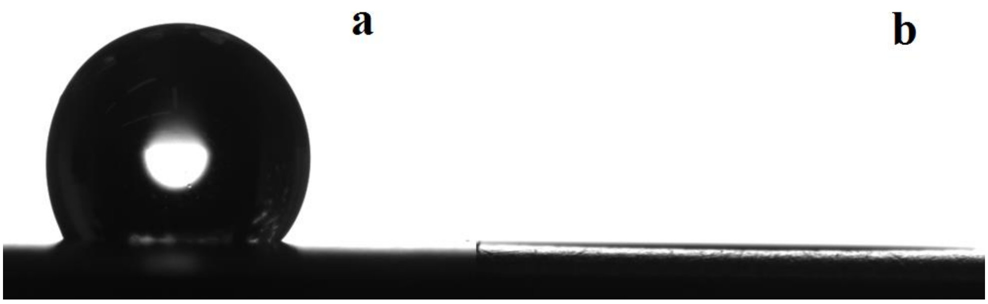

Fig.1 Microphoto of sessile drop of oligoelementosilazanes solution (OMGS -M) on surface of the same carbon material. a) OMGS -TaHf solution; b) OMGS -Zr solution.

Fine tuning of uranyl(VI) charge-transfer emission in hexacyanidometallate-based coordination frameworks

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Luminescent materials gather enormous interest due to a wide range of applications in display devices, light-emitting diodes, optical amplifiers, photovoltaics, chemical sensing, molecular thermometry and bioimaging.[1] Among them, a considerable attention is given to the uranyl-based coordination frameworks exhibiting attractive charge-transfer visible photoluminescence with the moderate control of emission color.[2] Despite having a rich chemistry, the UO_2^{2+} cation was rarely combined with policyanidometallates.[3,4] Metal cyanide complexes were extensively employed in generation of advanced physical properties, such as photomagnetism, negative thermal expansion and magnetization induced second harmonic generation.[5,6] Lately, cyanide complexes of transition metal ions were shown to efficiently sensitize and tune lanthanide(III) emission through the metal-to-metal energy transfer.[7-9] In this context, we have undertaken the challenge to investigate the impact of hexacyanido-metallates, $[M^{III}(CN)_6]^{3-}$ (Co, Rh, Ir) and $[Pt^{IV}(CN)_6]^{2-}$, upon the uranyl(VI) emission within functional materials. We present an unprecedented family of heterometallic coordination networks, three-dimensional $[(UO_2)_2(OH)(4,4'\text{-bpdo})_2][M(CN)_6]$ (M = Co, Rh, Ir) and layered $[(UO_2)_2(OH)_2(4,4'\text{-bpdo})_2][Pt(CN)_6]$, showing uranyl-based photoluminescence whose color is effectively tuned by d-block metal ions (Figure 1).[10]

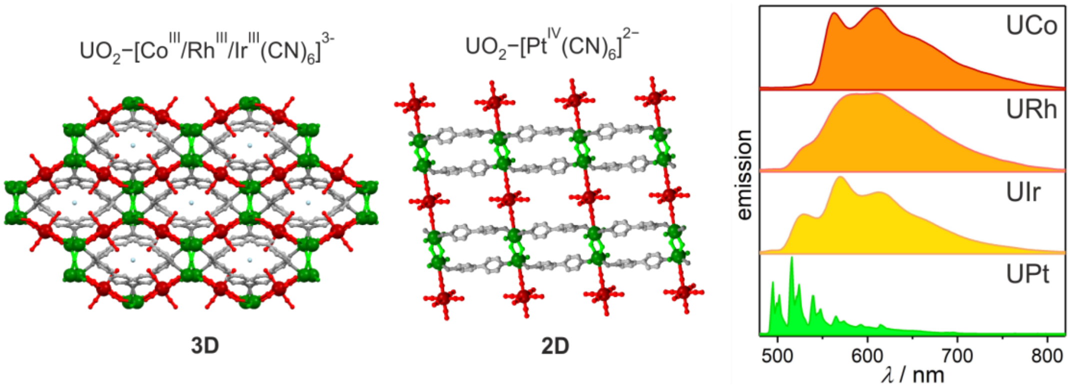

Figure 1. Bimetallic UO_2^{2+}–$[M(CN)_6]^{n-}$ coordination networks with tunable uranyl photoluminescence

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Crystallzation of calcium phoshates from solutions simulating the composition of human blood plasma

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Crystallization processes of slightly soluble compounds have always attracted the attention of researchers [1, 2]. Interest due to the fact that these compounds are part of pathogenic minerals and they are diseases of the human body, such as arteriosclerosis - disease associated with the deposition of calcium salts in the blood vessels. This disease is the second of the prevalence of all sclerotic lesions of blood vessels after atherosclerosis. Furthermore, the study of these compounds is of interest for the synthesis the promising biomaterials [3]. Information about the crystallization of pathogenic and necessary for human body slightly soluble compounds from biological fluids is very few in number [4].

The main difficulty of the study of such systems is their composition. Biological fluids consist of a plurality of components, both inorganic and organic [5-7].

For example, blood plasma is the link between all located outside the blood vessels fluids, that is why it was chosen as a model environment. Blood is liquid tissue. It carries out transportation of chemicals in the body. In addition, blood performs a protective, regulatory, and other thermoregulatory function.

This paper presents the results of studies on the nature of crystallization of slightly soluble compounds from solutions simulating the composition of human plasma, in under conditions close to the physiological.

Identified ranges of properties of the system that simulates the composition of the blood plasma, depending on the supersaturation: 3-15, 15-30, 30-90 according to the optical density, conductivity and pH. The order and constant nucleation ($n = 1.6$; $k = 88.61$) of calcium phosphates generated in the model solution of blood plasma are determined. Defined order and constants of the crystal growth of calcium phosphates formed in the model solution of blood plasma. Order is two. Constants varies depending on the pH and supersaturation, but not much different from each other in size ($k \approx 4.4E-06$). Types crystallization model solutions plasma are compared for systems with different initial supersaturation. As part of the sediment revealed the presence of calcium-deficient hydroxyapatite and calcium octophosphate. Influence of additives on the crystallization process model solutions of blood plasma was investigated, shown that: introduction of additives of magnesium, glucose, alanine does not affect the crystal growth reaction order ($n = 2$); rate constants of investigated systems with the introduction of different concentrations of magnesium supplements are not changed ($k = 0.2E-03$), and with increasing concentrations of alanine and glucose increase.

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Magnesium octa[(4’-benzo-15-crown-5)-oxy]phthalocyanine in phosphate buffer: supramolecular organization, phototoxicity, photo-induced generation of ROS and accumulation in tumor cells

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Photodynamic therapy (PDT) induces the use of three non-toxic components, namely, photosensitizer (FS), O_2 and light.[1] High reactive oxygen species (ROS) including singlet oxygen ($^1O_2$) are obtained under the laser irradiation in the presence of FS.

In the present work, octa[(4'-benzo-15-crown-5)-oxy]magnesium phthalocyanine (Mgcr$_8$Pc) is studied as a potential PDT agent. The presence of crown groups on the periphery of the macrocycle ensures the solubility of Mgcr$_8$Pc in the water environment and the possibility to control its supramolecular organization in solution. The purpose was to assess the phototoxicity, ROS levels, and accumulation of Mgcr$_8$Pc in HeLa tumor cells. Absorption and fluorescence spectroscopy, fluorescence microscopy using confocal laser scanning microscope were used in this study. The light toxicity found (IC_{50} dose) for Mgcr$_8$Pc was 1.83 μM. The ROS formation studied with use of fluorescent ROS detector $DCFH_2$ revealed the plateau on the curves of fluorescence intensity vs time (Fig. 1A) after 30 min of irradiation. Mgcr$_8$Pc (5 μM, 24 h) is absorbed by HeLa cells and localizes predominantly in the cytoplasm (Fig. 1B).

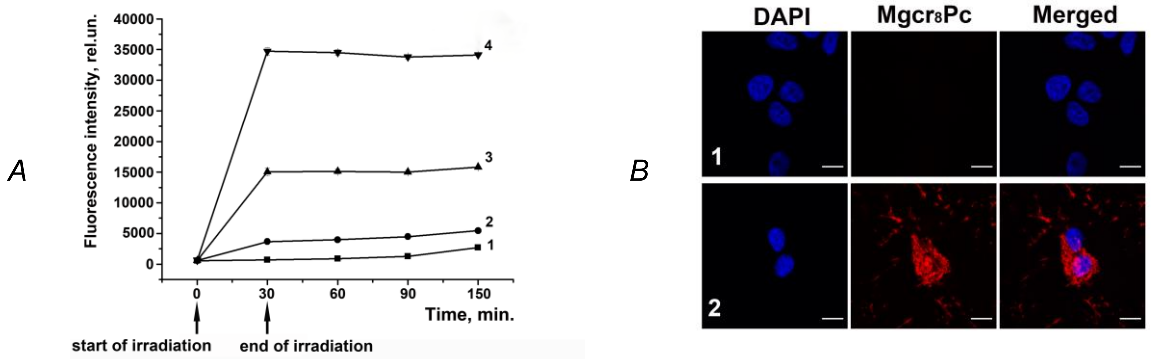

Figure 1. A1. Changes in the fluorescence intensity of DCF in HeLa cells without Mgcr8Pc (1) and in its presence at 1.56 μM (2); 3.1 μM (3) and 6.25 μM (4) after irradiation in time. **B1.** Merged set of confocal images combining DAPI (blue) and Mgcr8Pc (red) channels for HeLa cells obtained at 63X magnification. Panel 1 – untreated cells; panel 2 – cells treated with Mgcr8Pc (5 μM for 24 h). Scale bar – 10 μm.

Acknowledgments

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Spectrophotometric determination of stability constants of different amino acid complexes of magnesium

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Nowadays it looks very important to investigate negative factors which can influence on the processes of normal bone formation and can become a reason of different types of diseases. It is known that pathogenic organomineral aggregates usually crystallize in complex biological fluids. One of components of these fluids are ions of magnesium and different biogenic amino acids. They can interact to each other to form complexes which can participate in the normal physiological and pathogenic processes.

That's why the aim of our study is to investigate processes of formation and destruction of biogenic amino acid complexes of magnesium and calculate quantitative characteristics of their formation, such as overall stability constants.

Among numerous methods, the spectrophotometric method using mathematical means of treating data was applied. This method proved to be a very suitable one for the investigated systems in the ultraviolet spectral region. Also there was some researches using the same mathematical means of treating data on another objects of analysis.

To determine the stability constants of the complexes which are formed by the interaction of amino acids and Mg^{2+}, a method based on the mixing of solutions of participants of complexation and further spectrophotometric determination using a spectrophotometer is used. Using the obtained spectra of mixes like on Figure 1, the method of multiple linear regression is used. Then, we have calculated attenuation coefficients using the absorbance on different wavelengths and Optic-MLR software. After that, we have found equilibrium concentrations of all reaction participants and based on it, have calculated the overall stability constants.

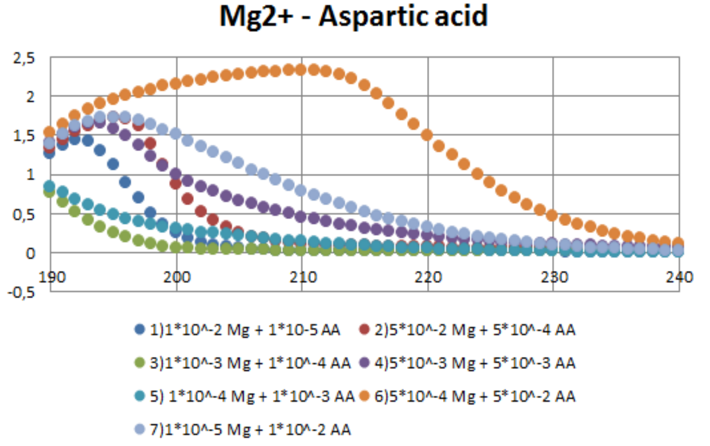

Figure 1. Spectra of Mg^{2+} and aspartic acid mixes

The first estimate of overall stability constants of all complexes of biogenic amino acids and magnesium are in the range between 10^2 and 10^5. These data can be used as a theoretical base and supporting material in diagnosing and treating diseases associated with the pathologic formation of minerals in the human body, and as a guide for development of the drugs with specific action.

Blood-brain barrier penetrating luminescent conjugate based on cyclometalated platinum(II) complex

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Transition metal complexes are widely studied and utilized as probes for bioimaging and luminescent microscopy.[1,2] The selectivity of labels towards specific compartments of the cell or tissue is of critical importance in biological visualization. Currently, the investigation of neurodegenerative disorders such as Alzheimer's disease (AD) becomes of great importance.[3,4] Using the luminescent labels capable of penetrating the blood-brain barrier (BBB) and bonding selectively to β-amyloids provides important information on the pathogenesis of AD and thus helps to create effective methods for its detection, prevention, and therapy.

Herein we report the synthesis, characterization of the structure, and photophysical properties of the cyclometalated Pt(II) complex and conjugate based on the complex and peptide, which is known to bind with amyloid-β (figure 1). Cytotoxicity of the conjugate was evaluated by using MTT method on HeLa and ECV cell cultures. Neuroimaging experiments on *Drosophila melanogaster* reviled that the compound penetrates BBB and distributes in the brain.

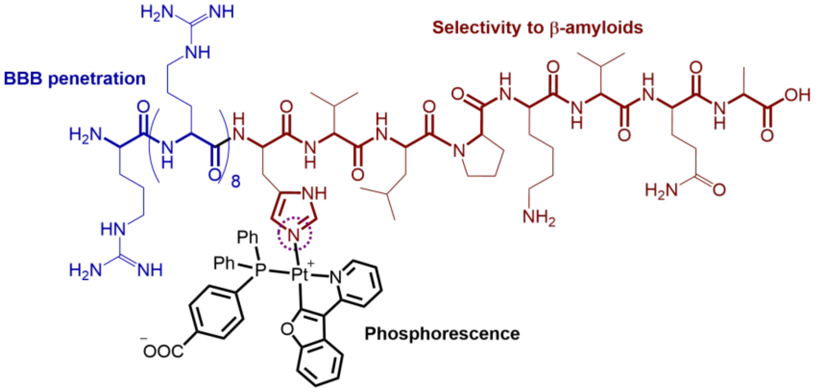

Figure 1. Structure of the conjugate under study

Acknowledgements

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Porphyrin Metal-Organic Framework Assembled in Layered Europium Hydroxochloride

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Metal-organic frameworks (MOF) based on porphyrin derivatives comprise a new class of functional porous materials offering useful properties of selective catalysts such as structural stability and widely varied functionalities for specific binding. However, MOFs may not be sufficiently stable in a course of the interactions with the reactive components. A possible strategy for solving this problem is the immobilization of MOF on the solid surface of inorganic layered templates. This approach makes it possible to obtain a stable hybrid material, which might exhibit a synergistic effect due to a combination of the properties of integrated organic and inorganic components. In this work we realize this idea through the intercalation of 5,10,15,20-tetrakis(4-carboxyphenyl) zinc porphyrinate (ZnTCPP) and a binuclear complex of zinc acetate as the MOF components into the microparticles of layered europium hydroxochloride (EuLH).

The catalytic activity of the material was demonstrated in the model reaction of the hydrolysis of bis(4-nitrophenyl) phosphate, which is widely used as a model for DNA phosphodiesterase. The UV-vis absorption spectroscopy was used to monitor the reaction with the hybrid catalyst comparing to a control system with pure EuLH. The data showed a difference in the reaction mechanisms in the BNPP-based system and the control system. We analyzed the composition of the reaction products in the hybrid catalyst to study the origin of this difference. The analysis of the catalysts was carried out using a combination of methods including X-ray diffraction, IR- and Raman-spectroscopy and MALDI-TOF mass-spectrometry. We pioneered the application of MALDI-TOF mass-spectrometry for a direct qualitative detection of low-molecular-weight organic components (BNPP and its products of hydrolysis) within such hybrid systems.

In summary, our results made it possible to determine the mechanism of the catalytic reaction and to assess the contribution of each component to the functional synergy of the hybrid system. We believe, that our method offers a labile platform for the development of efficient hybrid catalysts, suitable for conversion of organic phosphates and creation of elements of chemical sensors, sensitive to such compounds.

Acknowledgements

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Rare- and alkaline earth metal complexes with substituted diphenylmethanido ligands – synthesis, structures and reactivity

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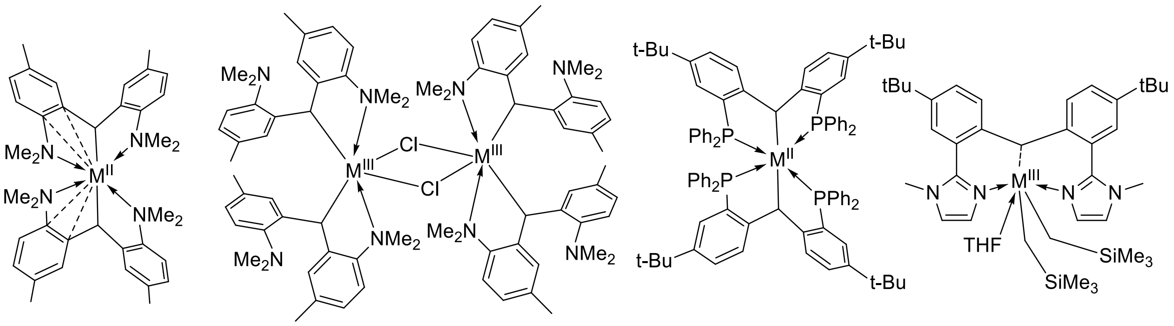
Alkyl complexes of rare earth metals have interest due to their unique reactivity and catalytic application for polymerization of alkenes and dienes, hydrofunctionalization of unsaturated hydrocarbons and are able to activate C–H bonds. Despite the huge number of currently known alkyl derivatives Ln^{III}, their analogues in the oxidation state +2 still remain extremely rare. The synthesis of new types alkyl complexes of rare and alkaline earth metals and the study of their reactive ability and catalytic activity are an topical task.

In our study new pincer diphenylmethanido ligands containing Lewis base groups in *ortho*-positions of the Ph rings (N-Me-imidazolyl-, - NMe_2, - PPh_2, - $P(O)Ph_2$ and - $P(S)Ph_2$) were used as alkyl ligands for preparation of rare and alkaline earth metal complexes. The presence of donor atoms capable to coordinate metal ion, can increase stability.

Novel Sc, Y, Yb^{II}, Sm^{II} and Ca bis(alkyl)s bounding with tridentate bis(2-(dimethylamino)-5-methylphenyl)methanido ligand $[2,2'\text{-}(4\text{-}MeC_6H_4NMe_2)_2CH]^-$ (Ca (**1**), Yb (**2**), Sm (**3**), Y (**4**), Sc (**5**)) or bis(4-(tert-butyl)-2-(diphenylphosphino)phenyl)methanido ligand $CH(C_6H_3\text{-}4\text{-}tBu\text{-}2\text{-}PPh_2)^-$ (Ca (**6**), Yb (**7**)) have been obtained by the salt-metathesis reaction of $MHal_n(THF)_x$ (M = Yb^{II}, Sm^{II}, Ca, Hal = I, n = 2; M = Y^{III}, Sc, Hal = Cl, n = 3) with two molar equivalents potassium diphenylmethanides. While heteroleptic tris(alkyl)derivatives of Sc and Y and Sc bearing tridentate bis(4-(tert-butyl)-2-(1-methyl-1H-imidazol-2-yl)phenyl)methanido ligand $[4\text{-}tBu\text{-}2\text{-}(1\text{-}MeC_3H_2N_2)C_6H_3]_2CH^-$ (Y (**8**), Sc (**9**)) have been obtained by the reaction of their tris(alkyl)derivatives with substituded diphenylmethane.



M = Ca (**1**), 73%
Yb (**2**), 84%
Sm (**3**), 58%

M = Y (**4**), 88%
Sc (**5**), 75%

M = Ca (**6**), 83%
Yb (**7**), 75%

M = Y (**8**), 78%
Sc (**9**), 81%

Figure 1. Alkyl complexes rare- and alkaline earth metals with tridentate diphenylmethanido ligands

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Synthesis, molecular structure and reactivity of O,N-heterocyclic germylenes.

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Interest towards the chemistry of the heavier analogues of carbene has not decrease over the past thirty years. At present a lot of stable metallenes derived from different heterocycles has been described. The N-heterocyclic analogues of carbenes on the basis of various diimines are the most studied for today. There are practically no data concerning O,N-heterocyclic metallenes.

In this work we present synthesis of new heterocyclic germylenes bearing N-(R)-substituted o-aminophenols, and investigation of their redox reactivity and acid-base properties. X-ray analysis of Ge(II) o-amidophenolates shows that they are monomeric in the solid state. This behavior is in contrast to the situation observed for related stannylenes and plumbylenes.

Redox active ligands such as o-aminophenoles can be used as reservoirs of electrons for bond-making and bond-breaking reactions and can support the multi-electron changes required to promote group- or atom-transfer reactions. Posessing a high degree of aromatically, heavy analogues of carbene can undergo one-electron reduction, which leads to formation butadiene-like dianion with four metalllocenters in the chain.

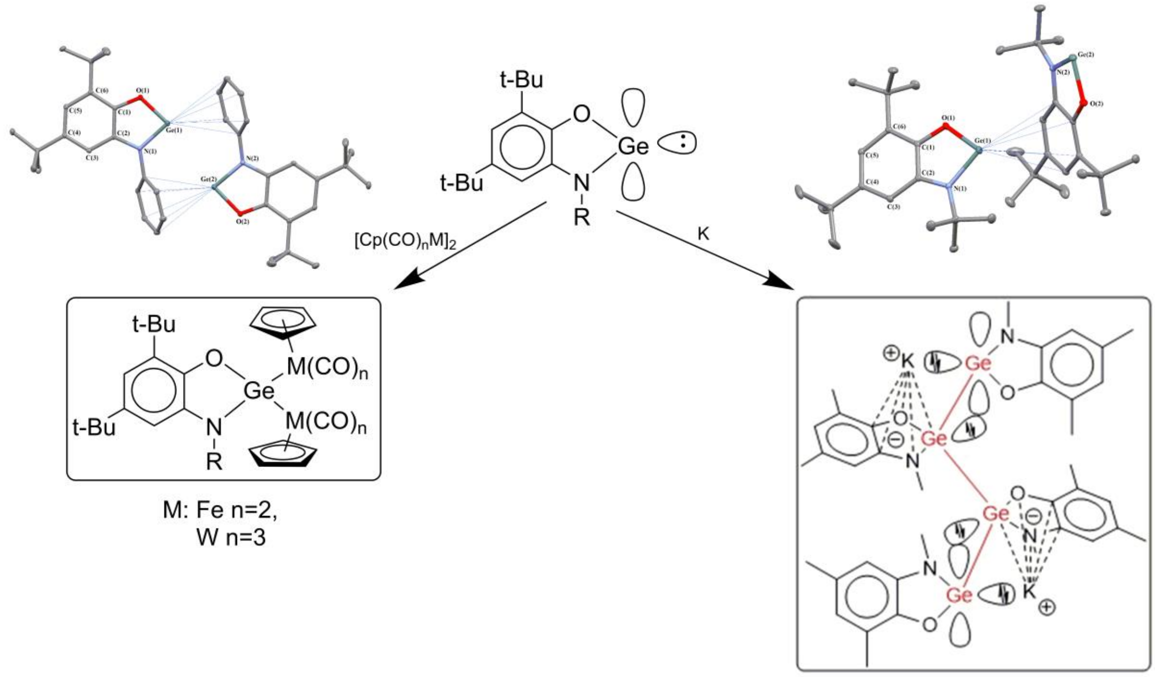

Figure 1. Reactivity of heavy analogues of carbene

Acknowledgements

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Synthesis of heteronuclear sandwich-type complexes of lanthanides with phthalocyanines

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Tetrapyrrole complexes are of special interest for materials chemistry. Among the wide range of phthalocyanines heteronuclear triple-deckers play a special role. When triple-deckers are formed by paramagnetic lanthanides, the coupling between unpaired f-electrons is observed. Together with large magnetic anisotropy, it makes these complexes promising for single-molecule magnet materials (SMM). However, in contrast to widely studied homonuclear complexes, heteronuclear tris-phthalocyaninates still remain relatively unexplored. Particularly, this is because of the lack of selective synthetic strategy toward complexes bearing two different metal.

Previously, we have found a new efficient reagent for the synthesis of heteroleptic sandwich phthalocyaninates – diphthalocyaninatolanthanum $LaPc_2$ which can be also effectively used for the synthesis of heteronuclear triple-deckers.[1,2]

In this work the developed early approach was applied to phthalocyanines with different substituent's nature including bulky butoxy groups and crown-ethers (Fig.1). The Y(III), Gd(III) and Tb(III) in different ligand environment were used as metal centres. Terbium(III) is of special interest as a very promising cation for SMM.[3] All target compounds were obtained in good yield (50-60%).

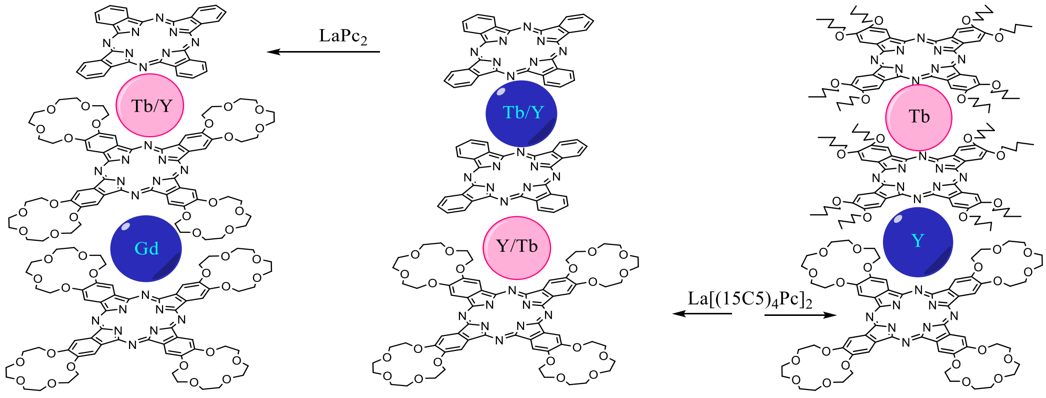

Figure 1.

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Salt metathesis reactions in synthesis of lanthanide arylthiolate and chalcogenide complexes supported by bulky β-diketiminate ligand

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Bulky organic ligands are often used to support lanthanide complexes, because they can kinetically stabilize the latter by blocking larger part of coordination sphere and thus making it possible to limit the overall coordination number and preclude oligomerization. The most used are cyclopentadienyl-based and N-donor chelating ligands, including β-diketiminates. The latter ones can be involved in intramolecular energy transfer as antenna-ligand. Soft chalcogen-based ligands are less favoured in lanthanide complexes than those with N- and O-donor groups. Heavy 16th group atoms in coordination sphere limit vibrational relaxation and may improve luminescent properties, but such complexes remain insufficiently studied because of difficulties in their handling, so the use of proper supporting ligand may be helpful in their studies.

We studied Ln complexes with bulky “nacnac” ligand (Ln = Sm, Nd; nacnac$^-$ = HC(C(CH$_3$)NDipp)$_2$$^-$, Dipp = 2,6-diisopropylphenyl). Starting from Ln triiodides, [Ln(nacnac)I$_2$(thf)$_2$] complexes were synthesized. The remaining iodides were shown to be easily substituted to thiolate ligands in reaction with corresponding potassium salts in THF, to give [Ln(nacnac)(SPh)$_2$(thf)] and [Ln(nacnac)(S(2-Py))$_2$] complexes (Figure 1*a*–*c*). IR-spectra studies showed dependence of ligand type, and ligand-specific bands were found which can be used for identification of the similar compounds.

As opposed to syntheses of chalcogenolate complexes, the salt metathesis substitution of I$^-$ for (poly)chalcogenide anions Q_n^{2-} was proven to be unfavourable. Thus, reactions of [Ln(nacnac)I$_2$(thf)$_2$] with K$_2$Q$_n$ in THF (n = 1, 2; Q = S–Te) did not proceed even at elevated temperatures. However, peculiar conversion happened only in the case of K$_2$Se, where a Sm(II) complex [Sm(nacnac)I(thf)$_2$] was obtained (Figure 1*d*). Possible grounds of this spontaneous reduction of Sm are discussed.

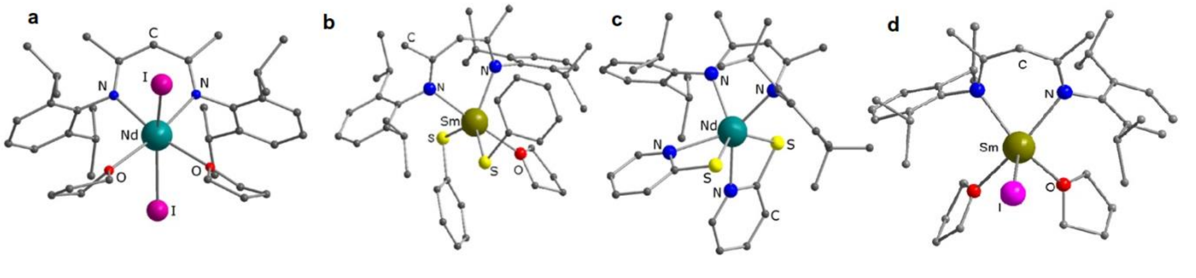

Figure 1. Examples of [Ln(nacnac)I$_2$(thf)$_2$] (a), [Ln(nacnac)(SPh)$_2$(thf)] (b) and [Ln(nacnac)(SPy)$_2$] (c) complexes; [Sm(nacnac)I(thf)$_2$] (d)

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Cyclometalated iridium (III) complexes with benzimidazoles/phenanthroimidazoles and various “anchoring” ligands: synthesis, structure, photophysical properties and application in dye-sensitized solar cells.

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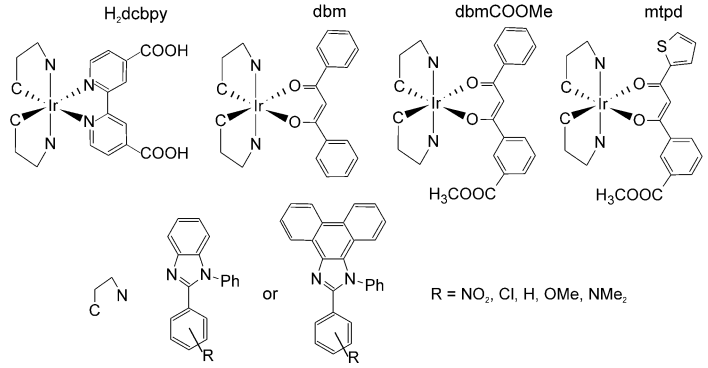
Cyclometalated Ir(III) complexes have attracted particular attention as more stable analogs of Ru(II) dyes in dye-sensitized solar cells (DSSC). Still, poor light-harvesting properties of Ir(III) photosensitizers prevent their widespread application in DSSC. Up to now, there have been many efforts to enhance the absorptivity of Ir(III) dyes either by varying cyclometalated (C^N or ‘antenna’) ligands or by changing the substituents in 2,2’-bipyridine-based ‘anchoring’ ligands. However, a substantial improvement of photophysical characteristics of the complexes has not been achieved. Based on our previous study of Ir(III) dyes, we have assumed that the desired significant increase of their light-harvesting properties can be achieved by drastic change in the chemical nature of the ‘anchoring’ ligand. Specifically, aromatic β-diketones acting as negatively charged chelating ligands are anticipated to be very promising for constructing efficient Ir(III) dyes.

Herein, we present a comprehensive study (X-ray, NMR, MS, UV-Vis, CVA, LS, DFT / TDDFT) of several series of iridium (III) complexes with 2-arylbenzimidazoles/2-arylphenantroimidazoles and different “anchoring” ligands: 4,4′-dicarboxy-2,2′-bipyridine (H_2dcbpy), dibenzoylmethane (dbm), 1-(3-methoxycarbonylphenyl)-3-phenyl-propane-1,3-dione (dbmCOOMe) and 1-(3-methoxycarbonylphenyl)-3-tiophene-propane-1,3-dione (mtpd) (Scheme 1).

We systematically studied the effect of the ligands structure on the optical and redox properties of the complexes as well as their electronic structures. Appropriate oxidation potentials, an optimal ground and excited states localization along with good light-harvesting characteristics of the complexes make them suitable candidates as photosensitizers in DSSC.



Scheme 1. Ligands and Ir(III) complexes studied in this work

Acknowledgements

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Synthesis, Investigation, and DFT Studies on Bis(Alkenylruthenium) Complexes with Free-Rotating and Rotationally Restricted Biaryl Bridges

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A series of biaryl-bridged dinuclear alkenylruthenium complexes with varied torsion angle ϕ between the planes of the phenyl rings have been prepared *via* regio- and stereospecific insertion of the -C≡CH bond of the corresponding terminal 4,4'-diethynylbiphenyl derivatives into the Ru-H bond of the hydride complex $HRu(CO)Cl(P^iPr_3)_2$ (Figure 1)[1]. These square pyramidal five-coordinated complexes have been characterized *via* IR, UV/Vis, and NMR spectroscopy, electrochemistry, UV/Vis/NIR-IR spectroelectrochemistry and DFT calculations. Our results indicate that the torsion angle strongly modulates and tunes the electronic coupling between the two ruthenium-vinyl moieties significantly. They confirm that σ-bonded divinylbiphenylenes constitute a particularly interesting class of non-innocent ligands in organometallic systems. Electrochemical studies showed that these complexes undergo two reversible, consecutive one-electron oxidation processes. The splitting of the redox waves, $\Delta E_{½}$, and the comproportionation constants (K_c) vary as the torsion angle changes, suggesting a strong electronic interaction between the two styryl ruthenium moieties (Kc = 2.9×10^3) when the two phenyl rings are planar, and a weak interaction (K_c = 18) when they are orthogonal to each other. In IR spectroelectrochemistry, the magnitude of the CO band shifts and the band splitting in the mixed-valent radical cations likewise depend significantly on the torsion angle between the planes of the two phenyl rings. Charge distributions in the radical cations vary from 67:33% when biphenyl bridge is close to planar to 97:3% when the phenyl rings are orthogonal to each other. Complexes with low torsion angle display strong electrochromic behaviour in three distinct states with a strong NIR band in their mixed-valent states. No such band was, however, observed in the case where the two phenyl rings are orthogonal to each other.

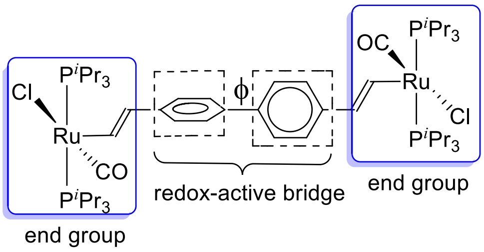

Figure 1. Biaryl-bridged dinuclear alkenylruthenium complexes

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Gold(I) complexes decorated by flexible alkynyl-terpyridine ligands: some features of luminescence

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Nowadays, a molecule capable to luminescent detecting of cations in solution are of great interest. Their feature is that they give a strong and stable luminescent response to different metal cations. Such complexes could be useful in biology and medicine sensing, and gold(I) complexes decorated by terpyridine moiety are good candidates because of them photophysical properties and structure architecture.

Herein we report synthesis of four new alkynyl-phosphine gold(I) complexes armed by terpyridine moiety (Fig. 1). All compounds obtained were characterized by ^{1}H and ^{31}P NMR spectroscopy, single crystal X-ray analysis, ESI mass spectrometry and CHN elemental analysis. Optical and photophysical properties of complexes, namely UV-vis, emission and excitation spectra, and excites state lifetimes have been carefully investigated in different media.

We found that on the one hand, the complexes demonstrate peculiar emission in solid state, and on the other hand, their luminescence responds to heterocations in solution.

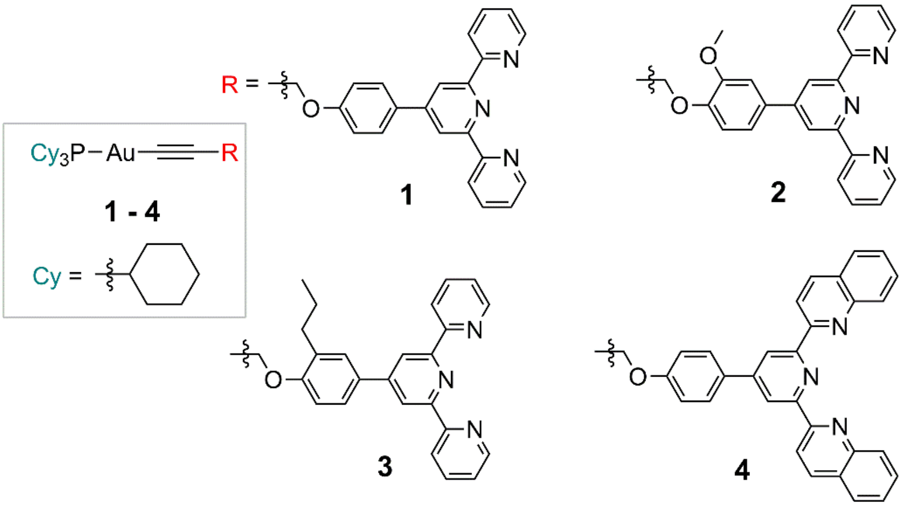

Figure 1. Structure of gold(I) complexes

Acknowledgements

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Physical factors controlling selectivity of the CuAAC reaction with diazides and dialkynes

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Over the past two decades the copper-catalyzed azide-alkyne cycloaddition (CuAAC), the most used “click” reaction, has become a robust and routinely utilized tool for creating a 1,2,3-triazole core in organic synthesis, as well as a very efficient bioorthogonal instrument for introduction of various labels and functional groups into systems of interest in biochemistry and molecular biology.[1]

In order to synthesize molecules containing two or more 1,2,3-triazole cores, corresponding azido-containing or alkynyl-containing 1,2,3-triazoles are needed as they seem to be the most synthetically simple precursors. And the most reliable way to access these materials is a multistep preparation avoiding formation of diazido- or diethynyl-species and thus eliminating chemo- and regioselectivity issues as well as formation of mixtures of mono- and diadducts in azide-alkyne cycloaddition (AAC) step. We studied influence of the solvent (no solvent or non-polar solvent) on the selectivity of CuAAC reaction with diazido- or dialkynyl substrates. It was found, that precipitation of products (in non-polar solvent) or significant increase in viscosity of the reaction medium (for neat reactions) may cause the reaction to stop at the stage of formation of the monoadduct.

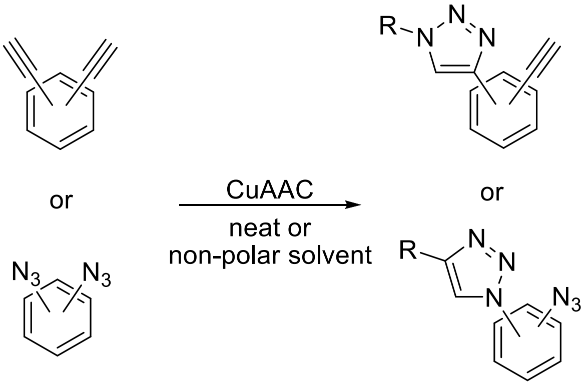

Figure 1. Selective synthesis of azido- and ethynyl-1,2,3-triazoles

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The efficiency of copper catalysts in Chan-Evans-Lam (CEL) reaction. Crucial role of metal ion numbers and counteranion nature.

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The copper-mediated C - C, and C - heteroatom bond formation is an important transformation and has been developed to include a wide range of substrates.[1] In 1998 Chan, Evans, and Lam in three back-to-back publications reported the oxidative coupling of amines with arylboronic acids promoted with copper salts in air. In comparison to the Ullmann reaction or Buchwald−Hartwig aminations catalyzed by palladium or copper, CEL-couplings proceed under much milder conditions, often at room temperature. In the following years, different research groups made considerable progress in expanding the scope of the copper-mediated coupling methodology.[2]

Typical for CEL-couplings is the requirement for a careful optimization of reaction conditions. The relative influence of base, water, solvent, counterions, and oxidants in CEL-couplings is still unclear. Furthermore, there are some undesirable couplings accompanying the main reaction (Fig.1).[3]

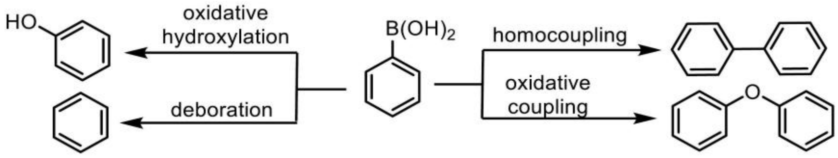

Figure 1. Side reactions in CEL-coupling

Evidently, there is a need to elaborate a new family of catalysts, selectively providing the desired CEL-coupling. Herein we synthetized and investigated more than 30 mono- and dinuclear copper(II) complexes in a CEL-reaction. The counterion nature and the number of copper(II) ions in the catalyst on acceleration of the CEL-reaction rate and the selective formation either C-C or C-N-bond was found to be crucial. The structure of the most efficient catalyst is depicted on Fig.2.

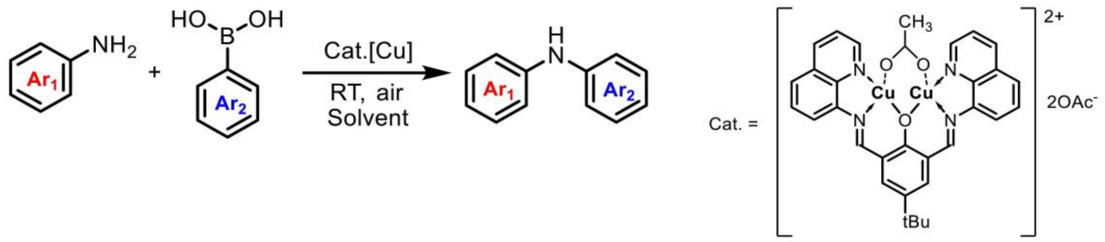

Figure 2. The Chan-Evans-Lam reaction

Acknowledgements

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Tricarbonylrhenium(I) complexes based on non-classical pincer ligands with central amide units as potential anticancer agents

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In pursuit of new anticancer agents, many research groups focus their attention on different transition metal complexes, including platinum, ruthenium, zinc, palladium, and gold derivatives. Organometallic rhenium(I) complexes are traditionally considered and used as radiopharmaceuticals in nuclear medicine and biological imaging, while their potential as anticancer agents is still essentially underestimated. Nevertheless, a range of rhenium complexes with bidentate heterocyclic, organophosphorus, labile alkoxide and hydroxide ligands have already demonstrated promising cytotoxic activities. At the same time, the efficiency of their multidentate analogs is almost unexplored. Therefore, we synthesized a series of tricarbonylrhenium(I) complexes based on non-classical pincer-type ligands with central amide units bearing ancillary donor groups both in the acid and amine components. The choice of functionalized carboxamides as the main research objects was dictated, in particular, by the ease of synthesis of a whole library of new ligands *via* modular assembling of readily available building blocks and their smooth cyclometalation under action of Re(I) precursors, affording pincer-type complexes (for selected examples, see Fig. 1). Furthermore, the use of pincer-type ligands having specific tridentate monoanionic frameworks, which offer multiple options for directed structural modifications, allows fine-tuning thermodynamic and kinetic stability of the resulting metal complexes. Despite the fact that these advantages of pincer complexes have been successfully used in catalysis and organic synthesis for the last two decades, in the field of anticancer drug design, this is a relatively new strategy. The preliminary evaluation of cytotoxic properties of the resulting complexes against several cancer cell lines allowed us to define the main structure–activity relationships for a principally new class of potential anticancer agents and to choose the most promising compounds for further studies.

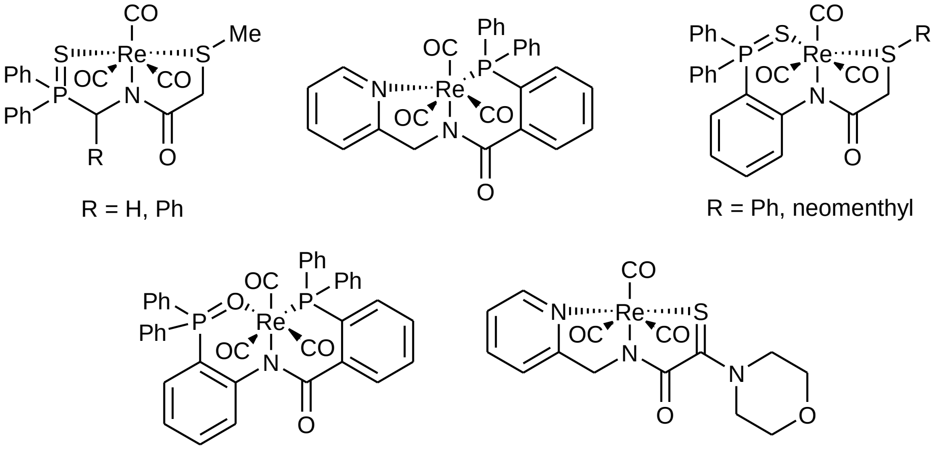

Figure 1. Cytotoxic tricarbonylrhenium(I) pincer complexes

Acknowledgements

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Copper-containing cage-like structures and their catalytic activity in Chan-Evans-Lam coupling reaction

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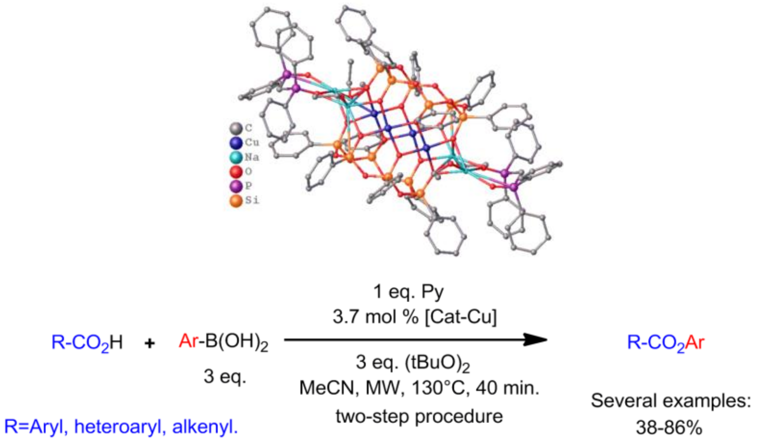
The cage-like structures based on metallsesquioxanes are attracted the attention of many research groups, because they demonstrate intriguing catalytic properties.[1] In recent years the Chan-Evans-Lam (CEL) coupling reaction, copper-catalyzed interaction of H-nucleophiles (amines, amides, sulfonamides, phenols etc.) and boronic acids, became popular instrument of fine organic synthesis.[2] Here we show that several copper-based cage-like silsesquioxanes catalyze coupling of boronic acids and carboxylic acids under microwave (MW) conditions. In comparison to published results,[3] Cu_4Na_4 complex (**Fig. 1**) exhibit high catalytic activity on conditions of low loading of copper source and added base.[4] To the best of our knowledge, this is a first example of CEL reaction by making C-O bond in MW.

Figure 1.



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Silver(I) complexes with coordinated and non-coordinated decachloro-*closo*-decaborate anion

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Silver complexation with the decachloro-closo-decaborate anion $[B_{10}Cl_{10}]^{2-}$ anion has been studied in DMF in the presence of Ph_3P and without it. It has been found that when a two-fold excess of Ph_3P is present in the reaction solution, complex $[Ag(PPh_3)_2(DMF)_2]_2[B_{10}Cl_{10}] \cdot DMF$ has been isolated, while $[Ag(Ph_3P)_3(H_2O)]_2[B_{10}Cl_{10}]$ 4DMF has been synthesized when $[Ag(Ph_3P)_3NO_3]$ has been used as the reagent. Both compounds contain silver(I) cationic complexes and the $[B_{10}Cl_{10}]^{2-}$ anion as counterions.

In order to synthesize a complex with coordinated $[B_{10}Cl_{10}]^{2-}$, the silver complexation has been carried out in DMF in the absence of competing ligands. In this case, complex $[Ag_2(DMF)_2[B_{10}Cl_{10}]]_n$ is formed where both DMF and $[B_{10}Cl_{10}]^{2-}$ are coordinated by the silver(I) atom. The obtained compounds have been characterized by ^{11}B NMR and IR spectroscopies as well as powder and single crystal X-ray diffraction technics.

Complex $[Ag_2(DMF)_2[B_{10}Cl_{10}]]_n$ is the first complex containing $[B_{10}Cl_{10}]^{2-}$ anion directly coordinated to the metal atom. Moreover, the Ag–Ag bonds are assumed to present in the crystal according to single crystal X-ray diffraction analysis (Ag…Ag 3.2023(8) Å). The formation of this bond can be confirmed by the Raman spectroscopy data.

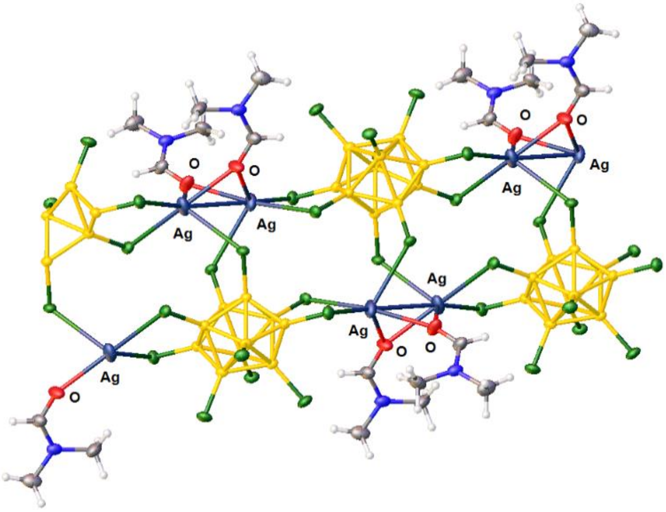

Figure 1. Fragment of infinite chains in crystal structure of $[Ag_2(DMF)_2[B_{10}Cl_{10}]]_n$

Acknowledgements

This study was performed within the framework of the state assignment of the Kurnakov Institute in the field of fundamental scientific research.

New Water-Soluble Copper(II) Complexes with Morpholine-Thiosemicarbazone Hybrids: Insights into the Anticancer and Antibacterial Mode of Action

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One of the major causes of cancer death is the malignant process, which is associated with the extensive formation of metastases, but it is not commonly mentioned that a significant number of immunocompromised cancer patients die due to infections, such as pneumonia and peritonitis. The simultaneous suppression of pathogenic microorganisms during anticancer chemotherapy could not only interrupt or abolish tumor growth but eventually protect cancer patients from infection. Hence, the development of novel drugs which exhibit dual anticancer and antibacterial properties in comparable concentration range would affect the malignant process and simultaneously decrease the risk of patients' death due to infection, febrile neutropenia and bacteraemia. In this project, we developed novel water-soluble thiosemicarbazone-morpholine hybrids and their Cu(II) complexes which demonstrated marked anticancer and antibacterial activity and improved therapeutic potential than clinically tested drug Triapine.

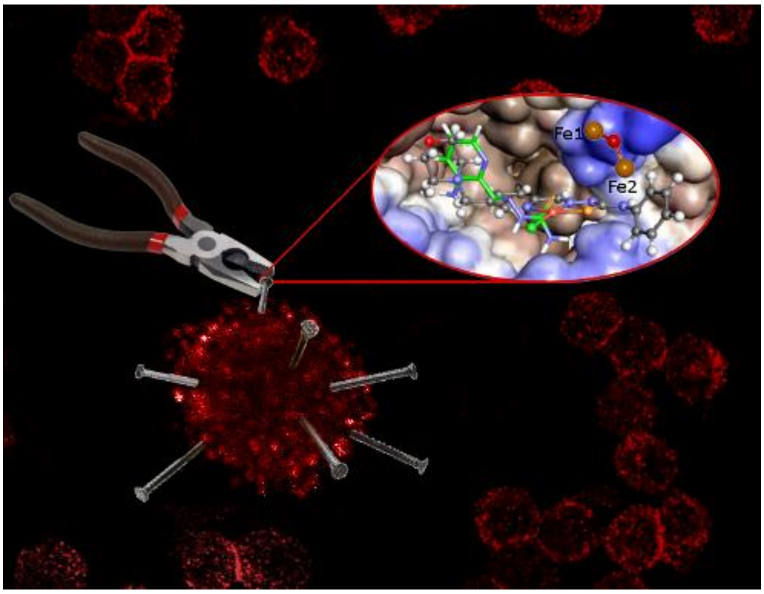

Figure 1. Marked antiproliferative and antibacterial properties of novel compounds might be related to their ability to induce endoplasmic reticulum stress and moderately inhibit ribonucleotide reductase as a result of intracellular iron chelation

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Spectroscopic and luminescence characteristics of solid solutions γ-$(Al_{1-x}Ga_x)_2O_3$

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A simple and original approach to the synthesis of solid solutions γ-$(Al_{1-x}Ga_x)_2O_3$ using the mixed hydroxoformate $Al_{1-x}Ga_x(OH)(HCOO)_2$ (x□0.4) as a precursor is reported. The X-ray diffraction, thermal analysis and vibrational spectroscopy methods were employed to study the formation conditions and the structure of several compositions $Al_{1-x}Ga_x(OH)(HCOO)_2$. The samples of $Al_{1-x}Ga_x(OH)(HCOO)_2$ are solid solutions holding the crystal structure of $Al(OH)(HCOO)_2$[1], where both Al and Ga occupy equivalent atom positions. The thermolysis of precursors was studied at 600-900°C in He atmosphere for 3 h. It was established that the thermolysis of $Al_{1-x}Ga_x(OH)(HCOO)_2$ (x□0.2) in He atmosphere at 700°C leads to the formation of solid solutions γ-$(Al_{1-x}Ga_x)_2O_3$. Changing the parameters of heat treatment, it was possible to control the particles' size of the thermolysis products and their defect structure determining the luminescence properties[2,3]. According to ^{27}Al MAS NMR data, Al^{3+} ions in the structure of γ-$(Al_{1-x}Ga_x)_2O_3$ occupy mainly the octahedral positions, and the intensities of NMR lines assigned to aluminate groups AlO_4 and AlO_5 decrease with increasing dopant concentration. The products of thermolysis of $Al_{1-x}Ga_x(OH)(HCOO)_2$ in He atmosphere at 700°C are characterized by blue emission, and the wide luminescence spectrum covers the whole visible range. Comparison of the emission spectra of γ-$(Al_{1-x}Ga_x)_2O_3$ oxides with different Ga content showed that the undoped oxide γ-Al_2O_3 has the most pronounced luminescence, and at x□0.1 an effect of Ga-concentration quenching of luminescence is observed. The DFT calculations of γ-$(Al_{1-x}Ga_x)_2O_3$ compounds confirmed the NMR data revealing the maximal exothermic effect for the formation of solutions with $x = 0.20$-0.25 and at the tetrahedral positions occupied by Ga3+ ions. Using the DFT calculations of electronic structure, the emission centers of luminescence in γ-$(Al_{1-x}Ga_x)_2O_3$ were related to the CH-groups remained after thermolysis of hydroxoformates. The emission activity of unoccupied C2*p* states located near the conduction band is suppressed by their overlap with the Ga4*p* states forming the bottom of conduction band and broadening at high concentration of Ga^{3+}.

Acknowledgements

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New phase within the SrO – RE_2O_3 – GeO_2 system

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Novel series cyclosilicates $Sr_3RE_2(Si_3O_9)_2$ (*RE* = Eu – Lu, Y) possessing the calcium yttrium silicate $Ca_3Y_2(Si_3O_9)_2$ crystal structure have been reported previously. These compounds crystallize in the monoclinic space group *C2/c* (*Z* = 4). Their structure can be related to a high-temperature polymorph of $CaSiO_3$ known as pseudowollastonite. Replacing the silicon by germanium we have explored an opportunity to extend the boundaries of this crystal type and to obtain the compounds $Sr_3RE_2(Ge_3O_9)_2$.

Counterintuitively, the club membership in cyclogermanates $Sr_3RE_2(Ge_3O_9)_2$ is shared at the moment only among *RE* = La – Er, while for lanthanides with smaller cation radii *RE* = Tm – Lu it is prohibited under known synthetic protocols. The products of $Sr_3RE_2(Ge_3O_9)_2$ with *RE* = Sm – Er have been obtained, yet, contaminated by numerous impurities in a large amount. One of these impurities was identified as the main phase in the products of Tm – Lu cyclogermanates. Henceforth, we attempted to characterize, if not to isolate this new phase.

The phase formation of the $Sr_3RE_2(Ge_3O_9)_2$, (*RE* = Dy, Ho, Er, Tm, Yb, Lu) cyclogermanates was studied at 1000 – 1100 °C in air. The samples with different metal ratios in the Sr – Tm – Ge – O system were prepared by a citrate method. $Tm_2Ge_2O_7$, $SrGe_4O_9$ and $SrGeO_3$ were registered as minor impurities in all samples. Based on the large collection of X-ray powder diffraction (XRPD) data, a projection of isobaric-isothermal phase diagram of the Sr – Tm – Ge – O system onto the compositional triangle SrO – 1/2 Tm_2O_3 – GeO_2 was constructed.

An analysis of the diagram predicts the general formula of the unidentified phase as $Sr_4TmGe_{5.667}O_n$. The sample with such composition contains the smallest amount of $Tm_2Ge_2O_7$ impurity, which can be decreased down to ~1 wt % after additional annealing at 1100 °C. Similar sample preparation with Yb has yielded $Sr_4YbGe_6O_n$ with $SrGe_4O_9$ impurity (2 wt % after annealing at 1000 °C).

The XRPD patterns were reminiscent of those for $Sr_3RE_2(Ge_3O_9)_2$ cyclogermanates, but no attempt to account for all observed peaks using monoclinic unit cell was successful. DFT calculations have predicted a structural relation of $Sr_4REGe_{5.667}O_n$ phase to wahlstromite-like lattices.

Thus, it may be concluded that the germanates of the general composition as $Sr_3RE_2(Ge_3O_9)_2$, (*RE* = Tm, Yb, Lu), which are isostructural to the $Sr_3RE_2(Si_3O_9)_2$ cyclosilicates, do not exist under 1000 – 1100 °C in air. Lanthanide ions of small radii yield the phases with the atomic ratio Sr/*RE* other than 3/2 and don't crystallize as the $Sr_3RE_2(Ge_3O_9)_2$ cyclogermanates.

Acknowledgements

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Sodium-ion transport in triple molybdates with pseudo-orthorhombic alluaudite-related structures

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In recent years, new functional materials based on alkaline containing compounds have attracted great interest mainly due to their promising applications for various electrochemical devices, and especially in energy storage systems (ESS). Although recent advances in lithium-ion battery (LIB) technology have increased the energy density to the level applicable to ESS, the high cost of lithium has led to the search for alternative batteries with a lower cost. Based on the abundance of sodium, the similarity of its electrochemistry to the well-proven LIB technology, the Na-ion batteries (NIB) have attracted considerable attention as an ideal candidates for ESS[1]. The compounds with the NASICON and alluaudite structures are currently considered among the most promising materials for NIB[1]. The $Na_{25}Cs_8R_5(MoO_4)_{24}$ (R = Sc, In) belongs to a family of compounds with pseudo-orthorhombic alluaudite-related structures. The ionic conductivity of these compounds reaches 10^{-3} $S{\cdot}cm^{-1}$ and is comparable to that for NASICON-type materials and other the best sodium conducting molybdates.[2,3] In this report, we present the results of NMR study of sodium diffusion mechanisms in the triple molybdate $Na_{25}Cs_8R_5(MoO_4)_{24}$ (R = Sc, In). In the ordinary alluaudite structure, for example, in $Na_5Sc(MoO_4)_4$, NaO_6 and (Na, Sc)O_6 octahedra and bridging MoO_4 tetrahedra form a 3D framework with Na^+ cations located in its channels. Such a crystal design implies the presence of 1D diffusion of sodium ions. However, due to cross-linking channels, ionic jumps can occur in the *bc* plane[4]. Although crystal structure of $Na_{25}Cs_8R_5(MoO_4)_{24}$ includes a numerous of non-equivalent sodium positions we could attribute tentatively the observed ^{23}Na NMR spectral components to distinct groups of similar sodium sites. Thus, based on the NMR spectra analysis and crystal structure data, it was supposed that, for $Na_{25}Cs_8R_5(MoO_4)_{24}$, the sodium diffusion occurs most likely in zigzag layers in the *ab* plane. Despite the fact that the crystal structures of $Na_{25}Cs_8R_5(MoO_4)_{24}$ (R = Sc, In) have an alluaudite framework, they are strongly distorted and the 1D channels along the *c*-direction are occupied mostly by cesium ions, therefore sodium ion transport through these channels is rather difficult.

Acknowledgements

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New effective phosphors based on fluorinated benzotiazolate lanthanide complexes

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The search for new efficient photo- and electroluminofors still remains an urgent task. Perfluorinated aromatic ligands are widely used for the design of luminescent lanthanide complexes. An increase in the luminescence efficiency in these compounds occurs due to the exclusion from the structure of multiphonon quenchers C–H, N–H, and O–H bonds with high vibrational energy, and their replacement by C–F groups.

A set of compounds $Ln(SON^F)_3(DME)_2$ (Ln = Nd, Sm, Eu, Gd, Ho, Er, Yb; $(H(SON^F)$=2-(3,4,5,6-tetrafluoro-2-hydroxyphenyl) -4,5,6,7-tetrafluorobenzothiazole) were synthesized by exchange reaction of respective (trimethylsilylamide)lanthanide with $H(SON^F)$ in DME solution. According to X-ray analysis the complex of erbium, in contrast to non-fluorinated analogs,[1,2] has a monomeric structure in which the erbium atom is bound by three monodentate ligands SON^F and four neutral methanol molecules. In the resulting compound, there is a strong intramolecular interaction Ln...F. The PL spectra of the obtained complexes contain intense ligand-centered (Gd, Ho) and metal-centered emission bands, both in the visible (Sm, Eu) and in the NIR range (Nd, Er, Sm and Yb). The PL intensity of all the obtained fluorinated compounds, as expected, is significantly higher than that of non-fluorinated analogs, which is associated with the substitution of C–H quenchers for C–F groups. For $Ln(SON^F)_3(DME)_2$ complexes the lifetime of excited states at 300K: Nd (1070 nm band) - 5 μs, Er (15540 nm band) - 4 μs, Yb (975 nm band) - 25 μs. These values are comparable with their predecessors.

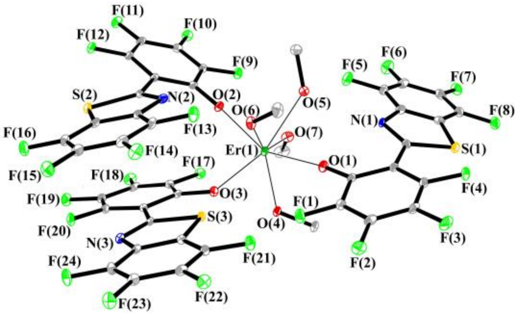

Figure 1. Molecular structure of $Er(SON^F)_3(OCH_3)_4$

Acknowledgements

The work was supported by the RSF (Grant No. 18-13-00066).

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Crystallochemical Engineering of Highly Correlative Layered Conductors

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Design of new materials that possess specific electronic properties requires deep knowledge of fundamentals that allows tracking of structural factor influence onto the electronic state of the solids under question. Materials where electronic correlations play critical role in the conductivity type are of paramount interest as minor modifications of the crystal structure may substantially differ the electronic state.

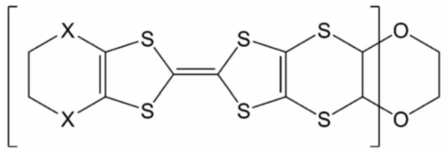
Radical cation salts of BEDT-TTF (*bis*(ethylenedithio)tetrathiafulvalene) are known for a plethora of charge and spin instabilities that produce transitions from metal to insulator and back together with more complex transitions involving "bad metal" state, superconductivity and so on. Accurate mapping of the states through traversing by temperature or pressure coordinates provides an investigator by an invaluable information about band structure peculiarities.

Layered character of the BEDT-TTF salts predetermines spatial segregation of anionic (usually non-conductive) and radical cation (conductive) counterpart. That provides valuable opportunity to realization of module-type construction strategy when organic molecule of single electron donor and (usually) inorganic anions are modified or synthesized separately and then are assembled in an ultimate single crystal with the required properties by an aid of electrocrystallization protocol.

For the target synthesis of highly correlative conductive salts with the required type of arrangement of donor molecules in the crystal lattice we developed new donors that are offsprings of original BEDT-TTF molecule.[1]

DOET molecule bears saturated dioxane ring annealed alongside long molecular axis of the donor molecule. The dioxane ring while is not included into intramolecular electron conjugation network play an important role of interlayer spacer that increases interlayer separation and thus, leads to increasing of electron-electron correlations. At the same oxygen atoms incorporated into a dioxan ring participate in global H-bonding system that strengthening crystal lattice framework.

DOEO is a further modified donor where additionally two terminal sulfur atoms in DOET molecule are replaced for oxygen. DOEO salts usually are more conductive than DOET ones as smaller size of oxygen atoms and their incorporation into H-bonding network results in effective contraction of conductive layers and increasing bandwidth (*W*) as a consequence leaving on-site Coulomb repulsion (*U*) nearly intact.



[X = S]: ET; All: (X = S): DOET, (X = O): DOEO

In the current work we present a set of DOEO and DOET salts where depending from the level of intralayer donor dimerization and value of correlative parameter *U*/*W* compounds with the properties ranging from stable metal to Mott insulator are obtained.

Acknowledgements

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The effect of substituents on the structure of new chromium(III) malonate complexes

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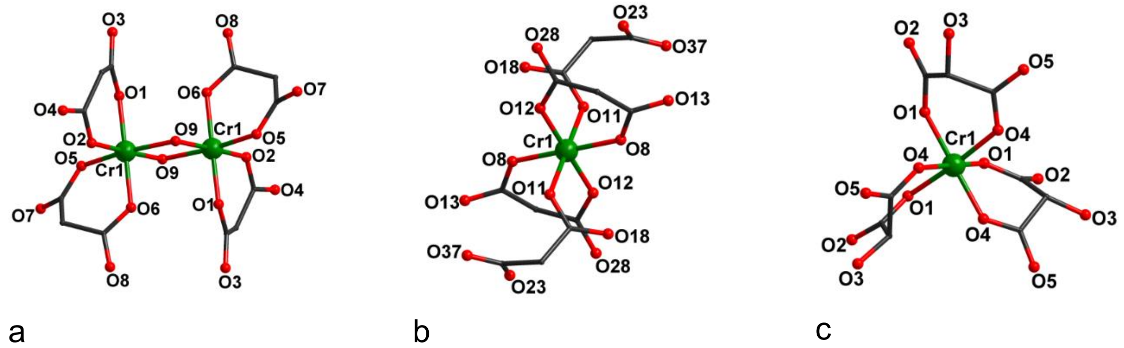
Octahedral complexes featuring paramagnetic Cr^{III} ions are of great importance for the development of new molecule-based magnets[1], luminophores and dyes for solar cells, their application in photoredox catalysis, and their use as sensitizers in upconversion processes[2]. Among numerous chromium(III) carboxylates the complexes with malonate anions are very rare, although this class of ligands is promising for the design of polynuclear compounds due to the diversity of coordination modes. In this work, we have investigated the interaction of Cr^{III} with anions of malonic acid (H_2mal) and its substituted analogs – dimethylmalonic (H_2Me_2mal) and hydroxymalonic acid (H_2(OH)mal)) and studied the crystal structure of the obtained compounds.

The reaction of $Cr(NO_3)_3$ with Ba(mal) or Ba(Me_2mal) in the molar ratio 1:3 was found to give the crystals of complexes $\{[BaCr(OH)(mal)_2(H_2O)_3]\cdot 2H_2O\}_n$ (**1**) or $\{[BaCr(OH)(Me_2mal)_2(H_2O)_3]\cdot H_2O\}_n$ (**2**), respectively, constructed from binuclear units $[Cr_2(OH)_2(R_2mal)_4]^{4-}$. These units are linked by Ba ions, resulting in the formation of 2D (**1**) and 1D (**2**) polymeric structures. The reaction similar to that for **2** but with the addition of a twofold excess of H_2Me_2mal gave crystals of the complex $[Ba_2Cr(Me_2mal)_2(HMe_2mal)_2(NO_3)(H_2O)_6]_n$ (**3**), in which mononuclear units $[Cr(Me_2mal)_2(HMe_2mal)_2]^{3-}$ (Fig. 1 b) are linked by Ba ions into a 2D polymeric structure. The replacement of Me_2mal^{2-} anions in similar reaction by $(OH)mal^{2-}$ anions led to formation of the 2D polymer $[Ba_3Cr_2((OH)mal)_6(H_2O)_{12}]_n$ (**4**) consisting of tris-chelate mononuclear units $[Cr((OH)mal)_3]^{3-}$ (Fig. 1 c).



a b c

Figure 1. Different types of Cr^{III}-malonate units: dinuclear unit of 1 (a), mononuclear bis-chelate unit of 3 (b, CH_3 groups of Me_2mal are omitted) and tris-chelate unit of 4 (c) (H atoms are omitted)

Acknowledgements

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Synthesis of metastable bismuth germanates and bismuth silicates and their solid solutions

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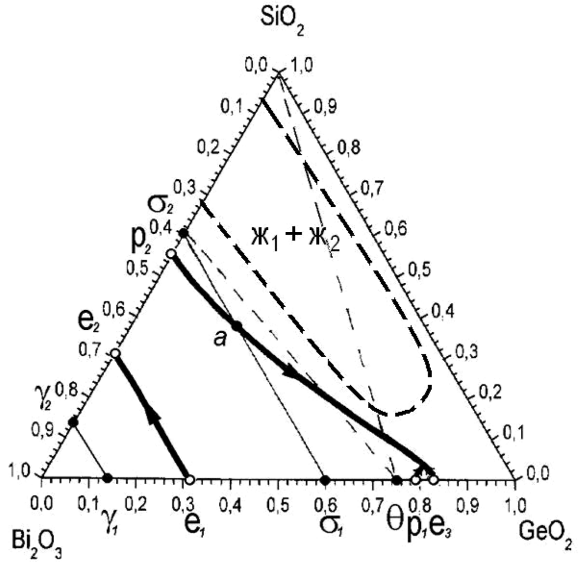
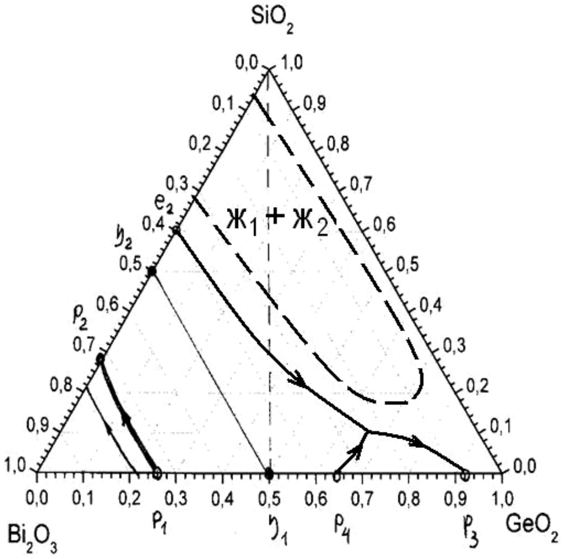
Stable germanates and bismuth silicates $Bi_{12}AO_{20}$ and $Bi_4A_3O_{12}$ with the structures of sillenite and eulitin, respectively, are important optical materials. Metastable Bi_2GeO_5 and Bi_2SiO_5 with the Aurivillius-type structure are of great interest as materials with high ionic conductivity in oxygen, ferroelectrics with high Curie temperature, unique photocatalysts and metastable solid phase binders for obtaining high-density ceramics at lower temperatures and reduced synthesis time.[1] Great prospects for the use of these metastable materials are associated with their solid solutions.

The implementation of metastable equilibria during the crystallization of the melt is a pressing, not only practical, but also theoretical task. One of the versions of the formation of metastable phases during crystallization of overheated melts in the systems Bi2O3-GeO2 and Bi2O3-SiO2, as well as in other similar systems based on bismuth (III) oxide, is associated with the assumption of their microheterogeneity.[2,3]

We have found macroscopic separation of the melt in the system Bi_2O_3-SiO_2 with a low-temperature critical delamination point of 1040 ºC. In the ternary system Bi_2O_3-GeO_2-SiO_2, the immiscibility region is shown for stable and metastable equilibria (Fig). At temperatures below 1040 ºC, the microheterogeneity of the melt should be expected, which, when cooled, overcools and forms metastable phases during crystallization.



a



b

Figure. Projections of the liquidus surface in the system Bi_2O_3-SiO_2-GeO_2 in stable (a) and metastable (b) equilibria

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New heteroleptic lanthanide (porphyrinato)(phthalocyaninates) with π-extended ligands

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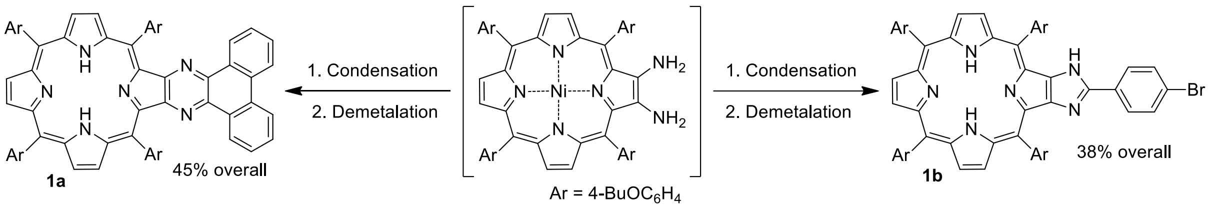
Heteroleptic lanthanide (porphyrinato)(phthalocyaninates) are promising compounds for the application in the development of molecular magnets, nonlinear optics and molecular information storage. Our efforts were recently aimed to the search of efficient synthetic methodology for the preparation of such type of compounds.[1] On the other hand, heterocyclic annelation allows to modify the electronic structure of the porphyrin molecules ant thus to tune their optical and electrochemical properties. In present work we focused on the preparation of heteroleptic lanthanide complexes with π-extended porphyrin ligands.



Scheme 1. Synthesis of π-extended porphyrins

The starting heterocycle-annelated porphyrins **1a** and **1b** were prepared from the corresponding diaminoporphyrin (scheme 1) following our previously reported procedures.[2] Further interaction of the obtained free-base porphyrins with dibutoxyphthalonitrile and lanthanum acetylacetonate allowed the preparation of the target heteroleptic complexes (figure 1). The obtained compounds were isolated and characterized with a set of spectral methods.

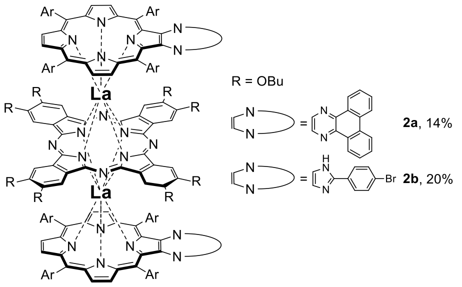


Figure 1. Heteroleptic lanthanum complexes with π-extended ligands

It is worth mentioning, that the annelation with imidazole and pyrazine heterocycles possess different influence on the electronic structure of the complexes. Thus, the UV-Vis spectrum of **2b** is quite similar to the typical spectra of lanthanum (porphyrinato)(phthalocyaninates). In contrast, the absorption maxima of **2a** are red-shifted by ca. 10 nm and 20 nm for Soret and Q-bands, with respect to related complexes.[1] The observed shifts of absorption bands of **1a** and **2a** clearly testifies the expansion of the aromatic system over the annelated arene-pyrazine fragment.

Acknowledgements

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Magnetochemistry of the Ln(III) complexes with semiquinones

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New heterospin mononuclear Ln(III) complexes with paramagnetic derivatives of 3,6-di-tert-butyl-1,2-benzoquinone (SQ) were synthesized and structurally characterized. Mononuclear $[Ln(SQ)_3(THF)_2]$ or heterometallic binuclear $[NaLn(SQ)_4(THF)_3]$ complexes (Figure 1) can be formed depending on 'NaSQ'[1] / $Ln(NO_3)3{\cdot}6H_2O$ ratio. THF ligands in the $[Ln(SQ)_3(THF)_2]$ may be substituted by other molecules, eg reaction of the $[Gd(SQ)_3(THF)_2]$ with Q yields a $[Gd(SQ)_3Q]$ complex. A coordination environment of the Ln(III) ions in the complexes is distorted square antiprism, formed by O atoms of SQ ligands and THF/Q molecules.

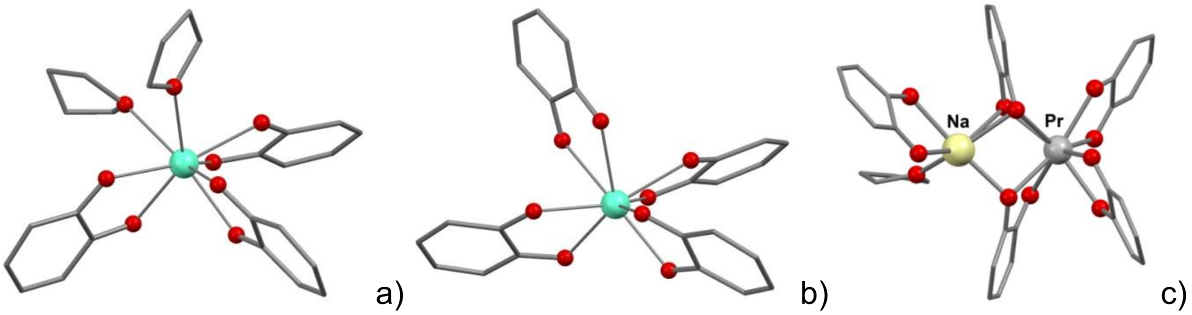

Figure 1. Structures of the $[Ln(SQ)_3(THF)_2]$ (a), $[Ln(SQ)_3Q]$ (b) and $[NaLn(SQ)_4(THF)_3]$ (c) complexes

Magnetochemical study of the complexes revealed presence of strong antiferromagnetic exchange coupling between spins of SQ ligands, whereas exchange interactions between Ln(III) and SQ are negligibly small.

It was found that $[Dy(SQ)_3(THF)_2]$ is metamagnetic at low temperature. Field dependencies magnetization for are nonlinear at low temperatures, and at 2 K magnetization almost linearly increases to 1 μ_B, and above 10 kOe it increases dramatically and reaches saturation, that typical for metamagnets.

Acknowledgements

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Structure transformation into $V_xTi_{1-x}O_2$ mesocrystals

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Titania mesocrystals have only recently been described and are best viewed as an entirely new class of inorganic materials.[1] Microstructural features of TiO_2 mesocrystals have been investigated thoroughly by several research groups. Obviously, to picture a full story, it is necessary to supplement these data with the crystallographic information on precursor NH_4TiOF_3 crystals that would help to explain correctly physical and chemical properties of TiO_2 mesocrystals. Here, we provide a first report on the full structural cascade from NH_4TiOF_3 to pure anatase TiO_2 mesocrystals prepared using Brijs and polyethyleneglycols with the different length. Results supporting these observations were obtained by XRD, EPR, XPS, SEM and FTIR spectroscopy. TEM and small-angle X-ray scattering data clearly show well-oriented assemblies of TiO_2 nanoparticles with average sizes of between several and tens of nanometers. Both single and powder XRD data were firstly collected and realised with synchrotron irradiation.[2] First time we demonstrate in-situ analyse thermal conversion of NH_4TiOF_3 crystals in presence of vanadium precursor into thermochromic mesocrystals VO_2-TiO_2 using powder diffraction. Beyond primary target we studied effect of V-doping into TiO_2 crystals and to estimate a potential of expeditious route to porous complex structural VO_2-TiO_2 materials

Moreover, in-situ Raman spectroscopy and in-situ TGA-MS, during heat treatment, allowed the evolution of NH_4TiOF_3 MCs undergoing transformation into anatase MCs to be followed so shedding light on the dynamics of MC formation.

We demonstrate that it is possible to obtain MCs of NH_4TiOF_3 via a non-classical method employing a gel of $(NH_4)_2TiF_6$ and H_3BO_3 with Brij-surfactant and PEGs templates. Finally, photocatalytic activity of the nascent TiO_2 (anatase) MCs has been demonstrated successfully so showing a potential application of these fascinating materials.

Acknowledgements

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Silica-supported tungsten oxide as oxo/imido heterometathesis catalyst

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Olefin metathesis is one of the key tools in modern organic synthesis. On the contrary, heterometathesis reactions, i.e. metathesis of multiple bonds containing heteroatom(s), are still poorly studied. We have previously reported that oxo- and imido- complexes of early transition metals (Mo, V, Nb, Ta, Ti) are efficient catalysts for oxo/imido heterometathesis reactions, in particular, imidation of aldehydes and ketones with *N*-sulfinylamines leading to the formation of imines. This reaction complements classical methods and allows obtaining imines based on sterically hindered ketones and electron-deficient anilines. However, routine application of this approach in organic synthesis is limited by the necessity of using air- and moisture-sensitive materials as catalysts.

In the present work we investigated the application of simple and commonly used industrial catalysts based on silica-supported early transition metal oxides prepared via wet impregnation (V_2O_5/SiO_2, MoO_3/SiO_2 and WO_3/SiO_2) as oxo/imido heterometathesis catalysts. It was found that MoO_3/SiO_2 and WO_3/SiO_2 revealed activities comparable with some of the previously reported systems prepared via Surface Organometallic Chemistry. W-based catalyst showed the highest activity, and thus, practical application and scope of WO_3/SiO_2-catalyzed reactions was further investigated.

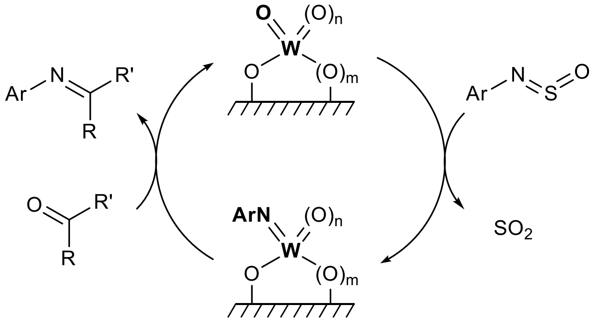

Figure 1. Heterometathetical imidation of ketones with *N*-sulfinylamines catalyzed by silica-supported tungsten oxide

Acknowledgements

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Metal hydrides as the novel intercalation agents in the synthesis of overstoichiometric Li-Mn-O, Mg-Mn-O and Li-Mg-Mn-O spinels

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The method of functional materials synthesis by intercalation is of particular interest due to it's wide potentialities [1]. It includes the reaction between matrix with definite structure and intercalation agent, that either directly inserts into the matrix host structure or undergoes the reaction producing the particles to be inserted.

One of the important aspects in the intercalation method development is the search of novel intercalation agents, that would enable the convenient and controllable insertion of definite particles with homogenous distribution of these under mild conditions and causing minimal contamination of material with byproducts. Unfortunately, the potential of the up to date intercalation methods is often limited with the chemical nature of intercalation agents.

Intercalation agents of the metal hydrides class was first suggested in the synthesis of lithiated spinel $Li_{1+x}Mn_2O_{4-\delta}$ [2-4]. This method exhibited high efficiency and included the annealing of mechanocomposites obtained by ball milling of stoichiometric spinel $LiMn_2O_4$ (matrix) and LiH (intercalation agent) with desired preset ratio under controlled partial oxygen pressure gas media. It allowed to synthesize the pure homogeneous spinel-structure solid solutions with record-high Li-content under mild conditions.

In the following presentation, the key advantages and potential of the hydride intercalation method as applied to the synthesis of overstoichiometric Li-Mn-O, Mg-Mn-O and Li-Mg-Mn-O spinels- promising materials for metal-ion batteries and oxidative processes catalytic systems- will be discussed. The peculiarities of hydrides usage as the intercalation agents as well as the experimental methods of chemical processes study accompanying the hydride intercalation will also be of consideration.

Acknowledgements

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Synthesis, characterization and photophysics of luminescent Ir(III) and Pt(II) β-diketonate complexes

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Nowadays phosphorescent imaging is an upcoming method for both *in vitro* and *in vivo* visualization of biological systems. Luminescent organometallic iridium(III) and platinum(II) complexes have often been proposed as useful luminophores for cell imaging due to their efficient luminescence and attractive photophysical properties.[1] Using selective vectors conjugated with luminescent probes provides unique information on the processes in living cells. Cell-imaging applicable complexes must be devoid of acute cytotoxicity, chemically stable in physiological conditions, and sufficiently soluble in aqueous media.[2]

Herein we report on a series of cyclometalated iridium(III) and platinum(II) β-diketonate complexes **1-4** bearing ether function (Figure 1). The compounds were obtained; their structure was intensively studied and characterized by ^{1}H-NMR spectroscopy and single-crystal X-ray diffraction analysis. For all the complexes absorption, excitation, emission spectra, lifetime of the excited state and quantum yields were measured to evaluate the impact of ligand properties onto photophysical characteristics of the compounds obtained. The ether function will be further utilized for conjugation with vectors or biomolecules.

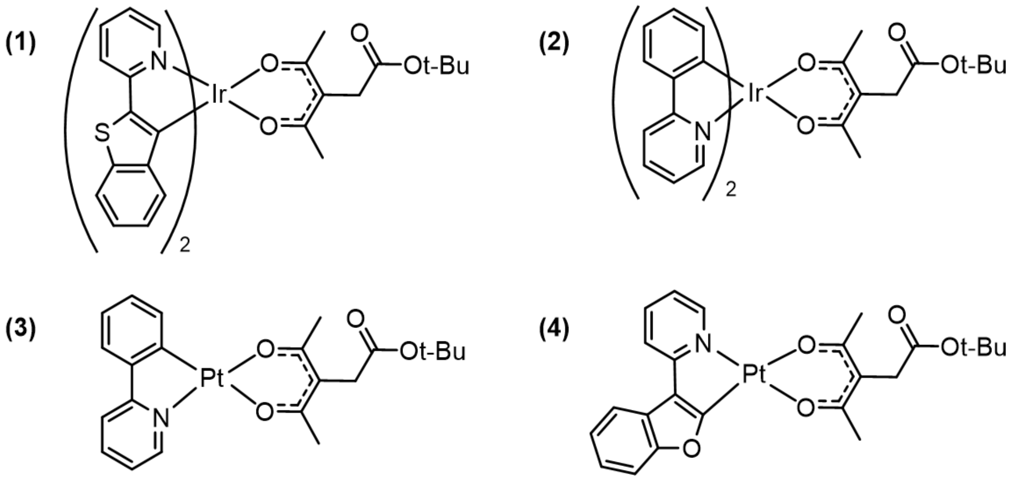

Figure 1. Structures of the complexes 1-4

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Distribution of Electron Density in Substituted η^6-Arene Tricarbonyl Chromium(0) Complexes: Experiment vs. Invariom Modelling

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In recent years, the invariom based approach[1] has been widely used to study a distribution of electron density (ED) in crystals of organic and inorganic compounds. Recently, it was proposed to use invariom modelling and "whole-molecule" scattering factors particularly to distinguish correct and incorrect central atoms in 3*d*-elements coordination compounds[2,3] and to analyzing of ED distribution in general.[4,5]

In this work, the molecular and crystal structures of η^6-[N-acetyl-(1,3-oxazine-6-yl)benzene]tricarbonylchromium(0) (**1**) and η^6-[spiro(cyclohexane-1,2'-(3,8-dihydro-2H-1,3-benzoxazine)]tricarbonylchromium(0) (**2**) have been studied. We carried out the comparative analysis of the topological characteristics of the electron density, obtained from high-resolution X-ray diffraction experiments and the "whole-molecule" scattering factors.

According to the data obtained, the invariom modelling (in it's "whole-molecule" variant) adequately describes the distribution of the deformation ED (Fig. 1) and the topological characteristics in the coordination sphere of chromium in **1** in **2**.

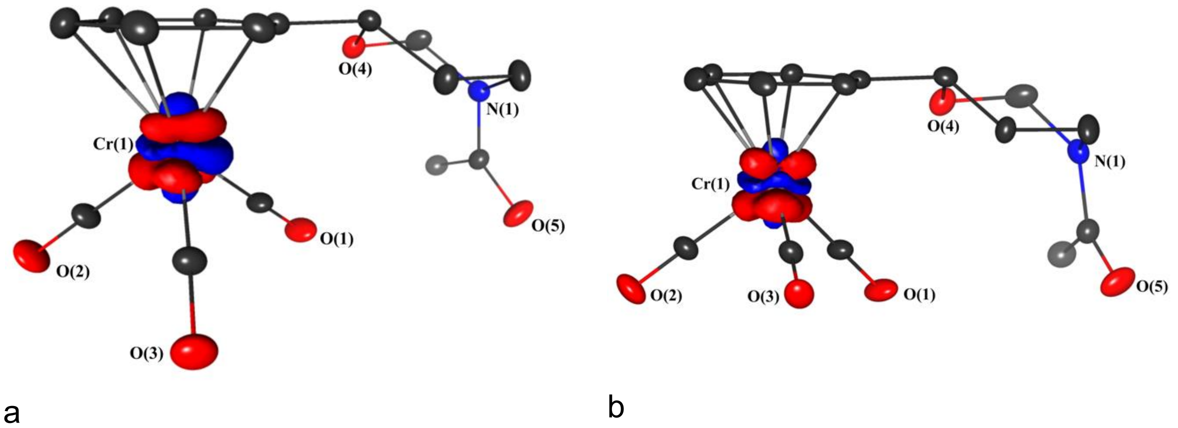

Figure 1. Distribution of DED in the coordination sphere of chromium in 1: X-ray diffraction experiment (*a*), invariom modelling (*b*)

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Single-crystal growth of iron phosphide-arsenide $FeP_{1-x}As_x$ by the chemical vapor transport

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Iron pnictides FeP and FeAs belongs to the large family of compounds, which crystallize in the MnP structural type (ortorhombic syngony, space group *Pnma*). Despite of the relatively simple structure and composition they show rather diverse magnetic property: antiferromagnetic ordering with the formation of a incommensurate helical magnetic structure (HMS), but the some features of this phenomenon still remains undisclosed. For a deeper understanding of the observed phenomena, it is of great interest to carry out measurements on large single crystals of $FeP_{1-x}As_x$ using such methods as solid-state on ^{31}P nuclear magnetic resonance and neutron spectroscopy.

To obtain large single crystals using the chemical vapor transport with iodine, a series of experiments were carried out, in which such parameters as evaporation and growth zone temperature, ampoule size, amount of transport agent, and transported substance were varied. As a result, conditions were selected that allow reproducible growing of FeP single crystals with sizes up to 1 cm and weights 0.3 - 0.5 g. For the mixed arsenide-phosphide $FeP_{1-x}As_x$ ($0 < x < 1$), it was possible for the first time to obtain crystals with dimensions 3x3x2 mm^3.

The obtained samples were characterized by XRD and EDX. The presence of HMS was demonstrated by neutron diffraction. Measurement of magnetic and transport properties showed good compliance with literature data. The study of the FeP single crystals by ^{31}P nuclear magnetic resonance made it possible to obtain new information about the features of the magnetic helicoidal structure of this compound.

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Transition-metal-free synthesis of 1,2-disubstituted indoles: a new life for the Madelung and Smith indole syntheses

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Madelung reaction is one of the classical approaches to assemble the indole core. It has served as a powerful tool to create heterocyclic systems from the very moment of its discovery back in 1912.[1] Original method involves harsh reaction conditions: heating of acylated *ortho*-toluidines to 250 – 350 °C in the presence of strong bases ($NaNH_2$ or KO*t*-Bu). However, classical conditions of Madelung cyclization along with several modifications are generally unable to afford 1,2-disubstituted indoles from unactivated tertiary amides. The problem can be solved by installation of some auxiliary groups on methyl group in *o*-toluidine moiety in order to make Madelung reaction feasible due to increased acidity of the resulting -CH_2- fragment (Figure 1). But is utilization of auxiliary groups the only option?

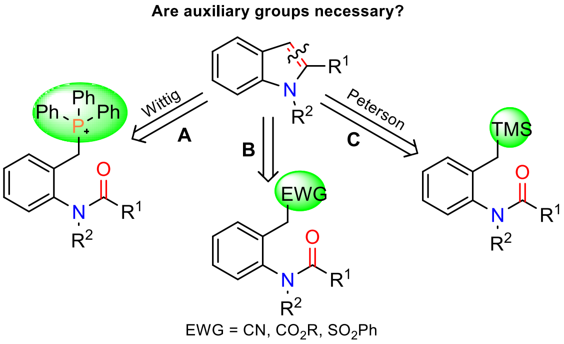

Figure 1

Our study deals with this important question. And the answer we got from the experiments is “No”. Metaloorganic base, LDA, is suitable reagent for transformation of unactivated tertiary amides into 1,2-disubstituted amides; yields are generally high. Furthermore, we found that the whole process of indole preparation from secondary amine can be done in one-pot two-step fashion. Mechanistic studies revealed that conventional mechanism of Madelung reaction is needed to be corrected. Moreover, success of the developed approach allwed us to consider application of Madelung cyclization to benzofurans and benzothiofenes synthesis.

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Highly cytotoxic palladium(II) pincer complexes based on cysteine and homocysteine derivatives

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Nowadays different types of transition metal complexes, including platinum, ruthenium, zinc, titanium, and gold compounds, are extensively explored as potential anticancer agents. Of particular interest are palladium derivatives which possess obvious similarities in structure and coordination behavior with platinum counterparts. One of the recent trends in the development of Pd(II) cytotoxic agents is the use of pincer-type and related tridentate ligands, which provide high thermodynamic and controlled kinetic stability along with the possibility to finely tune the properties of resulting complexes. Recently we showed that Pd(II) pincer complexes based on picolinamides functionalized with *S*-donor amino acids exhibit high cytotoxic activity against several cancer cell lines.[1–3] Modification of the ligand backbone by the sulfur or oxygen atom of the cysteine or homocysteine residue afforded several new series of κ^3-*S,N,N*-pincer complexes (Fig. 1). As well as their prototypes, these palladocyles display significant cytotoxic effects on human colon (HCT116), breast (MCF7), and prostate (PC3) cancer cells, but possess improved ability to induce cell apoptosis. The performed investigations allowed us to define the main structure–activity relationships and outline the most promising compounds for further investigations.

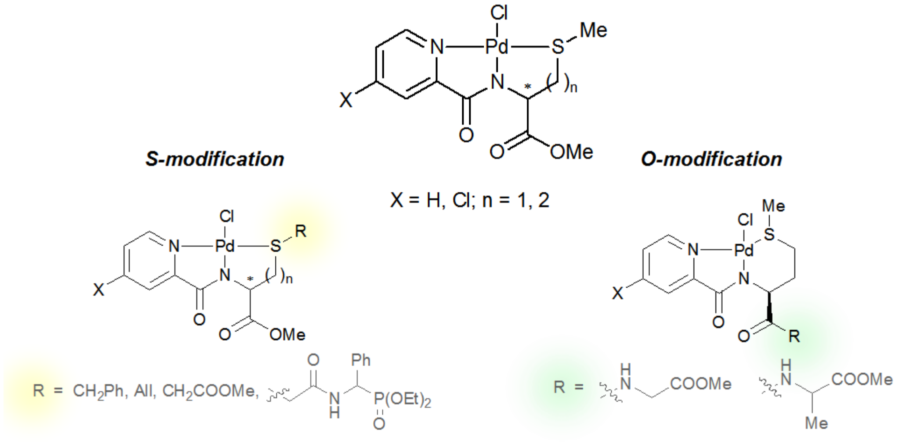

Figure 1. κ^3-*S,N,N*-Pincer complexes based on cysteine and homocysteine derivatives

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Silica-supported heteropoly acids: highly efficient catalytic systems for alkylation of aromatic hydrocarbons

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Keggin-type heteropoly acids (HPA's) are widely used as homogeneous and heterogeneous catalysts due to their unique physicochemical properties.[1-3] Their significantly higher Brønsted acidity, compared to the acidity of traditional mineral acid catalysts, is of great importance in determining catalytic activity. An additional feature of HPA's is their low corrosivity. In comparison to the traditional acid catalysts they reduce the negative environmental impact of the catalytic process. It is, however, important to note that heteropoly acids have an extremely low surface area. Their application as heterogeneous catalyst in organic reaction media therefore requires their dispersion on the surface of a support that increases the number of the available acidic sites and enhances catalytic activity.

The present report describes the synthesis, spectroscopic characterization and catalytic application of several silica-supported heteropoly acids. In the catalytic reactions the possible deactivation mechanisms of the catalysts are also discussed.

The new composites were synthesized by simple wet impregnation of the commercially available silica with the corresponding HPA (phosphotungstic acid, $H_3PW_{12}O_{40}$ or phosphomolybdic acid, $H_3PMo_{12}O_{40}$). Eight new heterogeneous catalysts have been prepared containing silica supports of different particle size and surface area and different HPA loading. The catalysts were thoroughly investigated by nitrogen gas porosimetry, FT-IR and ^{31}P MAS NMR techniques.

The novel silica-supported catalysts were then screened in Friedel-Crafts alkylation of aromatic hydrocarbons with 1-octene in a batch system. The catalysts proved to be extremely active even under mild reaction conditions (80 °C) in the alkylation reaction but rapidly deactivated upon recycling.

In contrast, the catalysts used in a continuous flow system provided the alkylated product with extremely high activity, selectivity and stability.

Acknowledgements

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Do metallophilic interactions exist in dimeric hydrides and halides of coinage metals?

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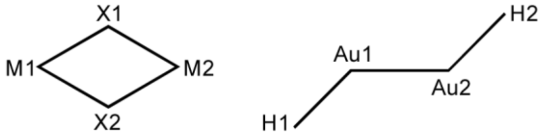
The interacting quantum atom (IQA) approach was employed to scrutinize the nature of metal···metal (M···M) interactions in dimers $(MX)_2$ (Chart 1) of hydrides (MH), fluorides (MF), and chlorides (MCl) of coinage metals (group 11 elements). The $(MX)_2$ molecules were optimized at CCSD(T) level using the fourth-order scalar-relativistic Douglas–Kroll–Hess (DKH) Hamiltonian (DKH4-CCSD(T) method henceforth) and relativistic all-electron basis sets for all atoms.



$(MX)_2$, D_{2h}:
M = Cu(I) (**1**), Ag(I) (**2**), Au(I) (**3**); X = H, F, Cl

trans-$(AuH)_2$, C_{2h} (**3**H, C_{2h})

Chart 1. DKH4-CCSD(T) optimized $(MX)_2$ molecules

The calculations performed indicate that interactions between M atoms in dimers **1-3** are really repulsive. The metallophilicity (the stabilizing interaction between metal atoms) is thus not exist in these complexes. The only exception is dimer **3H** of C_{2h} symmetry. The existence of the latter dimer on the potential energy surface of $(AuH)_2$ is an unambiguous evidence of the metallophilic Au···Au interaction in this dimer. Energies of M···M as well as X1···X2 repulsions are significantly outweighed by much higher energies of the interaction of two M atoms with two X atoms favoring thus the dimerization of the corresponding MX.

Analysis of electron density distributions in **1-3** allows one to conclude that electron populations of M atoms apparently dictate the nature of M···M interactions and the binding M atoms in the studied complexes. There exist certain critical values of positive charges on M atoms, on exceeding which M···M interactions in these complexes become repulsive despite negative formation energies of such complexes, small M···M internuclear distances, and the existence of a bond critical point (BCP) between M atoms. The same is presumably valid for other complexes of coinage and other transition metals with short intermetallic contacts.

The data obtained show that a comparison of internuclear M-M distances with the sum of the van der Waals radii of two transition metal atoms as well as the existence (the absence) of (3,-1) CP between M atoms are inappropriate criteria for solid decision about the existence or the nonexistence of the binding of M atoms.

For gamma-boron, a multiparameter infinite family of related forms of the general formula $(B_{12}^{-2})(B^{+1})_2$ is geometrically designed

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In 2008, two articles were published on the preparation at high pressure and determination of the structure of γ-boron.[1,2] When we did not have access to the full texts of these articles, we tried to reproduce this structure on the words of abstracts on the general formula $(B_{12}^{-2})(B_2^{+2}) = B_{14}$ and one schematic projection. To design boron structures, we used the MM+1 molecular mechanical method in the HyperChem program. It turned out that such a formula and projection have not one, but several theoretically possible forms of boron. Each intericosahedral B^{+1} atom forms two 2c2e-bonds with the boron icosahedra B_{12}^{-2} or with other B^{+1} and two 3c2e-bonds with the B_{12}^{-2}. Such B^{+1} atoms can be single, bound in chains of any even length or in infinite chains. These boron polymorphs can be formed from each other as the turns 180° (twinning) and (or) a polytypic shift of ½ the period in several orientations of the planes. For all new B_{14} forms, standardized crystallographic parameters in cif-format are calculated. For γ-boron, the difference between the calculated by MM+ and the experimental periods and density reaches 6%, so the structural data of the new B_{14} forms need to be clarified by quantum chemical methods. The closest in structure and density analogue of γ-boron has parameters: B_{14}, Pbcn (№ 60), z=4, a~5.12 Å; b~8.57 Å; c~8.54 Å; d~2.68 g/cm^3 (the same method for γ-boron calculated the same density). Densities of 2.54-2.59 g/cm^3 were calculated for 7 simplest B_{14} forms with single B^+ (Fddd, Cmce, $Pna2_1$, C2/m, C2/c, $P2_1/c$, C2/c). The simplest B_{14} forms with groups $(B^+)_2$ consist of a family of high-density forms 2.68 g/cm^3 (γ-boron and Pbcn-form) and a family of low-density forms 2.44-2.49 g/cm^3 (the remaining 5 forms: Cmcm, Pbcm, C2/m, P2/c, C2/c). The B_{14} form with infinite chains of B^+ has parameters: C2/c (No. 15); a~6.26 Å; b~11.74 Å; c~5.29 Å; β~98.8°; z=4 and also a high expected density of d~2.68 g/cm^3. Two B_{14} forms with groups $(B^+)_2$ belong to the space groups $P6_522$ and C2/c and have an intermediate density of ~2.58-2.61 g/cm^3. It is revealed that for the $(B^+)_2$-contained B_{14} form and α-rhombohedral boron structural hybrids are possible. The simplest such hybrides are $(B_{12}^{-2})_2(3c2e^{+1})_2(B^+)_2 = B_{26}$, P-1 (No. 2), a~8.31 Å; b~4.99 Å; c~4.60 Å; α~90.9°; β~102.4°; γ~101.9°; z=1, d~2.62 g/cm^3 and its monoclinic analogue $P2_1/m$. For some B_{14} forms, transformations with a decrease in symmetry and in the coordination number of atoms B^{+1} from the initial 6 to 5 are possible.

Acknowledgements

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Prediction of the structure of genetic molecules of possible carbon-free forms of life: phosphorus life (P-O-N-H-F) is the best alternative to our carbon life, and for life based on boron, sulfur or silicon there are serious difficulties.

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In order for a polymer chain to be capable of biological self-replication, a relationship between the binding energies of three different types must be performed: E_{chain} >> E_{pair} >> E_{tors}. Here, the E_{chain} is the energy of breaking chemical bonds in the polymer chain, the E_{pair} is the binding energy between mutually complementary links of different polymer chains, E_{tors} is the energy barrier of conformational rotation of the polymer chain. The simplest way to achieve intermediate Epair values is multiple hydrogen bonding between mutually complementary links. In the ICSD database, the simplest prototype of real nucleotides is structure $C_3N_3(NH_2)_3{\cdot}(CO)_3(NH)_3$ with triples of hydrogen bonds. In addition, it was found that in the structures of hexaaminotricyclotriphosphazene semi-ammoniate $[(P(NH_2)_2)_3N_3]_2{\cdot}NH_3$ and cyclotrimetaphosphimates of large cations $M_6[(PO_2)_3(NH)_3]_2$ (M = K, Rb, Cs) are dimers with six hydrogen bonds. On the basis of such dimers and their structural hybrids, the simplest polymers with such P-containing links ~((cyclo-$(PF)_2(PFNH_2)N_3$)(mu-NPF_2NH)$_x$((cyclo-$(PF)_2(PFO)N_3H$)(mu-NPF_2NH))$_y$~ (Fig. 1) are constructed using the HyperChem program, where NH_2 or OH groups can also be present instead of F. The polymer with the first type of links is geometrically optimized by the semi-empirical PM6 method using the MOPAC program. Such polymers are geometrically inclined to dimerize into self-complementary double helices. Also, I have constructed structurally similar polymers with the replacement of phosphorus with silicon, boron or sulfur, but for them, for a number of reasons, the chemical resistance will be so broken that the occurrence or maintenance of life will be almost impossible. the Hypothesis about the possibility of inorganic life put forward before, for example, Oganov for nitric life at high pressures in the depths of the giant planets.[1] However, no specific variants of the specific molecular structure of the inorganic polymer, making it possible to self-replication, before my work was not offered by anyone.

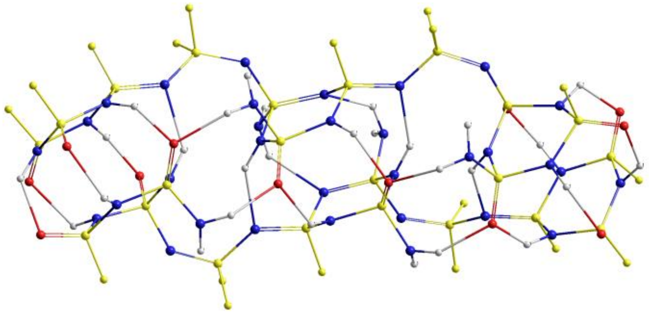

Figure 1. P-O-N-H-F double helix

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Synthesis and structure of new boron,antimony-capped iron(II) macrobicyclic tris-dioximate precursors of a transmetallation reaction with terminal donor group

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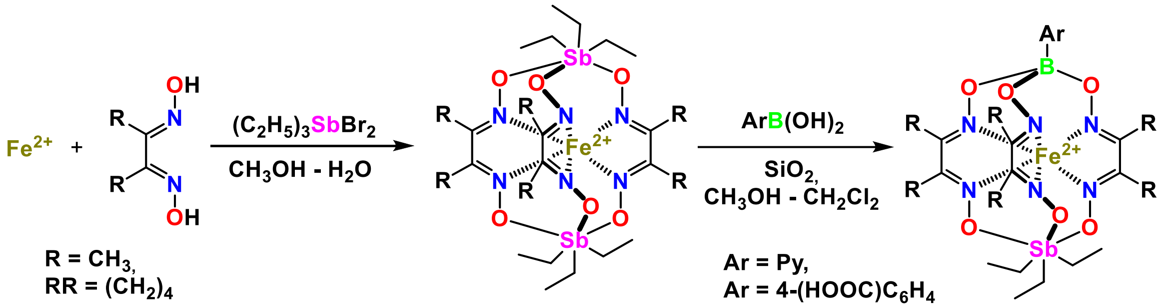
Cage metal complexes (clathrochelates)[1] with terminal reactive, donor or biologically relevant group(s) are prospective, chemically robust, three-dimensional molecular platforms and macrobicyclic building blocks for the design of new types of (photo)electronic devices, modern functional materials and prodrugs as well.
The above tris-dioximate iron(II) cage complexes were obtained using a two-step synthetic procedure. First of them included the synthesis in high yields of the bis-triethylantimony-capped clathrochelates by template coindensation of the corresponding α–dioxime with triethylantymony(V) dibromide as a Lewis acid on the iron(II) ion as a matrix.[2,3] The tris-dioximate iron(II) cage complexes with non-equivalent boron,antimony-containing apical cross-linking fragments were obtained by a stepwise transmetallation by Scheme 1 of one of the two apical fragments of the above bis-triethylantimony-capped complexes with equivalent of the corresponding boronic acids, in the presence of silica gel as a heterogeneous catalyst.



Scheme 1.

The obtained complexes were characterized using UV-Vis, MALDI-TOF MS, IR and ^1H and $^{13}C\{^1H\}$ NMR specta, as well as by single crystal X-ray diffraction.

Acknowledgements

The financial support from the Russian Foundation for Basic Research (grants 19-03-00357 and 18-29-23007) is gratefully acknowledged. The spectra measurements were performed using an equipment of CKP FMI IGIC RAS, which is financially supported in the framework of the IGIC RAS state assignment in the field of basic scientific research.

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Synthesis, characterization, cytotoxicity, and DNA binding studies of new Cu(II) complexes with tetrazole and isothiazole derivatives

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Nowadays chemotherapy is one of the main ways to treat various cancers, therefore a huge number of studies are carried out worldwide to develop new improved antitumor drugs. Mixed-ligand 1,10-phenanthroline based copper(II) complexes as anticancer drugs are of interest to scientists[1].

At the present work we were interested in the evaluation of the biological properties of mixed-ligand copper(II) complexes with tetrazole (5-phenyl-1H-tetrazole, 5-methyl-1H-tetrazole) and isothiazole (4,5-dichloroisothiazol-3-carboxylic acid) derivatives with 2,2'-bipyridine, 2,2'-bi-4-picoline, 1,10-phenantroline or 4,7-dimethyl-1,10-phenanthroline have been synthesized.

All of the complexes were characterized by various spectral and physical methods: elemental analysis, powder diffraction analysis, UV-Vis and IR-spectroscopy. The molecular and crystal structures of the complexes have been determined by single-crystal X-ray diffraction analysis.

The effect of the complexes and ligands on the viability of the MCF-7 and Hep-2 cell lines was investigated *in vitro* (48 hours, 1-50 μM) by means of IN Cell Analyzer 2200 using dual staining with Hoechst 33342/propidium iodide. Most of the complexes exhibit significant dose-dependent cytotoxic effect. Moreover, 1,10-phenanthroline based compounds were much more toxic than complexes containing 2,2'-bipyridine. For some of the complexes DNA binding study was performed (Fig. 1).

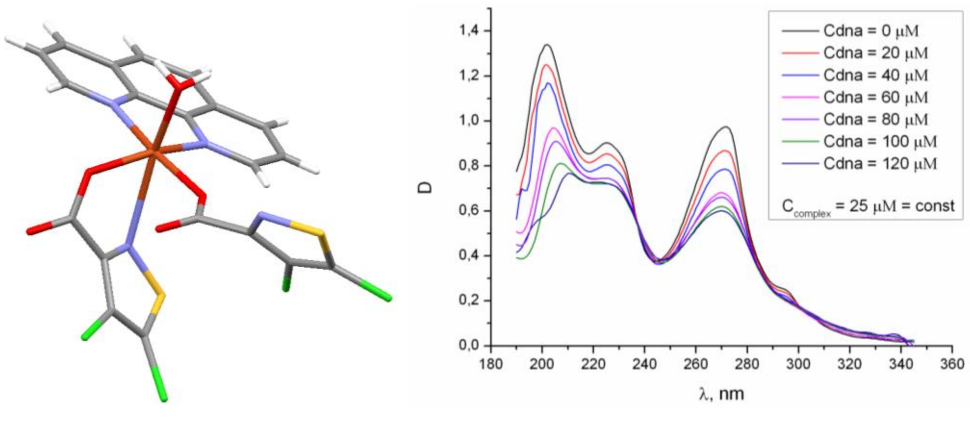

Figure 1. Structure and absorption spectra of the [Cu(1,10-phen)$L_2(H_2O)$] (where 1,10-phen – 1,10-phenantroline, L – 4,5-dichloroisothiazol-3-carboxylic acid) upon titration with ct-DNA

Acknowledgements

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Destruction of amino acids catalyzed by copper(II) complex

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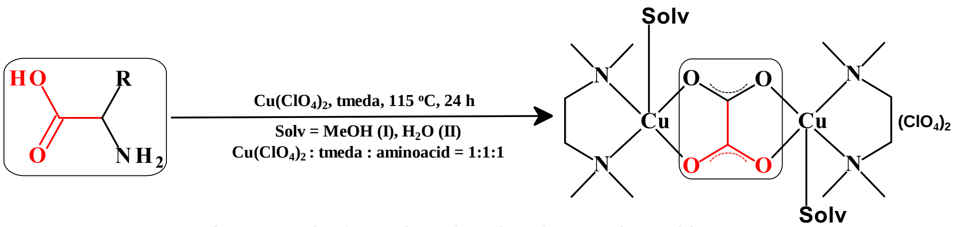
Since the beginning of 20th century, many examples of organic reactions catalyzed by d-metal ionshave been investigated. In particular, ethylene glycol, glycerin, mannite or methylamine in the presence of copper and its compounds oxidize in aerobic conditions to formic acid and formaldehyde, respectively[1]. Later, deamination reactions of amino acids, leading to the formation of their keto-carboxylic derivatives were described[2].

In case of the simplest amino acid, glycine, the reaction proceeds deeper, with the formation of oxalate ion[1, 3]. However, examples of such processes occurring under relatively mild conditions and leading to the destruction of more complicated amino acids, such as alanine or arginine, are not currently published.

Herein we describe an unexpected destruction of a number of amino acids (glycine, alanine, arginine, glutamine and p-chlorophenylalanine) under mild solvothermal conditions in the presence of the copper(II) aminate complex. In all cases, the main reaction product is the well-known binuclear oxalate bridging copper (II) complex [(tmeda)Cu^{II}(solv)(μ-*k*O,O,O`,O`-C_2O_4)Cu^{II}(solv)(tmeda)](ClO_4)$_2$, where (tmeda = N,N,N`,N`-Tetramethylethylenediamine; solv = H_2O, MeOH) (see scheme 1).

In case of alanine, arginine, glutamine and p-clorphenylalanine, complex **I**
is formed in a methanol solution, in the case of glycine and the use of an aqueous solution – complex **II**. The unit-cell parameters for **I**: monoclinic, $P\ 2_1/c$, a 11.3467(3), b 8.1186(2), c 15.7054(3) Å, β 100.018(2), V 1424.71 Å3, Z = 2, R = 0,0273; for**II**: monoclinic, $P\bar{1}$(2), a 7.5680(2) b 10.0083(2) c 18.7682(5) Å, α 87.913(2), β 80.579(2), γ 82.081(2), V 1388.87 Å3, Z 4, R 0,0372. Both **I** and **II** were characterized by elemental analysis, IR, UV-Vis spectroscopy and X-ray diffraction.

We propose two possible mechanisms for the formation of oxalate ion. The first one involves the deamination of an amino acid followed by the replacement of a radical R in amino acids with a hydroxyl group. The second proposed mechanism involves decarboxylation followed by fixation of CO_2 and the formation of oxalate.



Scheme 1. The formation of oxalate from amino acid

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Colored pyrophosphate powders for stereolitographic printing

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The method of stereolithographic printing is widely applied to produce porous ceramic materials of complex architecture[1]. Among them, the stereolithography (SL) technique is believed to be the most prominent and popular. 3D printing technology has been extensively used worldwide. Calcium phosphate (CP) ceramics is used to replace and reconstruct bone tissue over the past decades. To serve as a matrix inducing bone ingrowth, highly porous structures called scaffolds are developed. In the present work, calcium phosphate (CP) powder was obtained at room temperature using mechanochemical activation from calcium lactate and dibasic ammonium phosphate:

$$Ca(CH_3CH(OH)COO)_2+(NH_4)_2HPO_4+2H_2O \rightarrow CaHPO_4\ 2H_2O+CH_3CH(OH)COONH_4$$

Phase composition of powders after synthesis was represented by brushite ($CaHPO_4$ $2H_2O$). The phase composition of the powders after heat treatment at 500–700 °C was represented mainly by γ-calcium pyrophosphate γ-$Ca_2P_2O_7$ (γ-CPP). Heat treatment at 700 °C led to transformation of brushite to β-pyrophosphate. During heating ammonium lactate decomposed forming gas products (CO_2, NH_3 and H_2O) and partially amorphous carbon due to oxygen deficiency[2].

The CP-colored powders with products of degradation of ammonium lactate can be used to create suspensions based on light-cured monomers intended for stereolithographic printing of semi-finished porous openwork ceramic structures. For ceramics based on CP, intended for use as implants, microporosity provides the surface roughness that is necessary for the adhesion of proteins and osteoblasts.

The phase composition of ceramics obtained from the synthesized powders after calcination at 1100 °C is represented by biocompatible and bioresorbable β-CPP β-$Ca_2P_2O_7$ phases. The resulting ceramic materials based on CP from synthetic powders can be used as a material for bone implants.

Due to the large amount of amorphous carbon formed during the thermal decomposition of ammonium lactate, a local temperature increase occurs. This leads to the formation of the β-CPP phase at 700 degrees, which is significantly lower than the normal temperature of formation of this phosphate.

CP-powders synthesized from calcium lactate and ammonium hydrophosphate via two stage scheme including mechanochemical activation and thermal treatment can be used in the production of porous ceramics by 3D printing.

Acknowledgements

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Sawhorse-type ruthenium complexes with triazolopyrimidine ligands as an efficient catalysts of hydrogenation with sodium borohydride

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Hydrogenation is one of the backbones of the chemical industry because of its wide range of applications in the synthesis of various products such as fine chemicals, pharmaceuticals, food, dyes, functional polymers, and agrochemicals.[1] Ruthenium catalysts are widely used for selective hydrogenation.[2]

The dinuclear ruthenium complexes containing a $Ru_2(CO)_4$ backbone with a typical sawhorse geometry proved to provide a stable, versatile and tunable platform for the design of molecular catalysts, liquid crystals, supramolecular materials as well as of bioactive substances.[3] In most cases, carboxylato-bridged derivatives were involved in the catalytic hydrogenation reactions.

Following this research lines three new sawhorse-type ruthenium complexes of the general formula $[Ru_2(CO)_4(CH_3COO)_2(L)_2]$, where L=triazolopyrimidine derivatives (Figure 1) have been synthesized and characterized by NMR, IR, and X-ray.

The catalytic activity of new catalysts was tested in the hydrogenation of cyclohexene derivatives and ketones. Instead of using high pressures of H_2 sodium borohydride as a hydrogen source was applied.

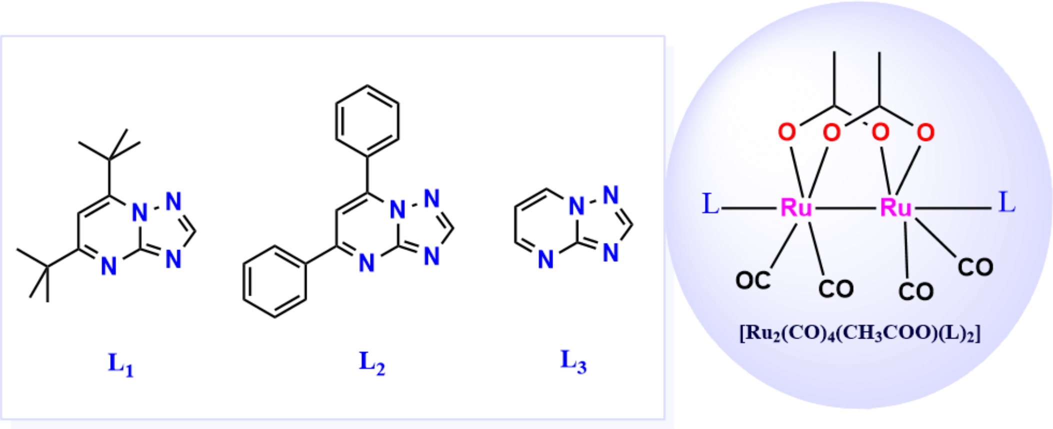

Figure 1. The structure of ligands and the general formula of used catalysts.
L = 5,7-ditertbutyl-1,2,4-triazolo[1,5-*a*]pyrimidine (L1), 5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (L2) and 1,2,4-triazolo[1,5-*a*]pyrimidine (L3)

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Palladium- and ruthenium-complexes of chiral tridentate P,N,O-ligands and their application in catalysis

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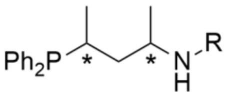
Chiral bidentate ligands containing different coordinating functionalities with distinct electronic and steric characteristics are a particularly interesting class of compounds. The majority of these compounds contain phosphorus as soft donor and nitrogen or oxygen as hard donor atoms.[1] The different electronic properties provide excellent catalytic behavior in transition metal catalyzed organic transformations. The activity of transition metal catalysts can be tuned by the introduction of a third coordination site with nitrogen or oxygen donor atom. The hemilabile character of this side arm can strongly affect the activity and the enantioselectivity of the catalyst.[2,3]

In the present work we evaluated the Ru(II) and Pd(II) coordination chemistry of new type of P,N,O-ligands (Figure 1). The coordination behavior of compounds **1**-**6** were thoroughly studied by X-ray crystallography, 1D and 2D NMR techniques and computational methods. The catalytic properties of the ligands were investigated in ruthenium-catalyzed enantioselective hydrogenations and in palladium-catalyzed asymmetric allylic substitutions. In the catalytic reactions high enantioselectivities and activities could be obtained.



1 (*S*,*S*): R = $(CH_2)_2OH$
2 (*S*,*S*): R = $(CH_2)_2OCH_3$
3 (*S*,*S*): R = (*S*)-$CH(CH_3)CH_2OH$
4 (*R*,*R*): R = (*S*)-$CH(CH_3)CH_2OH$
5 (*S*,*S*): R = (*S*)-$CH(CH_3)CH_2OCH_3$
6 (*R*,*R*): R = (*S*)-$CH(CH_3)CH_2OCH_3$

Figure 1. Novel, potentially tridentate P,N,O-ligands

Acknowledgements

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A new synthesis method of mesoporous oxides $Ce_xZr_{1-x}O_2$-SiO_2 using cyclodextrins

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Ceria attracts much attention of researchers due to its unique properties: large values of oxygen capacity and oxygen conductivity. These properties, as well as sintering resistance, can be improved by doping ceria with zirconium. However, the resulting solid solutions usually do not have large specific surface areas. To solve this problem it can be used a combination of these oxides with silica. In this work for the first time a sol-gel method using cyclodextrins as structure-forming agents was used for the production of such complex oxide systems.

Samples of $Ce_xZr_{1-x}O_2$-SiO_2 were obtained by hydrolysis of tetraethoxysilane in the presence of hydrochloric acid, as well as cyclodextrin (beta-cyclodextrin mixed with urea or methylated beta-cyclodextrin). Various combinations of inorganic salts (nitrates and chlorides) are used as sources of cerium-zirconium oxide. Moreover, the introduction of these salts was carried out both at the stage of gelation and by impregnation of previously obtained SiO_2 according to the wetness capacity.

Thermal decomposition of the gels was studied using thermogravimetric and differential thermal analyzes. The synthesized samples were investigated by a number of physicochemical methods. The uniform distribution of elements in the samples was confirmed by EDX method. The values of the surface area and pore size distribution were determined by BET method.

It was shown that all the samples obtained are uniform in composition. They are mesoporous and have relatively large specific surface areas (300-400 m^2/g). Samples obtained by the introduction of salts at the stage of gelation, have a narrower pore size distribution and smaller pores (average pore size of about 3-4 nm) compared with samples obtained applying salts on the wetness capacity of previously synthesized SiO_2 (average pore size of about 5-10 nm) .

Thus, in this work, we studied the effect of the type of the initial salts of cerium and zirconium, as well as the method of their introduction on the properties of the resulting oxides $Ce_xZr_{1-x}O_2$-SiO_2.

Diversity of Ag (I) complexes with 10-(aryl)phenoxarsines

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The complexation of triphenylarsine ligands with silver(I) ions is currently attracting increasing attention due to their unusual coordination chemistry. Thus, mononuclear silver(I) complex of triphenylarsine with thiocyanate[1], homo- and heteroleptic complexes based on silver nitrate and silver carboxylate[2-6], binuclear bridged complexes based on bromate and nitrite silver[7,8] were obtained.

Here we present the synthesis of Ag (I) complexes of 10-(aryl)phenoxarsines.

The reaction of 10-(aryl)phenoxarsines with silver (I) salts was carried out in a ratio of ligand:metal 2:1, 3:1 and 4:1 (Figure 1). The composition and structure of the complexes **1-5** depend on the ligand to metal ratio and on the counterion in the initial metal salt. All observed compounds were characterized by NMR, mass-spectrometry, elemental analysis and X-ray crystallography.

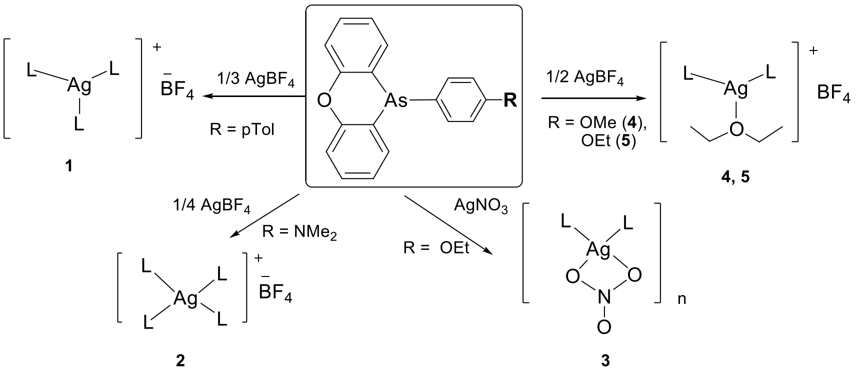

Figure 1. Synthesis of complexes 1-5

Acknowledgements

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Triangular molecules $E_{24}E'_{21}H_{21}$ (E, E′ = Si, Ge): a DFT study

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Triangulenes are alternant non-Kekulé hydrocarbons with high spin which depends of the molecular size. They are also could be described as triangular graphene-like flakes. Whereas carbon triangulenes are fairly well studied, their main group element analogues received much less attention. Various triangulene compositions of the group 14 elements were studied recently.[1] Modification of the triangulenes like a hole in the skeleton can change their spin state[2] and it is demonstrated at Figure 1. In this work we present DFT calculations on structures and properties of a series of group 14 elements (Si, Ge) holed triangulenes.

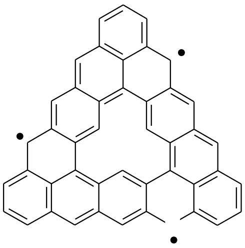

Figure 1. Holed triangulene, S=3/2

Acknowledgements

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Rare earth, alkaline earth and 3d elements lactates: synthesis, structure and application for oxide films deposition.

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Lactic acid is a low-cost and environmental friendly compound. Its salts demonstrate sufficient stability in solution being formed by chelating ligands. Metal lactates are widely applied in medicine (e.g. as contrast agents for MRI), in lanthanide-actinide separation and household chemistry. Nevertheless, the detailed synthesis, crystal structure and thermal behavior of lactates, except some transition metals, as well as their application for thin film deposition by Metal-Organic Chemical Solution Deposition (MOCSD) have not yet been studied. MOCSD is characterized by the low cost, high reproducibility, technical simplicity and highly effective control of the composition and thickness of obtained films. However, MOCSD requires the precursor solution in polar and volatile organic solvents, mainly alcohols, to be developed for each metal. Moreover, in case of complex oxide thin films these precursors must be compatible to each other. Thus, the object of the study are rare earth, alkaline earth and 3d elements lactates.

As a result of interaction of lactic acid and REE cations in water or methyl alcohol, REE lactates with different structure and amount of water molecules are formed, depending on the synthesis procedure and the location of the cation in the series. Wherein, mono-, di-nuclear molecules and linear polymers are formed, which are linked by a network of hydrogen bonds. The strength of the complexes formed is confirmed by the absence of formation of different-ligand complexes with diethylenetriamine and ethylenediamine in isopropyl alcohol. When moving along a series, the lactate-anion denticity consistently decreases from three (chelate-bridging type of coordination) down to two. Meanwhile the temperature of final dehydration increases, and the solubility decreases drastically, which is explained by the decrease in the radius of the central ion. In all structures, the central ion with coordination number 8 has an tetragonal anti-prismatic environment, in the case of coordination number 9 it is supplemented by a ‘cap’ of hydroxyl or carboxylic oxygen. Since for the crystal growth, the oxygens of the lactate anion should be involved in a network of hydrogen bonds, water molecules always present in the coordination sphere.

The successful synthesis of Li, Ca, Sr, Ba, Pb, Mn, Fe, Ni, Co, Cu lactates of general formula $[M(Lact)_n(H_2O)_m]$ are also reported. Composition, structure and thermal behavior of all the obtained compounds were studied by TGA, IR spectroscopy, powder and single crystal XRD as well as DFT simulations. Several crystal structures have been reported for the first time.

The utilization of N-donor ligands allows to increase the solubility of metal lactates and to obtain the precursor solutions in isopropyl alcohol. Moreover, the interaction of amine ligand with water traces under thermal treatment of precursor solution results in decreasing of it decomposition temperature. As a result a large variety of amorphous and crystalline homogeneous and uniform thin film were obtained: planarizing layers (Y_2O_3, La_2O_3), thermal barrier (ZrO_2:Y_2O_3), and functional ($LaNiO_3$, $LaMnO_3$, $LuFeO_3$) oxide thin films.

Solid-state organization of novel cyclometalated platinum(II) complexes through weak interactions

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Noncovalent interactions such as halogen bonding (HB), pi-stacking, H-bonding are widely used for design and fabrication of a variety of functional materials, constructed from inorganic, organic, or organometallic building blocks.[1] Moreover, weak interactions driven crystallization could cause assembly of systems with fascinating optical properties.[2]

Herein we present a series of novel cyclometalated platinum(II) complexes which are decorated by ligands suitable for making of weak interactions (Fig. 1). Crystallization of the complexes leads to realization of HB, pi-stacking and also classical donor-acceptor interactions in solid state.

All target complexes were obtained with good yields and were fully characterized by ^{1}H and ^{195}Pt NMR spectroscopy, mass spectrometry, IR spectroscopy and CHN elemental analysis. Single crystal XRD analysis provides a support that various weak interactions take place depending on the electronic properties of the ligands in coordination sphere of platinum(II).

Influence of observed weak interactions on photophysical properties of obtained platinum(II) complexes was investigated. UV/vis absorption spectra, excitation and emission spectra, excited state lifetimes and QY were measured for solution and solid state.

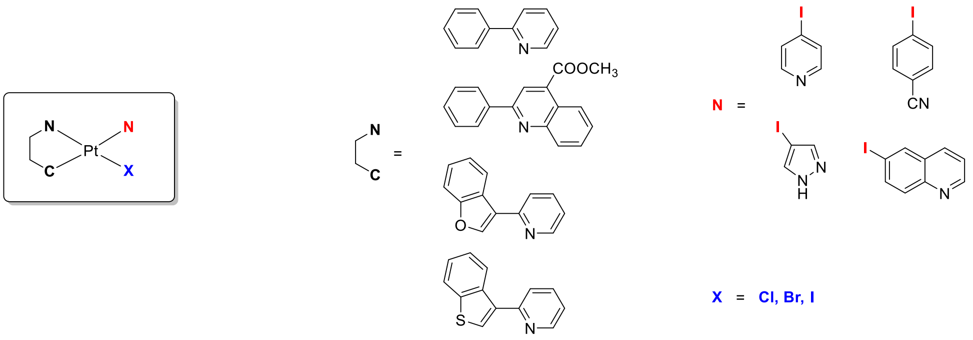

Figure 1. Cyclometalated platinum(II) complexes

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Chemical and structural features of new Cd(II) and Cd(II)-Ln(III) complexes with trimethylacetate anions and N-donor ligands

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Cadmium carboxylates are perspective as starting compounds for further modification and synthesis of heterometallic compositions with promising photoluminescent and magnetic properties[1]. Pivalate anion (piv) is an exactly usable ligand due to its lability and high solubility of the synthesized complexes[2,3].

It was shown that Cd forms polynuclear complexes $[Cd_2(piv)_4(L)_2]$ with piv anions and N-donors (L), such as Et_3N, Lut, 2,2'-bipyridine. In the case of 1,10-phenantroline the structure of the resulting compound depends on molar ratio of the components in the reaction mixture. Molar ratio equal to Cd:L=2:1 gives hexanuclear compound $[Cd_6(piv)_{10}(CO_3)L_2]\cdot 3MeCN$ (**1**) (Figure 1), that rearranges to binuclear complex $[Cd_2(piv)_4(L)_2]$ in the conditions of ratio Cd:L=1:1. It should be noted that in Ar atmosphere and compound $[Cd_2(piv)_4(L)_2]$ (**2**) was crystallized.

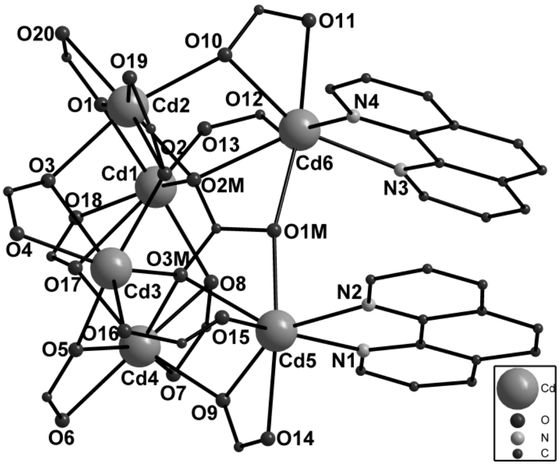

Figure 1. The structure of the complex 1 (H-atoms, t-butyl groups and solvates are omitted)

In the presence of Ln ions polymers $[LnCd_2(piv)_7(H_2O)_2]_n\cdot nMeCN$ (3) were isolated. Only combination with dicarboxylic acid anions (1,1-cyclogexanediacetic, $chda^{2-}$) allowed us to crystallize heterometallic complex $[Eu_2Cd_2(chda)_2(piv)_6(bpy)_2]$ (3) – the first example of Cd-Ln molecular complex with aliphatic acids.

Structural features of synthesized complexes and comparison with aromatic acids analogues will be discussed.

Acknowledgements

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$BiGeSbO_6$ - a new layered oxide for luminescent application

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A new layered compound $BiGeSbO_6$ with $PbSb_2O_6$ structure has been synthesized for the first time via solid state reaction. The $BiGeSbO_6$ systematic investigation, which includes Rietveld refinement of structure (Fig1a), isobaric heat capacity measurements and thermodynamic functions (entropy, enthalpy increment and Gibbs free energy) calculation in the 10 to 1200 K temperature range, as well as optical and luminescent properties studying has been carried out.

The structural feature of $BiGeSbO_6$ is the highly symmetric isolated site of the Bi^{3+} ions. The distances between the nearest bismuth ions are ~5 Å. The compound has a low-energy long-wavelength absorption edge, 800 cm^{-1}. Furthermore, $BiGeSbO_6$ has the ability to form solid solutions with lanthanide oxides, which has been demonstrated with Eu_2O_3 as an example. The results suggest that lanthanide ions in $BiGeSbO_6$ are not actively interacting with each other, which imply a weak concentration quenching. The aforementioned facts, as well as the thermodynamic stability of the compound up to 1250 K, lead us to believe that $BiGeSbO_6$ has great potential for further detailed study in order to produce from it an effective luminescent matrix for activation by REE ions.

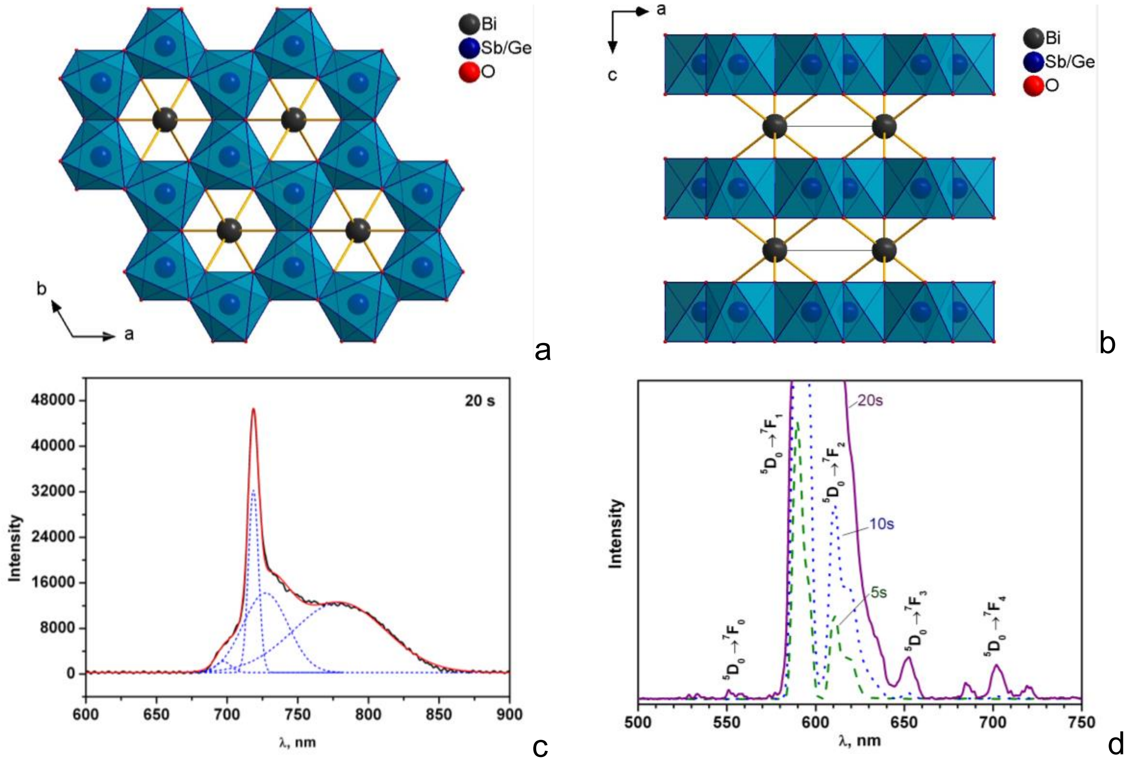

Figure 1. The structure (a, b) and X-ray luminescence spectra of $BiGeSbO_6$ (c) and $Bi_{0.97}Eu_{0.03}GeSbO_6$ (d)

Acknowledgements

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Thermodynamic calculation of the possibility of formation of calcium oxalate

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Currently, the causes and triggers of the processes leading to the formation of organomineral aggregates – OMA (renal, dental and salivary stones) have not been studied sufficiently and are still debatable. It is known that pathogenic OMA have a complex and heterogeneous composition, which is why some authors suggest such entities to be called mixed. So, the share of mixed oxalate-phosphate stones according to different researchers varies from 7 to 60%, urate – from 5 to 50% and so on. However, in general, the most common urinary stones are oxalate stones, composed of the minerals of whewellite $CaC_2O_4 \cdot H_2O$ (COM) and weddellite $CaC_2O_4 \cdot 2H_2O$ (COD), with predominance of COM. These substances are the most frequent components of the stones of the genitourinary system, in addition, they can be part of the dental, gallstones, stones of the salivary glands, they are found in mineral deposits in the lungs, vessels, spleen, in the prostate and pancreas, in the muscles and joints.

For the thermodynamic description of precipitation equilibrium, a solution in a system in which a slightly soluble compound is formed, stability fields were constructed. The principle of constructing such diagrams is to establish the functional dependence of the index of the minimum cation concentration that forms part of the precipitate, which must be created to initiate the precipitation of the phase at a certain pH value of the solution and anion concentration: pMq+ = f (pXq–; pH). In this case, the region above the critical plane obtained characterizes the conditions under which the formation of a given phase is thermodynamically impossible. Based on the constructed 3D diagrams in the pMq+ – pXq– – pH coordinates, conclusions were drawn about the stability of this system and predicting the nature of the change in equilibrium under varying conditions. Based on the thermodynamic values of the solubility products at 310 K, the functional dependences $pCa^{2+} = f(pC_2O_4^{2-}; pH)$ and 3D diagrams ("stability fields") for calcium oxalate monohydrate were determined. To estimate the effect of pH on the possibility of formation of a slightly soluble compound in solution, the graphical dependences of the supersaturation index ($SI = \lg \Omega$) on this factor were constructed: SI = f (pH). It is assumed that if $SI > 0$, then under these conditions it is more thermodynamically more probable that the phase is precipitated from the solution. The acidity of the medium exerts the greatest influence on the thermodynamic stability of substances, the state of the system, and the processes of crystallization. Thus, as the pH value increases, the driving force of crystallization of $CaC_2O_4 \cdot H_2O$ increases significantly. The described regularity is explained by the fact that with increasing pH the relative concentration of $C_2O_4^{2-}$ in the system increases, therefore, a positive correlation between supersaturation and pH is observed. It should be noted that the constructed thermodynamic model reflects the possibility of the formation of phases only on the basis of data on their thermodynamic stability in the standard state and does not take into account, in particular, the kinetic factors and hydrodynamic conditions that affect the process of solid phase formation under real conditions.

Mixed-metal lanthanide triazolecarboxylates for luminescent sensing

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Porous coordination polymers (MOF) based on REE complexes are of interest because of the combination of unique luminescent characteristics of f-ions and high sorption capacity of framework structures. This combination of properties is required to create chemical fluorescent sensors for gases and liquids.

The sensor functioning in a liquid medium must have a number of properties: high chemical stability (including resistance to solvents); thermal stability (necessary for the regeneration of the material); high luminescence intensity. The first two requirements are met by numerous MOF derivatives of REE, and to increase the luminescence intensity, ligands with a minimum number of quenching bonds (O–H, N–H, C–H) should be chosen. Literature analysis has shown that 1,2,3-triazole-4,5-dicarboxylic acid H_3TDA is a convenient ligand. Several of its REE derivatives with the MOF structure are described. In the course of our work, two groups of mixed-metal complexes were synthesized solvothermally: the one with composition of $[Eu_xTb_{1-x}(TDA)(H_2O)_3]*H_2O$ (A) and the other with composition of $(NMe_2H_2)[Eu_xTb_{1-x}(TDA)(HCOO)]$ (B), and their chemical and photophysical properties have been studied. For the compound $[Tb(TDA)(H_2O)_3]*H_2O$, the crystal structure was determined by X-ray diffraction. It is to be noted that it differs from the one described in [1], where the same (according to the XRD data and analytical methods) compound $[Tb_2(TDA)_2(H_2O)_5]*3H_2O$ is attributed to the compound. In the structure there are 4 nonequivalent Tb^{3+} cations, and the amount of coordinated water molecules is different. Replacing the solvent(water) in the solvothermal synthesis with a mixture of H_2O-DMF in a ratio of 1: 1 leads to the formation of completely new complexes with the MOF structure. Their composition corresponds to the formula $(NMe_2H_2)[Eu_xTb_{1-x}(TDA)(HCOO)]$. The dimethylammonium cation, as well as the formate anion, is formed during the hydrolysis of the solvent. The cation is located in a part of the pores of the framework structure, and the formate anion, along with the triazoledicarboxylic anion, creates this framework. Compounds have high thermal stability: the decomposition temperature exceeds 350°C. In addition, they are completely insoluble in organic media, including boiling xylene, acetonitrile, DMSO and DMF. Moreover, all compounds are characterized by intense luminescence of central REE ions. For both A and B, studies of the luminescent properties of the obtained complexes were carried out. In both cases, the luminescence spectra contain bands corresponding to the emission of Eu^{3+} and Tb^{3+} ions. The excitation spectra contain bands that are characteristic of both luminescence excitation directly through the REE ion and through ligand molecules, which allows us to expect the presence of excitation transfer in the complexes according to the TDA->Tb->Eu scheme. This assumption was confirmed after studying the kinetic parameters of the radiation of the complexes. Then a complex of composition $[Tb_{0.9}Eu_{0.1}(TDA)]$ was synthesized, in which the ratio of the luminescence intensities from the strongest transitions of terbium and europium is close to 1, which can be used as a sensory response to H_2O molecules.

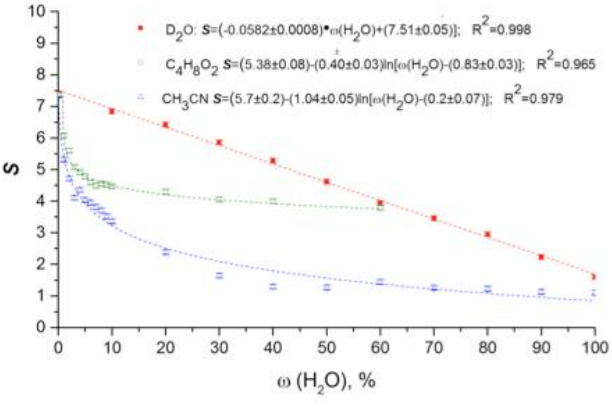

Figure 1. Calibration plots for determination of H_2O impurities in D_2O(red), dioxane(green) and CH_3CN(blue).

The occurrence of the sensory response is associated with different quenching efficiency of the luminescence of terbium and europium ions through O–H vibrations of water molecules. The sensory response was determined with respect to H_2O impurities in D_2O, CH_3CN and dioxane. It was shown that the complex of this composition can be effectively used as a sensor for the H_2O impurity in these media(Figure. 1).

Effect of synthesis conditions on the formation of the structure of the holmium-manganese complex with a tert-butylthiacalix[4]arene

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In recent years, polynuclear coordination compounds containing high-spin atoms of transition elements have been the subject of close attention of specialists in various fields. The interest is caused by the possibility of their use as molecular magnets. These substances, when placed in an external magnetic field, are magnetized and retain their magnetization after the field is turned off. Heteropolynuclear clusters are considered the most promising: due to the use in coordination polymers of various metal ions having unequal values of the total spin, it is possible to obtain a ferromagnetic system, which is characterized by all the necessary magnetic properties. During the synthesis of such a molecular magnet based on manganese and holmium salts with tert-butylthiacalix[4]arene, it was found that the formation of the structure of the complexes is influenced by the conditions of the synthesis, resulting in a change in the spatial arrangement of metal ions in the cluster site. X-ray diffraction analysis showed that both complexes are quad-core, crystallizing in the triclinic crystal system (sp. gr. P-1), the molecules of the complexes have a sandwich-like structure, in which between the anti-parallel tBuTCA ligands is a flat quadrilateral fragment with metal ions at the vertices and a bridge oxygen atom (μ_4-O) in the center (Figure 1). The complex, synthesized under normal conditions, has the same ions in the adjacent vertices of the site and a lower lattice density (1.257 Å^3). If the complex is synthesized in a microwave reactor (low-power microwave radiation, heating up to 145 °C, a closed volume and, as a result, slightly increased pressure), the metal ions in the coordination node are located at opposite peaks, and the density of the crystal lattice increases (1.901 Å^3).

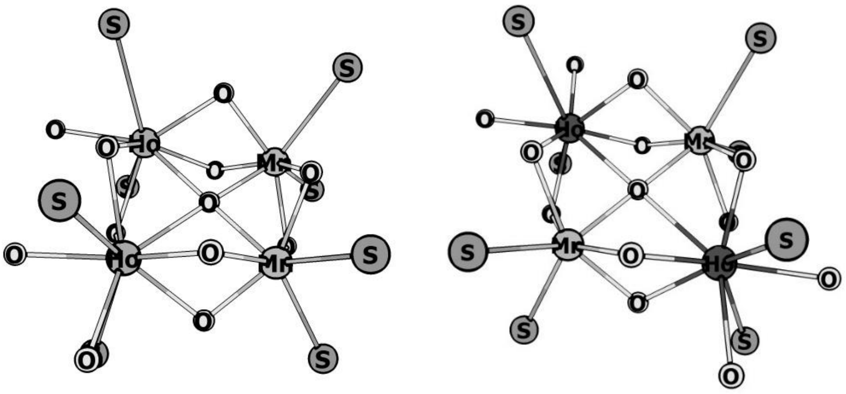

Figure 1. Node holmium-manganese complex, synthesized under normal conditions (left) and in a microwave reactor (right)

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Reactivity of ruthenium(II)-cymene complexes towards proteins

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Organometallic complexes have been the subject of various research studies, particularly with the respect to their potential medicinal application.[1] The half-sandwich ruthenium complexes are among the most promising efficient antitumour agents[2]. Within this frame, cymene-ruthenium complexes have been among the most investigated compounds, joining different research aspects, from syntheses, over biological activity towards versatile interaction with different biomolecules.[3] In a continuated research interest in this topic, over 40 of such compounds were prepared in our laboratory. Four of them, all containing ruthenium-cymene scaffold, but differing in the structure of chelating ligand and a number of coordinated chlorides, were chosen to be subject of the investigation of interactions with two proteins, horse heart cytochrome (Cyt) and hen egg white lysozyme (Ly) in carbonate buffer by ESI-MS, UV–Vis absorption and circular dichroism spectroscopy. The detailed analyses of their speciation as well as analyses of adducts were performed. Dehalogenated complexes are most likely species initially coordinating the proteins for all tested complexes and consequently the complexes with two chloride ligands were more reactive toward proteins than those with only one, and the complex with *S*,*N*-chelating ligand was less reactive than one with *O*,*N*-chelating ligand. In general, protein reactivity toward Ru(II) complexes is determined by protein structure and ligands in Ru(II) coordination sphere, but this reactivity should be described from both kinetics, as well as from stability aspect. In the cells there are many strong metal binding ligands present in mM concentrations, including carbonate ions. Their ability for exchange, e.g. to bind and to leave, determinate the extent, as well as mechanism of the binding of ruthenium complexes to the target biomacromolecules for cancer therapy, i.e. DNA and proteins.

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Synthesis and structure of ammonium peroxotellurates and application for nanomaterials preparation

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Ammonium peroxotellurates $(NH_4)_4Te_2(\mu\text{-}OO)_2(\mu\text{-}O)O_4(OH)_2$ (**1**) and $(NH_4)_5Te_2(\mu\text{-}OO)_2(\mu\text{-}O)O_5(OH)\cdot 1.28H_2O\cdot 0.72H_2O_2$ (**2**) were isolated from 5% hydrogen peroxide aqueous solutions of ammonium tellurate and characterized by single crystal and powder X-ray diffraction studies and by Raman spectroscopy and thermal analysis. Peroxotellurate anions in **1** and **2** contain a binuclear $Te_2(\mu\text{-}OO)_2(\mu\text{-}O)$ fragment with one μ-oxo- and two μ-peroxo bridging groups.[1]

Ammonium peroxotellurates solutions were used as precursors to obtain high-charge-capacity sodium- and lithium-ion battery anodes based on tin(II) and antimony(III) tellurides and graphene oxide composites. Graphene oxide/SnTe (Sb_2Te_3) electrodes exhibit exceptionally high reversible volumetric charge capacities above 3000 (2100) and 1300 (1651) mAh cm^{-3} at 100 mA g^{-1} charging rate for lithium- and sodium-ion batteries, respectively. [2,3]

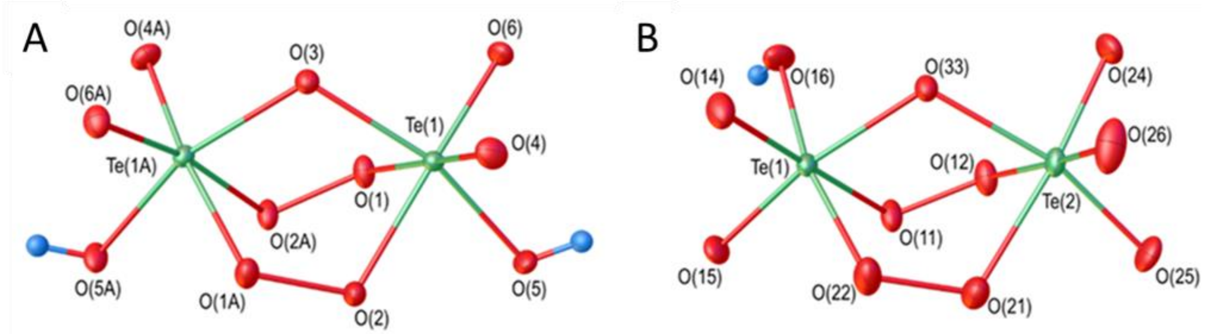

Figure 1. A) Binuclear anions $[Te_2O_{11}H_2]^{4-}$ in structure 1 and B) $[Te_2O_{11}H]^{5-}$ in structure 2

Acknowledgements

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Synthesis of novel carborane clusters of Ru(II) and its application in ATRP polymerization

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Ruthenium carborane clusters have found application as effective catalysis of Atom Transfer Radical Polymerization of vinyl monomers. This process is based on reversible halogen transfer from carbon to ruthenium atom and is as accompanied by Ru(II) – Ru(III) oxidation process []. The development of new types of catalysts is governed by the necessity of increase of the polymerization rate and the decrease catalyst load making this process more convenient for practical application.

In this work a series of *closo*-carborane clusters of ruthenim (II) with bi- and tridentate ligands were synthesized from the known from 5,6,10-{$Cl(Ph_3P)_2Ru$}-[5,6,10-(μ-H)$_3$-10-H-7,8-H-*exo-nido*-7,8-$C_2B_9H_8$] or its *closo*-isomer via ligand exhange reactions. The obtained clusters were characterized by means of NMR, MALDI MS and X-ray analysis confirmed its structures.

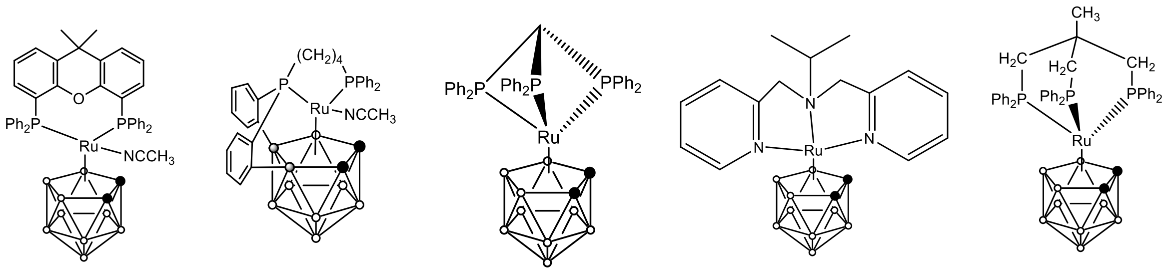

Figure 1. Structures of the obtained Ru(II) complexes

The performed electrochemical studies show that the synthesized Ru(II) clusters are capable to undergo reversible oxidation to Ru(III) being the prerequisite of its successful application in polymerization catalysis.

It was shown that complexes of Ru(II) bearing diphosphine ligands easily release auxiliary nitrile ligand and generate active 16-electron species being a real catalysts of polymerization process. The polymerization of methacrylate monomers conducted in the presence of such complexes proceeds with higher rate relative to the previously used Ru(III) species and results in formation of the polymers with low molecular weight distribution.

The catalytic activity of complexes with tridentate ligands is noticeably depends on the ligand structure and the steric constraints in the formed 18-electron clusters. The use of tris(diphenylphosphino)methane as a ligand results in formation of complex containing one labile arm capable for dissociation with further abstraction of chlorine atom and formation of radicals initiating polymerization process. The use of the less rigid triphosphine or triamine ligands results in very stable Ru(II) species incapable for participation in catalytic cycles inspite of the reversible Ru(II)-Ru(III) oxidation.

Acknowledgements

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Reversible Activation of NH, OH and CC Bonds by a Palladium(0) Complex

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The activation of water by oxidative addition is a key step in the catalytic splitting of water into hydrogen and oxygen.[1] Despite the prominence of palladium in cross-coupling catalysis, the intermolecular oxidative addition of water or amines to late transition metals is rare.[2]

We have recently reported the synthesis of a terminal palladium(II) imide complex from a palladium(0) precursor featuring a cyclic (alkyl)(amino) carbene ligand (CAAC).[3] Remarkably, this precursor is the first example of a heteroleptic, linear coordinated palladium(0) complex with a weakly bound *N*-donor ligand. This complex serves thus as a model for the elusive palladium(0) intermediate of the PEPPSI^{TM} precatalyst familiy.[4]

Herein, we report the oxidative addition of water, aniline and alcohols to this palladium(0) complex. All oxidative addition reactions proceed swiftly at room temperature and involve a hydride migration onto the carbene ligand. Furthermore, we report the reactivity with CC bonds. The mechanism will be discussed in detail based on reaction kinetics, isotopic labeling, DFT, isolated intermediates, solvent effects, and reactivity studies.

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Palladium N,C-metallacycles from *N*-substituted pyrazoles and pyrazolones

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N,C-metallocyclic compounds are attracting interest in the scientific community owing to their role in C-H activation chemistry. Palladium is a highly reactive metal in this approach and often used as catalysts for C-H functionalization reactions.[1]

Presented results describe the formation N,C-palladacycles from palladium(II) acetate and N-substituted pyrazoles and pyrazolones (Figure 1). Selected pyrazole derivatives are used as an efficient directing group in palladium-catalyzed C-H bond functionalization.[2]

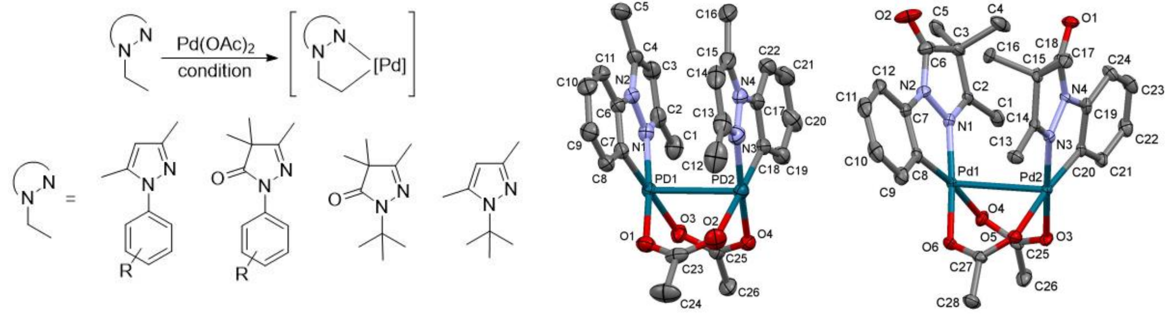

Figure 1. Scheme of preparation N,C-palladacycles and examples X-ray structures of them

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Field-induced single-ion magnet based on cobalt(ii) tiodiacetic complex

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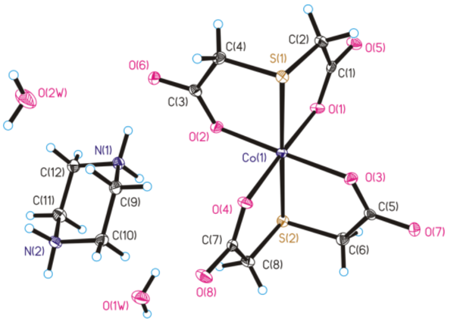
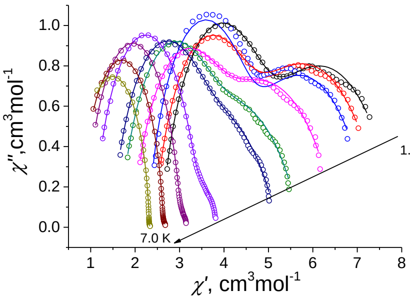
Wide interest in molecular magnetic materials was stimulated by promising revolutionary technological advances in the field of quantum computing, spintronics, ultra-high density memory storage devices and other applications.[1,2] Single molecule magnets (SMMs) and single ion magnets (SIMs) based on 3d-metals[3] are of great interest within coordination chemistry community, since they give to chemist flexibility to influence on local electronic structure and local magnetic anisotropy of metal ion by variation of ligand fields and symmetry of coordination polyhedra. Among such systems cobalt(II) complexes are especially promising as SIMs due to the strong spin–orbit coupling of the metal ion that can, in combination with ligand field effects, lead to high magnetic anisotropy.



Structure of complex **I**



Cole−Cole plot of complex **I** under 0.25T DC field.

This work presents the synthesis, structure and magnetic properties of a new mononuclear high-spin ($S = 3/2$) anionic Co (II) complex $(PipH_2)^{2+}[Co^{II}(TDA)_2]\cdot 2H_2O$ (**I**) (Pip = piperazine, H_2TDA = thiodiacetic acid) exhibiting slow magnetic relaxation in an applied magnetic field. Large ZFS parameter $D = +52.3$ cm^{-1}, obtained from fitting of experimental DC magnetic properties is rather close to calculated at CASSCF/NEVPT2 level value $+54.8$ cm^{-1}. It is interesting to note that this complex is the first example of SIM based on a high-spin hexacoordated cobalt(II) complex with donor sulfur atoms.

Acknowledgements

This work has been supported by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 14.W03.31.0001)

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Novel Pincer Pd(II) Borohydrides: Synthesis, Structural Properties and Reactivity

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Palladium catalysis is crucial in a state-of-art organic and organometallic chemistry. However, the data about palladium(II) tetrahydroborate complexes are very scarce. Herein we present synthesis, structural properties and reactivity of new palladium tetrahydroborate complexes with PCP and $^{\mathrm{CpRu}}$PCP ligands (Figure 1).

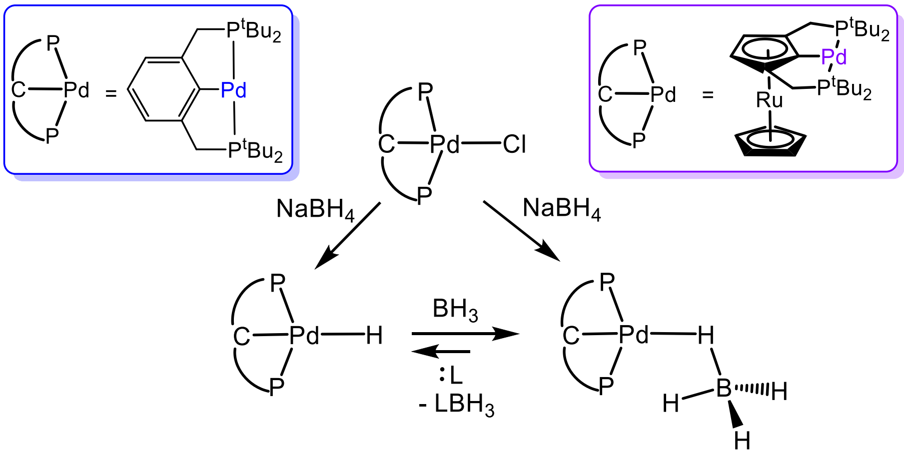

Figure 1. General scheme of formation of pincer (pincer)PdX complexes

Formation of palladium(II) tetrahydroborate complexes upon the reaction of starting palladium chlorides (pincer)PdCl with $NaBH_4$ was evidenced by FTIR, multinuclear NMR and X-Ray diffraction experiments. The thermodynamic stability of Pd(II) borohydrides toward BH_3 elimination yielding the corresponding hydrides was explored by theoretical calculations and multinuclear NMR measurements. The alcoholysis of Pd(II) tetrahydroborate ($^{\mathrm{CpRu}}$PCP)Pd(BH_4) ($^{\mathrm{CpRu}}$PCP = κ^3-[{2,5-(^{t}Bu$_2$PCH$_2$)$_2$C$_5$H$_2$}Ru(C$_5$H$_5$)]) is shown to yield the dinuclear cationic Pd(II) tetrahydroborate with bridging BH_4^- ligand [(LPd)$_2$(μ,η^{1,2}:η^{1,2}-BH$_4$)]$^+$. The bifurcate dihydrogen-bonded complexes were found to be the active intermediates of the first proton transfer in this step-wise alcoholysis yielding eventually [{($^{\mathrm{CpRu}}$PCP)Pd}$_2$(μ,η^{1,2}:η^{1,2}-BH$_4$)]$^+$. According to the X-ray and DFT/M06 geometry analysis, BH_4^- ligand in both mono- and dinuclear palladium tetrahydroborates has mixed coordination mode η^{1,2}. ($^{\mathrm{CpRu}}$PCP)PdH can be assessed in the reaction with excess organic bases (THF, Py). It turned out being very is reactive and rapidly activates CO_2 (ca. 15 min) yielding formiate complex ($^{\mathrm{CpRu}}$PCP)Pd$^{\mathrm{II}}$(η^1-OC(O)H). Hydrolysis of ($^{\mathrm{CpRu}}$PCP)PdH with the subsequent CO_2 insertion yields hydrocarbonate complex ($^{\mathrm{CpRu}}$PCP)Pd$^{\mathrm{II}}$(η^1-OC(O)OH).

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (RFBR; projects № 17-03-01128 and 19-03-00524) and the “RUDN University Program 5-100”

Study of Oxidation of Aluminum Powder Coated by Perfluoropolymer

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Oxidation process of spherical aluminum powder (ASD-1) encapsulated in perfluoropolymer (PFP) was investigated using thermal gravimetric – differential thermal analysis (TGA-DTA). There were following reasons for the choice of this powder. Earlier using TGA-DTA analysis it was shown that oxidation effectiveness of aluminum powder under high temperature increase with reduction in particles size[1]. Therefore aluminum powder with relative small specific surface 0,138 $м^2$/g, which had sufficient oxidative resistancece (ASD-1). Purity of the powder was 99.8 mass %. For exploration of oxidation process "Derivatograph" of F. Paulic system was applied. Measuring was carried out in the temperature range from 20 up to 1000°C with rate of heating 10 °C/min in the air. For comparison untreated ASD-1 was analyzed too. For powder encapsulation solution of the PFP (fluorine content 74.8 mass %) in the fluoroorganic solvent was used. One sample of aluminum powder was encapsulated in PFP by use solution contained fluorosurfactant (ammonium salt of perfluorocarbon acid). We expected that addition of fluorusurfactant (FS) would help to get more uniform coating on particles. Results of the TGA-DTA investigation are in the table.

Table 1

Influence PFP and FS content on powder particles on TGA-DTA characteristics

PFP content %	FS content , %	Relative mass loss in range 400-465°C	Temperature of the beginning of relative mass growth (exoeffect), °C	Relative mass growth in range 600-1000°C, %
0	-	0	680	+7.4
5	-	-0.8	675	+9.2
8	-	-4.3	675	+11.4
8	0.05	-6.2	670	+17.4

Table data indicate that mass of untreated ASD-1 doesn't change up to 680 °C. Encapsulated powder samples have temperatures of the beginning of mass loss in the range 670-675 °C. In a case of encapsulated aluminum powder one can see that mass loss take place in range 400-465°C. It is connected with PFP destruction. Maximal mass loss (-6.2 %) takes place for sample containing 8 % PFP и 0.05 %. Explanation of this fact is following: addition of FS lead (probably) to obtaining of more friable (porous) coating. As result hot air, easily pass through coating to aluminum surface. In this case heating of aluminum, PFP and its destruction progress more rapidly. Only this sample has maximal mass growth in comparison with untreated sample (+ 17.4 vs. + 7.4). Obtaining results give possibility assert that oxidation of encapsulated samples of aluminum powder occur more intensive than one for untreated sample.

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Phosphorescence in complexes of Eu(II)

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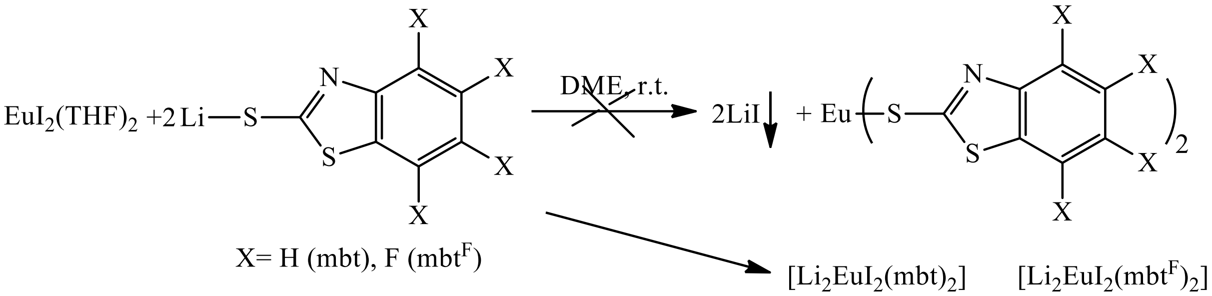
Luminophores which emit from a triplet state (phosphorescence) are in demand for some applications like organic light emitting diodes (OLEDs) for example. The most efficient triplet luminophores known to date are noble metal complexes with some organic ligands. In present work we describe the first example of phosphorescence that was achieved in derivatives of divalent europium at room temperature.

The reactions of europium diiodide with lithium salts of 2-mercaptobenzothiazole or its perfluorinated analogue in the 1,2-dimetoxyethane media do not lead to precipitation of LiI from solutions as expected. But the reactions result in a formation of highly phosphorescent complexes **1** or **2** (Figure 1).



1 **2**

Figure 1. Scheme of formation of phosphorescent complexes 1 and 2

The photoluminescence (PL) of the complexes was studied at room and nitrogen temperatures in the solutions and in the solid state. It was shown that the PL spectra of **1** and **2** at room temerature are close to those of the thiolate salts Ln(mbt$^{(F)}$)$_3$ of La and Gd at nitrogen temperature (Figure 2). The possible reasons of such efficient phosphorescence are discussed.

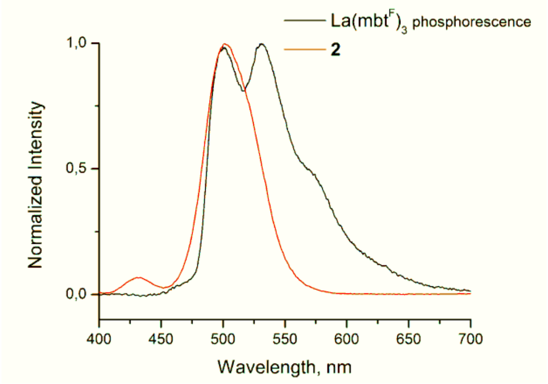


Figure 2. PL spectra of La(mbt^F)$_3$ and 2 in solid state

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Complexes of lanthanide arylphosphates: synthesis, structure and luminescent studies

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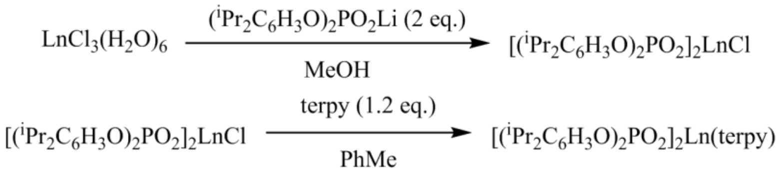
Lanthanide coordination compounds are well known for their luminescent properties[1]. In particular, they are proposed as new materials for high-efficient OLEDs[2].

Novel complexes of bis(2,6-diisopropylphenyl)phosphates of neodymium, europium, gadolinium and terbium with α,α'-terpyridine were synthesized according to the scheme below:



$$LnCl_3(H_2O)_6 \xrightarrow[\text{MeOH}]{(^iPr_2C_6H_3O)_2PO_2Li\ (2\ eq.)} [(^iPr_2C_6H_3O)_2PO_2]_2LnCl$$

$$[(^iPr_2C_6H_3O)_2PO_2]_2LnCl \xrightarrow[\text{PhMe}]{\text{terpy (1.2 eq.)}} [(^iPr_2C_6H_3O)_2PO_2]_2Ln(terpy)$$

All but neodymium complex were obtained as bis-phosphate chlorides, when neodymium complex was obtained as a tris-phosphate complex. Structures of all complexes were resolved by X-ray diffraction method (Figure 1). Luminescent study of terbium and europium complexes showed high quantum yields.

Obtained complexes are relatively air-stable. Synthesis, structure and photophysical properties of Nd, Eu Gd and Tb complexes with diarylphosphate ligands will be discussed in a poster.

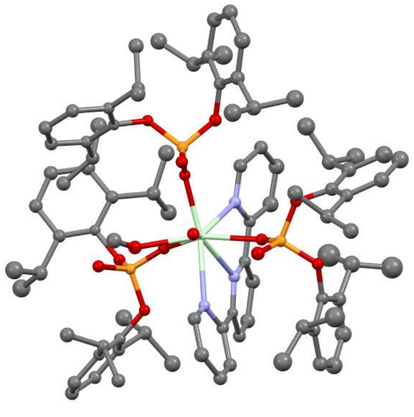


Figure 1. Structure of $[(^iPr_2C_6H_3O)_2PO_2]_3Nd(terpy)(MeOH)(H_2O)$

Acknowledgements

We thank the Russian Science Foundation for financial support (grant No. 17-13-01357).

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Polynuclear aminohydroximate Cu(II)-Ln(III) complexes as the single-source precursors for low-temperature growth of nanostructured cerium and copper oxides

Marina A. Katkova,[a] Kirill V. Kremlev,[a] Galina S. Zabrodina,[a] Roman V. Rumyantcev,[a] Sergey Yu. Ketkov,[a] Irina G. Fomina,[b] Igor L. Eremenko[b]

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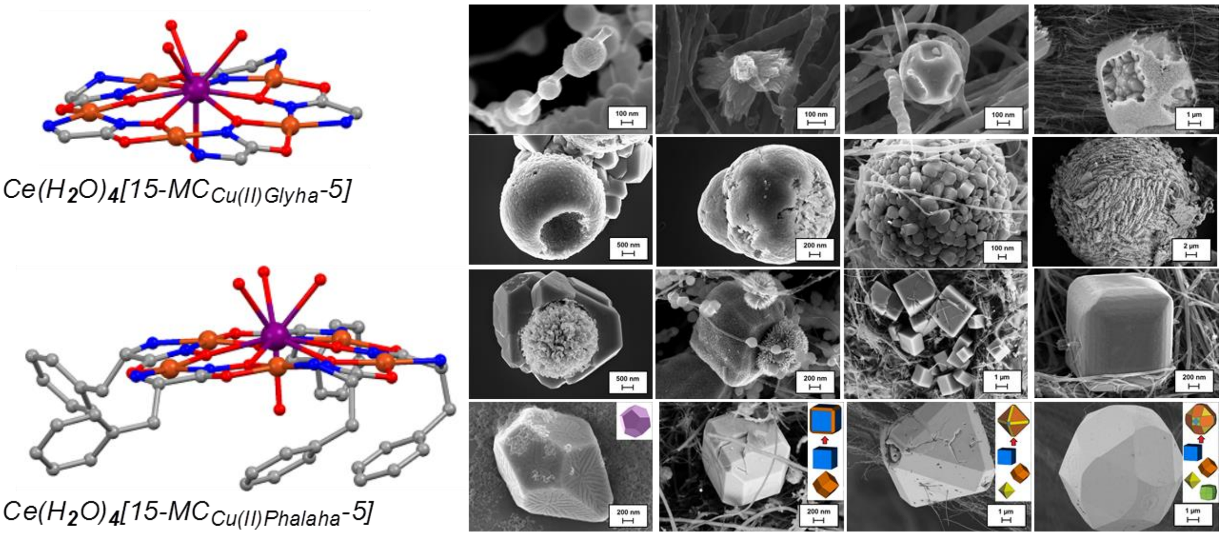
Water-soluble Cu(II)-Ce(III) aqua-complexes bearing aminohydroximate (glycine- and α-phenylalanine) ligands have been synthesized and tested for preparing the target copper and cerium oxides under hydrothermal conditions.[1] These polynuclear heterometallic metallamacrocyclic complexes represent the unique single-source precursors for a facile one-pot, surfactant- and template-free synthesis of nano- and mesocrystals with the intrinsic features of rough surfaces, high porosity, single-crystalline structures and complex morphology. The structures, morphologies and compositions of as-prepared samples have been characterized by means of powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive spectroscopy (EDS). Our results suggest a very simple chemical route to guide the formation of beautiful self-assembled nanostructures (Figure 1).



$Ce(H_2O)_4[15\text{-}MC_{Cu(II)Glyha}\text{-}5]$

$Ce(H_2O)_4[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]$

Figure 1. Molecular structures of glycinehydroximate and phenylalaninehydroximate Cu(II)-Ce(III) complexes (left) and SEM images of cerium and copper oxide nanostructures grown hydrothermally from these complexes as single-source precursors (right)

Acknowledgements

This work was supported by the Russian Science Foundation (projects № 18-13-00356).

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pH-Responsive switching behavior of water-soluble metallamacrocyclic phenylalaninehydroximate La(III)-Cu(II) complex: insight into tuning protonation ligand states

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In recent years increased attention has been paid to polynuclear metallamacrocyclic complexes, named as metallacrowns, not only for their esthetic aspect but also for their intriguing functions.[1,2] With an idea to explore the unique structure of the lanthanide 15-MC-5 complexes, the water-soluble La(III)-Cu(II) complex based on α-phenylalaninehydroximate ligands $La(H_2O)_4[15MC_{CuPhalaha}\text{-}5](Cl)_3$ has been synthesized and characterized structurally and spectroscopically. The X-ray structure demonstrated that the ring copper ions are placed in distorted square pyramidal geometries with different axial coordination ligands. UV-vis absorption spectra display the halochromic behavior of complex, which represents reversible color changes from blue to colorless in the aqueous solution in response to pH variations. This effect has been described as pH-induced "on-off-on" switch through protonation and deprotonation of the phenylalaninehydroximate ligands in this metallamacrocyclic complex. To confirm the mechanism of the observed halochromism, a computation analysis was accomplished on the fragments of model $La(H_2O)_4[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]^{3+}$ by density functional theory (DFT) calculations at the τ-HCTHhyb/x2c-TZVPall level.

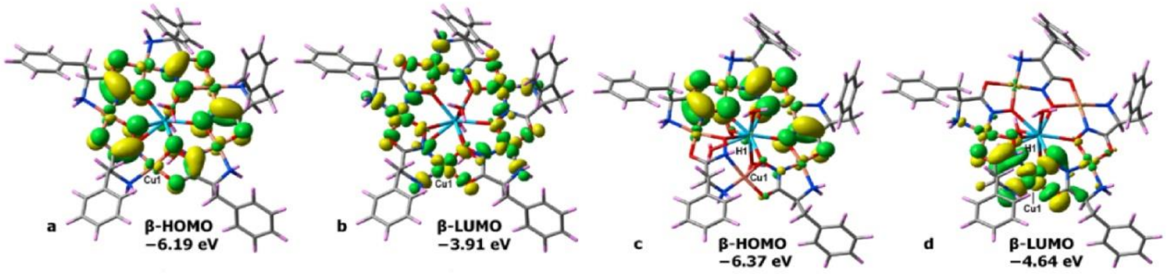

Figure 1. Frontier molecular orbitals obtained for optimized geometries of the cationic form $La(H_2O)_4[15MC_{CuPhalaha}\text{-}5]^{3+}$ **(a, b)** and protonated species $La(H_2O)_4[15MC_{CuPhalaha(H)}\text{-}5]^{4+}$ **(c, d)**

Acknowledgements

This work was supported by the Russian Science Foundation (project 18-13-00356).

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Diversity of single ion magnets in the solid state apatite matrix

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Single ion magnets typically represent linear or at least highly anisotropic complexes of d- or f-elements with more or less volumetric organic ligands. We suggest to use a purely inorganic compound with apatite structure as a matrix for d- or f-elements highly anisotropic ions with SIM properties. So compounds with composition $Ca_5(PO_4)_3[(CoO_2)_x(OH)_{1-2x}]$ or $Ca_{5-x}Dy_x(PO_4)_3[O_x(OH)_{1-x}]$ could be synthesized. In the first compound cobalt is characterized by very low coordination number 2 and bent geometry that causes a substantial orbital moment as well as a significant negative value of zero field splitting parameter *D* and therefore demonstrates SIM properties with remagnetization energy barrier U_{eff} about 63 cm^{-1}. In the second compound calcium cations are partially substituted by dysprosium. Coordination number of Dy is 7 but with one substantially shorter Dy-O contact so forming linear DyO^+ ion. Such ion is also characterized by a slow magnetic relaxation with U_{eff} about 790 cm^{-1}.

Except the thermal and chemical stability the apatite matrix allows us to influence on the nearest environment and crystal field parameters of magnetic ions and consequently tune the magnetic properties. So calcium replacement by strontium in the apatite composition leads[1] to increasing the remagnetization barrier of Dy containing SIM to 1040 cm^{-1}. Analogically calcium replacement by barium raised U_{eff} of cobalt containing samples[2] about six times to 387 cm^{-1}.

Another opportunity provided by an apatite matrix is possibility to change the concentration of magnetic centers so influencing on the distance between them that could be important for example for quantum tunneling suppression. It is also possible to influence on the nearest environment of magnetic ions that could change the crystal field and so the magnetic properties.

Acknowledgements

The work was supported by Russian Science Foundation, research grant №16-13-10031.

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DFT modelling of mechanisms for reactions of organogermanium and organoarsenic compounds bearing N-heterocycles with unsaturated substrates

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Heterocyclic germylene (*i*-Pr)$_2$NB(NDmp)$_2$Ge **(1)** **(D**mp = 2,6-Me$_2$C$_6$H$_3$) has been recently demonstrated to react with various alkynes under a controlled formation of respective 1,2-digermacyclobut-3-enes.[1] In this work its diverse reactivity with RN$_3$, RNCS and RNCO (R = t-Bu or Ad) is analyzed on the basis of DFT calculations at the M062X/DGDZVP level of theory. The reactions give a series of germanium heterocyclic compounds including a remarkable ring expansion caused by an insertion of the RNCO molecule (Scheme 1). The different behavior of the unsaturated molecules as well as the increased stability of the novel six-membered ring **2** is explained on the basis of orbital and electron density analyses leading to the plausible reaction mechanisms.

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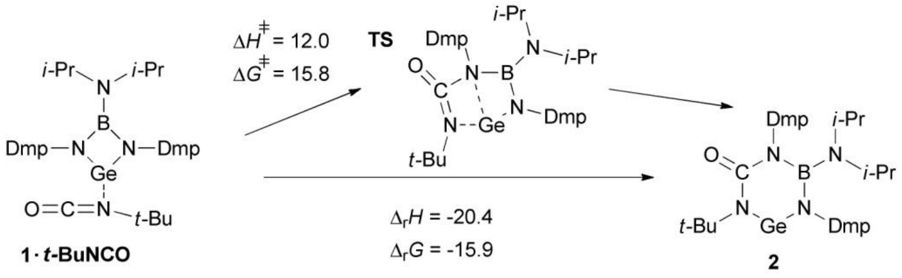
The organoarsenic compounds studied are represented by 1*H*-2,1-benzazaarsole (**3**) that showed a dienophile like behaviour in the reaction with alkynes RCCR (R = CO$_2$Me, C$_5$F$_4$N) thus forming 1-arsa-1,4-dihydro-iminonaphthalenes. Quite surprisingly, these products underwent facile C*H*->N*H* proton migration leading to stable substituted 1-arsanaphthalenes. The reaction mechanism and intermediate structures were elucidated by our theoretical studies.



Scheme 1. Calculated mechanism and parameters of the **1** -> **2** reaction.

Acknowledgements

This work was supported by the RFBR (projects № 18-33-01252 (germylenes) and19-03-00755 (organoarsenic compounds).

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Local structure approaches to stabilize complex intermetallics

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In the chemistry of intermetallics, due to complex nature of chemical bonding, the composition-structure dependence generally does not obey the usual notions about the valence and oxidation states of elements, hence the prediction tools for these compounds are limited to empirical and semi-empirical rules. The rules are based on two opposite approaches. The rules of the first group use as a criterion the total number of valence electrons per formula unit or atom of a certain type. The rules of the second group are based on the geometric criteria for the maximum filling of space with atoms. These rules, owing to heavy contribution of delocalized bonding, are dealing with the crystal structure on a large scale, averaging it and ignoring the difference in the electronic structure of elements of the same block.

However, not all intermetallics obey this generalized interpretation, and some complex crystal structures require different elements of the same block to at least preferentially occupy different sites in the crystal structure. In the present work, we have studied two groups of compounds with a nearly equal *d*- to *p*-element ratio T_6E_5 (T = Cr, Fe; E = Ga, Ge) and $Fe_{32+\delta}Ge_{35-x}E_x$ (E = Si, P, As), in which the structural stability is controlled by local electronic and size factors. The formation of compounds of the first group, T_6E_5, is governed primarily by electronic factors, specifically by the stability of the $(E)_n$ ($n = 2$-∞) chain fragments of connected *p*-element atoms. The $Fe_{32+\delta}Ge_{35-x}E_x$ family of compounds, on the other hand, is a showcase of importance of the geometric factors. The $Fe_{32+\delta}Ge_{35-x}E_x$ compounds are formed as a result of distortion of the $MgFe_6Ge_6$-type block in order to match the dimensions of the Co_2Al_5-type block, which distortion is promoted by the replacement of Ge atoms by another *p*-element at one specific site for each compound.

Acknowledgements

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The study of reaction products of eutectic Zr-Si melt with carbon fiber reinforced carbon precursors

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The ceramic matrix composites (CMC) are found themselves today in many different areas of applications in commercial sectors. The reactive melt infiltration (RMI) technics of CMC manufacturing are adventurous over the traditional ceramic processing methods due to low shrinkage and near-zero porosity of the final composites. The CMC manufacturing by reactive silicon melt infiltration of carbon fiber reinforced carbon (CFRC) precursors has been rather well studied and presented in the literature. However, the using of ultra-high temperature ceramics such as ZrC can improve ablation and erosion resistance of “ordinary” SiC matrix of CMC and further improve high-temperature performance. In this regard the study of the carbon fiber protection and carbide formation process as well as the reaction products in the system carbon fiber reinforced carbon – zirconium - silicon is an urgent and important task for manufacturing of Zr-Si-C-matrix composites with high performance properties.

The carbon fibers before CFRC synthesis were protected from reactive melt by polymer impregnation and pyrolysis technics using preceramic compositions based on polycarbosilane, oligovynilsilazane and rolivsan. The carbon matrix of CFRC were synthesized form resol phenol-formaldehyde resin and ethylene glycol with the using the polymerization induced phase separation step to achieve the desired porosity and transport properties. To minimize the processing temperature of RMI the eutectic Zr-Si was chosen.

It was shown that in the case of unprotected carbon fibers the Zr-enriched phases are located preferable along the perimeter of carbon fiber filaments. It was proposed that the infiltration and reaction rate in the interphase of carbon fiber and carbon matrix are higher than through the carbon matrix. The protection of carbon fibers with Si-C-N based interfacial coating allows protecting the reinforcing carbon fibers from reactive melt and undesired carbide formation.

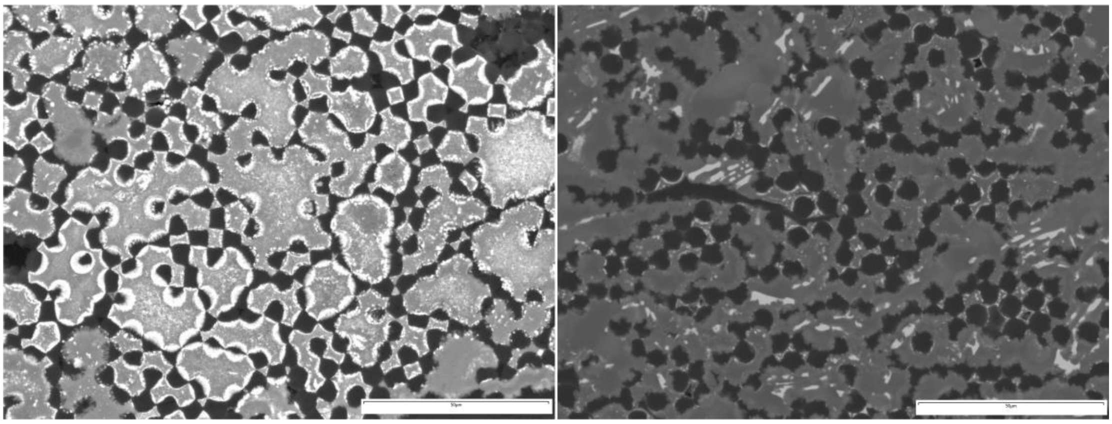

Figure 1. Microstructure of the reaction products of eutectic Zr-Si melt with CFRC based on unprotected carbon fibers (left) and protected by Si-C-N interfacial coating carbon fibers (right)

Acknowledgements

The reported study was funded by RFBR according to the research project № 17-03-01163.

The possible chemical engineering approach towards controlled carbide formation in the system carbon matrix – eutectic Zr-Si melt

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The ceramic matrix composites (CMC) are used nowadays as the structural materials in very extreme environments including high-temperatures, oxidative and corrosive media. One of processing method of the CMC with near-zero porosity is reactive melt infiltration (RMI), where the carbon matrix can be used as precursor for carbide-type CMC-matrix. The using of ultra-high temperature ceramics such as ZrC can improve ablation and erosion resistance of “ordinary” SiC matrix of CMC and further improve high-temperature performance. In this regard the controlled carbide formation in the system carbon – zirconium - silicon is an urgent and important task for processing Zr-Si-C-matrix composites by RMI method.

The phenol (cresol), formaldehyde and sodium hydroxide were used for resol resin synthesis. 4-Toluenesulfonyl chloride was used as catalyst of resol resin condensation. The final carbon matrixes were obtained after consecutive steps of polymerization induced phase separation (PIPS), post-curing and pyrolysis under the time-temperature regime derived from thermo-kinetic calculations.[1]

The synthesis conditions of carbon matrix with variable transport properties and chemical reactivity are regarded. The using of resol-type phenol/cresol-formaldehyde resin and pore forming agents (ethylene glycol) make it possible to synthesis the carbon matrix with variable porosity, transport properties and chemical reactivity. It was shown, that the PIPS conditions in the chosen system are the most important instruments to control the transport properties and porosity (Fig.1 left). The partial substitution of phenol by cresol in the step of resol resin synthesis makes it possible to vary the chemical reactivity of carbon matrix towards eutectic Zr-Si melt (Fig.1 right).

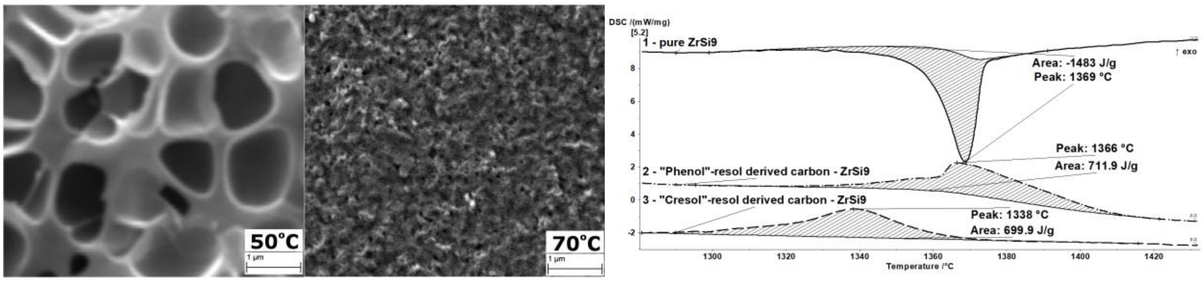

Figure 1. Microstructure of carbon matrix obtained at different temperatures of PIPS step **(left).** DSC curves of eutectic Zr-Si melt [1], exothermic effect of carbide formation of eutectic Zr-Si melt with “phenol”-resol derived carbon [2] and “cresol-phenol”-resol derived carbon [3] **(right)**

Acknowledgements

The reported study was funded by RFBR according to the research project № 17-03-01163

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Click-chemistry as a convenient way for bindig of metalloblocks: design principles for the construction of *multi-metallic* systems containing Ln(III)

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In recent years, the Cu(I)-catalyzed azide-alk~~i~~yne cycloaddition (CuAAC) has received considerable attention as a way of preparing substituted-1,2,3-triazoles for using in coordination chemistry. These molecules can act as N-donor ligands and posibility of generating polydentate triazole ligands is very attractive, in particular, they can be exploited to coordinate high coordination number ions such as lanthanides, which possess fascinating photophysical properties.[1]

As a sinton for the click reaction, a wide range of compounds may be used, among which there are both organic molecules and various inorganic compounds having an alkyne or azide fragment.[2,3] In this regard, it becomes possible to create organo-inorganic hybrids carrying additional coordination vacancies for the metal ion.

Herein, we report on the design and synthesis of bimetallic Ir(III)/Ln(III) complexes (Figure 1) and heterometallic hybrids based on polyoxometalate (POM) and Ln(III) complexes.

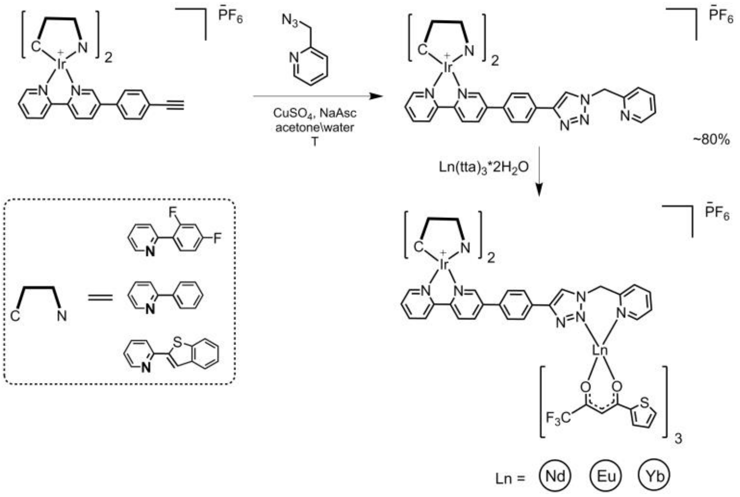

Figure 1. The design of the Ir(III)/Ln(III) dyads

Acknowledgements

The authors greatly appreciate financial support from the Russian Science Foundation, grant 16-13-10064. The work was carried out using equipment of St.Petersburg State University Research Park: Centers of Magnetic Resonance, Optical and Laser Materials Research, Chemical Analysis and Materials Research, for Physical Methods of Surface Investigation; and X-ray Diffraction Centre.

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Ru Complexes for C(sp3)-H Bond Activation

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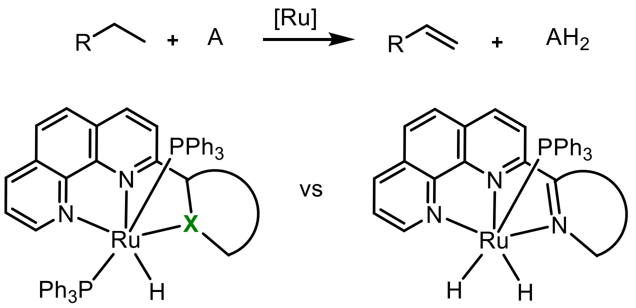
A great deal of interest to C-H bond activation and functionalization catalyzed by transition metal complexes led to the development of several efficient systems. However, some crucial queries still remain to be addressed in the area of sp^3 C–H bond activation. For the latter reactions mostly Ir, Rh and Pt complexes are extensively studied. Only few examples of sp^3 C-H activation by Ru and Os complexes were reported and mechanism of these catalytic processes are not well established. Herein, we report synthesis of various ruthenium hydride complexes bearing anionic and neutral ligands. Using these complexes detail mechanistic studies as well as theoritical calculations were carried out to understand the preferential catalytic pathway [Ru(II)/Ru(IV) vs Ru(0)/Ru(II) cycle] for the alkane dehydrogenation.



1. Ru(II)/Ru(IV) vs Ru(0)/Ru(II)
2. Mechanistic studies and Theoretical calculations

X = C and N anionic fragment

Figure 1. Transfer Dehydrogenation of Alkane

Acknowledgements

Some parts of this work were supported by DST-RFBR project No. 18-53-45026.

QTAIM and conceptual DFT study of derivatives of *closo*-borate anions with exo-polyhedral carbonile groups

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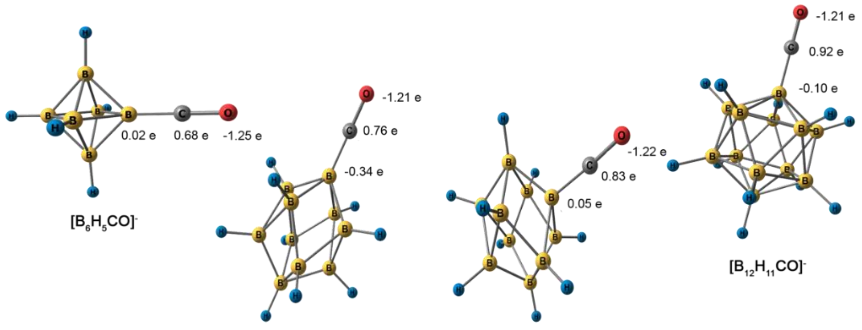
This study focused on the structure, bonding, and reactivity analysis of the derivatives of *closo*-borate anions $[B_nH_{n-1}CO]^–$ (n = 6, 10, 12) and $[B_nH_{n-1}COR]^–$ (n = 6, 10, 12, R=OH, OCH_3, NH_2, H, CH_3). DFT calculations at the ωB97X-D3/6-31++G(d,p) level of theory have been performed. The B–B, B–H, B–C and C–O bonding interactions have been theoretically studied under the perspective of the Quantum Theory of Atoms in Molecules (QTAIM) and several local and integral topological properties of the electron density involved in these interactions have been computed. We have discovered the good correlation between results of Wiberg bond order analysis and QTAIM analysis of B-C and C-O interactions. Also, different chemical reactivity descriptors have been calculated via conceptual density functional theory (DFT). The active sites suitable for nucleophilic attacks have been selected using the Fukui function indices based on the NBO and AIM atomic charges.

We have discovered the good correlation between results of Wiberg bond order analysis and QTAIM analysis of B–C and C–O interactions. Anion $[B_6H_5CO]^–$are characterized by the largest values of B–C bond order and *ρ(r), ∇²ρ(r),* H_b, and delocalization index*.* The values of main QTAIM characteristics of B–C interactions decreases with the increasing of boron cluster size. Anion $[B_{12}H_{11}CO]^–$ are characterized by the largest values of C–O bond order and *ρ(r), ∇²ρ(r),* H_b, and delocalization index*.* The value of main QTAIM characteristics of C–O interactions decreases with the increasing of boron clusters size.

Reactivity descriptors for model systems have been calculated via conceptual density functional theory (DFT). The active sites suitable for nucleophilic attacks have been selected using the Fukui function indices based on the NBO and AIM atomic charges. The most strong electrophile is $[B_{12}H_{11}CO]^–$, and the weakest one is $[B_6H_5CO]^–$. In all cases, the most electrophilic site of all mono-carbonyl derivatives of *closo*-borate anions is C-atom of carbonyl group.



$[B_6H_5CO]^-$

$[1\text{-}B_{10}H_9CO]^-$

$[2\text{-}B_{10}H_9CO]^-$

$[B_{12}H_{11}CO]^-$

Acknowledgements

This work was supported by the Russian Science Foundation (projects no. 18-73-00049).

An exact general form for Hohenberg-Kohn' functional

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Precision was given first[1] to the form of well-defined but commonly unknown Hohenberg-Kohn' energy functional E[ρ] of the electron density ρ for atoms, molecules and materials at equilibrium state, where proper energy functional representation for atoms was provided in terms of a solution of the Poisson equation for the quantum-statistical density and exploiting fermionic expression for energy. This recipe is given now for universal solution of the 1D Poisson equation which has not regular boundary condition. Accurate same energies for Elements are obtained, but in contrast to the boundary regularization the closed formula is figured out for atomic energy. This variety of representations completes the conclusion that energy is simply a homogeneous functional of a general form. Utilizing of Poisson equation with opportunity to get exact energy calculation instead of Schrodinger one, promises great prospects, as long as the former can be solved by highly efficient finite element methodology; computational complexity is defined by space volume of the system of interest rather than number of particles within. This is the basis for the development of substances and materials using the finite element method technology and fast Poisson solvers.

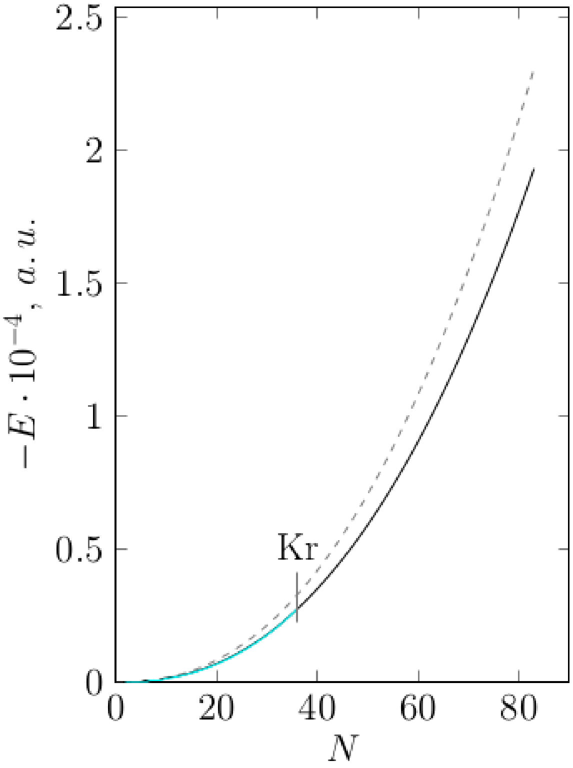

Figure 1. Energy for neutral atoms: black by $E = -0.6432\ Z^{7/3}$, cyan by CCSD(T), dashed by $E = -0.7687\ Z^{7/3}$ (Thomas-Fermi theory)

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Efficient hydroarylation of terminal alkynes with sodium tetraphenylborate performed in water

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Functionalization of alkynes via addition of aryl group, namely arylation of alkynes, presents a very attractive pathway to organic compounds such as arylalkenes.[1] These compounds are intermediates in the synthesis of biologically active species, pharmaceutical and agrochemical agents.[2] The medical properties of the stilbene derivatives, products of hydroarylation, have been extensively studied.[3]

Recently, we performed the highly selective and efficient hydroarylation of alkynes (**1**) (Fig.2) with sodium tetraphenylborate in the presence of a palladium(**II**) complex with imidazole ligands (Fig.1). Several reactions of various alkynes were carried out and in most cases two products were observed. The first one (**2**), arylalkene, was formed by addition of aryl group of tetraphenylborate to alkyne. The second product (**3**) was formed by two molecules of alkyne and one phenyl group originated from tetraphenylborate. Reactions were carried out under mild conditions in water.

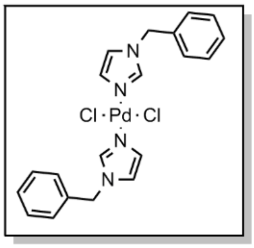

Figure 4. The imidazole complex

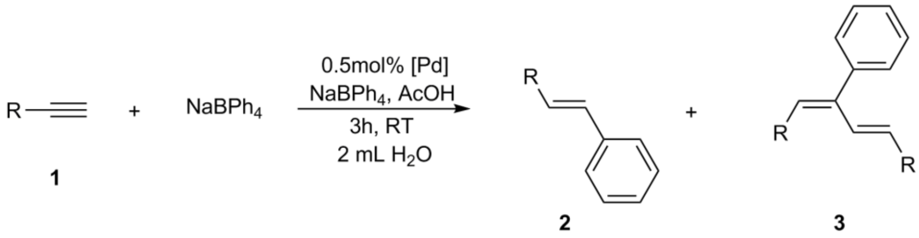

Figure 2. The reaction of hydroarylation of alkynes with sodium tetraphenylborate in the presence of palladium(**II**) catalyst

Very attractive results were obtained in reactions of alkynols with sodium tetraphenylborate in the same conditions. Alkynes with hydroxyl group formed only 2-type products with very high yields.

We proposed a plausible mechanism of the hydroarylation reaction, based on spectroscopic studies. Additionally, we evidenced that water is not only a solvent but also hydrogen source enabling formation of arylalkenes.

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Results of fundamental inorganic chemistry research in Russian Chemical Bulletin

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Russian Chemical Bulletin is the leading journal in chemistry, covering practically all areas of fundamental chemical research including General and Inorganic Chemistry, Physical Chemistry, Chemical Physics, Organic Chemistry, Organometallic and Coordination Chemistry, Chemistry of Natural Compounds, Bioorganic, and Medical Chemistry, Polymer Chemistry, Supramolecular Chemistry, Materials Chemistry. Papers on interdisciplinary topics are also accepted for publication.

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Antiferromagnetic inclusions in organic semiconductors $(DOEO)_4HgBr_4$•TCE

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The discovery of unusual properties of charge carriers in graphen significantly develops organic electronics modifying future promising materials. Series of the two-dimensional organic conductors is in hot list of modern researches. The DOEO molecule can be considered as simplest organic elements of the spintronics requiring simultaneous control over charge-carriers, anti-ferromagnetic clusters created and providing spin polarization of charge carriers in a thin layer. The antiferromagnetic-semiconductor interface is very important condition of antiferromagnetic spintronics. We found intriguing discrepancy between theoretical prediction of the magnetic properties of $(DOEO)_4HgBr_4$•TCE crystals and experimental data revealing antiferromagnetism. Direct antiferromagnetic interaction cannot occur in crystals with a lattice parameter much higher than the exchange radius. In organic semiconductors, structural defects and nanoclusters are the centers of holes localization. These clusters we observed in $(DOEO)_4HgBr_4$•TCE crystals by atomic force microscopy (AFM). Presence of the local antiferromagnetic "drops" provides direct exchange interaction between localized holes as well as RKKY indirect exchange interaction. Comprehensive study of the structural, magnetic, and electronic properties of heterostructures antiferromagnet-organic semiconductors heterostructures will be presented. The inclusions resolved by AFM had round shape and occupied 20-30% of the sample volume at room and low temperatures. The pan-cake shaped inclusions of 5-6 nm thickness were 90-150 nm in diameter. Coexistence of two magnetic centers (large antiferromagnetic inclusions, and separated paramagnetic centers capturing holes) was revealed at low and high temperatures in $(DOEO)_4HgBr_4$•TCE single crystals. Temperature correlation between magnetic moment M(T) and number of localized charge carriers extracted from conductivity N_{loc} (T) indicates contribution of the holes to magnetism of the compound. Field dependence of magnetization $M(H)$ is a superposition of Brillouin function (70 weight %) and a linear term (30 weight %). Localization of charge carriers leads to non monotonic temperature dependences of the electrical resistivity and magnetic moment. This non monotonic behavior results from the competition between the free charge carriers and AFM inclusions. Antiferromagnetic exchange interaction can be explained by strong electron-electron interactions. The structure of the sulfur S lines in the XPS spectra indicates the electrical conductivity of the crystals because of the transfer of holes between the short “tail-to-head” contacts of DOEO molecules containing sulfur atoms. The value of $(R_\perp – R_{||})/R_\perp$, where $R_{||}$ and $R_\perp$ are the electrical resistance along and across the conductive layers of the crystal, respectively, is usually used to characterize the anisotropy of the electrical conductivity. Using previously measured temperature dependences of the electrical resistance, we obtained the temperature dependences of $(R_\perp–R_{||})/R_\perp$, which are in good agreement with the temperature dependence of the ΔE shifts of the lines in XPS spectra. The shift of the lines in the XPS spectra, as well as the temperature variations of $(R_\perp–R_{||})/R_\perp$, indicate the localization of charge carriers in the process of changing the character of hole mobility from quasi-one-dimensional (at temperatures below 140 K) to quasi-two dimensional (at temperatures above 140 K).

Na- and Mg-codoped bismuth niobate pyrochlores: synthesis, structure, electrical properties

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Doped bismuth niobates with the pyrochlore structure are interesting due to the possibility of obtaining materials with a variety of properties (from dielectrics to mixed conductors). The $Bi_{1.5}MNb_{1.5}O_{7-\delta}$ (M – Mg, Zn) compounds attract attention as high-frequency ceramic capacitors.

In this work, Na- and Mg-codoped bismuth niobates $Bi_{1.5}Mg_{1-x}Na_xNb_{1.5}O_{7-\delta}$ (x = 0; 0.10; 0.25; 0.50) $Bi_{1.5}Mg_{0.65}Na_{0.25}Nb_{1.5}O_{7-\delta}$ and $Bi_{1.5}Mg_{0.5}Na_{0.4}Nb_{1.5}O_{7-\delta}$ were synthesized by the method of organic-inorganic precursors combustion. The phase composition and structure of compounds were studied by X-ray method on a SHIMADZU XRD-6000 diffractometer and by SEM on a TESCAN VEGA 3 SBU microscope (X-ACT (EDS) microanalyzer). It has been shown that $Bi_{1.5}Mg_{1-x}Na_xNb_{1.5}O_{7-\delta}$ (x = 0; 0.10; 0.25), $Bi_{1.5}Mg_{0.65}Na_{0.25}Nb_{1.5}O_{7-\delta}$ and $Bi_{1.5}Mg_{0.5}Na_{0.4}Nb_{1.5}O_{7-\delta}$ are single-phase and exhibit the pyrochlore-type structure (*Fd-3m*). Distribution of dopants over the pyrochlore sites was determined by fitting of X-ray diffraction pattern with Rietveld analysis. It has been established that the Na atoms are distributed in the Bi sites, and the Mg atoms – in the Nb sites predominantly. This fact is in good agreement with a theoretical first-principles prediction regarding the stability of pyrochlore models with a different distribution of Na and Mg atoms within cationic sites. Electrical properties of the samples were investigated by impedance spectroscopy (immittance analyzer E7-28) in the air, oxygen and "wet" atmospheres in the frequency range 25-10^6 Hz and in the temperature range 25-750 °C. The temperature dependence of the conductivity of the samples obeys the Arrhenius law with E_a of 0.3-0.5 eV ($T < 300$ °C) and of 1.2 eV ($400 \le T$ (°C) ≤ 750) in the air. Thus, the conductivity of the compounds is caused by different charge carriers. According to data of temperature programmed isotope exchange (TPIE) with $C^{18}O_2$ of the Cu- and Mg-codoped bismuth niobates the oxygen transport is activated up to 250 °C [1]. The conductivity of $Bi_{1.5}Mg_{0.5}Na_{0.4}Nb_{1.5}O_{7-\delta}$ is higher (240-360 °C) in the "wet" atmosphere that points to protonic conductivity. The permittivity (ε') of the obtained samples is comparable (x = 0.4, ε' = 143, tanδ = 0.002) with ε' for Li- and Mg-codoped bismuth niobates (x = 0.5, ε' = 142, tanδ = 0.002) at 1 MHz and 25 °C [2]. Thus, the Na- and Mg-codoped bismuth niobates with the pyrochlore structure are mixed conductors and can be used as high-frequency ceramic capacitors at room temperature.

Acknowledgements

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Novel heterometallic 3d-4f-complexes on a basis of 1,1´-cobaltoceniumdicarboxylic acid

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Heterometallic carboxylates containing one of the metal atoms as a part of stable organometallic ligand represent relatively poorly studied type of compounds. In recent years we have obtained and studied *3d-4f*-heterometallic complexes containing cymantrenecarboxylate $CymCO_2^-$ (Cym = $(\eta^5\text{-}C_5H_4)Mn(CO)_3$)[1,2] or ferrocenecarboxylate[2] $FcCO_2^-$ (Fc = $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe$) ligands.

Cobaltocenium ion $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+$ also belongs to stable organometallic compounds and the study of complexes of its carboxylate derivatives with lanthanides was also of interest. While $CymCO_2H$ in aqueous-organic media[1,3] and 1,1´-ferrocenedicarboxylic[4,5] acid form coordination polymers with Ln^{3+} ions, exchange reactions between Ln acetates and 1,1´-cobaltoceniumdicarboxylic acid in the form of its adduct with its hexafluorophosphate $[Co(\eta^5\text{-}C_5H_4CO_2)(\eta^5\text{-}C_5H_4CO_2H)]\cdot[Co(\eta^5\text{-}C_5H_4CO_2H)_2][PF_6]$ in $H_2O\text{-}CH_3CN$ media bring about the isostructural complexes built of the isolated ions $[Ln(H_2O)_8][Co(C_5H_4CO_2)_2]_2[PF_6]$ (Ln = Dy(**1**), Er(**2**), Yb(**3**)), which represent the first examples of *3d-4f*-heterometallic complexes including cobaltocene fragment (Fig. 1). Magnetic studies have shown that Yb complex **3** is a field-induced SMM with magnetization reversal barrier Δ_{eff}/k_B of 46 K under 2500 Oe constant field. Thermolysis of the complexes under air brings about $LnCoO_3$ perovskite phases exhibiting catalytic properties in oxidation processes as one of the products.

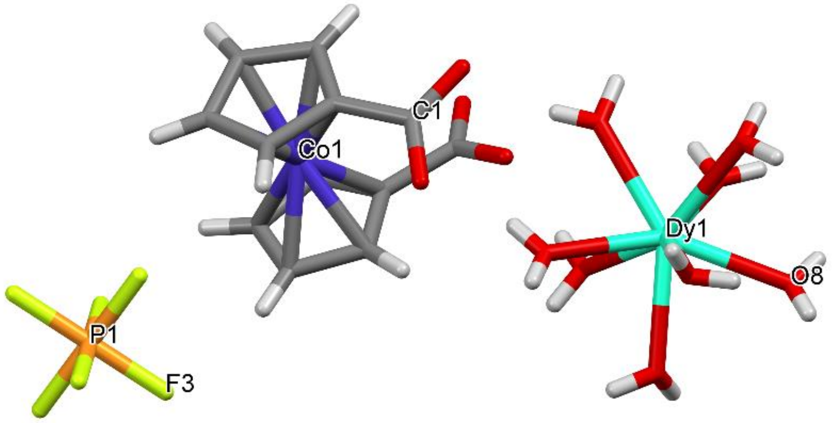

Fig. 1. Structure of complex 1.

Acknowledgements

The work was supported by the Russian Science Foundation (project 16-13-10407).

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Two novel series of 3d-3d´-4f-complexes on a basis of organometallic ligands

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Heterometallic complexes containing organometallic ligands are still poorly studied. In recent years we have obtained and studied several series of *3d-4f*-bimetallic complexes containing cymantrene[1] (CymH = (η^5-C_5H_5)Mn(CO)$_3$) or ferrocene[1,2] (FcH = (η^5-C_5H_5)$_2$Fe) and benchrotrene[3] ((η^6-C_6H_6)Cr(CO)$_3$) fragments.

Using $FcCO_2H$ and triethanolamine (H_3tea), we obtained new isostructural trimetallic complexes [$Ln_2Cr_2(OH)_2(FcCO_2)_4(NO_3)_2(H_2tea)_2$]·*Solv* (Ln = Tb (**1**), Dy (**2**), Ho (**3**), Er (**4**), and Y (**5**); *Solv* are the lattice solvent molecules) having defect-dicubane structure of the metal core (Fig. 1, left); for Tb, an isomeric complex **1a**, in which Tb^{3+} is chelated by triethanolamine as a tetradentate ligand, was also isolated. For Dy, a similar complex [$Dy_2Fe_2(OH)_2(CymCO_2)_4(NO_3)_2(Htea)_2$]·*Solv* (**6**) was obtained. DC magnetic studies revealed ferromagnetic interactions in the metal cores of **2** and **3** at T ≈ 25 K, and in **5** below 20 K. Complexes **1**, **2**, **3**, **4**, and **6** display the properties of single-molecule magnets (SMMs) with magnetization reversal barriers Δ_{eff}/k_B of 56, 80, 48, 14 and 20 K, respectively. Thermolysis of **1-5** under air gives $LnFe_{0.25}Cr_{0.75}O_3$ phases. Using $CymCO_2H$ and Fe(η^5-$C_5H_4P(O)Ph_2$)$_2$ ligand ($DppfO_2$), a series of new heteroleptic mononuclear *3d-3d´-4f*-complexes [$Ln(CymCO_2)_2(DppfO_2)_2$]NO_3·*Solv* (Ln = Tb (**7**), Dy (**8**), Ho (**9**), and Er (**10**)) was obtained. Both kinds of organometallic ligands in the unique bulky cations [$Ln(CymCO_2)_2(DppfO_2)_2$]$^+$ are bidentate (Fig.1, right). According to AC magnetic studies, complexes **9** and **10** are the SMMs with Δ_{eff}/k_B values of 3.8 and 10.1 K, respectively.

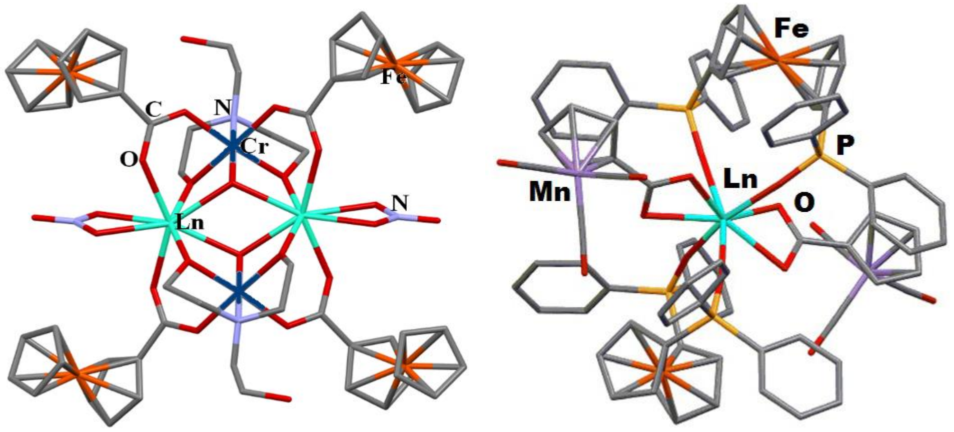

Fig. 1. Structures of complexes 1-5 (left) and of bulky cations in compounds 7-10 (right).

Acknowledgements

The work was supported by the Russian Science Foundation (project 16-13-10407).

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Microporous MOFs based on a pyridyl benzoic acid Schiff base ligand

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Metal–organic frameworks (MOFs) have attracted tremendous interest in the last decade due to their unique structural features[1] and potential applications in gas storage, separation,[2,3] magnetism,[4] catalysis,[5] sensing[6] and so on. The key factor for the discovery of MOFs with novel structural features and potentially interesting physical properties is the development of new synthetic strategies. Appropriate organic ligands are very important in this context, since even small changes in the flexibility, length, or symmetry of the ligands can result in a remarkable diversity of architectures and functions. [7]

An apparent strategy toward new MOFs with interesting properties consists of the use of N- and O-donor polytopic organic ligands.[8] Specifically, pyridyl-carboxylates have been confirmed as excellent ligands to assemble multidimensional coordination polymers due to the ability of the N donor atoms to bind most of the metal ions and the high bridging capability of the carboxylate groups. We will discuss the synthesis and characterization of three new compounds. These are $\{[Co_3(INIB)_6]\cdot 4DMF\}_\infty$ **$[1]_n$**, $\{[Mn_3(INIB)_6]\cdot 4DMF\}_\infty$ **$[2]_n$**, $[Cd(INIB)_2]\cdot DMF\}_\infty$ **$[3]_n$** and $[Zn(INIB)_2]\cdot DMF\}_\infty$ **$[4]_n$** ($INIB^-$ = the anion of 4-((pyridin-4-ylmethylene)amino)benzoic acid). All these complexes display 3-D microporous structures.

Acknowledgements

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New Pt(II) complexes with pincer NNC ligands; influence of the ligand on the photophysical properties

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The phosphorescent Pt(II) complexes attract considerable attention, owing to their potential applications as materials for OLEDs[1] and labelling agents in bioimaging.[2] The most important criteria for the applicability of this compounds are their photophysical characteristics: emission and excitation wavelengths, quantum yields, excited state lifetimes. Since the ligands coordinated to Pt metallocenter actively participate in the emissive excited states, they have a key influence on the photophysical parameters of the complexes and establishment of the relationship between the electronic structure of the ligand environment and the photophysical properties is one of the most important tasks.

Despite the fact that cyclometalated complexes of type [(N^N^C)Pt^{II}L] are well-known very few examples of the compound with 6, 6'-phenyl-substituted bipyridines as the pincer ligands are published, therefore detailed investigation of the systems based on the 6, 6'-phenyl-2, 2 '- bipyridines with various donor and acceptor groups is of particular importance.

In our resent research we focused on studying of cyclometalated platinum(II) complexes with the 6, 6'-substituted 2, 2 '- bipyridines as pincer N^N^C ligands and different ancillary ligands (Cl, alkynyl, phosphine) (Figure 1).

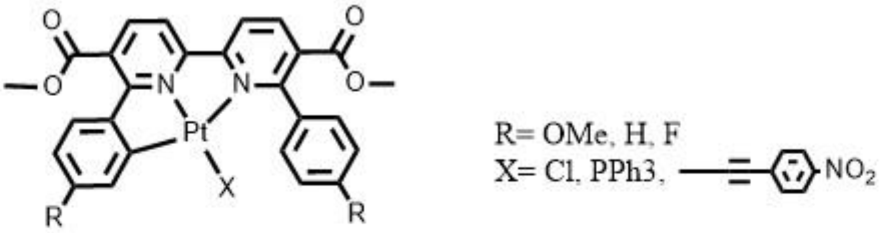

Figure 1. Schematic structure of new Pt(II) complexes.

All the new compounds were fully characterized by elemental analysis, X-ray crystallography, ESI-MS, 1D (^{1}H) and 2D (^{1}H-^{1}H COSY) NMR spectroscopy. The photophysical properties of the complexes obtained were thoroughly investigated. Dependence of the emission parameters on the nature of orthometalated (N^N^C) ligand substituent (R = OMe, H, F) and type of ancillary ligand was also established.

Acknowledgements

This research has been supported by grant of the RSF 19-73-20055. The work was carried out using equipment of the Centre for Optical and Laser Materials Research, the Centre for X-ray Diffraction Studies, the Magnetic Resonance Research Centre and the Centres for Chemical Analysis and Materials Research (St.Petersburg State University).

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Optical properties of copper (+2) ions in lead silicate glasses

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Copper (+2) ions give us wide possibilities for modifying glass colour from blue to green. In order to study the dependence of colour on glass composition 3 series of M_2O-PbO-SiO_2 (M = Li-Cs) glasses were prepared: *series 1* $10K_2O$-xPbO-(89,5-x)SiO_2-0,5CuO (x = 10÷60 mass%), *series 2* $11M_2O$-10,5PbO-$78SiO_2$-0,5CuO (mol%) (M = Li-Cs) and *series 3* $10K_2O$-10PbO-(80-x)SiO_2-xCuO (x = 0,5; 2 mass%) The glasses were molten at 1500ºC in alundum crucibles in an electric furnace with $MoSi_2$ heating elements. The melt was poured and quenched into 7-10 mm thick disks with further annealing in a muffle furnace. The material obtained is a transparent glass coloured from green to light-blue.

According to ESR data Cu^{+2} ions (d^9-configuration) occupy tetragonally distorted octahedral sites in glass matrix. Different alkali metals non-equally influence (Fig. 1) the tetragonal distortion that increases from Li to Cs. Various ways of colour tuning are available un this system. Increasing of PbO or CuO concentration leads to batochromic shift of the absorption edge. As a result glass becomes green instead of light-blue. In the same time d-d transitions intensity is responsible for the saturation of colour. Therefore, the more CuO is present in glass, the more deep colour can be obtained.

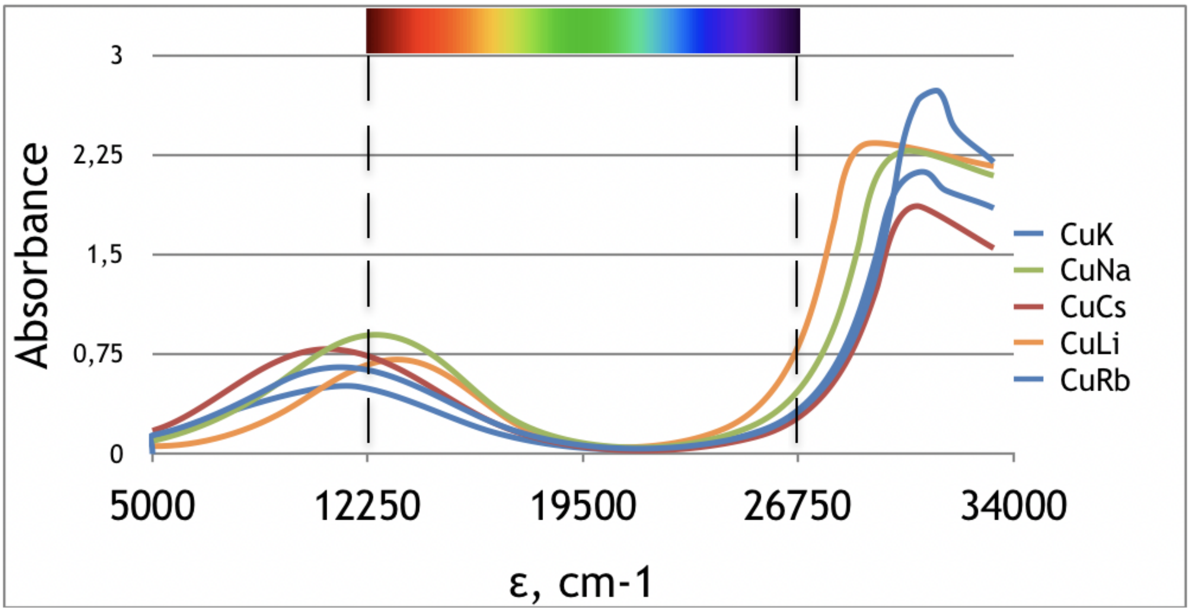

Figure 1. UV-Vis-NIR spectra dependence upon introducing different alkali metals

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Eu-, Ho-, Yb-doped $Bi_2Ti_2O_7$ pyrochlores: ab initio and experimental study

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Doped bismuth titanate pyrochlores may be interesting as materials with high dielectric constant, low leakage current, mixed electronic-ionic (proton) conductors, photocatalytic systems under visible lights, and host for photoluminescent active elements. Rare-earth elements have the suitable ionic radius, charge state for substitution Bi-atoms in $Bi_2Ti_2O_7$ and formation of the stable doped pyrochlore compounds. Moreover, chemical synthesis methods (*e.g.* co-precipitation) can realize metastable intermediate state in order to obtain new pyrochlore compositions with high dopant content.

Ab initio calculations were performed by means of the DFT using the PAW method as implemented in VASP. The generalized gradient approximation for exchange-correlation potential in the PBE form was used. Doping in the pyrochlore structure was simulated by the substitution one Bi (Ti) atom to one dopant atom (Eu, Ho, Yb) within the $Bi_4Ti_4O_{14}$ cell, which corresponded to the 25 at.% substitution. The cut-off energy of 500 eV and k-mesh 8×8×8 were used. The geometry optimization was performed until the forces on the atoms became less than 0.5 meV/Å. The calculations of the total and partial DOS, the band structure, dielectric and optical parameters for the pyrochlore models have been carried out after the geometry optimization.

The pyrochlore-type compounds $Bi_{2-x}M_yTi_{2-z}O_{7-\delta}$ (M = Eu, Ho, Yb) were obtained via co-precipitation method in the fine powder state. According results of DFT calculations the substitution of Bi-atoms by the dopant atoms is an energetically favorable process, rather than Ti-substitution. This fact is in good agreement with the synthesis of doped pyrochlores with appropriate element composition. Detail descriptions of the homogeneity regions for doped compounds, the study of the distribution dopant atoms in the crystallographic pyrochlore sites, thermostability, morphology, optoelectronic properties, and dielectric behavior of *f*-doped BTO are presented based on the comparative results of *ab initio* and experimental study.

Acknowledgements

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Non-covalent interactions in perchlorinated boron clusters as monitored by ^{35}Cl NQR

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The first attempts to use ^{35}Cl NQR for detecting and characterizing non-covalent interactions in supramolecular systems assembling $[B_{10}Cl_{10}]^{2-}$ clusters via halogen (chlorine) atoms were undertaken. NQR technique detects subtle disturbance in electron density distribution which occurs upon arising weak intermolecular interactions between atoms, hence selecting from the entire set of measured by X-ray “shortened” interatomic contacts those actually caused by non-covalent interactions.

A number of compounds of type $R_2[B_{10}Cl_{10}]$, the vast majority of which were solvates, have been studied (R = $[Ph_4P]^+$, $[Ag(NH_3)_2]^+$, $[Et_3NH]^+$, K+, Cs+ as well as the complexes of Cu(II) and Fe(II)).[1-5] The ^{35}Cl NQR data, supported by analysis of calculated electron density distribution and X-ray diffraction studies,[1] showed that cations and solvent molecules involve chlorine atoms in non-covalent interactions $N-H\cdots Cl$, $C-H\cdots Cl$ and $p\cdots\pi$, the latters occuring between lone pairs of Cl atoms and delocalized electron density of phenyl rings or C≡N groups of solvates. But no perturbation of the electron density on the Cl atoms was contributed by alkali cations ($M^+ = K^+$, Cs^+) in aqueous and non-aqueous solvates $M_2[B_{10}Cl_{10}].xL$ (L = solvate molecule), while the X-ray diffraction detected numerous $M\cdots Cl$ distances shorter than the sum of vdW radii.[2,3] The comparative strength of non-covalent interactions in the compounds based on decachloro-*closo*-decaborates was analyzed using the NQR data.

Acknowledgements

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Oxygen exchange on nanocomposites MO_x/WO_3 (M = Pd, Ru)

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Tungsten oxide WO_3 is an *n*-type semiconductor used as the sensitive material in conductometric gas sensors. The modification of WO_3 surface by PdO_x or RuO_x clusters improves sensors characteristics, mainly sensitivity and selectivity, in the detection of reducing gases CO and NH_3[1]. The formation of the sensor response as the change in the electrical conductivity of the material is due to oxygen chemisorption and chemical reactions between the chemisorbed or lattice oxygen and target gas molecules. Thus, determining the effect of modifiers on the interaction of a semiconductor matrix with atmospheric oxygen is one of the key aspects in the development of effective materials for semiconductor gas sensors.

In the present work, we investigated the activity of WO_3 and MO_x/WO_3 samples (M = Pd, Ru) in the interaction with oxygen using the temperature-programmed isotope exchange (TPIE) method[2]. Nanocrystalline WO_3 was synthesized by precipitating a H_2WO_4 hydrogel from $(NH_4)_{10}W_{21}O_{41}$ solution by nitric acid with subsequent annealing at T = 300, 450, 600°C. Chemical surface modification of the resulting WO_3 matrices with Pd and Ru additives (1 wt.%) was performed by the impregnation method. The TPIE experiments were effectuated by mass spectrometry in a flow-type reactor.

The interaction of WO_3 with oxygen occurs through the homogeneous exchange[2], which starts at ~650°C regardless of the WO_3 annealing temperature. A similar activity is demonstrated by PdO_x/WO_3 sample. The behavior of the RuO_x/WO_3 samples is significantly different: they demonstrate an oxygen exchange[2] with rapid increase in catalytic activity starting at 210-273°C with the maximum at 370-385°C. However, upon further heating, the activity of the RuO_x/WO_3 samples decreases non-monotonously with a local minimum at 450°C and a local maximum at 490-500°C. At 650°C, a homogeneous oxygen exchange begins, like for all other samples. The results obtained correlate with the previously studied behavior of the MO_x/SnO_2 nanocomposites[2,3]. Thus, the RuO_x/SnO_2 demonstrated the beginning of oxygen heteroexchange at ~200°C[3], while the PdO_x/SnO_2 nanocomposite was less active[2]. Moreover, at ~380°C the MO_x/SnO_2 samples also showed some deactivation; which however, was less pronounced, especially for RuO_x/SnO_2. Comparison of the behavior of WO_3- and SnO_2-based samples allows us to conclude that SnO_2 is more involved in oxygen heteroexchange due to oxygen spillover mechanism by PdO_x and RuO_x clusters, while WO_3 plays an active role in the deactivation of RuO_x nanoparticles.

Acknowledgements

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Radioluminescent properties of organo-lanthanides

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The absorption of ionizing radiation and subsequent transformation into visible light is important property of materials which can be widely used. One of these areas is the use of scintillator-based detectors - substances that convert ionizing radiation into visible light. Such detectors are often used in medical devices, radiography, biochemical analysis, and astrophysics. Currently, a large number of lanthanide-containing scintillators based on inorganic materials is known. However complexes of lanthanides with organic ligands as radioluminescent materials have not almost studied.

We have found that chalet complexes of Dy, Er, Nd, Sm and Tm upon x-ray irradiation show efficient emission specta of which is characteristic to respective Ln ion (Fig 1). Solid samples of the complexes were irradiated with x-rays at room temperature. The anode voltage on the tube was 45 keV, and the anode current was 150 μA.

To compare the luminescence intensity, the x-ray luminescence spectrum of anthracene is given. Comparison of the intensity of radio luminescence and photoluminescence showed that the latter was 300 times higher. With simultaneous excitation by X-ray and UV light, a total intensity is observed, which indicates the similarity of the mechanisms of both types of excitation.

The detected high efficiency of radioluminescence of the Eu and Tb complexes shows that it is possible in principle to use these compounds as functional materials in the design of radiation detectors.

It was found unexpectedly that the beta-irradiation does not cause luminescence of aluminium oxiquinolinate Al(Q)3 and europium beta-diketonate Eu(TTA)3.

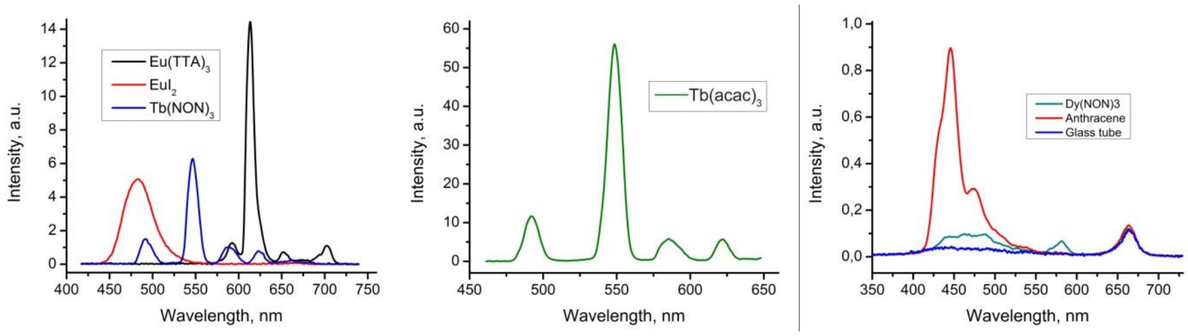

Figure 1. Radio luminescence spectra of organometallic complexes of lanthanides and anthracene

Acknowledgements

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Heterospin Compounds Based on Nitroxide and [$Cu_4(hfac)_2(L–X)_2$] where L–X is 2,4,6-tris(trifluoromethyl)- or 2-methyl-4,6-bis(trifluoromethyl)tetrahydropyran-2,4,6-triol

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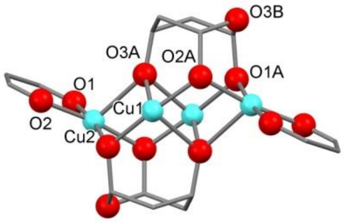
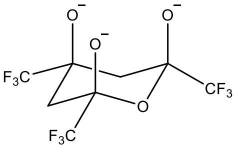
Recently we described the synthesis of polynuclear Cu(II) complexes [$Cu_4(hfac)_4(OMe)_4$] or [$Cu_{11}(hfac)_{10}(OH)_8(O)_2$].[1] It was found that recrystallization of these compounds from acetone/toluene mixture gave rise repeatedly to [$Cu_4(hfac)_2(ttpt)_2(Me_2CO)_2$], where ttpt was 2,4,6-tris(trifluoromethyl)tetrahydropyran-2,4,6-triol. This ligand enforces face-capping coordination geometry at the metal that attracted our attention. Such an availability of the {$Cu_4(hfac)_2(ttpt)_2$} building block prompted us to introduce it in design of heterospin compounds with nitroxides.



{$Cu_4(hfac)_2(ttpt)_2$}



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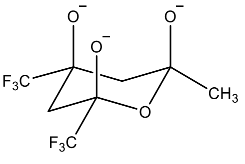
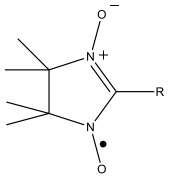
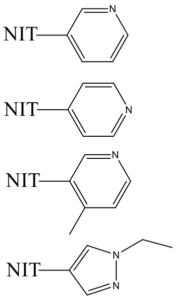


$mtpt^-$



NIT-R



We succeeded in synthesizing of a whole range of polynuclear and polymeric Cu complexes with NIT-R. Their structure and magnetic properties are under discussion. It was found that {$Cu_4(hfac)_2(mtpt)_2$} formation, where mtpt is 2-methyl-4,6-bis(trifluoromethyl)tetrahydropyran-2,4,6-triol, is possible as well. We discuss the possible mechanism of {$Cu_4(hfac)_2(mtpt)_2$} formation.

Acknowledgements

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A new type of supramolecular composites of anionic Zn(salen) complexes and organic polycations as self-improving catalysts for the addition of CO_2 to epoxides

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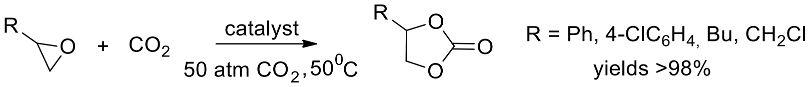
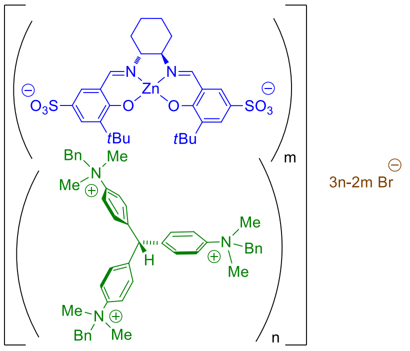
A set of assembled supramolecular ionic heterogeneous composites (**1-3**) *(Figure 1)* was synthesized and investigated. For compound **1**, the crystal structure is determined. Composites **1-3** were also analysed by nitrogen porosimetry. The heterogeneous system **3** was catalytically competent in the reaction between styrene oxide and carbon dioxide.



The system functioned as a bifunctional catalyst which could be easily separated and recycled by the addition of ether to the reaction mixture. The same batch of the catalyst could be employed for, at least, five runs with its catalytic properties improving as it was reused. Proposed *in situ* conversion of the initial composite 3 into a more catalytically active set of species is presented at *Scheme 1.* The new formed phenolic groups within the zinc (salen) complex may be additionally stabilized by hydrogen bond formation with the newly formed unprotonated dimethylamino groups. Thus, the *in situ* formed species can be considered as Lewis acid activated Brønsted acids and would be expected to be highly efficient catalysts for cyclic carbonate synthesis.



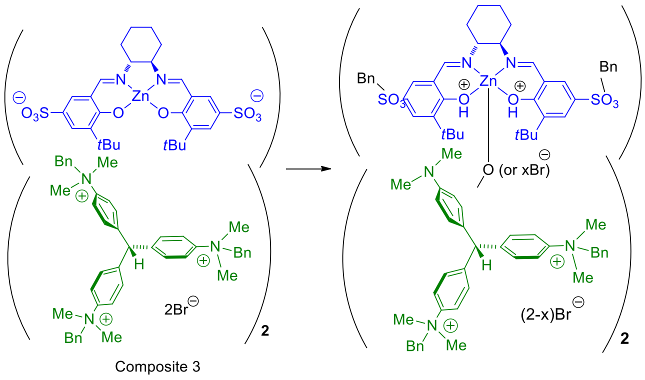


Figure 1 **Scheme 1**

Composites 1(m=3,n=2), 2(m=1,n=1), 3(m=1,n=2)

Acknowledgements

Financial support by the RFBR (Grant № 18-53-05004 Arm_a) is gratefully acknowledged.

Disorder in crystals of transition metal oxide fluoride complexes. Identification of O and F atoms

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Most transition metal oxide fluoride compounds are inherently orientationally disordered.[1] It is accepted in the literature that in disordered structures of oxide fluoride compounds it is impossible to differentiate oxygen and fluorine atoms by X-ray diffraction due to their similar ionic radii and scattering factors. Polar pseudo-octahedral MO_xF_{6-x} ($x = 1–3$) anions give rise to crystal structures, in which no oxide/fluoride ordering appears due to numerous local configurations as in the case of cubic *Fm*3*m* $A_2^+B^+M^{IV}O_3F_3$ (A, B = alkali metal; M = Mo, W) family.[1] However, we found that in the case of dynamically disordered oxide fluoride polyhedra it became possible to distinguish between O and F atoms on local scale and to determine the real polyhedral geometry.[2] During such a dynamics, the central atom is shifted towards the edge, face, or apex of octahedron giving its disordering on cuboctahedron, cube, or octahedron, respectively (Figure 1). Such a displacement of the central atom enables one to determine the real octahedral geometry where O and F atoms can be identified owing to the inherent differences between M–O and M–F bonding. Upon cooling, similar compounds undergo phase transitions of order-disorder type with a rather large value of entropy change. Meanwhile, in some cases, dynamic processes are so fast that the central atom does not keep pace with oxygen and remains near the polyhedron symmetry center. In this case, the M–O and M–F distances are physically equalized, which can be detected by the appearance of an IR band in the range of 700–800 cm^{-1} assigned to totally synchronous M–O and M–F vibrations. This is especially true for tantalum oxide fluoride complexes.[3]

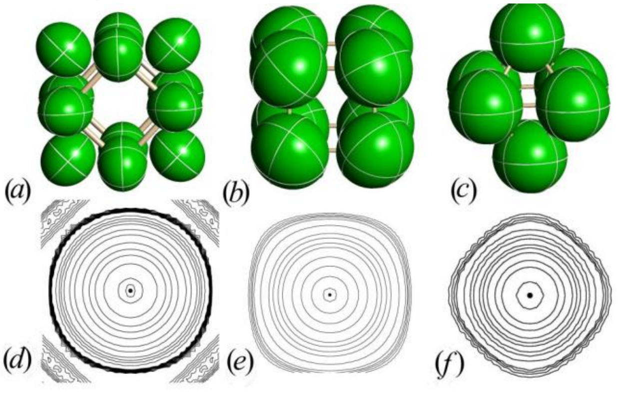

Figure 1. Dynamic displacement of M atom from the octahedral center of MX_6 on cuboctahedron, cube, or octahedron for $(NH_4)_3WO_2F_5$ ***(a)***, $(NH_4)_3WO_3F_3$ ***(b)***, and $(NH_4)_3TiOF_5$ ***(c)***, respectively, and the corresponding electron density profiles ***(d, e,*** and ***f)***.

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Interaction of the Sn(IV)-tetraphenylporphyrins with Ionic Surfactants: Fluorescent Properties and Photochemical Stability

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Hydrophilic annionic and cationic Sn(IV)-tetraphenylporphyrins [tetra(4-sulfophenyl)porphyrin (SnP1) and tetra(methylpyridyl)porphyrin (SnP2)] with hydroxyl and metoxidol axial ligands (L) were synthesized and their fluorescent properties and photochemical stability were investigated in phosphate buffer (pH 7.4). The processes of the Sn(IV)-porphyrin complexes interations with oppositely charged surfactants [SnP1 with the cetyltrimethylammonium bromide (CTAB) and SnP2 with the sodium salt of the dioctylsulfosuccinate (DSC)] were studied (Fig.).

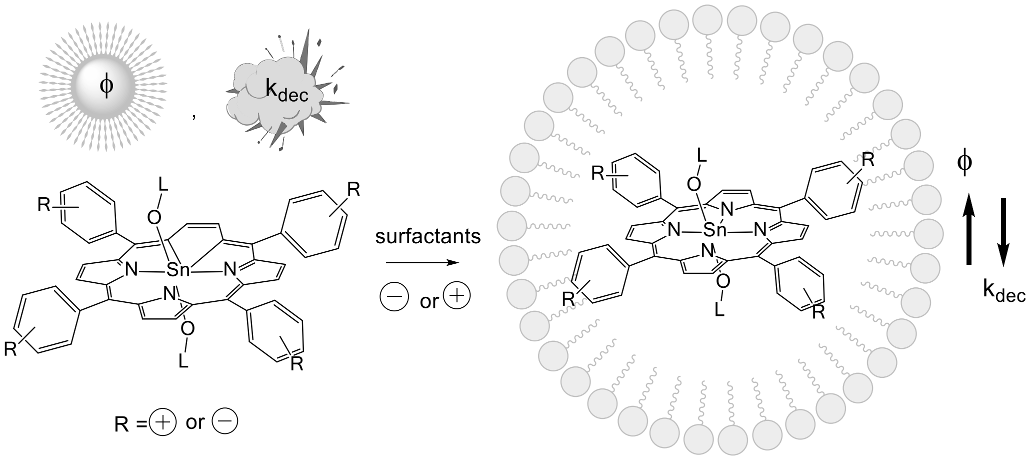

Figure. Schematic representation of surfactant micelles with porphyrinate molecule

It was established that upon localization of the Sn(IV)-porphyrin in surfactant micelles their fluorescent properties enhanced. When excited at 425 nm, each of the Sn(IV)-complexgave a two-banded fluorescence spectrumin the range of 607-610 (band I) and 658-665 nm (band II). As the porphyrinates are incorporated into micelles, the ratio of the bands intensity in the fluorescence spectra changes (it decreases in the I-st band and increases in the II-nd band).Porphyrin molecules, regardless of the nature of the macrocycle and the central metal cation in both aqueous and non-aqueous mediaundergo light destruction in the presence of peroxide compounds. It has been shown how the photochemical stability of Sn(IV)porphyrins in aqueous media depends on the presence of the antioxidant methoxidolmolecule on the Sn(IV) cation and on the inclusion of the macrocycle in surfactant micelles.

Acknowledgements

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Processes of the Sn(IV)-tetra(4-sulfophenyl)porphyrins*bis*-axial complexes interaction with copper cations in aqueous media

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Coordination polymers are one of the most important objects of supramolecular chemistry, which are organometallic framework structures with a given geometry and properties. Using of large porphyrin or phthalocyanine molecules with a rigid structure as the main sites for the creation of organometallic coordination polymers makes it possible to obtain highly porous hybrid materials with high catalytic or photo-activity. The purpose of this work was to study the possibility of chain polymers obtaining on the base of the Sn(IV)-porphyrins *bis*-axial complexes and Cu(II) cations.

Hydrophilic *bis*-tyrosin-Sn(IV)-tetra(4-sulfophenyl)porphyrin (L1-SnP-L1) and bis-diaminohydroquinone-Sn(IV)-tetra(4-sulfophenyl)porphyrin (L2-SnP-L2) were synthesized (Figure 1). The structures of the obtained complexes were characterized by UV-Vis and two-dimensional NMR spectroscopy and mass spectrometry and confirmed by quantum chemical calculations.

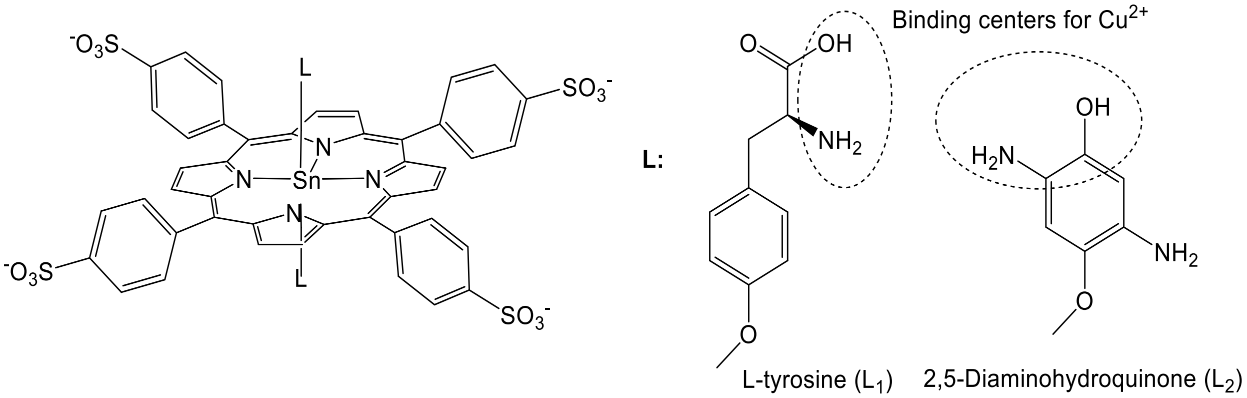

Figure 1. Structures of the bis-axial Sn(IV)porphyrin complexes

The processes of the Sn(IV)-porphyrin complexes (L-SnP-L) interation with Cu(II)-cations in phosphate buffer (pH 7.4) were studied by UV-Vis and NMR spectroscopy. It is shown how the composition and structure of the complexes$(\text{L-SnP-L})_n\cdot\text{Cu}^{2+}{}_m)$depends on the reaction ratio of the reactants and the interaction time. The structures of the compounds obtained $(\text{L-SnP-L})_n\cdot\text{Cu}^{2+}{}_m)$were characterized by a set of various physicochemical methods and optimized by calculation methods.

Acknowledgements

This research was funded by the Russian Foundation for Basic Research (project no 19-03-00078-A). We thank I. Khodov (ISC RAS) for ^{1}H NMR investigations of the porphyrins.

Generation of Air-Water Two-Phase Flow with Narrow Micro-Bubble Size Distribution

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Separations based on two-phase gas-liquid flows are widely implemented in industry. Despite the proven efficiency of single-size bubbles, until now, achieving two-phase air-water flows with unisize micron air bubbles was out of reach.

Here we describe a new bubble generator that has no moving parts. The generator can create bubbles in a wide range of diameters-from micron to several mm- by changing the ratio of the gas flow rate to that of the liquid. The core of the generator is a vortex chamber where liquid supplied through tangentially-oriented ducts meets air supplied in the radial direction through an orifice ducts. An obtained two-phase suspension is drained through an exit nozzle of the vortex chamber.

Micron bubbles were measured with a laser beam and mm bubbles with high speed camera. More than 90% (by number) of the generated air bubbles were in a size range between 1 and 20 □m. Changes of liquid to air flow ratio between 7 and 27 created bubbles with diameters between 0.05 and 2 mm.

The proposed generator creates pressure oscillations frequency which under test conditions were in the range 0.74-1.06 Hz. The frequency and amplitude of pressure oscillations is determined by the geometry of the vortex chamber. The proposed new generator might have profound theoretical and practical use in a variety of separation processes including oxidation, flotation, membrane separation and biotechnology.

Keywords: bubble velocity; gas-cavity zone; pressure frequency oscillation; vortex chamber.

$ReGa_2Ge$ and $ReGaGe_2$: new semiconducting intermetallics

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Intermetallics possessing semiconducting properties are a rare class of intermetallic compounds. As a rule, they are formed between atoms of different blocks of the Periodic Table of chemical elements. Most of them belong to three families of compounds: These are half-Heusler alloys, Nowotny chimney-ladder phases, and $IrIn_3$ structure type phases. A strong overlap of the transition metal *d*-orbitals with the *p*-element *s*- and *p*-orbitals leads to the gap opening in the band structure, and the Fermi level can fall into the gap at the certain concentration of valence electrons (VEC). To the date there are only local concepts, such as 18-n rule,[1] explaining this behavior for some groups of compounds. The search for new compounds of this class allows us to formulate rules that would help to explain and predict the appearance of new non-metallic intermetallic compounds.

In this work, we synthesized two compounds $ReGa_2Ge$ and $ReGaGe_2$; the former belongs to the $IrIn_3$ structure type, and the VEC = 17 anticipates its semiconducting properties confirmed by theoretical and experimental studies, whereas the latter, surprisingly, has its own crystal structure, the features of which reveal the semiconducting behavior to be realized in the 18-electronic system.

The details of the crystal and electronic structure, as well as the properties of new compounds will be discussed in detail in this report.

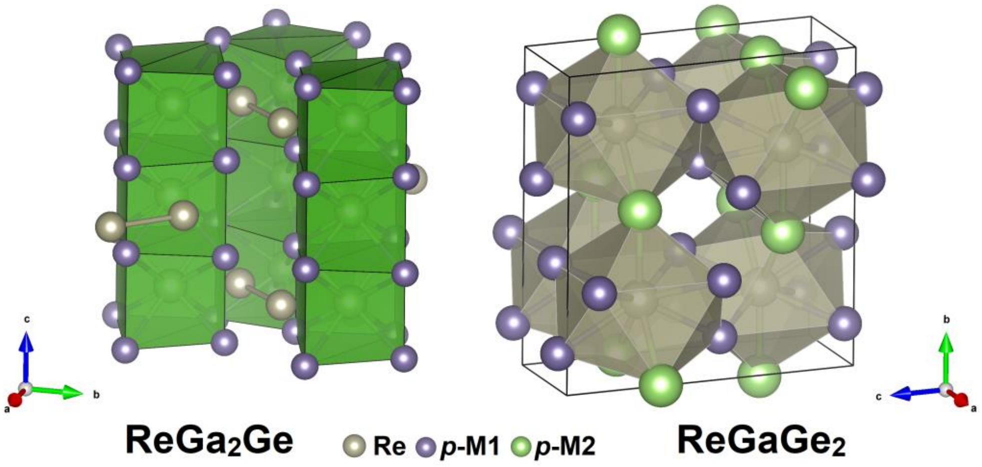

Figure 1. View of the crystal structures of $ReGa_2Ge$ and $ReGaGe_2$

Acknowledgements

This work supported by the Russian Science Foundation, grant # 17-13-01033

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Synthesis and characterization of well-dispersed carbon-coated pyrrhotite nanoparticles

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The cation-deficient iron sulfides $Fe_{1-x}S$ have attracted an increasing interest in the fields of nanomaterials because of the unique magnetic properties that may find application in nonvolatile phase-change magnetic memory devices and high-performance anode materials of lithium ion batteries.[1,2] In this work the well-dispersed carbon-encapsulated iron sulfide ($Fe_{1-x}S$@C) nanoparticles (NPs) with typical core/shell structure were synthesized by thermal pyrolysis of iron nitrate and sulfur powder with hexadecylamine at temperature (T_R) between 360 °C and 400°C in an atmosphere of air. All of the XRD reflections of samples could be indexed to the hexagonal phase with NiAs-type structure ($P6_3/mmc$). A Scherrer's formula analysis of the peak broadening indicates an average crystallite size of $Fe_{1-x}S$ NPs from 17.6 to 23.9 nm, depending on the T_R. Two peaks located at 212 and 276 cm^{-1} are detected in the Raman spectrum, which is typical to the asymmetric and symmetric stretching modes of FeS. Moreover, two characteristic peaks, D band and G band, of amorphous carbon were observed at around 1350 and 1591 cm^{-1}, respectively. The carbon-encapsulated $Fe_{1-x}S$ NPs have good uniformity and nearly monodispersity as shown in TEM images. In addition, the particle size of $Fe_{1-x}S$@C NPs is about 40 nm and the thickness of coated carbon shell is about 4-5 nm. Temperature-dependent magnetization M(T) on several repeated heating-cooling cycles were recorded in an applied field of 15 kOe. On the first heating branch, a peak transition in M(T) was observed starting around 410 ~420 K, with a maximum at 475~520 K, and then decreases slowly to Curie points 625~675 K. The magnetization of first cooling branch is clearly higher than the heating one. Moreover, during the first cooling branch from 650 K, the peak transition was not reproduced and increased with Weiss behavior back to room temperature. For the multiple, repeated heating-cooling cycles (2-5) show the thermal hysteresis behavior that the Curie transition on cooling curves lagged behind on heating curves by about 30 K. This phenomenon is most probably due to the non-stoichiometry in the $Fe_{1-x}S$@C NPs with a specific redistribution of vacancies which changes the initial composition of nanoparticles.

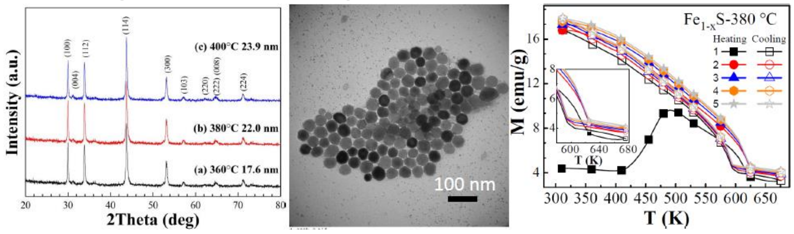

Figure 1. (a) XRD patterns of $Fe_{1-x}S$@C NPs prepared at different temperatures; **(b)**TEM image and **(c)** Temperature-dependent magnetization $M_{H=1.5T}$, obtained from hysteresis loops of $Fe_{1-x}S$@C NPs synthesized at T_R=380 °C.

Acknowledgements

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Multifunctional metal-organic frameworks based on rhenium octahedral clusters $[Re_6Q_8(CN)_6]^{4-}$ and rare-earth cations.

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Chemistry of metal-organic coordination polymers (CP) attracts a lot of attention for the last decades due to various physicochemical properties like luminescence, catalytic properties, permanent porosity and magnetism. One of the most common routes for obtaining of CPs is their self-assembly in solution from building blocks[1]. Octahedral cluster complexes $[Re_6Q_8(CN)_6]^{4-}$ (S, Se, Te) are convenient building block for synthesis of new coordination polymers[2]. Intensive luminescence and reversible oxidation accompanied with color and magnetic properties change makes such complexes interesting for obtaining of coordination polymers, which can be applied in different multifunctional materials.

Self-assembly of clusters complexes $[Re_6Se_8(CN)_6]^{4-}$ with Ln^{3+} and furan/tiophene/selenopehene – 2,5-dicarboxylic acid (fdc, tdc and sdc respectively) in the aqueous solution leads to construction of new metal-organic framework (MOF) with general formula $[\{Ln(H_2O)_3\}_2(L)Re_6Se_8(CN)_6]\cdot nH_2O$ (L = fdc, tdc, sdc; Ln = Gd, Tb)[3]. These compounds acquired all features of used building blocks owning a wide range of properties. All compounds are porous and display red photoluminescence of the cluster, paramagnetic behavior due to Ln^{3+} cations and demonstrate high CO_2/N_2 and CO_2/CH_4 selectivity. Besides that a presence of redox active cluster leads to the reversible oxidation in the solid state accompanied with drastic color change. Such properties make this compounds perspective for obtaining multifunctional materials due to highly selective gas sorption and sensitivity to such toxic technical agents as Br_2 and N_2H_4.

Moreover, a series of MOFs based on $\{Ln_4(\mu_3\text{-}OH)_4\}^{8+}$ oxo-clusters with general formula $[\{Ln_4(\mu_3\text{-}OH)_4(\mu\text{-}ina)_1(ina)_3(H_2O)_6\}\{Re_6S_8(CN)_6\}]\cdot nH_2O$ was obtained. In these compounds rhenium complexes $[Re_6S_8(CN)_6]^{4-}$ is act as linker for binding of zigzag chains $[\{Ln_4(\mu_3\text{-}OH)_4(\mu\text{-}ina)_{1/2}(ina)_{3/2}(H_2O)_6\}]^{4+}$ forming 3D structure. All nine compounds within the series can be obtained by simple synthetic procedure and good yields.

Acknowledgements

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Ligand-to-metal charge transfer excited states based on d^0 metallocene dicarboranyls

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Group 4 metallocenes are of particular importance for catalytic polymerization of olefins[1], activation of small molecules, molecular photonics, as antitumor agents, and so on. Properties of the complexes are largely determined by nature and localization of the frontier orbitals (HOMO, LUMO) being a subject of continuous discussions[2-4].

In the present work, photophysical and quantum-chemical methods were applied to study the orbital nature and extremely rare ligand-to-metal charge transfer (LMCT) excited states based on non-classical organometallic species − structurally complex d^0 metallocenes, bearing polyhedral boron-containing σ-ligands $M(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ (M = Ti, Zr, Hf). We conducted simulation at different levels of theory (DFT, HF and time-dependent ones) of molecular architecture, MO properties, and electronic spectra of $M(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$. A good agreement of the results of computational and photophysical studies (LMCT transition energies, oscillator strengths, etc.) was achieved. According to our computation data (DFT, TD-DFT), the observed first transition $S_0 \rightarrow S_1$ in the electronic excitation and absorption spectra of the metallocene dicarboranyls is caused by charge transfer from the HOMO centered predominantly on Cp π-ligands to the metal-centered LUMO, while in the related dimethyl derivatives $(\eta^5\text{-}Cp)_2MMe_2$, this transition is caused by charge transfer from the HOMO, localized on the Me σ-ligands. The dipole moment of the complexes, having all M−C σ,π-bonds, drastically (ca. 6 times) increases on going from dimethyl to dicarboranyl counterparts. In contrast to “structurally simple” dichlorides $(\eta^5\text{-}Cp)_2MCl_2$, the related sterically-hindered bridged metallocene dicarboranyls are emissive in liquids, most likely, due to their much higher structural rigidity. We note that related dimethyls $(\eta^5\text{-}Cp)_2Me_2$ are not emissive even at low temperature.

In conclusion, using quantum-chemical calculations at different levels of theory and photophysical methods, we revealed that despite the presence of metal−carbon σ-bonds, structurally-sophisticated metallocene dicarboranyls, in contrast to dimethyl analogues, possess LMCT excited states with charge transfer predominantly from Cp-ligands, high molecular dipole moment, and photoluminescent properties, making them similar to the dichloride analogues, lacking the M−C σ-bonds.

Acknowledgements

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Modeling of stereoisomers of metallocene (Zr, Hf) dicarboranyls

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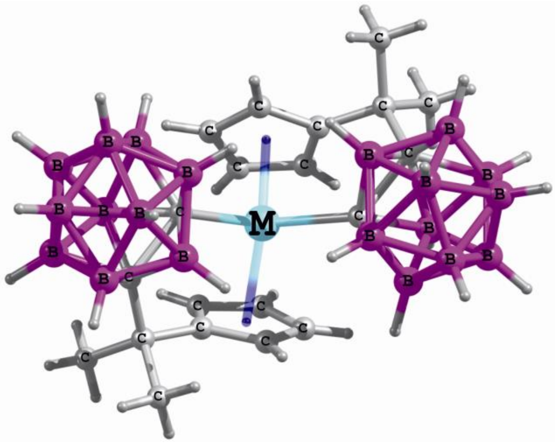
The group IV metallocenes are bent-sandwich complexes composed of a metal ion in d^0 electronic configuration and multiply-bonded π-donor ligands and unidentate σ-donor ligands. They are of particular importance for catalysis[1], activation of small molecules, photochemistry of coordination compounds, as antitumor agents, etc.[2]



Correct molecular geometry prediction is a necessarily prerequisite for further reliable theoretical calculations. In the present study, density functional theory (DFT) methods were applied to unravel molecular architecture of stereoisomers of sterically-hindered d^0 double-*ansa*-metallocene dicarboranyls $M(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ [M = Zr (**1**) and Hf (**2**)], having rare emissive ligand-to-metal charge transfer excited states. Figure shows the spatial isomer of **1** and **2** that crystallographic parameters are known. Our DFT-computing data agree well with the X-ray data for **1** and **2**. None of the density functionals, applied in this study, gives consistently superior description for the sophisticated structure of **1** and **2**.

Electric dipole moments μ_g of **1** and **2**, theoretically deduced, appear to be virtually the same (despite different spin-orbit coupling effects of Zr and Hf) and are twice larger than those of closely-related d^0 metallocene dichlorides $(\eta^5\text{-}Cp)_2MCl_2$ (M = Zr, Hf). The latter is also true for the isostructural titanocene dicarboranyl.[3]

Our computing reveals that species **1** and **2** can exist in the form of at least two stereoisomers, having identical lengths of the principle organometallic bonds: M–Cp$_{(centroid)}$ π-bonds and M–C$_{(carboranyl)}$ σ-bonds. Surprisingly, electric dipole moments of the stereoisomers of each complex **1** and **2**, respectively, little differ ($\Delta\mu_g$ = 0.1 – 0.3 Debye in gas phase, according to different DFT-methods). The complex structure of such systems requires more elaborated methodologies for an accurate description, such calculations can have strong impact on the interpretation of the experimental data; and an additional work on this point is in progress.

Acknowledgements

The financial support under the state contract 0089-2019-0003 and RFBR project 18-03-00359 is acknowledged.

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Ligand-to-metal charge transfer excited states in organometallic compounds

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Organometallic compounds are an important class of materials in many areas of science and technology. Many classes of organometallic complexes are regarded as rather unstable to air/water and, historically, this fact has drastically hampered development of organometallic photophysics and photochemistry. Besides, ambiguities in literature often resulted from rather difficult manipulation with sensitive organometallic compounds and experimental set-up and most studies in inorganic photophysics and photochemistry have been concerned with classical coordination compounds, while photophysics and photochemistry of organometallic compounds remain tremendously less understood.

Molecular excited states are of great fundamental and technological importance. In contrast to organic molecules, unambiguous determination of photophysical characteristics for organometallic complexes presents certain difficulties: the more complex the molecule or molecular system, the more complicated appears to be the problem. Design of complex molecules, those can be optically excited into long-lived excited or charge-separated state(s), has received enormous fundamental and theoretical efforts due to their perspective use in solar energy conversion, photocatalysis, and many other related fields of molecular photonics. The present contribution is devoted to the properties of ligand-to-metal charge transfer (LMCT) excited states as an extremely rare, much less studied type of electronically-excited states. The current state of the knowledge on LMCT excited states, based on organometallic complexes, will be surveyed and fundamental properties will be discussed and generalized. Principle emphasis will be given to studies on solvatochromism[1], relation between LMCT transition energies and differences in oxidation and reduction potentials[2-5], relation between emission[6] quantum efficiency and lifetime[7], electron-exchange (Dexter) resonant energy transfer[8,9], and photolysis of organometallic compounds in their LMCT excited states. There is great scope for novel chemical, photophysical, and photochemical studies of organometallic species, having long-lived emissive LMCT excited states, and their organized systems.

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Functional properties of Cu-substituted $La_2NiO_{4+\delta}$ as oxygen electrodes for protonic ceramic fuel cells

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Nowadays mixed ionic–electronic conductors (MIECs) derived from $La_2NiO_{4+\delta}$ (LNO) with a K_2NiF_4-type structure have received considerable attention as promising cathodes for solid oxide fuel cells (SOFC) due to their desirable transport, mechanical and catalytic properties[1]. It is well-known, that among the studied cathode materials, $La_2NiO_{4+\delta}$ has the relatively low thermal expansion coefficient (TEC) values, which are close to those of proton-conducting electrolytes. Nevertheless, in order to ensure stable operation of SOFC, it is necessary to further lower the TEC values. One of the effective ways of properties optimization is the partial substitution of nickel by a small amount of other 3d-elements[2]. In this work, copper was selected as a dopant in LNO in order to improve functional properties and sinterability.

Complex oxides of a general $La_2Ni_{1-x}Cu_xO_{4+\delta}$ system (LNCx, where x = 0, 0.1, 0.2 and 0.3) were prepared via a citrate-nitrate synthesis technique. The obtained precursors were calcined at 800 °C for 3 h and finally fired in air at 1050 °C for 5 h. The ceramic samples were sintered at 1300 °C. The phase state of the synthesised powders was studied by X-ray diffraction (XRD) analysis. Oxygen overstoichiometry for the synthesized LNCx materials was analysed by thermogravimetric method in a temperature range of 30–1000 °C in different atmospheres (air and 50%H2/Ar). Thermomechnical properties were studied employing a dilatometry technique between 100 and 1000 °C in static air. Electrical properties were studied by four-probe DC in a temperature range of 100–900 °C in static air.

A complex analysis of the data obtained shows that the partial replacement of Cu for Ni has a significant effect on the lattice structure, thermomechnical, electrical and electrochemical properties of $La_2Ni_{1-x}Cu_xO_{4+\delta}$. Cu-doping leads to an elongated Ni(Cu)O6octahedron in the perovskite layers, corresponding to the decreased a and b but increased c parameters. The thermal expansion coefficients were equal to $13.8\cdot10^{-6}$, $13.7\cdot10^{-6}$, $13.4\cdot10^{-6}$ and $12.8\cdot10^{-6}$ K^{-1} for x = 0, 0.1, 0.2 and 0.3, respectively. The Cu-doping decreases the total conductivity of nickelates, which can also be explained by the relatively low concentration of charge carries associated with the corresponding low oxygen overstoichiometry of such doped compounds. The substituting Cu also promotes the sintering process. The densification temperature for LNCx ceramics drops down to 1300 °C, while $La_2NiO_{4+\delta}$ ceramics were obtained at 1450 °C.

It can be concluded, that materials based on $La_2NiO_{4+\delta}$ with small additions of copper can be considered as promising electrodes for protonic ceramic fuel cells.

Acknowledgements

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Tris(pyrazolyl)methane – a versatile ligand for design of Ln(III) complexes featuring magnetic and luminescence properties

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Lanthanide Single-Molecule Magnets (SMM) captivate due to their possible applications in data storage, spintronics or quantum computing. In such coordination complexes, a slow relaxation of the magnetization originates from the appearance of an energy barrier that opposes two directions of the magnetization. The foundation of such remarkable property lies in the synergistic combination between the intrinsic nature of the Ln ion through its angular dependence of the 4f electronic density (oblate vs. prolate) with the crystal-field generated by the surrounding ligands. In this sense, mononuclear Ln SMM with tremendous magnetic properties represent a challenge for synthetic chemists in order to design optimized complexes with appropriate symmetry and coordination sphere in order to maximize the magnetic anisotropy of the ± m_J states. N-containing ligands, which are easily incorporate in the complexation with Ln ions due to their hard Lewis acidity, are suitable candidates for synthesis of complexes of these metals.

Herein we report synthesis, structure and magnetic and luminescence properties of a series of Ln(III) complexes of the general formula [Ln(Tpm)X_3] coordinated by Tpm ligand (tris(3,5-dimethyl-pyrazolyl)methane; Ln = Tb, Dy, Er, Yb; X^- = NO_3^-,Cl^-; Fig. 1).[1] The observation of a field-induced slow relaxation of magnetization of these derivatives is highly dependent on the anion's nature. NO_3^- moieties appear to be suitable to stabilize the oblate electronic density of Dy^{3+}, while Cl^- generate an equatorial crystal-field allowing the slow relaxation of the prolate Er^{3+} ions. More over Tpm ligand was found to be suitable coordination environment for Eu, Tb and Dy luminescence sensebilization.

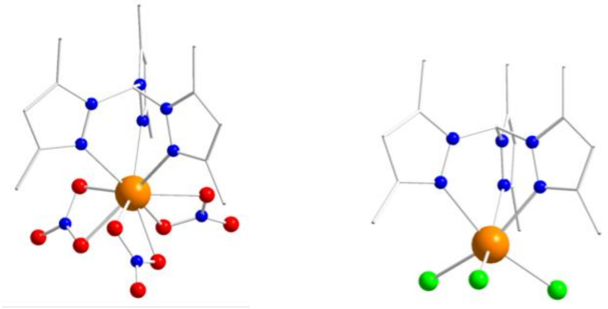

Figure 1. Molecular structures of [Ln(Tpm)(NO_3)$_3$] **(left)** and [Ln(Tpm)Cl_3] **(right)**

Acknowledgements

This work was supported by Russian Science Foundation (Project No 17-73-30036).

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Rare-earth metal bis(alkyl) complexes supported by tridentate amidopyridinate ligand

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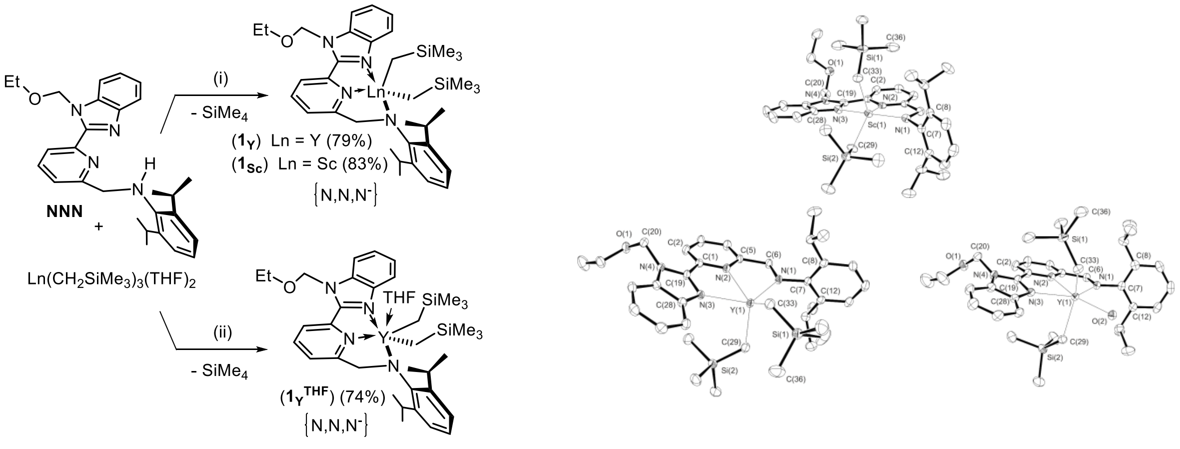
A range of new organo-rare-earth compounds incorporating N,N,N-amidopyridinate ligand has been prepared. Addition of **NNN** to $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y) affords bis(alkyl) compounds **1**$_{\mathbf{Ln}}$ in reasonable yields.

It was found that depending on the reaction and workup solvents different coordination compounds could be isolated in the case of yttrium. The reaction in toluene followed by slow crystallization from cold toluene afforded the pentacoordinate species **1**$_{\mathbf{Y}}$, while the use of hexane as reaction solvent with the subsequent recrystallization of the product from cold THF/hexane mixture (1/4) allowed the formation of hexacoordinate compound 1_{Y}^{THF}. As for scandium, the only non-solvated pentacoordinate compound **1**$_{\mathbf{Sc}}$ was isolated regardless the solvent. All obtained derivatives have been crystallographically characterized.

To widen the application range of the newly synthesized complexes, they were evaluated as catalysts precursors for the polymerization of isoprene. Ternary catalytic systems **1**$_{\mathbf{Ln}}$/$AlBu^i_3$/borate allowed the formation of polyisoprene with predominant 1,4-cis-content (up to 98%) within the period of 6–18 h. Notably, unlike in the case of scandium species, the catalytic performance of the yttrium compounds was found to be totally dependent on the borate nature.

All the complexes **1**$_{\mathbf{Ln}}$ were also tested as pre-catalysts for the intermolecular C-N, C-S and C-P bond formation reactions. For these hydroelementation trials, styrene was allowed to react with equimolar amounts of amines, phosphines and thiols in the presence of the compounds **1**$_{\mathbf{Ln}}$. The complexes showed 100% regioselectivity giving exlusively anti-Markovnikov addition products in all cases regardless the nature of E-H (E = N, S, P) reagent used.



Scheme 1. Synthesis of dialkyl compounds 1_{Ln}

Acknowledgements

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MOCVD of epitaxial vanadium dioxide films by pyrohydrolysis of vanadium(IV) b-diketonates

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The epitaxial vanadium dioxide films exhibit the sharp metal-insulator transition (MIT) at the closest-to-the-room temperature among oxide materials with intensive resistivity change (in >10^4 times). At the critical temperature (T_c) the vanadium dioxide transforms from a low-temperature insulating monoclinic phase (MoO_2 structure) to a high-temperature metallic tetragonal phase (TiO_2 rutile structure). The T_c value of vanadium dioxide can be changed by high pressure and doping [1]. Nowadays it is known that the phase transition in VO_2 thin films can be triggered by electrical or optical excitations. Also at MIT temperature the optical reflectance in IR and THz range changes in several times that opens prospective applications of VO_2 as a key component of different ultrafast switch electronic and optic devices.

The chemical vapor deposition (CVD) is one of the most effective industrial technology that is able to obtain high quality films of functional materials without using of ultrahigh vacuum system. To this moment the CVD method has not been widely using due to the absence of demonstrative results showing the formation of high quality VO_2 with excellent physical properties. Among chemical vapor methods of polycrystalline vanadium dioxide film synthesis the variety of metal-organic CVD (MOCVD) techniques based on destruction of volatile vanadium metal-organic compounds have been described.

To our opinion the pyrohydrolysis reaction based on the nonoxidative reaction of the vanadium(IV) precursor is the most perspective way for stabilization of pure VO_2 phase in the film composition and epitaxial growth from gas phase. In this work we investigate the CVD approach for deposition of epitaxial VO_2 films using reaction between different vanadium(IV) b-diketonate $VO(dik)_2$ (dik = acac, thd, hfa) and water vapor at temperature range 350-600°C. We considered the efficiency of vanadium precursors (volatility, thermal stability, deposition rate) and compared the structures, morphology and MIT characteristics of VO_2 films obtained on different substrates.

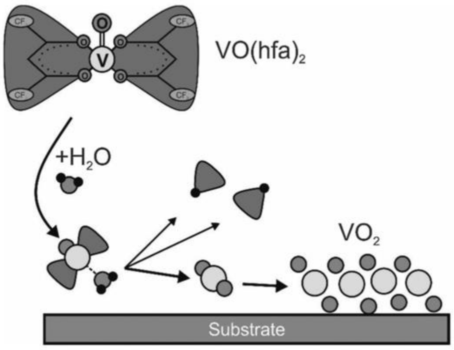

Figure 1. The scheme of reaction between $VO(hfa)_2$ molecule and water resulted in VO_2 formation.

Acknowledgements

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Synthesis and properties of layered phosphides $Ba(A_{1-x}B_x)_2P_2$ (A, B=Cr, Mn, Co, Ni)– analogues of superonducting family 122

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Layered phosphides $Ba(A_{1-x}B_x)_2P_2$ (A, B=Mn, Cr, Co, Ni) are isostructural analogues of $BaFe_2As_2$ – parent compound of superconducting family 122. The study of their crystal structure and physical properties is directly related with the research of unconventional superconductivity. Also, it is interesting to establish the influence of d-element nature on typical structure and magnetic transitions which are characteristic for family 122. Synthesis was conducted by crystal growth from tin flux. Synthesis conditions, specified in the literature, were modified in the course of increasing the quality and size of crystals. For example, to removing of tin residue and by-products of synthesis, different methods can be used: dissolving in hydrochloric acid, in ethanol, water, exposure to ultrasound. As it turned out, crystals with different composition react on the effects mentioned above in various ways. This is the reason why selection of conditions for flux removing was produced.

Firstly, single crystals with composition BaT_2P_2 (T = Mn, Co, Ni) were obtained. Compositions of crystals were confirmed by EDX and XRD. The dependence of the parameter c change for BaT_2P_2 in range of d-metals (Mn, Fe, Co, Ni) was built. The obtained decrease of parameter ***c*** is in good agreement with the dependence observed in the series BaT_2As_2. The study of single crystals by ARPES showed that there is a noticeable improvement in the quality of measurements in comparison with arsenide analogs. Secondly, series of mixed phosphides was obtained. According to the EDX, they have composition $Ba(Co_{0.9}Mn_{0,1})_2P_2$, $Ba(Mn_{0,89}Cr_{0,11})_2P_2$, $Ba(Co_{0,84}Cr_{0,16})_2P_2$. Compared to arsenide analogues, we couldn't obtain mixed phosphides with high level of substitution ($x > 0.1$□0.15). Research of $Ba(Co_{0.9}Mn_{0,1})_2P_2$ by single crystal XRD showed that tin is present in the structure, partially replacing barium. The effect of substitution on the crystalline and electronic structure of compounds is discussed.

This work was supported by RSF (Project 19-43-04129)

Boron cluster anions $[B_nH_n]^{2-}$ (n = 10, 12) in the synthesis of zinc(II) and cadmium(II) complexes with imidazole derivatives: structural features and properties

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The reactivity of the boron cluster anions $[B_nH_n]^{2-}$ (n = 10, 12) in Cd(II) and Zn(II) complexation in the presence of imidazole derivatives L (Fig. 1a) are studied. Inner- and outer-sphere complexes $[ML_2[B_nH_n]]$ or $[ML_3][B_nH_n]$ are formed.

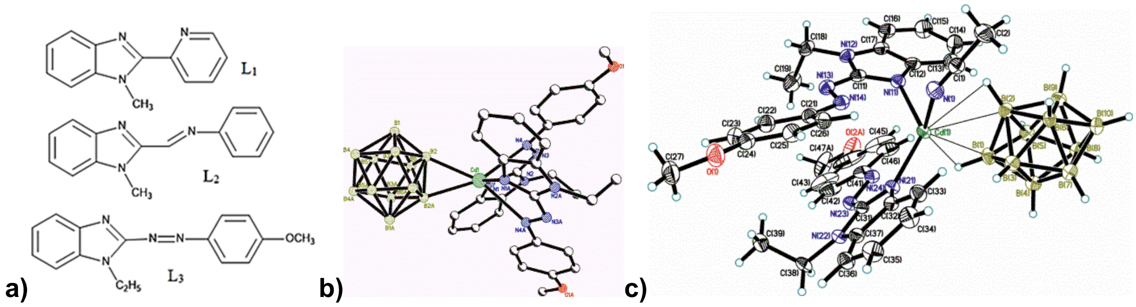

Figure 1. (a) Ligands used in the work; fragments of structures of **(b)** $[Cd(L^3)_2[B_{12}H_{12}]]$ and **(c)** $[Cd(CH_3CN)(L^3)_2[B_{10}H_{10}]]$.

tris-Chelate complexes $[ZnL_3][B_{10}H_{10}]$ were obtained by the interaction of $[Zn(H_2O)_6][B_{10}H_{10}]$ with a three-fold excess of ligand L in acetonitrile. According to X-ray diffraction, the coordination environment of the zinc atom in the complex with L^1 is formed by three imidazole N atoms and three pyridine N atoms.

The inner-sphere mononuclear Cd(II) complexes $[M(L^3)_2[B_nH_n]]$ were obtained by the interaction between $[Cd(DMF)_6][B_nH_n]$ with L^3 in acetonitrile. In the structure of $[Cd(L^3)_2[B_{12}H_{12}]]$ (Fig. 1b), the coordination polyhedron is formed by the N atom of the imidazole ring and the N atom of the azo group to form a five-membered metallocycle, and the BH bonds of the *closo*-dodecaborate anion. In complex $[Cd(CH_3CN)(L^3)_2[B_{10}H_{10}]]$ (Fig. 1c), acetonitrile forms the coordination sphere of the metal in addition to L^3 molecules.

The coordination mode of L^3 ligand (mono- or bidentate cyclic) and the coordination environment of the central atom affect the character of the luminescence spectrum. Thus, the presence of the *closo*-dodecaborate anion in the outer sphere of the complex led to a hypsochromic shift of the luminescence maximum, while the inner-sphere coordination resulted to its quenching.

Acknowledgements

This study was performed within the framework of the state assignment of the Kurnakov Institute in the field of fundamental scientific research.

Synthesis of Functionalized Selenophenes by Stepwise Assembly of Isocyanide, Alkynes and Se Units on a Diiron Frame

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The sequential reactions of the easily available $Fe_2Cp_2(CO)_4$ with CNMe/Me^+ (1),[1] NCMe/Me_3NO (2), a terminal alkyne (3), gray selenium/NaH (4) and an acetylene(di)carboxylate (5) leads to 1-(2-amino)-selenophene-alkylidene diiron complexes.[2,3] The bridging alkylidene carbon is displaced from coordination to the diiron frame upon straightforward treatment of the complexes, in solution of 1,2-dimethoxyethane, with water; this procedure results in the formation of multiply functionalized selenophenes, which have been isolated in high yields upon alumina purification.

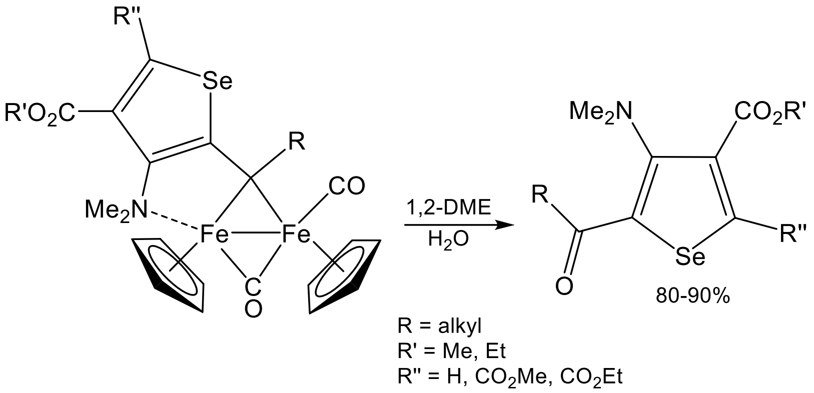

Figure 1. Hydrolysis of selenophene-alkylidene bridging ligand in diiron complexes

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Glass and ceramics formation in fluorozirconate-phosphate systems doped with REE

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Fluorophosphate glasses are potential precursors for glass ceramics and materials for modern photonics.[1] The effect of the sodium and lithium metaphosphates on the glass properties and ceramic in the fluorozirconate-phosphate systems doped with REE ions was investigated.[2, 3]

Glass formation and crystallization in the systems ZB – MPO_3, ZBLA – MPO_3, ZBLAN – MPO_3, (M = Li, Na) doped with REE trifluorides (EuF_3, ErF_3, NdF_3) were studied. The addition of the phosphate component up to 15-20 mol.% reduced the glass transition temperature (T_g) and the temperature of the onset of crystallization (T_x). According to NMR data, the structure of the obtained glasses is similar to that of fluorozirconate glasses. The depolymerization extent of the phosphate component is low. The temperatures of the transition of fluorine containing groups to local reorientational motions and onset temperatures of the fluoride ions translational motion are comparable to that for the fluoride glasses and have weak dependence on the glass composition. The heat treatment of glasses in the temperature range T_g-T_x caused the crystallization of nanoscale particles, the composition of which corresponded to β-$BaZrF_6$. SEM images of the samples confirmed the globular structure of the initial glasses and the obtained glass-ceramics. It has been established that REE ions are predominantly in the fluoride environment. Heat treatment decreased the luminescence intensity of the obtained ceramics in the visible region.

Introduction of lithium and sodium metaphosphates in the amount of 25-89 mol.% causes the crystallization processes in the studied systems. At 89-98 mol % $LiPO_3$ the crystalline phase of ZrP_2O_7 was formed, whereas at 89–97 mol.% $NaPO_3$ the $Zr_{2.25}(PO_4)_3$ was formed. The color of these vitreous samples changed from slightly opalescent to white depending on the content of ZBLA (ZB).

The most optimal conditions for the synthesis of glass ceramics are the composition of 5–10 mol % of $LiPO_3$ ($NaPO_3$), and the heat treatment time of 2–3 hours.

Acknowledgements

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Synthesis and characterization of new half-sandwich arene-ruthenium complexes with 11*H*-indeno[1,2-b]quinoxalin-11-one oxime analogs

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Chemistry of half-sandwich arene-ruthenium(II) complexes has been intensively developed in the recent years, due to their catalytic activity in hydrogen transfer reactions, alkene polymerization, ring opening metathesis polymerization, and olefin oxidation.[1]

Our group has been involved in the development of the coordination chemistry of new polycyclic ligands, containing N,N'- chelating fragment, which confers unusual physical and chemical properties on the corresponding Ru(II) complexes. Previously, we demonstrated the synthesis of new polycyclic N-containing ligands - 11*H*-indeno[1,2-b]quinoxalin-11-one oxime analogs.[2] Here we describe further studies of these ligands. It has been shown that such polycyclic compounds are capable of acting as chelating agents, forming mono- and binuclear coordination compounds. We report the synthesis of 4 new η6-arene-Ru(II) complexes with 11*H*-indeno[1,2-b]quinoxalin-11-one oxime analogs and tryptanthrin-6-oxime, a derivative of natural alkaloid tryptanthrine.

Complexes were prepared in high yield by the reaction between η6-arene-ruthenium dimer $[Ru(cym)Cl_2]_2$ (cym = p-cymene) and the appropriate ligand in methanol or methanol/DMF mixture. It was shown that even in the absence of a base, deprotonation occurs, and the ligands are coordinated in anionic form.

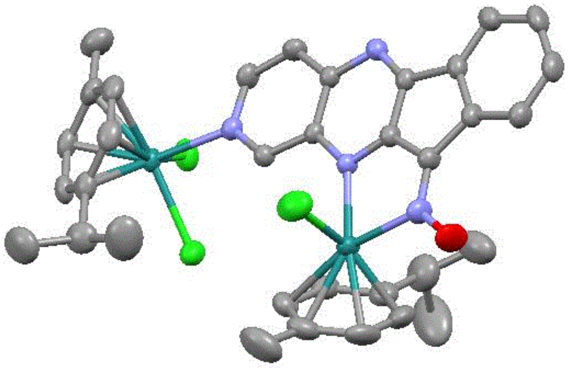

Figure 1.Molecular structure of binuclear η6-arene-Ru(II) complexe with 10H-indeno[1,2-b]pyrido[3,4-e]pyrazin-10-one oxime

Acknowledgements

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NP's in nanospheres produced with atomic precision

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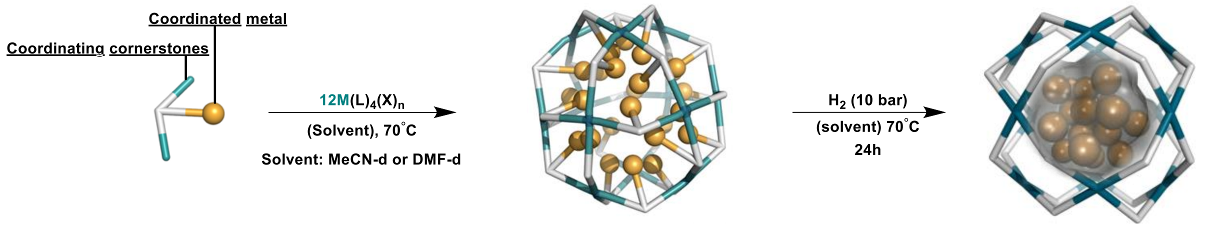
Recently it was discovered in our group that by reduction of coordinated Rh and Ir, pre-organized inside a nanosphere, nanoparticles can be prepared in a confined space (Figure 1).1) This phenomenon can be of great interest, because by pre-organizing the metals in a sphere, a nanoparticle with a precise number of metal atoms can be prepared.

With this atomic precision, detailed information could be obtained on the synergistic effects of alloying metals and specific nanoparticle size for the hydrogenation of olefins. Therefore, it is proposed to expand this concept to preparation of well-defined nanoparticles of other metals that would be promising as hydrogenation catalysts (individual or alloyed), and explore possibly unique activity and/or stability as a result of these precise compositions and/or sizes.



24 x monomer building block

$M_{12}L_{24}$ Nanosphere

A well defined nanoparticle: Containing a known number of metal atoms

Figure 1. Visual representation of self-assembly of the nanosphere and subsequent particle formation

Doubly coated, organic – inorganic paraffin phase change materials: ZnO_2ZnO coating of hermetically encapsulated paraffins

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A way to benefit from the favorable attributes of both organic microencapsulation, including the hermetic sealing of the organic PCM core, and inorganic microencapsulation, including dispersibility in aqueous and polar solvents and improved thermal conductivity, is outlined. The approach is demonstrated by uniformly coating organic polymer encapsulated PCMs with zinc oxide, which allows thermal percolation through the interconnected inorganic shells. We demonstrate that hydrogen peroxide sol-gel processing can be used to form such uniform zinc peroxide coatings which are then converted by chemical treatment to zinc oxide shells.

The way to overcome different challenges associated with the synthesis of thin film coatings of organic PCMs by zinc oxide are addressed, and the favorable attributes (thermal conductivity and dispersibility in solvents) of the new doubly coated PCM capsules are demonstrated.

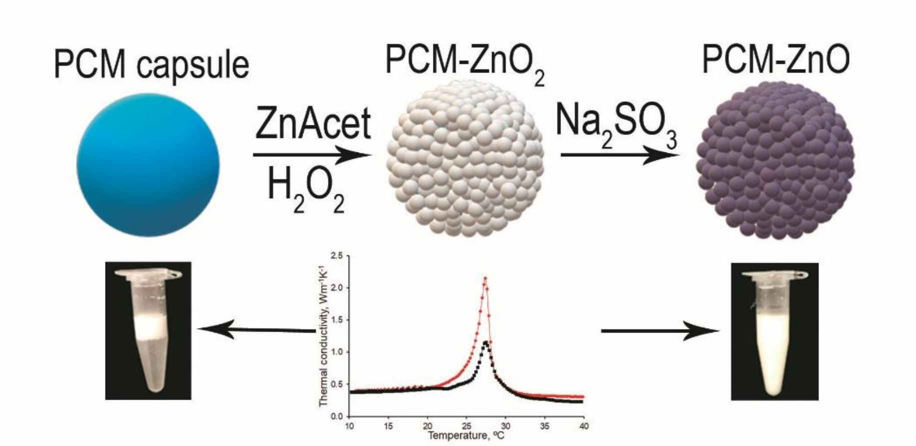

Figure 1. Scheme of ZnO coating formation on organic PCM surface

Acknowledgements

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Slow magnetic relaxation effect and sensitized near-infrared emission in lanthanide(III)(4,4’-azopyridine-1,1’-dioxide)[Co^{III}(CN)$_6$]$^{3-}$ layered frameworks

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Within the field of inorganic chemistry, there is a growing interest in searching for multifunctional materials combining optical and magnetic properties. Of special importance are metal complexes called Single Molecule Magnets (SMMs) which possess strong magnetic anisotropy giving rise to the slow magnetic relaxation.[1] As a result, they can exhibit the magnetic hysteresis of a molecular origin, similar to that observed in permanent magnets. SMMs are considered as promising candidates for applications in molecular spintronics, quantum computing and data storage.[2,3] Most promising elements in construction of SMMs are trivalent lanthanide ions showing strong magnetic anisotropy related to the combined role of spin-orbit coupling and crystal field effects. Among them, the magnetically axial complexes of Dy(III) exhibit the highest blocking temperatures exceeding 80 K.[4] By employing 4f metal ions in synthesis of SMMs one can also observe photoluminescence related to their f-f electronic transitions. Therefore, the attractive luminescent SMMs are achieved.[5] We focused on the preparation of emissive molecular magnets by using 4f metal ions inserted into coordination networks with cyanide metal complexes and supporting organic ligands.[6] We present a series of layered coordination polymers, $\{[\mathrm{Ln^{III}}(\mathrm{apdo})(\mathrm{H_2O})_4]\mathrm{Co^{III}}(\mathrm{CN})_6]\}\cdot 2\mathrm{H_2O}$ (**Ln(apdo)Co**, Figure 1, Ln = Nd, Tb, Dy, Er, Tm, Yb; apdo = 4,4’-azopyridine-1,1’-dioxide) exhibiting field-induced slow magnetic relaxation and photoluminescent properties, including sensitized NIR emission of Nd^{III} and Yb^{III}.[7]

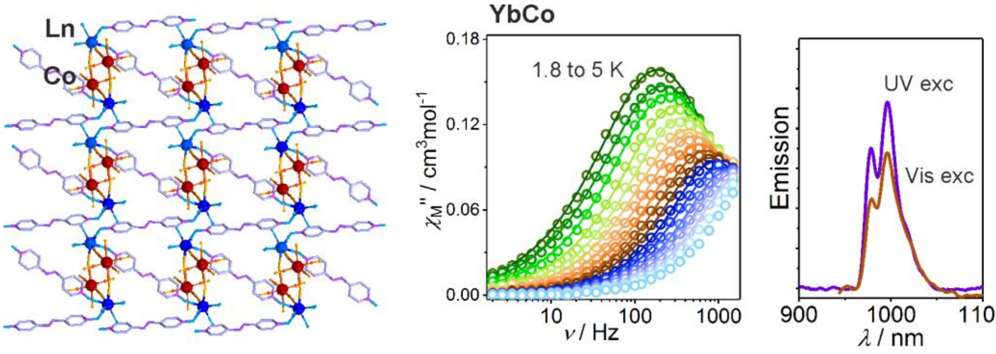

Figure 1. Crystal structure, slow magnetic relaxation and NIR luminescence of Ln(apdo)Co layers.

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A microporous Co(II) - based 3-D metal organic framework built from magnetic infinite rod-shaped secondary building units

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Metal organic frameworks (MOFs) is a class of porous materials that has attracted tremendous research attention over the past decade for many reasons. These include their intriguing crystal structures[1] and interesting physical properties that lead to potential applications in a series of areas[2] including gas storage and separation,[3] catalysis,[4] sensing,[5] magnetism,[6] etc. Particular attention has been devoted to multifunctional MOFs combining two or more interesting properties.

Recently we have been investigating the synthesis of new MOFs based on polytopic pyridyl carboxylate ligands. These have been proven to be excellent ligands for the construction of multidimensional coordination polymers due to the ability of their N donor atoms to bind most of the metal ions and the high bridging capability of their carboxylate groups. We will discuss the synthesis, characterization and properties of a new MOF **$\{[Co_5(INA)_3(HCOO)_7(DMF)(H_2O)]$**$\cdot 2DMF \cdot 4H_2O\}_\infty$ denoted as [**Co_5-INA**] (INA^- = the anion of isonicotinic acid). **Co_5-INA** exhibits a rigid 3D porous structure that is based on a rod secondary building unit (SBU) which consists of Co_5 repeating units with a unique Co/O core. **Co_5-INA** shows a BET area of 264.5 m^2g^{-1} and CO_2 uptake of 1.96 mmol g^{-1} at 273 K/1 bar. Magnetic measurements revealed that it displays a spin canting behavior with a spin glass relaxation process at ~5.0 K.

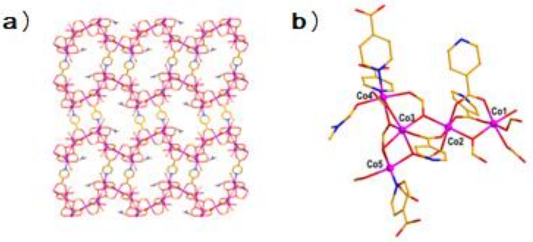

Figure 1. Representations of the **a)** 3D porous structure and **b)** Co_5 repeating unit of Co_5-INA**.**

Acknowledgements

The Project ΚΟΥΛΤΟΥΡΑ/BP-NE/0416/06 is financed by the Republic of Cyprus through the Research Promotion Foundation.

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Hydrotalcite-like hydroxides of Al, Mg, Ni, Co - catalytic materials for partial oxidation and dry reforming of methane.

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Catalysts based on hydrotalcite-like hydroxo salts $[AlMg_2Ni_xCo_y(OH)_{6.08}][(NO_3)nH2O]$, where x = 0, 0.005, 0.01, 0.02, 0.03, 0,035, 0.04 and y = 0.04, 0.035, 0.03, 0.02, 0.01, 0.005, 0 with a small total Ni and/or Co content of no more than 2 wt. % have been first studied In partial oxidation of methane and dry reforming of methane to synthesis gas. Synthesis gas (SG), a valuable intermediate product of petrochemistry, is predominantly produced by expensive endothermic methane steam reforming process. The SG with the ratio of $H_2/CO> 3$ obtained by methane steam reforming requires further processing for its further use in the synthesis of methanol and Fischer-Tropsch synthesis, and oxo synthesis. The SG with ratio of $H_2/CO = 2$, or less and acceptable for above mentioned processes can be obtained using the reactions of partial oxidation of methane (POM) or dry reforming of methane (DRM). Well-known Ni catalysts of POM and DRM are deactivated due to coke deposits formation or the formation of inactive nickel compounds with carriers. So, creation of selective and stable POM and DRM catalysts is actual task.

It has been shown that the catalysts with x= 0.03-0.04 and y= 0.01-0 provide a synthesis gas yield up to 98% in the case of partial oxidation and dry reforming of methane. In the presence of these catalysts, a trace amount of carbon nanotubes is formed. Ni catalyst demonstrates stability in POM and DRM more than 50 h time on stream.

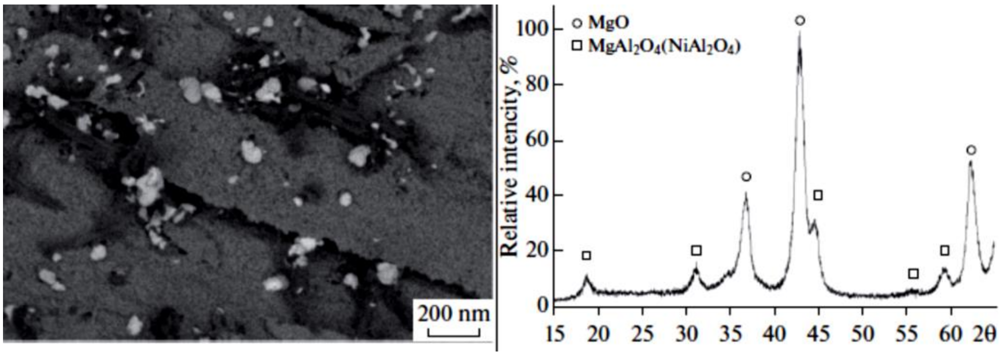

Figure 1. (left) SEM micrograph and (right) X-ray powder diffraction pattern of Ni sample after DRM catalysis

Acknowledgements

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Novel cyclopentadienyl rhodium iminophosphonamides

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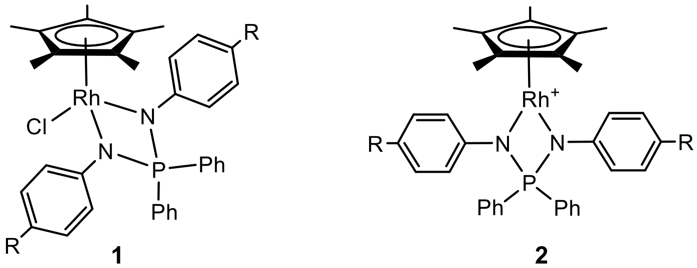
The iminophosphonamide ligand [RN-PR'$_2$-NR]$^-$ is a strong σ,π-donor and has been shown to efficiently stabilize electron-deficient species.[1] Its zwitterionic nature causes localization of high electron density on N-atoms making them reactive towards electrophilic centers, that has been recently demonstrated for arene ruthenium iminophosphonamides.[2]

Here we report on the synthesis of novel half-sandwich rhodium iminophosphonamides: a series of 18ē (**1**) and 16ē (**2**) complexes differing by aryl substituents at the N-atoms. Their physico-chemical properties will also be discussed.



1 **2**

R = Me, iPr, OMe, COOEt

Figure 1. Half-sandwich 18ē and 16ē rhodium iminophosphonamides

Acknowledgements

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Structural and magnetic phase transitions in double perovskite $BiMn_7O_{12}$: probe Mössbauer diagnostics

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In recent years, due to the development of high pressure - high-temperature (HP-HT) synthetic approach, the family of double manganites AMn_7O_{12} was significantly expanded: the perovskite-like phases were obtained, where *A* cations are "unusual" from point of view of geometric size as well as electronic structure. It was shown that the introduction of Bi^{3+} cations with a lone electron pair into the structure is of particular interest. In combination with the Jahn-Teller character of the Mn^{3+} cations occupying pseudo-square (*A*') and octahedral (*B*) positions in the $AA'_3B_4O_{12}$ double perovskite structure, this leads to a significant distortion of the crystal lattice and the appearance of a whole cascade of temperature-induced structural phase transitions. In this case, the lattice symmetry consistently changes from triclinic to cubic ($P1 \rightarrow I2/m \rightarrow I2/m(o) \rightarrow Im\overline{3}$) with temperature increasing ($T_3 \approx 290$ K, $T_2 \approx 460$ K, $T_1 \approx 608$ K, respectively).[1]
In this work we present the results of the probe Mössbauer study of the double manganite $BiMn_7O_{12}$. Previously, this approach was successfully applied to the investigation of the features of the charge and orbital orderings in AMn_7O_{12} manganites (A = Ca, Cd, Sr, Pb), which also have a double perovskite structure.[2] The ^{57}Fe atoms were used as probe Mössbauer nuclides, introduced into the structure of $BiMn_7O_{12}$ manganite. The samples of $BiMn_{7-x}{}^{57}Fe_xO_{12}$ (x = 0, 0.04) manganites were synthesized under high pressure and high temperature conditions (6 GPa, 1323 K).
As a result of the research, the effect of impurity iron cations on the macroscopic properties (temperatures of structural phase transitions T_i, Néel temperature T_N) of bismuth manganite was studied in comparison with the undoped sample. The Mössbauer measurements of $BiMn_{6.96}{}^{57}Fe_{0.04}O_{12}$ were carried out in a wide temperature range above and below $T_{N1} \approx 53$ K. It was shown that probe ^{57}Fe atoms isovalently replace the Jahn-Teller Mn^{3+} cations in the octahedral sublattice, and each temperature range is characterized by the specific type of Mössbauer spectrum. It was demonstrated that the number of partial spectra Fe(*i*) and their hyperfine parameters (first of all, the quadrupole splittings Δ_i) are highly sensitive to the type of crystallographic structure of $BiMn_7O_{12}$ as well as to the nature of splitting and local environment of the manganese octahedral positions (Mn*i*).
In the magnetically ordered temperature range ($T < T_{N1}$), the spectra were presented as a superposition of several Zeeman sextets with a relaxation structure. It is assumed that the observed complex magnetic hyperfine structure is due to the dynamic behavior of the frustrated states of the paramagnetic impurity centers $^{57}Fe^{3+}$.

Acknowledgements

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Conjugation in hydrogen-bond networks: the role and manifestation

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Hydrogen bonds play a key role in innumerous chemical and biochemical processes. H-bond networks predetermine properties of the unique and, at the same time, universal solvent, water, and all aqueous solutions where either hydrophilic or hydrophobic solvation effects locally strengthen or weaken the inherent H-bond system of water. Monoatomic alkaline, alkaline-earth, and halide ions that are present in aqueous solutions act as either the so-called structure breaking or structure-making agents. Almost all biologically important or active particles and macromolecules form hydrogen bonds of one or another strength, and typical functional groups that provide the bonding are hydroxyl and amino ones, although weak H-bonds can appear also when a π-electron system of some usually aromatic molecular fragment act as a proton acceptor. As a result, aqueous solutions are characterized by extended hydrogen bond networks that involve local defects of Bjerrum's D or L kind, which can be traps of electron-excessive or electron-deficient particles, and are more or less distorted due to thermal motion, as well as rotational and vibrational excitation. All the particles involved in the extended H-bonded system can be considered as constituting a supramolecular ensemble, the internal dynamics of which is determined by the aforementioned factors.

Our nonempirical quantum chemical simulations of diverse hydrogen-bonded clusters composed of water, hydrogen fluoride, and ammonia molecules of either individual or mixed chemical nature, as well as hydrates of different small ions and biologically important relatively small molecules, which involve hydroxyl and/or amino groups, enabled us to prove the hypothesis[1] about the conjugation effect in hydrogen-bond networks that takes place when covalent and hydrogen bonds alternate within extended either open or closed H-bond sequences. The effect is manifested in the higher stability of clusters and in the non-additivity of H-bond energies. Another important manifestation of the effect, which is related to the peculiarities in the electron density distribution, is the appearance of characteristic vibrations within the high-frequency range that can be treated as a fingerprint of the conjugated H-bond systems. The larger the spatial domains of conjugated H-bond networks, the higher the absorption intensity in this narrow characteristic range.

Acknowledgements

Simulations were carried out with the use of the facilities of the HPC computing resources at Lomonosov Moscow State University[2]. The work was partially financially supported by the Russian Foundation for Basic Research, project no 19-03-00215.

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Hybrid catalysts based on graphene oxide and porphyrin metal-organic frameworks

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Decomposition of toxic organic substances using heterogeneous catalysis under the visible light irradiation is one of the most promising methods of wastewater treatment. Metal-organic frameworks (MOFs) are good candidates for application as photocatalysts due to their unique properties such as high surface area values and porosity. However, their chemical stability is often unsatisfactory.[1] Using composite materials containing MOF and a stabilization matrix is a promising solution.

Here, we used graphene oxide (GO) sheets as the stabilizing matrix and porphyrin based MOF as the photocatalytic component. Zinc (II) acetate was used as the metal cations source and two porphyrins (*meso*-tetra-(4-pyridyl)-porphyrin and *meso*- -4-pyridyl)-di-(4-carboxyphenyl)-porphyrin) were used as the organic linkers. The catalytic activity of zinc (II) porphyrinates is well known and it was successfully used in organic synthesis reactions, photodegradation of aromatic compounds and water decomposition for hydrogen production[2].

We used the emulsion technique for synthesis of the composite GO/porphyrin MOF catalysts. Two solvent systems were applied: water/chloroform and DMSO/hexane for meso-tetra(4-pyridyl)-porphyrin and meso-di(4-pyridyl)-di(4-carboxyphenyl) porphyrin correspondingly.

The model reactions of rhodamine-6G and 1,5-dihydroxynaphthalene (DHN) photobleaching were chosen for evaluation of the catalytic activity of the obtained materials. It was found that the nature of porphyrin plays a key role in ensuring the catalytic activity of the composite material. While the material based on meso-tetra(4-pyridyl)-porphyrin does not exhibit any catalytic activity, materials containing meso-di(4-pyridyl)-di(4-carboxyphenyl)-porphyrin decompose solutions of rhodamine 6G (Fig.1) and 1,5-dihydroxonaphthalene under visible light irradiation, that was detected by UV-Vis spectroscopy.

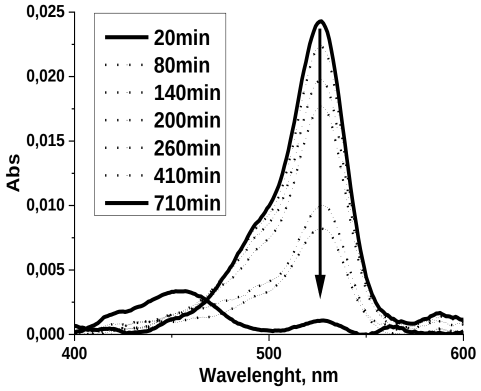

Figure 1. UV-Vis spectra of the photobleaching of a solution of rhodamine 6G under visible light irradiation in the presence of the composite based on meso-di(4-pyridyl)-di(4-carboxyphenyl)-porphyrin MOF

Acknowledgements

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A simple way from five-membered metallacyclocumulenes to five-membered metallacycloallenes

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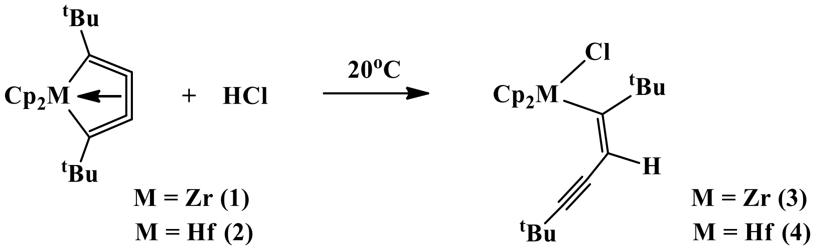
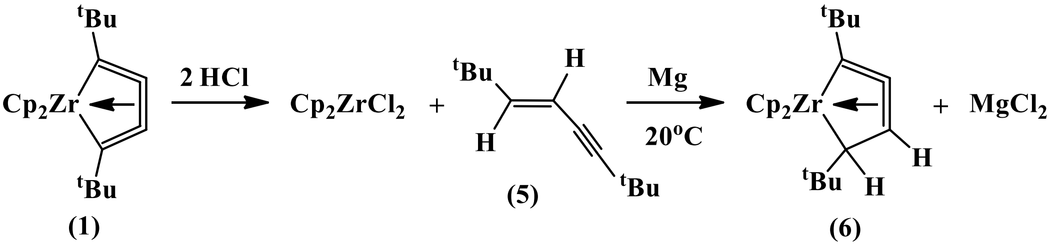
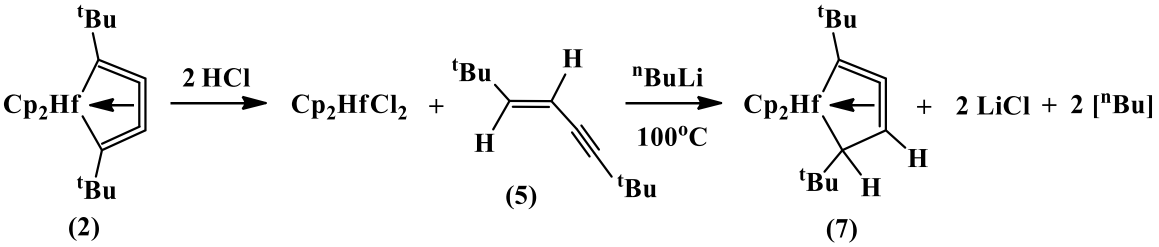
We have found that the reactions of five-membered zircona- and hafnacyclocumulenes (**1**) and (**2**) with equimolar amounts of HCl at 20°C result in the formation of σ-alkenyl complexes (**3**) and (**4**), respectively.



Under similar conditions, the interaction of **1** and **2** with two equivalents of HCl gives the corresponding metallocenedichloride and 1,4-di(*tert*-butyl)-*trans*-1-buten-3-yne (**5**). If a mixture of Cp_2ZrCl_2 and **5,** formed from **1** and HCl, is treated with Mg in THF at 20°C, the five-membered zirconacycloallene complex **6** is produced in 60% yield.



Analogously, the addition of two equivalents of ^{n}BuLi to the obtained mixture of Cp_2HfCl_2 and **5** followed by heating at 100°C affords the corresponding five-membered hafnacycloallene complex **7**.



Acknowledgements

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Palladium complexes of chiral diamine triphenylphosphine ligands: structural characterization and potential application to enantioselective catalysis

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Secondary structures play a key role in facilitating selectivity in supramolecular catalysis.[1] In nature, enzymes enable selectivity by having a well-defined tridimensional substrate binding site, supported by non-covalent interactions between amino acids in the backbone. In supramolecular catalysts, amino acids or other oligo-amides can also form well defined secondary structures, mainly by hydrogen bonding but also through other types of weak interactions, thus mimicking the natural active sites of enzymes.

In our previous work we have used supramolecular amino acid and diamine ligands in Rh (I) catalyzed enantioselective hydrogenation reactions with very high selectivity.[2] Since Rh (I) complexes can be prone to oxidation and problematic to study spectroscopically, we have synthesized and described Pt (II) Pd (II) complexes as model compounds to study these systems. The synthesized Pd (II) complexes are of additional interest as they form different structures than Rh (I) and Pt (II) complexes and can themselves be used as catalysts for different types of reactions such as allylation or hydroformylation. In this work we describe the solution structure of Pd (II) complexes by different instrumental methods (^{1}H, ^{13}C, ^{31}P NMR, UV, CD, x-ray, mass spectrometry) as a starting point for their application in enantioselective catalysis.

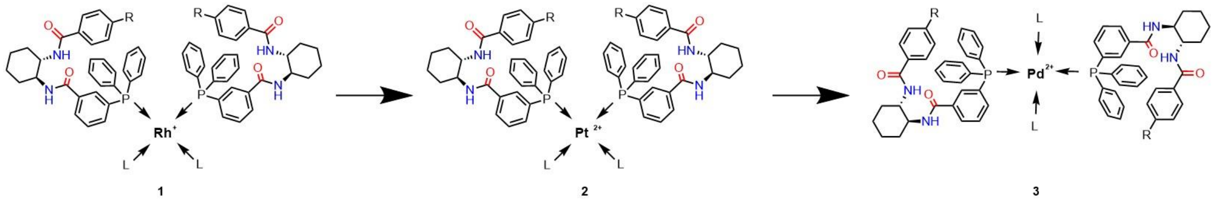

Figure 1. Catalytically active Rh complexes 1 which are modeled by Pt complexes 2 and the Pd complexes 3 currently under investigation

Acknowledgements

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INSERTION OF THE PhNCO AND CO₂ INTO TWO M-OR BONDS OF Ti(OEt)₄ ILLUSTRATED BY THE X-RAY DIFFRACTION STUDIES OF THE PRODUCT OF INNER-SPHERE HIDROLYSIS

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In a previous study [1] authors focused on the multiplet insertion by EtNCO into $Ti(OPr^i)_4$ on the basis of physical and chemical studies proposed that it contains the associated alkoxo-group on which there took place insertion, representing as 1-nylon. In contrast with our previous results the products of partial and complete hydrolysis of similar products of insertion into of W-Cl bond [2,3], for which there was or inner-sphere cyclization to formation of the corresponding ligand, or a formation of a heterocyclic compound. X-ray diffraction studies confirmed the initial assumption of the author [4] that in this case decarboxylation took place with the formation of isopropyl (Z) aniline (phenyl-imino) methyl (phenyl) carbamate. Apparently, this is due to the difference in heating modes in the experiment, namely due to the reaction at the boiling point of the solution, which, as might be expected, will stimulate decarboxylation.

X-ray microcrystalline x-ray diffraction data were obtained on the “Belok” beamline of the Kurchatov Synchrotron Radiation Source (National Research Center “Kurchatov Institute” Moscow, Russian Federation) in □-scan mode using a Rayonix SX165 CCD detector at 100K, the X-ray wavelength at 0.80246 Å. Primary indexing, refinement of the unit cell parameters, integration of reflections and correction for reflection intensity absorption were performed using the XDS program suite [5]. The complex structure was solved by direct methods and refined by full-matrix least squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were placed in the calculated positions and refined using the riding model with $U_{iso}(H) = 1.5 \times U_{eq}(C)$ for methyl and $1.2 \times U_{eq}(C)$ for methylene groups, respectively. The hydrogen atoms involved in the formation of hydrogen bonds were founded from the electron density map. The calculations were carried out using the SHELXTL software package [6]. Crystallographic data for the complex **I** have been deposited in the Cambridge Crystallographic Data Centre (CCDC 1896336). Main distances (Å.): of the molecule **I** :Ti(1)-O(1) 1.793(4) ;Ti(1)-O(2) 1.779(4); Ti(1)-O(3) 2.191(4); Ti(1)-N(1) 2.171(4); Ti(1)-N(2) 2.096(5); Ti(1)-N(5) 2.048(4) and angles (deg.) : O(1)-Ti(1)-O(2) 99.6(2); O(2)-Ti(1)-N(5) 102.5(2); O(1)-Ti(1)-N(5) 102.22(19); O(2)-Ti(1)-N(2) 96.96(19); O(1)-Ti(1)-N(2) 105.23(18); N(5)-Ti(1)-N(2) 142.97(18); O(2)-Ti(1)-N(1) 158.53(19); O(1)-Ti(1)-N(1) 90.45(19;); N(5)-Ti(1)-N(1) 93.76(18); N(2)-Ti(1)-N(1) 61.94(17); O(2)-Ti(1)-O(3) 92.61(19); O(1)-Ti(1)-O(3) 162.37(18); N(5)-Ti(1)-O(3) 62.44(16); N(2)-Ti(1)-O(3) 85.65(16); N(1)-Ti(1)-O(3) 82.41(15). This contrasts with the previously obtained results for products of partial and complete hydrolysis of similar products when embedded in the W – Cl bond [2, 3], which is accompanied either by cyclization within the coordination sphere with the formation of the corresponding ligand or the formation of a heterocycle, triphenyl (iso) cyanoureate. In the course of structural studies, it was confirmed by the authors [1] that the combined decarboxylation of the complexes followed by the hydrogenation of PhNCO leads to the formation of cyclohexyl fragments in the organic component.

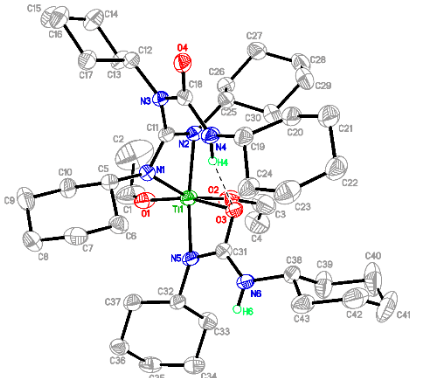

Figure 1. Molecular structure of complex **I**, thermal ellipsoids showed with 30% probability. Hydrogen atoms, except involved in the formation of intramolecular and intermolecular hydrogen bonds, are not shown.

Acknowledgements

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Heteroleptic phosphine-diimine Cu(I) and Ag(I) complexes: synthesis and photophysical properties

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Today growing interest toward heteroleptic phosphine-diimine Cu(I) complexes is observed due to their ability to demonstrate thermally activated delayed fluorescence (TADF) and thus potential usage as light-emitting materials for OLEDs.[1]

It is known that bulkiness of ligands plays the key role in photophysical properties of such complexes. Bulky surroundings can partly block excited-state flattening reorganizations and, thus, reduce emission quenching.

We synthetized a range of copper(I) complexes with bulky substituted 2,2'-bipyridines as diimine ligands and a set of various phosphines. It was found that an excessive bulkiness of symmetrical 2,2'-bipyridines prevents formation of heteroleptic complexes. By contrast, reaction with asymmetrical diimine ligand resulted in target compounds with high yields.

Although silver is nearest group analogue of copper and can form isostructural coordination compounds, Ag(I) complexes have different photophysical properties. However, recently heteroleptic Ag(I) complexes demonstrating TADF have been described.[2] Herein we report the silver(I) complexes, which are isostructural to copper(I) complexes described above.

The complexes obtained were characterized by polynuclear NMR spectroscopy, ESI mass spectrometry, and single X-ray analysis. Optical and photophysical properties of Cu(I) and Ag(I) complexes were investigated.

Acknowledgements

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Design of the convenient molecular precursors for the heterogeneous oxo/imido heterometathesis catalysts

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As a part of the research program aiming at application of early transition metal imido complexes in organic synthesis we have previously described a novel catalytic C=N bond formation strategy based on the oxo/imido heterometathesis reaction.[1] Being used as catalysts, silica-supported titanium imido complexes show high activity and allow reaching quantitative conversions and high yields in imidation of carbonyl compounds with *N*-sulfinylamines. In order to establish the structure–activity relationship and develop more active catalytic systems we synthesized and characterized a number of new monomeric titanium imido complexes having general structure shown in Fig. 1, which were then used as precursors for the silica-supported catalysts. In current study we took advantage of the accessibility of *tert*-butylimido starting materials and focused on the convenience of 2,5-dimethylpyrrolyl ligand easily and purely replaceable upon interaction with the surface hydroxyl groups of silica. Variation of the nature (donor/acceptor properties and steric hindrance) of the X-type ligands and coordination number of the metal allowed us to track the general trends in the catalyst activities.

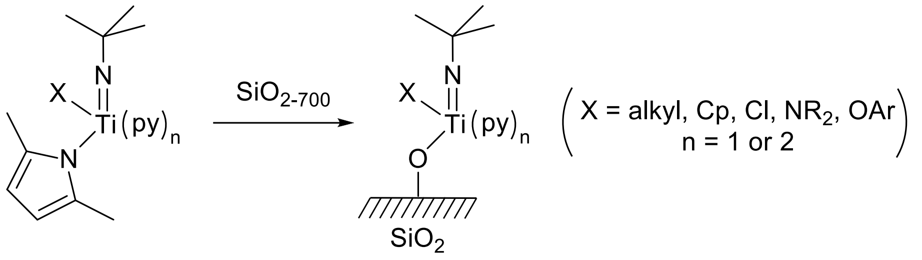

Figure 1

Acknowledgements

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$Cu_{26-x}Fe_xA_2Sn_6S_{32}$ (A = V, Ta) colusites: crystal and local structures and thermoelectric properties

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In recent years, unsubstituted colusites, $Cu_{26}A_2M_6S_{32}$ (A = V, Nb, Ta; M = Ge, Sn), and solid solutions on their base, have been actively studied as promising thermoelectrics[1], due to the combination of their high thermoelectric efficiency and ecological-friendly chemical composition. The actual problems are the precise study of crystal and local colusites structures and their correlation with the composition and thermoelectric properties.

In our work, we have shown for the first time an opportunity of obtaining Fe-contained colusites, $Cu_{26-x}Fe_xA_2Sn_6S_{32}$ (A = V, Ta; x = 0÷4.5). The homogeneity range was determined as 4.5 ÷ 5.0 atoms per formula unit. The structures of the compounds were accurately refined based on synchrotron diffraction experiments at room temperature. For analyzing the correlation between the local structure and iron content and to confirm the structural data ^{57}Fe Mössbauer study of $Cu_{26-x}Fe_xV_2Sn_6S_{32}$ (x = 1.0, 2.0, 3.0, 4.0) was performed. The presence of iron in both Fe^{2+} and Fe^{3+} oxidation states, changing within the homogeneity range, and its tetrahedral coordination were found. The thermoelectric properties measurements for $Cu_{26-x}Fe_xA_2Sn_6S_{32}$ (A = V, Ta; x = 1.0, 2.0, 3.0, 4.0) in the 300 ÷ 700 K temperature range have shown the perceptible difference in the Seebeck coefficient, electrical resistivity and thermal conductivity depending on the nature of the A and iron content. However, the thermoelectric figure-of-merit increases with the temperature for all samples, and at 700 K ZT_{max} reaches 0.8 and 0.3 for $Cu_{25}FeV_2Sn_6S_{32}$ and $Cu_{24}Fe_2Ta_2Sn_6S_{32}$ respectively.

Acknowledgements

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Electrical conductivity and structure of molten PCl_5−MCl_n (M - polyvalent metal) mixtures

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Phosphorus pentachloride forms of complex compounds $xPCl_5 \cdot yMCl_n$ with chlorides of polyvalent elements contain PCl_4^+ cations and $M_kCl_{kn+m}^{m-}$ (k = 1, 2) anions. All of these salts are low melting and volatile substances. In molten state near the melting point, they have very low values of electrical conductivity: 10^{-10} - 10^{-4} S/cm for molecular liquids PCl_5, $MoCl_5$, $TaCl_5$, $ZrCl_4$, $AlCl_3$, $GaCl_3$, $FeCl_3$, $TiCl_4$, $SnCl_4$ and 10^{-3} - 10^{-4} S/cm - for polymer-like melts $ZnCl_2$ and $BeCl_2$.

Due to the high vapor pressure of these melts, a special sealed cell was designed to measure their electrical conductivity. It was made of quartz and contained Ni, W or carbon electrodes. For measurements, an AC-bridge with an input frequency of 10 kHz was used. The mixtures were prepared by fusing the components in evacuated and sealed quartz ampoules.

The conductivity of all these molten mixtures increases with the temperature increase, as it is shown in Figure 1, using the example of the $ZnCl_2$-PCl_5 system. The inflection points on the electrical conductivity polytherms correspond to the crystalline $ZnCl_2$ or $ZnCl_2 \cdot PCl_5$ phases deposition upon cooling.

The electrical conductivity of molten MCl_n - PCl_5 mixtures is by 1-9 orders higher than that of pure molten salts. The greatest increase is observed at small additions of PCl_5 (0 - 15 mol.% PCl_5). The specific conductivity of molten mixtures containing 25 –50 mol.% of phosphorus pentachloride varies slightly with concentration. All highly concentrated mixtures demonstrate high values of electrical conductivity (~0.1 $Ohm^{-1} \cdot cm^{-1}$ at 400 ^{0}C), which is typical for ionic melts. Therefore, a great rise of conductivity, which is observed at non-conducting molecular or polymer-like salts mixing, can be explained by the formation of charged particles, like complex PCl_4^+ cation and complex anions like $TiCl_5^-$, $Ti_2Cl_9^-$, $SnCl_5^-$, $AlCl_4^-$, $Al_2Cl_7^-$, $TaCl_6^-$, as a result of chemical interaction. Such ions were found *in situ* in the melts containing phosphorus pentachloride by the Raman spectroscopy. The regularities revealed for the most of molten salt compositions are caused by the formation of complex chloride cations and anions of phosphorus and polyvalent metals, which makes possible the charge transfer.

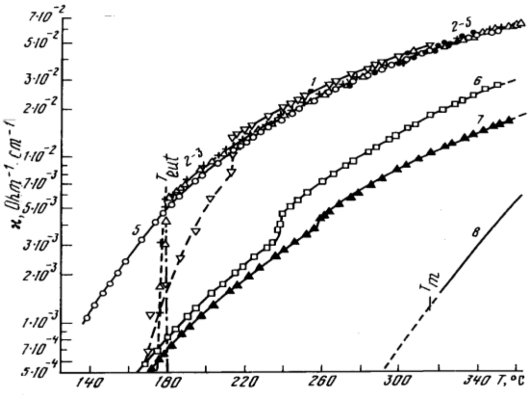

Figure 1. Temperature dependence of specific conductivity of $ZnCl_2$-PCl_5 molten mixtures (1-7) and $ZnCl_2$(8): 1 - 47; 2 - 31; 3 - 30; 4 - 26; 5 - 23; 6 -12; 7 - 6 mol.% of PCl_5

New rare-earth metal complexes coordinated by polydentate NNN ligand. Synthesis, structures and catalytic activity in hydrosilylation of unsaturated substrates

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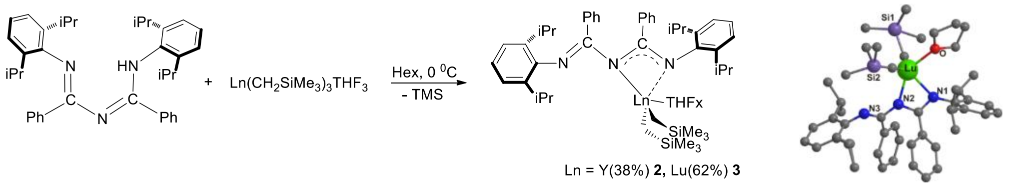
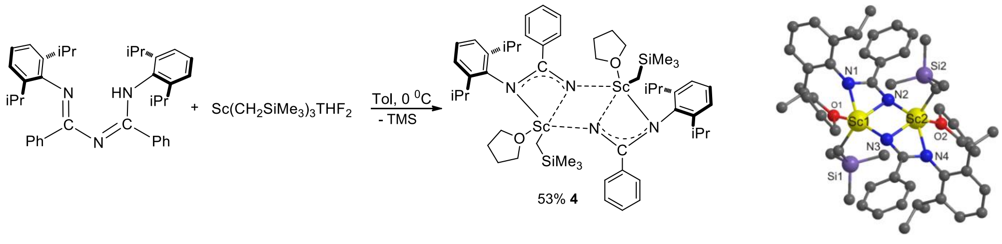
The reaction of 1,3,5-triazapentadiene $i\mathrm{Pr_2C_6H_3NC(Ph)NC(Ph)NHC_6H_3}i\mathrm{Pr_2}$ (**1**) with rare-earth tris(alkyl) complexes $\mathrm{Ln(CH_2SiMe_3)_3(THF)_2}$ (Ln = Y, Lu) in hexane at 0 °C is accompanied by TMS elimination and affords corresponding bis(alkyls) $[i\mathrm{Pr_2C_6H_3NC(Ph)NC(Ph)NC_6H_3}i\mathrm{Pr_2}]\mathrm{Ln(CH_2SiMe_3)_2(THF)_x}$ (Ln =Y (**2**), Lu (**3**)) (Scheme 1). However, in contrast to the complexes of transition metals in which the NNN ligand **1** coordinates to the metal centers forming six-membered NCNCNM metallocycles, in bis(alkyl) complexes **2** and **3** ligand **1**, coordinates to the metal ion in "amidinate" fashion resulting in the formation of four-membered metallocycle (Scheme 1).

The alkane elimination reaction of **1** with $\mathrm{Sc(CH_2SiMe_3)_3(THF)_2}$ in toluene is accompanied by the cleavage of C-N bond of 1,3,5-triazapentadiene and affords mono(alkyl) complex $[i\mathrm{Pr_2C_6H_3NC(Ph)NSc(CH_2SiMe_3)THF}]_2$ (**4**) coordinated by amidinate ligand (Scheme 2).

The catalytic hydrosilylation of unsaturated substrates with phenylsilane using complexes **2**–**4** as catalysts has been examined. Complexes **2**–**4** are active in the catalysis of hydrosilylation of 1-nonene, 1,5-hexadiene, 1-heptin with $\mathrm{PhSiH_3}$. The reactions selectively provide the anti-Markovnikov addition products in quantitative yields within 1 h at 20 °C. The reactions of $\mathrm{PhSiH_3}$ with 2-methylstyrene, styrene, divinylbenzene and cyclohexene proceed in quantitative yield in 48 h. The mono(alkyl) scandium complex **4** was found to be more active in the hydrosilylation reactions compared to the yttrium and lutetium bis(alkyl) compounds **2**–**3**.



Scheme 1. The synthesis of bis(alkyl) rare-earth complexes 2 and 3



Scheme 2. The synthesis of mono(alkyl) complex 4

Acknowledgements

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The 3rd degree of biomimetism: associating the cavity effect, Zn^{II} coordination and internal base assistance for guest binding and activation

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Supramolecular modeling of metallo-enzyme active sites[1] by Resorcinarene-based *Bowl Complexes* is reported. They display a biomimetic coordination core with either three[2] or four[3] imidazole groups at the large rim of the macrocycle (**Rim$_3$** and **Rim$_4$**, respectively). Both presents two labile coordination sites, one under the control of the resorcinarene cavity, the other exposed to the solvent. Their host-guest properties together with some reactivity studies will be presented and compared. Quite remarkably, the 4th imidazole arm promotes binding of an acidic molecule by acting as an internal base, which allows guest binding as an anion to the metal center in endo position. Most importantly, the presence of this labile imidazole arm makes the Zn^{II} complex active for the catalyzed hydration of acetonitrile. This system presents a high degree of biomimetism when considering zinc enzymes: a pocket for guest binding, a similar first coordination sphere, a coordination site available for water activation in cis position relative to the substrate and finally an internal imidazole residue that plays the role of a general base.

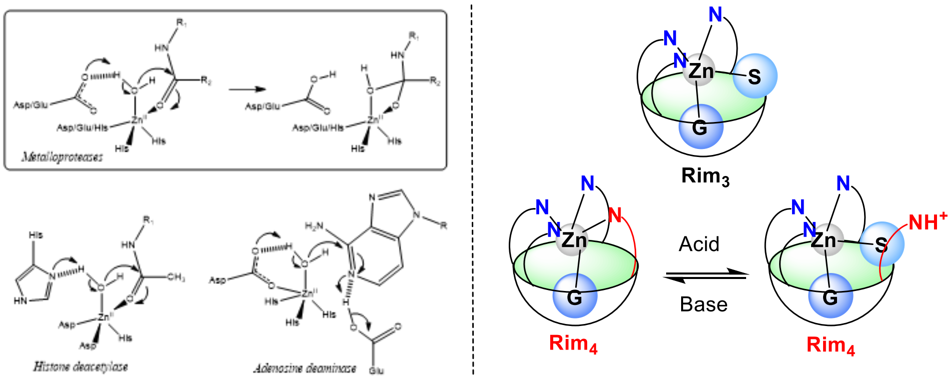

Figure 1 Left: Top: generic active site of Zn^{II} proteases and key step involving the assistance of an Asp or Glu residue as a general base. **Bottom:** example of variations of active site and nucleophilic attack occurring in other zinc hydrolytic enzymes. **Right:** Bowl complexes

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Corundum films with highly ordered porous structure

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Aluminium anodizing in acidic media results in a formation of the anodic aluminum oxide (AAO) with unique porous structure, which can be represented as an array of cylindrical channels aligned normal to the metal surface. As-prepared anodic alumina is amorphous, that makes it unstable in acidic and alkaline media. Chemical stability of AAO can be improved by the porous films annealing, which is accompanied by the crystallization of initially amorphous material into the low-temperature alumina polymorphs and finally into most-stable corundum. The latter phase transition without porous structure sintering is a main challenge in AAO thermal treatment.

Here we present approach to prepare porous alumina films with highly ordered structure in corundum (α-Al_2O_3) form. AAO films were obtained by Al anodizing in 0.3 M sulfuric acid at 25 V. As-prepared anodic alumina represents honeycomb-like porous structure (fig. 1, left) with interpore distance of 64 nm, pore diameter of ca. 18 nm (porosity of ~ 7%), and thickness of 50 μm.

Two crystallization processes at 956 and 1193 °C were revealed by simultaneous thermal analysis (STA). Based on STA data, thermal treatment sequence with a heating rate of 1 °C/min around the transition temperatures, final annealing at 1200 °C for 4 h and slow cooling down to room temperature was proposed. Resulted AAO films are flat, warp/crack-free and, according to X-ray diffraction data, consist of α-Al_2O_3 phase without any low-temperature alumina polymorphs.

According to electron back-scattering diffraction (EBSD), AAO films after crystallization into corundum consist of porous single-crystalline grains with average size of about 10 μm without any texture preferences. Slight increase in pore diameter up to 25 nm (porosity ~ 14%) due to volume shrinkage was observed (fig. 1, right).

To the best of our knowledge, porous corundum films with well-ordered porous structure and pore diameter less than 30 nm are demonstrated for the first time.

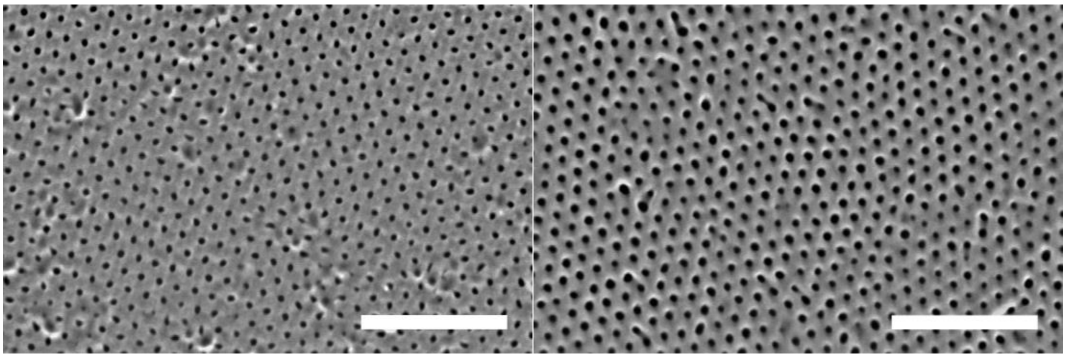

Figure 1. SEM images of the AAO bottom surface after barrier layer removing: as-prepared (left) and after crystallization into corundum phase (right). Scale bar – 500 nm.

Acknowledgements

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«Integrated precursors of silicon nitride multiceramics involving -Ti, Zr, Ta, Hf, Y».

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An efficient method of improving the heat resistance of ceramic-matrix composites is based on the use of polyelementosilazanes (OMHS-M) as impregnating compositions obtained through oligoorganosilazanes reaction with alkylamide metal compounds $M[N(C_2H_5)_2]_п$, where M=Ti, Zr, Ta, Hf, Y in various combinations. The pyrolysis of OMH-M is accompanied by the formation of highly heat-resistant silicon nitride ceramics, the heat resistance of which significantly exceeds that of ceramics based on unmodified polysilazanes. Therefore, comparative studies of the properties of OMHS-M and the features of their thermal behavior were performed, since insufficient attention has been paid to multi-ceramics with two or more refractory metals.

It is found that the kinematic viscosity of OMHS-M solutions in toluene in the range of 9-13 cSt provides a high impregnation ability and a decrease in the residual porosity of carbon frames from 24% to 8% during three impregnations. OMHS-M are characterized by good spreadability. The contact angle of carbon surface determined by the Young-Laplace method is 15.4° for OMHS-Ta, and for OMHS-TaTi it is 9.8°.GPC curves have a polymodal distribution. The presence of Si-N-M fragments in OMHS-M results in an increase in their thermal stability. The yield of inorganic residue during the pyrolysis increases at each stage of weight loss, especially with an increase of metal concentration. The thermal stability of OMHS-M ceramics obtained in the atmosphere of argon by pyrolysis up to 850°C was evaluated by weight loss after heat treatment of ceramics in the temperature range of 1100-1800°C. So the highest heat resistance was found for the OMHS-Ta, Hf multiceramics.

Studies of the morphology and composition of multi-ceramics using SEM and X-ray microanalysis showed that the nature of the metal has a significant impact on the characteristics of fibrous nanostructures

The morphology and composition of OMHS-M ceramics were studied by SEM and X-ray microanalysis, respectively. The obtained OMHS-M were studied by methods of elemental analysis, NMR-spectroscopy; IR-spectroscopy.

Probe Mössbauer Study of Manganite $ScMnO_3$

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Manganites $RMnO_3$ (R = rare earth elements) are an object of keen interest of science from both practical and fundamental point of view. For oxides containing rare-earth cations with large radius (La-Dy) an orthorombic perovskite structure is typical, whereas small radius rare-earth ions (Sc, Y, Ho-Lu) lead to a hexagonal structure. Many of the presented manganites manifest multiferroic properties that makes them promising for possible practical use. The ionic radius of R cation has a significant impact on specific features of magnetic and crystal structure of $RMnO_3$ manganites. For this reason Sc- and In-containing manganites stand out from the rest of similar oxides (Ho-Lu), especially in having an unusually high Néel temperature.

Below $T_N \approx 129$ K manganite $ScMnO_3$, just like most of $RMnO_3$ compounds, exhibits antiferromagnetic properties: in triangular Mn^{3+} sublatice spins form a 120° magnetic structure. However, below $T \approx 58$ K a reorientation of magnetic spins in hexagonal plane occurs.[1]

In present work a probe Mössbauer spectroscopy was used to study the crystallographic and magnetic structures of $ScMnO_3$ for the first time. For the research, samples $ScMn_{1-x}{}^{57}Fe_xO_3$ ($x = 0 \div 0.03$) doped with probe ^{57}Fe atoms were synthesized. At $T = 300$ K Mössbauer spectra represent a superposition of several quadrupole doublets. Semi-empirical calculations of electric field gradient (EFG), originating on ^{57}Fe nuclei, confirmed that observed subspectra correspond to the stabilization of probe ^{57}Fe cations in manganese position (triangular bipyramids) as well as in scandium positions (10-30% of the whole amount of iron). Distribution of impurity iron cations in $ScMnO_3$ structure does not depend on their concentration.

The analysis of the Mössbauer spectra at low temperatures ($T < T_N$) showed that the behavior of the hyperfine parameters of ^{57}Fe nuclei is “sensitive” to the peculiarities of changes in the magnetic structure of $ScMnO_3$. Based on the obtained results, we assume that above 80 K the magnetic structure of $ScMnO_3$ may contain the topological defects — vortices and anti-vortices, which is characteristical for several low-dimensional systems.

Acknowledgements

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3d Transition metal tris-imidazole-oximate complexes as potential single molecular magnets

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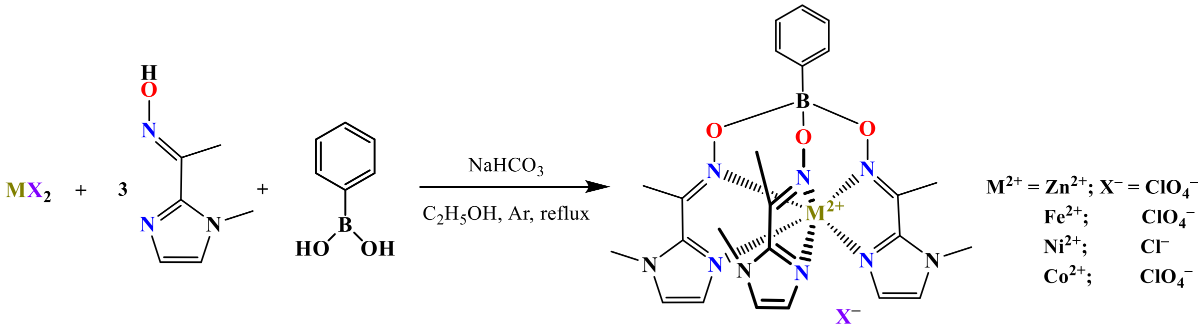
Since the discovery of single molecule magnets (SMMs), they attracted attention of both synthetic and material chemists owing to their individual molecules behaving as permanent magnets. Complexes with SMM behavior can also be used as paramagnetic tags for structure determination of biological macromolecules or as the model compounds for chiral discrimination by NMR spectroscopy. A combination of the rigid trigonal prismatic geometry and electronic configuration d^7 are necessary for the observation of their SMM behavior.

The boron-capped cobalt, nickel, iron and zinc(II) tris-imidazole-oximates were obtained by Scheme 1 by condensation of 1-(1-methyl-1H-imidazol-2-yl)ethanone oxime with phenylboronic acid on the corresponding metal(II) ion as a matrix. The use of their perchlorate salts is crucial for successful performing of this reaction due to the formation of less soluble products[1], except the nickel(II) complex, where chloride anion was used (Scheme 1).



Scheme 1.

Among a series of new 3d-metal complexes the cobalt(II) complex has a high barrier to magnetization reversal, whereas the complexes of other metals either show a very small magnetic anisotropy (iron and nickel(II) complexes) or is diamagnetic compound (zinc(II) derivative). All the complexes obtained were characterized by elemental analysis, MALDI-TOF mass spectrometry, UV-Vis, ^1H and ^{13}C NMR spectroscopy. Their structures were confirmed by single crystal X-ray diffraction.

Acknowledgements

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Single molecule magnet behavior in a Dy(III) pentagonal bipyramidal complex with quasi-linear Cl-Dy-Cl sequence

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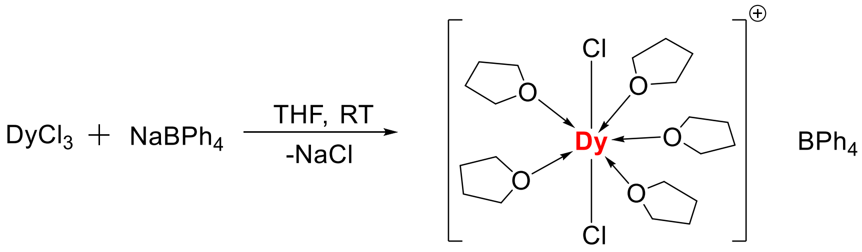
The ability of a coordination complex to present bistable magnetic states continues to attract attention of chemists and physicists since the discovery of this phenomenon nearly thirty years ago.[1,2] In this sense, the field of Single-Molecule Magnets (SMMs) has taken an upturn with the use of lanthanide ions to design highly magnetically anisotropic complexes exhibiting exceptional performances, making such molecular systems potential candidates for applications in datastorage, spintronics or quantum computing. In lanthanide SMMs, the slow relaxation of magnetization is directly correlated to the lanthanide crystal-field generated by the surrounding ligands that favours the creation of an anisotropic barrier, Δ, opposing two antiparallel directions of the magnetic moment (±m_J).



1, 86%

Figure 1.

We report the synthesis and magnetic investigation of a dysprosium pentagonal bipyramidal complex $[Dy(THF)_5Cl_2][BPh_4]$ (**1**) exhibiting a linear Cl–Dy–Cl sequence suitable for providing a coordination environment allowing a zero-field slow relaxation of the magnetization. Besides, the complex also shows dual luminescence originating from $[BPh_4]^-$ and Dy^{3+} ion.[3]

Acknowledgements

The authors thank the Russian Science Foundation Grant No. 17-73-30036

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Thin film metamaterials based on vanadium and titanium dioxides

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Vanadium dioxide based thin film materials are of great interest due to their unique optoelectronic properties. At a temperature of 68 ° C, an almost instantaneous (<1 ps) reversible dielectric-to-metal phase transition occurs with a sharp change in resistance (up to 10^5 times for single-crystal samples) and optical transparency in the IR and THz ranges. This allows the use of vanadium dioxide films as a key component of optoelectronic devices: microwave switches, RF and THz attenuators, radiation modulators, etc. Addition of TiO_2 in the film allows to obtain self-assembled structure formed in the process of spinodal decomposition of solid solutions VO_2-TiO_2, with the formation of alternating lamellae rich with vanadium and titanium, respectively. In this case, a significant change in the properties of the samples occurs as a result of stabilization of the high-temperature VO_2 phase due to the proximity of the parameters of the TiO_2(R) and VO_2(R) unit cells [1].

Vanadium and titanium dioxide thin films were obtained by chemical vapor deposition (MOCVD) by the reaction of pyrohydrolytic decomposition of vanadium (IV) and titanium (IV) coordination compounds at temperatures from 350 to 600°C in a stream of moist argon on the r-Al_2O_3 substrates. It was found that during the spinodal decomposition, which involves annealing at 900°C followed by exposure at a lower temperature, leads to the reduction of vanadium to +3 state, due to isostructural lattices of V_2O_3 and sapphire, which is confirmed by X-ray phase analysis. To avoid the influence of the substrate on the vanadium oxidation state, thin films of pure titanium dioxide were grown on sapphire, are subsequently used as the buffered layer for the growth of $V_xTi_{1-x}O_2$ solid solution composition.

In this work we show the formation of VO_2-TiO_2 thin film solid solution on the 2 inch sapphire substrates by reaction of volatile coordination compounds of V(+4) and Ti(+4) with water in the cold wall MOCVD reactor. As precursors the $VO(thd)_2$ and $Ti(i\text{-}PrO)_2(thd)_2$ were used. We have demonstrated similar volatility of substances by EDX analysis: the spatial distribution of vanadium and titanium throughout the film is very close to the original, which was laid during the preparation of the precursor.

Acknowledgements

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Low softening inorganic and hybride polyoxides and related materials

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Inorganic oxides (silicates, phosphates, aluminates, borates, etc.) is a class of polymers with incombustibility, high thermal and radiation resistance, no volatiles during thermal destruction, extremely low vapor pressure of melts, possibility of synthesis under "mild conditions", unlimited raw materials, the ability to refuse organic solvents. This makes them attractive from the point of view of polymer materials science.

Appeal to inorganic and hybrid polymers will allow partial solution of the problems associated with combustibility, low thermal stability, large natural assimilation times (50–600 years) inherent in organic polymers.

We have considered the possibility of obtaining, chemical modification and processing of low molecular weight - oligomeric oxides with softening temperatures (T_f) and yield (T_{flow}), close to the values of these parameters for organic polymers

(T = 20-200°C).

The search for polyoxides, whose highly elastic state is possible at "organic temperatures," was carried out in accordance with the energy theory that relates physical interactions in a polymer with their thermal characteristics .

The objects of study were oligomeric oxides of boron, phosphorus, silicon, and their derivatives. In the synthesis of oxides, the "solution method" was used with the use of aqueous solutions and in the formation of materials traditional plastic processing technologies were used.

Polyoxides were modified by residual hydroxyl groups, capable not only of entering into chemical interaction, but also forming strong hydrogen bonds that affect the rate of polycondensation of oxides and their relaxation properties.

The synthes[s of a wide range of oligomeric oxides and the literary analysis of publications on low-melting inorganic glasses made it possible to consider them as a new promising class of oligomers.

It were received polymer-polymer blends **-** a new type of composites produced by mixing melts of organic and inorganic polymers what can be concidered as a new way to obtain slow-burning and non-combustible materials without the use of flame retardants. .

It were synthesized polyoxide hybrids with organic and organoelement compounds· with an oxygen index OI = 65–90.

The resulting compositions based on oligomeric oxides and polymer-polymer binders allowed the development of non-combustible reinforced composites without thermal degradation products using glass, basalt, carbon and cellulose fabrics.Thermal and mechanical properties, oxygen index, water resistance of composites were measured.

Marked areas of application of the developed materials.

Boronic acid function as synthetic receptor of reagentless microsensor for rapid detection of microorganisms in aerosol

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Microbial contamination control of indoor air is important for occupational and public health. Microscopic fungi *Penicillium* are common airborne genera, they cause allergies, chronic diseases. Beside the harm to the human health there is also a negative influence of microorganisms on manufacturing processes of medicines, foods and microelectronics. However, conventional microbiological methods are laborious, time-consuming or expensive, and usually unsuitable for on-site analysis.

To overcome most of these drawbacks, it is possible to use synthetic receptors such as poly(3-aminophenylboronic acid) (poly(3-APBA)). Previously we reported on the novel reagentless detection principle allowing the discrimination of specific affinity bindings from nonspecific interactions.[1] Poly(3-APBA) is able to selectively bind compounds possessing 1,2- or 1,3-diol moiety which leads to poly(3-APBA) conductivity increase. Upon complexation, the hybridization of the boron center shifts from sp^2 to sp^3, with the boronic acid moiety becoming an anionic and tetrahedral hydroxyl coordinate species. Hence, the mechanism of the observed conductivity increase in the presence of polyols can be referred to as polyaniline self-doping by “freezing” negative charges in ring substituents upon complexation. Since 1,2- and 1,3-diol functions are common structural elements of saccharides incorporated within fungi cell wall, poly(3-APBA) is able to bind to fungal cell wall surface, which consists mainly of β-1,3-glycan.

In this work, we elaborated microsensor for direct detection of *Penicillium chrysogenum* in air. Impedimetric detection of *P. chrysogenum* in bioaerosol was carried out on interdigitated ultramicroelectrodes, modified with electropolymerized 3-APBA. It was first shown that the presence of the microorganism in air led to conductivity increase of poly(3-APBA) due to specific interaction of the cell wall functional groups with boronic acid moiety. Effect of poly(3-APBA) conductivity increase as a result of polymer self-doping in the presence of the fungi was confirmed by Raman spectroscopy.

Detection of fungi with microsensor requires less than 20 minutes which is approximately 100 times faster than agar plate cultivation. Furthermore, microsensor is applicable to monitor fungal content in air within concentration range including the hygienic standard. The novel reagentless detection principle that we propose will ensure the analysis reliability, since it is based on affinity interactions. No additional chemicals and sample preparation are needed either. These advantages and compact size of microsensors opens the possibility to create embedded systems of air control in manufacturing processes and even in everyday life.

Acknowledgements

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Hydrothermal synthesis of manganese pyrovanadate $Mn_2V_2O_7$

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Homogeneous precipitation method is widely used for obtaining oxide nanomaterials with controlled phase composition and microstructure. The method is based on controlled hydrolysis of metal salts in the presence of slowly hydrolyzing reagents, e.g. hexamethylenetetramine or urea. In order to obtain highly crystalline metal oxides this technique can be combined with hydrothermal treatment. The literature survey showed that information on the use of formamide for inorganic materials synthesis under hydrothermal conditions is currently rather scarce.

The work was aimed at the study of the routes of hydrothermal treatment of V_2O_5 and $KMnO_4$ in the presence of formamide at various pH and molar ratios of reagents.

The treatment of V_2O_5 and $KMnO_4$ was carried out under microwave hydrothermal conditions at 200°C during 20 min. Molar excess of formamide to divanadium pentoxide and potassium permangate was equal to 5:1, 25:1, 50:1. The pH of the mixtures was adjusted to 0.5/ 1.5/ 2.0/ 3.0/ 5.0 with a dilute (0.5 M or 2 M) nitric acid. Solid reaction products were collected, washed by distilled water, thoroughly dried and studied by means of X-ray powder diffraction analysis (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

As a result, a new selective and time-saving method for the preparation of manganese pyrovanadates $Mn_2V_2O_7$ was proposed. According to XRD data, the desired single-phase product was obtained at pH 1.5–3.0 when molar excess of formamide was 5:1-50:1 and also at pH 5,0 when excess was equal to 5:1. Both an increase and decrease of starting pH yielded mixtures of products. According to SEM data, the $Mn_2V_2O_7$ consisted of rectangular particles having thickness of 2–5 μm and length of 5–10 μm. EPMA showed an absence of potassium in the crystals.

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Tunable one-pot synthesis of different cerium(IV) phosphates

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Crystalline rare-earth phosphates are widely used in high-tech industrial applications as optical materials, heat-resistant ceramics, ion-exchangers, luminophores and radioactive waste sorbents. Cerium phosphates are of particular interest since they can contain cerium ions in both +3 and +4 oxidation states. The crystallographic data and properties of cerium(III) orthophosphates – monazite and rhabdophane – have been thoroughly studied. Surprisingly, information on cerium(IV) orthophosphates is extremely scarce, despite their long history and rich ceric coordination chemistry. The data on ceric orthophosphates are rather limited, since they tend to form amorphous phases when synthesized from aqueous solutions. High temperature treatment, in turn, eventually results in the decomposition of Ce(IV) compounds, with the formation of Ce(III) species. Apparently, the only rational pathway for the preparation of crystalline ceric orthophosphates is a mild hydrothermal treatment.

The present work was aimed at investigation of ceric orthophosphates' crystallization pathways under hydrothermal conditions. As a starting material, we used amorphous ceric phosphate gels.[1] The gels were synthesized by addition of distilled water, NH_4OH, HNO_3, H_2SO_4, dimethylformamide, or tetramethylammonium hydroxide to the ceric phosphate solution prepared by dissolving nanocrystalline ceria in excess of hot concentrated phosphoric acid. In some cases the gels obtained were purified from excess of orthophosphoric acid and then redispersed in aqueous acid solutions. Crystallization of the gels was performed by hydrothermal treatment at 180°C for 24 hours.

It was shown, that under certain conditions, hydrothermal treatment allows for the synthesis of new phases simply by adjusting the composition of hydrothermal media. Hydrothermal treatment of initial gels depending on the mineralizer and its concentration yielded $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$, $(NH_4)_2Ce(PO_4)_2(H_2O)$, monazite $CePO_4$ and previously unknown $NH_4Ce_2(PO_4)_3$. The structure of the latter compound was solved using powder X-ray diffraction data.[2] It appeared to be isostructural to ammonium thorium phosphate, $NH_4Th_2(PO_4)_3$; in this crystal structure, large channels (5.07 × 3.79 Å) located along the c-axis are occupied by NH_4^+ ions. Hydrothermal treatment of purified ceric phosphate gels in HNO_3 solutions yielded another novel ceric phosphate ($CeOHPO_4$) with a tunnel structure.

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The use of fullerene in obtaining biologically active compounds based on a derivative of vitamin B_{12}

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Approaches of preparing of biologically active substances based on transition metal complexes with biological substrates participation in closed to physiological conditions were developed for a number of years in INEOS RAS. As is known, transition metal complexes are active catalysts for many chemical reactions, similar to those which occur in living organisms under the action of metal enzymes. Under academician M.E.Vol'pin's idea, catalytic sources of active oxygen species (AOS) which are capable selectively accumulate in tumor, can be active in suppressing of tumor tissue grows. The native macrocyclic cobalt complexes — vitamin B_{12} and its derivatives (cobalamins, in particular, *e*-carbonic acid of B_{12}: *e*-COOH-Cbl-CN (I) introduce the most interest[1]. Also, firstly in INEOS RAS was elaborated the method of synthesis of aminoacids and peptides fullerene derivatives. It turned out to be that there is no toxicity of these substances and they have a wide spectra of biological activity. A complex of studies has shown that the most effective derivatives with antitumor activity are those compounds that contain nitrogroups or carnosine derivatives[2].

We assumed that the introduction of a pharmacophoric fullerene derivative of the active form of vitamin B_{12} into the molecule will significantly improve the efficiency of the antitumor action of the complexes. To do this, first of all it was necessary to show the fundamental possibility of the synthesis of such compounds. On the first stage of the work the addition to carboxylic group of a macrocyclic cobalt complex — derivative of cobalamin *e*-COOH-Cbl-CN (I) the fullerene frame of the amino acid fullerene C_{60} derivative — ether of N-(monohydrofullerenyl)-ε-aminocapronic acid: $HC_{60}NH(CH_2)_5COOCH_3$ (II) result in the new type of mixed biologically targeted cobalamin-fullerene complexes CN-Cbl-C(O)-$C_{60}NH(CH_2)_5COOCH_3$ (III). The next derivative (IV) is obtained directly by the addition of (I) to (II), but after the additional introduction of a spacer — an ethylene bridge with the formation of the following structure: CN-Cbl-B_{12}-C(O)OCH_2CH_2-$C_{60}NH(CH_2)_5COOCH_3$ (IV). The structure of obtained substances (III) and (IV) was established by UV, IR, CD spectroscopy and elemental analysis[3].

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“Cage” cation’s iodobithmutates: features of the formation and crystal structures

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Inorganic-organic hybrid halogen bithmutates have attracted much attention due to the huge structural diversity and promising physical properties[1]: photochemical and photophysical properties, ferroelectricity, and others. Bismuth(III) forms quite a number of halide complexes with various cations. The halobithmutate’s anions assembling occurs as a result of {BiX_6} octahedral sharing by vertex, edges or faces, resulting in polynuclear anions involving from 2 to 10 octahedra or coordination polymers. In cases where X = I or Br, the anionic substructure may be completed with X_2, X^-, X_n^- moieties. The physical properties of the resulting hybrid compounds are associated both with the dimension of the anion, the nature of the cation, and the strength and number of weak interactions between them: N-H···I, O-H···I, I···I. However, an unambiguous relationship between the structure of selected organic cations, the synthesis conditions and the structure of formed halogen bithmutates not yet been identified.

Herein we report on the crystal structure and synthesis of iodobismuthates of different adamantane’s derivations: azomethines and amino-. We present the possibility of formation different iodobismuthates for the same cation, depending on the synthesis conditions and the ratio of the Bi:cation. We would draw your attention to the comparable system of the weak interactions for the same cations in the iodobismuthates, and also some cation’s iodides.

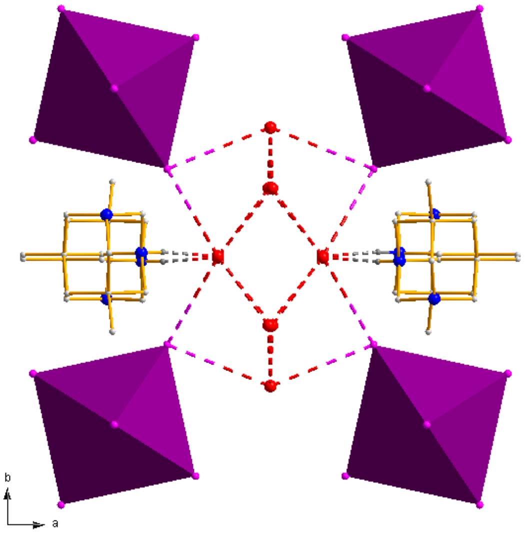

Figure 1. View of the crystal structure of $(C_{10}N_2H_{19})_2(H_3O)BiI_6{*}5H_2O$

Acknowledgements

Authors wish to thank Dr. A. V. Medved’ko for the providing organic substances.

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Probable graphite oxide layer structure

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Graphite oxide (GO) is an interesting material that can scarcely be referred to as a substance because of its irregular and variable structure and composition. Having been known for more than a century and a half, it still did not unlock all secrets of the nature, mutual arrangement, and even relative amounts of different functional groups that cover graphite layers and determine numerous promising properties of the substance. Even the C/O ratios in samples obtained according to different oxidation techniques differ, not saying about the inevitable nonzero content of hydrating water that may be as high as 10-17%. It is worth noting that arrangement of functional groups on a GO surface partly covered with water molecules, which naturally form hydrogen bonds with the groups, can be considered as a very interesting supramolecular system where all important oxygen-containing building blocks are strongly grafted to a carbon skeleton and interconnected either directly or via H_2O molecules.

According to XPS and solid-state NMR studies, graphite oxide contains chiefly oxidized carbon in the form of epoxide and hydroxide groups and non-oxidized carbon, as well as a much smaller amount of carboxyls, ketones, and geminal diols. Absorption ir spectra seem to be most informative due to the presence of several clear signals in the fingerprint range and a broad band from 3700 to 2200 cm^{-1}, which can be deconvolved into a series of Gaussians that may give rise to ideas about the probable nature of the functional groups. However, for the same reason as in the case of XPS and NMR, namely the absence of adequate tabulated reference data, the spectra cannot be interpreted if no additional information is used. The source of such information is quantum chemical modeling.

We have carried out nonempirical simulations of model $C_{54}H_p(O)_k(OH)_l(COOH)_m(H_2O)_q$ systems that represent hypothetic fragments of an oxidized carbon sheet at an assumption about different kinds of prevailing functional groups and their combinations. Calculated absorption spectra of the systems (based on the results of the normal-coordinate analysis) were visualized with the use of Lorenzian broadening and compared to the recorded infrared absorption spectrum of the synthesized specimen. The comparison enabled us to formulate certain conclusions about the nature of spectral signals in the fingerprint range. In particular, it became clear that there are mutual effects of different functional groups, solvating water molecules, and carbon skeleton, which can by no means be predicted without theoretical consideration.

Acknowledgements

Simulations were carried out with the use of the facilities of the HPC computing resources at Lomonosov Moscow State University.[2]

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The role of redox, microwave activation and complexes of metals in the synthesis of organic sulfur derivatives from hydrogen sulfide

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As is well known, the radical process of thiolation of organic compounds with participant of hydrogen sulfide is rather laborious. This is because the generation of the thiyl radical by breaking the S–H bond requires high energy costs. The significant practical value of organic sulfur derivatives, many of which are biologically active and used as pharmaceuticals, requires a search of new approaches to increase the reactivity ability of hydrogen sulfide.

Previously, we have successfully carried out the synthesis of sulfur derivatives of aromatic, unsaturated, and alicyclic hydrocarbons using direct redox activation of H_2S in organic solvents at room temperature.[1,2] In this work, a number of methods for generating thiyl radicals from hydrogen sulfide have been expanded by microwave irradiation and indirect activation in the presence of the reactive form of 3,6-di-tert-butyl-o-semiquinolate complexes of chromium(III) and indium(III).The first option can significantly reduce the duration of the reaction of H_2S with organic compounds in comparison with electrosynthesis by 5-10 times. The second method allows to decrease reduce the energy consumption for obtaining organic sulfur derivatives due to the indirect activation of H_2S in the presence of anodic-activated complexes by 0.8 V compared with the oxidation potential of H_2S on platinum.

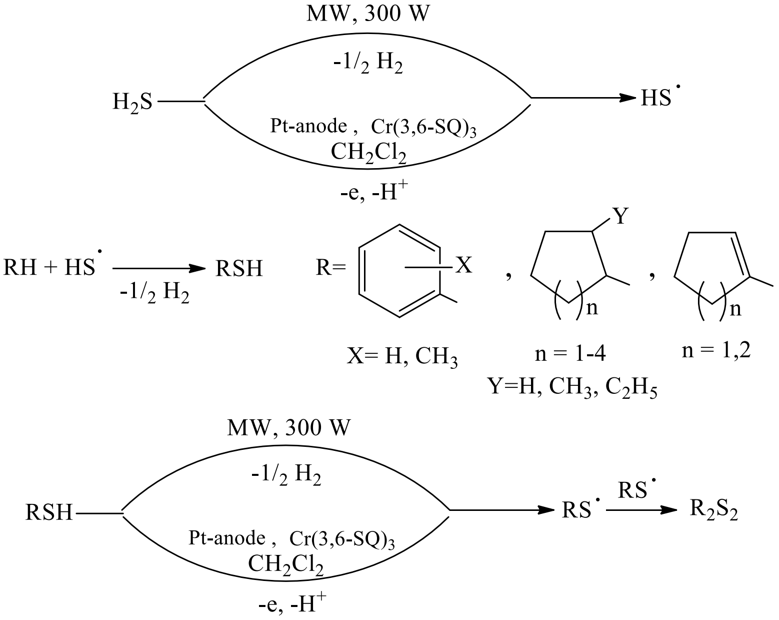

Figure 1. Scheme of the radical reaction mechanism of organic compounds thiolation under different conditions of H_2S activation

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Photochemistry of iodine and polyiodides in hybrid perovskites

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Modern perovskite photovoltaics demonstrates extraordinary progress among all types of solar cells. By now, perovskite solar cells (PSCs) have already reached a record power conversion efficiency (PCE) of 24.2%. This achievement together with low cost and production simplicity makes PSCs a favorite candidate for commercialization. All these advantages of PSCs are related to unique electrical properties of hybrid perovskites with a general formula $APbX_3$ (where A = $CH_3NH_3^+$ (MA), $CH(NH_2)_2^+$ (FA), or Cs^+; X = I^-, Br^-) such as defect tolerance, small exciton binding energy, long carrier diffusion lengths, and a high light absorption coefficient.

Unfortunately, hybrid perovskites suffer from poor stability to humidity, oxidation, high temperatures, and photochemical degradation. The encapsulation approach allows to get rid of the first two factors but thermal and photochemical stability depends mainly on intrinsic properties of perovskite materials. In the literature, photostability and photodegradation of hybrid perovskite is elucidated insufficiently. The goal of this work is to reveal new details of photo-induced processes in hybrid perovskites to suppress possible degradation mechanisms.

An analysis of photoluminescence (PL) dynamics of $MAPbI_3$ and $FAPbI_3$ thin films under constant blue light illumination (465 nm) shows complete photodegradation accompanied by the film color shift and appearing PL from PbI_2. In the case of periodic illumination with dark pauses, PL intensity of hybrid perovskite demonstrates reversible changes. This feature might be caused by photo-induced formation of point defects and sequential defect structure relaxation in darkness. We experimentally demonstrate photochemical generation of molecular iodine from most of hybrid perovskites which can further react with surrounding lead halides via a reversible process: $MAPbI_3$ (solid) + I_2 (gas) $\leftrightarrows$ PbI_2 (solid) + MAI_3 (liquid). This important reaction was discovered by Raman spectroscopy revealing instantly strong vibrational modes of I_3^- and I_5^- under 514nm laser illumination.

The photochemical degradation mechanism of hybrid perovskites proposed here depends strongly on either the shift of reaction equilibrium or overall chemical stability of adjacent materials inside PSCs. As an example, we demonstrated for the first time incompatibility and deep chemical degradation of gold as one of widely used electrode materials via its interaction with photochemically generated polyiodide melts in hybrid perovskite $MAPbI_3$.[1] The latter suggests to search for novel iodine and polyiodide resistant materials and strengthening the control over concentrations of possible volatile degradation products inside PSCs.

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Praseodymium (III) complexes with Pyridine-N-Oxides: synthesis, structure, properties

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Over the past two decades, the design of single-molecule magnets (SMM) has attracted increasing attention due to the prospect of their potential use: processing and storing magnetic information at the molecular level [1]. In recent years, due to a more in-depth study of the magnetic-chemical properties of heavy lanthanide ions: Tb (III), Dy (III), Ho (III) and Er (III)), salts of these rare earth elements (REE) have become much more frequently used for designing new mmm. This is due to the significant magnetic anisotropy arising due to their large orbital angular momentum. Thus, a series of MMMs were found, including complexes of Ln (III) with polyoxometalates, phthalocyanine, macrocyclic ligands — Schiff bases, β-diketones, and nitronyl nitroxide radicals [2].

In this work, two ligands were used - pyrithione, which exists as a pair of tautomers, the main form of which is 1-hydroxy-2 (1H) -pyridinethione, and the other form is 2-mercaptopyridine-thiol N-oxide (see. Figure 1) and 2,2'-dithiobis (pyridine-N-oxide) (see. Figure 2). Ligands possess suitable structural characteristics: (i) can be easily coordinated with REE (III) ions through two donor atoms; (ii) The N-hydroxy group of ligands can act as a separate magnetic center between neighboring REE (III) ions. Using these advantages of ligands, two new Pr (III) complexes were synthesized and the relationship between their structure and magnetic properties was studied.

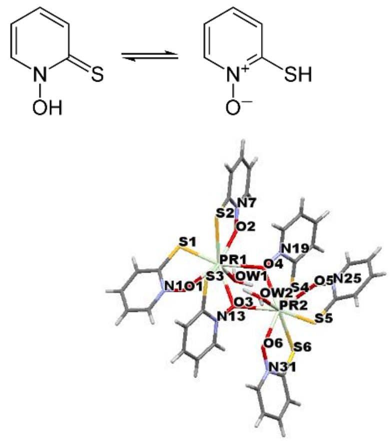

Figure 1. 2-mercaptopyridine-thiol N-oxide

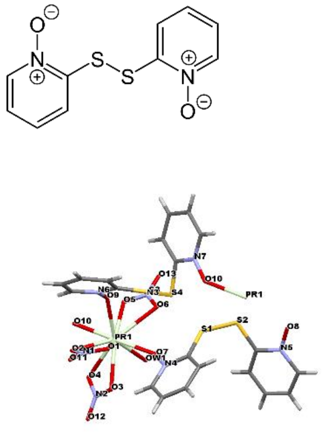

Figure 2. 2,2'-dithiobis (pyridine-Noxide)

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The transition metals bisphosphonates complexes with spacer-armed 2-pyridyl-1,2,4-triazoles

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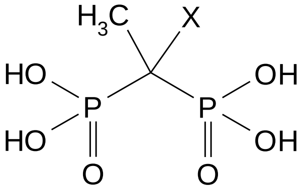
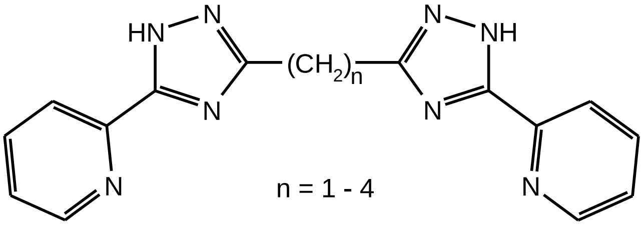
Bisphosphonates can show multiple coordination modes, and this combined with the different geometries of the metal polyhedron lead to a large number of compounds with versatile structures. Most of them display layered structures with different layer topologies and the organic groups filling in the interlayer spaces. Low dimensional metal bisphosphonates such as chains, clusters and coordination polymers can be obtained at additional functional groups and organic extra ligands introducing.

Here we describe the synthesis and structure heteroleptic transition metals complexes of same biphosponates and spacer-armed 2-pyridyl-1,2,4-triazoles, which are a convenient matrix for for assembling coordination compounds of various nuclear and topology.



X = OH,NH$_2$



Title complexes were obtained by usual synthesis in water solution. Coordination compounds were fully characterized by various means including elemental analysis, UV-Vis, IR-spectroscopy, EPR and X-Ray analysis.

The modes of binding and types of structures formed during self-assambly of the complexes are studied. It is shown that the of bridging ligands binding is determined by the length of polymethylene spacer. The following types of complexes have been described.

1. Spacer-armed binuclear complexes with one binucleating bridge triazoles and two terminal bisphosphonates di-anion.
2. Spacer-armed binuclear complexes with two binucleating bridge triazoles and two binucleating bridge bisphosphonates di-anion.
3. Spacer-armed binuclear complexes with two binucleating bridge triazoles, one binucleating bridge bisphosphonates di-anion, and one trinucleating bisphosphonates di-anion.

In all case non-coordinated P-OH groups or water molecules involved in the H-bands system that lead to creation of interesting supramolecular structure.

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Synthesis and Effect of P Doping on Magnetic Order and Superconductivity in LaFeAsO

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Many theoretical and experimental studies were conducted on iron-based superconductors (IBSC), although their superconducting mechanism hasn't been defined yet. 1111-type compounds are composed of layer of Fe and Pn atoms which is separated by a non-iron layer such as La-O (for LaFeAsO)[1].

Superconductivity emerges when the tetragonal-orthorhombic structural transition and antiferromagnetic phase transitions are suppressed. The analysis of the experimental data suggests that superconductivity can be induced using external pressure, carrier-doping by aliovalent substitution, and chemical pressure by lanthanide contraction, however carrier doping and chemical pressure were identified to appear simultaneously[2].

In this study powder samples of $LaFeAs_{1-x}P_xO$ (x=0.15-0.4) were synthesized by solid state reaction. We have investigated synthesis conditions such as starting reagents, temperature and pressure conditions can influence phase purity and their superconducting properties with P-substitution. Samples were studied using following methods: room-temperature standard XRD, energy dispersive x-ray (EDX) microanalysis, magnetic susceptibility, Mossbauer spectroscopy, nuclear quadrupole resonance (NQR) and nuclear magnetic resonance(NMR).

Rietveld refinement on XRD patterns confirms that synthesized compound has expected structural properties as tetragonal crystal structure with P4/nmm space group with smaller unit cell parameters reflecting the smaller ionic radius of P with respect to As. Small amounts (up to 5%) of Fe_2P and La_2O_3 were observed in some samples. Phosphorus (P) content found in the samples was less than nominal by 5-10%.

^{57}Fe Mössbauer spectra of $LaFeAs_{1-x}P_xO$ (x = 0.2 - 0.25) in the paramagnetic and magnetically ordered phase are consistent with spectra obtained for another P-doped 1111-type compound CeFeAsO[3]. Presence of Fe_2P magnetic impurity which has a ferromagnetic ordering was also confirmed. Both samples obtained under normal conditions and via high-pressure synthesis reportedly become superconducting at 25% level of P-doping, yet we found out that samples synthesized at ambient pressure aren't superconducting and demonstrate antiferromagnetic order[4].

^{75}As NMR measurements show that the magnetic order is suppressed by P doping, but no superconductivity has been found. Possible reasons for the absence of superconductivity will be discussed.

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Synthesis and reduction properties of lanthanide (Ho, Dy) complexes with sterically hindered o-iminobenzoquinone ligand

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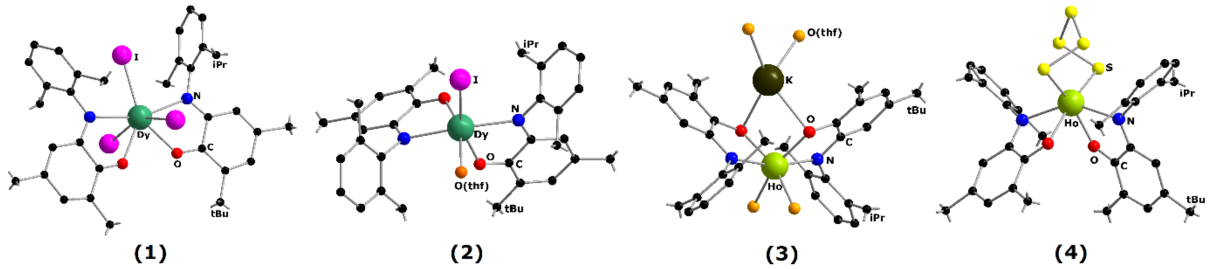
Ortho-benzoquinones play an important role in coordination chemistry, because these ligands, upon coordination to a metal, can reversibly accept one or two electrons with the formation of anion-radical or dianionic form, respectively (redox-active ligands). Their analogs – o-iminobenzoquinones – are much less studied among other related ligands. In this ligands the substituent at the nitrogen atom provides an opportunity to change steric hindrance caused by the ligand. Still, there are very few lanthanide complexes with this type of ligands, especially those with known structures.[1] This complexes can possess interesting structural and magnetic properties because of presence of several paramagnetic centers. The redox-active ligands can provide additional reactivity, while acting as an electron reservoir.

In this work we describe synthesis, structures, and some properties of lanthanide complexes (Ln = Dy, Ho) with the ligand 4,6-di-*tert*-butyl-N-(2,6-di-isopropylphenyl)-*o*-iminobenzoquione (dipp-IQ), which can be reduced to monoanionic iminosemiquinone radical (ISQ$^{–}$) or amidophenolate dianion (AP$^{2–}$). Resulting quinone complexes [LnI_3(dipp-IQ)$_2$] are isostructural. Reduction of these complexes by two equivalents of KC_8 results in formation of iminosemiquinone derivatives [LnI(dipp-ISQ)$_2$(thf)]. Successive addition of the same amount of KC_8 results in formation of amidophenolate complexes [K(thf)$_2$][Ln(dipp-AP)$_2$(thf)$_2$]. This amidophenolate complexes can react with elemental chalcogens (E = S, Se) to form molecular pentachalcogenide complexes [K(18-crown-6)(thf)$_2$][Ln(E_5)(dipp-ISQ)$_2$(thf)$_2$], while direct reaction with elemental tellurium proceeds only with additional activation. Reduction of quinone complexes with 3 equivalents of KC_8 results in mixed-ligand complexes [Ln(dipp-ISQ)(dipp-AP)(thf)$_2$]. All complexes were isolated and characterized by X-ray diffraction, IR, and CHN.



(1) **(2)** **(3)** **(4)**

Figure 1. Crystal structures of complexes: [DyI_3(dipp-IQ)$_2$] **(1),** [DyI(dipp-ISQ)$_2$(thf)] **(2),** [K(thf)$_2$][Ho(dipp-AP)$_2$(thf)$_2$] **(3),** [K(18-crown-6)(thf)$_2$][HoS_5(dipp-ISQ)$_2$(thf)$_2$] **(4)**

Acknowledgements

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Mechanistic diversity in ketone transfer hydrogenation catalyzed by ruthenium iminophosphonamides

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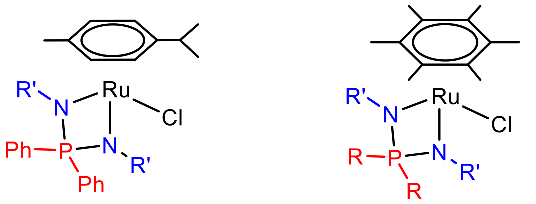
We have recently reported the synthesis and chemical properties of a series of half-sandwich 18ē and 16ē arene ruthenium complexes with a strong σ,π-donating zwitterionic iminophosphonamide (NPN) ligand [(arene)Ru{(R$_2$P(NR’)$_2$}(X)] (X = Cl$^-$, PF$_6^-$).[1,2] We showed that [(p-cymene)Ru{(Ph$_2$P(NTol)$_2$}(X)] (**1**, X = Cl) can readily transform in basic isopropanol to the hydride complex (X = H), which efficiently catalyzes the transfer hydrogenation of acetophenone.[3] The proposed catalytic mechanism involves an outer-sphere hydride transfer to ketone via a zwitterionic intermediate on the basis of an experimental kinetic study as well as DFT calculations. Interestingly, the arene and the N and P substituents affect the catalyst activity and stability. Hexamethylbenzene and P-aryl groups significantly improve the catalyst long-term stability, while electron-releasing alkyl substituents at the N atoms enhance the catalyst activity (**5**,**6**) at the expense of its stability in isopropanol. Surprisingly, complexes **5**,**6** are highly active even in the absence of base and have good long-term stability. The Eyring analysis showed that the N-aryl substituted complexes **1-4** have very similar activation parameters, which differ strongly from those of the N-alkyl analogs (**5**,**6**). We propose a Noyori-type mechanism for transfer hydrogenation by **5**,**6**, which apparently involves highly basic N atoms for H-bonding/deprotonation of isopropanol, followed by assistance in substrate activation.



1, R' = *p*-Tol,
2, R' = *p*-C$_6$H$_4$COOEt

3, R = Ph, R' = *p*-Tol,
4, R = Et, R' = *p*-Tol,
5, R = Ph, R' = Me,
6, R = Ph, R' = Me/*p*-Tol

Figure 1. Half-sandwich arene ruthenium iminophosphonamides

Acknowledgements

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Rare earth complexes with radical-anionic iminopyridine ligands

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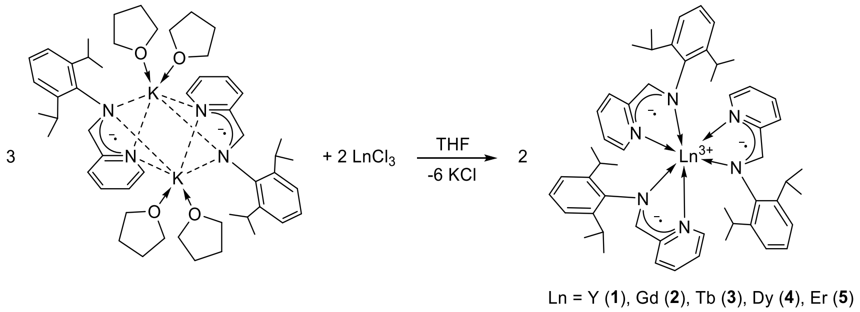
Complexes Ln(IPy$^{\bullet -}$)$_3$ (Ln = Y (**1**), Gd (**2**), Tb (**3**), Dy (**4**), Er (**5**)) were prepared by the treatment of the radical-anionic adduct of potassium and iminopyridine[1] with LnCl$_3$ in 3:2 molar ratio (Scheme 1).

Rare earth complexes **1**–**5** were obtained as dark green crystalline solids in 73, 71, 75, 72 and 70 % yields, respectively. X-ray single crystal diffraction analysis (Figure 1) shows that compounds **1**–**5** crystallize in the hexagonal $R\overline{3}$ space group as the solvates **1**·0.5(Toluene), **2**·0.5(Toluene), **3**·0.5(THF), **4**·0.5(Toluene) and **5**·0.5(Toluene). The bonding situation within the planar diimino fragment N$_{Py}$–C–C–N$_{imine}$ in **1**–**5** is consistent with the radical anionic form of the iminopyridine ligand.[2] Remarkably, the dysprosium complex **4** reveals a zero-field slow relaxation reflecting a genuine SMM behaviour.



Scheme 1. Synthesis of Ln^{3+} complexes 1–5 coordinated by radical-anionic iminopyridine ligands

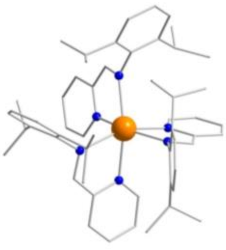


Figure 1. Molecular structure of 4

Acknowledgements

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Zinc(II) and cadmium(II) complexes with bis(azolyl)alkane derivatives: synthesis, structure and luminescent properties

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Nowadays the luminescent properties of cadmium(II) and zinc(II) coordination compounds are widely investigated, because their emitting mechanism differs from the luminescence of materials based on lanthanides. Zinc and cadmium ions have a completely filled d-shell therefore d-d transitions don't occur and the luminescence of these metal-organic complexes is mainly caused by intra-ligand electronic transitions (π–π* transitions) or rarely by the process of charge transfer from metal to ligand (MLCT).

In this work four bis(azolyl)alkane derivatives were used as ligands: bis(benzimidazol-2-yl)methane (L^1), 1-(1*H*-benzimidazol-1yl-methyl)-1*H*-benzo-triazole (L^2), bis(benzotriazol-1-yl)methane (L^3) and 1,3-bis(1,2,4-triazol-1-yl)propane (L^4). Methods of synthesis a number of complexes, which contain cadmium(II) or zinc(II) halides and nitrates with these ligands, have been developed. All compounds were characterized using elemental and powder diffraction analysis, thermogravimetry and IR-spectroscopy. Single crystals some of the complexes were obtained by slow crystallization and molecular and crystal structures have been determined by single-crystal X-ray diffraction analysis. It was found that L^1 is coordinated to the metal ions by bidentate-cyclic mode to form cation-anion compounds: $[Cd(L^1)_2(EtOH)_2][Cd(L^1)(NO_3)_3]_2 \cdot 6EtOH$ (fig.1) and $[Cd_4(L^1)_4Cl_6(EtOH)(H_2O)][CdCl_4] \cdot 6EtOH$. The complex with L^2 – $[Zn(L^2)_2Cl_2]$ – is a mononuclear compound with monodentate coordination of the ligand to the metal center. The complexes $[Zn(L^3)Br_2]_n$, $[Cd(L^3)I_2]_n$ and $[Cd(L^4)(H_2O)_2(NO_3)_2]_n$ are polymeric chains, where organic ligands perform the bridge function, connecting metal ions.

Spectra of luminescence excitation and emission of polycrystalline samples (ligands and complexes) were received at room temperature, the quantum yields and lifetimes of the excited states were measured.

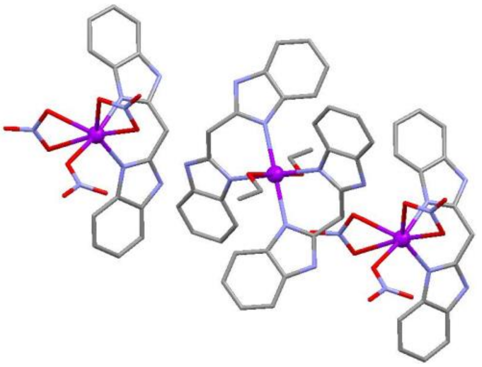

Figure 1. Structure of $[Cd(L^1)_2(EtOH)_2][Cd(L^1)(NO_3)_3]_2$

Acknowledgements

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A general synthesis of unnatural α-amino acids with γ-tertiary and quaternary carbon centers via chiral Ni(II) complexes

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Chiral α-amino acids (AA) with γ-tertiary and quaternary carbon centers display various biological activity.[1] However, the design of the safe and simple methods for their production is still limited, underexplored and, from the point of the synthetic chemistry, is challenging task. Currently, the safe, promising and attractive protocol for the asymmetric synthesis of unnatural α-AAs becomes the addition of the generated *in situ* radicals to the alkene or imine derivatives based on chiral auxiliaries.[2]

We report about the efficient and practical protocol for the asymmetric synthesis of the unnatural α-amino acids with γ-tertiary and quaternary carbon centers via selective intermolecular iron-catalyzed olefin-olefin coupling of a chiral Ni(II) complex of dehydroalanine Schiff base ((S)-BPB-Ni-Δ-Ala)[3] with different olefins (Figure 1).[4] Diastereomeric Ni(II) complexes with a ratio of up to *dr* >20:1 were isolated in 42–93% yields (18 examples). The target unnatural α-AAs were isolated with excellent enantioselectivity and yields up to 83%.[4]

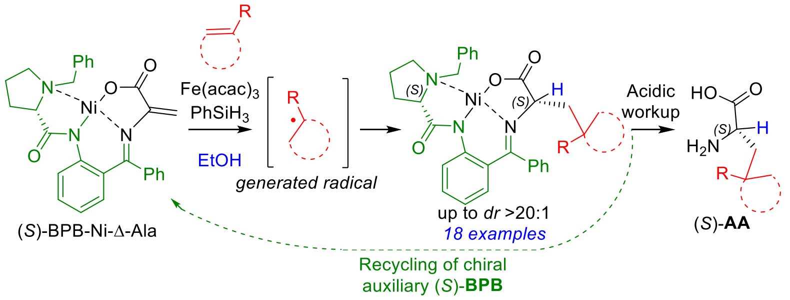

Figure 1. Asymmetric synthesis of α-AAs via chiral Ni(II) complex

Acknowledgements

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New metal-rich nickel-aluminum chalcogenides based on the $AuCu_3$-type heterometallic fragments

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One of the relatively recent discoveries in the field of metal-rich inorganic compounds has been a family of metal-rich nickel - *p*-metal chalcogenides $Ni_{7-x}MCh_2$ and $Ni_{10-x}M_2Ch_2$ (M = group 13-15 metal; Ch = S, Se, Te) containing $AuCu_3$-type heterometallic fragments. In their structures, single- or double-stacked along the *c* axis Ni_3M heterometallic fragments alternate with nickel-chalcogenide Ni_3Ch_2 fragments. Another important structural feature of these compounds is the possibility of varying the Ni_3Ch_2 fragment type (antifluorite plus defective Cu_2Sb, or defective Cu_2Sb).[1]

Presently, the least studied compounds of this type are those containing group 13 metals, particularly aluminum-containing ones, most probably due to the serious difficulties in obtaining single-phase samples by standard solid-state synthesis. In this work, we have synthesized samples of the compounds $Ni_{6.01}AlS_2$, $Ni_{5.61}AlSe_2$ and $Ni_{7-x}AlTe_2$ containing minimum amount of impurities by high-temperature ampoule synthesis using the KCl-LiCl salt mixture as a flux.

The crystal structures of $Ni_{6.01}AlS_2$ and $Ni_{5.61}AlSe_2$ were refined by the full-profile Rietveld method against powder diffraction data. The $Ni_{6.01}AlS_2$ profile was described in the tetragonal system (a = 3.5438(3) Å, c = 18.1058(2) Å, V = 227.38(5) Å^3, $R_p/R_w/R_{Bragg}$ = 0.025/0.033/0.0051). It was found that nickel-sulfur fragments have two types — defective Cu_2Sb-type and antifluorite type, as in other previously described sulfides $Ni_{7-x}MS_2$. The nickel-aluminum selenide profile can also be described in the tetragonal system within the $Ni_{7-x}MSe_2$ structure model (a = 3.5886(5) Å, c = 18.555(3) Å, V = 238.96(5) Å^3, $R_p/R_w/R_{Bragg}$ = 0.053/0.069/0.014); however, this compound only has one type of nickel-selenium blocks, the one with Cu_2Sb-type structure. It should be noted that the samples contained a small amount of a metallic nickel impurity (~ 1%) in case of $Ni_{6.01}AlS_2$, and Ni_3Se_2 (~ 6%) in case of $Ni_{5.61}AlSe_2$.

Electronic structure of $Ni_{7-x}AlCh_2$ (Ch = S, Se) was characterized based on the DFT calculations and electron localization function topology. All compounds are expected to be 3D metallic conductors and display an array of multi-centered heterometallic bonds.

Acknowledgements

This work was supported by Russian Foundation for Basic Research (Grant 18-03-01201a) and the Programme of Presidium of Russian Academy of Sciences (Grant No.I35.2.3). The computations were carried out using the equipment of the shared research facilities of the HPC computing resources at Lomonosov Moscow State University.

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Photochemical properties of 1-cymantrenylalkyl derivatives of N,S-substituted thioureas

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Currently the field of the synthesis and investigation of compounds with photochromic properties which can potentially be used as molecular switches, memory elements and chemical sensors is being actively developed. There are examples of effective photochromic systems based on organometallic compounds of Re, Ru, Co, and other metals.[1] We have previously shown that manganese derivatives exhibit photochromic properties.[2] With the aim of creating photochromic systems and materials, we obtained monosubstituted bifunctional cymantrene derivatives, cascade structures among them, containing isothioureido fragments as n-donor groups capable of chelating reversibly to manganese (Figure 1) and studied their photochemical properties.

We found that the photolysis tricarbonyl complexes in solution (λ□$_{max}$ = 330 nm) yields stable dicarbonyl chelates (λ□$_{max}$ = 380 nm and 440 nm) (Figure1). In a closed system in the presence of CO, they add CO to form the parent tricarbonyls thus forming intermolecular photochromic systems. The molecular structure and relative thermodynamic stability of chelates formed was established by IR, UV-Vis and NMR spectra and confirmed by B3LYP / LanL2DZ calculations. The presence of the third functional group capable of coordinating to Mn, allowed us to create for the first time an intramolecular three-component photochromic system with fine tuning of optical properties. The photochromic systems obtained are stable and withstand many irradiation – thermal reaction without spectral changes.

Acknowledgements

The authors acknowledge the Russian Science Foundation (grant 17-73-30036) for financial support.

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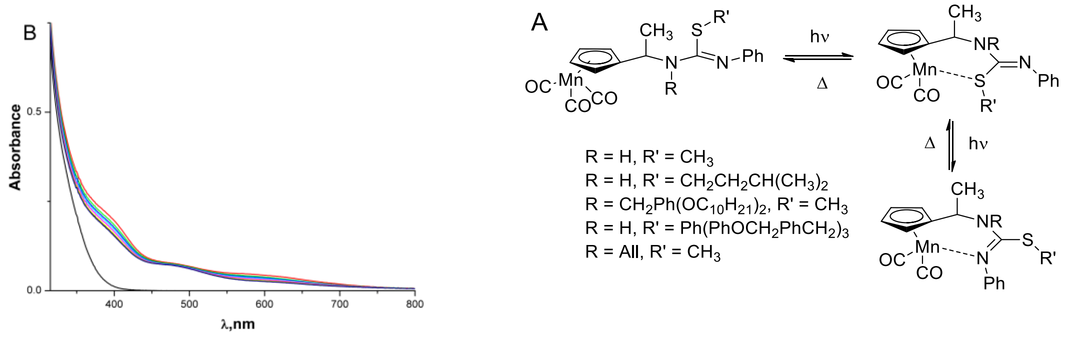

Composition systems based on ZIF-8 and alumina nanofibers as materials with tunable properties for catalysis

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A novel composition materials based on zeolitic imidazolate framework (ZIF-8) and alumina nanofibers (Nafen^{TM}) were synthesized according to a two-step template approach by a solvothermal procedure. According to HR-TEM data, the ZIF-8 content affected its nanocrystal dispersity in the ZIF-8/Nafen composite. The DRIFT spectroscopy study of the basicity of Nafen and ZIF-8/Nafen materials using $CDCl_3$ as a probe molecule revealed that the amount of basic sites can be tailored by the ZIF-8 nanoparticle content in the composites. Basic sites in the ZIF-8 matrix were suggested to form by the Zn-OH groups and N-moieties of nonbridging linkers in ZIF-8 framework defects, whereas the bridging oxygen atom (Al-O-Al) and -OH groups of the Nafen support can act as basic sites. The increasing ZIF-8 content in the composite leads to rising the amount of these basic sites. The strength of the strongest basic sites of Nafen and ZIF-8 materials are 955 and 858 kJ/mol, respectively.

Catalytic properties of ZIF-8/Nafen were investigated in two catalytic reactions. The first reaction was synthesis of propylene glycol methyl ether (1-methoxy-2-propanol, PGME) from methanol and propylene. PGME is widely used in chemical, cosmetic and pharmaceutical industry as pollution-free solvent. It was found that the reaction rate and yield of PGME rise with the increasing content of the ZIF-8 crystals in ZIF-8/Nafen composites (Fig. 1) that is correlated to the amount of basic sites in the composites. The selectivity to PGME depends on the nature and amount of active sites that can be adjusted by the ZIF-8 content in ZIF-8/Nafen. The maximum activity and selectivity to PGME (93.8%) are observed in the presence of the pure ZIF-8 material with the smallest nanocrystal size (100-150 nm).

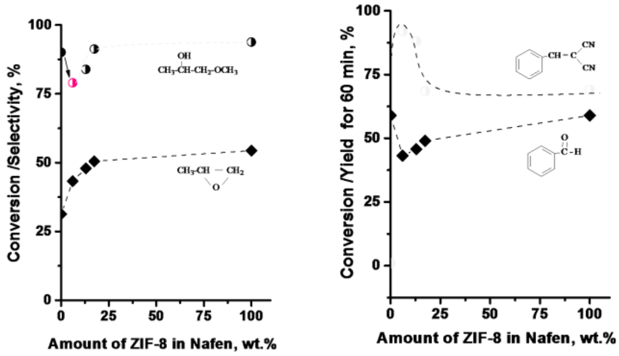

Figure 1. Dependence of catalytic properties of ZIF-8/Nafen on ZIF-8 content in composite in studied reactions

The second reaction for testing catalytic properties of composite materials were the Knoevenagel condensation of benzaldehyde (BA) with malononitrile to 2-benzylidenemalononitrile. Reaction rate was demonstrated to rise with increasing ZIF-8 content in composite (Fig. 1), whereas selectivity reaction towards benzylidenemalononitrile (BMN) decreased due to the side reaction of aldol condensation of BA.

Tuning the catalytic performance of zinc zeolitic imidazolate frameworks in the synthesis of 1-methoxy-2-propanol from methanol and propylene

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Nowadays, a new subclass of metal-organic frameworks (MOFs), such as zeolitic imidazolate frameworks (ZIFs), have attracted considerable attention as materials for catalysis due to combination of structure od zeolites and physicochemical properties of MOFs in one material. Here we demonstrated investigation of catalytic potential of zinc zeolitic imidazolate frameworks based on 2-methyl- (ZIF-8) and 2-ethylimidazolate (MAF-5 or ZIF-14) linkers in synthesis of propylene glycol methyl ether (1-methoxy-2-propanol, PGME) from methanol and propylene. PGME is widely used in chemical, cosmetic and pharmaceutical industry as pollution-free solvent.

In the presence of ZIF-8 and MAF-5 materials reaction was found to proceed at 110-120°C with 92.1-93.8% selectivity towards PGME. Reaction rate in the presence of MAF-5 was higher in compared with ZIF-8 that was related to the higher in the basicity and in the accessibility of active sites. The lower basicity of ZIF-8 (858 kJ/mol) than MAF-5 (884 kJ/mol) due to the difference in pK_a of conjugate acids of 2-methylimidazole (7.85) and 2-ethylimidazole (8.0).

It was demonstrated that catalytic properties of ZIF-8 strongly depended on the crystal size. The conversion of PO and yield of PGME decreased rapidly with increasing crystallite size. Such behavior can be related with (a) the mass transfer resistance changes with the crystal size and morphology, and (b) varying localization of active sites. Moreover, the reaction selectivity is also determined by the crystal size of ZIF-8 materials. The lower the crystal size of the ZIF-8 sample, the higher the selectivity toward PGME that was explained by (a) different density of active sites on the external surface, and (b) electronic structure effects of the surface.

The reaction mechanism in the presence of ZIF-8 catalyst was investigated by IR spectroscopy. According to the IR study, reaction between MeOH and PO in the presence of ZIF-8 systems proceeds on "Lewis acid site - basic site" pairs, where Lewis acid sites are preferably formed by Zn^{2+} ions without three or two organic linkers, whereas basic sites are formed by Zn-OH species or N atom of 2-methylimidazole.

MAF-5 and ZIF-8 materials showed good reusability for 5 recycles in catalysis that can point to their high potential for catalytic application. Compared with reported catalysts, studied ZIFs, especially MAF-5, showed not only the highest conversion of PO but also the highest selectivity for 1-methoxy-2-propanol under the similar reaction conditions.

Single Molecule Magnets based on Dy^{3+} complexes supported by diazabutadiene ligands.

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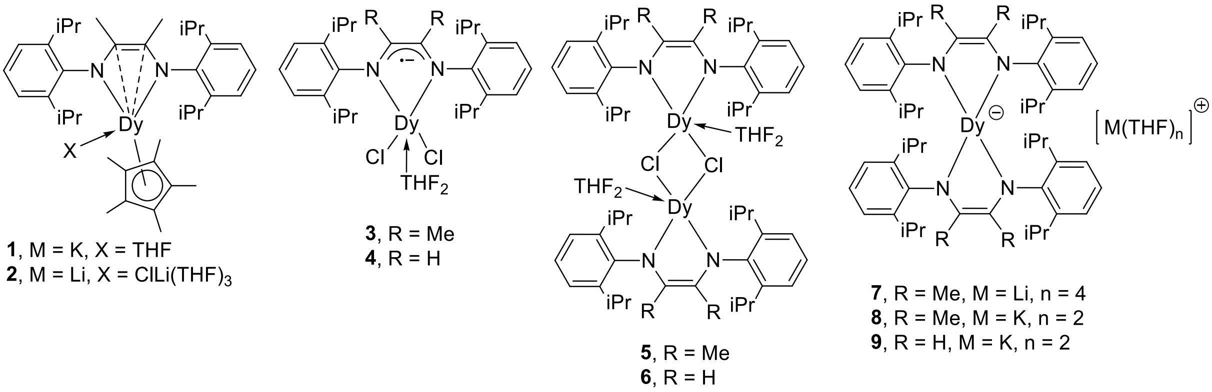
Coordination complexes exhibiting slow relaxation of their magnetization associated with magnetic bistability show tremendous potentialities for information storage or spin-based computing[1]. Single-Molecule Magnets (SMM) have been greatly enhanced by taking advantage of the fascinating properties of lanthanide ions[2]. Lanthanide ions such as Dy^{3+} exhibiting oblate electronic density are efficiently stabilized by axial crystal-field that maximizes the splitting of the m_J levels, while minimizing the Quantum Tunneling of the Magnetization (QTM)[3].

The overall approach to the design of new dysprosium SMM is to create highly symmetrical axial enviroments around the Dy^{3+} ion and stabilize thereby the 4f electronic density. In this aim, a series of heteroleptic half-sandwich[4], chloride and homoleptic Dy^{3+} complexes containing diazabutadiene ligands in [DAD^{2-}] as well as [$DAD^{\bullet -}$] forms was synthesized.



1, M = K, X = THF
2, M = Li, X = ClLi(THF)$_3$

3, R = Me
4, R = H

5, R = Me
6, R = H

7, R = Me, M = Li, n = 4
8, R = Me, M = K, n = 2
9, R = H, M = K, n = 2

Figure 1. All obtained homo- and heteroleptic Dy^{3+} complexes exhibit distinct slow relaxation of the magnetization dynamics and geniune Single-Molecule Magnet (SMM) behaviour.

Acknowledgements

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Blue luminescence of cyclometallated 1,2,3-triazol-5-ylidene iridium(III) complexes

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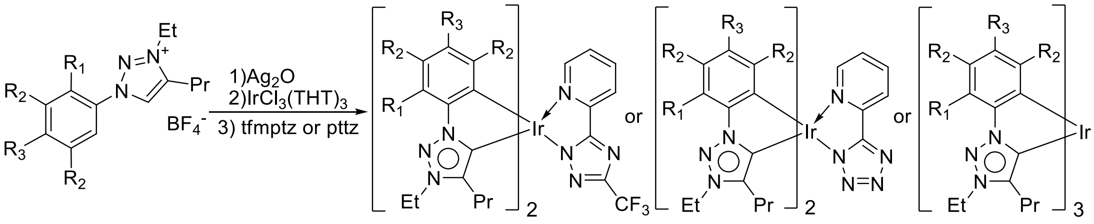
Phosphorescent Ir(III) complexes are widely used as photosensitizers in photodynamic therapy, photocatalysts for water splitting, phosphorescent labels in biomolecules, and oxygen sensors. The most important field of application of Ir(III) complexes is their use as phosphorescent pigments in electroluminescent devices, such as organic light-emitting diodes and light emitting electrochemical cells.

Most of Ir(III) complexes used in OLEDs are homoleptic tris-cyclometallated Ir(III) complexes [Ir(C^N)$_3$] or neutral heteroleptic bis-cyclometallated complexes [Ir(C^N)$_2$(L^X)] (C^N = C-, N-donor cyclometallated ligand, L^X = auxiliary ligand).

N-heterocyclic carbenes are widely investigated as ligands, allowing to elevate the energy of the lowest unoccupied molecular orbital (LUMO). They are strong-field ligands due to weak π-acceptor and strong σ-donor properties, which leads to higher LUMO level and, consequently, higher energy of emitted photons (that is, blue shift of the spectrum), together with high-energy d–d level of the excited state, which reduces the probability of thermally activated non-radiative MC decay. In addition to classic NHC ligands, intense attention is directed towards a new class of NHCs, mesoionic carbenes (MIC) based on the 1,2,3-triazol-5-ylidene core. Recently, we reported that 1,2,3-triazol-5-ylidene ligands can serve as tunable platform for synthesis of luminescent iridium(III) complexes.[1]

A series of homoleptic and heteroleptic iridium(III) complexes was synthesized and their molecular structures were established by X-Ray crystallography. All complexes exhibit luminescence in blue (**1** and **2**, 460-490 nm) or green (**3**, 520-550 nm) region.



1 (NHC)$_2$Ir(tpmptz) **2** (NHC)$_2$Ir(pttz) **3** (NHC)$_3$Ir

Figure 1. Synthesis of homo- and heteroleptic iridium(III) luminescent complexes

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Intercalation of Halogen Bond Acceptor Molecules in the Molecular Co-crystals of $(HBpz_3)ReOCl_2$

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In the co-crystallization with various halogen bond (XB) donors (C_2I_2, 1,4-$C_6F_4I_2$, 1,4-$(CF_2)_4I_2$ *etc*), the molecules of $(HBpz_3)ReOCl_2$ ($HBpz_3$ = *tris*-pyrazolylborate) forms identical double layers, which hosts the layers of guest XB-donor molecules between them. Consequently, the only variable parameter of the packing is the distance between the double layers, and the resulting co-crystals differ just by *c* dimension, while the rest parameters of their unit cells are almost identical.

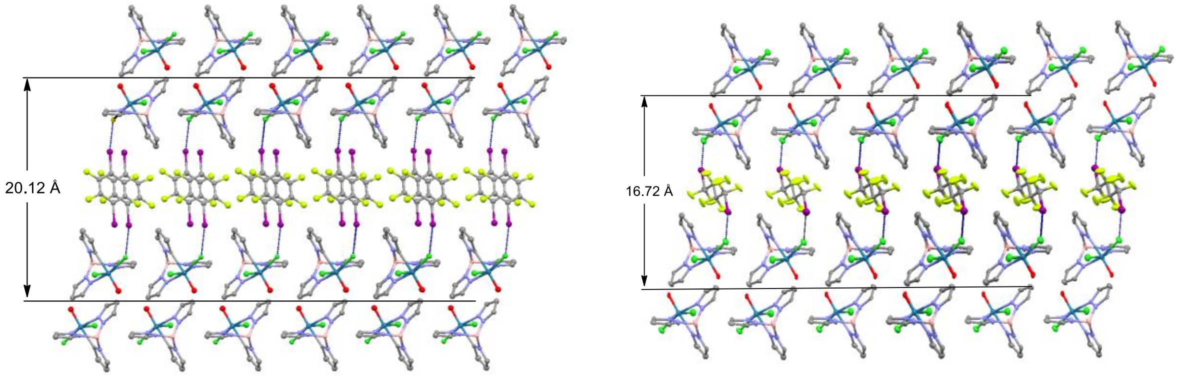

Figure 1. Intercalation of 1,4-$C_6F_4I_2$ and 1,4-$C_6F_4I_2$ and between the double layers of $(HBpz_3)ReOCl_2$

$(HBpz_3)ReOCl_2$ - 1,4-$C_6F_4I_2$ **a** 7.810, **b** 8.218, **c** **20.121** □ 87.00 □ 82.19 □□64.05
$(HBpz_3)ReOCl_2$ - 1,4- $(CF_2)I_2$ **a** 7.990, **b** 8.145, **c** **16.721** □ 82.54 □ 79.75 □ 64.51

It worth noting, that parent $(HBpz_3)ReOCl_2$ crystals suffers from the severe twinning and O/Cl positional disorder [1], so that Re-O and Re-Cl bonds cannot be distinguished from one another, but in its XB co-crystals, where I---Cl-Re XBs are formed, this problem can be resolved. Therefore, in general, XB can assist to overcome twinning and disorder in crystals, by means of co-crystallization of a subject compound with an appropriate halogen (or other σ–hole) donor or acceptor. In most cases σ–hole interactions are quite weak to produce considerable or undesired effect on the molecular geometry, but can assist in organizing them into well-crystallized form, which can be analyzed by routine single crystal XRD methods.

Acknowledgements

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Luminescent Mn(II) complexes based on N,O-hybrid pyridyl-containing phosphine oxides

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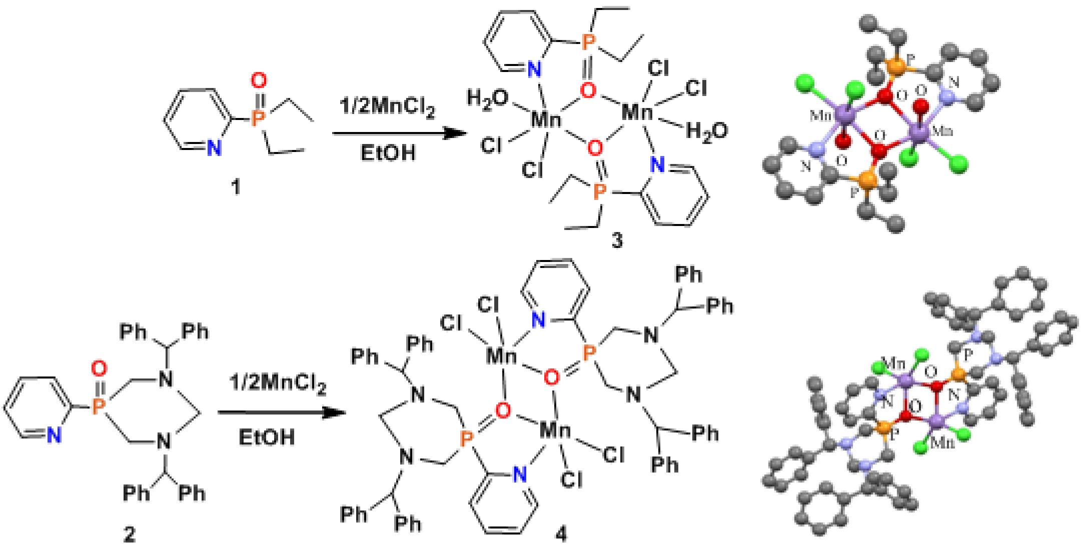
Manganese(II) complexes attract a great interest for researchers due to high emissive quantum yields make them potential candidates for use in organic light-emitting diodes[1].It is also well known complexes based on Mn(II) sources have “red” luminescence in the solid phase[2,3]. Recently novel N,O-hybrid pyridyl-containing phosphine oxide ligands and their metal complexes with Mn(II) metal-ion were synthesized (Scheme 1).



Scheme 1. Synthesis Mn(II) complexes with ligands 1, 2

Ligands **1**, **2** reacts with manganese(II) chloride in EtOH in 2:1 metal:ligand ratio giving the corresponding binuclear complexes **3**, **4**. The composition and structure of **3, 4** were determined using a set of physicochemical analysis methods including X-ray analysis.

It was found that complexes **3**, **4** in CH_3CN, $CHCl_3$ solutions, correspondingly, exhibit luminescence with λ_{em} at *ca* 400 nm.

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Copper Complexes Bearing Bis(pyrazol-1-yl)acetic Acids

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Copper-dioxygen reactions have aroused more and more attention in the recent years due to their remarkable reaction properties observed in nature. Thus, we previously reported on a dinuclear cupric complex $[\mathrm{Cu^{II}}_2(\mathrm{bd}t\mathrm{bpza})_2(\mathrm{NO_3})_2]$ bearing the κ^4-*N,N,O,O*- coordinating bis(3,5-di-*tert*-butylpyrazol-1-yl)acetate (bd*t*bpza).[1]

To gain more knowledge about structural and functional models of dinuclear type 3 copper enzymes, we synthesized the cuprous compounds $[\mathrm{Cu^I}(\mathrm{Hbd}t\mathrm{bpza})\mathrm{Cl}]$ (**1**) and $[\mathrm{Cu^I}(\mathrm{Hbdppza})\mathrm{Cl}]$ (**2**), bearing the corresponding *N*,*N*,*O*-heteroscorpionate ligands in a κ^2-*N*,*N* coordination mode. X-ray structure determination of **2** revealed a trigonal planar coordination geometry of the copper center. Exposure of the cuprous complexes to air led to the activation of dioxygen. Hereby, **1** was converted to the cupric $[\mathrm{Cu^{II}}_2(\mathrm{Obd}t\mathrm{bpza})_2]$ complex by an intramolecular C-H activation, resulting in a self-hydroxylation on the *tert*-butyl moiety. Complex **2**, however, was oxidized to result in the homoleptic bisligand complex $[\mathrm{Cu^{II}}(\mathrm{bdppza})_2]$, with the release of H_2O_2 as a byproduct. To obtain more insight into the reaction mechanism, DFT-calculations focusing on the dinuclear μ-η^2:η^2-peroxido- and bis-μ-oxido-intermediates have been performed.

Additionally, we present electrocatalytic studies regarding the hydrogen evolution reaction catalyzed by the homoleptic cupric complexes $[\mathrm{Cu^{II}}(\mathrm{bpza})_2]$ and $[\mathrm{Cu^{II}}(\mathrm{bdmpza})_2]$ under acidic conditions.

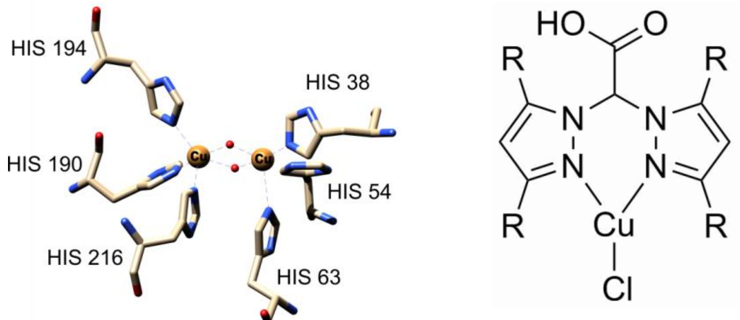

Figure 1. A) Tyrosinase as an example of dinuclear type 3 copper enzymes. (PDB 3AWV) **B)** Cuprous complexes bearing bis(3,5-disubstituted pyrazol-1-yl)acetic acids (R = ^{t}Bu (1), Ph (2))

Acknowledgements

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The structures of new chloroacetate complexes of uranyl with organic cations

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The investigation of chemical compounds that contain uranyl cations UO_2^{2+}, the most stable form of existence of uranium(VI), is an important field of inorganic and coordination chemistry. The permanently developing interest to this particle is connected with the crucial role of uranium as an energy source in nuclear industry. The carboxylate complexes of uranium are explored intensively for several decades[1] and some of them, for example acetates and oxalates, are applied in analytical practice and processing of uranium. Nevertheless, the data about uranyl ions interacting with halogenated analogues of acetic acid are absent in literature.

Yellow crystals of $(CH_3)_4N[UO_2(L)_3]$ (I), $(C_2H_5)_2NH_2[UO_2(L)_3]$ (II), $(PhNH)_2CNH_2[UO_2(L)_3]$ (III) and $(C_2H_5)_3C_7H_7N[UO_2(L)_3]$ (IV) (where L = CH_2ClCOO^-) were obtained after a few days of isothermal evaporation of the reaction mixtures at ambient conditions. The crystal structures of complexes I−IV are determined with the method of X-Ray diffraction analysis of single crystals.

In the structures I−IV the uranium atoms have CN = 8. The coordination polyhedra of U atoms have the form of hexagonal bipyramids, while dual to them Voronoi-Dirichlet polyhedra have the form of hexagonal prisms. The volumes of Voronoi-Dirichlet polyhedra of U atoms are equal to 9.43 (I), 9.39 and 9.43 (II), 9.42 (III) and 9.46 (IV) $Å^3$. These values are in a good agreement with the known[2] value of 9.3(2) $Å^3$ for UO_8. In all the synthesized compounds the uranyl ion coordinates three monochloroacetic-anions (coordination mode B^{01}-4)[3] and forms complex units $[UO_2(L)_3]^-$. The evaluation of noncovalent interactions was conducted with the application of the method of molecular Voronoi-Dirichlet polyhedra. According to the calculation, the bonding between uranium containing complexes and outer-sphere cations and the formation of supramolecular structures of the obtained compounds are realized through intermolecular interactions, in particular C−H/O contacts.

Acknowledgements

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Synthesis, structure and redox properties of the cluster complexes [$Re_6Q_8(bpy)_4Hal_2$]

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Octahedral rhenium cluster complexes with N-donor heteroaromatic terminal ligands make it possible to combine properties from various functional groups, which makes them interesting from the point of view of varying electrochemical, photophysical and spectroscopic properties.[1,2] The possibility to obtain cluster complexes with different symmetry allows us to consider them as building blocks for supramolecular compounds.

In this work, clusters with the general formula [$Re_6Q_8(bpy)_4Hal_2$]·2bpy (Q = S, Se; Hal = Cl, Br, I) were obtained using the ampoule synthesis in the melt of 4,4′-bipyridine (bpy). Structures of the compounds have been studied by X-ray structural analysis. Four bpy molecules have been found to be coordinated in equatorial plane, whereas the labile halide ligands occupy *trans*-position. Solvate 4,4′-bipyridine molecules can be removed by washing with polar solvents, and resulting compounds [$Re_6Q_8(bpy)_4Hal_2$] are soluble in DMSO and *N*-methyl-2-pyrrolidone.

Cyclic voltammetry (CV) revealed that, unlike most well-known cluster complexes with N-donor heterocyclic ligands, compounds [$Re_6Q_8(4,4'\text{-bpy})_4Hal_2$] exhibit several consecutive reversible ligand-centered redox processes. On the other hand, reversible one-electron oxidation of the cluster core has not been displayed in the positive potential region. From a comparison of CV of cluster complexes and free 4,4′-bipyridine, it can be assumed that the first redox wave belongs to the reduction process bpy ↔ $bpy^{\bullet-}$, which leads to the formation of the [$Re_6Q_8Hal_2(4,4'\text{-bpy})_4$]$^{\bullet-}$ anion. The redox potential shifts to the positive region approximately by 0.5 V, which can be correlated with the influence of the coordination of organic ligands to the cluster core.

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Structure and magnetic properties of heterometallic coordination polymers based on methoxy-substituted beta-diketonates of transition metals and lanthanides of the type $[TM(dik)_2Ln(dik')_3]$

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Metal complexes with methoxy-substituted □-diketonates (R-CO-CH-CO-$C(OCH_3)_xR'_{3-x}$, x=1, 2) have been proposed for the preparation of various heterometallic coordination polymers [1, 2]. It was shown that cocrystallization of transition metal complexes (Cu (II), Ni (II), Co (II), Mn (II)) with $Ln(thd)_3$ from organic solvents allows to obtain various heteroleptic and heterometallic complexes. The use of mono-methoxy ligands allows volatile heteroleptic binuclear and anhydrous homoleptic complexes of lanthanides with fluorinated ligands as a result of ligand exchange reactions. Cocrystallization with participation of the transition metal complexes with dimethoxy-substituted ligands results in heterometallic complexes which are isostructural linear coordination polymers of alternating monometallic fragments linked by bridging oxygen atoms of the methoxy groups (Figure 1). The composition and structure of products after cocrystallization of transition metal β-diketonates with lanthanides complexes can be varied depending on the combination of metals and structure of the ligands involved. Magnetic properties of the complexes were investigated depending on TM and Ln involved.

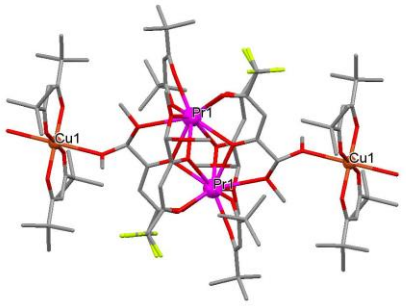

Figure 1. A fragment of $[(PrL_2(thd))_2Cu(thd)_2]$ coordination polymer. L= trifluoro-5,5-dimethoxypentane-2,4-dionate, thd= 2,2,6,6-tetramethylheptane-3,5-dionate

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Cyano-substituted phthalocyanines of *d*-elements. Synthesis, spectroscopic, fluorescent, coordination properties and catalytic activity

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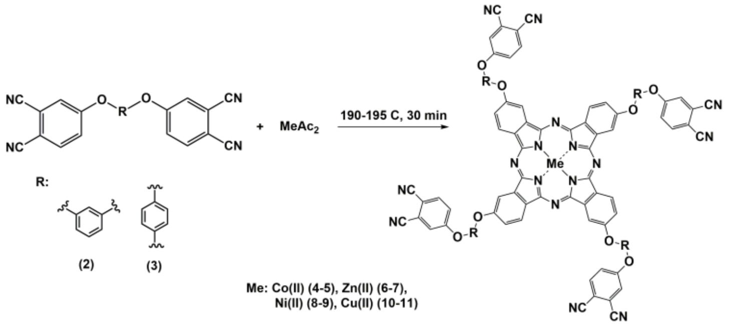
Coordination compounds containing complex organic ligand and several coordination centers are very promising in smart-materials construction.[1-2] Present report deals with the synthesis of a number d-metals complexes with substituted phthalocyanines, having cyano- groups in the terminal positions of peripheral substituent, as well as its physic-chemical properties study. The synthesis was carried out by template condensation method, the phthalocyaninates obtained were characterized by ^{1}H NMR and IR spectroscopy and MALDI-TOF mass-spectrometry. For the complexes obtained spectroscopic characteristics in various organic solvents were determined, extra-coordination prosses in a weakly coordinating solvent were studied by the example of interaction with DABCO, pyridine and pyrazine. It was established the complexes stability depends on steric factors of the peripheral substituent and decreases in the series Py < Pz < DABCO. Further, fluorescent properties of the phthalocyaninates described were studied both in the individual state and as part of the molecular complex with N-ligand.



Scheme 1. Synthesis of Co(II), Zn(II), Ni(II), Cu(II) tetrakis-(dicyanophenoxy)phthalocyanines

Catalytic activity of the phthlocyanines synthesized in the liquid-phase oxidation of N,N-carbomodithiolate varies in the series Ni<Cu<Zn<Co. It correlates with the stability of molecular complexes with pyridine (1:1), which confirms the coordination path of disulfide bond formation reaction.

Acknowledgements

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The family of Mo_4Ga_{21}-based superconductors

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Superconductivity is often inherent in families of compounds with common structural features. Recently, endohedral Ga clusters centered by atoms of a 4*d* or 5*d* transition metal were proposed as a structural motif favorable for superconductivity in Ga-based intermetallic compounds.[1] In this family, Mo_8Ga_{41} with T_C ~ 10 K, Mo_6Ga_{31} (8 K), Rh_2Ga_9 (2 K), Ir_2Ga_9 (2 K), and $ReGa_5$ (2.3 K) superconductors were reported, among which Mo-based compounds are distinguished by relatively high critical temperatures. Moreover, Mo_8Ga_{41} attracted interest as a strong-coupling superconductor[2] and as a candidate for multiband superconductivity[3-5] that motivates the search for new endohedral Ga cluster superconductors and investigation of their properties.

The Mo-based endohedral Ga cluster superconductors are represented by the Mo_8Ga_{41} and Mo_6Ga_{31} compounds, which have closely related crystal structures where $Mo@Ga_{10}$ and $Ga@Ga_{12}$ clusters are the main building units. From the structural point of view, another related compound, Mo_4Ga_{21}, can be anticipated, however, it does not form in the respective binary system. Exploratory syntheses in the Mo-Ga-S ternary system indicate that Mo_4Ga_{21} can be stabilized when Ga is partially substituted by S.[6] Here, we present the family of Mo_4Ga_{21}-based superconductors, which are formed when Ga is partially replaced by an E element from groups 14-16. Six representatives with E = Sn, As, Sb, S, Se, and Te were synthesized and investigated by means of crystal and electronic structures, and thermodynamic and transport properties. The studied compounds exhibit superconducting properties at low temperatures with indications of anisotropy of the order parameter.

Acknowledgements

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Reactivity of coordinatively unsaturated gold(I) derivatives towards manganese and rhenium phenylvinylidenes

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Gold (I) complexes have received considerable attention of researches for their possible application in functional material development, molecular devices design, biochemistry.[1,2] These complexes are also especially versatile and selective catalysts for a growing number of synthetic transformations.[3,4] Therefore, there is continuous interest in understanding the reactivity of gold (I) derivatives towards carbon-carbon triple bonds of organic alkynes and organometallic acetylides. However, at the same time, no information is available regarding the reactions of gold (I) complexes with compounds containing a metallaallene system M=C=C. There is only one study on reactions between vinylmethyltitanium derivatives and $XMPR_3$ (M = Cu, Au) where a binuclear vinylidene complex containing TiAu metal core was characterized.[5] Here we report our study on the interaction of rhenium and manganese phenylvinylidenes $Cp(CO)_2M{=}C{=}CHPh$ (M = Mn, Re) with gold(I) complexes (L)AuX (X = Cl, -C≡C-Ph, -C≡C-(2-C_5H_4N)), containing labile ligands L such as dimethylsulfide, tetrahydrothiophene, or pyridine. Obtained heterometallic compounds are characterized by IR, and NMR spectroscopy, their redox-properties are established. The molecular structures are determined by X-ray diffraction study.

Acknowledgements

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Pd/Cu-Catalyzed M-C coupling reactions in synthesis of functionally substituted σ-acetylide iron complexes

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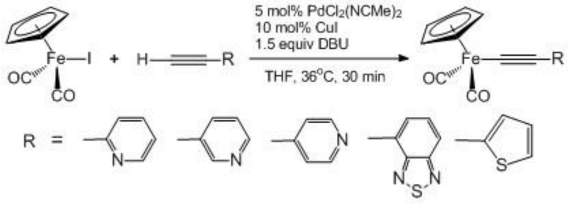
σ-Alkynyl complexes are of great interest due to their possible application in molecular electronics, nonlinear optics, and proton reduction catalysis.[1-3] Common synthetic routes to the transition metal acetylides involve the reaction of alkali metal acetylides with transition metal halides or the reaction of metal carbonylates with 1-chloroalkynes. Both routes require the use of sensitive reagents, give low yields of desired products, and result in a number of by-products.[4] Pd/Cu-catalyzed cross coupling could be an efficient tool to prepare σ-acetylide complexes from terminal alkynes. However, the reactivity of terminal alkynes toward metal-carbonyl halides under cross-coupling conditions has enough not been studied. In looking for ways to extend our understanding of Pd/Cu-catalyzed M-C coupling process, we studied the reactions between alkynes (2-, 3-, 4-ethynylpyridine, 4-ethynyl-2,1,3-benzothiadiazole, and 2-ethynylthiophene) and $CpFe(CO)_2I$ under Pd/Cu-catalyzed conditions. In course of the work we found out that depending on the catalyst and reagents used, the reactions could proceed in different ways to give the desired alkynl complexes or different by-products.

The conditions, catalysts and reagents that provide the highest yields of the desired product were determined. Synthetic approaches to σ-acetylide iron complexes of the type $Cp(CO)_2Fe\text{-}C{\equiv}C\text{-}R$ (R is *o*-, *m*-, *p*-pyridyl, 2-tenoyl, 2,1,3-benzothiadiazole) were elaborated (Scheme 1).



Scheme 1

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Electrochemical deposition of corrosion resistance alloys containing chromium phosphides

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In the last time, the development of theoretical principles of new deposition techniques of chromium and chromium alloy coatings from environmentally friendly baths based on Cr(III) compounds is attracting progressively increasing attention from researchers[1-5]. One topical problem is the production of thick deposits (up to several tens of microns) that can be used as corrosion and wear resistant coatings[5,6].

Corrosion–resistant materials Cr–P and Cr–P–W coatings were obtained by electrodeposition from aqueous and aqueous–organic (DMFA : water) solutions, respectively. Inclusion of phosphorus into the deposits formed on the cathode is confirmed using the EDX and XPS techniques. Sodium hypophosphite addition into solutions applied for coatings electrodeposition led to substitution of carbon by phosphorus in the electrolytic deposits. XPS results showed that P(+5) was found at the coating surface, while the contribution of P(–3) was significant already at the depth of 10 nm. This allows stating the formation of chromium phosphides in the course of electrolysis[7,8].

The materials obtained by electrolysis were X–ray amorphous. This fact might be considered as promising from the point of view of corrosion protection[9].

It is shown that addition of phosphorus into the coatings results, as compared to Cr–C coatings, to disappearance of the region of potentials corresponding to active metal dissolution in the anodic polarization curves and enhancement of their corrosion resistance. It is essential that this effect was found also in the chloride–containing solution. Therefore, one may conclude that the surface of alloys is passive under conditions of corrosion process[10].

Acknowledgements

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Increase in Wear Resistance of Composite Coatings Nickel–Phosphorus–Modified Copper Phthalocyanate

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Loss of energy during friction and wear is a large problem in the operation of actuated parts of most mechanisms. An alternative to the use of conventional liquid, plastic, and solid lubricants may be represented by antifriction compositions, which are deposited on parts and friction units using chemical and electrochemical deposition.[1, 2] Some phthalocyanine (Pc) derivatives possess necessary features of triboactive additives, in particular, structure-formation ability at an interface.[3] However, when using water-insoluble phthalocyanines for the preparation of coatings, it is a problem to maintain their suspension stability in electrolyte solutions. To solve this problem, the modification of Pc particles by reaction with 4-benzenediazonium-carboxylate are used.[4] It was shown (Fig. 1a) that the electrokinetic (ζ-) potential of the particles in aqueous dispersions changes greatly (from -25 mV to -45 mV) as well as the average size aggregates reduces from ~3000 nm to ~250 nm. This provided the significant increase of colloidal stability of Pc aqueous suspensions. The introduction of additives of the disperse phase of modified (carboxylated) CuPc in an amount of 0.1–0.2 g/L into weakly acidic solutions for chemical deposition of the Ni-P alloy provides composition coatings with the wear resistance, which is increased by two to three times, under rubbing friction (Fig. 1b). The wear resistance of coatings increases with growth of the number of carboxyphenyl fragments in the modified CuPc

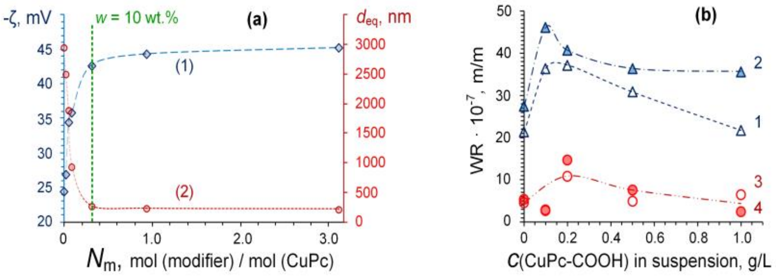

Figure 1. (a) ζ-potential of CuPc particles (1) and the mean diameter (d_{eq}, 2) of their aggregates in aqueous suspensions depending on the molar ratio modifier-CuPc. **(b)** Dependence of the wear resistance at the path length of (1, 3) ~0 and (2, 4) 1 km in the case of (1, 2) Ni-P-CuPc-coatings and (3, 4) tribocontact of the Ni-P-CuPc-coating/steel-45 on the concentration of CuPc-COOH

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Physico-mechanical properties of composite coatings based on chromium and various forms of carbon

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To improve the operational properties of chromium coatings a dispersed phase (DP) is introduced into solutions for the electroplating of chromium[1,2,3]. In this study various carbon modifications were used as the dispersed phase: graphite, multi-walled carbon nanotubes (MWCNT) and detonation nanodiamonds (DNA).

Composite coatings (CP) Cr-C were obtained by electrolysis from a solution (250 g/l CrO_3, 2,5 g/l H_2SO_4) containing DP (C_{DP} = 4-40 g/l) at 50°C and with current density 0,5 A/cm^2.

The graphite distribution (fig. 1) in the obtained composite coatings was determined by the method of secondary ion mass spectrometry (SIMS) on a CAMECA IMS 4f mass spectrometer (France). When the concentration of DP in the chromium plating solution increase from 0 to 8 and 16 g/l, the concentration of carbon in the CP increases from 0 to 10 and 31% by volume, respectively. The fracture toughness of coatings (K_{1c} was determined by indentation on a micro Vickers hardness tester Shimadzu HMV-G21DT, Japan) reaches the highest value (0,52±0,05 MPa*$m^{1/2}$) with a graphite content of 8 g/l.

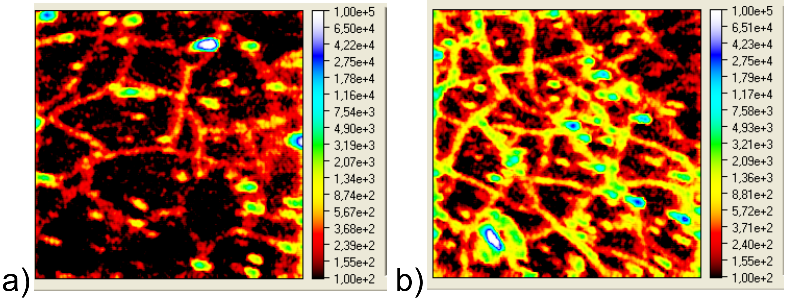

Figure 1. Graphite distribution maps in CP: a) C_{DP} = 8 g/l; b) C_{DP} = 16 g/l

With the DNA and MWCNT addition the fracture toughness remains at the level of the coating without the dispersed phase – 0,37±0,05 MPa*$m^{1/2}$.

The wear rate (W) under dry friction conditions of tribo-couple «steel (HV 4,6 GPa) – the coating with a chromium matrix» was determined on a Taber Linear Abraser 5750 (USA) unit with a load of 10,8 N (0,38 MPa). The obtained values of total wear rate of CP with graphite are 1,3 times less than the coating without DP, and the coefficient of friction was 0,2, against 0,32 for a chromium coating without graphite.

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Characteristics of Nickel complexes and deposition of electroless Nickel alloys

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The proposed by various scientists' mechanisms for the reduction of Nickel ions[1-3] does not consider the influence of the characteristics of complex Nickel ions on the parameters of the electroless of coatings. At the same time, by the example of electrodeposition of chromium and various alloys, the significant role of complex compounds is shown and models of ligand selection are proposed.[4, 5]

The characteristics of the ligands (denticity D) and Nickel complexes (NC) (charge Z, and the stability constants (SC) lgβ) on the rate (mg cm^{-2} h^{-1}) of deposition of the coatings Ni-P (V), Nickel (V_{Ni}) and the phosphorus content (wt.%) in them (w_P) the chemical reduction of complexes of Nickel hypophosphite-ion was studied. To assess the degree of influence of each of the factors, mathematical models were obtained.

$$V = 0.594 - 0.081D + 0.086Z$$

$$V_{Ni} = 0.540 - 0.074D + 0.085Z$$

$$w_P = 13.631 - 0.820Z - 0.377\lg\beta$$

The deposition rate of Nickel-phosphorus coatings increases with a decrease in the dentisity of the ligand and an increase in the charge of the Nickel complex.

The greatest influence on the phosphorus content in the coating shows the charge and stability of the complex ion.

Rules for the selection of ligands and/or Nickel complexes for the designing of new highly effective solutions of autocatalytic deposition of Nickel-based coatings with different phosphorus content are formulated.

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Electrospun metal oxides nanofibers for gas sensing in humid air

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Semiconductor gas sensors are widely used to control the concentration of toxic gases in the air. N-type oxides, such as SnO_2, ZnO, In_2O_3, are typical sensitive materials, but the detecting in humid air is limited due to the strong reduction of the signal value. The negative influence of water should be reduced and this work is devoted to the synthesis and studying of nanocomposites, based on the zinc oxide, modified by cobalt oxide ([Co]/[Co]+[Zn] = 5÷26%).

The nanofibres of zinc-cobalt oxides were obtained by electrospinning from polymer solutions of the $Zn(CH_3COO)_2 \cdot 2H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$. The acetates were dissolved in the equal mixture of 2-methoxyethanol and isopropanol, and then PVP (M_w=1300000) was added. The decomposition temperature was determined by TG-MS. The obtained samples were characterized by XRD and BET method. The study of microstructure of the samples was carried out by HAADF-STEM, EDX maps were acquired. The sensory properties of fibers to NO_2 (1 ppm), CO (20 ppm) and H_2S (0.5–2 ppm) were studied under different air humidity conditions at the temperature 80-270 ^oC. The sensor signal to H_2S in the humid air is dramatically smaller than in the dry air for pure ZnO, but for the nanocomposites with 5 mass percents of Co the signal is quite high even when the humidity is not 0% r.h. The value of the sensor signal to NO_2 for pure ZnO is higher than for all other samples.

Acknowledgements

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Polyfunctional boron synthons under cross-coupling conditions

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Series of amidine-iodine-*closo*-decaborates was synthesized and its reactivity under palladium catalyzed cross-coupling conditions was investigated.

Introduction of positively charged exo-polyhedric substitutes into boron carcass changes general charge of the system and electron density distribution in substituted *closo*-decaborates, which drastically affects reactivity of such compounds under conditions of further cross-coupling processes. Nitrile groups and its derivatives can be introduced into boron cluster to reduce the system charge. Under the conditions of Kumada reaction, it's impossible to use $[ee\text{-}B_{10}H_8I(NCR')]^{1-}$ (R' = Me, Et, tBu, Ph) anions due to electrophilic nature of nitrile group. Because of that we've synthesized series of iodine derivatives of *closo*-decaborates with general formulae $[ee\text{-}B_{10}H_8I(NHC(NH_2)R')]^{1-}$ (R' = Me, Et, tBu, Ph). Such second-generation *closo*-decaborates can be obtained either from iodine-*closo*-decaborates, unsubstituted amidines $[2\text{-}B_{10}H_9(NHC(NH_2)R'')]^{1-}$ or nitrile derivatives of *closo*-decaborate anion.

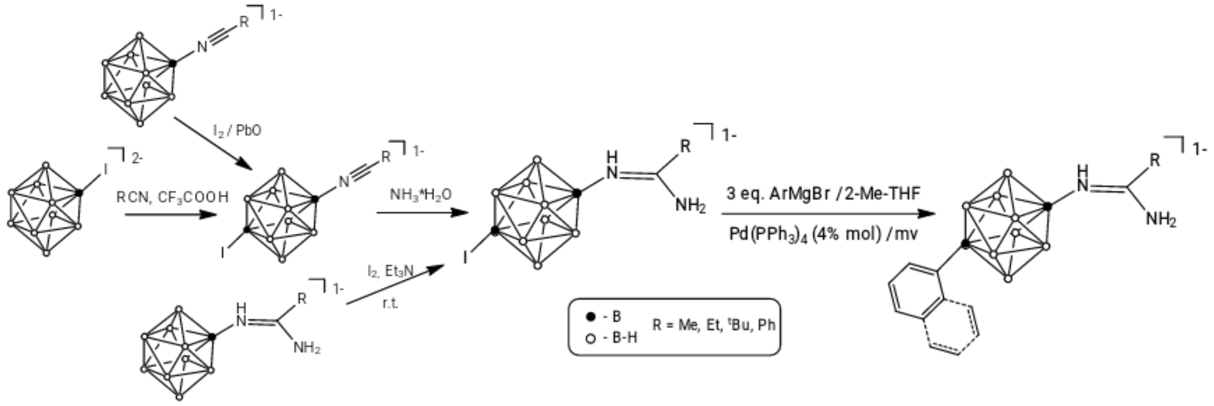

Figure 1. General reaction scheme

Further, disubstituted derivatives of *closo*-decaborate anion was introduced into palladium catalyzed cross-coupling reaction with Grignard reagents in ether solvents (THF, 2-Me-THF, 1,4-dioxane) in order to prevent oxidation side processes.

Acknowledgements

This research was supported by RFBR (17-03-01013 A) and Grant of the President of the Russian Federation 2845.2018.3.

Trihydroxo[dihydroxo(oxo)borato]dicopper(II) $Cu_2\{BO(OH)_2\}(OH)_3$: synthesis, thermal stability and magnetic properties

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Basic copper(II) dihydroxoborate $Cu_2\{BO(OH)_2\}(OH)_3$, first synthesized in 1985[1] and later found in nature as the mineral Jacquesdietrichite, occupies a special place among basic copper(II) salts. The structure of $Cu_2\{BO(OH)_2\}(OH)_3$ consists of chains, formed by square fragments $[CuO_4]$ with the common edges (Fig.1a). Taking into account two additional distances Cu···O 2,65 and 2,68 Å each chain represents octahedron, combined by opposite edges. The bridging groups $BO(OH)_2$ connect octahedron layers, forming a frame structure. Chains in Jacquesdietrichite structure are considerably distant from each other, so this compound appears an interesting object for studying magnetic properties. Meanwhile, the synthesis conditions, mentioned in the only article dealt with the preparation of this substance, are not fully described.[1] Thus, this work is devoted to the optimization of the synthesis method of the basic copper(II) dihydroxoborate $Cu_2\{BO(OH)_2\}(OH)_3$, investigation of its thermal stability and magnetic behavior.

Carrying out the synthesis by pouring two solutions together in accordance to the conditions, noticed in the article[1], led to the formation of X-ray amorphous powder. Therefore, to obtain the target product, the series of experiments, variation of reagents, their ratio, pH of reaction mixture, temperature, heating duration and the presence of stirring included, were realized. A single-phase well-crystalized sample of basic copper(II) dihydroxoborate $Cu_2\{BO(OH)_2\}(OH)_3$ was obtained by adding of a homogeneous mixture of solid reagents $Na[B(OH)_4]$ and $CuCl_2 \cdot 2H_2O$ to the distilled water with following heating at 50 °C in sealed container during 12 days. To separate the large crystals of $Na_2B_4O_7 \cdot 10H_2O$ the resulting blue precipitate was washed several times with water. Purity of the sample was proved by X-ray diffraction method and infrared spectroscopy. The gradual formation of cubic crystallites (Fig. 1b) from the initially unstructured sediment is well described by the model of oriented splicing.

Magnetic susceptibility and heat capacity measurements in wide temperature range show no evidence of formation of long-range magnetic order in $Cu_2\{BO(OH)_2\}(OH)_3$ down to 2 K. Experimental data are best described by weakly alternating Heisenberg spin-1/2 chain model.

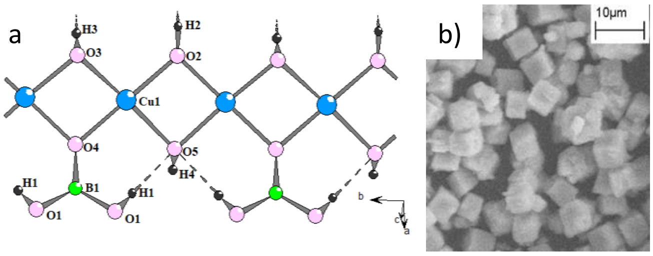

Figure 1. Chain fragment of $Cu_2\{BO(OH)_2\}(OH)_3$ (a); microphotograph of $Cu_2\{BO(OH)_2\}(OH)_3$ (b).

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This work was supported by the RFBR, grant number 19-03-01059.

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Novel platinum-based heterometallics: synthesis, structure and catalytic performance

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Currently palladium-based mixed-metal complexes, such as $PdIn(OOCMe)_5$, are widely studied as homogenous catalysts[1] and as precursors for heterogeneous catalytic systems[2], but analogous platinum carboxylic compounds are much less available. In this work we used two synthetic approaches for the preparation of heterobimetallic platinum-based carboxylic complexes:

1. by the reaction of the platinum acetate blue[3] ($Pt(OOCMe)_{2.5}$ (PAB) with the supplementary metal acetate:

$Pt(OOCMe)_{2.5} + M^{III} \rightarrow \{M^{III}Pt(OOCMe)_5\}$

2. by two-stage protocol starting from Pt^{IV} (and $K_2[Pt(OH)_6]$ as platinum source):

(*i*) $K_2[Pt^{IV}OH)_6] + M^{II} \rightarrow M^{II}Pt^{IV}(OH)_6\downarrow + 2\,K^+$

(*ii*) $M^{II}[Pt^{IV}(OH)_6] + 6\,MeCOOH \rightarrow \{Pt^{IV}M^{II}(OOCMe)_6\} \rightarrow Pt^{II}M^{II}(OOCMe)_4$

Using this techniques, we synthetized a series of heteronuclear comlexes, including alkaline-earth metals[4], which showed high potential in homogeneous catalysis of alkene hydrogenation (fig. 1-2). In some cases we investigated intermediate complexes of platinum in higher oxidation state (fig. 3).

The structures of the synthetized complexes were established by low-temperature single-crystal XRD (synchrotron radiation, tuned wavelength 0.79373-0.96990 Å, "Belok" beamline, Kurchatov Center for Synchrotron Radiation and Nanotechnology).

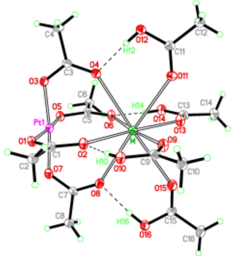

Fig. 1. Molecular structure of the complexes $Pt^{II}(OOCMe)_4M^{II}(HOOCMe)_4$, M = Ca, Sr, Ba

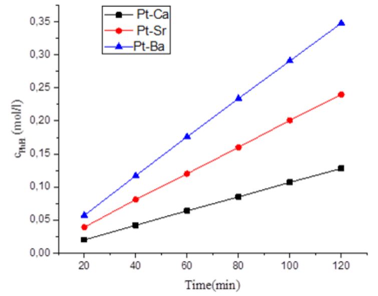

Fig. 2. Catalytic activities of various complexes during styrene hydrogenation (H_2 1 atm, 20°C)

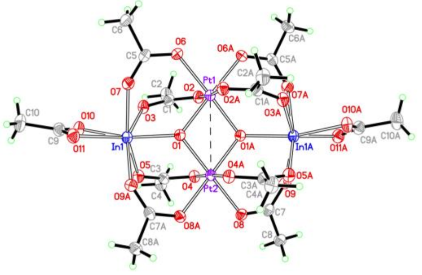

Fig. 3. Molecular structure of tetranuclear complex $Pt_2(O)_2In_2(OOCMe)_{10}$

Acknowledgements

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Mononuclear complexes based on FeI_2 and diverse N- (P-)donor ligands: synthesis, structural features and magnetic behavior.

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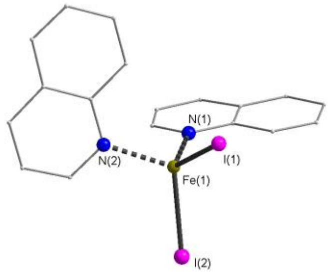
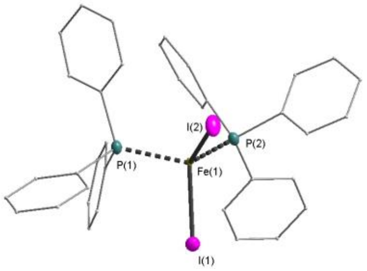
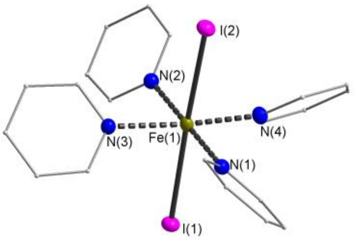
During the past decade many polynuclear compounds with Single Molecular Magnet behavior has been reported[1]. These complexes are often synthesized in one-pot reaction in one step with a little synthetic control but the latter is highly important in tuning the SMM parameters. It is relatively easy to control the coordination sphere of only the one metal ion. The first example of a monometallic 3d SMM was the high spin compound of iron (II) $K[(tpa^{Mes})Fe]$[2]. Fe (II) ions seem to be the most promising candidates for single-ion magnet creation due to specific features of the electronic structures of these ions.

In this work we carried out the synthesis a number of FeI_2 complexes with N- and P-donor ligands using a simple and cheap synthetic approach. Measured magnetic behavior of synthesized complexes, we compared it with similar Co (II) compounds. Changing the coordination sphere of Iron (II) ion using different ligands, we can regulate the angle iodine-iron-iodine' tuning the magnetic parameters.

Synthesis of the title coordination compounds, peculiarities of their structures and results of their magnetic behavior investigation will be discussed in the report in details.







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Ternary layered rare earth hydroxides (Eu, Gd, Tb) intercalated with 4-sulphobenzoate anion: synthesis and luminescent properties

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Layered rare-earth hydroxides (LRHs) that have been discovered recently represent a new class of pillared inorganic materials with anion-exchange properties. These compounds are considered as structural analogues of well-known layered double hydroxides (LDHs) with the general formula $Ln_2(OH)_{6-x}(A^{m-})_{x/m}\cdot nH_2O$ (Ln = RE, A = anion, x = 1-2, n = 0-2). LRHs are currently the focus of attention due to their unusual properties, combining specific features of host rare-earth matrices and guest intercalated anions. Today's most promising LRH applications include the design of luminescent materials and biomaterials. The luminescent properties of LRHs are comparable with corresponding rare-earth complexes, but they are insoluble, low toxic and the size of their particles can vary widely. Luminescent properties of LRHs can be finely tuned both by the cationic composition (rare-earth solid solution) and by changing the anionic composition that sensitizes or quenches the lanthanide luminescence.

Sensitization of Eu^{3+} luminescence in LRHs is caused by intercalation of anions of the organic acids. Most of those belong to the class of aromatic carboxylates forming luminescent complexes with Tb^{3+} и Eu^{3+}, which are known for their high stability and their intense and tunable luminescence (by introducing substituents and heteroatoms into the aromatic cycle). Sulphobenzoates are analogues of benzenedicarboxylates previously not intercalated into the structure of LRHs. The presence of a sulphonic group implies their more active participation in ion exchange reactions with LRHs and the formation of more ordered structures with rare-earths, as compared to benzenedicarboxylates.

This work presents the hydrothermal microwave (HTMW) synthesis of layered rare-earth (Gd, Eu, Tb) hydroxides containing 4-sulphobenzoate anion of composition $(Gd_{1-x}Tb_{0.9x}Eu_{0.1x})_3(OH)_7(C_7H_4O_5S)\cdot H_2O$. 4-Sulfobenzoate anions sensitize both the Eu^{3+} and Tb^{3+} luminescence in the LRHs. For solid solutions of $Gd_{1-x}Tb_{0.9x}Eu_{0.1x}$ intercalated with 4-sulfobenzoate anion the $Eu^{3+}(^5D_0 \rightarrow {}^7F_2)/Tb^{3+}(^5D_4 \rightarrow {}^7F_5)$ ratio can be easily tuned by changing x (gadolinium content). In case of x<0.5 only luminesce of Eu^{3+} is observed. Then x exceeds 0.5 both luminesce of Eu^{3+} and Tb^{3+} are observed.

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Synthesis and structural analysis of aluminum oxyhydroxide aerogel

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The oxidation of metallic aluminum through the amalgam layer upon exposure to humid air has been known for over a century [1]. Brittle amorphous aluminas which form during such an oxidation consist of fibres having a nanometric diameter. Optimization of the process (air humidity, temperature, addition of chemical modifiers *etc.*) allows obtaining large size alumina monoliths (several centimeters and even higher). The water content in such materials is close to 40%, their bulk density being only 13 kg m^{-3} [2], thus they could be considered as alumina oxyhydroxide aerogels. However, the structure of these materials in mesoscopic range is still virtually unstudied. Such data are of primary importance to understand the mechanism of fibrous alumina monoliths formation.

The work presents the results of the comprehensive studies of the micro- and mesostructure of aluminum oxohydroxide aerogels, special attention was paid to the structural changes in these materials upon thermal annealing. Structural characterization of as-prepared and annealed aerogels was performed by means of complementary methods including X-ray diffraction, nitrogen adsorption-desorption, transmission electron microscopy, thermal analysis. Important structural information was obtained using small-angle scattering techniques (SAXS, SANS and USANS).

It was found that the structure of aluminum oxohydroxide monoliths can be described within the three-level model: the primary particles (typical size of $r_c \approx 9–19$ Å) form the fibrils (cross-sectional radius $R \approx 36–43$ Å and length $L \approx 3200–3300$ Å) or lamellae (thickness $T \approx 110$ Å and width $W \approx 3050$ Å) which in turn are aggregated in large-scale structures (typical size $R_c \approx 1.25–1.4$ µm) with an almost smooth surface. High specific surface area of as-prepared aerogels (~200 m^2/g) remains nearly unchanged upon thermal treatment up to 900°C. Sintering of alumina particles at higher temperatures (1150°C) results in decrease of specific surface area down to ~100 m^2/g.

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The synthesis, characterization and theoretical calculation of a poly hydroxyl functional Schiff base Cu(II) complex, and the investigation of its polymerizability to metal containing epoxy polymer

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Metal containing polymers (MCP) are the macromolecules usually containing metal-ligand coordination units, and are a multidisciplinary research field mainly based at the interface between coordination chemistry and polymer science[1]. The progress of this area has also been reinforced by the growth of several other closely related disciplines including macromolecular and crystal engineering, organic synthesis, supramolecular chemistry and material science[2], [3]. Bis(N(2-(hydroxylethoxy ethyl)-2-oxy-4 hydroxybenzaldimine) cupper(II), [Cu(DHBEE)$_2$] (**2**) was synthesized as the poly-hydroxyl functional monomer for preparing of metal containing epoxy polymers. The characterization of the prepared ligand, its Cu(II) complex and the epoxy polymer was performed by the combination of conventional spectroscopic techniques. The crystal structure of [Cu(DHBEE)2] (2) was determined by XRD technique. The complex, Cu(C11H13NO4)2, crystalizes monoclinic space group P21/n with a=12.3978 (6) Å, b=7.6016 (3) Å, c=13.5109 (7) Å, β=114.566 (4)° and Z=2. The molecular structure, energies, molecular electrostatic potential, NBO analysis of the ligand (**1**) have been investigated using density functional theory (DFT) calculation. To investigate the tautomeric stability, optimization calculations at the DFT/B3LYP level were performed for the enol (OH) and keto (NH) forms of the title compound.

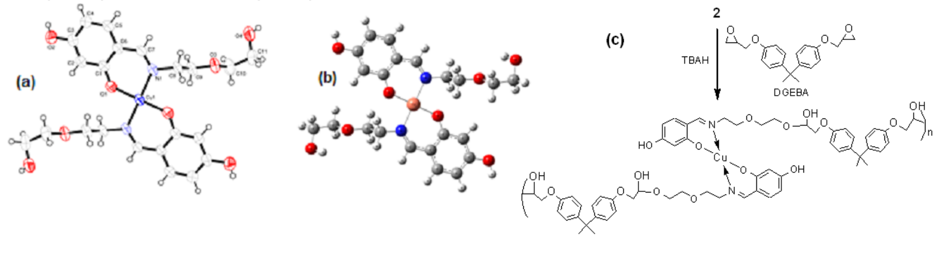

Figure 1. (a) The molecular structure of 2 showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, **(b)** the optimized geometry of 2 obtained using B3LYP/LanL2DZ level, (c) reaction pathway for metal containing epoxy polymer formation.

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Prussian Blue Based Composite Nanoparticles Defeating Natural Enzyme Peroxidase as Catalytic Labels For Immunoassay

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Nowadays nanozymes – inorganic nanoparticles mimicking enzymatic activity – are an important object of research. For instance, using peroxidase-mimicking nanozymes as catalytic labels for immunoassay may allow substituting costly and unstable horseradish peroxidase (HRP), the most widely used label.

Such nanoparticles have to possess enzymatic specificity and retain high activity in physiological pH (7.0-7.5). Among known nanozymes[1] both characteristics are intrinsic only to “catalytically synthesized” Prussian Blue (PB) based nanozymes, which peroxidase-like activity exceeds even that of HRP[2]. However, for immunoassay applications nanozymes need to be functionalized to conjugate them with an antibody.

In the present work we suggest a method of the nanozymes’ functionalization by using monomers (aniline and 3,4-(2-(azidomethyl)ethylenedioxy)thiophene) of conductive polymers as reductants for Fe_{3+} and $[Fe(CN)_6]^{3-}$ mixture. While reducing the $Fe[Fe(CN)_6]$ complex into PB, monomers undergo oxidative polymerization and form conductive polymers. This allows functionalizing the nanoparticles on the stage of their synthesis and controlling their diameter (30-60 nm) by varying the concentrations of reagents.

X-ray powder diffraction pattern confirms that obtained nanozymes are of Prussian Blue crystalline structure. Moreover, the nanoparticles formed in this reaction are indeed composite ones, which was confirmed by Raman spectra containing characteristic signals of both PB and corresponding polymers. Moreover, their colloidal stability is significantly increased compared to their predecessors, according to measured zeta potential, which is up to three times higher (-33.3 mV).

Kinetics of H_2O_2 reduction catalyzed by obtained nanoparticles in the presence of 3,3’,5,5’-tetramethylbenzydine, most common HRP substrate were investigated spectrophotometrically monitoring the accumulation of TMB^{2+}. Dependency of initial reaction rate on TMB concentration obeys Michaelis-Menten equation. Calculated k_{cat} are volume dependent, thus, H_2O_2 penetrates the bulk of nanoparticles. For 46 nm diameter particles k_{cat} is 460 s^{-1}, which is more than two times higher than k_{cat} for HRP in identical conditions. Moreover, in the absence of H_2O_2 no TMB oxidation was registered, indicating that obtained nanozymes do not display oxidase activity.

Modification of nanoparticles with azide and amino functional groups will allow linking them with antibodies. Together with the high stability and specificity of the obtained nanoparticles it may allow for substitution of natural and recombinant peroxidases in immunoassays.

Acknowledgements

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Composite metal hexacyanoferrates based sorbents in chitosan binding matrix

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Inorganic compounds (oxides/ hydroxides, some salts - ferrocyanides of transition metals, molybdenum phosphates, etc.), which are used as inorganic ion exchangers, show various selectivity to a number of elements, that is their advantage over other sorbents. Their sorption properties depend on a number of factors: the composition and the crystallographic arrangement of inorganic exchanger, particularly on the compatibility in the size and charge of exchangeable cations with target elements. In addition to these characteristics the crucial ones for the sorption properties of materials are particle size, which determines the active surface area, their hydrolytic stability, etc. All these parameters can be adjusted by changing the conditions of synthesis of compounds (the order of adding precursors, their ratio, temperature, aging, etc.).

There are three groups of ion exchangers: “intrinsic” inorganic ion exchangers without use of any additives, supported ones or embedded into a matrix [1]. The use of composite sorbents allows to overcome technical disadvantages of “intrinsic” inorganic exchangers (column clogging, peptisation) and simplifies the process of separating the solid sorbent from the liquid phase.

The paper studies the processes of immobilization of common sorbents on cesium – hexacyanoferrates of transition metals (Ni, Cu, Zn), into the chitosan biopolymer matrix to produce composite sorbents [2]. The yielded composite sorbents were also deposited onto the support – carbon fiber.

Preparation of composite materials followed generally next main phases:

a) synthesis of suspensions of hexacyanoferrates and their deposition together with the biopolymer chitosan in alkaline media;

b) synthesis of hexacyanoferrates from precursors combined with chitosan deposition;

c) synthesis of the sorbent by homogeneous deposition of hydroxide (Ni) and chitosan in the presence urea as a hydrolyzing agent, followed by modification with ferrocyanide.

Composite sorbents were characterized using X-ray diffraction, SEM-EDX. The hydrolytic stability of sorbents in mineralized solutions and at high pH values was tested. Sorption properties with respect to ^{137}Cs were determined.

Acknowledgements

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New synthesis method of N-monosubstituted ammonio-closo-decaborates

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In the work, the process of interaction of nitrilium derivatives of the *closo*-decaborate anion with lithium aluminum hydride was studied. Reduction process proceeds under mild conditions and leads to the formation of N-alkylammonio-*closo*-decaborate with high yields and selectivity.

The composition of the product mixture and yields depend on the ratio of reactants. The complete conversion of the initial nitrilium derivative is not observed at equimolar ratio of reactants. It can be explained by the fact that the reaction proceeds heterogeneously, and a part of the reducing agent is spent on side processes involving the solvent. The best result is given by the of reagent ratio equal to 1:3. The further increase in the reducing agent amount causes cluster destruction processes and decrease of the target product yield.

For the structure of $(N^{n}Bu_4)[2\text{-}B10H_9NH_2CH_2CH_3]$ was confirmed by single crystal X-ray diffraction.

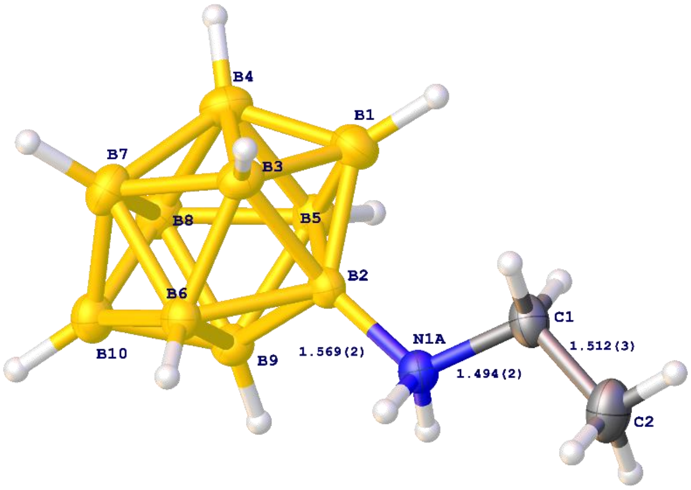

Figure 1. Structure of the $[B_{10}H_9NH_2Et]^-$ anion

Acknowledgements

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Influence of barium, calcium and strontium atoms on magnetic properties of iron-containing solid solutions $Bi_2MNb_2O_9$ (M – Ba, Sr, Ca)

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Magnetic dilution and NEXAFS spectroscopy were used in the study of iron-containing solid solutions $Bi_2MNb_2O_9$ (M – Ba, Sr, Ca) with layered perovskite-like structure. The analysis of the NEXAFS Fe2p-spectra of iron-containing solid solutions and iron oxides revealed that the studied Fe atoms were mainly in the +3 oxidation state. The study of magnetic susceptibility of the $Bi_2Ba(Sr, Ca)Nb_{2-2x}Fe_{2x}O_{9-\delta}$ solid solutions showed the influence of atoms of the second coordination sphere on the distribution, degree of clustering, and intensity of exchange interactions in clusters of iron atoms. It was established that iron (III) atoms exhibited selectivity in filling the cation positions, preferring less distorted octahedral positions. The substitution of barium with strontium(calcium) atoms led to intensification of the exchange of the ferromagnetic type and to a decrease in the degree of clustering of iron atoms in the solid solutions $Bi_2MNb_{2-2x}Fe_{2x}O_{9-\delta}$(M-Sr, Ca).

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Mn doped $BiNbO_4$ ceramics: magnetic properties, thermal stability, phase transitions, NEXAFS and ESR spectroscopy

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Thermal stability, magnetic properties, NEXAFS and ESR spectra of the solid solutions $BiNb_{1-x}Mn_xO_{4-\delta}$ in orthorhombic and triclinic modifications have been studied. X-ray diffraction determined the reversibility of the phase transition from the high-temperature triclinic modification to the orthorhombic modification at 950 °C in the $BiNb_{1-x}Mn_xO_{4-\delta}$ solid solutions. The ESR spectra of $BiNb_{1-x}Mn_xO_{4-\delta}$ of the orthorhombic modification revealed a broad axial-symmetric absorption band with the values of $g_{||} \sim 3.8$ and $g_{\perp} \sim 2.0$, against the background of which, the poorly-resolved structure of hyperfine splitting of Mn (II) was detected. The ESR spectra of triclinic $BiNb_{1-x}Mn_xO_{4-\delta}$ revealed the sextet structure of Mn(II) ions with 8.4 mT splitting and some features at g = 3.80 and 1.47, and a broad diffuse band with $g \sim 2.2$ having a sextet with 8–9 mT splitting and g = 2.0 against its background. The measurements of magnetic susceptibility allowed us to calculate the parameters of exchange interactions in dimers and the distribution of manganese atoms (II), (III) and (IV) in dependence on concentrations of the solid solutions in the orthorhombic and triclinic modifications. The solid solutions $BiNb_{1-x}Mn_xO_{4-\delta}$ as well as manganese oxides MnO, Mn_2O_3 and MnO_2 were studied by the NEXAFS spectroscopy in order to determine the degrees of oxidation of manganese atoms. The DSC curves of the samples $BiNb_{1-x}Mn_xO_{4-\delta}$ revealed the endothermic effects associated with the phase transition from the orthorhombic modification to the triclinic one at 1050 °C (x=0.03) and 1048 °C (x=0.06). The temperatures of the melting peaks were 1231 °C (x=0.03) and 1220 °C (x=0.06), respectively.

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Synthesis and photophysical properties of europium complexes with heterocyclic ligands from 2,2'-bipyridyl-6,6'-dicarboxamide

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Lanthanide complexes with heterocyclic ligands possess significant luminescent properties, which allow using them in time-resolving immunofluorescence technique. Here we report preparation of the ligands based on substituted 2,2'-bipyridyl-6,6'-dicarboxylic acid and their complexes with Eu^{3+}. Ligands were obtained in two different ways (Fig. 1), complexation of these ligands with europium salts lead to formation of LM and LM_2 complexes. Luminescence spectra of the complexes were studied. Luminescence spectra of prepared europium complexes show two maxima typical for europium ion: at 592 nm and at 615 nm. The emission intensity was studied for various solvents. Using the D_2O solutions the number of coordinated water molecules was estimated. Complexes possesses bright phosphorescence in various protonic environment namely for complex with R=H in methanol (4.7% QY) and water (1.2% QY). The lifetimes found 0.7 and 0.5 ms correspondingly.

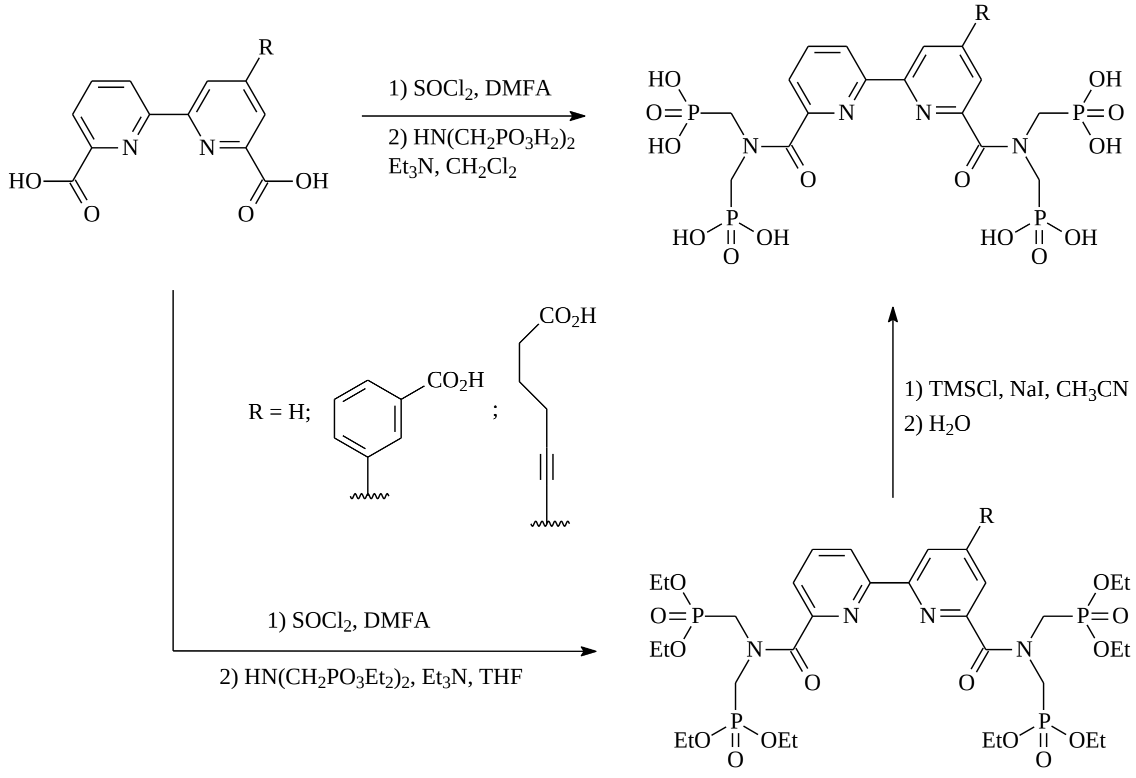

Figure 1.

Dy^{III} single molecule magnets with Schiff base ligand

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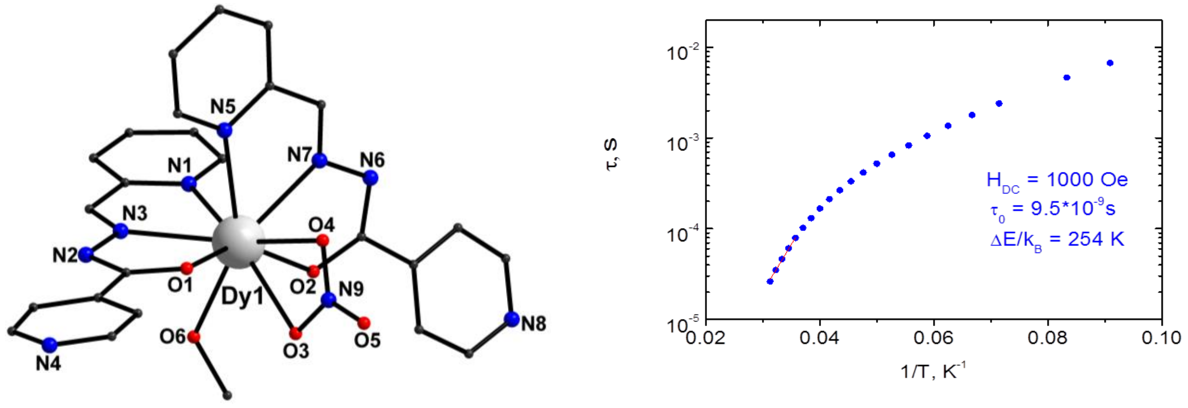
The chemistry of lanthanide complexes has been attracting intense interest over the last decades due to the possibility of obtaining of single-molecule magnets (SMMs). Such magnetic molecules can be potentially used for quantum computing, molecular spintronics and for creation of high-density data storage devices.

We synthesized the series of new mononuclear complexes of Dy^{III} with Schiff base (HL) obtained by the condensation of 2-pyridinecarbaldehyde and 4-pyridinecarboxylic acid.

The resulting HL is an N,N,O-tridentate chelating ligand. The complex $[Dy(H_2O)(CH_3OH)(NO_3)_2(HL)]$ (**1**) was formed as a result of the reaction of $Dy(NO_3)_3 \cdot 5H_2O$ with HL in methanol at the 1: 1 reagent ratio. The changes in the ratio of the initial reagents of lanthanide(III) nitrates and HL to 1: 2 with simultaneous introduction of Et_3N in the mixture of methanol-acetonitrile led to the formation of a complex with two anions of ligand: $[Dy^{III}(CH_3OH)(NO_3)(L)_2] \cdot CH_3CN$ (**2**). Crystallization of compounds **2** from methanol led to the formation of complexes $[Dy^{III}(CH_3OH)(NO_3)(L)_2] \cdot CH_3OH$ (**3**). The use of $Dy(OAc)_3$ instead of $Dy^{III}(NO_3)_3 \cdot 5H_2O$ while maintaining the Dy^{III}: HL ratio of 1: 2 resulted in new complexes $[Dy^{III}(L)_3] \cdot 2H_2O$ (**4**).

All new complexes were structurally characterized as well as their magnetic behavior (AC and DC) were studied. According to magnetic measurements, all compounds are SMMs.



a b

Figure 1. Complex 2 molecule structure (***a***) (hydrogen atoms are omitted); inverse temperature dependence of the relaxation time in the optimal field H=1000 Oe for complex 2 (***b***)

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Novel Nd-based single-ion magnet with remagnetization energy barrier of 93 cm^{-1}

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Investigating of paramagnetic substances that could maintain macroscopic magnetic moment without external magnetic field due to a substantial magnetic anisotropy (single ion magnets) is a rapidly growing research field at the moment. The main vector is searching new single-ion magnets with as high as possible remagnetization energy barrier U_{eff} as well as the highest blocking temperature. The most impressive Dy based complex[1] at the moment is characterized by U_{eff} more than 1500 cm^{-1}. Recently we suggested a purely inorganic Dy containing single-ion magnet representing phosphate with apatite structure.[2] The highest observed U_{eff} in such substances is more than 1000 cm^{-1}.

Among the Nd based single-ion magnets the most successful is polyoxometalate[3] with U_{eff} about 50 cm^{-1}. In this work we report a new inorganic phosphate Nd-based single-ion magnet: calcium phosphate apatite $Ca_{5-x}Nd_x(PO_4)_3O_x(OH)_{1-x}$ with partial calcium substitution on neodymium.

Neodymium in this structure partially substituting calcium is surrounded by 6 oxygen atoms of phosphates and one oxygen that is situated in the centre of trigonal channel replacing hydroxide. This last oxygen is located much closer to the neodymium than 6 others so rare-earth cation is characterized by coordination number 6+1 with one much shorter contact and represents a highly anisotropic ion.

ac magnetic measurements of this compound showed a typical features of single ion magnets with narrow relaxation time distribution and U_{eff} about 93 cm^{-1}. No impact of dilution was observed: two samples with different neodymium concentration show nearly the same magnetic properties.

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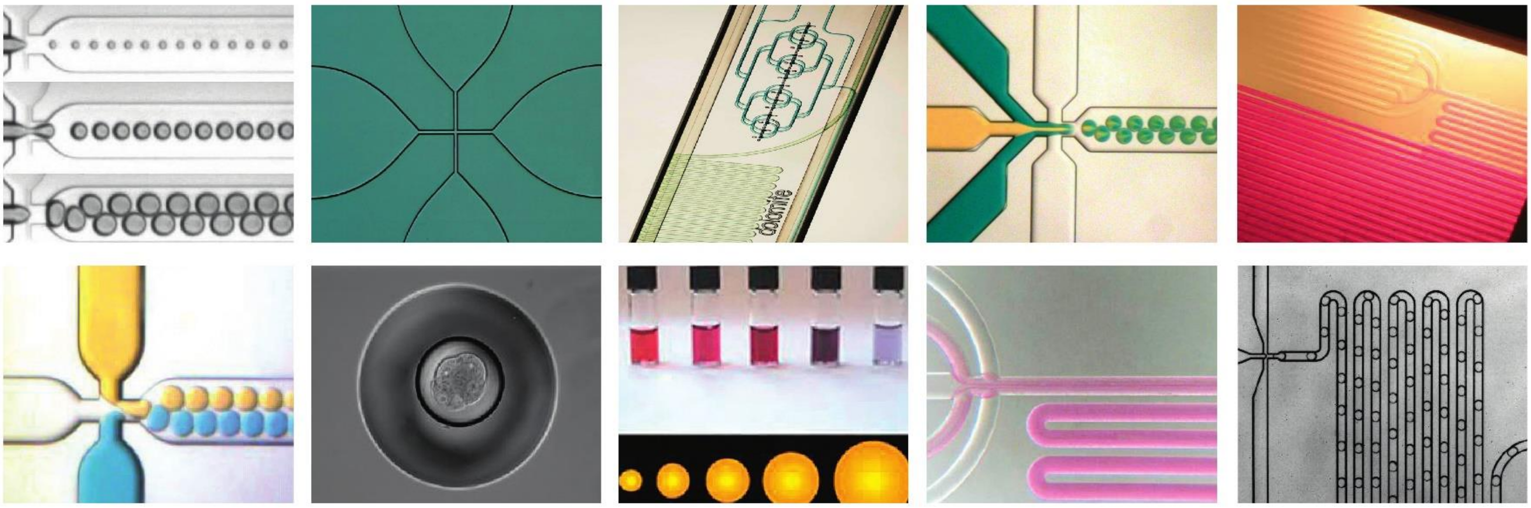

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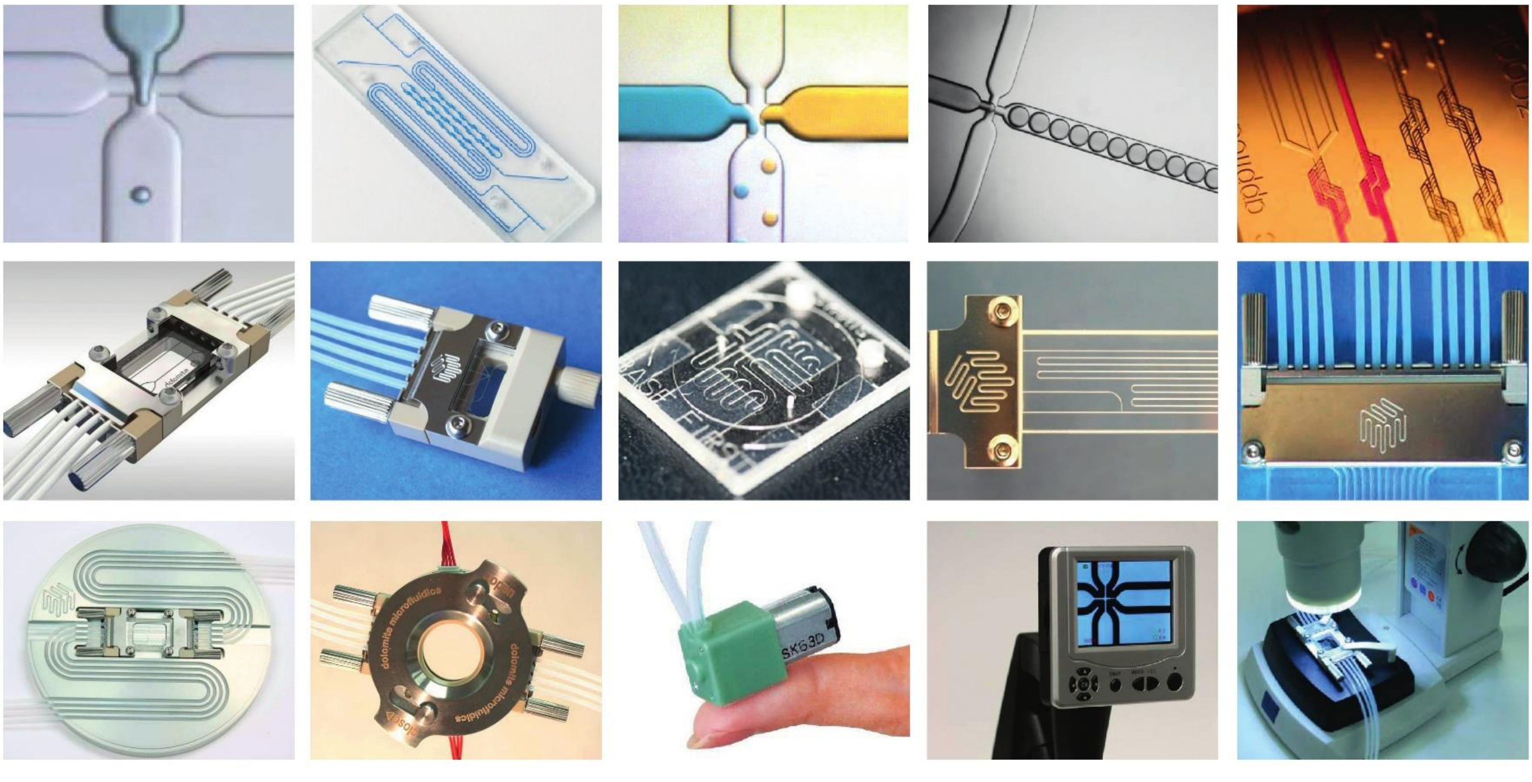

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