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IVth INTERNATIONAL WORKSHOP ON TRANSITION METAL CLUSTERS

IWTMC – IV

September 8 – 11, 2014

Book of abstracts

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International Workshop on Transitional Metal Clusters (IWTMC) is a representative meeting assembling scientists who are working in the area of fundamental and applied cluster chemistry including application of clusters in catalysis, material science, bio-modeling, medicine etc. The workshop promotes a forum of discussion between academy and industry, and is aimed to strengthen collaborations between cluster chemists. The previous editions of this meeting were held in France (University of Rennes, 2008), Germany (Rostock, 2010) and Spain (Benicassim (Castellón), 2012).

IVth edition of the International Workshop on Transitional Metal Clusters is held in Russia in the famous Novosibirsk scientific center Akademgorodok which is located on the beach of artificial sea "Obskoe".

Topics of the IWTMC-IV include inorganic and hybrid cluster compounds, cluster functionalization, molecular and supramolecular assemblies, nanomaterials, cluster-based catalysis and activation, MOFs, quantum chemistry, functional surfaces, clusters in biology and medicine etc.

The main peculiarity of the IWTMC-IV is its integration with IDeMat-2 meeting («Innovative Design» of New Generations of Materials built up from Oxo and Metal-Clusters). The IDeMat network involves seven French Universities (Versailles Saint Quentin, Rennes 1, Lille 1, Lyon 1, Grenoble, Strasbourg and Toulouse) and the three main Universities of Siberia (Novosibirsk, Irkutsk and Tomsk). Previous IDeMat meeting took place in Rennes in June, 2013. Goal of seminar is brainstorming on cluster chemistry to give high level lessons to master and PhD students that could attend the conference for free.

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INTERNATIONAL WORKSHOP ON TRANSITION METAL CLUSTERS
IWTMC-IV
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BARTHELEMY

Sponsors of the conference

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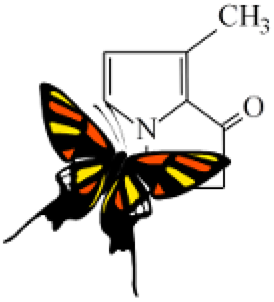

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PROGRAM

SEPTEMBER, 8th			
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15:30 – 16:00	Shevelkov Andrei V. “TRANSITION METALS IN NON-AQUEOUS CLATHRATES: STRUCTURE PATTERNS AND BONDING”	30 min	25
16:00 – 16:30	Liu Chen-Wei “ENCAPSULATING HYDRIDES AND MAIN-GROUP ANIONS IN d^{10}-METAL CLUSTERS STABILIZED BY 1, 1-DICHALCOGENO LIGANDS”	30 min	26
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	CONFERENCE DINNER		

SEPTEMBER, 11th			
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LUNCH			

FIFTY-YEAR ANNIVERSARY OF CLUSTER CHEMISTRY. LOOKING BACK: AS EVERYTHING BEGAN IN SIBERIA

Fedorov V.E.[1,2]

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This year the scientific community celebrates 50-year anniversary of the metal cluster chemistry. In anniversary days there is a natural desire to look back and to sum up some results obtained in this field.

In this report, the author recalls the scientific research on metal cluster chemistry, which was carried out by scientists of Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, which from the very beginning actively joined in development of the new very interesting direction and made a significant contribution to cluster chemistry.

Key results of the researches in the field of cluster chemistry executed by scientists of Nikolaev Institute of Inorganic Chemistry are presented. Structure and properties of some representative chalcogenide cluster compounds of niobium, tantalum, molybdenum, tungsten and rhenium for the first time synthesized in the Institute are briefly discussed. Some original results which are conceptually important in chemistry of metal cluster complexes are noted.

NEW NANOSIZED Ag- AND Au-CLUSTERS; SYNTHESIS, STRUCTURES AND PHOTOPHYSICAL PROPERTIES

Fenske D.,[1] Fuhr O.[2]

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[2]*Lehn Institute of Functional Materials, Sun-Yat Sen University, Guangzhou, China*

There are a number of metal chalcogenide ions known in the gas phase. Obviously it is possible to stabilize these species with protecting tertiary phosphine ligands.

An easy route to such compounds is the reaction of transition metal halides with silylated derivatives of S and Se. An alternative way to get this compounds is the reaction of AgSR (R = organic group) with $E(SiMe_3)_2$ (E: S, Se, Te). This yields to the formation of core-shell clusters consisting of an Ag_2E core covered by a shell of AgSR-group. Examples are phosphine-stabilized clusters with hundreds Ag atoms.

These materials may be regarded as sections cut out of the structure of binary phases, which are effectively shielded by an envelope of PR_3 ore sometimes SR ligands. The structures, properties and results from ab initio calculations will be reported. Under high vacuum conditions the PR_3 ligands can be removed from the cluster surface. This results in the formation of an amorphous nano composite material. The size of the particles is between 3.0 – 5.0 nm with narrow size distribution.

During the last time we are also able to synthesize Au clusters . Examples are ionic clusters like: $[Au_{10}Se_4(dppe)_4]Br_2$, $[Au_{18}Se_8(dppe)_6]Br_2$, $[Au_{34}Se_{14}(tpep)_6(tpepSe)_2]Cl_6$. These compounds show interesting photophysical properties.

ASSEMBLING APPROACHES IN CLUSTER CHEMISTRY FOR ENHANCED COOPERATIVITY

Braunstein P.[1]

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The use of assembling ligands has long been implemented to facilitate the selective synthesis of cluster complexes, in particular of heterometallic clusters since it allows the sequential construction of complex molecules. Furthermore, assembling ligands provide additional stability to the molecule. Examples will focus on 3 electron donor phosphanido bridging ligands (μ-PR_2), whose flexibility allows reversible breaking of metal-metal bonds without cluster decomposition and on 4 electron donor short-bite diphosphine ligands, such as $Ph_2PCH_2PPh_2$ and $Ph_2PNHPPh_2$. N-Functionalization of the latter allows an easy anchoring of metal clusters onto various supports and to nanoparticules endowed with unique catalytic properties.

NEW INSIGHTS INTO THE CHEMISTRY OF TRANSITION METAL CLUSTER CHALCOGENIDES AND THEIR POTENTIAL APPLICATIONS

Llusar R.[1]

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Transition metal cluster chalcogenides are very versatile systems due to the robustness of their cluster core and the easy modification of their coordination environment. The work of our group has been devoted to explore this versatility through functionalization of molybdenum and tungsten cuboidal M_3S_4 units with diphosphines, and more recently with aminophosphines and diamines [1-2]. The synthesis, structure and reactivity of the new amino and aminophosphino complexes will be presented and compared with that of their corresponding diphosphino derivatives. Special emphasis will be placed on applications of these trimetallic cluster chalcogenides as catalysts for the selective reduction of organic substrates [3]. Detailed mechanistic studies that combine spectrometric and spectroscopic techniques with theoretical investigations will be presented.

The final part of the presentation will be dedicated to the development of homo- and heteroleptic cluster complexes containing redox active ligands, such as dithiolenes and/or diimines [4]. The photophysical properties of these compounds will be discussed as well as their potential applications in photocatalysis.

Acknowledgements. Financial support from the Spanish MINECO and Generalitat Valenciana is gratefully acknowledged. Special thanks go to the members of my group, former and present, and collaborators along these years for their efforts and dedication.

1. Llusar R., Vicent C. *Inorg. Chem. In Focus III (chapter 7)*, ed. G. Meyer, D. Naumann, L. Wesermann, **2006 ,** Wiley-VCH, Weinheim
2. Beltrán T. F. *Ph. D. Thesis* **2013**, Universitat Jaume I of Castellón, Spain.
3. Sorribes I., Wienhöfer G., Vicent C., *Angew. Chem. Int. Engl. Ed.* **2012,** *51*, 7794.
4. Recatalá, D., Gushchin A., Llusar R., *Dalton Trans.* **2013**, 12947.

RECENT ADVANCES AND OUTLOOKS IN THE ELABORATION OF MULTIFUNCTIONAL MATERIALS BUILT UP FROM METAL ATOM CLUSTERS

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At the occasion of the fiftieth birthday of the introduction of the term ‘metal atom cluster’ by F. A. Cotton in inorganic chemistry [1], it is the good time to make a review on the advances in the engineering of solid state compounds, molecular assemblies and nanomaterials based on metal atom clusters.

In this contribution, it will be evidenced in a first part how the concept of cluster building blocks is an efficient tool in order to describe and explain the physical and electronic properties of cluster-based inorganic solid state compounds. This part will focus on M_4 tetrahedral and M_6 octahedral cluster-based inorganic compounds which exhibit great potential respectively for the design of Random Access Memories and as thermoelectric component for energy conversion devices [2].

In a second part, recent advances in the engineering of multi-functional materials and nanomaterials based on octahedral metal atom cluster buildings blocks will be presented [3]. The latter exhibit unique intrinsic structural and physicochemical properties (orthogonal disposition of metallic sites that can be selectively functionalized, photoluminescence and photocatalysis, redox, generation of singlet oxygen) that make them relevant building blocks for the structuration at the nanometric scale and functionalization of hybrid organic-inorganic materials and supramolecular frameworks. After synthesis by solid state chemistry techniques at high temperature, inorganic precursors built up on face-capped $[(M_6Y^i{}_8)Y^a{}_6]$ cluster units (Y = chalcogen and/or halogen) can be functionalized via solution chemistry techniques or organic melts to form $[(M_6Y^i{}_8)L^a{}_6]$ (L = CN, OH, various organic ligands…). This contribution will give an overview on advances in the synthesis of $[(M_6Y^i{}_8)Y^a{}_6]$ and $[(M_6Y^i{}_8)L^a{}_6]$ cluster units as well as on their use in the elaboration of supramolecular frameworks, nanoparticles, hybrid nanomaterials (co-polymers and liquid crystals) and active molecular junctions.

Acknowledgements. We thank the France-Russia programs PICS (2011-2013 N°5822) and International Associate Laboratory (2014-2017) as well as the IDEMAT chemistry project in the frame of the Franco-Siberian Center of Training and Research.

1. Cotton F.A., *Inorg. Chem*, **1964**, *3*, 1217.
2. Gougeon P., Gall P., Al Orabi R.A., *Chem. Mater.*, **2012**, *24*, 2899.
3. Cordier S., Molard Y., Brylev K.A., *J. Clust. Sci.*, **2014**, Review in press, DOI 10.1007/s10876-014-0734-0.

RECENT INSIGHTS INTO THE MECHANISM OF SUBSTITUTION REACTIONS IN M_3Q_4 CLUSTERS

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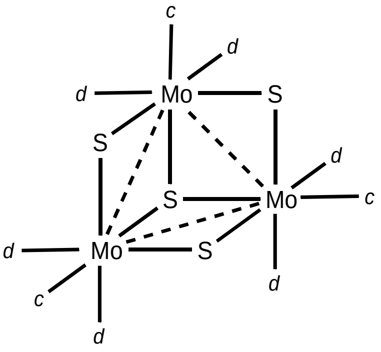
The M_3Q_4 clusters (M= Mo, W; Q= S, Se) adopt a cuboidal structure with M and S atoms occupying the corners, although one of the corners corresponding to the metals is unoccupied, as shown in the figure for Mo_3S_4. This leads to a structure with one capping Q atom and three bridging Q ligands. Because the M-M and M-S bonds do not fully satisfy the coordination environment of the metal centres, there are three coordination sites at each metal centres available for ancillary ligands as water molecules: $M_3Q_4(H_2O)_9^{4+}$ clusters. Because of the cluster symmetry, the coordination sites are not equivalent and two types of water can be distinguished: those trans to the capping Q (*c* in the figure) and those trans to a bridging Q (*d*). Substitutions in these clusters were comprehensively studied by the group of Sykes in Newcastle, so that the fundamentals of reactions in which H_2O is substituted by monodentate ligands as Cl^- or NCS^- are well established.[1] Three important conclusions derived from this classical work are: i) the reactions at the different metal centres occur sequentially with statistically-controlled kinetics, ii) water trans to bridging Q (*d*) are more labile than those trans to the capping Q (*c*), and iii) the rate of reactions are pH-dependent because of the acidity of coordinated water.



In this communication, some recent results on those reactions will be presented, with particular emphasis on the lability of the different types of water molecules and the operation of statistical kinetics. In addition, some mechanistic information on substitution reactions inorganic solvents will be also commented.

Acknowledgements. financial support by the Spanish Ministerio de Economía y Competitividad and the E.U. FEDER program (Grant CTQ2012-37821-C02-02) and Junta de Andalucía (Grupo FQM-137) are gratefully acknowledged.

1. Hernández-Molina R., Sykes A.G., *J. Chem. Soc., Dalton Trans.*, **1999**, 3137 and refs therein.

MOLYBDENUM OCTAHEDRAL CLUSTERS ANCHORED ON GRAPHENE OXIDE SURFACES WITH POTENTIAL APPLICATIONS IN PHOTOCATALYSIS

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The trend towards a sustainable development implies the development of new photocatalytic semiconductor materials with applicability in solar energy conversion and environmental protection, such as H_2 generation, pollutant degradation and eco-friendly catalytic transformations. In the last years, graphene oxide (GO) materials have attracted a lot of attention due to their exceptional semiconductor properties, and as carriers of photoactive transition metal particles and complexes. The development of photoactive GO catalysts would encompass, for example, photoactive transition metal complexes or nanoparticles with a large absorption window from UV to the visible region. Metal atoms clusters are nanosized units that could exhibit very interesting catalytic and photocalytic properties. It has been found that octahedral hexametallic molybdenum, tungsten and rhenium clusters have interesting photophysical and redox properties, and they can also be used as red dye building blocks in the elaboration of hybrid nanomaterials (copolymers, liquid crystals, MOFs…).

The integration of metal cluster complexes on graphene oxide (GO) for the preparation of graphene-based nanohybrid materials would result in nanocomposites with excellent properties and improved functionalities due to the synergetic effects between GO and the inorganic components. Recently, the properties of GO and the photocatalytic performance of $Na_2[Mo_6Br_8(N_3)_6]$ have been combined in a new class of composite materials with high photocatalytic activity for the degradation of organic pollutants.[1] Here we present the preparation of anchored $Mo_6X^i_8Y^a_6$ (X^i = Cl, Br, I; Y^a = apical ligand) clusters on GO surfaces, and their characterisation by using spectroscopic techniques with the aim of prepare graphene-based semiconductor photocatalysts with potential applications in sun-light driven water splitting for H_2 generation and CO_2 photoreduction to provide methanol.

Acknowledgements. The financial support of the Spanish Ministerio de Economia y Competitividad (research project MAT2011-28009), and Universitat Politècnica de València (PAID-06-12/SP20120740) is gratefully acknowledged.

1. Barras A., Das M.R., Devarapalli R, *Appl. Catal. B*, **2013**, *130-131*, 270.

ENANTIOSELECTIVE SYNTHESIS OF M_3Q_4 TRIMETALLIC CLUSTER CHALCOGENIDES

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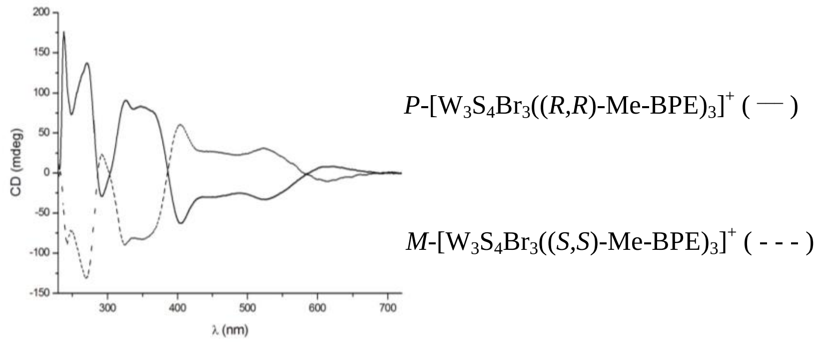
Cuboidal transition-metal clusters constitute a large family of multimetallic compounds which are present in both industrial and biological catalytic processes. In particular, molybdenum and tungsten M_3S_4 and $M_3M'S_4$ sulfides have a special relevance in such fields since they have been used as model for metalloenzimes or as contrast agents in medicine [1, 2]. In spite of all applications found for cubane-type M_3S_4 and $M_3M'S_4$ complexes as catalysts, their role in asymmetric catalysis is very limited due to the scarce number of optically pure cuboidal complexes [3].

Along the years we have prepared and isolated a large number of molybdenum and tungsten diphosphino clusters of formula $[M_3Q_4X_3(\text{diphosphine})_3]^+$ (M=Mo, W; Q=S, Se; X=Cl, Br, H, OH; diphosphine=dmpe, dppe, dppen), mainly, through excision reaction of polymeric phases according to equation 1. However, in the absence of an optically pure source, these complexes are obtained as racemic mixtures [4].

$$2\{M_3Q_7X_4\}_n \quad + \quad 9 \ \text{diphos} \ \xrightarrow[\text{reflux}]{CH_3CN} \ 2\,[M_3Q_4X_3(\text{diphos})_3]X \quad + \quad 3 \ \text{diphos}(S)_2 \qquad (1)$$

We have explored the generality of this excision reaction of polymeric $\{W_3Q_7Br_2Br_{4/2}\}_n$ phases with enantiomerically pure diphosphines, as a rational route to access enantiopure cuboidal $[W_3Q_4X_3(\text{diphosphine})_3]^+$ clusters. CD measurements have revealed the enantiomeric character of such compounds.



Acknowledgements. The financial support of the Spanish Ministerio de Economía y Competitividad (grants CTQ2011-23157), Universitat Jaume I (research project P1.1B2013-19) and Generalitat Valenciana (Prometeo/2009/053 and ACOMP/2013/215) is gratefully acknowledged.

1. Yang K.Y., Haynes C.A., Spatzal T., *Biochemistry*, **2014**, *53*, 333.
2. Liu Y.L., Liu J.H., Ai K.L., *Contrast Media & Molecular Imaging*, **2014**, *9*, 26.
3. Seino H., Hidai M. *Chem. Sci.*, **2011**, *2*, 847.
4. Feliz M., Guillamon E., Llusar R., *Chem. Eur. J.*, **2006**, *12*, 1486.

THERMAL DETECTION OF METASTABLE TUNGSTEN HALIDE CLUSTERS

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Chemical reactions performed at low heating temperatures offer opportunities to obtain thermally metastable solids. With a combined DSC-XRD study we are exploring a soft reduction methodology for the preparation and characterization of series of metal-rich tungsten halide compounds. Experiments are carried out to scan, characterize, and to systematically study metal-rich systems. This is achieved by a reaction procedure departing from reactive halide compound. Within the experimental procedure the reactive starting material (e.g. WCl_6) is reduced by a non-conventional reduction agent (C_2Cl_6 [1], Sb [2,3], Fe [3], Co [4], Mn, P [5], …) to allow the observation of series of compounds being formed during the successive reduction steps. Individual reduction steps (from W^{6+} to W^{2+}) are monitored by differential thermal analyses (DTA/DSC) (Figure 1). Conditions derived from the thermal analysis are used for subsequent syntheses of individual compounds. Compounds are characterized (XRD, etc.) and some properties are examined.

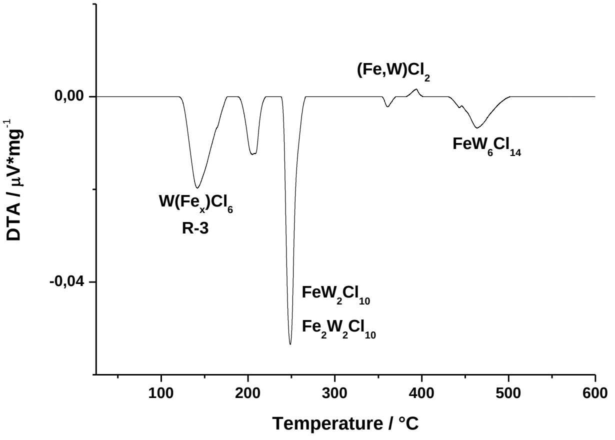

Figure 1. Successive reduction of β-WCl_6 with excess of iron powder, monitored by DTA.

1. Ströbele, M., Meyer, H.-J., *Inorg. Chem.* **2010**, *49*, 5986.
2. Ströbele, M., Meyer, H.-J., *Z. Anorg. Allg. Chem.* **2012**, *638*, 94.
3. Ströbele, M., Mos, A., Meyer, H.-J., *Inorg. Chem.* **2013**, in press; Ströbele, M., Meyer , H.-J., *Z. Anorg. Allg. Chem.* **2011**, 637, 1024.
4. Mos, A., Ströbele, M., Meyer, H.-J., *J. Cluster Sci.* **2014**, in press.
5. Ströbele, M., Eichele, K., Meyer, H.-J., unpublished; Ströbele, M., Eichele, K., Meyer, H.-J., *Eur. J. Inorg. Chem.* **2011**, 4063.

TRANSITION METALS IN NON-AQUEOUS CLATHRATES: STRUCTURE PATTERNS AND BONDING

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Clathrates are compounds possessing aesthetically beautiful crystal structures of the host-guest type [1]. There is a vast family of alternative clathrate compounds apart from the well-known gas hydrates. They comply with the Zintl rule and their three-dimensional host frameworks are mostly built of four-bonded main-group elements that tend to complete their electronic octet by forming two-centre, two-electron bonds and localizing lone electron pairs [2]. Clathrates containing transition metal atoms compose a special subgroup of this family. Though having the same crystal structure as proper Zintl clathrates, they show remarkable distinctive features of bonding and properties; that is why they deserve particular exploration. In this report, discussed will be the details of the d-metal atoms distribution and its influence on the superstructure formation as well as the peculiarities of bonding involving d-metal atoms. Other properties will be briefly presented, including localized vibrations, magnetic ordering, charge carrier and heat transport, keeping in mind the potential application of Zintl clathrates as thermoelectric materials.

Acknowledgements. This research is supported by the Russian Foundation for Basic Research, grant № 14-03-00571-a.

1. Geffrey G.A. In: Inclusion Compounds. Eds: Atwood J.L., Davies J.E.D., MacNicol P.D. Academic Press, London, U.K., **1984**.
2. Shevelkov A.V., Kovnir K., *Struct. Bond.* **2011**, *139*, 97.

ENCAPSULATING HYDRIDES AND MAIN-GROUP ANIONS IN d^{10}-METAL CLUSTERS STABILIZED BY 1,1-DICHALCOGENO LIGANDS

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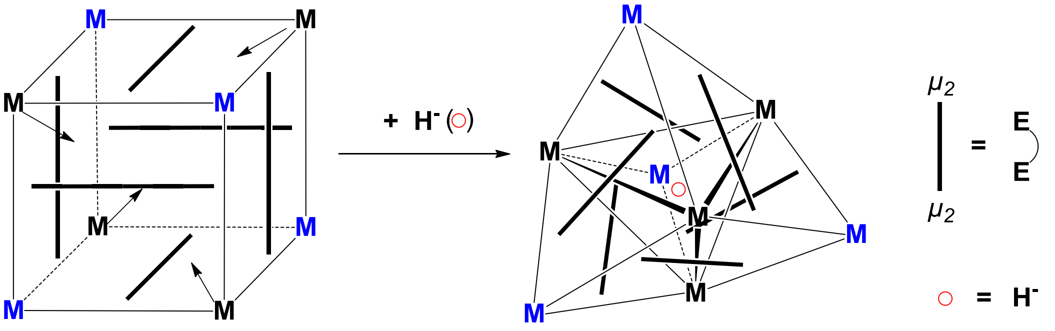
Cu(I) and Ag(I) can form with 1,1-dithio or 1,1-diseleno ligands various types of clusters of various nuclearities, the framework of which being maintained by the metal-chalcogen bonds provided by the bridging ligands. The metal centers are generally tricoordinated and consequently are bearing an accepting orbital of valence s and/or p character. There is no formal metal-metal bonding between the 16-electron, but only weak d^{10}-d^{10} interactions which tend to slightly favor the overlap between the metal-centered accepting orbitals. The bonding combinations of these orbitals are generally perfectly suited for interacting with the occupied valence orbitals of an encapsulated anion. This is the reason why many of these clusters are able to encapsulate hydrides or main-group anions, a situation which tends to stabilize the whole structure through the building of significant bonding between the hosting cage and its anionic guest. Not only is the effect of anion encapsulation to stabilize the cluster cage, but it can also significantly modify its structure, such as hydride in octanuclear species (Scheme 1), or even act as a template in the stabilization of species which would not be stable as empty clusters. The latter occurs most often with cluster nuclearities larger than 8. This presentation focuses on the synthesis and structure of all the known clusters of d^{10} metals decorated with 1, 1-dichachogeno ligands and containing entrapped saturated atomic anions. Their structures are analyzed with respect to cluster nuclearity and shape. The photoluminescence properties of some of them are discussed.



Scheme 1. The tetrahedral distortion induced by an encapsulated hydride in a $[M_8(E^\frown E)_6]^q$ cage (M = Cu(I), Ag(I); E = S, Se)

DFT MODELING OF ANION-CONTAINING Cu(I) AND Ag(I) CLUSTERS STABILIZED BY DI-CHALCOGENO LIGANDS

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Copper(I) and silver(I) are known for their ability to form, in association with various types of bridging and terminal ligands, cluster species of various shapes and sizes in which weak bonding interactions between the 16- or 14-electron closed-shell metal centers is generally present. The association of this weak interaction with the existence of a vacant orbital of s/p_z character on each metal center leads to the formation of one or several accepting orbitals of metal-metal bonding character. These vacant orbitals are particularly well suited for interacting with the occupied orbitals of entrapped hydrides or main-group anions. In the clusters of smaller nuclearities, these anions are encapsulated in the middle of the metallic polyhedron, whereas in the larger clusters, they can also cap the metallic faces, both from inside or outside the cage envelope, as in the large polyhydrides $[Cu_{20}H_{11}(S_2P(O^iPr)_2)_9]$ or $[Cu_{28}(H)_{15}(dtc)_{12}]^+$ synthesized in the Taiwan group.

In this talk we discuss the contribution provided by DFT calculations in the understanding of the structure, bonding and properties of a series of Cu(I) and Ag(I) clusters stabilized by dithio and diseleno ligands and containing hydrides or main-group anions. A comparison is made with structurally related gold, silver or copper nanoclusters stabilized by inorganic ligands, the electron count of which satisfying the superatom (jellium) closed-shell closure model.

SYNTHESIS AND PROPERTIES OF HEXANUCLEAR RHENIUM AND TECHNETIUM COMPLEXES WITH ISOTHIOCYANATE LIGANDS

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The hexarhenium(III) chalcogenide cluster complexes are intriguing for synthetic versatility, luminescent and redox active properties. We previously synthesized the chalcogenide capped hexarhenium(III) complexes with isothiocyanate ligands at the terminal positions of the clusters.[1] In the present study, the reactions of hexarhenium(III) chalcohalide clusters with thiocyanate were investigated. Moreover, we studied the reactions of hexatechnetium(III) clusters with thiocyanate.

The new complexes $[\mathrm{Re}_6(\mu_3\text{-}\mathrm{Q}_7\mathrm{X})(\mathrm{NCS})_6]^{3-}$ (Q = S, Se; X = Cl, Br) were obtained by the similar reaction of $[\mathrm{Re}_6(\mu_3\text{-}\mathrm{S})_8\mathrm{Cl}_6]^{4-}$ with KNCS.[1] The reactions of the corresponding chalcohalide complexes $[\mathrm{Re}_6(\mu_3\text{-}\mathrm{Q}_7\mathrm{X})\mathrm{X}_6]^{3-}$ with molten KSCN for 1 h gave $[\mathrm{Re}_6(\mu_3\text{-}\mathrm{Q}_7\mathrm{X})(\mathrm{NCS})_6]^{3-}$. The X-ray structures of $[\mathrm{Re}_6(\mu_3\text{-}\mathrm{Q}_7\mathrm{Br})(\mathrm{NCS})_6]^{3-}$ were determined. All of the thiocyanate ligands coordinate at their nitrogen sites to the rhenium cluster. The mean Re-N bond distances are 2.06 Å for both chalcobromide complexes. The values are similar to those of $[\mathrm{Re}_6(\mu_3\text{-}\mathrm{Q})_8(\mathrm{NCS})_6]^{4-}$. The capping chalcobromides are disordered. The reactions of $[\mathrm{Re}_6(\mu_3\text{-}\mathrm{Q}_6\mathrm{X}_2)\mathrm{X}_6]^{2-}$ (Q = S, Se; X = Cl, Br) with molten KSCN were not occurred, although the reaction was prolonged for 12 h. This may be due to the strong bond between rhenium and the terminal halide in the μ_3-$\mathrm{Q}_6\mathrm{X}_2$ capped complexes compared with those in the μ_3-$\mathrm{Q}_7\mathrm{X}$ and μ_3-Q_8 complexes, because $\{\mathrm{Re}_6(\mu_3\text{-}\mathrm{Q}_6\mathrm{X}_2)\}^{4+}$ core is more positive than $\{\mathrm{Re}_6(\mu_3\text{-}\mathrm{Q}_7\mathrm{X})\}^{3+}$ and $\{\mathrm{Re}_6(\mu_3\text{-}\mathrm{Q})_8\}^{2+}$.

The reaction of $[\mathrm{Tc}_6(\mu_3\text{-}\mathrm{S})_8\mathrm{Br}_6]^{4-}$ with molten KSCN gave $[\mathrm{Tc}_6(\mu_3\text{-}\mathrm{S})_8(\mathrm{NCS})_6]^{4-}$. Figure 1 shows the X-ray structure of $[\mathrm{Tc}_6(\mu_3\text{-}\mathrm{S})_8(\mathrm{NCS})_6]^{4-}$. All of the thiocyanate ligands coordinate at their nitrogen sites to the technetium cluster. The mean Tc-Tc, Tc-S, Tc-N bond distances are 2.575, 2.38 and 2.11 Å, respectively. These values are similar to those of $[\mathrm{Re}_6(\mu_3\text{-}\mathrm{S})_8(\mathrm{NCS})_6]^{4-}$, $[\mathrm{Tc}_6(\mu_3\text{-}\mathrm{S})_8\mathrm{Br}_6]^{4-}$, $[\mathrm{Tc}_6(\mu_3\text{-}\mathrm{S})_8(\mathrm{CN})_6]^{4-}$.[1-3] The reactions of $[\mathrm{Tc}_6(\mu_3\text{-}\mathrm{S}_7\mathrm{X})\mathrm{X}_6]^{3-}$ (X = Cl, Br) with molten KSCN were also investigated.

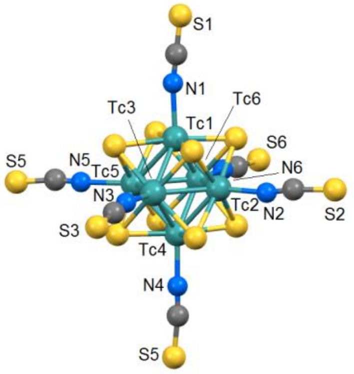

Figure 1. The X-ray structure of $[\mathrm{Tc}_6(\mu_3\text{-}\mathrm{S})_8(\mathrm{NCS})_6]^{4-}$

1. YoshimuraT., Chen Z.-N., Itasaka A., *Inorg. Chem.*, **2003**, *42*, 4857.
2. Yoshimura T., Ikai T., Tooyama Y., *Eur. J. Inorg. Chem.*, **2010**, 1214.
3. Yoshimura T., Ikai T., Takayama T., *Inorg. Chem.*, **2010**, *49*, 5876.

ALKOXIDES OF RHENIUM AND d-ELEMENTS OF V–VII GROUPS: SYNTHESIS, PROPERTIES AND APPLICATIONS

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The report summarizes the results of work on the development of methods for the synthesis of mono-and heterometallic alkoxy derivatives of rhenium and heavy transition metals with different ligands, including containing cluster M_4 (M = Re, Mo).

The results of quantum chemical calculations (method C.A.C.A.O.) in case of complexes with different ligands) have shown that the existence of complexes $Re_4O_n(OEt)_x(O\text{-}iPr)_y$ with structures of ethylate and isopropylate [1] is equiprobably. For a preliminary assessment of the possible existence of isopropylate containing heterometallic cluster M_4 (M = Re, Mo, W, Ru). Program «Priroda-04» was used.

The synthesized complexes and their thermal decomposition products were characterized by CA, XRD, DTA, IR spectroscopy, mass spectrometry, electron microscopy. It was shown that thermal decomposition products in the air represented by ultrafine (nano sized) oxides of the corresponding metals, reduction in hydrogen produces metals, alloys and ligatures at low temperatures.

The expediency of use of rhenium and heterometallic oxoalkoxocomlexes of d-elements (V) and (VI) groups as precursors for producing heterogeneous catalysts for conversion of ethanol or its mixture with glycerol in an olefin-alkane fraction favored in the production of a new generation of motor fuels is shown. Methods to obtain high-performance catalysts (W, Re/Al_2O_3 and $Re\text{-}Ta/Al_2O_3$) for reductive dehydration reaction of alcohols, the precursors for which were bimetallic complexes $Re_{4-x}WxO_6(OCH_3)_{12}$ and $Ta_4O_2(OCH_3)_{14}(ReO_4)_2$ were developed. It was established that the catalyst $Re\text{-}Ta/Al_2O_3$ exhibits selectivity on output of olefins and the catalyst W, Re/Al_2O_3 - on output of alkane-olefin fraction of hydrocarbons [2].

Acknowledgements. The research was carried out under the support of the RFBR grants №№ 09-03-00328a and 12-03-00699a.

1. Drobot D.V., Seisenbaeva G.A., Kessler V.G., *J. Cluster Sci.*, **2008**, *20*, 23.
2. Patent №2391133 (RF). Tsodikov M.V., Chistyakov A.V., Yandiev F.A., Kugel V.Y., Buhtenko O.V., Zhdanov T.N., Gekhman A.E., Moiseev I.I., Drobot D.V., Petrakova O.. Reported 06.10.08; publ. 10.06.10, Bull. Number 16.

OCTAHEDRAL CLUSTERS WITH MIXED INNER LIGAND ENVIRONMENT: SELF-ASSEMBLY, MODIFICATION AND ISOMERISM

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Octahedral complexes are one of the most representative class of compounds in the chemistry of transition metal clusters. There are two main structural types of the octahedral cluster complexes that are defined by composition and structure of the cluster core. Complexes of the first type are typical for halides of niobium and tantalum and represent an octahedral metal cluster M_6 with edges coordinated by halide ions resulting in the core $\{M_6(\mu_2\text{-}X)_{12}\}^{m+}$ (M = Nb or Ta; X = F, Cl, Br, or I). In halides and chalcogenides of molybdenum, tungsten and rhenium each face of the octahedron M_6 is coordinated by a ligand forming the cluster core $\{M_6(\mu_3\text{-}X)_8\}^{m+}$ (M = Mo, W, or Re; X = Cl, Br, I, S, Se, or Te).

Octahedral clusters with homoleptic inner ligand environment $[\{M_6(\mu_2\text{-}X)_{12}\}L_6]$ and $[\{M_6(\mu_3\text{-}X)_8\}L_6]$ possess high local symmetry. Introduction of a second type of ligand into the cluster core decreases the local symmetry of complex distorting metal cluster. In addition, mixed ligand inner environment leads to isomery of cluster cores.

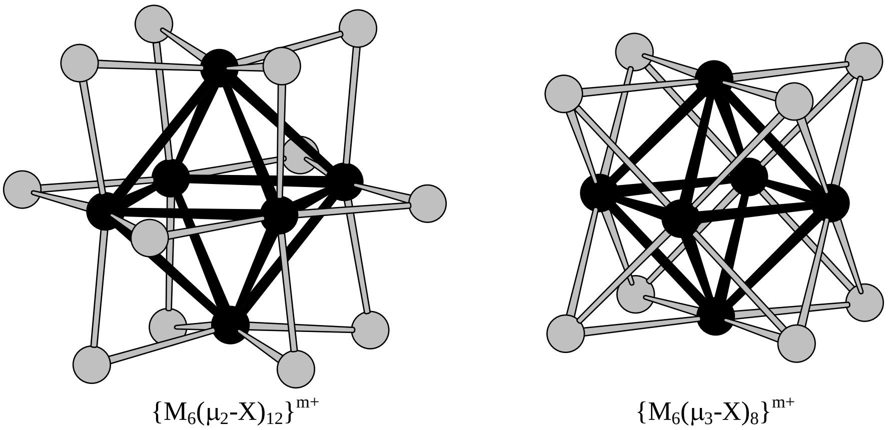

Fig. 1. Two types of cluster cores in octahedral cluster complexes.

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This work summarizes preparation methods of mixed ligand cluster complexes with the general formulas $[\{M_6(\mu_2\text{-}X)_{12}\}L_6]^n$ or $[\{M_6(\mu_3\text{-}X)_8\}L_6]^n$ and their structural features. Special attention will be paid for compounds with ordered ligand arrangements in crystal structure.

Authors thank the International Associate Laboratory (2014-2017) as well as the IDEMAT chemistry project in the frame of the Franco-Siberian Center of Training and Research.

ACUTE INTRAVENOUS TOXICITY OF OCTAHEDRAL RHENIUM CLUSTER COMPLEXES $Na_4[\{Re_6Q_8\}(CN)_6]$ (Q = Se/S/Te)

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Octahedral rhenium cluster complexes may have considerable potential as metallic therapeutic and diagnostic drugs due to its luminescent and X-ray contrast properties. However, its potential biological effects and toxicity in vivo are rather far from being understood. The properties of metal-based drugs are dependent on the metal ion, its oxidation state, and ligand structure [1]. Considering that ligands forming the metal-based agent are able to modify the biological properties of the drug, the correct choice of the ligand could improve significantly the adverse effects associated to metal ion overload and facilitate metal ion distribution [2].

We study the acute toxicity of several octahedral rhenium cluster complexes with different inner ligands after intravenous injection in mice. All cluster complexes were diluted in sterile phosphate buffer saline (pH = 7,4). No evidence of toxicity were seen in the group of mice received 500 mg/kg of $Na_4[\{\mathbf{Re_6Te_8}\}(CN)_6]$. After intravenous injection of 500 mg/kg $Na_4[\{\mathbf{Re_6Se_8}\}(CN)_6]$ 60% of mice lived for two weeks and then were sacrificed for morphological analysis. Other 40% of mice have dead at the first day. However, the injection of 500 mg/kg $Na_4[\{\mathbf{Re_6S_8}\}(CN)_6]$ resulted in instant death of mice, so the dose was reduced by a factor of 2. Seventy five percent of mice, received 250 mg/kg of $Na_4[\{\mathbf{Re_6S_8}\}(CN)_6]$ lived for 2 weeks and 25% mice of this group dead at the first day. Morphological analysis has shown that liver and kidney are target organs for these cluster complexes.

Consequently, the cluster complexes based on $\{\mathbf{Re_6Te_8}\}$-cluster core is the safest agent for biomedical application. Unfortunately the chemistry of octahedral rhenium telluride cluster compounds is weakly studied and the cyanide complex is only one soluble complex for this cluster core. However, the $Na_4[\{\mathbf{Re_6Se_8}\}(CN)_6]$ also showed rather good tolerance in vivo (since the dose 500 mg/kg more than 12 times higher presumed clinical dose). Moreover chemistry of $\{\mathbf{Re_6Se_8}\}$-based compounds is studied well enough to create highly water soluble compounds with properties suitable for use as metallic therapeutic and diagnostic drugs.

Acknowledgements. This work was supported by the Russian Science Foundation (Grant №14-14-00192).

1. Thompson K.H., Orvig C., *Science*, **2003**, *300*, 936.
2. Storr T., Thompson K.H., Orvig C., *Chem. Soc. Rev.*, **2006**, *35*, 534.

HETEROMETALLIC CLUSTERS WITH A $\{Re_3Mo_3S_8\}$ CORE: SYNTHESIS, REACTIVITY AND DFT CALCULATIONS

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A series of new heterometallic clusters with $\{Re_3Mo_3S_8\}^{-1/0}$ cluster core has been obtained using the combination of high-temperature synthesis and solution methods [1]. Reaction of ReS_2 and MoS_2 in molar ratio 1:1 in sealed silica ampoule with excess of KCN at 750°C led to formation of black octahedral crystals of compound $K_6[Re_3Mo_3S_8(CN)_5]$ (**1**). Reaction of polymeric compound **1** with an aqueous solution of KCN led to the cleavage of intercluster bonds and formation of stable 23e paramagnetic cluster anion $[Re_3Mo_3S_8(CN)_6]^{6-}$. Black crystals of paramagnetic compound $CaK_4[Re_3Mo_3S_8(CN)_6]\cdot 8H_2O$ (**2**) has been crystallized from the solution. During the dissolution 24-electron cluster core $\{Re_3Mo_3S_8\}^-$ of compound **1** were oxidized to paramagnetic 23-electron core $\{Re_3Mo_3S_8\}^0$ of compound **2**.

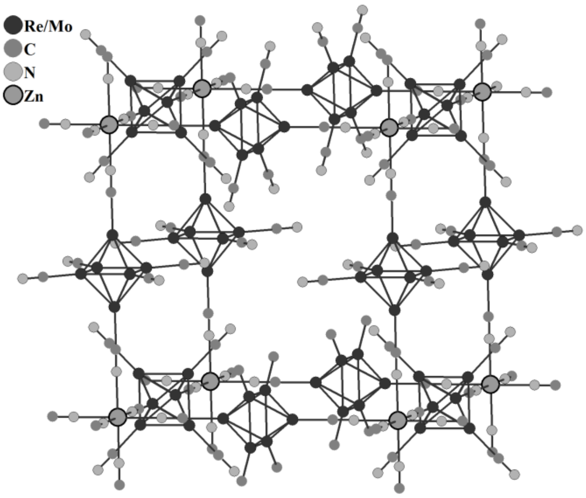

Figure 1. Polymeric framework of **3**. The inner ligands, $[Zn(NH_3)_4]^{2+}$ cations and water molecules have not been represented for clarity.

Compound **2** readily reacts with 3*d* metals salts in aqueous or aqueous ammonia solutions forming polymeric products mainly. Particularly, reaction of **2** and $ZnCl_2$ in aqueous ammonia solution resulted in formation of polymeric compound $[Zn(NH_3)_4]_8Zn[Re_3Mo_3S_8(CN)_6]_3\cdot 8H_2O$ (**3**). Compound **3** crystallizes in a cubic $Pm\bar{3}m$ space group with $a = 14.9831(3)$ Å and has the "*anti*-Prussian blue" structure (Fig. 1). Polymeric framework consist of the Zn^{2+} ions which are octahedrally connected to six cluster anions through the CN-groups, and each cluster anion is connected with only two Zn^{2+} ions in *trans*-position, giving the formula of the polymeric framework $\{Zn[Re_3Mo_3S_8(CN)_6]_3\}_{\infty\infty\infty}^{16-}$. Framework cavities are occupied by $[Zn(NH_3)_4]^{2+}$ cations and H_2O molecules.

Compound **3** is stable at the room temperature in the mother solution, but air storage resulted in partial loss of NH_3 molecules and structural rearrangement. The resulting compound $[Zn(NH_3)_4]_2[ZnRe_3Mo_3S_8(CN)_6]\cdot nH_2O$ (**4**) has the Prussian blue type structure with cluster anions connected through octahedral Zn^{2+} ions bonded to each CN-group. Compounds **3** and **4** are paramagnetic with g-value equal to 2.280.

We thank the IDEMAT chemistry project in the frame of the Franco-Siberian Center of Training and Research. Work was also supported by RFBR grant № 12-03-01099-a.

1. Gayfulin Y.M., Naumov N.G., Rizhikov M.R., *Chem. Comm.*, **2013**, *49*, 10019.

POROUS METAL ORGANIC FRAMEWORK MATERIALS FOR GAS STORAGE AND SELECTIVITY

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The storage, sequestration and selective binding of fuel gases in a safe and compact form represents a significant current challenge. There is wide-ranging interest in the development of stable materials that can store and release hydrogen, carbon dioxide, sulphur dioxide and methane with fast kinetics and high reversibility over multiple cycles. Porous co-ordination framework compounds have enormous potential in this regard. We report the synthesis, structural characterisation and gas adsorption studies of a range of metal-organic materials derived from stable carboxylate-linked complexes that exhibit high porosity and surface area coupled with high storage capacities and selectivities. Of particular interest are *in situ* structural and dynamic studies of gas-loaded materials that define the binding of substrates within pores at a molecular level [1-7].

We describe the synthesis, structure and properties of a unique non-amine-containing porous solid NOTT-300 in which hydroxyl groups within the pores bind selectively to CO_2, SO_2, acetylene, ethylene and ethane. NOTT-300 exhibits highly selective uptake of CO_2 versus N_2, CH_4, H_2, CO, O_2, Ar, and *in situ* powder X-ray diffraction (PXRD), neutron diffraction and inelastic neutron scattering (INS) studies, combined with density functional theory (DFT) modelling, reveal that these hydroxyl groups bind CO_2 and SO_2 *via* the formation of $O{=}X{=}O(\delta-)\cdots H(\delta+)$—O hydrogen bonds [1]. These are reinforced further by weak supramolecular interactions with C-H hydrogen atoms on the phenyl rings. This offers exciting potential for the application of new capture systems based on the soft binding of CO_2 and SO_2 via the use of an “easy-on“ and “easy-off“ model.

This work has been extended to the study of the storage and binding of acetylene and ethylene which bind to the metal-organic host *via* hydrogen bonding between hydroxyl group and the π-electron density of the unsaturated guest. Excellent gas capacities and selectivities between alkene vs alkyne are observed representing a methodology for purification of ethylene from acetylene.

1. Yang S., Sun J., Ramirez-Cuesta A.J., *Nature Chemistry*, **2012**, *4*, 887.
2. Yang S., Lin X., Lewis W., *Nature Materials*, **2012**, *11*, 710.
3. Yang W., Davies A.J., Lin X., *Chem. Sci,* **2012**, *3*, 2993.
4. Yang S., Liu L., Sun J., *J. Am. Chem. Soc.*, **2013**, *135*, 4954.
5. Yan Y., Suetin M., Bichoutskaia E., *Chem. Sci.*, **2013**, *4*, 1731.
6. Yan Y., Yang S., Blake A.J., *Acc. Chem. Res.*, **2014**, *47*, 296.
7. Savage M., Yang S., Suyetin M., *Chem. Eur. J.*, **2014**, *20*, 8024.
8. Alsmail N.H., Suyetin M., Yan Y., *Chem. Eur. J.*, **2014**, *20*, 7317.

PROPERTIES OF HYDROGEN BONDED NETWORKS

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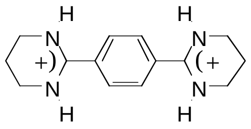
The bisamidinium dications (**1**, **2**, or **3**, see scheme) are molecular building blocks particularly suited to build molecular networks by self-assembly with hexacyanometallates type anion $[M^{III}(CN)_6]^{3-}$ (M = Fe, Co, Cr) or $[M^{II}(CN)_6]^{4-}$ (M = Fe ou Ru) or other hydrogen bonds acceptors metallic anions. The strength and the adaptability of the formed networks arise from the involved charge assisted hydrogen bonds [1].



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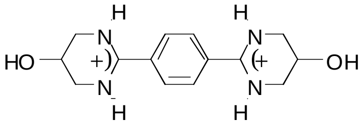

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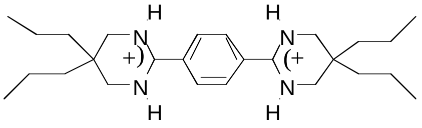

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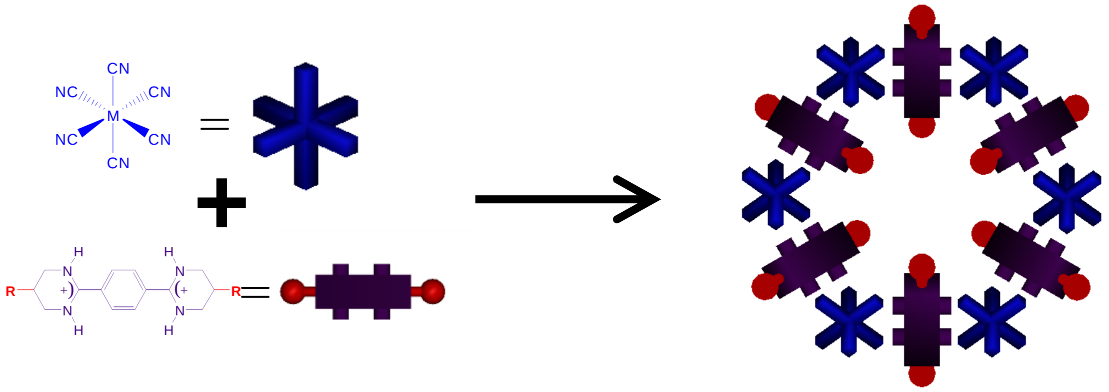

Scheme: Formation of hydrogen bonded molecualr networks $(\mathbf{X}\text{-}2H^+)_3[M^{III}(CN)_6]^{3-}{}_2$ (**X**=1, 2 or 3, and M = Cr, Fe or Co) or $Y(\mathbf{3}\text{-}2H^+)_3[Fe^{II}(CN)_6]^{4-}{}_2$ (Y=Na, K, Rb, Cs)

Mono or two-dimensional molecular networks may be obtained in the crystalline state [2]. These networks may be porous, presenting optical properties like luminescence [3] or liquid crystals [4]. A particular material processing, "crystal of crystal" may also be presented [5].

1. Ferlay S., Hosseini M. W. "*Functional Supramolecular architectures for organic electronics and nanotechnology*" Ed. Wiley-VCH. **2011**.
2. (a) Ferlay S., Félix O., Hosseini M.W., *Chem. Comm.*, **2002**, 702; (b) Ferlay S., Bulach V., Félix O., *CrystEngComm*, **2002**, 447; (c) Dechambenoit P., Ferlay S., Hosseini M.W., *New J. Chem.*, **2006**, *30*, 1303; (d) Dechambenoit P., Ferlay S., Hosseini M.W., *J. Am. Chem. Soc.*, **2008**, *130*, 17106; (e) Dechambenoit P., Ferlay S., Hosseini M.W., *Chem. Comm.*, **2009**, 1559
3. (a) Paraschiv C., Ferlay S., Hosseini M.W., *J. Chem. Soc., Chem. Comm.*, **2004**, 2270; (b) Dechambenoit P., Ferlay S., Hosseini M.W., *CrystEngComm*, **2011**, *13*, 1922.
4. Dechambenoit P., Ferlay S., Donnio B., *Chem. Commun.*, **2010**, *47*, 734.
5. (a) Ferlay S., Hosseini M.W., *J. Chem. Soc., Chem. Comm.*, **2004**, 788; (b) Dechambenoit P., Ferlay S., Hosseini M.W., *Cryst. Growth & Design*, **2005**, *5*, 2310; (c) Dechambenoit P., Ferlay S., Kyritsakas N., *Chem. Commun.*, **2009**, 6798; (d) Dechambenoit P., Ferlay S., Kyritsakas N. *Chem. Commun.*, **2010**, 868.

HETEROGENEOUS LIQUID-PHASE SELECTIVE OXIDATIONS OVER TEREPHTHALATE-BASED METAL-ORGANIC FRAMEWORKS

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Metal-organic frameworks (MOFs) have attracted considerable attention as prospective materials for heterogeneous catalysis due to a unique ensemble of properties, such as high surface areas, crystalline open structures, tunable pore size and functionality, and high contents of uniformly distributed accessible metal sites [1]. Here we summarize on our experience in the use of terephthalate-based MOFs, Cr- and Fe-MIL-101(100) and Ti-MIL-125 as heterogeneous catalysts for the liquid-phase selective oxidation of various classes of organic substrates (alkanes, alkenes, arenes) with environmentally benign oxidants, such as molecular oxygen, aqueous hydrogen peroxide and *tert*-butyl hydroperoxide (TBHP).

Cr- and Fe-MIL-101 are highly efficient, true heterogeneous and recyclable catalysts for the solvent-free selective oxidation of cyclohexane with TBHP and/or molecular oxygen under mild conditions [2]. Both Cr-MIL-101(100) and Fe-MIL-101(100) catalyze solvent-free allylic oxidation of alkenes (cyclohexene, terpenes) but the selectivity strongly depends on the metal nature: the Cr-MOFs give predominantly α,β-unsaturated ketones while the Fe-MOFs afford mainly unsaturated alcohols, thus pointing out a biomimetic behavior [3]. Cr-MIL-101 revealed a superior catalytic performance in the oxidation of anthracene with TBHP, producing 9,10-anthraquinone with a nearly quantitative yield [4]. Finally, Ti-MIL-125 converted alkyl-substituted phenols to corresponding *p*-benzoquinones with >99% selectivity and moderate efficiency of the oxidant (H_2O_2) utilization [5].

Catalyst stability, reusability and nature of the catalysis have been thoroughly investigated. Stability toward destruction was found to reduce in the order Cr-MIL-101, Cr-MIL-100 > Fe-MIL-100 > Fe-MIL-101 > Ti-MIL-125. Although the structural integrity of MIL-125 was destroyed by the reaction medium, this MOF acted as a precursor for a highly active, selective and recyclable amorphous catalyst, stable toward titanium leaching.

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1. Hwang Y.K., Férey G., Lee U.-H., in *Liquid Phase Oxidation via Heterogeneous Catalysis* (Eds: M. G. Clerici, O. A. Kholdeeva) Wiley, New Jersey, **2013**, Ch. 8.
2. Maksimchuk N.V., Kovalenko K.A., Fedin V.P., *Chem. Commun.* **2012**, *48*, 6812.
3. Skobelev I.Y., Sorokin A.B., Kovalenko K.A., *J. Catal.* **2013**, *298*, 61.
4. Kholdeeva O.A., Skobelev I.Y., Ivanchikova I.D., *Catal. Today*, **2014**, DOI: 10.1016/j.cattod.2014.01.010
5. Ivanchikova I.D., Lee J.S., Maksimchuk N.V., *Eur. J. Inorg. Chem.* **2014**, 132.

EFFECT OF MODIFICATION ON HIGH-PRESSURE HYDROGEN STORAGE PERFORMANCE OF METALL-ORGANIC FRAMEWORKS

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Development of advanced hybrid hydrogen storage systems based on integration of solid-state adsorption materials into lightweight composite high-pressure tanks requires new H_2 sorbents effective under such conditions. Metal-organic frameworks demonstrate spectacular adsorption ability toward hydrogen at cryogenic temperatures but it vanishes when approaching the ambient one. Besides, the excess adsorption capacity which refers to the substantial storage performance as compared with compressed gas reaches its maximum value at a certain moderate pressure and then gradually decreases with rising pressures.

Two approaches to enhancement of MOF's adsorption behaviour at high pressures have been explored in the present work:

- doping of the porous framework with ionic clusters to increase the dipole-induced dipole interactions between sorbent and hydrogen molecules;
- formation of composites containing a catalyst of dissociative chemisorption of H_2 molecules.

Chromium(III) terephthalate MIL-101 and a series of commercial MOF Basolite C300, F300, and Z1200 as porous matrices, anionic cluster complexes $[Re_4S_4F_{12}]^{4-}$ and $[SiW_{11}O_{39}]^{7-}$ as doping species, Pt/C and the hydride-forming intermetallic compound $LaNi_5$ as catalysts have been used.

The measured adsorption-desorption isotherms were fully reversible for all studied systems, which indicates that there were no side chemical reactions under experimental conditions. The presence of ionic clusters (especially, Re-containing one) in the pores of the framework led to a remarkable increase of density of the hydrogen adsorbed layer at room temperature.

A drastic change of high-pressure adsorption has been found for the composites containing chemisorption catalysts. Those materials kept high storage capacity within the whole studied pressure range without the typical maximum of excess adsorption at low pressures. As the amount of the adsorbed hydrogen at room temperature increased gradually with pressure, the modification applied resulted in a substantial shift of the upper pressure limit of the efficiency of the adsorbents as compared with the pristine MOFs. Such a remarkable enhancement allows us to consider the guest-modified MOFs as promising materials for advanced hybrid high-pressure storage systems.

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THE INFLUENCE OF DIAMAGNETIC SUBSTRATES ABSORPTION ON MAGNETIC PROPERTIES OF POROUS COORDINATION POLYMERS

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Porous coordination polymers (PCPs) can be used as a basis for creation of multifunctional materials and active bodies of sensors due to combination of their ability to absorb different compounds and other functional properties [1,2]. Paramagnetic PCPs can reveal unique tunable magnetic properties, that can be modulated by chemical reactions or adsorption of different substrates [1,2]. Interaction of PCPs with guest molecules can modify magnetic susceptibility (χ_M) in wide temperature range, as well as can lead to change of the magnetic ordering or spin-crossover temperature and other magnetic characteristics. It is shown, that PCP's magnetic behavior modification upon guests exchange can be caused by one of the following reasons: guest molecule coordination to metal ion or decoordination (fig. 1,a); formation or breaking of bonds in the group, which transmits exchange interactions between metal ions; or change of bond lengths or angles in coordination polymer because of crystal lattice adaptation to the guest molecule (fig. 1,b) [1]. The report will focus on the known examples of modifications in the magnetic properties of PCPs by reacting with diamagnetic substrates.

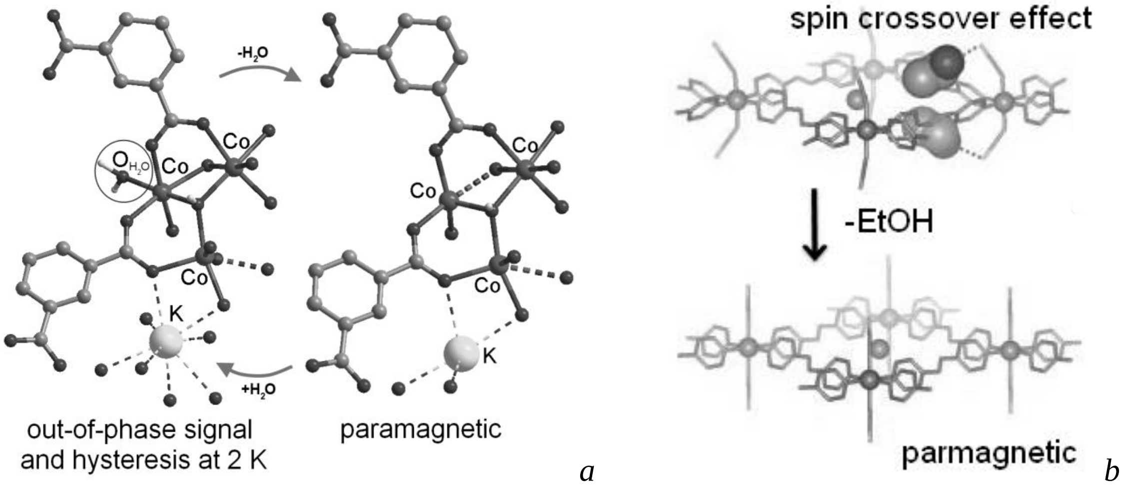

Figure 1. Examples of magnetic behavior modification upon "guests" exchange (see details in the text).

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1. Kolotilov S.V., Kiskin M.A., Eremenko I.L., *Curr. Inorg. Chem.*, **2013**, *3*, 144.
2. Coronado E., Espallargas G.M., *Chem. Soc. Rev.*, **2013**, *42*, 1525.

THEORETICAL ASPECTS OF ATOMISTIC LEVEL DESCRIPTION OF NANOPOROUS MATERIALS

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With tremendous progress in computer technologies and applications during the last decade, atomistic-level simulation is rapidly becoming an essential tool in materials science for the study of the physical and chemical properties of various materials. The recent advent of metal–organic framework materials (MOFs), as new functional adsorbents has attracted the attention due to scientific interest in the creation of unprecedented regular nano-sized spaces and in the finding of novel phenomena, as well as commercial interest in their application for storage and separation. For MOFs the structural versatility of molecular chemistry has allowed the rational design and assembly of materials having novel topologies and exceptional host-guest properties that are important for urgent sustainable applications [1]. Due to the regularity of MOF structures, in a computer simulation we are easily able to build structural models of MOFs that are very helpful to find new materials with desired characteristics.

Here, our recent achievements have been reported. The high sorption ability for acetylene on specific MOF material was determined [2], using both different experimental measurements and first-principles calculations which ascribe to the double hydrogen bond support between the acidic acetylene proton and its acceptor basic site on the channel surface. In collaboration with experimentalists, the absorption of several chiral sulfoxides, which constitute an important class of biologically active compounds and therapeutic drugs, into the homochiral porous coordination polymer has been also investigated [3]. The specific nanoporous material that selectively adsorbs CO with adaptable pores has been studied using first-principles calculations. The high selectivity of CO has been achieved from a mixture with nitrogen by both the local interaction between CO and accessible Cu^{2+} metal sites and the modification of nanopore size. The obtained results have been compared with CO adsorption into HKUST1 structure [4].

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1. Kitagawa S., et al., *Angew. Chem. Int. Ed.*, **2004**, *43*, 2334.
2. Matsuda R., et al., *Nature*, **2005**, *436*, 238.
3. Dybtsev D.N., et al., *Chem. Eur. J.*, **2010**, *16*, 10348.
4. Sato H., et al., *Science*, **2005**, *343*, 167.

UNUSUAL HEAT CAPACITY IN ~62% GUEST FREE HIGH POROUS COMPOUND $Zn_2(C_8H_4O_4)_2{\cdot}N_2(CH_2)_6$: QUANTUM EFFECTS

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Crystal structure of high-porous metal-organic sorbent $Zn_2(C_8H_4O_4)_2{\cdot}N_2(CH_2)_6$ is made up of tetragonal 2D-layers $Zn(C_8H_4O_4)$ intermitted by molecular ligands $N_2(CH_2)_6$. The crystal symmetry is tetragonal, space group ***P***4/*mmm*, *a* = 10.929 and *c* = 9.608 Å, Z = 1 [1]. The figure shows the arrangement of metal Zn^{2+} cations, terephthalate anions $[C_8H_4O_4]^{2-}$, and ligand molecules of 1,4-diazabicyclo[2,2,2]octane $N_2(CH_2)_6$.

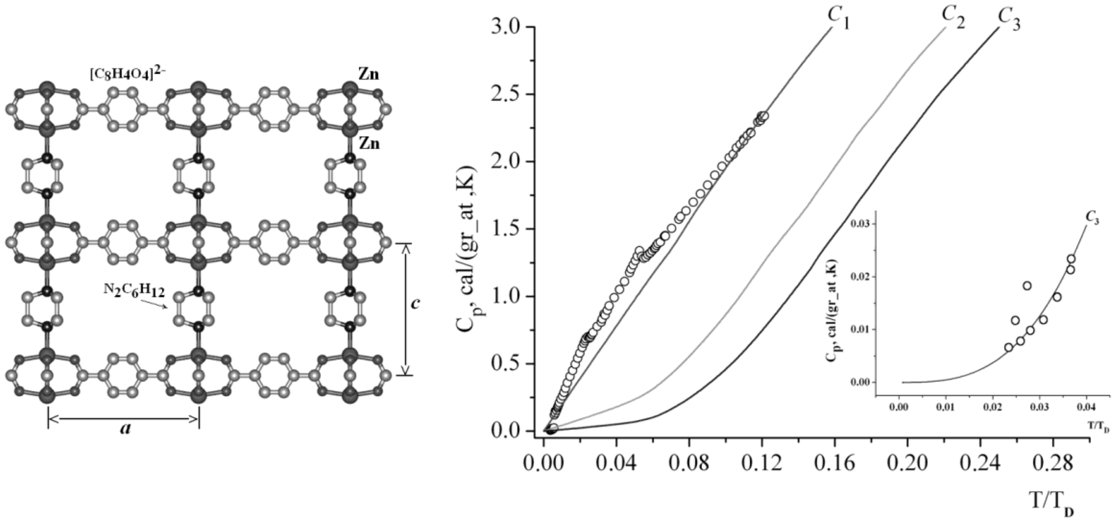

Figure 1. The positions of empty areas in the structure of $Zn_2(C_8H_4O_4)_2{\cdot}N_2(CH_2)_6$ (left), and specific heat Cp of the compound (right). C_1,C_2,C_3 are specific heats of 1D-chain, 2D-layered, and 3D bulk crystal, respectively.

According to ^{1}H NMR spin-lattice relaxation study [2], in the low temperature region some remarkable features were found to characterize intracrystalline rotational mobility and chiral polarization of $N_2(CH_2)_6$ molecules below 20 K.

In this work we report data on thermodynamic properties of $Zn_2(C_8H_4O_4)_2{\cdot}N_2(CH_2)_6$ studied at 8-300 K using low-temperature adiabatic calorymetry (Figure). Phase transitions were observed at ~15, ~60, and ~135 K. It is shown that specific heat of the compound obeys the classical Debye law Cp ~ T^3 only below 15 K, whereas above 15 K it is proportional to the first degree of temperature, Cp ~ T, to indicate strong anisotropy of crystal vibrations corresponding to 1D vibration continuum (C_1). The report will also contain discussion of quantum effects.

Acknowledgement. This work was supported by RFBR (project № 14-03-00036).

1. Chun H., Dybtsev D.N., Kim H., *Chem. Eur. J.* **2005**, *11*, 3521.
2. Gabuda S.P., Kozlova S.G., Samsonenko D.G., *J. Phys. Chem. C.* **2011,** *115*, 20460.

RATIONAL DESIGN OF PHOTOMAGNETIC CHAINS: BRIDGING SINGLE-MOLECULE MAGNETS WITH SPIN-CROSSOVER COMPLEXES

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The rational design of molecule-based systems displaying tunable optical and/or magnetic properties under external stimuli has received a great deal of attention recently. This interest is driven by the potential applications in the high-performance molecule-based electronic devices in the area of recording media, switches, sensors, and displays. As examples, Fe(II) complexes and cyanido-bridged compounds notably demonstrate the concomitant change in magnetic and optical properties by thermally and light-induced spin crossover or metal-to-metal electron transfer respectively [1,2].

The foregoing remarkable properties in the cyanido-bridged networks prompted many researchers to design new photomagnetic compounds through a building-block approach [3]. In this presentation, we will present recent systems that we obtained with the association between Fe(II) spin crossover units and Mn(III) single-molecule magnets through cyanido bridges. The optical reflectivity and photomagnetic experiments reveal that the photomagnetic properties of the Fe(II) unit is kept after its coordination to the acceptor Mn^{III}/saltmen complexes, allowing to switch "on" and "off" the magnetic interaction between the photo-induced Fe^{II} HS unit (S = 2) and the Mn(III) ions [4]. To the best of our knowledge, the reported compounds represent the first examples of coordination networks of Single-Molecule Magnets linked by spin-crossover units inducing thermally- and photo-reversible magnetic and optical properties.

Acknowledgements. This work was supported by the University of Bordeaux, the ANR, the Région Aquitaine and the CNRS and the IUF (Institut Universitaire de France).

1. Decurtins S. et al., *Chem Phys. Lett.* **1986**, *1*, 105.
2. Sato O. et al., *Science* **1996**, 272.
3. Sato O. et al., *Angew. Chem. Int. Ed.*, **2007**, *46*, 2152; Bleuzen A. et al., *Inorg. Chem.*, **2009**, *48*, 3453; Berlinguette C.P. et al., *J. Am. Chem. Soc.*, **2005,** *127*, 6766; Li D. et al., *J. Am. Chem. Soc.*, **2008**, *130*, 252; Zhang Y. et al, *Angew. Chem. Int. Ed.*, **2010**, *49*, 3752; Mercurol J. et al., *Chem. Commun.*, **2010** *46*, 8995; Nihei M. et al., *J. Am. Chem. Soc.*, **2011** *133*, 3592; Funck K.E. et al, *Inorg. Chem.*, **2011**, *50*, 2782; Liu T. et al., *Angew. Chem. Int. Ed.*, **2012**, *51*, 4367.
4. Ababei R., Pichon C., Roubeau O., *J. Am. Chem. Soc.*, **2013**, *135*, 14840.

OPTICAL AND MAGNETIC MOLECULAR SWITCHES FROM SOLID STATE TO SOLUTION

Clérac R.[1,2], Koumousi E.[1,2,3,4], Jeon I.-R.[1,2,3,4], Mathonière C.[3,4], Mitcov D.[1,2], Siretanu D.[1,2]

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The design of molecule-based systems displaying tunable optical and/or magnetic properties under external stimuli received a great deal of attention in the past few years. This interest is driven by the potential applications in high-performance molecule-based electronics. As an example, 3D Fe/Co Prussian blue compounds exhibit a concomitant change in magnetic and optical properties due to a temperature- or light-induced metal-to-metal electron transfer (ET). The foregoing remarkable properties in Prussian blues prompted us to design soluble molecular fragments of these coordination networks through a rational building-block approach in order to mimic their properties on a single molecule [1-3]. With a judicious choice of the ligands for metal ion molecular precursors, we prepared an octanuclear [1], tetranuclear [2], and dinuclear [3] (Fig. 1) cyanido-bridged Fe/Co complexes. In the solid state, while an intramolecular ET is observed for the $[Co_4Fe_4]$ and $[Co_2Fe_2]$ complexes, the Co ion of the dinuclear complex exhibits a spin crossover (SCO) involving a $[Fe^{III}_{LS}\text{-CN-}Co^{II}_{LS}]$ ground state and a thermally populated $[Fe^{III}_{LS}\text{-CN-}Co^{II}_{HS}]$ state. To our knowledge, this compound is the only example of a heterobimetallic complex exhibiting a Co^{II} SCO. Remarkably, our studies of these $[Co_nFe_n]$ complexes in solution reveal important optical and magnetic changes induced by an intramolecular metal-to-metal ET triggered and modulated by a controlled protonation of the complex or by temperature. Therefore, these molecules act as different molecular switches depending on their physical state and external stimuli.

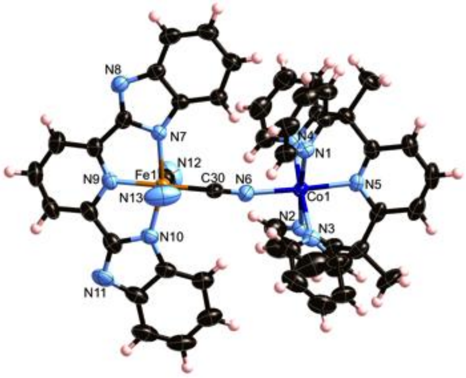

Figure 1. ORTEP-type view of the dinuclear complex $[(BBP)Fe(CN)_3Co(PY5Me_2)]\cdot 2.5CH_3OH$ (with H_2BBP = 2,6-*bis*(benzimidazol-2-yl)pyridine and $PY5Me_2$ = 2,6-*bis*(1,1-*bis*(2-pyridyl)ethyl)pyridine) at 370 K. The thermal ellipsoids are drawn at the 50 % probability level.

Acknowledgements. This work was supported by the University of Bordeaux, the ANR, the Région Aquitaine and the CNRS. All the authors of the references are acknowledged for their work, collaboration, expertise and assistance.

1. Li D. et al., *J. Am. Chem. Soc.*, **2008**, *130*, 252.
2. Zhang Y. et al., *Angew. Chem. Int. Ed.*, **2010**, *49*, 3752; Siretanu D. et al., *Chem. Eur. J.*, **2011**, *17*, 11704.
3. Jeon I.-R. et al., *Chem. Sci.*, **2013**, *4*, 2463.

CATALYTIC BEHAVIOR OF METAL-ORGANIC FRAMEWORKS IN PHOTOCATALYTIC DECOLORIZATION OF METHYLENE BLUE IN AQUEOUS SOLUTION

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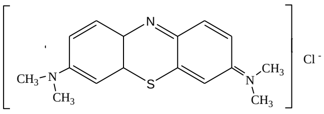
Nowadays, numerous studies of metal-organic frameworks (MOFs) have attracted wide scientific attention devoted to their applications in photocatalysis, because MOFs behave as semiconductors under exposed to light. However, the understanding of the dependence of catalytic behavior of MOFs on the chemical composition and structure of MOFs is still limited.

Here, we investigated effect of the variation of both the nature of metals and the organic ligands on physicochemical and photocatalytic properties of isoreticular UiO-66-R (H, $-NH_2$, $-SO_3H$ and $-NO_2$), isostructural MIL-100(M) (M – Fe, V and Cr), MIL-125(Ti) and $Cu_2(BTC)_3$ in the photocatalytic degradation of methylene blue (MB) by air oxygen in an aqueous solution at pH = 7.0 and 20 ^{o}C of under solar radiation.



It was found that catalytic activity of isostructural MIL-100(M) correlated with the band gap value (E_g). The decreasing of E_g value leads to the increase in catalytic activity of MOFs (Fig. 1).

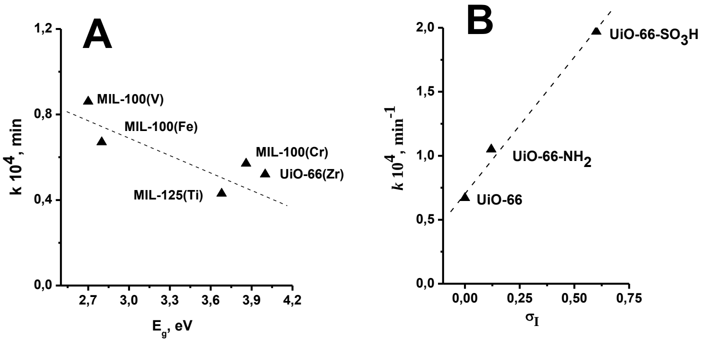


Figure 1. (A) Correlation between E_g of MOFs and reaction constant of MB decolorization over MOFs under the irradiation; (B) Correlation between σ_I and reaction constant in MB decolorization over isoreticular UiO-66-R.

Activity of isoreticular UiO-66-R depends on the inductive effect (σ_I) of substituent group in organic linker of MOFs (Fig. 1). Decreasing order of -I effect (or increasing order of +I effect) favours the decreasing of photocatalytic activity. It was demonstrated that MOFs potentially have much greater photooxidation efficiency than TiO_2 powder.

A LINK BETWEEN CATALYTIC PERFORMANCE AND PHYSICOCHEMICAL PROPERTIES OF METAL-ORGANIC FRAMEWORKS IN THE KNOEVENAGEL CONDENSATION REACTION

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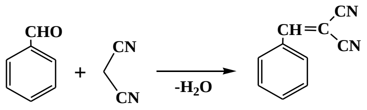
Chemistry of metal-organic frameworks (MOFs) is new field, which captures the attention and imagination of so many during the past two decades due to the possibility of adjustment their textural and physicochemical properties. The change of chemical compositions and structure opens up the broadly possibility of using MOFs in catalysis. With this perspective, we investigated effect of the variation of both the nature of metals and the organic ligands on red-ox and acid-base properties of MOFs, such as isoreticular family UiO-66-R (-H and -NH_2) and isostructural family MIL-100(M) (M – Al, Fe, V and Cr) in Knoevenagel condensation of benzaldehyde with malononitrile to 2-benzylidenemalononitrile.



It was demonstrated that catalytic activity of MOFs rises with increase in amount of basic sites and the ionic covalent nature of the metal-oxygen bond in metal-carboxylates. The reaction mechanism can be ascribed to the “M^{+n}–O^{2-} Lewis acid–base” pair that participates in the catalysis via the deprotonation, aldol and dehydration steps. Using the ionic covalent parameter (ICP) to analyze the influence of the covalence of metal-oxygen bonds on the acid-base properties of a metallic cation, i.e. the ability of oxygen to donate electron density to a metal ion, it can predict a catalytic activity of MOFs (Fig. 1). The generation of carbanion of malononitrile on the surface of UiO-66 and MIL-100(Al) was proved by IR and DR-UV-vis spectroscopies.

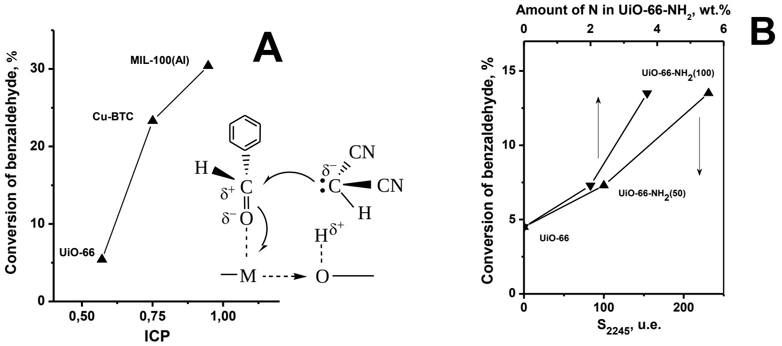


Figure 1. (A) Correlation between conversion of benzaldehyde for 270 min and ICP; (B) Correlations between conversion of benzaldehyde for 210 min and amount of NH_2-groups in UiO-66-NH_2 and amount of basic sites determined by IR spectroscopy using $CDCl_3$ as probe molecule.

The insertion of NH_2-groups into the linker ligand of UiO-66 led to an increase in the catalytic activity of UiO-66-NH_2, since increasing the amount of basic sites increased the activity of UiO-66-NH_2 catalysts.

LIQUID PHASE SEPARATION OF BENZENE FROM SATURATED ALIPHATICS BY ADSORPTION ON METAL-ORGANIC FRAMEWORK HKUST-1

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Purification of aliphatics by removing aromatics is challenging in the petrochemical industry [1]. Application of porous metal-organic frameworks (MOFs) for the separation and purification of hydrocarbons represent considerable interest [2]. In the present work the comparison of three different commercially available MOFs Basolite C300, A100 and F300 was performed in the liquid phase separation of benzene from saturated aliphatic compounds. Basolite C300 (HKUST-1) consists of copper paddlewheel metal clusters linked by 1,3,5-benzenetricarboxylate ligands [3], Basolite A100 (MIL-53(Al)) consists of infinite chains of octahedra formed by coordination of Al^{III} by terephthalate and OH^{-} groups [4] and Basolite F300 is porous iron benzene-1,3,5-tricarboxylate with unknown structure.

MOFs were purchased from Sigma-Aldrich. Before the using these solids were vacuum dried at 200 °C during 2 hours. For batch experiments MOF (30 mg) was added to solution of benzene in heptane (2 mL) containing n-decane (1.0 vol.%). After stirring the mixture for 2 h at room temperature the adsorbent was collected by filtration. The concentration of benzene in the filtrate was determined by GC using *n*-decane as an internal standard. Breakthrough experiments and chromatographic separation were performed at room temperature and the flow rate of 0.15 mL min^{-1} on a 30 mm stainless steel column with an internal diameter of 4 mm (cartridge CatCart®30) filled with MOF (100 mg), placed in H-Cube Pro instrument equipped with HPLC pump. For breakthrough experiments solutions of benzene in heptane containing n-decane (1.0 vol.%) was fed into the column. For chromatographic separation 0.1 mL of a heptane mixture containing benzene (1 mg) and cyclohexane (1 mg) were placed on the inlet of the column and eluted by heptane. The effluent fractions were collected every 3 minutes and concentrations were determined by GC.

It was found that, Basolite C300 exhibits an excellent capacity for benzene providing adsorption of 0.25 g of benzene per 1 g of Basolite C300 from heptane solution at ambient temperature. This solid is an efficient adsorbent for the liquid phase separation of benzene from saturated aliphatics. Significant amounts of heptane solution can be purified on a column of Basolite C300 before the breakthrough point. Using Basolite C300 as the stationary phase allows realizing liquid chromatographic resolution of benzene and cyclohexane mixture. In contrast to Basolite C300, Basolite A100 and Basolite F300 demonstrate significantly worse adsorption capacities insufficient for successful purification of saturated aliphatics. This observation can be explained by coordinative interaction of benzene molecules with copper sites in the framework of Basolite C300 via π-complex formation.

Acknowledgements. This research was supported by RFBR Grant no. 14-03-31124.

1. Takahashi A., Yang R.T., *AIChE J.*, **2002**, *48*, 1457.
2. Li J.-R., Sculley J., Zhou H.-C., *Chem. Rev.*, **2012**, *112*, 869.
3. Chui S.S.-Y., Lo S.M.-F., Charmant J.P.H., et al., *Science*, **1999**, *283*, 1148.
4. Loiseau T., Serre C., Huguenard C., et al., *Chem.–Eur. J.*, **2004**, *10*, 1373.

SUPRAMOLECULAR PROPERTIES OF VERY LARGE CLUSTERS

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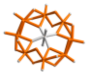
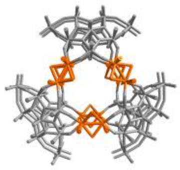
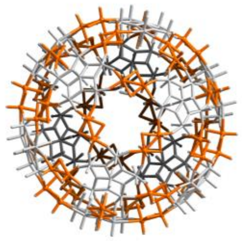
Softening of polyoxometalates through inclusion of sulfido groups within the $\{M_xO_y\}$ framework [1,2] is expected to modify significantly the POM properties e.g. structural and electronic, and thereby appear be an “ideal” strategy to associate and cumulate complementary properties at the molecular level, such as the electrocatalytic function of the {M-S} core combined with the electrons storage capacity of the polyoxometalate.


$\{Mo_9\}$


$\{Mo_{40}\}$


$\{Mo_{63}\}$


$\{Mo_{132}\}$

We will report on the synthetic approaches for the formation of the literally “polyoxo**thio**metalate” compounds with special emphasis on the unique reactivity of the preformed sulphur-containing cationic cluster as building blocks $\{Mo_2O_2S_2\}^{2+}$ toward polyoxometalate building blocks. Such simple systems, based on chemical and structural complementarities between ionic reactive moieties have allowed producing a series of relevant clusters with unrivalled large nuclearity structural arrangements, like rings, sphere, cylinder and boxes.[3,4] Specific reaction parameters and considerations will be pointed out showing that a deliberate *pure* inorganic supramolecular chemistry based on weak interactions, flexibility and dynamic is possible with polyoxometalates.

1. Cadot E., Sokolov M., Fedin V., *Chem. Soc. Rev.* **2012,** *41,* 7335.
2. Sokolov M.N., Kalinina I.V., Peresypkina E.V., *Angew. Chem. Int. Ed*. **2008**, *47, 8,* 1465.
3. Marrot J., Pilette M.-A., Haouas M., *J. Am. Chem. Soc.*, **2012**, *134*, 1724.
4. Shäffer C., Todea A.M., Bögge H., *Angew. Chem. Int. Ed.* **2011**, *50*, 12326.

HIGH-VALENCE CLUSTERS, POLYOXOMETALATES AND ORGANOMETALLICS – A SYMBIOSIS

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The results of half-a-century development of cluster chemistry, together with a remarkable progress in the field of coordination and organometallic chemistry make it possible to attack a challenging problem of a rational design of complex molecules, which would combine various building blocks, in a rational way. In this presentation various approaches to achieve combination of high-valence clusters with polyoxometalates (POM-cluster hybrids) and introduction of M-C bonded functionalities into POM and high-valence clusters will be discussed. Examples will be given of introducing cluster units (Re_2^{6+}, Ir_2^{4+}, Rh_2^{4+}, $Mo_3S_4^{4+}$) into lacunary POM, such as $PW_{11}O_{39}^{7-}$, $SiW_{10}O_{38}^{8-}$, $W_5O_{18}^{6-}$, $\{AsW_9\}$ and $\{AsW_{15}\}$. A strategy for introduction of M-C bonds into POM, based upon i) incorporaion of a noble metal (Rh, Ir, Ru) following by ii) metallation or trans-metallation at the noble metal site, will be presented. First organometallic Au POM will be reported. A way of elaboration of the $Mo_3S_4^{4+}$ clusters to achieve direct fullerene coordination will be presented. First fully-substituted organometallic derivatives of $\{M_6I_8\}$ (M = Mo, W) clusters will be discussed.

1. Sokolov M.N., Adonin S.A., Sinkevich P.L., *Dalton Trans.* **2012**, *41*, 9889.
2. Cadot E., Sokolov M.N., Fedin V.P., *Chem. Soc. Rev.* **2012**, *41*, 7335.
3. Sokolov M.N., Kalinina I.V., Peresypkina E.V., *Eur. J. Inorg. Chem*. **2013**, 1772.
4. Sokolov M.N., Korenev V.S., Izarova N.V., *Inorg. Chem.* **2009**, *48*, 1805.
5. Sokolov M.N., Mikhailov M.A., Brylev K.A., *Inorg. Chem*. **2013**, *52*, 12477.

IONIC LIQUID CRYSTALS BASED ON POLYOXOMETALATES: SYNTHESIS, CHARACTERIZATIONS IN THE SOLID STATE AND LIQUID CRYSTAL PROPERTIES

Watfa N.[1,2], Floquet S.[1], Terazzi E.[3], Haouas M.[1], Taulelle F.[1], Hijazi A.[2], Naoufal D.[3], Cadot E.[1]

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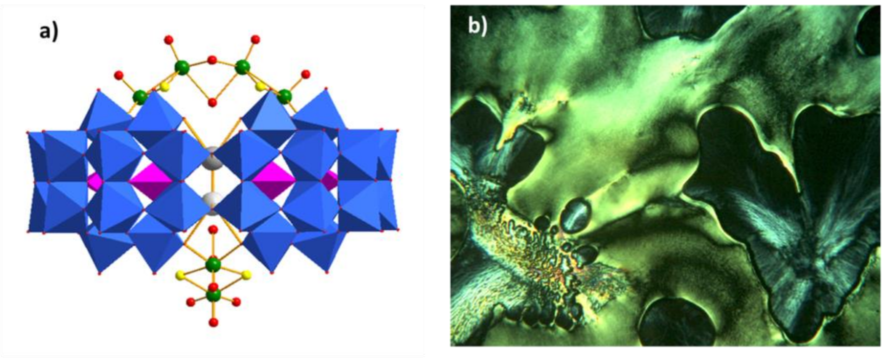
Current activity in the chemistry of Polyoxometalates (POM) is widely driven by potential applications in catalysis, medicine, magnetism, materials sciences and nanotechnology. The ionic interaction between POMs and organic cations can lead to the formation of soft materials and especially ionic liquid crystals [1]. This contribution will be focused on the combinations of the highly charged polyoxothiometalates $[Na_2K_2\{Mo_4O_4S_4(H_2O)_3(OH)_2\}_2(P_8W_{48}O_{184})]^{32-}$ [2], $[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$ and $[Mo_{132}O_{312}S_{60}(SO_4)_{30}(H_2O)_{72}]^{72-}$ [3] with various organic cations such as $DODA^+$ and substituted imidazolium cations. After description of the structure of the POMs, this contribution will be focused on the characterizations performed in the solid state and especially solid state NMR. Finally, the liquid crystals properties of some new materials will be described on the basis of DSC, Polarized Optical Micrscopy and SA-XRD studies [4,5].



a) Structural representation of the POM $[Na_2K_2(Mo_4O_4S_4(OH)_2(H_2O)_3)_2(P_8W_{48}O_{184})]^{32-}$
b) Polarized Opitcal Microscopy picture of the association between POM and $DODA^+$ cation at 200°C

1. Li W., Yin S., Wang J. *Chem. Mater*. **2008**, *20*, 514.
2. Korenev V.S., Floquet S., Marrot J., *Chem.*, **2012**, *51*, 2349.
3. Korenev V.S., Boulay A.G., Haouas M., *Chem. Eur. J.*, **2014**, *20*, 3097.
4. Floquet S., Terazzi E., Hijazi A., *New J. Chem.* , **2012**, *36*, 865.
5. Floquet S., Terazzi E., Korenev V.S., *Liquid Crystals* , **2014**, *41(7)*, 1000.

COORDINATION ABILITIES OF THE [Mo_2] CLUSTER FRAGMENTS WITHIN THE FRAMEWORK OF THE KEPLERATE

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Anionic compounds obtained at the end of the last century by Professor Muller [1] which were called keplerates are notable not only for their unique structural features but also because of their host-guest properties. Each spherical capsule of such anion is constructed of 12 pentagonal building blocks connected together by 30 mono- or binuclear linkers. More than 10 years the only one binuclear linker was used − {Mo_2O_4} cluster unit. But several new studies [2-5] in the field of keplerate chemistry showed that it is also possible to obtain compounds with similar oxothiomolybdenum binuclear fragments (Fig. 1).

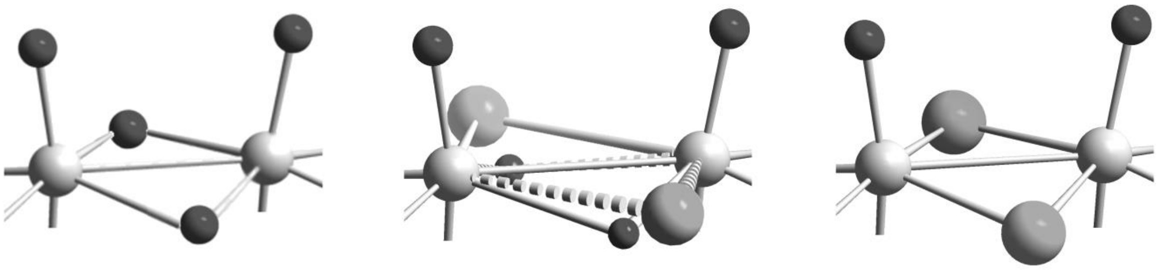

Figure 1. Schematic representation of {Mo_2O_4}, {Mo_2O_3S} (*two possible options*) and {$Mo_2O_2S_2$} binuclear units.

Binuclear bridges in the keplerate structure additionally coordinate anionic ligands directed inside the sphere (Fig. 2). Some ligands are labile, such as acetate, and can be replaced, other ligands coordinated much stronger and remain connected during the various manipulations.

Herein, we will discuss the patterns of coordination of these ligands to the cluster linkers shown in Figure 1.

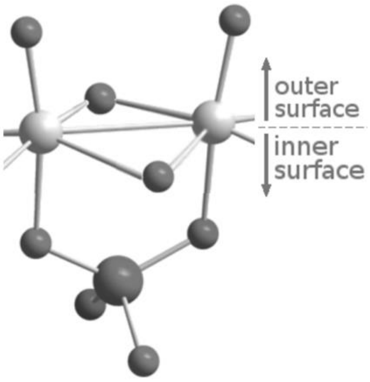

Figure 2. Model of {$Mo_2O_4(SO_4)$}.

Acknowledgements to the grant of the Russian President (project МК-4318.2013.3).

1. Müller A., Krickemeyer E., Bögge H. et al., *Angew. Chem. Int. Ed.*, **1998**, *37*, 3360.
2. Schäffer C., Todea A.M., Bögge, H. et al., *Angew. Chem.*, **2011**, *123*, 12534.
3. Bannani F., Floquet S., Leclerc-Laronze N. et al., *J. Am. Chem. Soc.*, **2012**, *134*, 19342.
4. Schffer C., Todea A.M., Bögge H. et al., *Dalton Trans.*, **2013**, *42*, 330.
5. Korenev V.S., Boulay A.G., Haouas M. et al., *Chem. Eur. J.*, **2014**, *20*, 3097.

RELATIONSHIPS BETWEEN THE PROTONATION STATE AND CATALYTIC PERFORMANCE OF $[\gamma\text{-}XW_{10}M_2O_{40}]^{n-}$ POLYOXOMETALATES (X = Si, P; M = Ti^{IV}, V^{V}) IN H_2O_2-BASED OXIDATIONS

Maksimchuk N.V.[1], Zalomaeva O.V.[1], Ivanchikova I.D.[1], Maksimovskaya R.I.[1],
Maksimov G.M.[1], Kholdeeva O.A.[1]

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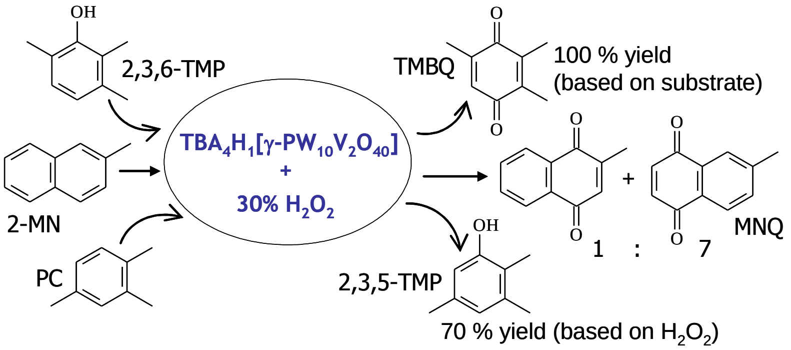
Di-metal-substituted γ-Keggin polyoxometalates (POMs), $[\{\gamma\text{-}SiW_{10}Ti_2O_{36}(OH)_2\}_2(\mu\text{-}O)_2]^{8-}$, $[\gamma\text{-}SiW_{10}V_2O_{40}]^{6-}$ and $[\gamma\text{-}PW_{10}V_2O_{40}]^{5-}$, are known as efficient catalysts for a range of selective oxidations with aqueous H_2O_2 [1-2]. We explored effects of the cation nature on the catalytic performance of these POMs in H_2O_2-based oxidation of alkylsubstituted arenes and cyclohexene (CH).

Tetrabutylammonium (TBA) salts differing in the ratio of TBA cations and H^+ have been prepared and fully characterized. The protonation/deprotonation of the di-vanadium-substituted POMs in MeCN was studied using ^{51}V and ^{31}P NMR, and forms with different protonation state, $[H_2SiW_{10}V_2O_{40}]^{4-}$ (**Ia**), $[HSiW_{10}V_2O_{40}]^{5-}$ (**Ib**), $[SiW_{10}V_2O_{40}]^{6-}$ (**Ic**), $[HPW_{10}V_2O_{40}]^{4-}$ (**IIa**), and $[PW_{10}V_2O_{40}]^{5-}$ (**IIb**), have been identified.

Forms **Ia** and **IIa** ensured a blend of high activity and selectivity in CH epoxidation. The addition of extra protons to **IIa** led to increasing activity but decreasing selectivity. The replacement of TBA for tetrahexylammonium (THA) cations in $TBA_5H[\gamma\text{-}SiW_{10}V_2O_{40}]$ produced a noticeable increase in both catalytic activity and epoxidation selectivity. On the contrary, substitution of TBA for THA in $TBA_8[(\gamma\text{-}SiW_{10}Ti_2O_{38}H_2)_2O_2]$ decreased the catalyst activity in the oxidation of CH.

Form **IIa** revealed a superior catalytic activity and selectivity in the oxidation of 2,3,6- and 2,3,5-trimethylphenols (TMP) to 2,3,5-trimethyl-1,4-benzoquinone (TMBQ, Vitamin E key intermediate). For oxidation of alkylaromatic hydrocarbons, pseudocumene (PC) and 2-methylnaphthalene (2-MN), to 2,3,5-TMP/TMBQ and methylnaphthoquinones (MNQ), respectively, addition of extra proton is required. Unusual regioselectivity, i.e., predominant formation of 6-methyl-1,4-naphthoquinone, has been found in the oxidation of 2-MN.



The research was supported by RFBR (grant No. 13-03-12042).

1. Goto Y., et al., *Inorg. Chem*. **2006**, *45*, 2347.
2. Mizuno N., Kamata K., *Coord. Chem. Rev*. **2011,** *255*, 2358.

H_2O_2-BASED SULFOXIDATION OF THIOETHERS CATALYZED BY KEGGIN-TYPE POLYOXOMETALATE $[(\gamma\text{-}SiW_{10}Ti_2O_{38}H_2)_2O_2]^{8-}$: KINETIC AND DFT STUDY

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The mechanism of thioanisole (PhSMe) sulfoxidation with aqueous hydrogen peroxide catalyzed by a Keggin-type polyoxometalate (POM), $[(\gamma\text{-}SiW_{10}Ti_2O_{38}H_2)_2O_2]^{8-}$ (Ti_4-POM) [1], was investigated by a combination of kinetic modeling and DFT calculations. The formation of an active form of the catalyst proceeds through interaction of H_2O_2 with POM that can be either initial dimeric Ti_4-POM or monomeric $[(\gamma\text{-}SiW_{10}Ti_2O_{38}H_2)(OH)_2]^{4-}$ (Ti_2-POM) formed via hydrolysis of Ti-O-Ti bonds linking two Keggin moieties in Ti_4-POM. Therefore, two alternative mechanisms of sulfoxidation were evaluated (A and B).

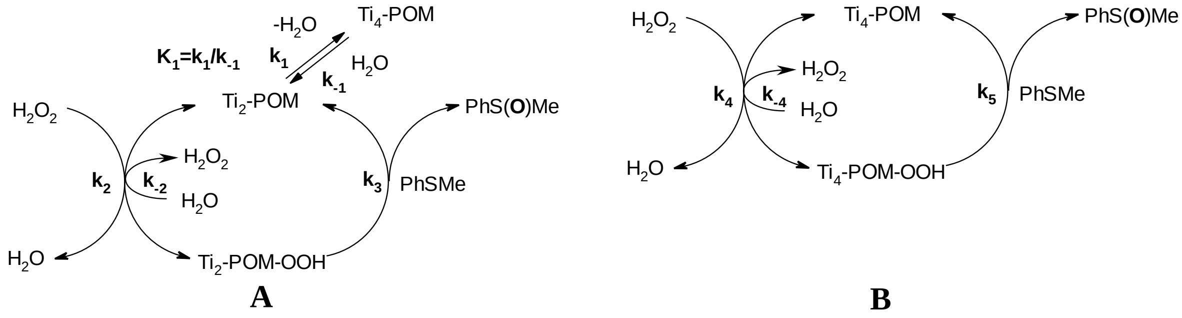

Fig. 1. Alternative mechanisms for PhSMe sulfoxidation with H_2O_2 catalyzed by Ti_4-POM

The rate law for both mechanisms was derived using a steady-state approximation. To fit the experimental initial rates, a chi-square error function was used. Based on the kinetic modeling, mechanism **A** that involves a hydrolysis step is proposed. The DFT study of the sulfoxidation process also supports this mechanism. The formation of a titanium hydroperoxo complex is more favorable for Ti_2-POM: the corresponding transition state is 6.5 kcal·mol^{-1} lower in energy relative to Ti_4-POM. The activation barrier for oxygen atom transfer is 3.6 kcal·mol^{-1} lower for Ti_2-POM relative to Ti_4-POM. The activation barriers of the hydroperoxo complex formation and oxygen atom transfer to the substrate are very close to each other, so that there is no definite rate-limiting step, which agrees with the experimental data. Computed ΔG for the Ti_4-POM hydrolysis, hydroperoxide activation, peroxo complex formation and sulfoxidation are in good agreement with the experimental data.

Acknowledgements. I.Y.S. acknowledges Polyoxometalate Chemistry for Molecular Nanoscience (PoCheMoN) action in the framework of European Cooperation in Science and Technology (COST) program and Universitat Rovira i Virgili for financial support. The research was partially supported by RFBR (grant No. 13-03-12042).

[1] Goto Y., et al. *Inorg. Chem.* **2006**, *45*, 2347.

THE FIRST EXAMPLE OF S-ELEMENT ACTING AS CENTRAL ATOM IN POM: NEW KEGGIN-TYPE ANION $[BeW_{12}O_{40}]^{6–}$

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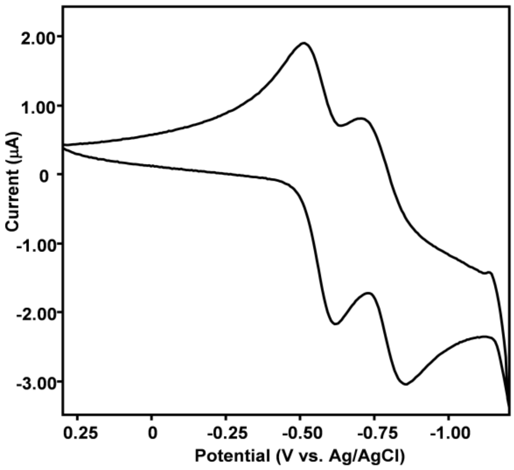

Figure 1. Cyclic voltammogram of $(Me_2H_2N)_6[BeW_{12}O_{40}]$ solution in H_2O.

In this work preparation and characterization of Keggin-type (“1:12”) $[BeW_{12}O_{40}]^{6–}$ (**1**) was reported as the first example of an s-element incorporation in a heteropolyoxotungstanate anion as a part of the tetrahedral building block. It was characterized by set of methods including monocrystal X-ray diffraction, multinuclear NMR and IR-spectroscopy, ESI-MS and CV. Cyclic voltammogram shows two successive quasi-reversible reduction waves with $E_{1/2}$ = -0.560 V and -0.792 V (vs. Ag/AgCl), which were assigned to W(V)/W(VI) couples (figure 1). Room temperature ^{9}Be NMR spectrum of **1** in CD_3CN exhibits one signal at 0.65 ppm, and ^{183}W NMR spectrum – one signal at -146.1 ppm, in agreement with the retention of the α-Keggin-type structure in solution. Negative ESI mass spectrum of **1** recorded in H_2O displayed a group of signals attributed to 4-, 3- and 2- charged species due to $[BeW_{12}O_{40}]^{6–}$ adducts of protons and other cations (figure 1). Condensation reactions also were studied for another cations (Mg^{2+}, Cd^{2+}) with $WO_4^{2–}$. The work was supported by RFBR grants 13–03–01261a and 13–03–00012a.

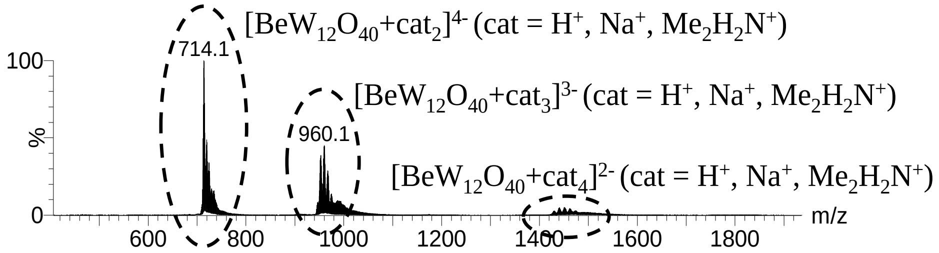

Figure 2. Cyclic voltammogram of $(Me_2H_2N)_6[BeW_{12}O_{40}]$ solution in H_2O.

PLATINUM CONTAINING POLYOXONIOBATES

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The chemistry of polyoxometalates (POM) is a rapidly growing area of modern coordination chemistry. One of the emerging research lines in this field is chemistry of polyoxoniobates and tantalates, which offer various chemical challenges like generation of pentagonal building blocks [1], nanosized catalysts for water splitting (WS) [2] etc. The diagonal analogy between Ti and Nb gives a possibility to consider polyoxoniobates as soluble models of nanosized TiO_2. In order to increase the energy conversion efficiency in the WS reactions combining of polyoxoniobates with noble metals is a viable perspective. However, this field is rather underdeveloped [3]. In the present work complexation of platinum(IV) with $[Nb_6O_{19}]^{8-}$ was studied with different techniques. Thus, a dimeric complex $Cs_2K_{10}[Nb_6O_{19}\{Pt(OH)_2\}]_2\cdot 13.4H_2O$ (Fig. 1) when hexaniobate $[Nb_6O_{19}]^{8}$ reacts with Pt(IV) in 1:1 molar ration, while increasing of the Pt/Nb_6 ration to 2:1 gives crystals of a sandwich-type $Cs_2K_{10}[(Nb_6O_{19})_2Pt]\cdot 18.06H_2O$ complex (Fig. 2). The complexes were characterized with ^{195}Pt NMR, electrospray- mass-spectrometry, capillary electrophoresis, X-ray analysis. Reactivity in solutions is discussed.

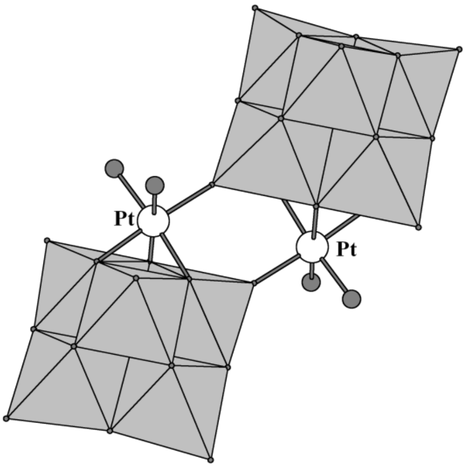

Figure 1. Structure of $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$

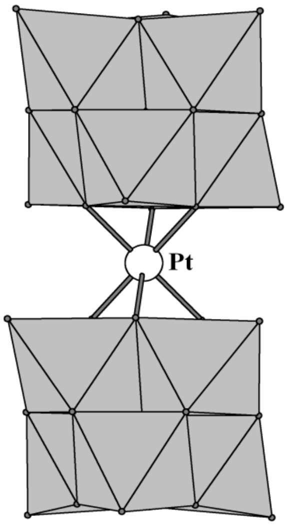

Figure 2. Structure of $[(Nb_6O_{19})_2Pt]^{12-}$

Acknowledgements. This work was supported by RScF grant 14-13-00645.

1. Tsunashima R., Long De-L., Miras H.N., *Angew. Chem. Int. Ed.* **2010**, *49*, 113.
2. Huang P., Qin C., Su Z.-M., *J. Am. Chem. Soc.* **2012**, *134*, 14004.
3. Laurencin D., Thouvenot R., Boubekeur K., *Dalton Trans.* **2007**, 1334.

QUANTUM CHEMISTRY EVALUATION OF THE MICROSCOPIC PARAMETERS AT THE ORIGIN OF THE MAGNETIC PROPERTIES OF REDUCED POMs

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The aim of this presentation is to give a general overview of a theoretical approach that has been developed and applied by the authors to the study of the magnetic properties of reduced Polyoxometalate ions (**POMs**).

In a first part, I will briefly describe a two-step approach based on wave function (**WF**) and model Hamiltonian calculations. I will show the precision that can be reached by WF embedded fragment calculations to extract the amplitude of the main microscopic electronic interactions and by model Hamiltonian to reproduce the properties of the whole reduced POM [1].

Then, results obtained for some POMs will be presented and I will insist on the precise understanding offered by this approach concerning the role played by each microscopic interaction on the magnetic properties of POMs [2-7].

Finally, some theoretical results about a para- to antiferro-magnetic transitions induced by an external electric field and the possibility to tune this behavior by weak chemical changes of the POM will be discussed [8].

1. Suaud N., Poblet J.M. *et al*, to be submitted ;
2. N. Suaud *et al*., *Euro. J. Inorg. Chem*, **2009**, 5109;
3. Calzado *et al*., *Inorg. Chem*., **2008**, *47*, 5889;
4. J.M. Clemente-Juan *et al*., *J. Phys. Chem. A*, **2007**, *111*, 9969;
5. N. Suaud *et al*., *Chem. Euro. J*, **2004**, *10*, 4041;
6. N. Suaud *et al*., *J. Am. Chem. Soc*., **2002**, *124*, 15134;
7. Suaud N., Cadot E. *et al*, to be submitted ;
8. S. Cardona-Serra *et al*., *Chem. Comm*., **2013**, *49*, 9621.

NEW CUBOIDAL MOLIBDENUM AND TUNGSTEN CLUSTER SULPHIDES COORDINATED BY BIPYRIDINE LIGANDS

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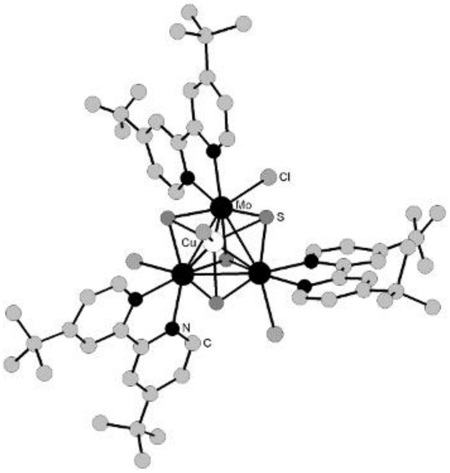
Triangular clusters containing M_3S_4 (M = Mo, W) units have received long-term attention because they have been shown to be efficient catalysts for the different kind of reactions (ex., regioselective defluorination of pentafluoropyridine, selective reduction of nitrobenzene derivatives, hydrogen evolution reactions) and due to their potential as metalloligands in front of a second transition metal M′ to yield cubane-type $M_3M'S_4$ clusters that share similarities with some biological catalytic active sites. Catalytic activity based on the heteroatoms has been also demonstrated.

Herein, we report the synthesis of new $\{M_3M'S_4\}^{4+}$ (M = Mo, W; M' = Cu, Ni, Pd) clusters coordinated by functionalized bipyridine ligands such as 4,4'-dinonyl-2,2'-bipyridine (dnbpy) and 4,4'-di-*t*-butyl-2,2'-bipyridine (dbbpy). Molecular structure of $[Mo_3S_4(CuCl)Cl_3(dbbpy)_3]^+$ is shown below:



Heterometallic complexes of general formula $[M_3S_4(M'\mathbf{X})Cl_3\mathbf{L}_3]Cl$ (**L** = dnbpy or dtbubpy, **X** = Cl, thiourea) have been synthesized and characterized by different techniques. Redox behavior of synthesized compounds is also studied in this work.

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UNPRECEDENT REACTIVITY OF TANTALUM DIMETHYLAMIDE

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Transition metal amides are highly reactive compounds which are much employed as reagents, ligand transfer agents, or precursors for more complex molecules. The ready cleavage of the highly polar M-NR_2 bond makes the amides particularly important synthons for a wide range of new compounds and materials. The M-NR_2 bond can be easily cleaved by protonation using various reagents with acidic E-H bonds (alcohols, thiols, secondary phosphines, pyrazoles etc.). Reactive small molecules such as CS_2 or CO_2 undergo insertion with the formation of dithiocarbamates and carbamates. In this work we report synthesis of new Ta coordination compounds and clusters by reactions of $Ta(NMe_2)_5$ with CS_2, Ph_2PH and pyrazol; with or without subsequent treatment with sulfur. $Ta(NMe_2)_5$ easily react with CS_2 with the formation of $[Ta(S_2CNMe_2)_3(\eta\text{-}CH_2\text{-}NMe)]$ (1). The formation of 1 can be explained as triple insertion of CS_2 followed by α-elimination of $HNMe_2$ molecule. Excess of CS_2 leads to the formation (in CH_2Cl_2) of $[Ta(S_2CNMe_2)_4]Cl$ (2). Cyclic voltammetry shows that $[Ta(S_2CNMe_2)_4]^+$ can be reversibly reduced to the neutral $[Ta(S_2CNMe_2)_4]$, the Ta(V)/Ta(IV) couple having $E_{1/2}$ – 0.74 V vs. Ag/AgCl. Reaction with CS_2 in the presence of S_8 leads to a complex mixture of Ta(V) dithiocarbamates $[TaS(S_2CNMe_2)_3]$ (3), $[Ta(S_2)(S_2CNMe_2)_3]$ (4), and a perthiocarbamate complex $[TaS(S_3CNMe_2)(S_2CNMe_2)_2]$ (5).

Diphenylphosphine rapidly reacts with $Ta(NMe_2)_5$ with the formation of an unstable product, which after treatment with S_8 yields green crystals of a cuboidal cluster, $[Ta_4S_4(\mu\text{-}S_2PPh_2)_4(S_2PPh_2)_2]$ (6), which is, to the best of our knowledge, the first cluster with the $\{Ta_4S_4\}$ core. Long Ta-Ta distances (2.97-3.05 Å) correspond to electron-deficient (only six of the required 12 e^-) M-M bonding in the cluster core.

3,5-dimethylpyrazole (PzH) as stronger N-H acid than Me_2NH reacts with $Ta(NMe_2)_5$ with the formation of yellow crystals of the pentakis(pyrazolate) [1], $[Ta(Pz)_5]$ (7). Which under treatment with CS_2 activates it forming $[Ta(Pz)_2SCPz_3]$ (8).

All the compounds have been characterized by single crystal X-ray analysis. Reactivity of complexes 1-8 is being investigated.

Acknowledgements. The work was supported by RFBR grant No. 12-03-33028.

1. Guzei I.A., Yap G.P.A., Winter C.H., *Inorg. Chem.* **1997**, *36*, 1738.

EXCITED TRIPLET STATES OF OCTAHEDRAL HEXANUCLEAR METAL CLUSTERS

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The excited state of an octahedral hexametal cluster with the general formula of $[M_6E_8L_6]^z$ (M = Re(III), Mo(II), W(II); E = S, Se, X (= Cl, Br, I); L = X, CN, SCN, etc., see Figure 1) experiences large spin-orbit (SO) coupling and, thereby, the degenerated emissive excited triplet state of the cluster splits in energy into (at least) 4 spin-sublevels (zero-magnetic-field splitting: zfs) as predicted theoretically by Azumi et al.: see Figure 2 [1]. Reflecting such SO coupling in the excited state, $[M_6E_8L_6]^z$ represented by $[Mo_6Cl_{14}]^{2-}$ or $[Re_6S_8X_6]^{4-}$ exhibits very large temperature (T) - dependent spectroscopic/photophysical properties since the Boltzmann distribution between the spin-sublevels varies with T and, at a given T, the emissions from several spin-sublevels contribute to the observed emission [1, 2]. Thus, the emission spectrum (maximum energy (ν^{em}) and full-width at half maximum (fwhm)), lifetime (τ^{em}), and quantum yield (Φ^{em}) of the cluster are very sensitive to T and the spectroscopic/photophysical properties of the cluster are governed by the zfs parameters: energy difference between the spin-sublevels, emission rate constant/lifetime of each spin-sublevel, and so forth. We have studied T dependences of the spectroscopic and photophysical properties of various $[M_6E_8L_6]^z$ clusters in the T range of 3 ~ 300 K and determined the zfs parameters of the clusters. The characteristics of the zero-magnetic-field splitting in the excited triplet state and T-dependent emission of the clusters will be discussed.

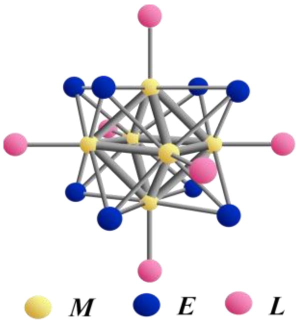

Figure 1. Structure of $[M_6E_8L_6]^z$.

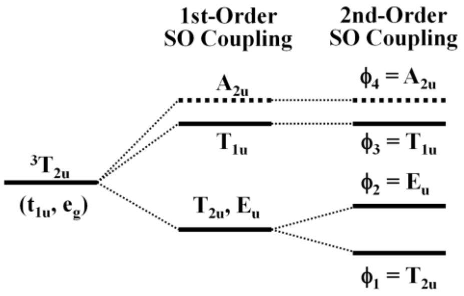

Figure 2. Spin-orbit (SO) coupling in the excited triplet state of $[M_6E_8L_6]^z$.

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1. Azumi T., Saito Y. *J. Phys. Chem.*, **1988**, *92*, 1715.
2. Kitamura N., Ueda Y., Ishizaka S., *Inorg. Chem.*, **2005**, *44*, 6308.

LUMINESCENT CLUSTERS OF COPPER SUBGROUP: UNUSUAL STRUCTURES, UNPRECEDENT EMISSION, HIGH POTENTIAL FOR APPLICATIONS

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During the last decade it was found that supramolecular complexes of copper subgroup represent an outstanding class of organometallic compounds with intriguing synthetic chemistry, extremely rich structural diversity and unique photophysical properties. The particular features of these complexes stem from ability of d^{10} ions (Cu^I, Ag^I and Au^I) to form networks of non-covalent metal-metal interactions, so called metallophilic bonds. Self-assembly of multi- and hetero-nuclear cluster cores through metallophilic interaction assisted by additional bonding with polydentate ligands results in formation of fascinating structural motifs, with specific electronic structure and properties determined to a great extent by both metallophilic bonding and effects of heavy metal ions. Synthetically this gave beautiful examples of huge (e.g. $[Au_{21}Ag_{30}(C_2Ph)_{36}Cl_9(Ph_2P(C_6H_5)_5PPh_2)_3]^{6+}$) cluster complexes, [1] unusual “rods-in-belt”, “envelop” [2, 3] and catenane [4] architecture of these complexes dictated by the nature and geometry of the polydentate ligands used to design targeted compounds. The latter allows for fine tuning of the product properties and makes possible a wide range of applications in bioimaging, sensing, OLED technology and material chemistry. These areas of applied usage are mainly determined by unique photophysics this class of compounds which are able to demonstrate extremely effective phosphorescence [2–4] (up to 100% quantum yield, absence of oxygen quenching) both in solution and in solid state and high two photon absorption cross-section [1, 3, 5].

Our international research group works in this area for quite long time and in the present communication we report novel results related to the synthesis, study of electronic structure and photophysics of the copper subgroup heterometallic complexes based on alkynyl and polyphosphine ligands, together with application of the compounds obtained in bioimaging, sensing and preparation of nanomaterials for analytics and energy storage.

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1. Koshevoy I.O., Karttunen A.J., Shakirova J.R., *Angew. Chem. Int. Ed.* **2010**, *49*, 8864.
2. Koshevoy I.O., Yi-Chih Lin, Karttunen A.J., *Inorg. Chem.*, **2009**, *48*, 2094.
3. Koshevoy I.O., Karttunen A.J., Tunik S.P., *Organometallics*, **2009**, *28*, 1369.
4. Koshevoy I.O., Yuh-Chia Chang, Karttunen A.J., *Inorg. Chem.* **2012**, *51*, 7392.
5. Koshevoy I.O., Yi-Chih Lin, Karttunen A.J., *Chem. Comm.*, **2010**, *46*, 1440.

NEW COPPER(I) CHALCOGENIDE CLUSTERS – SYNTHESES, STRUCTURES AND OPTICAL PROPERTIES

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This talk will describe the syntheses and structures of copper(I) chalcogenide clusters with special focus onto their optical properties.

Reactions of copper(I) acetat with silylated sulfur or selenium species lead to a bunch of different cluster compounds. The larger ones resemble small cutouts of the binary copper selenide or sulfide phases: e.g. $[Cu_{93}Se_{42}(Se–C_6H_4–SMe)_9(PPh_3)_{18}]_2$ or $[Cu_{136}S_{56}(S–CH_2–C_4H_3O)_{24}(dpppt)_{10}]$ [1]. The latter one can be interpreted as a nano-sized fraction of cubic Cu_2S with a HOMO-LUMO gap of 1.87 eV. The two dodecanuclear clusters $[Cu_{12}S_6(dpppt)_4]$ and $[Cu_{12}S_6(dppo)_4]$ show significant red/orange luminescence [2].

The use of *para*-substituted phenyl chalcogenolato compounds yields different smaller clusters with functional groups in the ligand shell some of them showing strong luminescence. With $–NMe_2$ as substituent a series of five clusters with green, blue or yellow emission was synthesized [3]. A recent study gives the conclusion that mainly the electron donating nature of the substituent is important whether these species are luminescent or not [4].

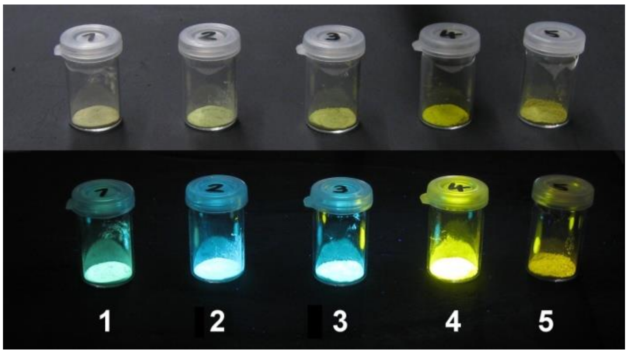

Figure 1. Photographs of a series of copper(I) N,N-dimethylanilinothiolate compounds with nuclearities from two to seven at daylight (top) and under UV light (λ = 366 nm; bottom) [3].

1. Fu M.-L., Issac I., Fenske D., *Angew. Chem.*, **2010**, *122*, 7052; *Angew. Chem. Int. Ed.*, **2010**, *49*, 6899.
2. Yang X.-X., Isaac I., Lebedkin S., submitted to *Chem. Commun.*
3. Langer R., Yadav M., Weinert B., *Eur. J. Inorg. Chem.*, **2013**, 3623.
4. Hu B., Su C.-Y., Fenske D., *Inorg. Chim. Acta.* **2014**, DOI 10.1016/j.ica.2014.05.009.

OCTAHEDRAL METAL CLUSTER COMPLEXES AS PRECURSORS FOR PHOTO- AND ELECTROLUMINESCENT MATERIALS

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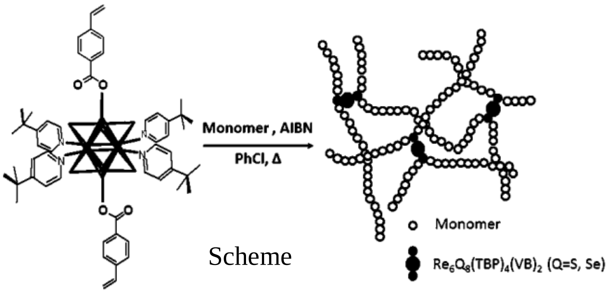
Octahedral molybdenum and rhenium metal cluster complexes of general formula $\{M_6Q_8\}Y_6$ (where M is either Re or Mo, Q are halcogens or chalcogens and Y are terminal ligands) show bright photoluminescence in the red and near-infrared regions with high quantum yields and photoluminescence life times of 1-100 µs. Many cluster complexes also have the capability for undergoing reversible oxidation/reduction with retention of the original structure. The electrochemical and photophysical properties of the cluster complexes can be tuned readily simply by substitution of the outer ligands in course of conventional chemical transformations. Such a combination of physical and chemical properties makes molybdenum and rhenium cluster complexes highly attractive for light-emitting applications (e.g. OLEDs, lasers, displays etc). However, naked clusters are not ideally suited for any of these applications, as they must be supported by a media that tailors them to a certain application. Incorporating inorganic Mo/Re cluster complexes into organic polymer matrices offers great opportunities in terms of integrating the excellent photophysical/electrochemical properties of metal clusters with the bespoke properties of various organic polymer matrices and thus to create designer materials tailored to specific applications.



Scheme

The presentation will describe recently developed approaches to modify cluster complexes to facilitate their incubation into conventional polymer matrices and use of these materials in light-emitting diodes. As example, we have synthesised and characterize novel soluble, readily polymerizable photoluminescent octahedral cluster complexes *trans*-$[\{Re_6Q_8\}(TBP)_4(VB)_2]$, where Q = S or Se, TBP = *tert*-buthyl pyridine VB = vinyl benzoate. These compounds have good solubility and therefore they can be easily copolymerised with organic monomers using the most widely-employed free-radical solution-based polymerisation techniques (Scheme). The resultant materials were shown to fully adopt the physical properties of the host polymer (*e.g.* thermal stability, molecular weights and solubility) and photoluminescent properties of a parent cluster complex. Accordingly, we have incorporated these rhenium cluster complexes into conductive polymer poly(N-vinylcarbazole) (PVK). The obtained hybrid materials were used as the active layer of polymer light emitting diodes (PLEDs). We have discovered that the electroluminescent emission spectra of PLEDs facilitate two picks: in blue region from the host (PVK) and red region from cluster complexes with no energy transfer to the dopant. The working devices that incorporated neat rhenium cluster complexes in the active layer were also fabricated.

Acknowledgements. The research is supported by Marie Curie Inter-European Fellowship (project “PolyMoRe”, No 327440)

PHOTOPHYSICAL PROPERTIES OF TETRANUCLEAR Au^I–Cu^I ALKYNYL-PHOSPHINE CLUSTERS BASED ON TRIDENTATE PHOSPHINE TEMPLATE: ALKYNE MAKES THE DIFFERENCE

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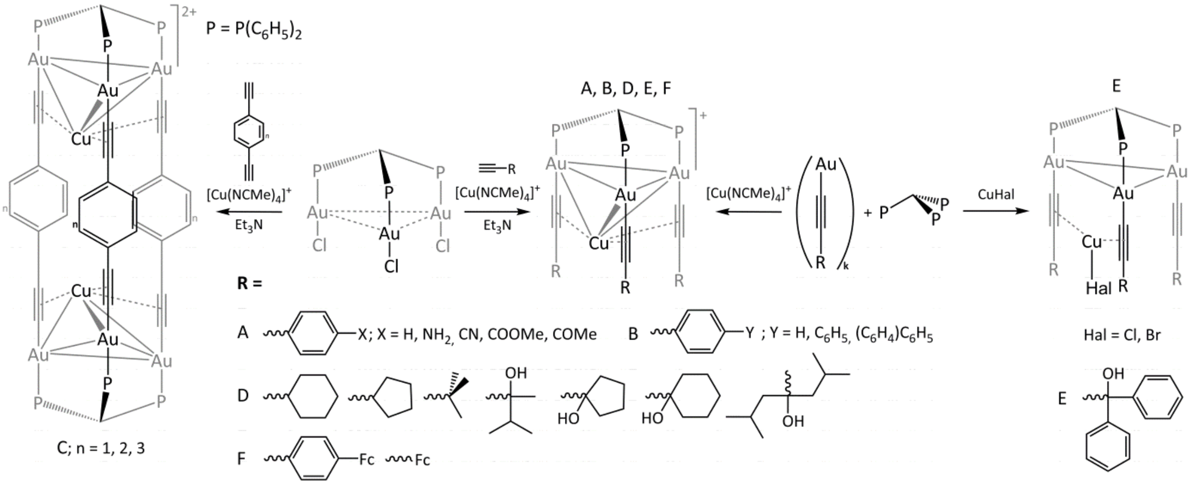
Several series of the structurally similar Au^I-Cu^I alkynyl-phosphine clusters stabilized by tridentate phosphine were obtained and them photophysical properties have been systematically investigated. It has been found that the luminescence properties of all complexes depend dramatically on alkyne ligands nature:

- **A** reveal a substantial shift of the emission maxima in-line with the change in electron donicity of the alkynyl ligands substituents [1].
- **B** and **C** display dual singlet and triplet luminescence, the former component of which can be completely suppressed in concentrated solution by self-absorption phenomenon [2].
- **D** solid state emission depends dramatically on alkynyl ligands nature that can be a result of the different packing mode due to presence/absence of H-bonding.
- **E** show luminescence vapochromism for detection of some organic solvents [3].
- **F** demonstrate no luminescence [4].



The theoretical calculations showed that variations of the alkynyl ligand display very little effect on cluster core structural parameters but show appreciable influence onto the orbital energies and the luminescent properties of the compounds under study.

Acknowledgements. The authors greatly appreciate financial support of SPbSU research grant 0.37.169.2014, RFBR grant 14-03-32077. The work was carried out using equipment of the Resource Centers “Analytical centre of nano- and bio-technology of SPbSPU”; and “Center of magnetic resonance”, “Center of Optical and Laser Methods for Material Investigation”, “Xray Diffraction Centre” of SPbSU.

1. Shakirova J.R., Grachova E.V., Gurzhiy V.V. et al., *Dalton Trans.* **2012**, *41*, 2941.
2. Shakirova J.R., Grachova E.V., Melekhova A.A. et al., *Eur. J. Inorg. Chem.*, **2012**, 4048.
3. Shakirova J.R., Grachova E.V., Melnikov A.S. et al., *Organometallics*, **2013**, *32*, 4061.
4. Shakirova J.R., Dau Thuy Minh, Domenech A., et al., *Eur. J. Inorg. Chem.*, **2013**, 4976.

ANTENNA EFFECT IN LUMINESCENT Mo_6 CLUSTER COMPLEXES

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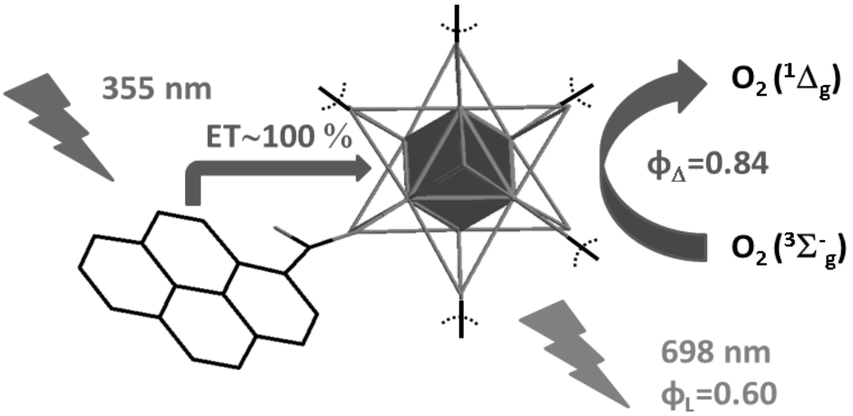
In the field of photofunctional materials, the octahedral molybdenum cluster complexes $[Mo_6L_{14}]^{2-}$ have recently emerged as inexpensive alternatives to the commonly used phosphorescent dyes thanks to relevant photophysical properties and simple synthetic protocols. Upon irradiation from the UV to the green spectral regions, the $[Mo_6L_{14}]^{2-}$ complexes form long-lived triplet states that relax *via* a broad red-NIR phosphorescence. Their emission is efficiently quenched by oxygen leading to the production of the reactive singlet oxygen in high yields. Such properties were already exploited in various materials such as $Mo_6@SiO_2$ nanocomposites for oxygen sensing in aqueous media [1], Mo_6-sensitized IR emitters [2], or light concentrators in solar cells [3].

In the optic of optimizing the photophysical properties of the Mo_6 cluster complexes towards applications, the choice of the ligands is essential as it allows for fine tuning of intrinsic key photophysical parameters. For instance, the $[Mo_6I_8(R\text{-}COO)_6]^{2-}$ complexes display the highest emission efficiencies [1, 4]. However, the molar absorption coefficients of the luminescent Mo_6 cluster complexes remain relatively modest.

In this contribution, we will show that it is possible to increase significantly the UV absorption of the Mo_6 cluster complexes while keeping high emission efficiencies thanks to an antenna effect between carboxylated fluorophores and the $\{Mo_6I_8\}$ core.



Acknowledgements. This work was financially supported by the Czech Science Foundation (13-05114S).

1. Kirakci K., Kubát P., Dušek M., *Eur. J. Inorg. Chem.* **2012**, 3107.
2. Molard Y., Labbé C., Cardin J., *Adv. Func. Mater*. **2013**, *23*, 4821.
3. Zhao Y., Lunt R.R., *Adv. Energy Mater*. **2013**, *3*, 1143.
4. Sokolov M.N., Mihailov M.A., Peresypkina E.V., *Dalton Trans*. **2011**, *40*, 6375.

PHOTOPHYSICAL PROPERTIES OF MOLYBDENUM CLUSTERS IN WATER

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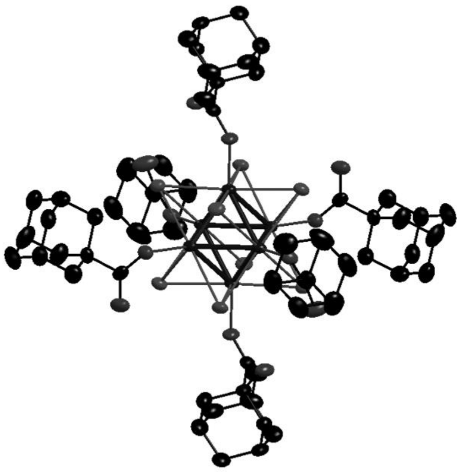
Water soluble phosphorescent dyes are of high interest for biological studies. Among various applications, the phosphorescent dyes allow for quantification of dioxygen level in aerobic systems and are useful sensitizers of singlet oxygen, *e.g.*, in photodynamic therapy of cancer. In this respect, the hexanuclear molybdenum cluster complexes constitute an inexpensive alternative to the commonly used phosphorescent oxygen probes such as Ru or Pd complexes thanks to relevant photophysical properties [1,2].

A barrier for the use of the clusters in water is their propensity to hydrolyse and form insoluble aggregates. This difficulty can be solved by the embedding of the clusters in silica nanoparticles [1] or by the grafting of azide ligands in apical positions [3]. An unexplored way to increase the solubility and stability of the clusters in water lies in the grafting of apical ligands capable of forming inclusion complexes with container molecules. These molecules may act as molecular shields providing protection against cluster hydrolysis and aggregation while keeping the hydrophilic character of the assembly. Typical systems are based on hydrophobic guest molecules such as adamantane or *closo*-carborane derivatives and hosts such as cyclodextrins.

In this communication, we report on the molybdenum cluster complexes based on the $\{Mo_6I_8\}$ core with adamantane-1-carboxylate and *closo*-carborane carboxylate apical ligands. These complexes display suitable photophysical properties and their stability in water is enhanced *via* host-guest interactions with cyclodextrin. The properties are further compared with the clusters bearing azide and thiocyanate ligands. All the described complexes show potential for oxygen sensing and singlet oxygen production in water solutions.



Determined molecular structure of $(Bu_4N)_2[Mo_6I_8(\text{Adamantane-COO})_6]$.

Acknowledgements. This work was financially supported by the Czech Science Foundation (13-05114S).

1. Kirakci K., Kubát P., Dušek M., *Eur. J. Inorg. Chem.* **2012**, 3107.
2. Kirakci K., Kubát P., Langmaier J., *Dalton Trans.* **2013**, *42*, 7224.
3. Barras A., Cordier S., Boukherroub R., *Appl. Catal. B: Environ.* **2012**, *1*, 123.

SOLUBILIZATION OF 4f HEXANUCLEAR COMPLEXES AND RESULTING LUMINESCENT PROPERTIES

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Polynuclear lanthanide based entities have been studied since several years at the laboratory. We investigate the possibilities of using such entities, once synthesized and characterized, for further chemistry. Replacing single metal ions by polynuclear entities in lanthanide organic frameworks would be of great interest for some properties (magnetism, luminescence for example).

One key point of this work is the balance between stabilisation and reactivity; in fact in most solvents tested entities are either destroyed or totally inert [1]. We finally found some operating conditions allowing good stabilisation and potential reaction [2]. The polyols (especially ethylene glycol) solubilize and stabilize these polynuclear entities. The solution of solubilised entities in ethylene glycol can be diluted several times by almost any classical solvent without observing any destruction of the entities. We tried to figure out how ethylene glycol prevents these polynuclear entities from destruction with the help of luminescent properties and ^{89}Y NMR.

In a second time, we have exploited this potential reactivity. Work is still under progress but we already obtained interesting compounds. For example we studied luminescent properties of a new family of hydroxybenzyl alcohol compounds.

1. Guillou O., Daiguebonne C., Calvez G., *J. Alloys Comp.* **2008,** *451* (1-2), 329
2. Calvez, G.; Daiguebonne, C.; Guillou, O., *Inorg. Chem.*, **2011,** *50* (7), 2851

PHOTO-ACTIVE HYBRID GELATORS AND MESOGENS BASED ON THE LUMINESCENT INORGANIC [Cu_4I_4] CLUSTER CORE

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The tetracopper(I) clusters formulated [$Cu_4X_4L_4$] (X = Cl, Br, I; L = organic ligand) possess rich photophysical properties [1]. The molecular structure of these cubane-type clusters is formed by four copper and four halide atoms occupying alternatively the corner of a cube (Fig. 1). Their remarkable photoluminescence properties and especially their emission sensitive to the environment conditions such as the temperature [2], the rigidity of the medium [3], or the pressure [4], make these clusters particularly appealing for the synthesis of stimuli-responsive materials exhibiting original optical properties.

In this context, we have demonstrated that the functionnalization of the inorganic [Cu_4I_4] cluster core by cholesteryl derivatives lead to the formation of hybrid gelators able to gel solvent through the formation of a globular network displaying thermochromic luminescence properties. The exceptional luminescence rigidochromism properties of the cluster core were also used in an original way to probe the dynamic of the gelation phenomenon [5].

More recently, the grafting of mesogenic promoters on the inorganic [Cu_4I_4] cluster has also allowed the emergence of [Cu_4I_4] cluster containing liquid crystalline materials displaying intriguing luminescent properties which can be modulated with electrical fields and polarizers.

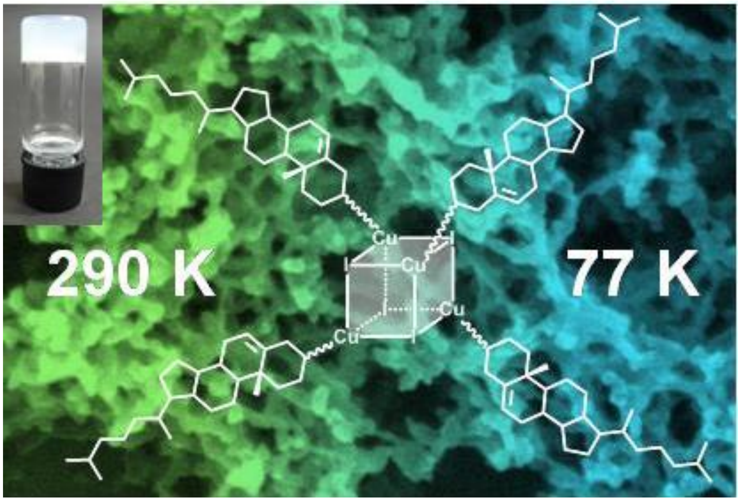

Figure 1. Illustration of the thermochromic luminescent properties of an original gel obtained with a hybrid [Cu_4I_4] cluster tetrahedrally functionalized with cholesteryl fragments. The formation of a 3D dense network of interlocked beaded-like filaments is responsible for the observed gelation of the

1. (a) Barbieri A., Accorsi G., Armaroli N., *Chem. Commun*. **2008**, 2185. (b) Ford P.C., Cariati E., Bourasssa J., *Chem. Rev*. **1999**, *99*, 3625. (c) Yam V.W.-W., Lo K.K.-W., *Chem. Soc. Rev*. **1999**, *28*, 323.
2. (a) Radjaipour M., Oelkrug D., Ber. Bunsen-Ges. *Phys. Chem*. **1978**, *82*, 159. (b) Tard C., Perruchas S., Maron S., *Chem. Mater*. **2008**, *20*, 7010
3. Tran D., Bourassa J.L., Ford P.C., *Inorg. Chem*. **1997**, *36*, 439.
4. Perruchas S., Le Goff X.F., Maron S., *Am. Chem. Soc*., **2010**, *132*, 10967.
5. Benito Q., Fargues A., Garcia A., *Chem. Eur. J*., **2013**, 15831

CHEMICAL DESIGN OF CHALCOGEN-CONTAINING ORGANOMETALLIC CLUSTERS

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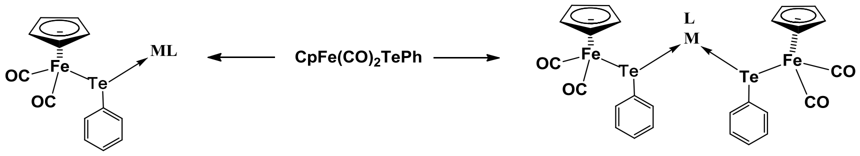
The chalcogen-containing organometallic complexes were used as ligands to complexes of different transition metals (M). X-Ray analyses data showed the common features: a) sharp shortening (from 0.15 to 0.3 A) of formally ordinary M–E bonds (E = S, Se, Te) and M–P bonds [1] compared to the covalent radii sum (CRS) [2]; b) electron-compensating rearragment of clusters.

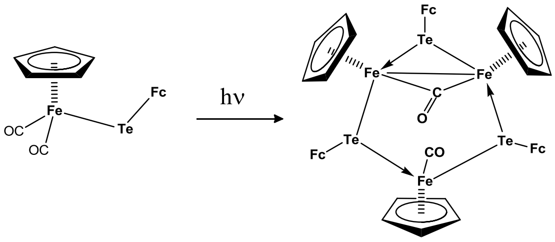
The coordination of $CpFe(CO)_2TePh$ as ligand:



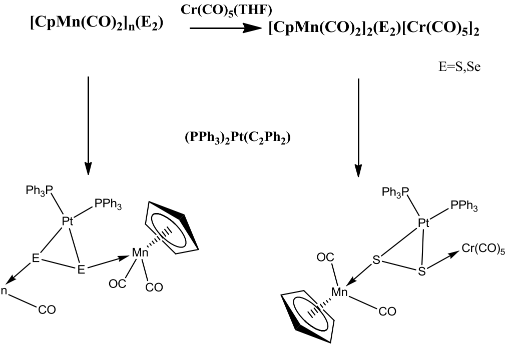
ML = $MeC_6H_4Pr^iRuI2$
$CpMn(CO)(NO)$

ML = $CpFe(CO)^+$,
$Re(CO)_3Cl$

The cyclization of $CpFe(CO)_2TeFc$:



The coordination and transmetallation of $[CpMn(CO)_2]_nE_2$ (E = S, Se, n = 2; E = Te, n = 3)



Acknowledgements: this work was financially supported by RFBR (12-03-00860, 12-03-33101) The Council on Grants of the President of Russian Federation (MK-5635.2013.3)

1. Pasynskii A.A., *Russ. J. Coord. Chem.*, **2011**, *37*, 801
2. Cordero B., Gomez V., Platero-Prats A.E., et al., *Dalton Trans.*, **2008**, 2832

SYNTHESIS OF HOMOMETALLIC, BIMETALLIC AND CHALCOGEN STABILIZED METAL CARBONYL CLUSTERS

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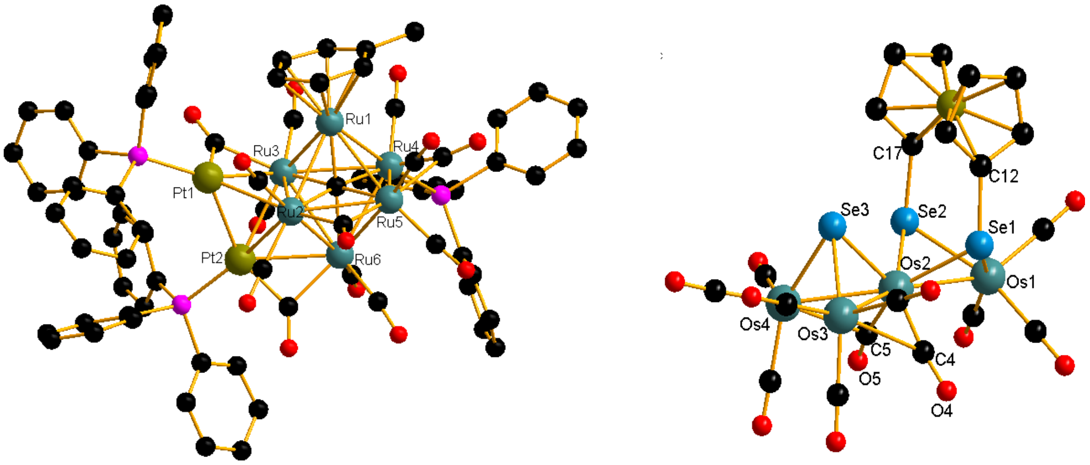
Synthesis and catalytic applications of homo and heteronuclear metal clusters has become one of the most rapidly flourishing area of research within the organometallic and organic chemistry field. Presence of chalcogens provide the additional stability and applicability (in the synthesis of nanomaterials, semiconducting materials) to the clusters. The development of systematic pathways for synthesis of these clusters is the promising challenge. In this context $[Ru_6(\mu_6\text{-}C)(C_6H_5CH_3)(CO)_{14}]$ has been found to be a suitable precursor for the preparation of high-nuclear Ru-Pt cluster with unique structural features. Further, reaction of 1,2,3-triselena[3]ferrocenophane and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(\eta^1\text{-}C\equiv CPh)]$ [1] with various metal carbonyls under thermal and photochemical condition has proved to be a suitable method for the synthesis for the synthesis of chalcogen stabilized metal carbonyl clusters.



(a) (b)

Figure 1. Molecular Structure of (a) Ru_6-Pt_2 cluster and (b) Os_4Se_3 cluster

Acknowledgements: CSIR, DST and IIT Bombay.

1. Mathur P., Raghuvanshi A., Ji R.S., *J. Organomet. Chem.*, **2013**, 731, 55.

METAL CARBONYL CLUSTER CHEMISTRY OF ORGANOTELLURIUM LIGANDS

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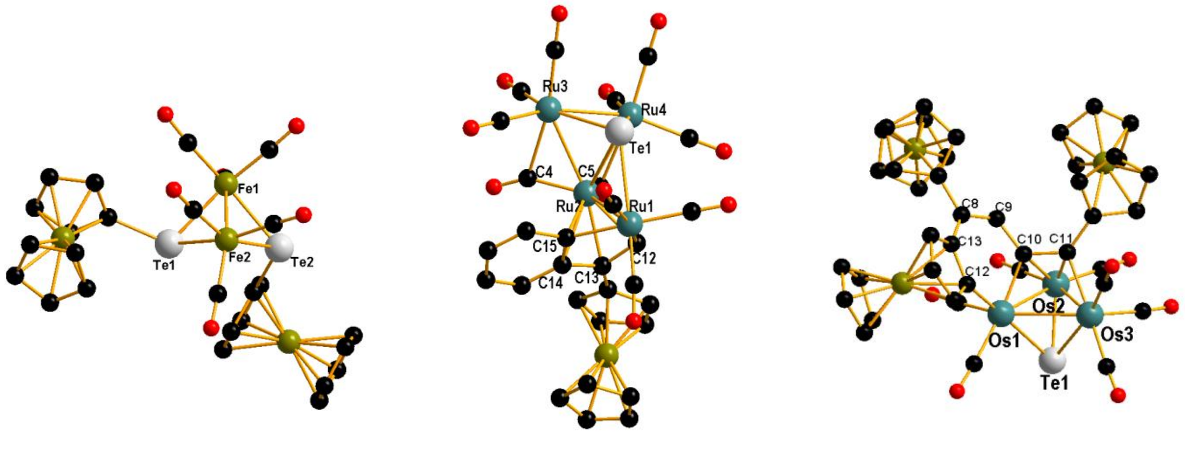
Chalcogens ligands have been used for the stabilization of transition metal carbonyl compounds in cluster growth reactions. Although this strategy has been extensively employed using lighter congeners S and Se, the utility of tellurium containing complexes in cluster growth processes has been little explored. This presentation highlights the role of organotellurium ligands in cluster formation.

Mononuclear metal carbonyls with diferrocenylditelluride ligand form mono-, di- and butterfly coordinated diferrocenylditelluride metal carbonyl complexes, whose interconversion has been shown under varying reaction conditions [1]. The diferrocenylditelluride upon treatment with FcC_4Fc and PhC_2H in reducing environment undergoes Te-Te bond cleavage and yields a multifunctional organotellurium ligands, (Z)-1-ferrocenyltelluro-1-ferrocenyl-4-ferrocenyl-1-buten-3-yne and phenylethynyl ferrocenyl telluride. The promising character of these ligands in cluster growth is due to its ability to interact with metal system through tellurium lone pair as well as through C-C π- system. The facile cleavage of Te-C bond also renders this ligand to be an important reagent for the stabilisation of high nuclearity clusters. Moreover, Presence of ferrocenyl and phenyl groups also offers additional features as orthometalation of ferrocene and phenyl may afford unusual products (fig. 1).



(a) (b) (c)

Figure 1. Molecular structures of Te- bridged metal carbonyl clusters

Acknowledgements: UGC, DST and IIT Bombay.

1. Mathur P., Tauqeer M., Torubaev Y.V., Mobin S.M., Lahiri G.K., Pasynskii A.A., Pavlova A.V., *J. Organomet. Chem.*, **2014**, 758, 55-59.

SYNTHESIS AND STRUCTURES OF MIXED-METAL RHENIUM COMPLEXES WITH BRIDGING SULFIDO LIGANDS

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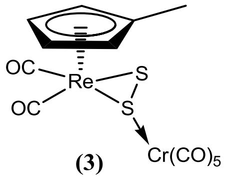
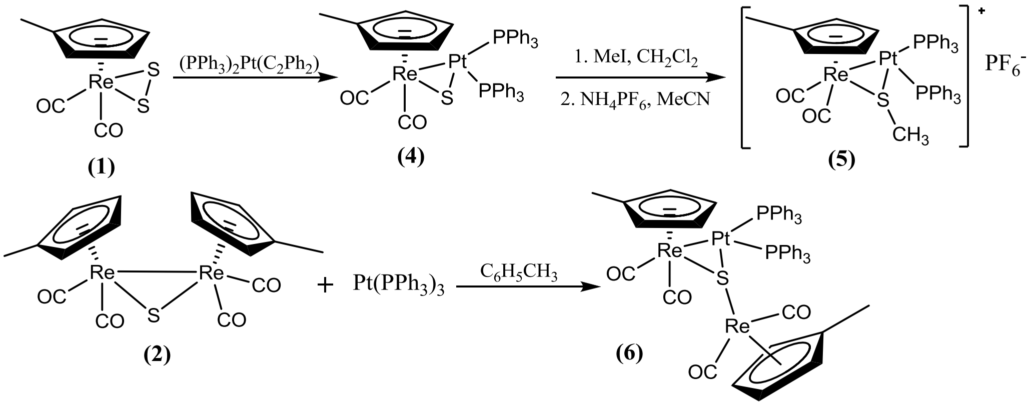
Mixed-metal clusters of platinum draw considerable attention as precursors for the catalysts for fuel cells [1]. Usually they could be prepared by insertion of Pt(0) complexes into the metal-metal, metal-hydrogen and chalcogen-chalcogen bonds [2].

The new disulfide rhenium complex Cp'Re(CO)$_2$S$_2$ (Cp'=C$_5$H$_4$Me) (**1**) was synthesized similarly to the known complex CpRe(CO)$_2$S$_2$ [3] by the reaction of S$_8$ with Cp'Re(CO)$_2$THF, which was generated by photolysis of Cp'Re(CO)$_3$ in THF solution. Binuclear complex (Cp'Re(CO)$_2$)$_2$S (**2**) containing metal-metal bond was also obtained as a side-product in this reaction.



(3)

Addition of Cr(CO)$_5$THF to complex (**1**) resulted in formation of complex Cp'Re(CO)$_2$S$_2$Cr(CO)$_5$ (**3**). The coordination of Cr(CO)$_5$ fragment proceeded without significant changes in the structure of ReS$_2$ core.



The reaction of **(1)** with (PPh$_3$)$_2$Pt(C$_2$Ph$_2$) in benzene produced an unstable intermediate, which degraded yielding new rhenium-platinum complex Cp'Re(CO)$_2$SPt(PPh$_3$)$_2$ **(4)** with one sulfide bridging ligand. The ionic product Cp'Re(CO)$_2$(SCH$_3$)Pt(PPh$_3$)$_2$PF$_6$ **(5)** was synthesized by the reaction of **(4)** with MeI in the CH$_2$Cl$_2$ solution followed by anion exchange. The reaction of binuclear rhenium complex (Cp'Re(CO)$_2$)$_2$S with zero valence platinum compound resulted in Re$_2$S ring opening and addition of Pt(PPh$_3$)$_2$ fragment to one of Re-S bonds producing new heterometallic complex [Cp'Re(CO)$_2$]$_2$SPtPPh$_3$ **(6)**. Structures of all synthesized compounds were confirmed by means of X-ray diffraction.

Acknowledgements. This work was financially supported The Council on Grants of the President of Russian Federation (MK-5635.2013.3)

1. Grinberg V.A., Pasynskii A.A., Kulova T.L. *Russ. J. Electrochem.*, **2008**, *44 (№2),* 187
2. Pasynskii A.A., Skabitsky I.V., Torubaev Yu.A. *J. Organomet. Chem.*, **2009**, *694*, 3373
3. Herberhold M., Schmidkonz B., *J. Organomet. Chem.*, **1988**, *358*, 301

NEW METHOD TO CERTIFY *AB INITIO* SIMULATION OF ATOMIC CLUSTERS

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Atomic clusters are expected to be useful in industries using nanotechnology based on the widely controllable physical and chemical properties depending on their size. To be able to predict new useful atomic clusters theoretically without experimental help, it is necessary to certify what we theorists predict. The present day state of art standard computer simulation method is density functional theory (DFT) invented by Professor Walter Kohn in 1964, which is an exact ground state theory for many electron systems. However, DFT does not give any functional form for electron exchange and correlation E_{xc}. He indicated an example of local density approximation (LDA) for E_{xc} which assumes uniform charge distribution. For metallic clusters a number of researchers apply generalized gradient approximation (GGA), which adds gradient of charge distribution to LDA and most atomic structures predicted by GGA agree well with experimental observations. DFT results with most of the types of E_{xc} give smaller HOMO-LUMO gap value, and recently LDA+U or hybrid functional are used frequently, which serve better HOMO-LUMO gap value comparable to experiment. These are basically phenomenology and no power of prediction, since DFT is a ground state theory and not possible to compute excited states (by diagonalization of the Hamiltonian the same number of states as the basis functions applied result, but no physical meaning above the Fermi level except for symmetry).

All theories should satisfy the necessary conditions of energy, momentum, and angular momentum conservations, Pauli's exclusion principle, and virial theorem for equilibrium state. Most of computer simulations to study stable ground structures of atomic clusters minimize the total energy of the system, and confirm no imaginary frequency in phonon dispersion. However, this standard method is not good enough. It is necessary to check the virial ratio (V/T=-2). Especially LDA+U and hybrid functional are very dangerous to violate the virial theorem badly some times, which results other properties much distorted from reality.

We have applied better computing methodologies of Quantum Diffusion Monte Calro simulation (QDMC) and multiconfiguration Hartree–Fock mothod (MCHF) to solve this fundamental problem and contribute to establish a new paradigm for theorists to have confidence in their numerical results. In the talk several typical examples will be introduced to clarify the advantage of our new methodology to certify *ab initio* computer simulation predicting atomic structures and physical and chemical properties of atomic clusters; (1) silicon fullerene as an example of atomic clusters not studied experimentally before theoretical prediction and (2) methylene CH_2 as an example of molecules for which previous theory violates the virial theorem.

SOLID-STATE REACTIONS IN NANOMATERIALS BASED ON MONOLAYERED CHALCOGENIDES OF TRANSITION METALS

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Monolayered dichalcogenides of transition metals MX_2 (X = S, Se, Te; M = Ti, Zr, Mo, W, etc.) have been considered lately as a new and very prospective class of compounds to be used as electronic devices. The compounds are known to exist in two polymorphic modifications H-MX_2 and T-MX_2. Here we report a theoretical discovery of a transition state TS-TiS_2 associated with the reaction H-TiS_2→TS-TiS_2→T-TiS_2 (Reaction 1) and two transition states associated with two possible reactions T-MoS_2→TS-MoS_2→H-MoS_2 (Reaction 2 and Reaction 3). Interestingly, for TiS_2 compound T-TiS_2 modification is lower in energy than H-TiS_2 modification, while for MoS_2 compound, to the contrary, H-TiS_2 modification is lower in energy than T-TiS_2 modification. Though all three reactions are shown to be exothermic in nature, activation energy for Reaction 1 (0.12 eV) is shown to be substantially lower than activation energies for Reactions 2 and 3 (1.39 and 1.03 eV). Correspondingly, the reproduction factor k_1 = 4.75 for Reaction 1 notably exceeds the reproduction factors k_2 = 1.62 and k_3 = 1.83 for Reaction 2 and 3, respectively. We therefore conclude that Reaction 1, if triggered by some external stimulus, can be though to propagate over the monolayer in a self-sustained manner, while this self-sustained process is much less probable for Reactions 2 and 3.

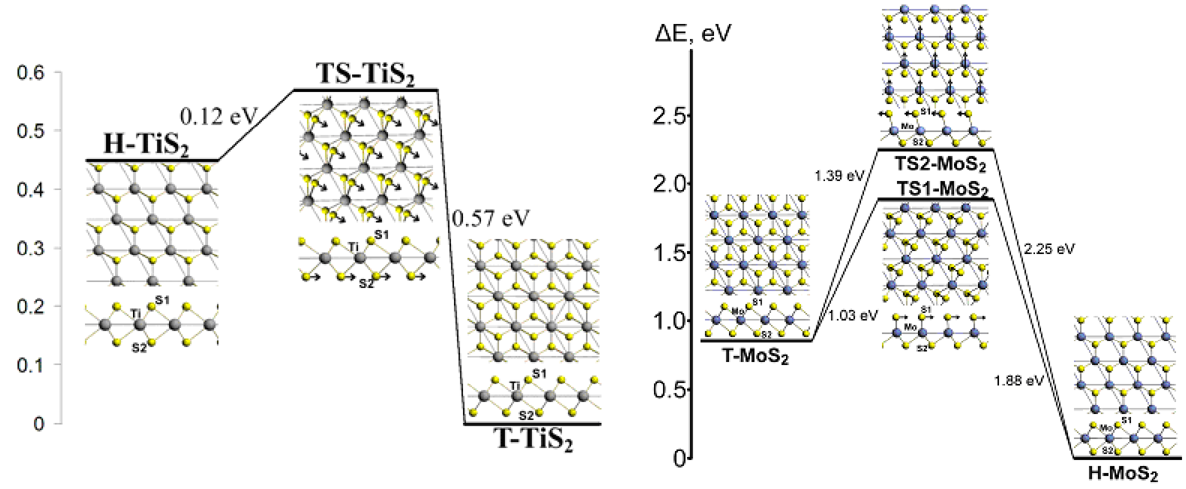

Figure 1. Reaction H-TiS_2 →TS-TiS_2→T-TiS_2 and two reactions T-MoS_2 → TS-MoS_2→ H-MoS_2.

The reactions were further studied with topological methods of quantum chemistry «Atoms in molecules» (QTAIM) and Electron Localization Function (ELF) to describe electron rearrangements and evolution of chemical bonding occurring in the systems in the course of the reactions.

Acknowledgements. The work was supported by RFBR grants (projects 12-03-00158).

XPS, XES AND QUANTUM CHEMICAL STUDY OF THE ELECTRONIC STRUCTURE AND ELECTRON DENSITY DISTRIBUTION IN THE COMPLEXES OF Cu(acac)$_2$, Cu(hfac)$_2$ AND COMPLEXES WITH NITROXYL LIGANDS BASED ON THEM

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The character of the electron density distribution on the atoms in chelate transition metal complexes containing the nitroxyl group near the metal ion is of interest in view of studying intracomplex exchange interactions and the nature of spin density redistribution channels in molecular magnetics. Therefore, it is relevant to examine the character of the integral electron density distribution and the location of the unpaired electron density on the atoms of free and coordinated radicals.

Methods of X-ray emission and X-ray photoelectron spectroscopy possessing the atomic characteristic are allowed to receive detailed information on the nature of the localization of the unpaired spin of the electron density on the atoms of the metal complex, the energy spectrum and partial composition of occupied and free molecular orbitals of the studied systems. In this paper for the first time an experimental study of the nature and distribution of the electron spin density of Cu(acac)$_2$, Cu(hfac)$_2$ as well as complexes of copper (II) with nitroxyl radicals is carried out by XES and XPS methods.

In order to interpret the X-ray photoelectron and emission spectra we are performed quantum chemical calculations of the electronic structure, charge and spin density, as well as the HOMO structure of corresponding nitroxyl radicals and complexes on their basis. It is shown that the analysis of the structure of X-ray photoelectron O(1s), N(1s), Cu(3s), Cu(2$p_{3/2,\ 1/2}$) spectra is allowed to determine the charge and spin states of the respective atoms of the complex and the nature of the redistribution of the spin density at coordination nitroxyl ligands to the metal atom.

It is shown that the structure of X-ray photoelectron O(1s) and N(1s) spectra is determined by the exchange interaction of the unpaired electron on the HOMO and the unpaired electron on the 1s-level as well as charge transfer processes between the different fragments of the molecule in the X-ray screening hole. Analysis of the calculated and experimental data of X-ray complexes of copper (II) with nitroxyl radicals is showed the possibility of transfer of electron density from the nitroxide group of the ligand in the chain of chemical bonds to the copper atom.

XPS study of charge and spin state of the multi-core heterospin copper complexes is performed in comparison with the data of quantum-chemical calculations. It is established that the copper ions in the complex $Cu_4(OH)_2(OAc)_4(DMF)_2(\mathbf{L})_2$ have similar charge and spin state. It is shown that the structure of the spectra of copper due to the superposition of the relevant electronic states $|C^{-1}3d^9>$ и $|C^{-1}3d^{10}\underline{\mathbf{L}}>$ ($C^{-1} = 2p^5$ or $3s^1$).

These examples show that the X-ray emission and X-ray photoelectron spectroscopy methods can be effectively used to study the electronic structure of transition metal complexes with nitroxyl ligands.

A JOINT THEORETICAL AND SPECTROSCOPIC STUDY OF STRUCTURAL PROPERTIES OF $K_6Re_3Mo_3S_8(CN)_5$ WITH A NEW HETEROMETALLIC OCTAHEDRAL CLUSTER

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The solution chemistry of rhenium and molybdenum hexanuclear M_6Q_8 (Q = S, Se) chalcogenide clusters is in a stage of rapid development. An enhanced research activity is caused by the opportunity to examine the redox chemistry of the electron-rich molecular forms, as well as to explore their ligand substitution and coordination chemistry. Recently, the synthesis of $K_6Re_3Mo_3S_8(CN)_5$ (**1**) containing a new Re_3Mo_3 octahedral core have been reported [1]. Compound **1** is isostructural with $K_6[Mo_6Se_8(CN)_5]$, which was previously reported [2]. The metal atoms in the basal plane of each $\{Re_3Mo_3S_8\}$-cluster are bound to four terminal CN-ligands, and the clusters are covalently linked by the two remaining cyanide ligands into linear chains, $[Re_3Mo_3S_8(CN)_4(CN)_{2/2}{}^{6-}]_n$, that lie along the c-axis. By reason of high symmetry of the cluster anions in crystal structure of **1**, Re and Mo atoms share the same crystallographic positions; thus, isomers were not distinguishable.

Solid-state NMR experiments can provide useful informations on the local environment and is therefore a very sensitive and efficient method for studying disordered materials. For inorganic compounds without protons or fluorine atoms, the two dominant interactions responsible for the appearance of the NMR spectrum are the chemical shift anisotropy and the quadrupolar interaction tensors. It appears that in many cases, the complexity of the experimental results require a theoretical analysis for their complete understanding.

To go further in the structural characterization of this new compound, we present the combined application of solid-state NMR and DFT calculations for the study of **1**. ^{95}Mo and ^{13}C solid-state NMR parameters of potential Re_3Mo_3 isomers have been computed using both molecular and periodic DFT based methods. These computed parameters have been compared with the one measured at high magnetic field.

1. Gayfulin Y.M., Naumov N.G., Rizhikov M.R., *Chem. Commun.* **2013**, *49*, 10019
2. Magliocchi C., Xie X.B., Hughbanks T., *Inorg. Chem.* **2000**, *39*, 5000

ONE POT SYNTHESIS, CRYSTAL STRUCTURES AND TOPOLOGY OF A SERIES OF CLUSTER-BASED HYBRID SUPRAMOLECULAR SOLIDS BUILT UP FROM $Re_6S^i_8(OH)^a_{6-x}(L)^a_x$ (L = BIPYRIDINE, AMINOPYRIDINE, PYRAZINE, BENZIMIDAZOLE, DABCO; X = 0, 2, 4, 6)

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Metal-Organic Frameworks (MOFs) have become during the past decade one of the most promising classes of synthetic compounds. These materials possess a wide array of applications in various fields like gas storage purification and separation, heterogeneous catalysis, or even controlled drug delivery [1]. Among them, luminescent porous coordination frameworks are promising for molecular recognition, non-linear optics or specific radiation detection. MOFs properties mainly rely on the framework design which can be controlled by making a judicious choice of both the organic and inorganic parts. Most studies have focussed on the use of various organic building units, while the inorganic ones are mainly polyhedra or polynuclear complexes. In the frame of IDEMAT network and IAL CLUSPOM, and based on former joint works between the groups of Rennes and Novosibirsk dealing with the use of octahedral cluster cores as building blocks for the design of nanomaterials and functional surfaces, we entered the field of the design of new coordination frameworks built from rhenium clusters. Indeed, rhenium octahedral clusters are known to exhibit very interesting chemical and physical properties [2] that make them attractive for the generation of such solids. In this frame, and among all possible starting cluster precursors, $K_4[Re_6S_8(OH)_6]^{4-}$ containing $[Re_6S_8(OH)_6]^{4-}$ was chosen because it is highly soluble in water, wherein it easily reacts with organic bases, such as pyridine derivates, pyrazine, DABCO or benzimidazole to undergo substitution of hydroxyl groups. New materials arising from this interesting reactivity have been synthesized and their crystal structures have been determined from single-crystal X-ray diffraction data. This communication will enhance the richness of the crystal frameworks that are accessible via multiple substitutions for hydroxyl groups on the cluster unit by distinct ligands, arising from 2 for pyridine derivates to 6 for benzimidazole. The topology of the resulting supramolecular frameworks will be discussed on the basis of weak bonds, protonation of the cluster units and then their charge. Some luminescent properties will also be presented.

1. (a) *Chemical Reviews*, Special issue, **2012**, *112*. (b) “Metal-Organic Frameworks: Applications from Catalysis to Gas Storage” ed. D. Farrusseng, *Wiley-VCH Verlag GmbH & Co.*, **2011**.
2. Cordier S., Molard Y., Brylev K.A., *J. Clust. Sci.*, **2014**, DOI 10.1007/s10876-014-0734-0.

NATURAL PRODUCTS: AN INFINITE SOURCE OF INSPIRATION

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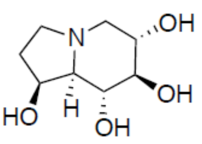
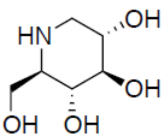
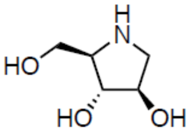
Natural products represent the most prolific source of drugs and have inspired many structures of non-natural drugs. It is also an infinite source of inspiration for organic chemist for the development of novel strategies to shorten synthetic routes, and afford a very flexible access for the synthesis of numerous natural products analogues. In this context, we will present our most recent results for the synthesis of polyhydroxylated alkaloids through ring closing metathesis involving heterosubtituted olefins.



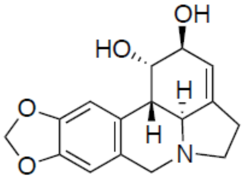
(+)-Castanospermine



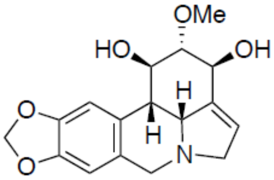
(+)-1-Déoxynojirimycine



(+)-DAB-1



(−)-Lycorine



(−)-Siculinine

PREPARATION AND PROPERTIES OF POLYFUNCTIONAL PYRIDINES AS VERSATILE SCAFFOLDS

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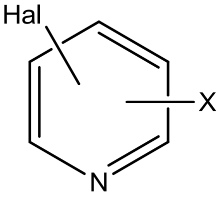
A novel syntheses of pyridines bearing high active functional groups are presented. Our synthetic approach is based on readily available pyridinamines and sequential reactions of electrophilic iodination and diazotization [1-5]. As a result we could prepare a new pyridine scaffolds containing such active substituents as iodo, tosylate, triflate, and azido groups in various positions of the core (**1, 2**).



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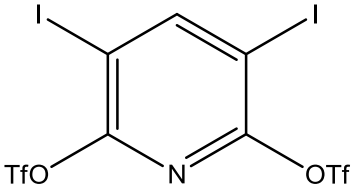

2

Hal= Br, I; X= OTs, OTf, N_3

Reactivity and leaving ability of the functional groups of the pyridine's family **1, 2** in halogenation, arylation and Pd-catalyzed cross-coupling reactions were investigated. It have been shown possibilities and restrictions for using of the functionalized pyridine scaffolds **1, 2** for organic synthesis and for preparation of composite organic materials.

Acknowledgements. This research was supported by RFBR grant 14-03-00743. E.A.K and V.D.F acknowledges the Scientific Programmes “Nauka” N 3.1333.2014 and 3.1344.2014 accordingly.

1. Tretyakov A.N., Krasnokutskaya E.A., Gorlushko D.A., *Tetrahedron Lett.* **2011**, *52*, 82.
2. Krasnokutskaya E.A., Semenischeva N.I., Filimonov V.D. *Synthesis* **2007**, 81.
3. Filimonov V.D., Trusova M.E., Postnikov P.S., *Org. Lett*. **2008**, *10*, 3961.
4. Krasnokutskaya E.A., Kassanova A.Zh., Estaeva M.T., *Tetrahedron Lett.* **2014**, *55*, 3771.
5. Kutonova K.V., Trusova M.E., Postnikov P.S., *Synthesis* **2013**, *45*, 2706.

NITRONES AND PYRROLES: A STRAIGHTFORWARD ACCESS TO *N*-HYDROXYLAMINES AND BIS(HETEROARYL)ALKANES

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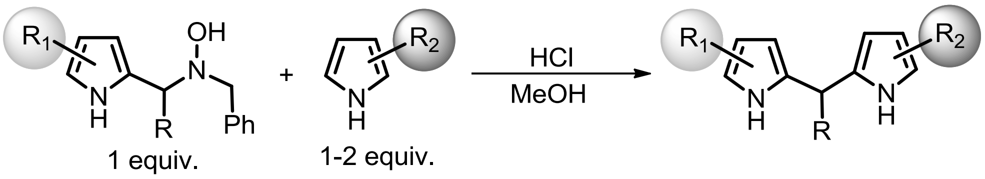
2,2’-Bis(pyrrolyl)alkanes are convenient synthetic precursors of porphyrins and fluorescent BODIPY dyes. They are usually prepared by the addition of pyrroles to aldehydes. The reaction pathway goes through a highly unstable carbinol intermediate which could not be isolated in most cases. As a consequence of this unstability, the preparation of 2,2’-bis(pyrrolyl)alkanes, especially those having some unsymmetrical substitution patterns, is usually a low yielding process.

To overcome this problem, we have developed a method involving the addition of pyrrole derivatives onto nitrones to give either *N*-hydroxylamines, or 2,2’-bis(pyrrolyl)alkanes [1].



This strategy allows the control of the second pyrrole addition onto a pyrrolic *N*-benzylhydroxylamine, which is a stable and easily purified compound. First, we studied these *N*-hydroxylamines and their possible applications in total synthesis of natural products [2]. Then, symmetrical and unsymmetrical bis(pyrrolyl)alkanes have been prepared in (good yields [3], and some of them have been transformed into the corresponding BODIPY dyes. Finally, this methodology was efficiently extended to other unsymmetrical bis(heteroaryl)alkane patterns [4].

1. Berini C., Minassian F., Pelloux-Léon N., *Tetrahedron Lett*. **2005**, *46*, 8653.
2. a) Berini C., Minassian F., Pelloux-Léon N., *Org. Biomol. Chem*. **2008**, *6*, 2574. b) Berini C., Pelloux-Léon N., Minassian F., *Org. Biomol. Chem*. **2009**, *7*, 4512. c) Murat-Onana M.L., Berini C., Denis J.-N., *Eur. J. Org. Chem*. **2014**, 3773.
3. Murat-Onana M.L., Berini C., Minassian F *Org. Biomol. Chem*. **2010**, *8*, 2204.
4. Christen A., Oueîny C., Piard R., *unpublished results*.

SOLVENT EXTRACTION OF METALS IN THE PRESENCE OF IONIC LIQUIDS

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Solvent extraction is one of the most important hydrometallurgical processes in the refining of metals, especially of precious metals, rare-earths and cobalt-nickel, by separation and purification [1]. Traditional extracting systems are composed of a metal ion, dissolved in an acidified aqueous solution, from which it is extracted toward a molecular organic solvent such as dodecane, kerosene, chlorinated solvents, *etc.* with the help of an extracting agent dissolved in it. However, the use of these volatile compounds causes the safety problems and they have the negative effects on the human health and environment.

Ionic liquids are a new class of solvents which are considered as excellent alternative to conventional organic solvents for liquid/liquid extraction of metals [2, 3]. Today, ILs are defined as semiorganic salts with a low melting point, typically below 100°C and many of them are even liquids at room temperature.

Actually, ILs possess unusual physicochemical properties such as negligible vapor pressure, nonflammability, high thermal and chemical stability, *etc.*, which lead them to be regarded as "green solvents" [5]. Furthermore, they can also be considered as "designer solvents" because their properties can be tuned by an appropriate choice of the constituent ions [6]. Besides, in the field of solvent extraction of metal ions, ILs have proven to be highly efficient media, as compared to traditional molecular solvents [7].

Here we present our experimental results on the solvent extraction of lanthanides and transition metals from aqueous acidic solutions by various ligands with the use of ILs as: replacement solvent, extracting agent, extractant and solvent at the same time and additive to traditional extraction systems. To confirm the extraction mechanism and the unusual composition of the extracted metallic species, we applied the spectroscopic techniques, namely UV-Vis and EXAFS.

Recently we have proposed a chemical model which describes the extraction process in the presence of ILs by cationic, anionic or neutral exchange [7]. We show that our model could be applied to various IL extraction systems and it provides a very good agreement between experimental and calculated data.

1. Wellens S., Thijs B., Moller C., *Physical Chemistry Chemical Physics* **2013**.
2. Sun X., Luo H., Dai S., *Chemical Reviews*, **2012**, *112* (4), 2100.
3. Billard I., Ouadi A., Gaillard C., *Anal Bioanal Chem*, **2011**, *400* (6), 1555.
4. Chaban V.V., Prezhdo O.V., *J. Phys. Chem. Lett.*, **2013**, 4 (9), 1423.
5. Freemantle M., RSC Pub., **2009**.
6. Freemantle M., *Chemical & engineering news*, **1998**, *76* (13), 32.
7. Billard I., Bünzli&Pecharsky, **2012**, *43*, 213.

GAS PHASE GLYCEROL VALORIZATION TO ACROLEIN OVER HETEROPOLYANION-BASED HETEROGENEOUS CATALYSTS

Dumeignil F.[1,2], Melendez R.[1,3], Capron M.[1], Fatah N.[1,3], Rey P.[4], Pariente S.[5],
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Due to the high amounts of glycerol by-produced with biodiesel, its upgrading by dehydration to acrolein is driving much attention [1]. This reaction can be catalyzed by various solid acid catalysts, which have all in common that they deactivate by coking. We studied the possibility of *in situ* regeneration of spent catalysts based on Keggin-type silicotungstic acid (STA - $H4SiW_{12}O_{40}$). Two samples were prepared with 20 wt.% STA, the first one supported on bare SBA-15, and the second one supported on SBA-15 in which 20 wt.% of ZrO_2 nanoparticles were dispersed [2]. The acidity of the catalysts was determined by NH_3-TPD and the thermal stability of the active phase was studied by TGA. The catalytic performances were determined at 275 °C in a fixed bed down flow reactor. The STA/ZrO_2/SBA-15 catalyst showed significantly increased long-term performance (69 % *vs.* 24 % yield in acrolein after 24 h of reaction) [3,4]. Grafting with zirconia led to a decrease in the acid strength of the STA, which was assigned to a modified electronic interaction between the active phase and the support, with further an increased thermal stability of the active phase. Thanks to this latter property, STA decomposition during one-shot regeneration of the catalyst by coke burning under air was suppressed, and the initial catalytic performance could be essentially recovered. In contrast, over the ZrO_2-free catalyst, the regeneration step led to a significant loss in acrolein yield (30 %) due to thermal destruction of STA. As this decomposition proceeds *via* the loss of constitutional water from the Keggin-structure, addition of water in the regeneration feed enabled recovering a slightly higher yield in acrolein (42 %), due to equilibrium displacement. Finally, cyclic regeneration of the catalyst was performed using iso-chronical cycles of 10 min for reaction and coke burning. The STA/ZrO_2/SBA-15 catalyst exhibited then poor performances (35 % yield in acrolein), which was explained by the longer activation period needed by this catalyst. On the other hand, the non-grafted catalyst exhibited rather stable performances (74 % yield in acrolein), without STA destruction. This was attributed to the shortness of the cycles, with thus only small amounts cokes to be burnt, then preventing the formation of harmful hotspots during regeneration [5]. At last, we developed an integrated process for simultaneous reaction and regeneration, based on a Two-Zone Fluidized Bed Reactor (TZFBR) technology we patented [6].

1. Katryniok B., Paul S., Dumeignil F., *ACS Catalysis*, **2013**, *3*, 1819.
2. Katryniok B., Paul S., Capron M., *J. Mater. Chem.*, **2011**, *21*, 8159.
3. Katryniok B., Paul S., Capron M., *GreenChem*, **2010**, *12*, 1922.
4. Paul S., Katryniok B., Dumeignil F., Capron M., WO 2011/08325, **2011**.
5. Katryniok B., Paul S., Capron M., *ChemSusChem*, **2012**, *5*, 1298.
6. Pariente S., Bellière-Baca V., Paul S., Fatah N., WO 2012/05166A1, **2012**.

BIO-INSPIRED SUPRAMOLECULAR ASSEMBLY OF GELATIN AND INORGANIC POLYANIONS

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In the last few years, the investigation on hybrid organic–inorganic materials has received very important attention for numerous application domains (catalysis, environment, energy, medicine…). The association between inorganic polyanions and naturally occurring polymers provides a convenient, low cost and environmentally-friendly way for the synthesis of new functional bio-nanocomposite materials [1].

In the present communication, new hybrid materials with promising properties have been synthesized by assembling thiometalate or polyoxometalate clusters with gelatin as a biopolymer through a coacervation process. This liquid-liquid phase separation is currently used with organic polyelectrolytes and polymers as a microencapsulation tool in pharmacy and cosmetic domains. We have showed that the charge, size and nature of the inorganic clusters strongly influence this liquid-liquid phase separation. We will describe here the characterization of the coacervates obtained from $[BW_{12}O_{40}]^{5-}$, $[PW_{11}O_{39}]^{7-}$, $[Mo_3S_4(HNTA)_3]^{2-}$, $[H_7P_8W_{48}O_{184}]^{33-}$, and $[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$. The mechanical properties of these hybrid materials have been studied at large strain by performing uniaxial tensile tests showing the possibility of finely tuning the extensibility of these materials by varying their cross-links density as well as the charge and the diameter of the inorganic polyanions. Finally the last part of this presentation will be focused on gelatin – $[BW_{12}O_{40}]^{5-}$ based modified glassy carbon electrodes which present interesting electrocatalytic properties for the detection of nitrite [2].

1. (a) Carn F., Durupthy O., Fayolle B., *Chem. Mater.* **2010**, *22*, 398. (b) Carn F., Steunou N., Djabourov M., *Soft Matter,* **2008**, 4, 735.
2. Khadro B., Baroudi I., Goncalves A.-M., *J. Mater. Chem. A*, **2014**, 2, 9208.

PRECISION POLYMER SYNTHESIS IN SUPPORT OF INNOVATIVE CATALYSIS

Manoury E.[1], Chen S.[1], Gayet F.[1], Poli R.[1], Zang X.[2], Zhang W.[2], Lansalot M.[2], D'Agosto F.[2],
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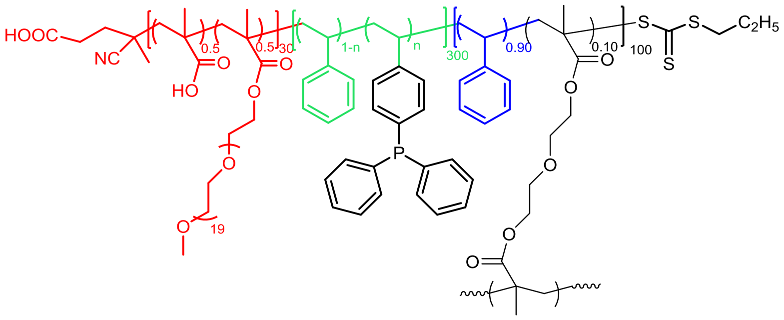
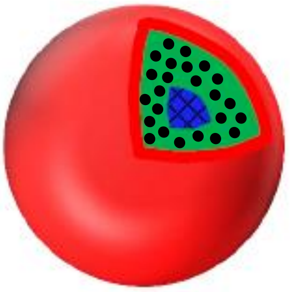
Aqueous biphasic catalysis is a most convenient protocol for industry but is limited to the conversion of organic substrates with non zero water solubility when the catalyst is water soluble. The most famous example is the Ruhrchemie hydroformylation of propene catalyzed by Rh/TPPTS, which is not applicable to the less soluble higher olefins [1]. Actively investigated stratagems include the use of additives (e.g. cyclodextrines), thermomorphic systems and micelles. The latter hold promise but are negatively affected by the formation of stable emulsions due to swelling, and catalyst loss at the water/organic interface. We propose an innovative solution consisting of core-cross-linked micelles to yield unimolecular amphiphilic core-shell catalytic nanoreactors. The presentation will highlight the synthesis and characterization of these nano-objects and their first catalytic application to the hydroformylation of 1-octene. Small organic molecules and the Rh precatalyst easily cross the hydrophilic polymer corona and interesting information was obtained on the intra- and inter-particle Rh exchange dynamics. The 1-octene hydroformylation occurs efficiently in the core of the particles under aqueous biphasic conditions and the catalyst could be recycled several times by simple decantation with low Rh leaching [2].





Acknowledgements: *This work was supported by the Agence Nationale de la Recherche (project no. ANR-11-BS07-025-01).*

1. (a) R. Tudor and M. Ashley, *Platinum Met. Rev.*, 2007, **51**, 164-171. (b) R. Tudor and M. Ashley, *Platinum Met. Rev.*, 2007, **51**, 116-126.
2. X. Zhang, A. F. Cardozo, S. Chen, W. Zhang, C. Julcour, M. Lansalot, J.-F. Blanco, F. Gayet, H. Delmas, B. Charleux, E. Manoury, F. D'Agosto and R. Poli, *Chem. Eur. J.*, in press.

MESOPOROUS CARBONS PREPARED BY HARD-TEMPLATE FROM CYCLODEXTRINS AND HOST-GUEST COMPLEXES AND THEIR POTENTIAL USES IN LIQUID-PHASE CATALYSIS

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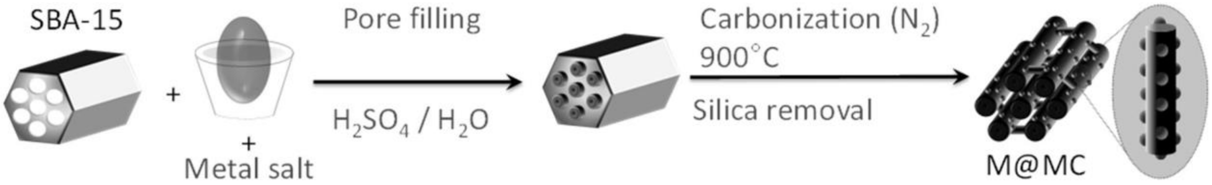
Over the past decade, porous carbon materials with high surface areas and large pore volumes have received increasing attention in a wide range of applications of technological importance, such as catalysis [1,2]. Efforts have been directed towards the development of ordered nanoporous arrays of carbon with well-defined pore structures by nano-replication. Generally, the synthesis procedure involves three main steps, i.e. *(i)* the preparation of the nano-structured silica, *(ii)* filling of the silica pores by the carbon precursor followed by carbonization and *(iii)* removal of the silica template. Interestingly, the formation of meso-structured carbons can be designed in terms of surface area, pore size distribution and pore shape while the hydrophobic/hydrophilic balance can be tailored by choosing appropriate carbon sources and optimizing the reaction parameters. In this communication, we will report on the synthesis of ordered mesoporous carbons prepared by nanocasting using SBA-15 and cyclodextrins (CDs) as carbon sources. Examples of the soobtained ordered nanomaterials will be presented and we will show that these materials can be employed as mass transfer promoters in the Pd-catalyzed Tsuji–Trost reaction. Moreover, we will also show that the use of CDs or host-guest assemblies in the presence of metal salts allows the direct synthesis of P6mm mesoporous carbon with uniformly dispersed metallic nanoparticles (Scheme1) [3]. The potential of these metal-carbon replicas for heterogeneous catalysis will be examined in liquid-phase catalytic reactions, such as the hydrogenation of long-chain olefins and fatty methyl esters.



Scheme 1. Incorporation of metallic NPs in mesoporous carbons through hard-template procedure.

1. Ryoo R., Joo S.H., Jun S., *J. Phys. Chem.* B, **1999**, *103*, 7743.
2. Gokulakrishnan N., Kania N., Léger B., *Carbon*, **2011**, *49*, 1290.
3. Gokulakrishnan N., Péru G., Rio S., *J. Mater. Chem. A*, **2014**, *2*, 6641.

METALLIC NANOPARTICLES STABILIZED BY CYCLODEXTRINS DERIVATIVES: RECENT DEVELOPMENTS IN AQUEOUS CATALYSIS

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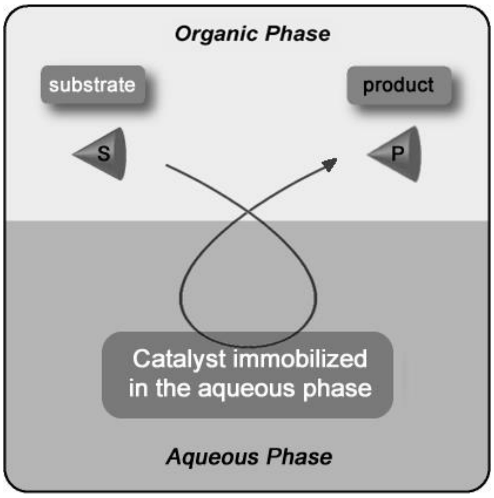
The immobilization of homogeneous or heterogeneous transition-metal catalysts in an aqueous phase appears as an eco-friendly technique to produce organic compounds. Indeed, the catalyst can be easily recovered in an active form at the end of reaction by decantation of the aqueous and organic phases and the production costs are significantly lower.



In this lecture, we will demonstrate that chemically modified cyclodextrins or cyclodextrin-based polymers are very useful compounds to stabilize catalytically active noble metal nanoparticles in water. Future developments of this technology will be discussed.

1. Herbois R., Noël S., Léger B., *Chem. Commun.*, **2012**, *48*, 3451.
2. Léger B., Menuel S., Ponchel A., *Adv. Synth. Catal.*, **2012**, *354*, 1269.
3. Noël S., Léger B., Herbois R., *Dalton Trans.* **2012**, *41(43)*, 13359.
4. Chau N.T.T., Guégan J.-P., Menuel S., *Appl. Catal. A Gen.* **2013**, *467*, 497.
5. Noël S., Léger B., Ponchel A., *Chem. Eng. Trans.*, **2014**, *37*, 337.
6. Noël S., Léger B., Ponchel A., *Catal. Today*, **2014**, DOI: 10.1016/j.cattod.2014.03.030

PALLADIUM CLUSTERS STABILIZED WITH PHOSPHONIUM SALTS AS EFFICIENT CATALYST IN SUZUKI CROSS-COUPLING REACTION

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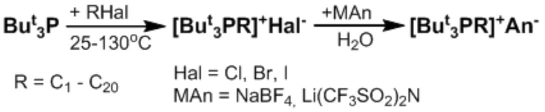
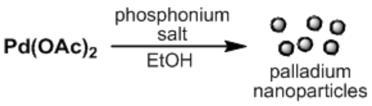
Palladium nanoparticles (PdNPs) are widely used as the catalyst in palladium catalysed reactions such as Suzuki cross-coupling [1, 2]. The problem of nanoparticles aggregation could be solved by using sterically hindered phosphonium ionic liquids (PILs) (Scheme 1) as stabilizers.

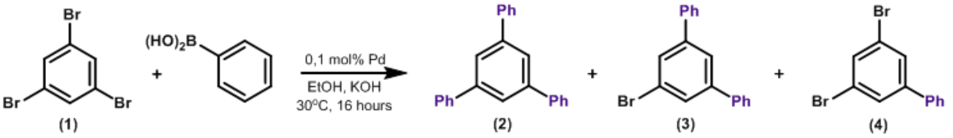


Scheme 1. Synthesis of the PIL.



Scheme 2. Palladium reduction.

PdNPs were obtained *in situ* by stirring of palladium acetate in ethanol in the phosphonium salt presence (Scheme 2). The PdNPs formation has been proved by electron microscopy (Fig. 1).



Scheme 3. The Suzuki reaction.

A number of synthesized PILs was tested as the stabilizers of PdNPs in Suzuki cross-coupling of 1,3,5-tribromobenzene **(1)** and phenylboronic acid (Scheme 3). We have demonstrated that the structure as well as the concentration of the coating agent in reaction mixture influence on the catalytic process. The quantity of PIL determines the mechanism of nanoparticles stabilization and as a consequence the activity of catalytic system.

Furthermore we have found that varying the length of the linear alkyl substituent of the sterically hindered phosphonium salt allows to change aggregation properties of the system and to tune catalytic activity of formed PdNPs.

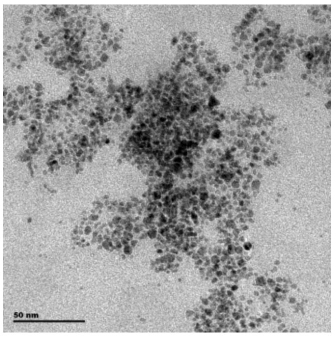


Figure 1. Palladium nanoparticles stabilized by $Bu^t_3P^+C_{10}H_{21}BF_4^-$.

Acknowledgements. Authors are grateful for the financial support to the Ministry of Education and Science of the Russian Federation (8451, MK 4440.2013.3) and the Russian Foundation for Basic Research (13-03-12170).

1. Balanta A., Godard C., Claver C., *Chem. Soc. Rev.*, **2011**, *40*, 4973.
2. Scholten J.D., Leal B.C., Dupont J., *ACS Catal*., **2012**, *2*, 184.

INTEGRATION OF TRANSITION METAL CLUSTERS ONTO HYDROGEN-TERMINATED SILICON SURFACES: CHARACTERIZATION AND ELECTRONIC PROPERTIES OF THE HYBRID JUNCTIONS

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The integration of redox-active functional units onto conducting surfaces is a necessary step toward the development of novel electrically addressable and switchable functional devices. For such applications, technologically relevant semiconducting surfaces, such as doped silicon, constitute particularly attractive substrates for the immobilization of molecular species. This approach has significant advantages in light of the extensive technologies and fabrication methods already built up around silicon in the existing semiconductor industry. The fabrication of functional devices incorporating redox-active molecules will benefit from the current development on CMOS structures and direct availability of industrial integration.

In this context, oxide-free, hydrogen-terminated silicon (Si-H) surfaces covalently derivatized with organic monolayers terminated by various redox-active centers (e.g. ferrocene, tetrathiafulvalene, organometallic complexes and transition metal clusters) have been prepared in our group [1] and examined to determine if charge storage or transfer devices could result from such electrically addressable hybrid junctions.

In this frame, we performed a full study of molecular junctions based on Mo_6I_8 cluster cores immobilized on Si(111) surfaces via an organic monomolecular layer containing terminal pyridine groups [2]. We have demonstrated that the presence of grafted Mo_6I_8 cluster changed the electronic properties of the junctions and provided new features evidenced in the charge transport characteristics. Moreover, in order to evaluate the effect of the type of clusters on the electronic properties of the hybrid junctions, molecular junctions including Re_6Se_8 cluster cores immobilized on both *n*- and *p*-type Si(111) surfaces have been also considered [3]. A simpler immobilization process has been established using the acido-basic reaction between the OH groups present in the cluster and the bound carboxylic acid groups end-capping an alkyl monomolecular layer covalently bound to the Si-H surface. This study shows that the cluster coverage can be finely controlled using mixed monolayers prepared from mixtures of 1-dodecene and undecylenic acid at different molar ratios in the first step of the grafting process. The effect of the Re_6Se_8 cluster coverage on the physical properties will be discussed and compared with those reported for Mo_6I_8 cluster-terminated monolayers immobilized on Si surfaces.

1. (a) Fabre B., *Acc. Chem. Res.*, **2010**, *43*, 1509. (b) Fabre B., Li Y., Scheres L., *Angew. Chem. Int. Ed.*, **2013**, *52*, 12024. (c) Yzambart G., Fabre B., Lorcy D., *Langmuir*, **2012**, *28*, 3453. (d) Grelaud G., Gauthier N., Luo Y., *J. Phys. Chem. C*, **2014**, *118*, 3680.
2. Fabre B.; Cordier S., Molard Y., *J. Phys. Chem. C*, **2009**, *113*, 17437.
3. Cordier S.; Fabre B., Molard Y., *J. Phys. Chem. C*, **2010**, *114*, 18622.

FORMATION, INTERLAYER DIFFUSION, AND THERMO – STABILITY OF NANOSTRUCTURE TME: Cu, Pd, Ni/GRAPHENE INTERFACES. MD-ANALYSIS

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The thermal evolution of transition metal (TM) nanoclusters and thin films deposited on a single- and two-layered grapheme (G) have been studied in a molecular-dynamics model in the temperature range 300 K $\leq T \leq$3900 K to analyze the formations and thermal stabilities of structure interfaces TM/G so as the diffusion processes and defect forming. The interface between graphene and a metallic substrate is of great importance for the use of graphene in integrated electronics, as heat-insulating materials, and in electromechanical devices, including those for protecting their microscopic units under heating and from aggressive environmental factors, activated interlayer diffusion, defect Creation**,** structure changing processes and lowering thermo –stability of the whole system. The initial arrangement of TM atoms on the graphene sheet is optimal from the standpoint of their interaction with the substrate, but it is not equilibrium for a metallic system with regular atomic packing at a temperature of 300 K. Because of this, even at this temperature, the atoms significantly approach to each other, so that the metallic film size decreases, and this reduction is more substantial in the transverse (“armchair”) direction as compared to the longitudinal (“zigzag”) direction. The longitudinal film size of two-layer graphene decreases more smoothly with increasing temperature, but the transverse size decreases not so fast as in the case of single-layer graphene. As a result, at T = 3300 K, the length of the metallic film more significantly decreases in the “zigzag” direction for two-layer graphene and in the “armchair” direction for single-layer graphene. Also the stresses in the systems were decreased with increasing temperature and reach the minimum even at a temperature of 1800 K. It was above this temperature that a significant increase in the elongation per unit length of the films in the “zigzag” and “armchair” directions of the graphene sheet begun to occur with a substantially stronger effect in the presence of metallic films on both sides of the sheet. The self-diffusion coefficient, which characterizes the displacement of the Ni atoms in the horizontal and vertical directions, also were increased at temperatures above 1800 K. Furthermore, in the horizontal directions, the steepest increase in the coefficient of mobility of the Ni atoms was observed for the single-sided metallic film. The advantages of a copper substrate as compared to, e.g., a nickel substrate are that the formation of graphene on copper was occured without carbon diffusion to the metal bulk, i.e., it took place immediately on the copper foil surface.

MULTIFUNCTIONAL NANOPARTICLES AND COLLOIDS BASED ON CLUSTERS OF TRANSITION ELEMENTS AND LANTHANIDES COMPLEXES

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The control of the luminescence property of nanomaterials is mandatory for applications in photonic and biomedical areas. By exploiting important colloidal phenomena, the goal of our work is to synthesize new luminescent and stable nanomaterials (colloidal solution, liquid crystal or thin films). This contribution highlights our efforts to elaborate and to characterize various colloidal nanostructures based on different luminophors such as: lanthanide coordination polymers or γ-Fe_2O_3-Mo_6X_{14}@SiO_2 or γ-Fe_2O_3-Mo_6X_{14}@SiO_2@Au.

In the first part, this contribution will summarize our results on the synthesis and characterization of luminescent Mo_6X_{14}@SiO_2 colloidal solution. Such nanoparticles including Mo_6X_{14} metal atom clusters (MC) as phosphors are good candidate for photonic crystal or bioimaging knowing that the red/infrared Mo_6 emission range could be selectively transmitted through tissues due to the low absorption at these wavelengths[1]. In addition, we will show the possibility to encapsulate γ-Fe_2O_3 and luminescent molybdenum clusters units in silica nanoparticles through a W/O microemulsion process and the evolution of the luminescence properties as a function of the size of the magnetic core. To our γ-Fe_2O_3-Mo_6X_{14}@SiO_2 MPs[2], small gold nanoparticles can be deposited on the surface of silica NPs allowing the preparation of gold nanoshells. Thus, thanks to the strong absorption of the plasmon band in the visible region, gold NPs can convert the absorbed light into heat, allowing the local destruction of cancer cells.

In the second part, we will show the possibility to stabilize solutions of polymer coordination nanoparticles[2] by solvation in a green chemistry solvent. For more than a decade, lanthanide-based coordination polymers have attracted great attention, because of their topologies coupled with their great potential applications in luminescence and molecular magnetism. These solutions exhibit intense luminescence using very little quantities of heteronuclear lanthanide terephtalate coordination polymers and are stable over time: no particle aggregation or decrease in luminance is observed.

The real challenge was to synthetize a non-toxic solution that combines the luminescence of the clusters in the NIR and lanthanide-based coordination polymers so it would be useful in several fields such as: nanomedicine, magnetic resonance imaging, fluorescence microscopy and to create luminescent surfaces.

1. Aubert T., Cabello Hurtado F., Esnault M.A., *J. Phys. Chem. C*, **2013**, *117*, 20154.
2. Nerambourg N., Aubert T., Neaime, C. *Colloids Inter. Sci.*, **2014**, *424*, 132

SYNTHESIS AND PROPERTIES OF CARBONYL POLYELEMENT CLUSTERS $[Fe_3(\mu_3\text{-}Q)(\mu_3\text{-}AsR)(CO)_9]$ AS POTENTIAL PRECURSORS FOR DESIGN OF NANOOBJECTS

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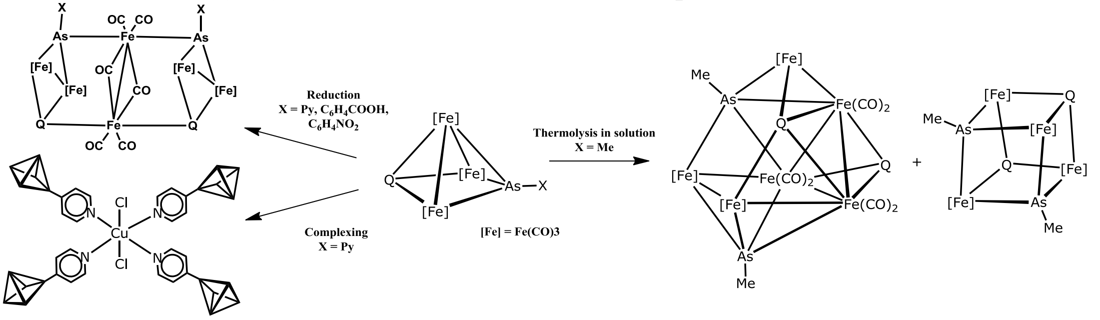
Chemistry of cluster compounds is an intriguing branch of modern inorganic chemistry. Metalloclusters may be regarded as intermediate species between the extremes of the bulk metal and the single metal atoms or ions that causes its unique physical and chemical properties which allow its further application in nanoscience. They can be used as precursors for different types of materials: nanocapacitors [1] and catalysts [2, 3], X-ray contrast agents in medical diagnostic imaging [4] and optical limiting materials [5, 6]. At the same time one of the problems of carbonyl clusters for the construction of functional materials is binding nonpolar cluster fragment with the supporter materials or association of cluster fragments in the crystal structure of a define structural motif. To be able to influence on the directional aggregation and binding of the cluster particles, we propose to functionalized clusters with donor polar group, which will determine the chemical affinity of the cluster particles and their binding into larger units, and will not compete with the carbonyl ligands to coordinate to metals in the cluster. For this purpose, as the model compounds were selected clusters with a core $Fe_3Q(ER)$ (Q and E are elements of 16 and 15 groups, respectively), for which we had previously studied a wide range of the cluster core modification reactions. For the introduction of functional groups methods of synthesis of clusters $[Fe_3Q(AsR)(CO)_9]$ on the basis of $K_2[Fe_3Q(CO)_9]$ and $RAsI_2$ have been developed.



The obtained complexes were characterized by various techniques (XRD, IR, NMR, ESMS, and CHN). In addition they were investigated by termogravimetric analysis and cyclic voltammetry analysis. It was shown that the type of organic fragment R in clusters make strong influence on thermal decomposition. Cyclic voltammetry analysis of clusters showed that the Te-containing clusters may participate in the reversible one- and two-electron reduction. Single-electron reduction of functionalized clusters $[Fe_3(\mu_3\text{-}Te)(\mu_3\text{-}AsR)(CO)_9]$ leads to their dimerization, accompanied by a rearrangement of the cluster core. There is also a possibility to use clusters as ligands. Complexes $[\{(CO)_9Fe_3QAsPy\}_4CuCl_2]$ and $[\{(CO)_9Fe_3QAsPy\}_2CuCl]_2$ were synthesized as the example.

1. Femonia C., Iapaluccia M.C., Kaswaldera F. et al, *Coord. Chem. Rev.*, **2006**, *250*, 1580.
2. Faure M., Vallina A.T., Stoeckli-Evans H., Süss-Fink , *J. Org .Chem.*, **2001**, *621*, 103.
3. Albonetti S., Bonelli R., Delaigle R., *Appl. Catal. A*, **2010**, *372*, 138.
4. Yang G.Y., Ang S.G., Cheng L.L., *Chem. Eur. J.*, **2003**, *9*, 900.
5. Yu S., Droege M., Downey S., *Inorg. Chem.*, **2001**, *40*, 1576.
6. Powell R.D., Halsey C.M., Liu W., *J. Struct. Biol.*, **1999**, *127*, 177.

STRUCTURAL ASPECTS OF NEW THREE-DIMENSIONALLY CONNECTED NIOBIUM CLUSTER COMPOUNDS

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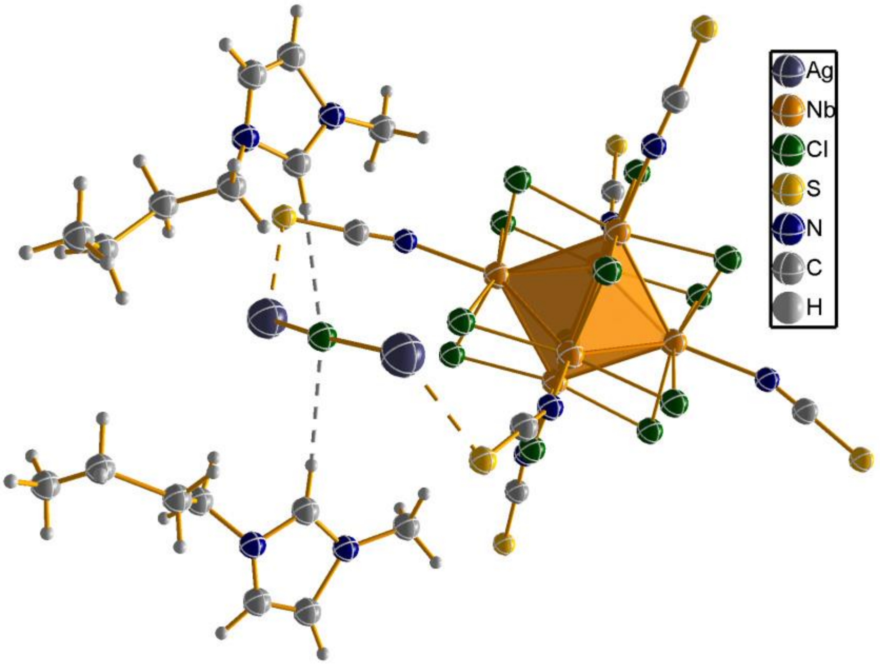
The research field of transition metal atom cluster compounds can be seen as a medal with two sides. On one side is the high temperature solid state chemistry which often leads to threedimensional expanded networks built up by metal atom cluster cores and ligands bridging in between. On the other side there is a solvent-based excision chemistry starting from high temperature solid state products leading to non-bridged isolated cluster cores. The synthetic route backwards to bridged M6 cluster units by connecting them utilizing organic ligands leads to new interesting metal-organic cluster frameworks of which one example is presented below.



$(BMIm)_2[Nb_6Cl_{12}(SCN)_6\{Ag_2(\mu_2\text{-}Cl)\}]\cdot 2CH_3CN$

The structure of the compound under investigation contains a Nb_6 octahedron that is surrounded by twelve inner chlorido ligands. The exo positions are occupied by isothiocyanato ligands leading to S-terminal functions. Thiophilic interactions between these ligands and soft Lewis acids such as Ag^+, respectively introduced through silver trifluoroacetate, $AgO_2CCF_3\cdot 0.5C_6H_6$, leads to the formation of the title compound in low crystalline yield (<5%). The solid state structure determined with the aid of x-ray diffraction techniques shows an unusual complex cation $[Ag_2(\mu_2\text{-}Cl)]^+$ (see figure above) which is known in the literature for several years [1] but structurally characterized for the first time in this work. The title compound can be seen as the first compound, consisting of octahedral transition metal cluster units ligated by a chelate ligand (see figure above) connecting two outer positions intraoctahedral whereas the remaining four ligands built inter-octahedral connections.

1. D. C. Luers and K. Abate, J. Inorg. Nucl. Chem., 1968, 30, 549-553

RECENT DEVELOPMENTS IN POLYPNICTIDE LANTANIDE CHEMISTRY

Konchenko S.N.[1, 2], Pushkarevsky N.A.[1, 2]

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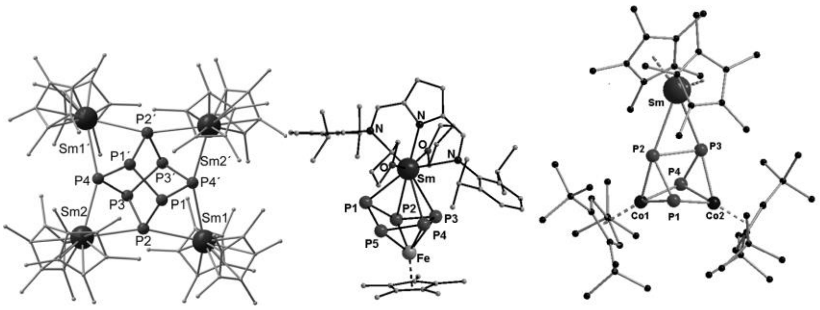
In the well-developed chemistry of organometallic transition metal (TM) complexes the compounds in which, besides M–C bonds, the metals are bonded with different main group elements are substantially evaluated as really common. In contrast to TM, only compounds with N- and O-donor ligands are well-represented among the rare- and alkaline-earth metals (RAM). Analysing CCDC structural data one may see that even complexes with P- and S-donor ligands are not really numerous, and heavier elements are represented just by solitary examples.

The lecture overviews different synthetic approaches to homo- (only RAM) and heterometallic (RAM/TM) complexes and their structural and electronic features [1-6].



1. Li T., Arleth N., Gamer M.T., Köppe R., Augenstein T., Dielmann F., Scheer M., Konchenko S.N., Roesky P.W., *Inorg. Chem.*, **2013**, *42*, 14231.
2. Li T., Gamer M.T., Scheer M., Konchenko S.N., Roesky P.W., *Chem. Commun.* **2013**, 49, 2183.
3. Li T., Wiecko J., Pushkarevsky N.A., Gamer M.T., Köppe R., Konchenko S.N., Scheer M., Roesky P.W., *Angew. Chem. Int. Ed.*, **2011**, *50*, 9491.
4. Konchenko S.N., Pushkarevsky N.A., Gamer M.T., Köppe R., Schnöckel H., Roesky P.W., *J. Am. Chem. Soc.*, **2009**, *131*, 5740.
5. Huang W., Diaconescu P.L., *Eur. J. Inorg. Chem.*, **2013**, 4090.
6. Huang W., Diaconescu P.L., *Chem. Commun.*, **2012**, *48*, 2216.

Acknowledgements The authors are grateful to the Russian Foundation for Basic Research (project no. 13-03-01088) and the Ministry of Education and Science of the Russian Federation (project of Joint Laboratories of Siberian Branch of the Russian Academy of Sciences and National Research Universities) for financial support.

ISOCYANATO- AND ISOTHIOCYANATO-SUBSTITUTED TRIANGULAR CLUSTERS OF MOLYBDENUM AND RHENIUM

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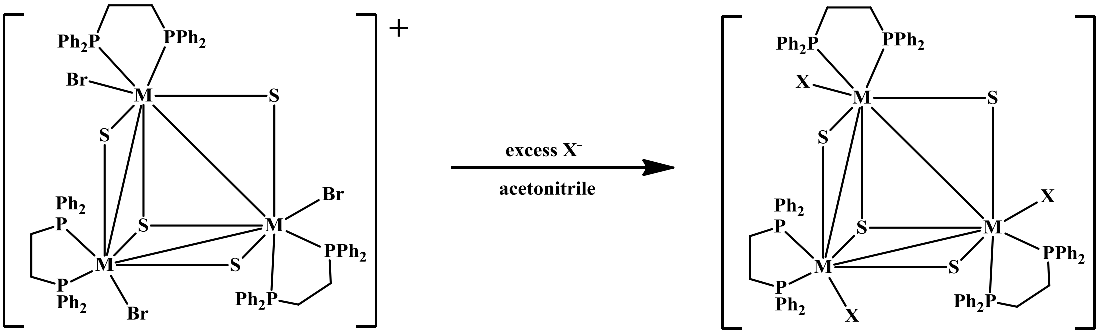
The metal clusters containing ambidentate ligands regarded as suitable building blocks for the assembly of (heterometallic) coordination polymers or oligomers. Using this approach, we developed the synthesis of new molybdenum and rhenium clusters with pseudohalide ligands $[M_3S_4(dppe)_3(NCX)_3]^+$ (M = Re, X = S; M = Mo, X = S, O). Magnetic susceptibility measurements showed that $[Re_3S_4(dppe)_3(NCS)_3]Br$ possesses the high-spin ground state with *S* = 3/2 observed earlier for its precursor $[Re_3S_4(dppe)_3Br_3]Br$.



An attempt to utilize the thiocyanate linkages of $[Mo_3S_4(dppe)_3(NCS)_3]NCS$ to coordinate $Cu(hfac)_2$ (hfac = hexafluoroacetylacetonate) lead to the formation of double complex salt $[Mo_3S_4(dppe)_3(NCS)_3][Cu(hfac)_3]$. The coordination of Cu *via* NCS bridges seems to be unfavorable due to phenyl substituents of dppe ligands.

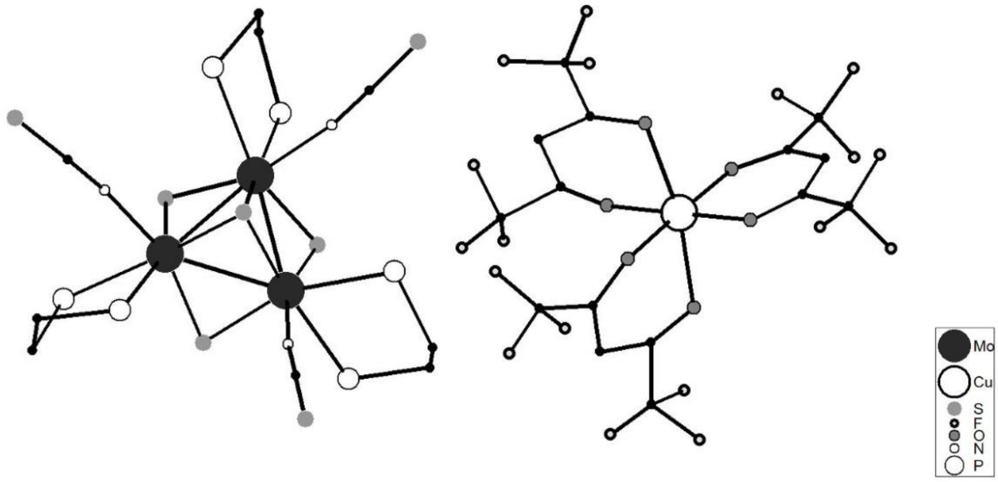


Figure 1. The structure of complex $[Mo_3S_4(dppe)_3(NCS)_3][Cu(hfac)_3]$. Phenyl rings are omitted for clarity.

Acknowledgement. The work was supported by the Russian Foundation for Basic Research (projects 13-03-01088 and 12-03-33028) and Russian Ministry of Education and Science.

EXCITED TRIPLET STATE OF (^{n}Bu$_4$N)$_2$[Mo$_6$X$_8$(C$_3$F$_7$COO)$_6$] (X : I, Br, Cl)

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One of the characteristic properties of an octahedral hexametal cluster is the temperature (T) dependences of the photophysical properties. In particular, although the emission maximum energy is constant below 30 K, it shifts to a low energy with an increase in T from 30 K to 70 K, while it shifts to a high energy above 70 K. Furthermore, the emission lifetime varies dramatically below 70 K. Although such emission characteristics have been observed for some metal complexes, very large T dependences observed for the emission properties of the octahedral hexametal clusters are quite rare, and several research groups have reported T-dependent emission models. Among these models, a spin-sublevel model in the emissive excited triplet state is in particular important.

Since an octahedral hexametal cluster experiences a large spin-orbit coupling, the degenerated excited triplet state splits into three spin-sublevels. Furthermore, it splits into four spin-sublevels under the assumption of second-order spin-orbit coupling as demonstrated by theoretical calculations. Since it has been reported that the symmetry of an octahedral hexametal cluster deviates from O_{h} to $D_{4\mathrm{h}}$ in the excited state, the excited triplet state splits into five spin-sublevels. Although the emission from the lowest-energy spin-sublevel (Φ_1) is observed at an extremely low temperature, the emission from the higher-energy spin-sublevels (Φ_2, Φ_3, Φ_4) can be observed upon T elevation with the Boltzmann populations of the spin-sublevels being varied with T [1].

Although octahedral hexametal clusters show very broad emission spectra compared with a common transition metal complex, [Mo$_6$I$_8$(C$_3$F$_7$COO)$_6$]$^{2-}$ shows a very sharp emission spectrum with a high quantum yield in a high energy at room temperature [2]. In this research, the photophysical properties of [Mo$_6$X$_8$(C$_3$F$_7$COO)$_6$]$^{2-}$ (X = I, Br, Cl) in the solid states were studied at low temperature, and the zero-field splitting parameters of the emissive excited triplet states were estimated to clarify the factors controlling the excited triplet states of the clusters. The results were explained by a large contribution of the emission from Φ_3 with a minor contributions from Φ_4, despite emission of general octahedral hexametal cluster was explained by a large contribution of the emission from Φ_4 with a minor contributions from Φ_3.

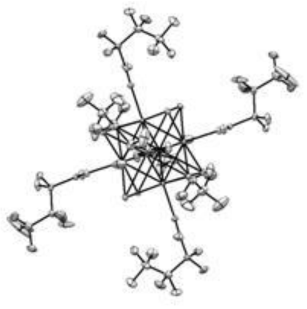

Figure 1. Structure of [Mo$_6$I$_8$(C$_3$F$_7$COO)$_6$]$^{2-}$ [2].

1. Kitamura N., Ueda Y., Ishizaka S., *Inorg. Chem.*, **2005**, *44*, 6308.
2. Sokolov M.N., Mihailov M.A., Peresypkina E.V., *Dalton Trans.*, **2011**, *40*, 6375.

[Mo$_6$X$_8$(C$_3$F$_7$COO)$_6$]$^{2-}$ (X = I, Br, Cl) were gifted by Dr. Brylev K.A. group (*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences*).

SYNTHESES AND PROTON CONDUCTIVITY OF MIL-101 DOPED BY TRIFLIC AND *PARA*-TOLUENESULFONIC ACIDS

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Metal-organic frameworks (MOFs) are supramolecular compounds consist of metal ions connected by bridge organic ligands. Special interest is caused by porous and stable 3D structures because of their possible applications such as sorbents, catalysts, proton and electron conductors. Mesoporous MOF MIL-101(Cr) (MIL – material of Institute Lavoisier) based on chromium(III) carboxylates linked by terephthalate anions is one of the most widely studied MOFs [1]. It has a topology of MTN zeolite with 2 types of mesopores 2.9 and 3.8 nm. Owing to the fact that it demonstrates unique chemical stability and huge BET surface area (~3500 m^2/g) MIL-101(Cr) is a good candidate for introduction of different chemically active molecules.

Proton exchange fuel cells are the most perspective types of fuel cells thanks to short starting time and long operation life. Main feature of these devices is proton exchange membrane (PEM). Nowadays commercially successful proton conductive material is Nafion with conductivity $\sigma = 10^{-3}$ S/cm at 80 °C and 34% relative humidity [2]. Such low value of conductivity and ability to work just in a highly humid atmosphere make searching of novel proton conductors very perspective.

In the current work we report about introduction of strong acids such as trifluoromethanesulfonic (TfOH) and *para*-toluenesulfonic (TsOH) acids in MIL-101(Cr) [3]. Both resultant hybrid materials acid@MIL-101 demostrate proton conductivity. TfOH@MIL-101(Cr) shows high value of conductivity $\sigma = \sim 10^{-1}$ S/cm at 70 °C and relative humidity (RH) 15 and 100%. Such indifference to atmosphere humidity is unique and may be explained by a strong hydration of material. All this makes TfOH@MIL-101(Cr) a good candidate to create low temperature PEM. Another compound TsOH@MIL-101(Cr) shows low proton conductivity $\sigma = 10^{-5}$ S/cm at 70 °C and 100% RH. At the same time decreasing of atmosphere humidity upto 15% RH leads to the dramatic lowering of conductivity (10^{-7} S/cm at 70 °C). Such strong dependence of proton conductity on atmosphere humidity makes TsOH@MIL-101(Cr) perspective for creation sensors of water molecules.

Acknowledgements.This research was supported by Grant № 14.Z50.31.0006 of Department of Education and Science, Russian Federation.

1. Ferey G., Mellot-Draznieks C., Serre C., *Science*, **2005**, *309*, 2040.
2. Lu J., Lu S., Jiang S.P., *Chem. Commun*., **2011,** *47*, 3216.
3. Dybtsev D.N., Ponomareva V.G., Aliev S.B., *ACS Appl. Mater. Interfaces*., **2014**, *6*, 5161.

EXFOLIATION OF LAYERED TRANSITION METAL CHALCOGENIDES IN LIQUID MEDIA: COLLOID SOLUTIONS AND FILMS

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Layered transition metal chalcogenides attract a great attention due to their some remarkable useful properties. The di- and trichalcogenides MQ_2 and MQ_3 (M=Nb, Ta, Mo, W; Q = S, Se) are regarded as perspective objects for microelectronics and optoelectronics, they can use as solar cell elements, electrodes in lithium batteries, effective catalysts, materials with charge density waves and lubricating property, and others. Layered structure of such type compounds allows exfoliating them which results in obtaining of nanoparticles with different thickness down to single layers.

Here we report the exfoliation of layered niobium and molybdenum chalcogenides MQ_2 and MQ_3 [1 for NbQ_3] by solution method. Stable colloidal dispersions of di- and trichalcogenides were prepared using ultrasonic treatment of bulk materials in different organic solvents – CH_3CN, dmf, ^{i}PrOH, EtOH, EtOH/H_2O (vol. 1/1), *n*-BuOH. The colloidal dispersions were characterized by electronic spectroscopy, DLS and AFM methods. According to the DLS and AFM data the particles sizes in different solutions extend from 70 to 400 nm, the mean sizes are in range 150 – 200 nm.

Using colloidal dispersions thin films of the chalcogenides were prepared by different approaches. Raman spectra and X-ray powder patterns for films are presented and discussed.

Acknowledgements. The work is supported by Russian Scientific Foundation (Project 14-13-00674).

1. Fedorov V.E., Artemkina S.B., Grayfer E.D., et al., *J. Mater Chem. C*, **2014**, DOI: 10.1039/C4TC00459K

NEW TETRANUCLEAR 8-QUINOLINOLATE COMPLEX OF YTTRIUM. SYNTHESIS, STRUCTURE AND LUMINESCENT PROPERTIES

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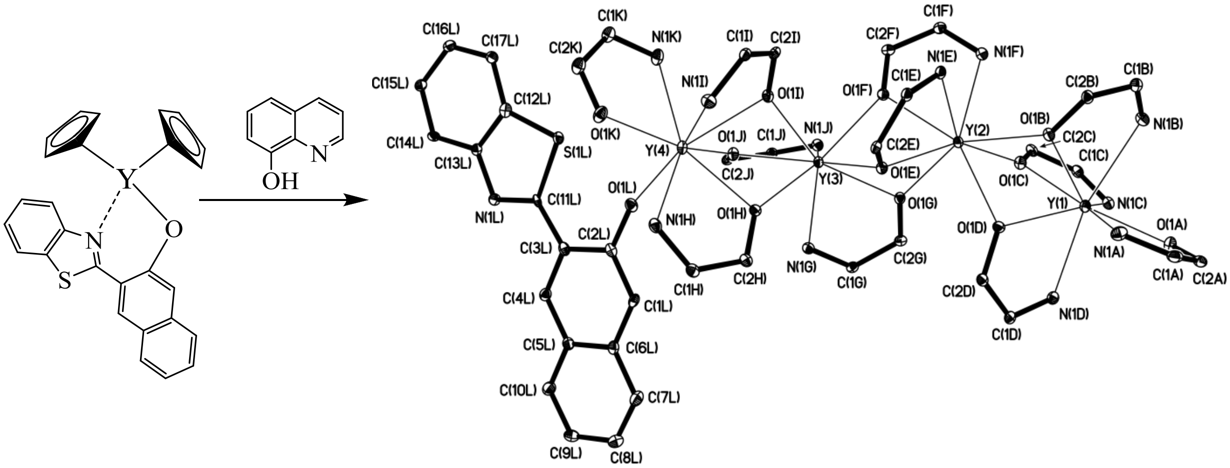
Complexes of rare earth metals with 8-hydroxyquinoline are still attracting the attention of much researchers as an emissive material in organic light-emitting diodes (OLEDs). Previously we have obtained mono-, bi- or trinuclear 8-quinolinolate complexes of rare earth metals [1]. Herein we present new tetranuclear 8-quinolinolate yttrium complex of general formulae $Y_4(NpSON)Q_{11}$ (**1**). It was prepared by the reaction of $Y(NpSON)Cp_2$ with 8-hydroxyquinoline in DME at room temperature. The X-ray structure analysis revealed that the molecule of **1** contains a rare zigzag chain of four Y^{3+} ions surrounded by two terminal quinolinolate ligands (Q) , nine bridging Q ligands chelately bonded to the metal ions and one terminal 2-(2-hydroxy-3-naphthyl)benzothiazolyl ligand (NpSON) bonded to yttrium monodentately.



The absorption spectra of the complex contained intense bands in the near UV region at 236, 283, 332, 344 nm, which were assigned to the intraligand π - π* transitions in aromatic fragments of quinolinolate and benzothiasolyl-naphtholate ligands. Photoluminescence spectra of **1** (λ_{ex} = 360 nm) in THF solution contained two bands of the ligand-centered emission: at 415 and 528 nm.

The analogous Yb complex was synthesized in a similar manner. Its absorption spectrum is identical to that of **1**. In its photoluminescence spectrum in THF solution the band of the metal-centered emission is observed at 988 nm with the luminescence of the ligands at 417 nm.

Acknowledgements The work is supported by the RSF (project № 14-13-01158).

1. Baranov E.V., Fukin G.K., Balashova T.V., *Dalton Trans*., **2013**, *42*, 15699.

SYNTHESIS AND CRYSTAL STRUCTURE OF HETEROMETALLIC V^{IV}-M^{II} (M^{II} = Mn, Co, Zn, Cd) COMPLEXES WITH 1,1-CYCLOBUTANEDICARBOXYLIC ACID ANIONS

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In present work we have studied the formation of the new heterometallic complex compounds with combination of metals V^{IV}-Mn^{II}, V^{IV}-Co^{II}, V^{IV}-Zn^{II}, V^{IV}-Cd^{II} and 1,1-cyclobutanedicarboxylic acid (H_2Cbdc) anions. Single crystals of obtained compounds were isolated and characterized by X-ray diffraction analysis.

Complex $\{[Cd(V^{IV}O)(Cbdc)_2(H_2O)_5]\cdot H_2O\}_n$ (**1**) with 1D polymeric structure crystallizes from reaction mixture obtained by interaction of water solutions of $VOSO_4\cdot 3H_2O$, $3CdSO_4\cdot 7H_2O$ and barium 1,1-cyclobutanedicarboxylate in the ratio 1:1:2. Polymeric chains of **1** are built of bis-chelate metal fragments $[(V^{IV}O)(Cbdc)_2(H_2O)]^{2-}$, linked by Cd atoms, which coordinate two carboxylate oxygen atoms and four O atoms of water molecules.

It was found that the replacement of $3CdSO_4\cdot 7H_2O$ by $ZnSO_4\cdot 7H_2O$ in the similar synthesis and the slow evaporation of water solution give crystals of molecular complex $[Zn(V^{IV}O)(Cbdc)_2(H_2O)_5]\cdot H_2O$ (**2**). Dinuclear structure of **2** is formed by linked together metal fragment $[(V^{IV}O)(Cbdc)_2(H_2O)]^{2-}$ and zinc atom, which is located in octahedral coordination environment of two carboxylate ligand O atoms and four O atoms of water molecules (fig. 1).

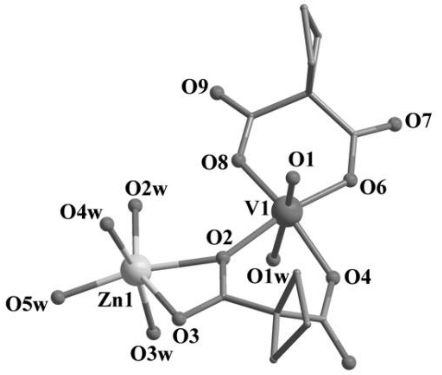

Figure 1. Molecular structure of **2**.

The attempt to obtain single crystals of V^{IV}-Mn^{II} and V^{IV}-Co^{II} 1,1-cyclobutanedicarboxylates in similar to **1** and **2** terms failed. The crystals of isostructural compounds $[M(V^{IV}O)(Cbdc)_2(H_2O)_3(EtOH)_2]_n$, M = Mn (**3**), Co (**4**) were obtained during the slow diffusion of ethanol vapor into the saturated water solutions. The structure of polymeric chains of **3** and **4** are similar to that for previously obtained compounds $\{[Mn(V^{IV}O)L_2(H_2O)_5]\cdot H_2O\}_n$ (L = Me_2mal and Bumal) with dimethylmalonic and buthylmalonic acid anions [1], but they are distinguished by the presence of two ethanol molecules coordinated to Mn and Co atoms.

Acknowledgements. This study was supported by the Russian Foundation for Basic Research (projects Nos. 13-03-12430, 14-03-01116 and 14-03-31292), the Russian Academy of Sciences, the Council on Grants of the President of the Russian Federation (grants MK-2917.2014.3 and NSh-4773.2014.3).

1. Bazhina E.S., Aleksandrov G.G., Bogomyakov A.S., *Polyhedron*, **2014**, *77*, 47.

EFFECT OF STRUCTURE AND CHEMICAL MODIFICATION ON GAS SORPTION FEATURES OF POROUS ALUMINIUM TEREPHTHALATES

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Dybtsev D.N.[2,3], Fedin V.P.[2,3]

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Elimination of CO_2 from methane containing gas mixtures is an important technological problem. Metal-organic frameworks are considered as promising materials for selective adsorption from gaseous mixtures due to a feasibility to adjust their pore structure and surface features in order to make them suitable for a certain adsorbate. Porous aluminium terephthalates of the MIL family (Materials of Institut Lavoisier) demonstrate a spectacular combination of both micro- and mesopores with a high specific surface area (MIL-101), an unique framework flexibility (MIL-53), and an opportunity of various synthetic modifications.

Sorption of methane and carbon dioxide on porous polymers Al-MIL-101-NH_2, Al-MIL-53 and Al-MIL-53-NH_2 in comparison with Cr-MIL-101 was investigated by volumetric and calorimetric techniques within a temperature range of 79 K to 308 K and pressures up to 3 MPa. Adsorption isotherms of Al-MIL-101-NH_2 showed the Langmuir type behaviour and complete reversibility regardless of the adsorbate nature. The flexible frameworks Al-MIL-53 and Al-MIL-53-NH_2 demonstrated hysteretic adsorption with several plateaus. The mechanism of adsorption and the isotherm shape for these materials depended on the experimental temperature and the gas used.

As it was shown by direct calorimetric measurements, the amino surface modification in the case of Al-MIL-101-NH_2 did not affect the adsorption heat of the CO_2 and CH_4. On the contrary, the heat of adsorption was reduced by 35% (CH_4) and 20% (CO_2) for Al-MIL-53-NH_2 as compared with unmodified Al-MIL-53.

An ideal adsorption selectivity of CO_2/CH_4 increases in the sequence Al-MIL-101-NH_2 < Al-MIL-53 < Al-MIL-53-NH_2, and reaches the value of $S(CO_2/CH_4) = 385$ at 223 K in the latter case. Thus, the flexible frameworks of the MIL-53 type, able to "distinguish" adsorbates of different nature, have a potential for practical applications to separate CO_2/CH_4 mixtures. Besides, the modification of such flexible porous materials by amino groups enhances their ability to the selective adsorption.

Acknowledgements. This work was supported in part by Russian Foundation for Basic Researches, grants No 13-03-12424 and 14-03-00520.

BI- AND TRIMETALLIC GOLD COMPLEXES OF DIPHENYLPHOSPHINOETHYL-FUNCTIONALIZED IMIDAZOLIUM SALTS AND THEIR N-HETEROCYCLIC CARBENES: SYNTHESIS AND PHOTOPHYSICAL PROPERTIES

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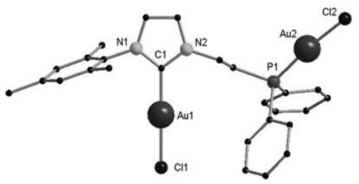
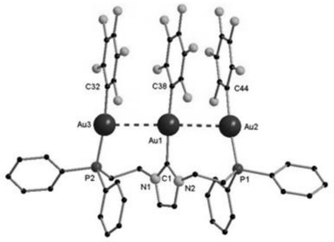
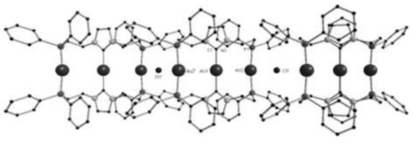
By attaching phosphine groups to NHCs, polydentate ligands are obtained, which can be either used as pincer-type ligands or as building blocks for multimetallic complexes. Gold complexes have been thoroughly investigated for their application in catalysis and their photophysical properties; photoluminescent compounds with attractive aurophilic d^{10}-d^{10} interactions are of particular interest [1]. It is, for example, still questionable whether two cationic gold centers are involved in certain catalytic steps [2] and if they are influenced by relativistic effects [3]. Hence, we used two known phosphinoethyl-tethered imidazolium salts [4] to synthesize bi- and trimetallic gold compounds. Although a few macrocyclic cationic gold complexes with N-phosphorylated or N-phosphinomethyl-substituted NHCs were reported by Braunstein and Kostyuk [5], to the best of our knowledge, neutral gold complexes with phosphorous-containing NHCs are still unknown. Herein we present a full account of phosphinoethyl-tethered NHC ligands in gold(I) chemistry.







The bimetallic complex of the single functionalized NHC was synthesized via transmetallation from the corresponding silver NHC-transfer reagent. The potentially tridentate disubstituted imidazolium salt was used to form acyclic and macrocyclic dinuclear complexes as well as trinuclear complexes after having activated the carbene function. Thereby, we obtained triply charged Au_3L_2 compounds with different anions as well as a neutral $L[Au(C_6F_5)]_3$ complex after having varied the starting material. All compounds display aurophilic interactions of different strength and they were investigated for their photoluminescent properties, which proved to be remarkable in some cases.

Acknowledgements. SFB/TRR 88 is gratefully acknowledged. S.B. thanks the Fonds der Chemischen Industrie (FCI) for generous fellowship.

1. Yam V.W.-W., Cheng E.C.-C., *Chem. Soc. Rev.* **2008**, *37*, 1806.
2. Gómez-Suárez A., Nolan S.P., *Angew. Chem. Int. Ed.* **2012**, *51*, 8156.
3. Gorin D.J., Toste F.D., *Nature* **2007**, *446*, 395.
4. (a) Lee H. M., Zeng J. Y., Hu C.-H., *Inorg. Chem.* **2004**, *43*, 6822; (b) Lee H.M., Chiu P.L., Zeng J.Y., *Inorg. Chim. Acta* **2004**, *357*, 4313.
5. (a) Ai P., Danopoulos A.A., Braunstein P., *Chem. Commun.* **2014**, *50*, 103; (b) Marchenko A.P., Koidan H.N., Hurieva A.N., *Organometallics* **2013**, *32*, 718.

SYNTHESIS, STRUCTURE AND PROPERTIES OF POROUS Zn(II) THIOPHENEDICARBOXYLATES WITH VARIABLE BRIDGING LIGANDS

Bolotov V.A.[1,2], Dybtsev D.N.[1,2]

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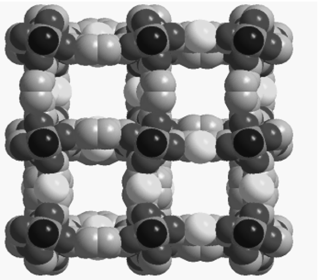
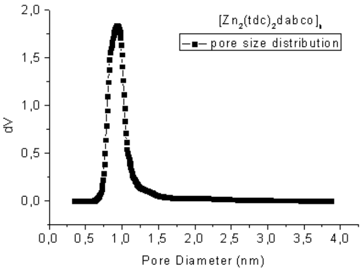
Porous metal-organic coordination polymers are built from metal cations, connected by organic linkers into periodic crystalline networks. Such type of materials provides almost infinite possibilities to the solid-state engineering and possesses many valuable material properties, especially the highest surface areas, great adsorption properties, selective gas uptakes, *etc*.

Our work describes the synthesis of three new isoreticular coordination polymers based on 2,5-thiophenedicarboxylic acid (H_2tdc) and N-donor linear bridging ligands of variable length. All compounds features isoreticular coordination network [Zn_2(tdc)$_2$L], where L = dabco, 1,2-bis-(4-pyridile)ethylene or 1,3-bis-(4-pyridile)propylene. The crystalline compounds were investigated by a number methods, such as single-crystal and powder X-ray diffraction, chemical, thermogravimetric analysis, IR spectroscopy. Interestingly, the [Zn_2(tdc)$_2$(dabco)] framework undergoes reversible changes of the pore volume, depending on the presence of the guest molecules. The N_2 adsorption of the activated samples shows reversible type I isotherm, typical for microporous materials. The BET surface areas vary from 420 to 1160 m^2/g, depending on the L. The gas adsorption data support the porous structure of the materials, established from the X-ray diffraction methods.





Acknowledgements. This work is supported by te Grant of the Ministry of Education and Science of the Russian Federation (grant 14.Z50.31.0006).

PROTON-CONDUCTING MATERIALS BASED ON POROUS METAL-ORGANIC FRAMEWORKS

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Metal-organic frameworks (MOFs) are compounds which consist of metal ions or clusters linked by organic moieties. MOFs are marked by high porosity and surface area. These factors and possibility of modification both organic and inorganic parts play crucial role in their functional properties, e. g. gas separation, gas storage, catalysis, nanoreactors, sensing and particularly proton conductivity.

H_3PO_4@Cr-MIL-101 and H_2SO_4@Cr-MIL-101 obtained by impregnation of stable mesoporous MOF by acids are described in [1]. They demonstrate high proton conductivity that can be compared with Nafion. The idea was developed and dependence proton conductivity on amount of phosphoric acid included into pores of Cr-MIL-101 and on structure of MOF (microporous Cr-MIL-53, mesoporous Cr-MIL-100 and Cr-MIL-101) was studied.

The substances synthesized were characterized by XRPD, IR-spectroscopy, elemental analysis and TGA. These compounds demonstrate high proton conductivity of 1×10^{-2} $S \cdot cm^{-1}$ at room temperature for sample with maximum amount of about 4 phosphoric acid molecules per formula unit. Generally reducing the acid composition in broad range leads to significant decrease in proton conductivity. On the other hand altering the MOF structure strongly affects both values of conductivity and its temperature behavior.

Proton-conducting materials based on Zn-containing MOFs are also of interest. Possibility of using SS NMR and single-crystal XRD analysis are advantages of these materials (in comparison with Cr-based MOFs), but they are not hydrolytically stable.

This study deals with hydroquinone ($C_6H_6O_2$), 1,4-benzoquinone ($C_6H_4O_2$) and quinhydrone incorporated in microporous Zn-ndc-ur. $C_6H_6O_2$@Zn-ndc-ur and $C_6H_4O_2$@Zn-ndc-ur were characterized by MAS NMR, XRPD, IR-spectroscopy and elemental analysis. Proton transfer was studied by broad-line ^1H NMR.

1. Ponomareva V.G., Kovalenko K.A., Chupakhin A.P., *J. Am. Chem. Soc.*, **2012**, 134, 15640.

PERSPECTIVES OF MOLYBDENUM OCTAHEDRAL HALIDE CLUSTERS IN BIOLOGY

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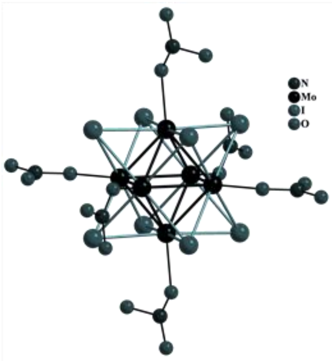

Structure of $[\{Mo_6I_8\}(NO_3)_6]^{2-}$

Molybdenum octahedral halide complexes are interesting for scientists, because they have got a lot of useful properties. On our opinion, luminescence is the most actual property. Such feature makes them perspective agents for bioimaging.

$[\{Mo_6X_8\}(NO_3)_6]^{2-}$ (X = Cl, Br, I) are good precursors of biology agents. We have shown that cluster complex with iodine core has the highest photophysical characteristics. For example, quantum yield of powered sample of $(Bu_4N)[\{Mo_6I_8\}(NO_3)_6]$ is 0.26.

A presence of labile NO_3^- groups gives opportunity for different reactions in solutions. Thus, for increase of stability we have chosen method of dispersive polymerization. Materials based on the cluster cores $\{Mo_6X_8\}^{4+}$ and the modified organic matrix - polystyrene (functional groups: -SH [1], -COOH, -Py) were obtained. Materials with -COOH, -Py were studied at different quantity of cluster and polymerization time. As a result we found that complexes are inhibiting the radical polymerization. For samples $\{Mo_6X_8\}$@PS-SH, $\{Mo_6X_8\}$@PS-COOH (1% of cluster to styrene, 18 hours, diameter of spheres is 0,7 – 1,0 nm), $\{Mo_6X_8\}$@PS-Py (1% of cluster to styrene, 18 hours, diameter of spheres is 0,7 – 1,0 nm) was carried out MTT test on human cancer cells (Hep2), which shows that concentration 7 mg/ml of materials doesn’t influence on cell proliferation.

Acknowledgements. This work was supported by the Russian Science Foundation (Grant №14-14-00192).

1. Efremova O.A., Shestopalov M.A., Chirtsova N.A., *Dalton Trans.*, **2014**, *43, 6021.*

HYDROGEN ADSORPTION ON BASOLITE C300 AND ITS COMPOSITES WITH LaNi$_5$ AND Pt/C AT PRESSURES UP TO 750 BARS

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A commercial MOF Basolite C300 represents copper benzene-1,3,5 tricarboxylate (HKUST-1) and is considered as a promising hydrogen adsorbent. To estimate its adsorption ability under high pressures that is of special interest for some applications the influence of chemisorption catalysts on hydrogen adsorption behavior of C300 at pressures up to 750 bars has been studied in the present work. Platinum on carbon black (E-TEK) and hydride-forming intermetallic compound LaNi$_5$ were used as catalysts.

Excess adsorption isotherms of pristine C300 at 81 K demonstrate a pronounced maximum of 3.74 wt% at 37 bars. The behaviour at room temperature can be described by a conventional Langmuir type isotherm with saturation at pressure above 250 bars (figure 1).

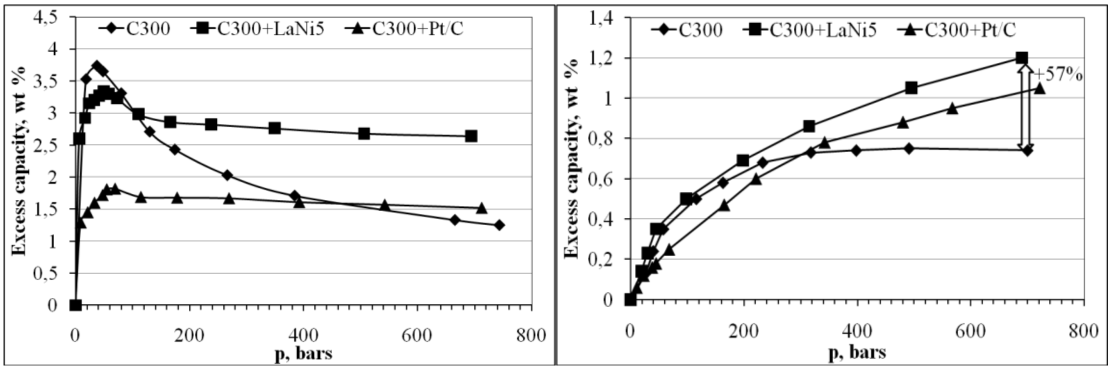

Figure 1. Hydrogen adsorption isoterms of C300, C300+Pt/C and C300+LaNi$_5$ at 81K (left) and 298K (right).

Production of the platinum containing composite comprised ball milling of a ternary mixture C300+Pt/C+glucose (10:1:1) followed by heat treatment according the procedure described in [1]. The modification applied led to a partial destruction of the metal-organic framework with formation of metallic copper. Meanwhile, an increase of hydrogen capacity at room temperature within the pressure range of 300 to 750 bars compared to the pristine C300 has been revealed.

The use of LaNi$_5$ prevented degradation of the porous matrix and resulted in the similar effect on hydrogen adsorption. A surplus of 57% in excess capacity has been recorded for the modified material C300+LaNi5 at 298 K (figure 1).

Acknowledgements. Financial support from the Russian Foundation for Basic Research (grant 14-03-00520) is gratefully acknowledged.

1. Li Y., Yang R.T., *J. Am. Chem. Soc.* **2006**, 128, 8136.

SYNTHESIS OF ZnO NANOPARTICLES WITH CONTROLLABLE PARTICLE SIZE BY A SYSTEMATIC THERMOLYSIS OF ISORETICULAR Zn-ORGANIC COORDINATION POLYMERS

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Porous coordination polymers are a recently emerged class of coordination compounds. Many of such materials can be synthesized relatively easily, with high yields from readily available starting compounds. Therefore, significant efforts are now directed to the synthesis of the other functional materials using the coordination polymers as precursors. Thermolysis of metal-organic compounds is a convenient way to prepare porous carbon materials, metal or metal oxide nanoparticles as well as various composite materials. Recently it was shown, that during the solid-state chemical transition the particle size of the product is reciprocally proportional to the relative contraction of the unit cell during the process. Following this concept, collapse of great unit cell of the porous coordination framework to the relatively dense product upon thermolysis should results in even smaller product particles. This open new possibilities to employ porous coordination polymers as precursors due to their high unit cell volumes and open porous structures. The goal of our project was to prove the above mentioned concept on the new class of coordination compounds with potential to achieve smaller particle size than with conventional precursors.

In this work we carried out thermal decomposition of series of isoreticular zinc(II)-containing coordination polymers [$Zn_2(bdc)_2$dabco], [$Zn_2(ndc)_2$dabco], [$Zn_2(bpdc)_2$dabco] (bdc = terephthalate, ndc = 2,6-naphthalanedicarboxylate, bpdc = 4,4′-byphenyldicarboxylate) in oxygen atmosphere at 400 °C. The resulting ZnO powder, indeed, consist of nanometer-scale particles, which was revealed by various methods. More importantly, the size of the ZnO crystallites, calculated from the X-ray peak broadening, inversely depends on the length of the dicarboxylate bridging linker in the precursor. The dimensions vary from *ca*. 2.0 to 4.4 nm upon the change of the linker. At the same time, the thermolysis of “conventional” zinc(II) basic carbonate at exactly the same conditions results in ZnO nanocrystallites of *ca*. 6.0 nm size. The average particle diameter of the bulk phase could be estimated by the measurement of the specific surface areas of the powder samples, assuming the spherical shape of the particles. The BET surface area measurements of ZnO samples clearly support the results of X-ray diffraction data: the longer organic linker used – the higher surface area of the ZnO product becomes, which indicates smaller particle size. Our results clearly demonstrate the rich yet underestimated potential of metal-organic frameworks as precursors for the synthesis of nanomaterials.

Acknowledgements. This work is supported by the Russian Foundation for the Basic Research (grant 14-03-00291)

PHOTOPHYSICAL PROPERTIES OFOCTAHEDRAL HEXA-MOLYBDENUM CLUSTERS HAVING A SERIES OF TERMINAL CARBOXYLATE LIGANDS

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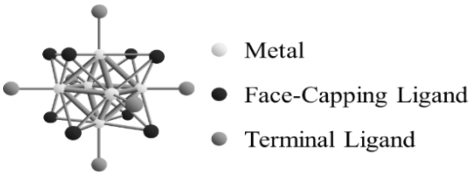

Fig. 1: Structure of octahedral hexametal cluster.

Octahedral hexametal clusters show in general very broad emission spectra compared with a common transition metal complex. In particular, hexanuclear molybdenum cluster $[Mo_6Cl_{14}]^{2-}$, shows relatively intense red emission and,therefore, has attracted as luminescent materials. The cluster can be depicted as an octahedron of molybdenum atoms associated with eight face-capping ligands and six terminal ligands (Fig. 1). Recently, Sokolov and his co-workers reported that $(Bu_4N)_2[Mo_6X_8(n\text{-}C_3F_7COO)_6]$ (X = Br, I) show extraordinarily bright and long-lived red phosphorescenceboth in solution and solid states with the highest emissionquantum yields and the longest emission lifetimes among hexanuclear metal cluster complexes [1]. In particular,$[Mo_6I_8(C_3F_7COO)_6]^{2-}$ shows a very sharp emission spectrum with a high quantum yield at room temperature. In this study, we focused on the hexanuclear molybdenum cluster with a $[Mo_6I_8]$ core and studied the photophysicalproperties of $[Mo_6I_8L_6]^{2-}$ (L: a series of carboxylate ligands) in acetonitrile.We discuss on the relationship between the excited-state properties of clusters and chemical properties of L.

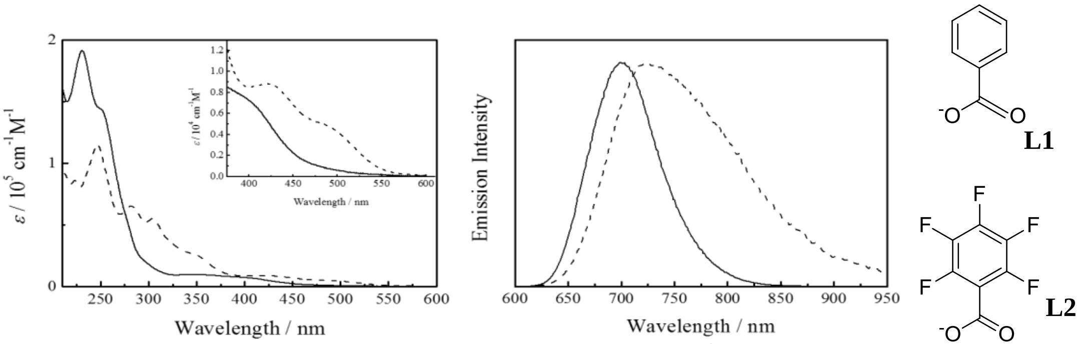

Figure 2. Absorption and emission spectra of $[Mo_6I_8L_6]^{2-}$ in acetonitrile. (: L1, gray : L2)

Fig. 2 shows the absorption and emission spectra of $[Mo_6I_8L_6]^{2-}$ (L1 = benzoic acid, L2 = perfluoro benzoic acid) in acetonitrile. $[Mo_6I_8L2_6]^{2-}$ shows red emission compared with $[Mo_6I_8L1_6]^{2-}$. More detailedexperiments on the photophysical properties of the clusters demonstrated that the non-radiative decay path of $[Mo_6I_8L2_6]^{2-}$ was different from those of other L ligands.

1. Sokolov M.N., Mihailov M.A., Peresypkina E.V., *Dalton Trans.*, **2011**, *40*, 6375.

This work was collaborated with Dr. K. A. Brylev and Prof. M. N. Sokolov groups at Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences.

X-RAY EMISSION AND X-RAY PHOTOELECTRON SPECTRA OF MONONUCLEAR AND MULTINUCLEAR MANGANESE COMPLEXES

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Transition metal complexes with the imidazoline nitroxyl radicals are magnetically active compounds. Magnetic properties of such complexes are determined by the nature of electronic interactions of paramagnetic centers: metal - nitroxyl group ligand $\{M\text{-}(N\text{-}O^{\cdot})\}$. In this regard the study of nature of the electron density distribution and localization of the unpaired electron density on the atoms of free and coordinated ligands as well as on the atoms of complexes metal centers is the actual. In the present work to study the assigned tasks were involved methods of X-ray emission and X-ray photoelectron spectroscopy.

The X-ray photoelectron spectra $Mn2p_{3/2,1/2}$, $Mn3s$, $Mn3p$, $O1s$, $N1s$, $C1s$ for multinuclear manganese complexes, $[Mn_6(O)_2(Piv)_{10}(THF)_4]\cdot THF$, $[Mn_6(O)_2(Piv)_{10}L_2]\cdot 3Me_2CO$ and $[Mn_6(O)_2(Piv)_{10}L_2]\cdot 2EtOAc$ were obtained. The X-ray emission MnL_α, MnL_β, MnL_η, MnL_l, OK_α spectra of mononuclear $MnL_2^{CF_3}$(DFMA) and $MnL_2^{COOCH_3}$ and multinuclear $[Mn_6(O)_2(Piv)_{10}L_2]\cdot 3Me_2CO$ and $[Mn_6(O)_2(Piv)_{10}L_2]\cdot 2EtOAc$ manganese complexes were studied. The data of X-ray measurements showed that significant redistribution of electron and spin density at coordination of the ligand in multinuclear complexes was not observed.

The analysis of experimental X-ray photoelectron measurements of the $Mn3s$ binding energy indicates that two groups of nonequivalent manganese atoms (4 Mn^{2+} atoms and 2 Mn^{3+} atoms) were contained in the complexes $[Mn_6(O)_2(Piv)_{10}(THF)_4]\cdot THF$, $[Mn_6(O)_2(Piv)_{10}L_2]\cdot 3Me_2CO$ and $[Mn_6(O)_2(Piv)_{10}L_2]\cdot 2EtOAc$. The availability of the satellite structure typical for 3d transition metal complexes was connected with the processes of charge transfer from the ligand atoms on metal atom $(Mn^{2+}L^{-})\leftarrow(Mn^{3+}L)$.

The X-ray emission MnL_α, MnL_β, MnL_η, MnL_l spectra had a similar structure for all studied complexes. X-ray emission L_α and L_β lines were connected with the transition of electron from the valence 3d-states on the internal $2p_{3/2}$ and $2p_{1/2}$ levels. Estimation of intensity ratio $I(L_\beta)/I(L_\alpha)$ led to the conclusion that the manganese ions of study complexes were located in two charge states with a large contribution of Mn(II) that corresponds to the XPS data.

The X-ray emission MnL_α, MnL_β and OK_α spectra of study complexes were built in the unified energy scale that gave the value of contributions of manganese atoms 3d-AO and oxygen atoms 2p-AO in the HOMOs. MnL_α, MnL_β and OK_α of compounds $[[Mn_6(O)_2(Piv)_{10}L_2]\cdot 3Me_2CO$ and $[Mn_6(O)_2(Piv)_{10}L_2]\cdot 2EtOAc$, $MnL_2^{CF_3}$(DFMA) and $MnL_2^{COOCH_3}$. The data about the nature of electronic metal - ligand interactions of the study complexes were obtained by the analysis of X-ray emission MnL_α, MnL_β and OK_α spectra.

DIAZONIUM TOSYLATES FROM PYRROLE DERIVATIVES

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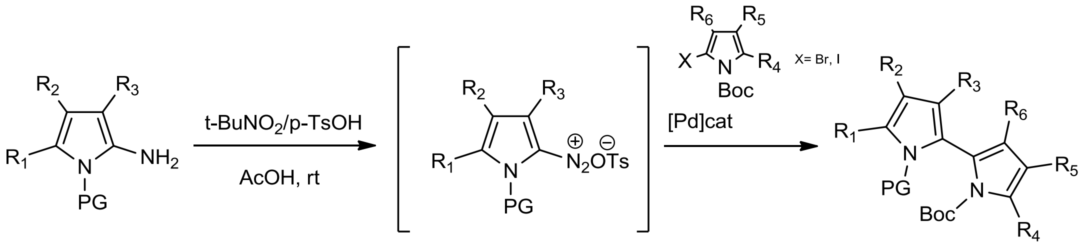
Recently, diazonium salts have been attracting more and more the attention of chemists as substrates for C-C cross-coupling reactions and C-H arylation [1, 2]. Today, there are many types of aromatic diazonium salts presenting various types of counter-cation, with a large variety of synthetic applications.

For example, diazonium tosylates [3], which were developed at the Chair of Organic Chemistry and Biotechnology of Tomsk Polytechnical University, proved to be more stable and more reactive than the related tetrafluoroborate salts. We are currently trying to extend the scope of this family to heteroaryl diazonium tosylates, especially in the pyrrole and indole series, which remains poorly described in the literature. Indeed, only few examples of pyrrolyl diazonium salts are already described [4].

Bi-heteroaryl units, such as 2,2' or 2,3'-bipyrroles, are included in a number of bio-active molecules, as well as in synthetic pharmaceuticals. Therefore, heteroaromatic diazonium tosylates would represent some suitable starting materials for cross coupling reactions leading to these interesting bi-heteroaromatics.



1. Robinson M.K., Kochurina V.S., Hanna J.M., *Tetrahedron Lett*. **2007**, *48*, 7687
2. Honraedt A., Raux M.-A., Le Grognec E., *Chem.Commun*. **2014**, *50*, 5236.
3. Filimonov V.D., Trusova M. E., Postnikov P. S., *Org. Lett*. **2008**, *10*, 3961.
4. Diana P., Barraja P., Lauria A., *et al*. *Synthesis* **1999**, 2082.

NOVEL POLYNUCLEAR CADMIUM CARBOXYLATES: APPROACHES TO SYNTHESIS AND STRUCTURAL FEATURES

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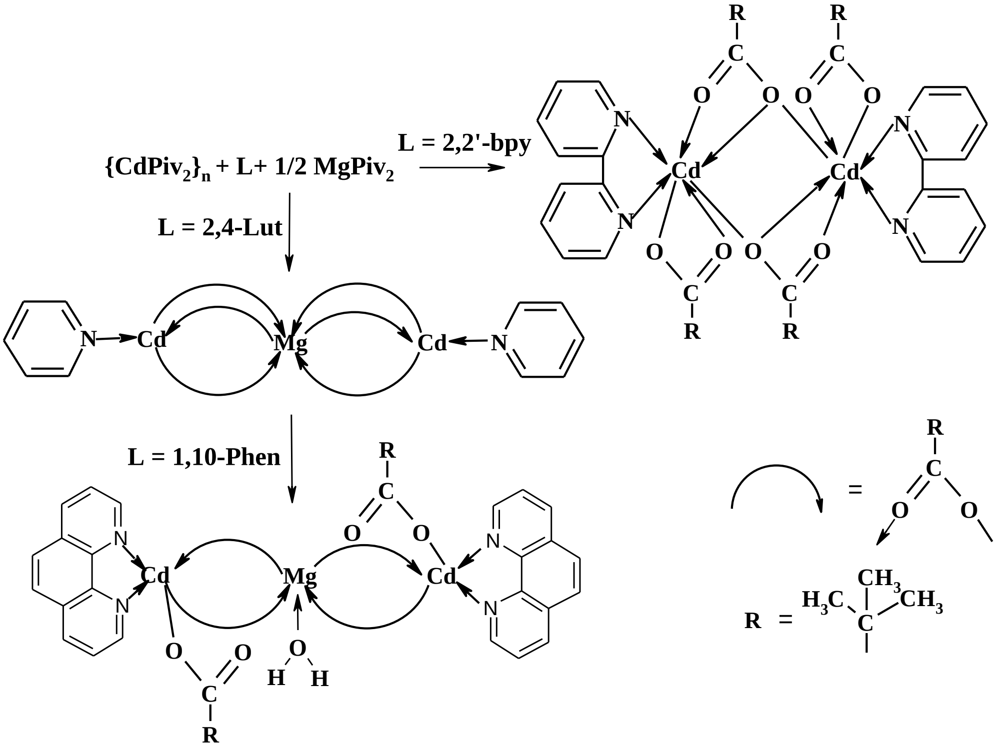
Approaches to synthesis of heterometallic cadmium pivalates (piv$^-$) were investigated. It was found that Cd-Li complex $[Cd_2Li_2(bpy)_2(piv)_6]\cdot 4MeCN$ can be obtained as a product of the reaction between Cd, Li pivalates and 2,2'-bipyridine (bpy). Compound $[Cd_2(bpy)_2(piv)_4]$ was crystallized in analogous reaction in the presence of magnesium in place of Li. It was found that heterometallic complex was not detected in such conditions. Trinuclear heterometallic complex $[Cd_2Mg(Lut)_2(piv)_6]$ was obtained using 2,4-lutidine (Lut) as monodentate N-donor ligand. In this complex molecules of Lut can be replaced by molecules of chelating ligand 1,10-phenantroline (Phen). As a result formation of unusual compound $[Cd_2Mg(Phen)_2(piv)_6(H_2O)]$ took place. In the structure Mg atom coordinates water molecule.



An attempt to crystallize Cd-Ln trimethylacetate was made. The reaction of Cd and lanthanide pivalates with Lut led to formation of 1D-polymer $[EuCd_2(piv)_7(H_2O)_2]\cdot MeCN$. Addition of 2,2'-bipyridine to the reaction mixture allowed us to crystallize homometallic complex $[Eu_2(bpy)_2(piv)_6]$.

Presented compounds were characterized by X-Ray diffraction analysis, CHN and IR-spectroscopy.

Acknowledgements. This study was supported by Russian Foundation of Basic Research (№ 14-03-01116, 14-03-31292, 13-03-12430, 13-03-00682, 14-03-90423, 14-03-31580), the Council on Grants of the President of the Russian Federation (MK-2917.2014.3, NSh-4773.2014.3), the Russian Academy of Science.

FATE OF EMERGING CONTAMINANTS IN THE ENVIRONMENT A MULTISCALE APPROACH

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These two last decades, many studies have reported the presence of new compounds, called "emerging pollutants", in wastewater and aquatic environments mainly coming from wastewater treatment plant (WWTP) effluents and soil amendments (sewage sludge, manure, slurry, …). These emerging pollutants including pharmaceuticals and new chemicals synthesized by chemists whose concentrations can reach up to a few tens μg in surface waters. Their presence can produce damaging effects on ecosystems as well as on human health. It is therefore fundamental to study their fate in the environment.

Such studies require combining macroscopic (sorption isotherms and column experiments, figure 1) to molecular scale experiments using powerful analytical tools (figure 2) in order to have a complete understanding of processes involved and of the contaminant speciation [1-3]. Molecular scale study provides structural information about the adsorbed contaminant and how it is bounded to the solid surface, whereas sorption experiments primarily monitor the mechanisms of (co-)sorption processes.

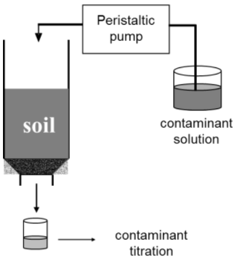

Figure 1. Column experiments

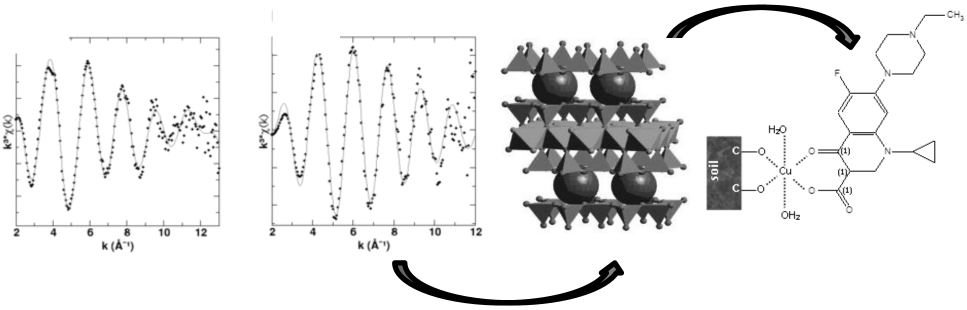

Figure 2. Molecular approach

Finally, besides the understanding of the biogeochemical processes governing transfers of contaminants in the environment, these studies have potential implications for the development of models allowing to establish relevant predictive systems of contaminated environments and for risk assessment of such pollution.

Overall, in this poster we presented the methodology that we apply to significantly advance the fundamental understanding of the fate of organic pollutants in presence of metallic cations in the environment and provide the knowledge basis for better risk assessment of these compounds in the environment. Such a methodology could be extent to all contaminants including transition metal clusters.

1. Grouer-Bacart M., Sayen S., Guillon E., *J. Colloid Interf. Sci.*, **2013**, *408*, 191.
2. Mamindy-Pajany Y., Sayen S., Mosselmans J.F.W., *Environ. Sci. Technol.*, **2014**, *48*, 7237.
3. Vo Dang Nguyen K., Guillon E., Dupont L., *J. Phys. Chem. C*, **2014**, *118*, 4465.

RIGID MEDIUM EFFECTS ON MLCT EXCITED STATES OF TRANSITION METAL COMPLEXES

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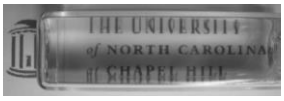
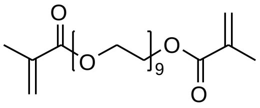
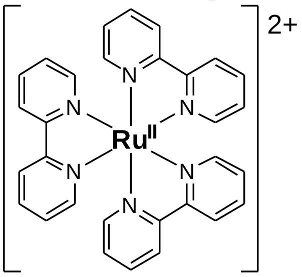
The excited-state characteristics (i.e., light absorption, emission, photoinduced reactions, and so forth) of metal complexes are controllable by the surrounding environment effects as well as by chemical modifications/derivatizations. Although the effects of temperature and polarity around the molecule are well understood, the influence of the rigidity of the medium and the transition between fluid and rigid/semi-rigid media on the excited-state properties of the metal complexes are not satisfactorily documented. In this study, a series of polypyridyl complexes showing the Metal-to-Ligand Charge Transfer (MLCT) excited states were introduced into rigid/semi-rigid media, and the spectroscopic and photophysical properties of the complexes under rigid environment were evaluated in detail.

Polymerization of poly(ethyleneglycol)dimethacrylate (PEG-DMA) fluids provides a means for preparing thin (mm to cm), chemically inert PEG-DMA films that are optically transparent throughout the visible region of the spectrum, as a photograph of PEG-DMA550 (PEG-DMA containing nine ethylene glycol spacers) film containing $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) is shown in the figure, and are conformable to surface structure on the nanoscale. The emission energies from the MLCT excited states of polypyridyl Ru(II) and Os(II) complexes, including $[Ru(bpy)_3]^{2+}$, increase upon film formation by polymerization of PEG-DMA550 while the MLCT absorption energies and spectral band shapes are similar in both media. The higher-energy excited states in the film lead to enhanced emission quantum yields and longer excited-state lifetimes. The latter was shown to be consistent with quantitative predictions of the energy gap law for nonradiative excited-state decay [1,2].





PEG-DMA550



$[Ru(bpy)_3]^{2+}$

$[Ru(bpy)_3]^{2+}$ and related complexes were also introduced into functionalized resins as rigid media. The complexes in the resins showed high-energy, long-lived and enhanced emission from the MLCT excited states as observed in PEG-DMA550 films.

Acknowledgements. This work was partly supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-FG02-06ER15788 and Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Young Scientists (B), under Grant Number 26810040.

References

1. Knight T.E., Goldstein A.P., Brennaman M.K., *J. Phys. Chem. B*, **2011**, *115*, 64.
2. Ito A., Knight T.E., Stewart D.J., *J. Phys. Chem. A*, **2014**, DOI: 10.1021/jp5019873.

RADIOCONTRAST MATERIALS BASED ON OCTAHEDRAL CHALCOGENIDE RHENIUM CLUSTER COMPLEXES

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Radiocontrast agents are used to improve visibility of inner body structures in X-ray based imaging techniques. Currently the most of radiocontrast agents are based on organic 1,3,5-triiodobenzene derivatives. Low toxicity and high solubility allowed these compounds to integrate into a medical field. However, their application has some drawbacks like cardiovascular, anaphylactic (allergic), painful consequences, and probability of emergence contrast-induced nephropathy. We suppose that octahedral chalcogenide rhenium cluster complexes can be one of the alternative radiocontrast materials. In these compounds a cluster core will act as a radiocontrast component and ligand environment similar to substituent in 1,3,5-triiodobenzene radiocontrast agents will provide biocompatibility.

Initial stage of this work included preparation of rhenium cluster complexes with simple organic ligands – triphenylphosphine (PPh_3), 4-aminopyridine (4-NH_2-py), pyrazine (pyz). Thus we have received cluster complexes: *trans*-$[\{Re_6Q_8\}(PPh_3)_4X_2]$, $[\{Re_6Q_8\}(4\text{-}NH_2\text{-}Py)_6]Br_2$, *trans*-$[\{Re_6Q_8\}(pyz)_4I_2]$ (Q = S, Se, X = Cl, I) by reactions of chalcogenide cluster rhenium complexes $Cs_4[\{Re_6S_8\}X_6]$ and $Cs_3[\{Re_6Se_8\}X_6]$ (X = Cl, Br, I) with molten triphenylphosphine, 4-aminopyridine or pyrazine respectively. All obtained compounds were characterized by X-ray diffraction on the single crystal and powder, IR-spectroscopy and element analysis. For complexes with triphenylphosphine and 4-aminopyridine luminescence spectra were recorded. These complexes are soluble in DMF, but insoluble in water and we were unable to examine their radiocontrast properties.

Also this work include preparation of rhenium cluster complexes with functional organic ligands – isonicotinic acid and phospine derivatives. Reactions of rhenium cluster complexes with functional organic ligands isonicotinic acid (4-py-COOH), isonicotinamide (4-py-$CONH_2$) and 3-(diphenylphosphine)propionic acid ($PPh_2(CH_2)_2COOH$) led to the cluster complexes: $[\{Re_6Q_8\}(PPh_2(CH_2)_2COOH)_6]Br_2$ (Fig. 1), $[\{Re_6Se_8\}(4\text{-py-}COOH)_4Br_2]$, $[\{Re_6Se_8\}(4\text{-py-}CONH_2)_4Br_2]$ (Q = S, Se). Complexes with 4-py-COOH, 4-py-$CONH_2$ were characterized by NMR and IR spectroscopy and element analysis. Complexes with $PPh_2(CH_2)_2COOH$ were characterized by X-ray diffraction on the single crystal and powder, IR-spectroscopy and element analysis.

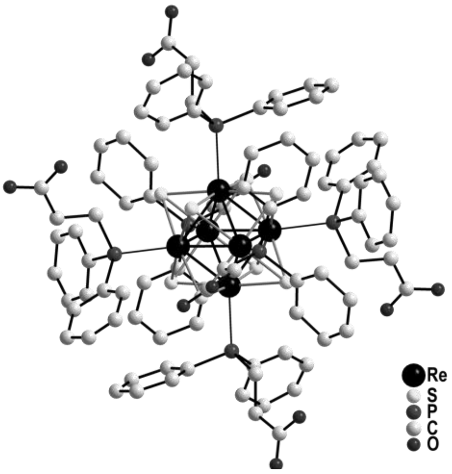

Fig. 1
$[\{Re_6S_8\}(PPh_2(CH_2)_2COOH)_6]^{2+}$

Acknowledgements. The work was financially supported by the Russian Foundation for Basic Research (project № 13-03-90402, № 14-04-01816).

WATER-SOLUBLE POLYNUCLEAR COPPER(II) 15-METALLACROWN-5 LANTHANIDE(III) CLUSTER AS A POSSIBLE CANDIDATE FOR BIOACTIVE DELIVERY

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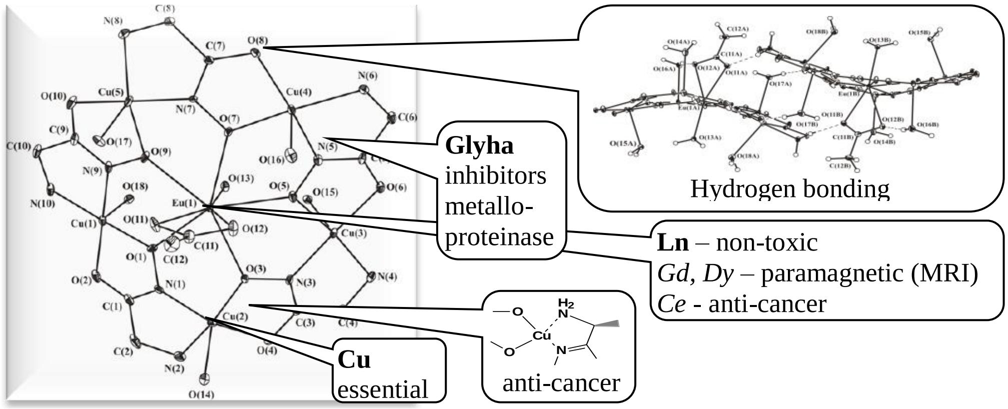
Metallacrowns present a unique group of inorganic cluster complexes, where 3*d*-4*f* compounds have attracted considerable attention because of their excellent architectures and remarkable magnetic properties. $Ln^{3+}[15\text{-}MC_{Cu(II)}\text{-}5]$ complexes contain a planar metallamacrocycle with an open lanthanide central metal surrounded by five Cu^{2+} ring metals. The positive Ln^{3+} charge is balanced by three anions, usually only one being coordinated to the lanthanide ion. Despite a large amount of systematic structural studies of the affinity of Ln complexes derived from α-aminohydroxamic acids for various organic carboxylates, there are no examples of metallacrowns based on the simple glycinehydroximate (Glyha) and acetate ligands. Note, that acetate ions have not been previously seen to bind to the $Ln^{3+}[15\text{-}MC\text{-}5]$. Herein, we present the first $Eu(OOCCH_3)[15\text{-}MC_{Cu(II)Glyha}\text{-}5](NO_3)_2$ metallacrown with acetate binding to the central lanthanide ion.

X-ray crystallography revealed that this metallacrown is pseudo-fivefold symmetric as a consequence of the –Cu(II)Glyha- repeat unit that rotates around the central Eu(III) ion.
The Eu(III) ion is eight-coordinate and contains the bidentate acetate and inner-sphere coordinated water. All five copper(II) ions also have weakly bound H_2O molecules. This system also possesses an interesting network of hydrogen bonds. The acetate ion bound to Eu(III) has hydrogen bonds to the H_2O species connected with the copper(II) ions. There are hydrogen bonds between the water molecules coordinated to Eu(III) and Cu(II). A weak bond is formed between the acetate oxygen and an amine group of another molecule. Additional nitrate ions required for the charge balance are found in the lattice. Remarkably, they do not coordinate to the copper ions.

As water-solubility is a criterion highly desirable for biological applications, we present new, stable, and easily synthesized water-soluble $Ln^{3+}[15\text{-}MC_{Cu(II)Glyha}\text{-}5]$. Analysis of the pharmacophore descriptors (Fig. 1) can also predict the biological activity of these complexes.



Glyha inhibitors metallo-proteinase

Hydrogen bonding

Ln – non-toxic
Gd, Dy – paramagnetic (MRI)
Ce - anti-cancer

Cu essential

anti-cancer

Figure 1. Pharmacophore descriptors of $Ln^{3+}[15\text{-}MC_{Cu(II)Glyha}\text{-}5]$

Acknowledgements. This work was supported by the RSF (Project 14-13-00832).

^{2}H NMR STUDY OF THE ROTATIONAL DYNAMICS OF TEREPHTHALATE PHENYLENES IN METAL-ORGANIC FRAMEWORKS Co-MOF, Ni-MOF AND Zn-MOF: EFFECT OF DIFFERENT METAL CENTERS

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Metal organic framework (MOFs) materials represent a new class of hybrid crystalline porous materials whose pore structure and chemical properties can be very diverse depending on the chemical composition and synthesis procedure. Their unique properties allow exploiting of MOFs in many fields such as adsorptions or separation of gases and liquids, catalysis and others. The MOFs are composed by inorganic nodes (*i.e.* the metal centers) bridged together by organic linkers.

Fragments of organic framework may be mobile and their motion is a huge source of structural information. There are two major mechanisms influencing the rate of molecular motions: steric and the electronic structure. On the fundamental level there exists an unresolved problem: what contribution does each of these mechanisms make?

To investigate this question a set of materials with identical structure but different nature of the metal center was examined. In such approach the steric component remains the same for all materials while the electronic component is affected by different electronic structure of the metal cation. As result, the influence of the MOF metal center variation (Co, Ni, Zn) on the dynamics of terephthalic fragment was observed.

The phenylene dynamics investigation was performed by experimental detection of the ^{2}H NMR spectra line shapes at different temperatures followed by numerical simulation of the registered spectra.

POROUS COORDINATION POLYMERS WITH REDOX-ACTIVE ORGANIC AND METAL-CONTAINING BRIDGES AS HETEROGENEOUS ELECTROCATALYSTS FOR REDUCTIVE ORGANIC HALIDES DEHALOGENATION

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Porous coordination polymers (PCPs) are promising for creation of selective adsorbents and catalysts of organic reactions, in particular, PCPs may be active electrocatalysts of electrochemical organic halides dehalogenation. Usage of heterogeneous catalysts simplifies the separation of products from the catalyst and may lead to size discrimination of substrate molecules. So, the synthesis of PCPs with desired electrochemical properties and the study of their catalytic activity is an important task. The aim of the work was to reveal the influence of PCP structure on its ability to undergo redox transformations, on the characteristics of such transformations (E_p, reversibility) and on PCP's catalytic activity in electrochemical dehalogenation of organic halides.

Redox-active PCPs were obtained by linking of $Fe_2MO(Piv)_6$ or $Cu_2(Piv)_4$ complexes (M = Co, Ni, Piv^- = pivalate) by redox-active units – discrete complexes $M(L1)_2$ (M^{II} = Fe, Co, Ni, Zn, and L1H is a Schiff base from 2-pyridylcarbaldehyde and hydrazide of 4-pyridinecarboxylic acid) or organic compounds. The electrochemical properties of the PCPs were studied by cyclic voltammetry using thin layers of the PCPs on GC electrode or suspensions in the working solution. Electrocatalytic effect was observed as PCP’s cathodic peak current growth after substrate addition to the working solution.

It was found that the redox-activity of $M(L1)_2$ preserved after incorporation of these compounds into PCPs $[\{Fe_2CoO(Piv)_6\}\{Ni(L1)_2\}_{1.5}]_n$ (**1**) and $[\{Fe_2NiO(Piv)_6\}\{Co(L1)_2\}_{1.5}]_n$. The catalytic activity of **1** in reactions of $CHCl_3$ or $CF_2Cl\text{-}CFCl_2$ dechlorination correlated with sorption capacity of this PCP in respect to substrates from vapor-air mixture at 1 atm [1].

Similarly, the redox-activity of L2 (2,6-*bis*(4-pyridyl)-4-(1-naphthyl)pyridine) and L3 (2,6-*bis*(4-pyridyl)-4-(9-anthracyl)pyridine) ligands preserved upon their inclusion in PCPs $[Cu_2(Piv)_4(L)]_n$ and $[Fe_2NiO(Piv)_6(L)]_n$ (L is L2 or L3). $[Cu_2(Piv)_4(L2)]_n$ exhibited weak electrocatalytic effect in 1-bromobutane dehalogenation.

It was shown that calculation of the energy profile for molecule diffusion along the pore in the frames of molecular mechanics approach allowed to estimate the accessibility of pores in PCPs for substrates.

Acknowledgements. The work was partially supported by joint grant of the NAS of Ukraine and the RFBR (Nos. 10-03-13(U), 03-03-14(U) and 14-03-90423), the Council on Grants of the President of the RF (NSh-4773.2014.3), and Russian academy of Science.

1. Lytvynenko A.S., Kolotilov S.V., Kiskin M.A., *Inorg. Chem.*, **2014**, *53*, 4970.

CHIRAL COORDINATION COMPOUNDS OF COBALT(II) FOR CHROMATOGRAPHIC SEPARATION OF OPTICAL ISOMERS OF ALCOHOLS

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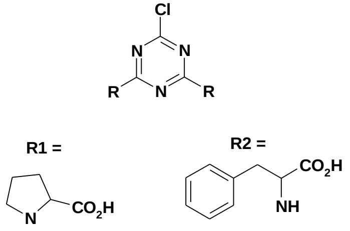
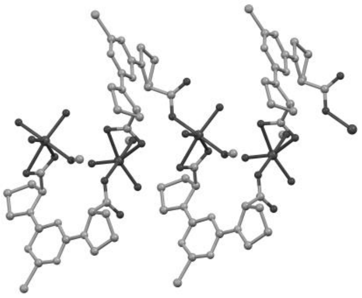
Analysis and preparative separation of optical isomers of organic compounds is important task of biochemistry, pharmacy, etc. Chromatography is one of the most promising methods for such processes. The aim of this work was to study the efficiency of new chiral coordination polymers as stationary phase for chromatographic separation of optical isomers.

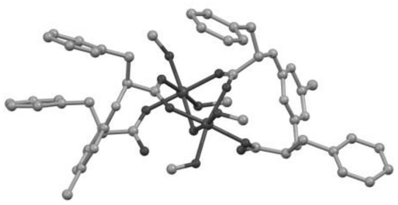
1D coordination polymer $[Co(bpct)(H_2O)_2(MeOH)]_n$ (**1**) and dimer $Co_2(bphact)_2(H_2O)(MeOH)_4$ (**2**) were synthesized using ligands, prepared from S-isomers of aminoacids (ligands are shown on the figure, fragments of aminoacids are N-substituted).



R1 L^{2-} = bpct
R2 L^{2-} = bphact



$[Co(bpct)(H_2O)_2(MeOH)]_n$ (**1**)



$Co_2(bphact)_2(H_2O)(MeOH)_4$ (**2**)

Compound **1** and its desolvated form $[Co(bpct)]_n$ (**3**) were studied as solid phases in chromatographic separation of racemic alcohols. The composition of the mixtures after separation was analyzed using standard chiral analytical column. It was shown that studied sorbents allowed to achieve 3.3 % enantiomeric excess of one of the isomers in conditions of the experiment (Table 1). Among studied alcohols, separation of isomers 2-butanol was the most efficient, and desolvation of the coordination polymer did not improve its efficiency.

Table 1. Values of enantiomeric excess of alcohols after chromatographic separation of racemates on a columns, filled by chiral coordination polymers (± 0.05 %)

Coordination polymer	*ee* (2-butanol), %	*ee* (2-hexanol), %	*ee* (3-hexanol), %
$[Co(bpct)(H_2O)_2(MeOH)]_n$ (**1**)	3.32 (R) [1]	0.19	2.79
$[Co(bpct)]_n$ (**3**)	2.22 (R) [1]	-	-

[1] The letter in brackets indicates the isomer, which is better retained on a column

Acknowledgements. This work was supported by the National Academy of sciences of Ukraine, joint grant of the National Academy of Sciences of Ukraine and RFBR (Nos. 03-03-14(U) and 14-03-90423), the Council on Grants of the President of the RF (NSh-4773.2014.3), and Russian academy of Science.

COORDINATION POLYMERS BASED ON POLYNUCLEAR SODIUM COMPLEXES AND CUCURBIT[5,6]URILS

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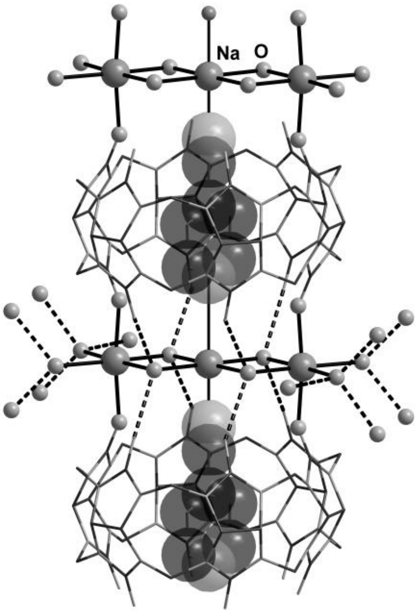
The chain coordination polymers $[Na_2(\mu\text{-}H_2O)(H_2O)CB[5]]Cl_2{\cdot}6H_2O$, $[Na_3(\mu\text{-}H_2O)_4(H_2O)_4(CNPy@CB[6])]Cl_3{\cdot}8H_2O$ were prepared by heating (110°C) of a mixture of sodium chloride, cucurbit[n]uril (CB[n], where n = 5, 6), 4-cyanopyridine, and water. According to X-ray diffraction data, binding of polynuclear cations with CB[n] occurs through coordination of the oxygen atoms of the cucurbit[n]uril portals to sodium atoms. Both complexes of the above composition isolated to the solid phase as supramolecular compounds with CB[n] were structurally characterized for the first time.

The crystal structure of $[Na_3(\mu\text{-}H_2O)_4(H_2O)_4(CNPy@CB[6])]Cl_3{\cdot}8H_2O$ is composed of alternating $[Na_3(\mu\text{-}H_2O)_4(H_2O)_4(CNPy@CB[6])]^{3+}{}_\infty$ polymeric chains, solvent water molecules, and chloride anions. The polymeric chain consists of alternating CB[6] molecules linked through carbonyl groups to the centrosymmetric linear trinuclear aqua complex cations $[Na_3(\mu\text{-}H_2O)_4(H_2O)_4]^{3+}$. The increase in the macrocycle size from CB[5] to CB[6] is responsible for the formation of trinuclear rather than binuclear complex. Each cucurbituril molecule is connected to two trinuclear complexes, the terminal sodium atoms are connected to two cucurbituril molecules (via the carbonyl group of one cucurbituril molecule and the carbonyl group of the other molecule). The terminal sodium atoms are also coordinated by two oxygen atoms of the bridging aqua groups and two oxygen atoms of the terminal aqua ligands. The central sodium cation is coordinated by the nitrogen atom of 4cyanopyridine, which is located in the cavitand cavity and is disordered over two positions, and by four oxygen atoms of the bridging aqua ligands. The coordination number of all sodium atoms are 6.



Acknowledgements. The work was financially supported by the President of the Russian Federation Grants (program of state support of leading scientific schools and young PhD grant EA Kovalenko MK-2514.2014.3).

NANOPARTICLES OF BiOCl IMMOBILIZED IN METAL-ORGANIC FRAMEWORK: A HYBRID MATERIAL WITH ENHANCED PHOTOCATALYTIC PERFORMANCE

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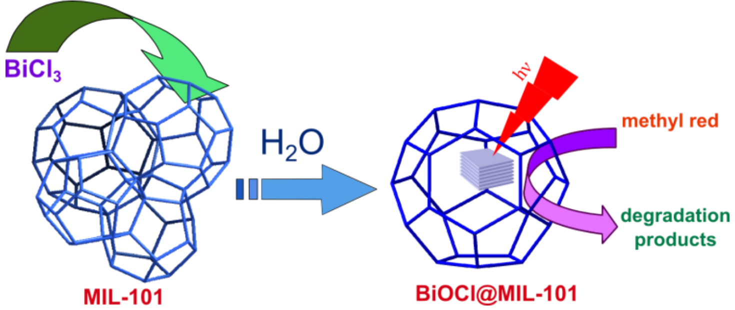
Research aiming the development of highly efficient photocatalysts remains a very actual task, i.a. in terms of treatment of various toxic pollutants. Among the whole palette of photocatalysts, there is a large family of materials based on bismuth oxohalides (BiOCl, BiOBr and BiOI) which are known to be active in degradation of different organic and inorganic substrates. The main factors affecting the activity of the photocatalyst are morphology, surface area and size of particles. These characteristics determine the goal of further development of synthetic methods and approaches which currently include solvothermal, microwave-assistant, ionic-liquid and many other routes. The ultimate objectives are: 1) to achieve the biggest surface area, 2) to maximize the stability of catalyst morphology and 3) to find the simplest and cheapest method of synthesis.

In this work, we present the original synthetic route to hybrid catalyst based on mesoporous chromium(III) terephthalate MIL-101 with embedded bismuth(III) oxychloride which reveals perfect activity in degradation of methyl red. Nanoparticles of BiOCl have been immobilized into MIL-101 matrix via two step procedure: 1) impregnation of MIL-101 by $BiCl_3$ solution; 2) hydrolysis of $BiCl_3$ by water washing of solid product. Only a small amount of Bi was determined by elemental analysis: 0.22 Bi atoms per formula unit or about 13 atoms per mesocage of MIL-101. Such small additive of guests do not affect on crystal structure of framework according to XRD analysis. The photocatalytic behavior was tested on methyl red degradation process. The methyl red solution (~5 mM) is fully discolored after 10 min of irradiation by Hg lamp (1 kW). The kinetic law for this process has first order and rate constant 0.11 min^{-1} which is one of the best constant for bismuth oxohalides based catalysts and exceeds the values for BiOCl catalysts in several times.



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PHOTOGENERATION OF THE TRIPLET STATES AND SINGLET OXYGEN BY HEXANUCLEAR MOLYBDENUM CLUSTERS

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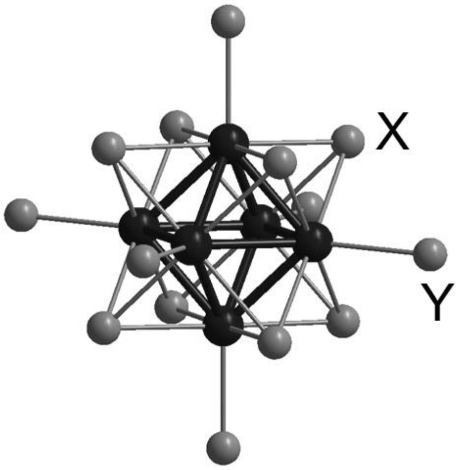
Metal complexes with luminescence originating from the triplet states have attracted a broad interest over the past few years for various applications such as light-emitting devices, dye-sensitized solar cells, optical oxygen sensors, and singlet oxygen, $O_2(^1\Delta_g)$, sensitizers. For each of these applications, various key parameters such as excitation and emission spectral features, quantum yields of luminescence, and singlet oxygen formation, as well as chemical, redox and photochemical stability have to be assessed for optimal performances. These complexes are usually based on noble metals like Ir, Pt, Ru, or Os that are relatively expensive. In this respect, hexanuclear molybdenum clusters constitute a relevant alternative to the complexes so far used thanks to their tunable photophysical properties [1-3].

The hexanuclear molybdenum clusters are effective in producing of $O_2(^1\Delta_g)$ by intermolecular energy transfer. Quenching of the cluster triplet states (i.e., luminescence or transient absorption signals) by oxygen is characterized by kinetics parameters that allow comparison with other systems. The formation of $O_2(^1\Delta_g)$ can be directly determined by steady-state and time-resolved luminescence spectroscopy based on monitoring weak phosphorescence around 1270 nm, by chemical quenching methods, or by ESR spin trapping.



Molecular structure of $[Mo_6X_8Y_6]^{2-}$

In this contribution, we report on the excited-state dynamics, luminescence, and generation of $O_2(^1\Delta_g)$ of a series of hexanuclear molybdenum cluster complexes $[Mo_6X_8Y_6]^{2-}$ in acetonitrile and in aqueous solution. The properties are correlated with the nature of ligands. Our results show that varying the type of the attached ligand on the Mo_6 cluster core allows for fine-tuning of their photophysical and optical properties. An ideal combination is the iodine inner ligands and the trifluoroacetate apical ligands. In this case, the Mo_6 cluster possesses efficient red luminescence, effective quenching of the triplet states by oxygen, and high yields of singlet oxygen formation.

This work was financially supported by the Czech Science Foundation (13-05114S).

1. Jackson J.A., Turro C., Newsham M.D., *J. Phys. Chem.* **1990**, *94*, 4500.
2. Kirakci K., Kubát P., Dušek M., *Eur. J. Inorg. Chem.* **2012**, 3107.
3. Kirakci K., Kubát P., Langmaier J., *Dalton Trans.* **2013**, *42*, 7224.

SPIN-CROSSOVER IN THE IRON(II) COMPLEXES WITH TRIS(PYRAZOL-1-YL)METHANE AND CLUSTER ANIONS $[Mo_6Hal_{14}]^{2-}$

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Spin-crossover (spin transition, SCO) appears in transition metal complexes with the electron configuration d^4-d^7 in an octahedral environment of ligands. Changing the spin multiplicity is influenced by temperature, pressure, or light of a specific wavelength. Complexes of iron(II) with polynitrogen-containing ligands have SCO $^1A_1 \leftrightarrow {}^5T_2$. These include compounds with *tris*(pyrazol-1-yl)methane ($HC(pz)_3$), which are bifunctional, therein spin crossover is accompanied by thermochromism (color change from white to pink (magenta)). Currently a number of complexes of various salts of iron(II) with $HC(pz)_3$ have been synthesized [1,2]. They have a high temperature SCO. At high temperature of the transition, in some cases T_c is close to the decomposition temperature of the complex that makes difficulties in the interpretation of magnetochemical data. Because of this, a search of compounds of iron(II) with $HC(pz)_3$ and the outer-anions, which may lower the temperature of SCO, is carried out.

The complexes of Fe(II) with $HC(pz)_3$, containing the outer sphere cluster anions, of the composition $[Fe(HC(pz)_3)_2][Mo_6Cl_{14}]\cdot 2H_2O$ (**I**) and $[Fe(HC(pz)_3)_2][Mo_6Br_{14}]$ (**II**) have been synthesized. Investigation of temperature dependence $\chi(T)$ shown that in both complexes spin crossover $^1A_1 \leftrightarrow {}^5T_2$ with hysteresis is observed (Fig. 1.2). For **I** the direct transition temperature, when heated, $T_c\uparrow$ is equal to 271 K, the return transition temperature, when cooled, $T_c\downarrow$ is equal to 268 K; for **II** – $T_c\uparrow = 270$ K, $T_c\downarrow = 267$ K.

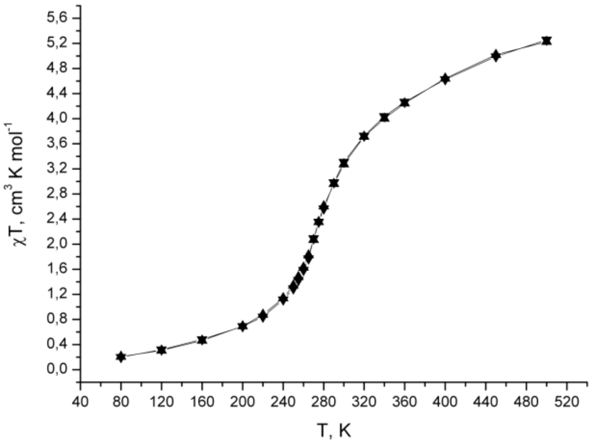

Рис. 1. Curve $\chi T(T)$ of **I**.

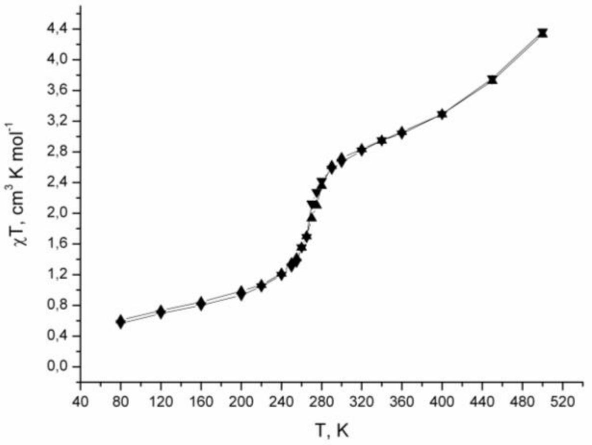

Рис. 2. Curve $\chi T(T)$ of **II**.

Spin-crossover in mentioned complexes is accompanied by thermochromism, color change for **I** from beige to pink, for **II** – from yellow to orange.

1. Long G.J., Grandjean F., Reger D.L., *Top. Curr. Chem.*, **2004**, *233*, 91.
2. Lavrenova L.G., Shakirova O.G., *Eur. J. Inorg. Chem.*, **2013**, 670.

OCTAHEDRAL RHENIUM CLUSTER *TRANS*-$[Re_6S_8(CN)_4L_2]^{n-}$ AS A PRECURSORS FOR LIQUID CRYSTAL PHASES

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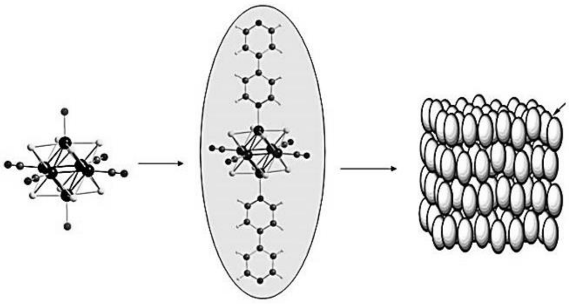
Octahedral cyanide rhenium clusters are well known as a good building blocks for obtaining of new frameworks as Super Prussian Blue analogues. Other properties of octahedral rhenium clusters are magnetic, electronic and luminescent related to the number of metallic electrons available for metal–metal bonds (VEC). However, their use as a functional material is limited due to the ceramic-like behavior of the solid-state forms. Preparation of a hybrid cluster-organic materials that possess the properties of the cluster and an organic part is a promising direction of development of cluster chemistry. For example, liquid-crystalline materials containing metallic clusters are an attractive emerging class of multifunctional molecular hybrid nanomaterials. As metallomesogens, they combine the specific properties of metallic clusters with the anisotropy-related properties of liquid crystals. The simplest way to obtain LC containing clusters is self-organization process combined negative charged inorganic cluster with organic specific mesogenic organic cations. In this way lamellar mesophases based on $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se, Te) with $(C_nH_{2n+1}(CH_3)_3N^+$, n = 14, 16, 18) and $[Re_6Q_8(CN)_6]^{4-/3-}$ with cyanobiphenylyloxydecyldimethylammonium action have been obtained [1, 2].

Authors propose a new approach for obtaining LC phases based on octahedral rhenium cluster complexes. Recently cluster complex *trans*-$[Re_6S_8(CN)_4(OH)_2]^{4-}$ was synthesized. Four cyano groups in equatorial plane are stable for substitution, two hydroxo groups in trans-position can be protonated or replaced to halides [3, 4]. The substitution of hydroxo to N-donor organic ligand with long carbonic chain should lead to formation of LC mesophases. Herein we report substitution of hydroxo groups to model N-donor ligands: pyridine, 4,4'-bipyridine, 4-aminopyridine and their derivatives.



Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Grant No 14-03-31860).

1. Suh M.J., Vien V., Huh S. et al., *Eur. J. Inorg. Chem.*, **2008**, *5*, 686.
2. Molard Y., Ledneva A. Amela-Cortes M et al., *Chem. Mater.*, **2011**, *23*,. 5122.
3. Naumov N.G., Ledneva A.Y., Kim S. J. et al., *J. Cluster Sci.*, **2009**, *20*, 225.
4. Ledneva A.Y., Brylev K.A., Smolentsev A.I. et al., *Polyhedron*, **2014**, *67*, 351.

Co AND Ni POLYOXOMOLYBDATES AS CATALYST PRECURSOR FOR CCVD SYNTHESIS OF FEW-WALLED CARBON NANOTUBES

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Catalytic chemical vapor deposition (CCVD) has several advantages making it the most widely used method for the synthesis of carbon nanotubes (CNTs). This method is based on the decomposition of carbon-containing molecules on catalyst particles of transition metals such as Fe, Ni and Co. CCVD synthesis is a multivariable process, however, the main influence on the structure, properties and yield of carbon material provides the catalyst. Adding metals such as W and Mo to the catalyst allows influencing the properties of the carbon product. However, the role of Mo during a CNT nucleation growth is still ambiguous.

Today grow the CNTs with an identical or near the same structure is priority direction. According to the experimental data there is an obvious dependence of CNT diameter on the size of catalytic particles. This fact had motivated to use metal-containing molecular clusters for the formation of discrete catalyst particles with a controlled size. Polyoxometalates, where metal atoms are linked by oxygen bridges in a compact cluster, satisfy these requirements. Among this class of inorganic compounds, the polyoxomolybdate clusters combining Mo with a transition metal are most attractive for the CCVD synthesis of CNTs. In the present paper we firstly report the use of ε-Keggin-type polyoxomolybdate clusters $Mo_{12}O_{28}(\mu_2\text{-}OH)_{12}\{Ni(H_2O)_3\}_4$ and $Mo_{12}O_{28}(\mu_2\text{-}OH)_{12}\{Co(H_2O)_3\}_4$ as a catalyst precursor for the CCVD synthesis of CNTs. A study of cluster decomposition products allowed developing idea about involvement of Mo in the formation of CNTs. The structure of CNTs was analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

Investigation of thermal behavior of the clusters showed formation of $NiMoO_4$ and $CoMoO_4$ together with MoO_3, which is sublimated starting from ~740°C. Decomposition of polyoxomolybdate clusters inserted into MgO yielded supported nanoparticles with an average size of ~3 nm. Using these nanoparticles, the CNTs were produced from ethylene at 900°C. Based on analysis of the products of polyoxomolybdate decomposition and CCVD synthesis we concluded that growth of CNTs is catalyzed by the Ni/Mo and Co/Mo alloys. TEM investigation indicated that the CCVD products contain individualized few-walled CNTs with narrow diameter distribution, which are not contaminated by amorphous carbon species. From the CK-edge NEXAFS spectra the walls of CNTs are well-graphitized and have only an insignificant amount of oxygen-containing surface groups. We suppose that carbon has the lower solubility in Ni/Mo and Co/Mo alloys than in corresponding transition metals. As the result, the rate of tubular carbon growth is slowed thus improving the quality and purity of the CNT product.

Acknowledgements. This work was supported by RFBR 14-03-32089 number.

ACTIVATION AND TRANSFORMATION OF HALOCARBONS AND AMINES IN THE COORDINATION SPHERE OF THE OSMIUM CLUSTER METALATE-ANION

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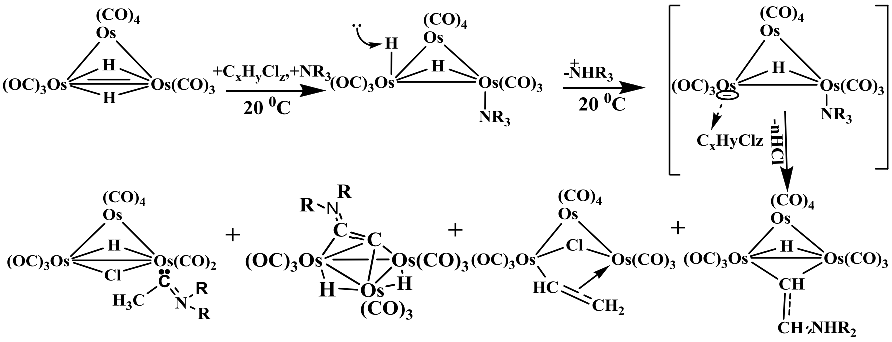
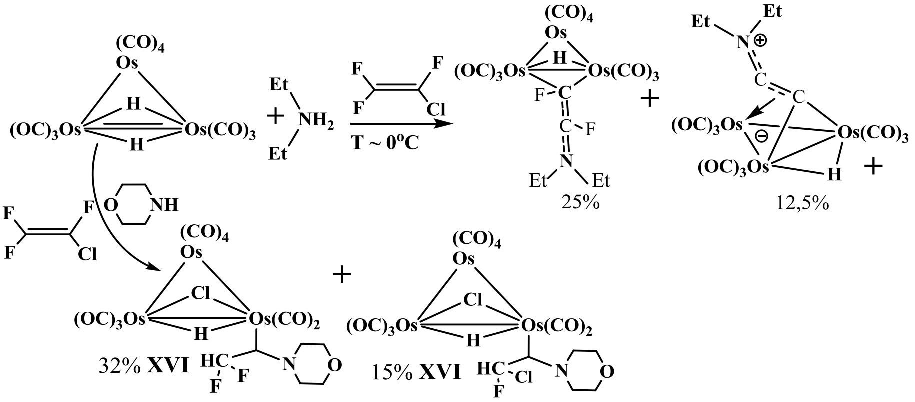
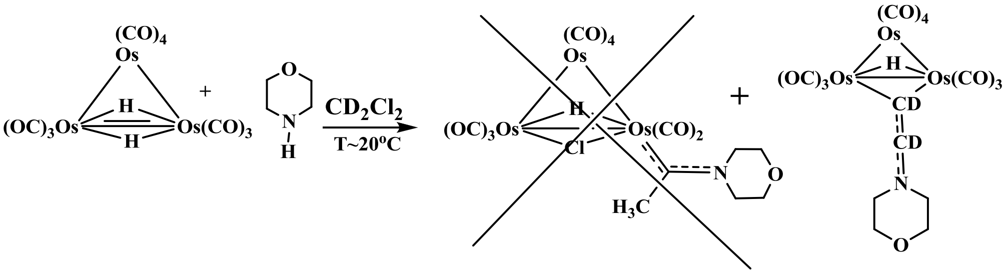
New reactions were studied in which the cluster metalat-anions $R_3NH[(\mu\text{-}H)Os_3(CO)_{10}NR_3]$, $PPN[(\mu\text{-}H)Os_3(CO)_{11}]$ and $K_2[H(\mu\text{-}H)\ Os_3(CO)_{10}]$ readily react with halocarbons (CH_2Cl_2, $C_2H_2Cl_2$, C_2HCl_3, CF_3Cl, etc) and various amines in normal conditions. A typical conversion scheme of a halohydrocarbon and an amine in the coordination sphere of the $R_3NH[(\mu\text{-}H)Os_3(CO)_{10}NR_3]$ is shown below.



All organic ligands in new complexes contain no chlorine. In the case when ftorohloroethylene is used, not only fluoro, but even chloro remain in the ligand.



We attribute this to a higher energy bond of C-F compared with C-Cl. When CD_2Cl_2 is used in the reaction, deuterium is included in the enamine ligand.



THE OCTAHEDRAL IODIDE CLUSTERS OF Mo(II) AND W(II)

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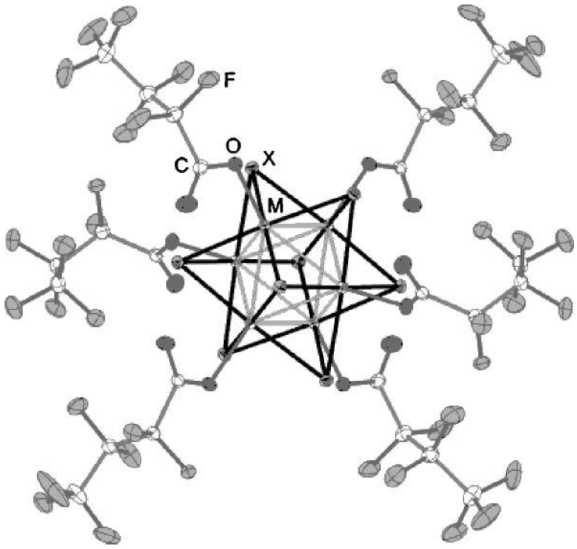
The octahedral halide bridged clusters of Mo(II) and W(II) of a general formula of $[\{M_6(\mu_3\text{-}I)_8\}L_6]$ (M = Mo, W; L = anionic or neutral; $\{M_6(\mu_3\text{-}I)_8\}^{4+}$ is the cluster core) possess remarkable photophysical properties which can be used in new luminescent materials. In particularly, the complex $(Bu_4N)_2[Mo_6I_8(C_3F_7COO)_6]$ (fig. 1) displays extraordinarily bright long-lived red phosphorescence both in solution and solid state, with the highest emission quantum yields (λ_{em} = 668 nm, φ_{em} = 0.59, τ_{em} = 303.0 ms) among hexanuclear metal cluster complexes of Mo [1]. The emission spectra of clusters with $\{W_6(\mu_3\text{-}I)_8\}^{4+}$ core, their excited state lifetimes and emission quantum yields have not been reported so far. To follow qualitative change of phosphorescent properties of cluster complexes of molybdenum and tungsten, a representative set of carboxylate complexes $[\{M_6(\mu_3\text{-}I)_8\}(OOCR)_6]^{2-}$ (M = Mo, W; R = CF_3, C_2F_5, C_3F_7, $C_{10}H_7$, C_6H_5, C_6F_5) was synthesized in this work, because the photophysical characteristics of the clusters of Mo(II) and W(II) are dependent on both the inner halide ligands, X, in the cluster core and terminal (outer) ligands, L and extraordinarily bright long-lived phosphorescence in the red/orange region of the spectrum can be expected for iodide molybdenum and tungsten clusters complexes with fluorinated organic ligands. The complexes were characterized by X-ray single-crystal diffraction (as well as by mass spectrometry, ^{19}F and ^{13}C NMR, luminescence spectroscopy).



Such luminescent complexes are of practical interest for design of a new generation of sensor materials and farmaceuticals (for conversion of triplet O_2 into singlet for killing cancer cells), for experimental cytology and histology (as luminescent markers of different sites in cells and tissues).

Acknowledgements. The authors thank Dr. P.A. Abramov (IIC SB RAS) for X-ray analysis.

1. Mihailov M.A., Brylev K.A., et al., *Dalton Trans*., **2011**, *40*, *6375*.

INTERATOMIC INTERACTIONS AND RELATIVISTIC EFFECTS IN NMR OF Rh AND Ir COMPLEX COMPOUNDS

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NMR of transition metal complex and cluster compounds may give lots of measurable parameters for interpretation. Unfortunately, today in this area there are no well established structure-property relations. This is mostly due to great variety of interatomic interactions with transition metal atoms, but also due to the impact of various relativistic effects. In this work, two pairs of complex compounds, $[Cp^*M(SnCl_3)_3]^-$ and $[Cp^*_3M_3Se_2]^{2+}$ M = Rh, Ir [1,2], are compared in terms of how the change of the metal affects the bonding structure and NMR of ^{119}Sn and ^{77}Se nuclei (so-called, HALA effect). In both cases geometrical structures of Rh compounds are almost identical to their Ir counterparts. Nevertheless, NMR shifts for ^{119}Sn (19 ppm for $[Cp^*Rh(SnCl_3)_3]^-$ and –307 ppm for $[Cp^*Ir(SnCl_3)_3]^-$) and ^{77}Se (1683 ppm for $[Cp^*_3Rh_3Se_2]^{2+}$ and 943 ppm for $[Cp^*_3Ir_3Se_2]^{2+}$) are noticeably different.

DFT calculations were performed in ADF program suit [3] using TZP basis and BP86 functional. To account for relativistic effects, zeroth-order regular approximation was used. NMR parameters were calculated with GIAO method. To characterize interatomic interactions, the topological analysis of electron density and Electron Localization Function (ELF) was performed within DGrid-4.6 [4].

Topological properties of interatomic interactions in $[Cp^*M(SnCl_3)_3]^-$ M = Rh, Ir pair of complexes are quite similar, with a great portion of 5s Sn orbital in M–Sn bond (according to MO analysis). This agrees with the fact that ^{119}Sn NMR shifts calculated with only scalar relativistic effects are almost equal for both complexes (220 ppm for $[Cp^*Rh(SnCl_3)_3]^-$ and 209 ppm for $[Cp^*Ir(SnCl_3)_3]^-$), while the shifts calculated with Spin-Orbit effects lie at 42.5 ppm for $[Cp^*Rh(SnCl_3)_3]^-$ and –257.5 ppm for $[Cp^*Ir(SnCl_3)_3]^-$, which is much closer to experimental data. Thus, here we observe large Spin-Orbit HALA relativistic effects.

For the $[Cp^*_3M_3Se_2]^{2+}$ M = Rh, Ir pair of complexes, the topological analysis of electron density shows the presence of M-M bonds for Ir complex, while, for Rh complex, there are no such bonds. ^{77}Se NMR shifts calculated with only scalar relativistic effects 1849 ppm for $[Cp^*_3Rh_3Se_2]^{2+}$ and 1131 ppm for $[Cp^*_3Ir_3Se_2]^{2+}$. Therefore, in this case, changing Rh to Ir significantly affects the bonding structure of the complex but does not increase the impact of Spin-Orbit relativistic effects on NMR shielding of ^{77}Se nuclei.

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1. Abramov P.A., Sokolov M.N., Mirzaeva I.V., *J. Organomet. Chem.* **2014**, *754*, 32.
2. Abramov P.A., Sokolov M.N., Mirzaeva I.V., *Russ. J. Coord. Chem.* **2013**, *39*, 379.
3. ADF: SCM, Vrije Universiteit, Theoretical Chemistry: Amsterdam, The Netherlands, http://www.scm.com.
4. Kohout, M. DGrid, version 4.6, Radebeul, http://www.cpfs.mpg.de/~kohout/dgrid.html.

STRUCTURE AND MAGNETIC PROPERTIES OF BINUCLEAR Ni(II) COMPLEXES WITH AROMATIC CARBOXYLATE ANIONS AND 2,3-LUTIDINE

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Molecular binuclear complexes are of wide interest for studying of exchange interactions between unpaired electrons of paramagnetic centers. Type and intensity of exchange interactions can vary depending on type and number of bridging ligands. That makes possible to obtain compounds with specified properties such as carboxylate bridged complexes $[M_2(O_2CR)_4L_2]$ (L= N- or O-donor ligand) with paddlewheel geometry. Correlation between geometry features and magnetic behavior of such relatively simple molecules is a task of inorganic chemistry.

Here we present new three nickel(II) complexes $[Ni_2(O_2CR)_4(2,3\text{-lut})_2]$ (HO_2CR is 3,5-di-tert-butylbenzoic (**1**, Fig. 1), 3,5-di-tert-butyl-4-hydroxybenzoic (**2**) or 1-naphthoic (**3**) acids) with bulky carboxylate substituents. All compounds have been characterized by elemental, IR, single crystal X-Ray, and XPRD analysis.

Magnetic measurements of **1** (Fig. 2) showed strong interactions between nickel(II) ions in molecule of the complex. Fitting of experimental data in full range of temperatures (T = 2-300 K) using Van Vleck's Equation (the case $S_1 = S_2 = 1$ and subject to presence of noninteracting paramagnetic ions Ni^{2+}) allows to calculate following parameters $g = 2.36\pm0.03$ and $-2J = 60\pm0.4\ cm^{-1}$ (percentage of noninteracting paramagnetic sites is less than 2%). The value of exchange interactions in **1** is typical for paddlewheel nickel(II) complexes.

The structural features of the isolated compounds and details of magnetic calculations in comparison with the known data will be presented to the report.

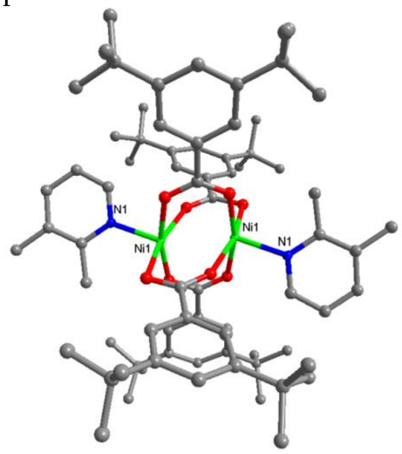

Figure 1. Molecular structure of **1**.

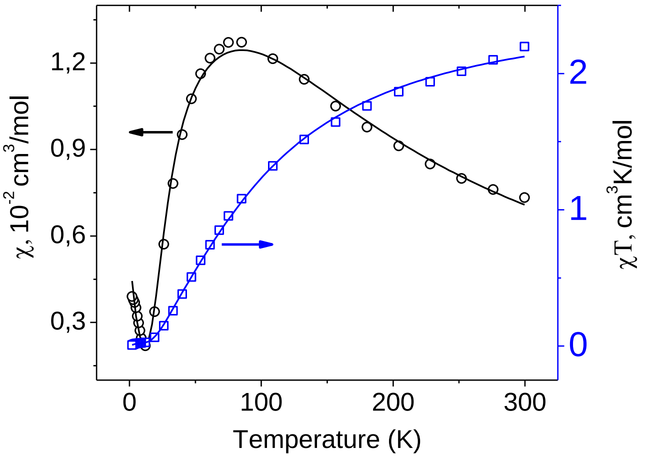

Figure 2. χ (o) *vs T* and χ*T* (□) *vs T* plots for **1** along with calculated curves.

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SOME NEW RESULTS IN THE CHEMISTRY OF $\{Mo_2S_2O_2\}$ COMPLEXES

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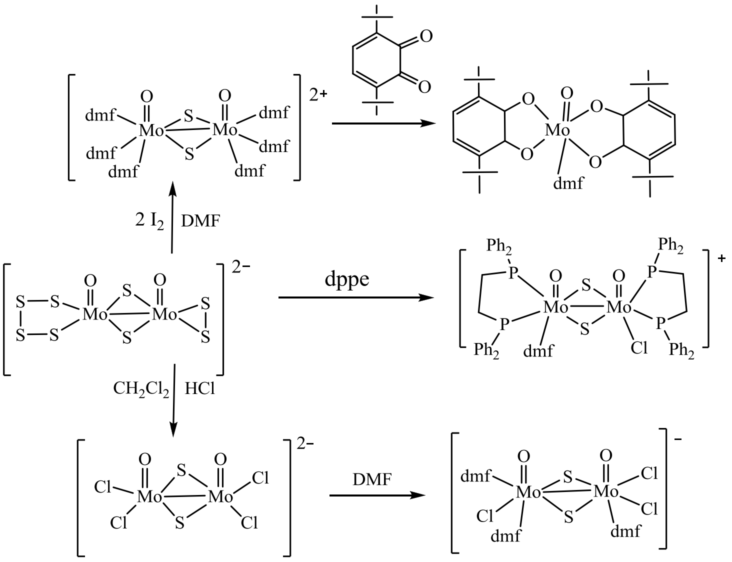
Complexes containing $\{Mo_2S_2O_2\}$ moiety are known from 1960s. Interest towards such compounds is concerned with a number of areas of potential application: from bioinorganic to catalysis.

This work is focused on synthesis and structural characterization of some new and known $\{Mo_2S_2O_2\}$ complexes containing labile ligands as well as some reactions of them. Main results of the work are shown in the scheme below.

$[Mo_2S_2O_2(DMF)_6]I_2$ is well-known more than 20 years [1], but it was not structurally characterized. Single crystals were obtained in this work and the structure was determined by X-ray.

$(Me_4N)_2[Mo_2O_2S_2Cl_4]$ was prepared using reaction of $(Me_4N)_2[Mo_2O_2S_8]$ with HCl in CH_2Cl_2. This compound does not contain O-donor ligands and is assumed as a suitable precursor of different $\{Mo_2S_2O_2\}$ derivatives. Lability of the Cl^- ligands is exhibited by reaction with DMF resulting in substitution of anionic ligand with a neutral one.
The presentation is focused on discussion of these and several other reactions and structures.



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1. Coucouvanis D., Toupadakis A., Lane J.D. et al., *J. Am. Chem. Soc.*, **1991**, *113*, 5271.

SYNTHESES, STRUCTURAL CHARACTERIZATION OF LITHIUM CARBOXYLATE FRAMEWORKS AND GUEST-DEPENDENT PHOTOLUMINESCENCE STUDY

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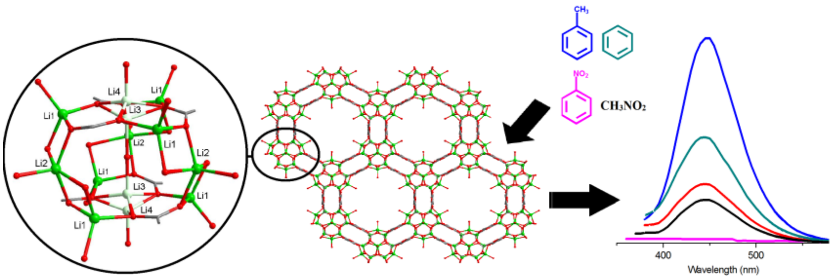
Five novel 3D lithium-organic frameworks $[Li_2(H_2btc)]\cdot C_4H_8O_2$ (**1**) (H_4btc − 1,2,4,5-benzenetetracarboxylic acid), $[Li_2(H_2btc)]$ (**2**), $[Li(H_2tatab)]\cdot 5H_2O$ (**3**) (H_3tatab − 4,4',4"-*s*-triazine-1,3,5-triyltri-*p*-aminobenzoic acid), $[Li_{11}(H_3O)(H_2O)_5(tml)_6)]\cdot 8C_4H_8O_2$ (**4**) (H_3tml − 1,2,4-benzenetricarboxylic or trimellitic acid), $[Li\{Li(nmp)\}\{Li(H_2O)(nmp)\}\{Li(nmp)_2\}_2(H_2tms)(Htms)_2]\cdot NMP\cdot EtOH$ (**5**) (H_3tms − 1,3,5-benzenetricarboxylic or trimesic acid, nmp − 1-methyl-2-pyrrolidinone) were synthesized by solvothermal method and characterized by X-ray crystallography, IR spectroscopy and TG analysis. Compounds **1** and **2** feature the same framework composition but different guest-controlled structures and topology. Compounds **1** and **3** have highly opened structures with pore sizes 4.5 × 4.5 Å and 8 × 10 Å correspondingly. Compound **4** consists of unique undecanuclear Li carboxylate complex $\{Li_{11}(H_2O)_5(RCOO)_{18}\}$ and contains pores with diameter 7 Å. This impressive unique $\{Li_{11}\}$ fragment is an interesting example of rare lithium polynuclear complexes. Furthermore, compound **4** is capable of reversible solvent exchange process. The photoluminescence properties of this porous compound were shown to depend on the nature of the guest molecules, providing the opportunity for the selective detection of dangerous explosive aromatic molecules.



$\{Li_{11}(H_2O)_5(RCOO)_{18}\}$ **$(H_3O)[Li_{11}(H_2O)_5(Html)_6]$**

Acknowledgements. This work is supported by the Grant of the Government of the Russian Federation (14.Z50.31.0006, leading scientist M. Schröder).

STEP-BY-STEP ACTIVATION OF A BIPOROUS COORDINATION FRAMEWORK

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Metal-organic frameworks, which possess nano-structured voids within their structure, are the objects of an ever-growing interest in the recent decades due to their prominent sorption, luminescent and catalytic properties. Generally the framework's channels demonstrate geometrical and chemical uniformity. More rare case presents so-called biporous materials, which have two distinct isolated cages or 1D channels with different chemical interface. Their co-existence broads the host-guest chemistry of such porous compounds since the difference in the chemical behaviour of the pores allows the selective sorption governed by the chemical affinity.

Recently we reported an interesting porous compound $[Zn_4(dmf)(ur)_2(ndc)_4]$ (ndc^{2-} = 2,6-naphthalenedicarboxylate, ur = urotropin, **1d**) and its guest-selective luminescence properties [1]. According to the single-crystal X-ray diffraction data, this framework $[Zn_4(ur)_2(ndc)_4]$ has complicated structure containing two types of channels. First ones (channels α) are hexagonal with characteristic dimensions 9.5×11 Å, second ones (channels β) are ellipsoidal with characteristic dimensions 4×5 Å.

Both type of channels in the as-synthesized crystals **1d**$\cdot$5DMF$\cdot H_2O$ are filled with DMF/H_2O solvent molecules: five guest DMF and one H_2O in the α-channels and one DMF in the β-channels having relatively long Zn–O(dmf) coordination interaction (2.282 Å). Common thermal activation of **1d**$\cdot$5DMF$\cdot H_2O$ at low pressure removes the solvent molecules from the α-channels only, resulting in a permanently porous **1d**. The further treatment destroys the framework, making it impossible to obtain fully activated $[Zn_4(ur)_2(ndc)_4]$ (**1**) at higher temperature.

Herein we report serendipitous, yet successful step-by-step activation of both types of channels in **1**, meditated by S_4N_4 guest molecules. The reaction of the compound **1d** with S_4N_4 acetone solution yields to the orange crystals of the compound $[Zn(S_4N_4)(ur)_2(ndc)_4]\cdot x Me_2CO$ (**1s**). The further treatment of **1s** in acetone with subsequent activation in the dynamic vacuum allowed us to obtain the compound **1**. As could be expected, the total pore volume and the surface area of **1** are gradually increased, compared to **1d**. More strikingly, the truly biporous nature of the compound **1** was demonstrated by selective adsorption experiments through quantative separation of the molecular mixture of S_4N_4 and benzene onto the corresponding channels with appropriate functionality.

Acknowledgements. This work was supported by the Government of the Russian Federation (Grant 14.Z50.31.0006) and Russian Foundation for Basic Research (Grant 14-03-31985).

1. Sapchenko S.A., Samsonenko D.G., Dybtsev D.N., Melgunov M.S., Fedin V.P. *Dalton Trans.*, **2011**, *40*, 2196.

TRANSFORMATIONS OF VARIOUS AMINES AND CHLOROCARBONS WITHIN COORDINATION SPHERE OF $[(\mu\text{-}H)_2Os_3(CO)_{11}]$

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In the metal complex catalysis, central metal atoms provide their vacant orbitals and usually act as electrophiles. Stone F.G.A and King R.B *et al.* have shown that the metalate- anions can react with organic electrophiles such as alkyl iodides, bromides and fluorides. It was believed that no clustered carbonyl anions can be effective nucleophiles because their charge is distributed onto a large number of carbonyl ligands.

In this report, we discuss the reactions of the cluster carbonyl-anion generated *in situ* with various halocarbons and heterocyclic amines. Complexes which are formed in these reactions contain coordinated haloethylenes which can interact with various amines to form enamine ligands. Activation of the organic molecules results in formation of C-C, C-N, C-Os, Os-Hal bonds at room temperature. New cluster complexes containing carbene or enamine ligands are formed in these reactions.

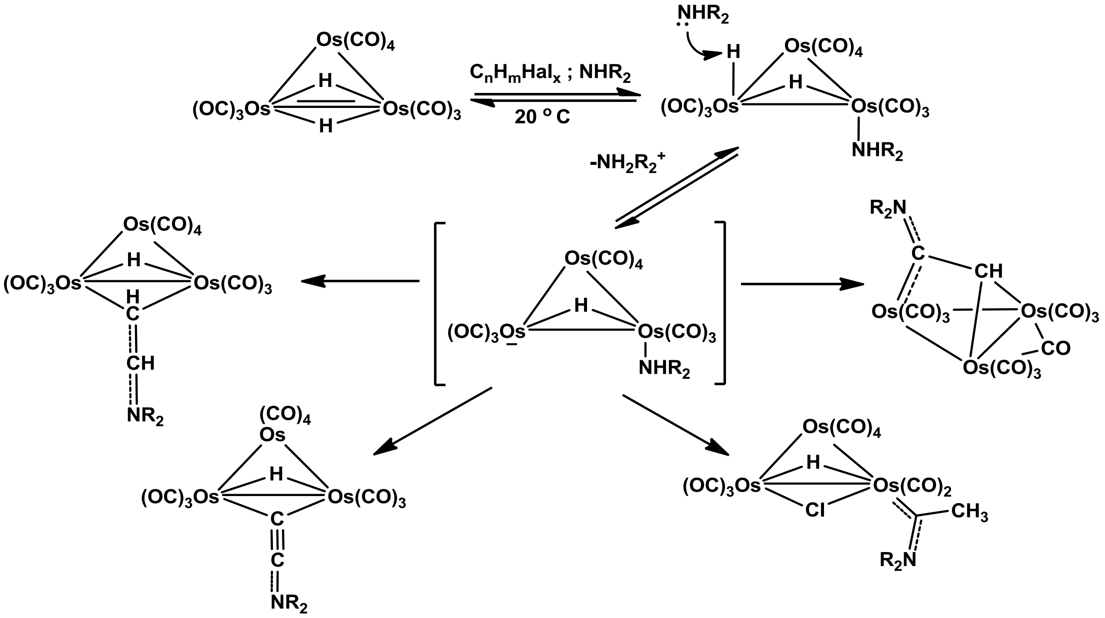

Figure 1. Reaction pathways.

Primary, secondary, tertiary, acyclic or cyclic amines, aminoacid esters, chloroethylenes and trifluorochloroethylene are used. Yields and the types of the resulting products strongly depend on both amines and halocarbons structures. All synthesized compounds were identified by IR and NMR-spectroscopy, elemental analysis and X-Ray difraction analysis.

PHOTOCHEMISTRY OF HYBRID PHOTOCHROMIC MATERIAL FORMED METALLORGANIC FRAME AND DIARYLETHENE.

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Great interest for microelectronics are compounds exhibiting photochromism in the solid state. Generally, side reactions with the solvent to cause photodegradation and thus photochromic in solid state are more stable. But, a few photochromic active in solid phase and the quantum yield is much smaller than in the solution.

The approach developing in this work is to use metal-organic coordination polymers (called metal-organic framework (MOF)[1]) for producing supramolecular compounds with organic photochroms. We believe, that this can result in creation of hybrid photochromic material with a high quantum yield and a high resistance to photodegradation.

Figure 1. The structure of Adduct-1 (by X-ray diffraction analysis).

The MOF $[Zn_4(dmf)(ur)_2(ndc)_4]$ (ndc^{2-} is 2,6-naphtalenedicarboxylate, ur is urotropin, and dmf is N,N`-dimethylformamide) [2] with the size of channels 10.5×10.5 Å was used for the synthesis of hybrid photochromic material. The material of MOF with diarylethene DMTC (2,3-bis-(2,5-dimethylthiophen-3-yl-cyclopent-2-en-1-one [3]) (1:1) (Fig.1) was synthesized and it photochemical properties were studied. DMTC is diarylethene which demonstrating high colorability. Adduct was found to demonstrate photochromic properties caused by transitions between colorless (open) and colored (closed) forms, which is typical for diarylethenes.

This work demonstrates that the incorporation of organic photochroms into MOF is a prospective approach to the formation of new hybrid photochromic materials. Currently, the work on synthesis of MOF adducts with more stable diarylethenes is in progress.

The financial support of the Russian Foundation of Basic Research (grants №№ 14-03-00212, 14-03-31539) is gratefully acknowledged.

1. Yutkin, M.P.; Dybtsev, D.N.; Fedin, V.P. *Russ. Chem. Rev.* **2011**, *80*, 1009.
2. Sapchenko, S.A.; Samsonenko, D.G.; Dybtsev, D.N.; Melgunov, M.S.; Fedin, V.P. *Dalton Trans.* **2011**, *40*, 2196.
3. Shirinian, V.Z.; Shimkin, A.A; Lonshakov, D.V.; Lvov, A.G.; Krayushkin, M.M. *J. Photochem. Photobiol. A: Chem.* **2012**, *233*, 1.

HEXARHENIUM CLUSTER COMPLEXES WITH A 1*H*-BENZOTRIAZOLE LIGAND ENVIRONMENT: SYNTHESIS, LUMINESCENCE AND BIOLOGICAL PROPERTIES

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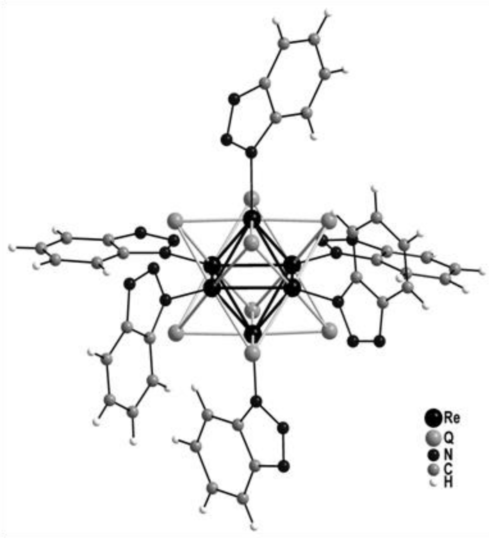
The first water-soluble hexarhenium cluster complexes with a heterocyclic outer ligand environment $[\{Re_6(\mu_3\text{-}Q)_8\}(BTA)_6]^{4-}$ (Q = S or Se, BTA = benzotriazolate ion) were obtained by reaction of $[\{Re_6(\mu_3\text{-}Q)_8\}(OH)_6]^{4-}$ with molten 1*H*-benzotriazole. The complexes exhibit red phosphorescence with the lifetimes and quantum yield values to be among the highest ones reported so far for chalcogenide cluster complexes making them promising bioimaging and PDT agents. The investigation of singlet oxygen generation was carried out by NMR experiment using 2,3-diphenyl-para-dioxene as a singlet oxygen sensor.



Structure of $[\{Re_6Q_8\}(BTA)_6]^{4-}$

To prove the potential, the cellular uptake and the toxicity were evaluated for the complexes. It was found that both clusters were taken up by the cells and at the same time did not exhibit acute cytotoxic effects at the concentration level of practical biological applications. The complexes $[\{Re_6(\mu_3\text{-}S)_8\}(BTA)_6]^{4-}$ and $[\{Re_6(\mu_3\text{-}Se)_8\}(BTA)_6]^{4-}$ were localized in the cell's cytoplasm. Thus, we have shown that the amphiphilic ligand environment allows the cluster complexes smoothly penetrate through cell membrane. The preparation of such complexes may constitute the first step toward the creation of a new class of NIR phosphorescent dyes based on of hexanuclear metal clusters.

Acknowledgements. This work was supported by the Russian Science Foundation (Grant №14-14-00192).

NEW TETRANUCLEAR HETEROLIGAND LANTHANIDE COMPLEXES: SYNTHESIS AND LUMINESCENT PROPERTIES

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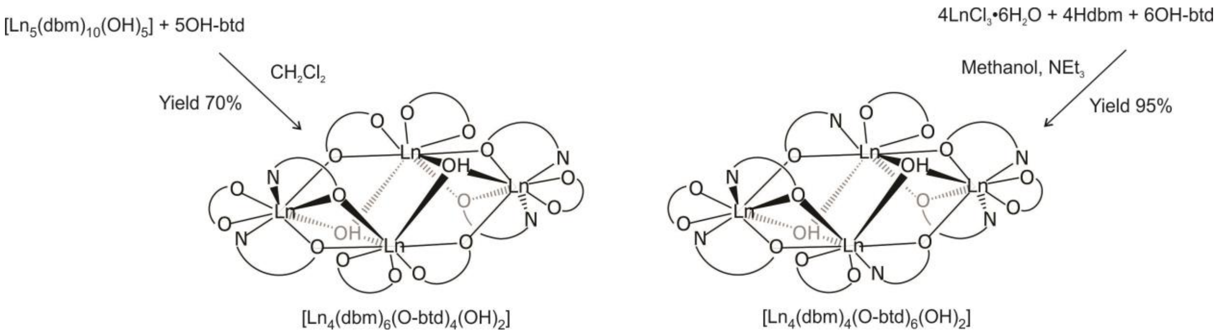
There is currently high interest for the design of lanthanide complexes displaying metal-centered luminescence emission in the visible and near-infrared region because of the wide variety of applications in material science, lighting and telecommunication technology and in bioanalysis [1-2]. Given that the Ln(III) centers cannot efficiently absorb light the way of choice to sensitize their luminescence is to employ chromophores as antennas for light absorption. In this scope, the use of 4-hydroxo-2,1,3-benzothiadiazole (OH-btd) as antenna ligand seems promising. Herein, we report the syntheses, structures and luminescent properties of the lanthanide complexes containing 4-hydroxy-2,1,3-benzothiadiazole.



The required conditions were found to isolate tetranuclear heteroligand complexes $[Ln_4(dbm)_4(O\text{-}btd)_6(OH)_2]$ and $[Ln_4(dbm)_6(O\text{-}btd)_4(OH)_2]$ (Ln = Dy, Er, Eu, Sm, Tb, Yb; dbm = dibenzoylmethanate) selectively and in moderate yields. Structures of the complexes have been established by single crystal X-Ray diffraction and other routine methods. The $\{Er_4(OH)_2\}$ core is similar in all compounds whereas the differences of the structures consist in $(dbm)^-/(O\text{-}btd)^-$ ligand ratio. The luminescence properties of the compounds have also been studied.

Acknowledgements The authors are grateful to the Russian Foundation for Basic Research (projects no. 13-03-01088, 14-03-31268, 14-03-31466) and Ministry of Education and Science of RF for financial support.

1. Ma Y., Wang Y., *Coord. Chem. Rev.*, **2010,** 254, 972.
2. Artizzu F., Mercuri M. L., Serpe A., *Coord. Chem. Rev.*, **2011**, *255*, 2514.

STRUCTURAL PECULIARITIES OF FERROCENYLTELLURIM HALIDE AND METAL-CARBONYL DERIVATIVES

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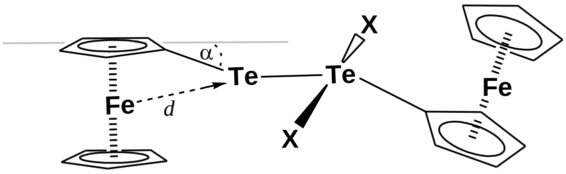
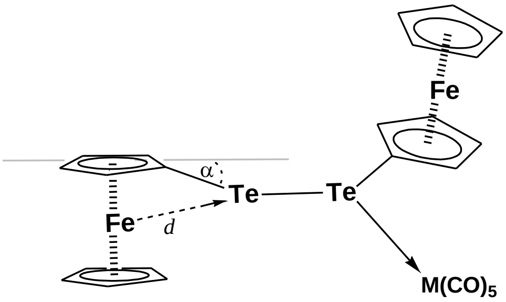
In the structures of mixed-valent ferrocenyl-tellurenyls [FcTe-TeX$_2$Fc] (X=Cl (**1**), X=Br (**2**), X=I (**3**)). all three structures **1** - **3**, non-halogenated atom of Te^{II} bents towards the Fe atom of ferrocenyl so that the deviation of Te(2) atom from the plane of the related Cp ring (thr dip angle) increases from 15.5° to 20.3° as we move . from the iodo- **3** to the chloro- **1** (the Fe(2)---Te(2) distance decreases from 3.3714(6) Å in the iodo- **3** to 3.293(3) Å in the chloro- **1**). This lays within the range of 14.6° ~ 20.7° observed in α-ferrocenyl carbocations $[C_5H_5FeC_5H_4C(C_6H_5)_2]^+[BF_4]^-$ [1], $[C_5H_5FeC_5H_4(cyclo\text{-}C_3(C_6H_5)_2)]^+[BF_4]^-$ [2]





α = 20.3° X = Cl
α = 15.4° X = Br
α = 15.4° X = I

α = 9° X = Cr
α = 8° X = Mo
α = 7° X = W

Similar, but less pronounced bent of non-coordinated Te atom towards the Fe atom of ferrocene was observed in M(CO)$_5$(Fc$_2$Te$_2$) – products of diferrocenyl ditelluride (Fc$_2$Te$_2$) interaction with VIb group metal carbonyls.

The most obvious explanation of in terms of interaction of filled nonbonding 3*d* t$_2$g orbitals of Fe with the tellurium localized LUMO is not supported by Mossbauer and DFT study and the last suggests the major contribution of Cp π-density donation to the tellurium localized LUMOs.

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1. Behrens U., *J Organomet. Chem*. **1979**, *182*, 89.
2. Sime R.L., Sime R.J., *J. Am. Chem. Soc*., **1974**, *3*, 892.

STRONTIUM-BASED METAL–ORGANIC FRAMEWORKS AS A DIELECTRIC MATERIALS FOR MICROELECTRONICS APPLICATIONS

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Highly porous structures with good thermal stability make strontium-based metal–organic frameworks, a candidate for use as a dielectric material for potential electronics applications. A strontium-based metal–organic framework $\{[Sr(C_6H_4O_6)(H_2O)]\}_n$ (**1**) was prepared through the reaction of $Sr(NO_3)_2$ with btc (1,2,4-benzenetricarboxylic acid) ligand under hydrothermal conditions. A single-crystal X-ray diffraction analysis revealed that compound **1** forms a 3D coordination network with a triclinic ($P\bar{1}$) space group. A symmetric unit consists of a strontium ion, one btc ligand and one water molecule. Metal ions are connected through the oxygen of btc ligand to form two dimensional layers. The two adjacent layers are connected through ligand to extend the structure into a 3D network. A thermogravimetric (TG) analysis showed that the structure is highly stable up to 250 °C. Dielectric measurements were performed to investigate the dielectric behavior of compound **1**.

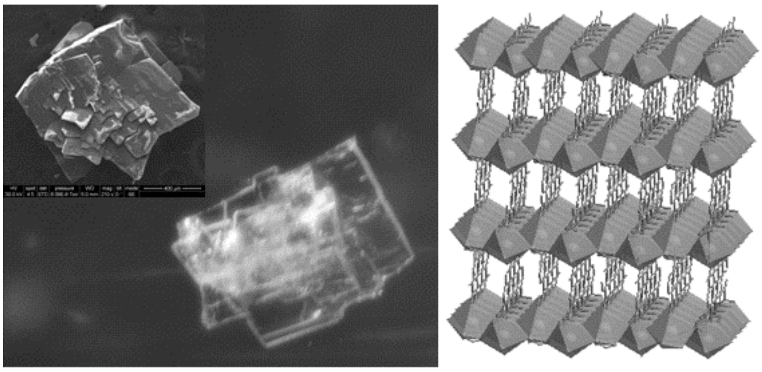

Figure 1. Crystal images showing a layered structure of compound **1**.

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OCTAHEDRAL RHENIUM CLUSTER COMPLEXES WITH S-DONOR APICAL LIGANDS

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At present, a large number of octahedral rhenium cluster complexes with the general formula $[\{Re_6Q_8\}L_6]^x$, where Q = S or Se; L – various organic or inorganic ligands, is known. However, there aren´t any structurally characterized examples of soluble Re_6 complex with S-donor outer ligands (L).

This work is devoted to the synthesis of first hexarhenium cluster complexes with S-donor apical ligands.

It was found that boiling of aquahydroxo complexes $[\{Re_6Q_8\}(H_2O)_4OH)_2]\cdot12H_2O$ (Q = S or Se) in aqueous solution of sodium sulfite leads to the formation of hexasubstituted sulfite complexes $[\{Re_6Q_8\}(SO_3)_6]^{10-}$ which structure is shown in Figure.

These anionic complexes were isolated as sodium salts of the composition $Na_{10}[\{Re_6Q_8\}(SO_3)_6]\cdot nH_2O$ and investigated by a set of physic-chemical methods. Notably, the complexes have the highest charge (10–) reported so far for hexanuclear transition metal cluster complexes, and are the first soluble octahedral rhenium cluster complexes with a doubly charged ligand. In addition, several insoluble compounds based on the anions $[\{Re_6Q_8\}(SO_3)_6]^{10-}$ and strontium, barium or cobalt cations were crystalized and characterized.

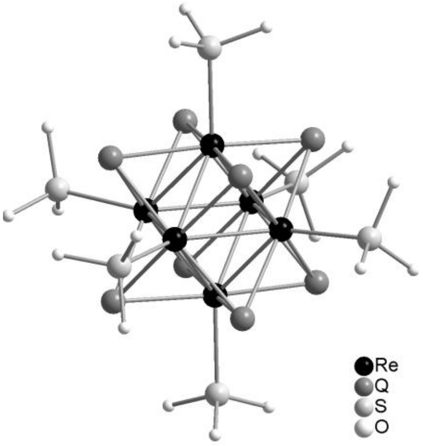

Figure 1. Structure of $[\{Re_6S_8\}(SO_3)_6]^{10-}$

Also, the reaction of hexahydroxo complexes $[\{Re_6Q_8\}(OH)_6]^{4-}$ (Q = S or Se) with molten $Na_2S\cdot9H_2O$ was studied. As a result sodium salts of anionic complexes $[\{Re_6Q_8\}(SH)_6]^{4-}$ were obtained.

Acknowledgements. This research was supported by the Russian Foundation for Basic Research Grant № 12-03-00477.

LUMINESCENT MATERIALS BASED ON OCTAHEDRAL MOLYBDENUM CLUSTER COMPLEXES AND SILICON DIOXIDE

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Octahedral molybdenum cluster complexes with the general formula $[\{Mo_6X_8\}Y_6]^n$ (where X is an inner ligand (Cl, Br or I) and Y is an outer organic/inorganic ligand) exhibit photoluminescence in the visible and near-infrared regions with high emission quantum yields and lifetimes, and have excellent potential for singlet oxygen generation. Due to these properties molybdenum cluster complexes can find a number of applications in the fields of medicine and biology. Despite the great potential of molybdenum cluster complexes, they are not suitable for use in biological purposes, since they are often insoluble in water and can potentially react in physiological environments. Thus, they must be either coated with appropriate organic ligands or encapsulated into an organic or inorganic inert matrix.

Silica is the most often used inorganic matrix for obtaining of luminescent materials intended for biological applications. In particular, silica particles are resistant to microbial attack, stable in aqueous solutions, nontoxic, and biocompatible. Furthermore, the size of particles can be easily adjusted, that is not always possible for other matrices. Thus, molybdenum cluster complexes and silicon dioxide have been chosen for obtaining of luminescent materials.

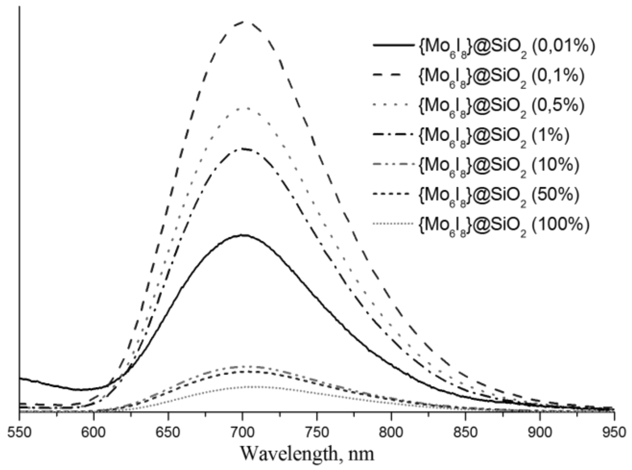

Figure 1. Luminescence spectra of the powderd samples $\{Mo_6I_8\}@SiO_2$ with different concentrations of cluster complexes.

The Mo_6 cluster containing luminescent silica particles ($\{Mo_6X_8\}@SiO_2$) were synthesized through Stöber method. This method consist in the alkaline hydrolysis of tetraethoxysilane (TEOS) in the presence of cluster complexes $[\{Mo_6X_8\}(NO_3)_6]^{2-}$ (X = Cl, Br, I). By this method, perfectly smooth spherical particles of ~500 nm in diameter were obtained. They were characterized by a number of physical and chemical methods. Inter alia, the luminescence properties of the obtained materials were studied (Figure). A dependence of the luminescence quantum yield on the concentration of encapsulated cluster complex was revealed.

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RIGID 1D COORDINATION POLYMERS WITH TUNABLE METAL CATION AND CHIRAL PENDANT MOIETIES

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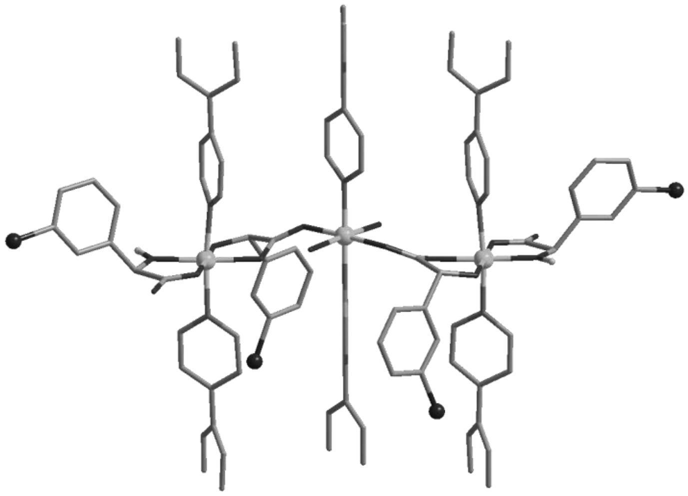
Coordination polymers are made of both inorganic and organic moieties and allow flexible control of both chemical composition and structural features of the compound. The incorporation of chiral molecules into coordination polymer network guarantees the presence of the asymmetric centers thus non-centrosymmetric structure of the material.

In this work a series of homochiral chain coordination polymers based on structurally robust 4,4'-bipyridyl (bpy) linker with tunable 3d metal cations (Co^{2+}, Ni^{2+}, $Cu^{+/2+}$, Zn^{2+}) and chiral auxiliary ligands (*R*-3-chloromandelate, *S*-3-phenyllactate, and *S*-3,3-dimethyllactate) were synthesized and characterized with X-ray crystallography. All the compounds are based on chain motifs $\{M(bpy)\}_\infty$, decorated with chiral acid residues and other ligands. One structure represents rare example of triple-chained ribbon, while five others are nearly isostructural, featuring robust metal-organic chains, decorated by chiral pendant ligands. Two structures contain Cu^+ cations connected with organic linkers forming double chains.



Acknowledgements. The work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006).

POLYNUCLEAR COMPLEXES OF Co^{II} AND Ni^{II} WITH THE ANION OF CYCLOPROPANE-1,1-DICARBOXYLIC ACID

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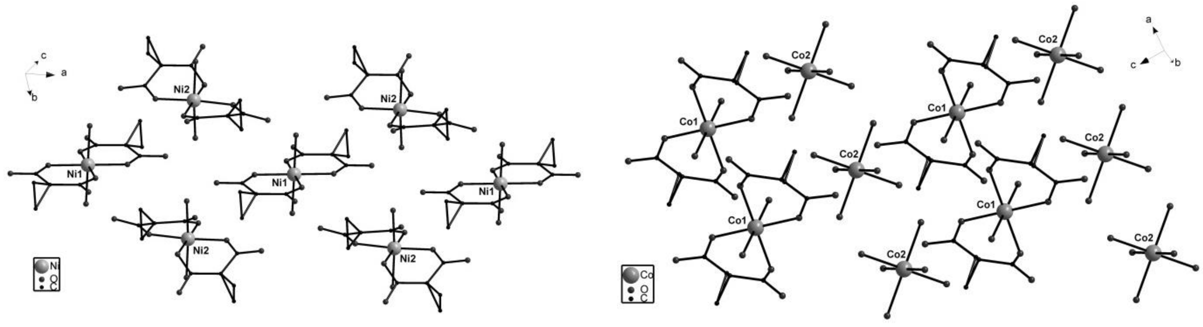
Nowadays for 3d-metal with anions of cyclopropane-1,1-dicarboxylic acid are described in the literature a number of homo- and heterometal compounds. The corresponding complexes of Co^{II} and Ni^{II} are isolated only in the form of polycrystalline samples [1] and heterometallic compounds were prepared exclusively for oxovanadium(IV) ion with strontium and barium atoms [2].

The reaction of nickel(II) acetate and potassium salt of cyclopropane-1,1-dicarboxylic acid, K_2CPDC, in water-ethanol mixture gives a new compound with layered structure $\{[K_6Ni_3(CPDC)_6(H_2O)_{14}]\cdot 4H_2O\}_n$ (**1**), the main structural motif which are formed by bischelate fragments of acid anions with nickel(II) atoms (fig.1.a). Nickel(II) atoms environment completed to octahedral by oxygen atoms of water molecules.



a b

Figure 1. Packing of mononuclear fragments formed by anions of cyclopropane-1,1-dicarboxylic acid in complexes **1** (a) and **2** (b)

Boil the suspension of cobalt acetate(II) with Na_2CPDC in ethanol, followed by recrystallization from water resulted in the formation of the coordination polymer $[Na_2\{Co(H_2O)_6\}\{Co(CPDC)_2(H_2O)_2\}]_n$ (fig. 1.b). In this complex all the atoms of cobalt(II) are located in an octahedral environment, but acid anions form bischelate fragments only with atoms Co(1). Environment of the atoms Co(2) is formed only by oxygen atoms of water molecules.

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1. Schwartz., Petri A., Schilling J., *Acta Cryst. C.: Cryst. Struct. Commun.*, **1998**, *54*, 1104.
2. Bazhina E.S., Nikiforova M.E., Aleksandrov G.G., *Russ. Chem. Bull.*, **2011**, *5*, 779.

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