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CATALYSIS, AND CRYSTAL ENGINEERING»

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BOOK OF ABSTRACTS

Novosibirsk 2024

Compiled by Prof. Pavel A. Abramov and Dr. Ekaterina A. Radiush

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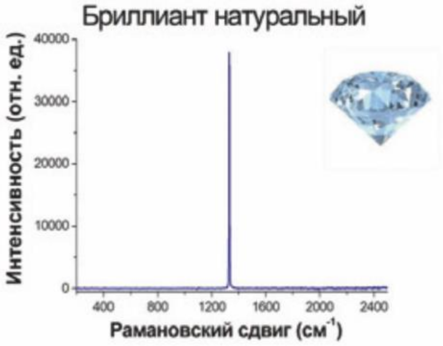
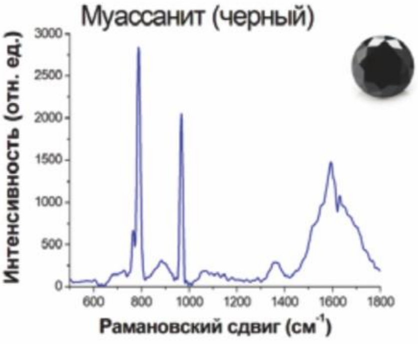
Определение и идентификация химических веществ – распространенная задача в области аналитической химии. Спектрометры **RamanLife**, работающие по принципу комбинационного рассеяния (КР) света (метод более известный как Рамановская спектроскопия), способны выполнять эту задачу очень легко. Будь то жидкость, твердое вещество, порошок, взвесь или гель – определение можно проводить даже через упаковку.

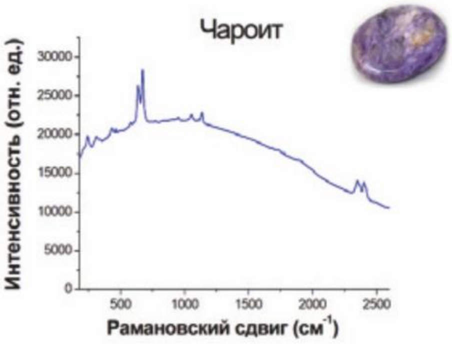
Линии сдвига, получающиеся при неупругом рассеянии света для каждого химического вещества уникальны, поэтому идентификация, например, с использованием базы данных спектров, не представляет проблемы. Библиотека спектров, которую можно приобрести к прибору **RamanLife** содержит более чем 24 000 спектров, а для удобства узкоспециализированных клиентов основная библиотека разбита по категориям, стоимость которых существенно ниже полной базы.

Рамановская спектроскопия безусловно является мощным инструментом для структурной идентификации молекулярных соединений и используется в различных отраслях промышленности, науки, медицины, сельского хозяйства и т.д. Наиболее эффективно сочетание двух методов – ИК-Фурье спектрометрии и КР, т.к. некоторые молекулярные колебания очень ярко проявляются в ИК и слабо в КР и наоборот. В связи с этим, спектроскопия комбинационного рассеяния может применяться не только как отдельный метод исследования, но и в сочетании с ИК для получения наиболее полного представления о природе образца.

Примеры спектров:







До недавних пор, стандартная установка для исследования Рамановского рассеяния света и люминесценции включала в себя мощный лазер, тройной спектрометр и охлаждаемый матричный фотодетектор. Все это приводило к тому, что приборы были большие и очень дорогие, вследствие чего метод получал недостаточное распространение среди специалистов. В последние годы ситуация на рынке научного приборостроения радикально изменилась, что позволило уменьшить и удешевить все компоненты Раман-люминесцентных установок. Во-первых, вместо громоздких и дорогих газовых лазеров появились мощные миниатюрные твердотельные лазеры. Во-вторых, тройной спектрометр удалось заменить значительно более простым, дешевым и компактным одиночным спектрометром благодаря появлению многослойных интерференционных фильтров с узкими спектральными характеристиками. В-третьих, за счет быстрого развития и оптимизации элементной базы

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CONTENTS

PLENARY LECTURES

Noncovalent Interactions and Functional Properties of GUEST@MOF Supramolecular Systems

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An important scientific problem is the creation of a fundamental basis for the chemistry of inclusion compounds based on porous metal-organic frameworks (MOFs). Noncovalent interactions in supramolecular GUEST@MOF systems largely determine the potential of using porous frameworks for the development of a new generation of functional materials. Due to noncovalent interactions, MOFs exhibit highly selective adsorption of gases, which will make it possible to effectively separate complex mixtures (for example, industrially important hydrocarbons) into individual components, as well as get rid of harmful impurities, such as greenhouse gases in industrial emissions [1-5]. The dependence of luminescence on the type of guest molecules in the pores of metal-organic frameworks makes it possible to create highly selective and highly sensitive luminescent sensors that respond to the presence of hazardous substances in air or water [6,7]. Intermolecular contacts direct the orientation of the guest molecules within the host channels, which drives, foe example, photoaddition reaction in a facile and diastereoselective fashion [8]. Monitoring the chemical transformations of guest molecules in porous frameworks using SCXRD allows the development of highly selective synthesis processes and obtaining structural information about unique reaction intermediates and products.

Acknowledgements

Our research was supported by grants from the Russian Science Foundation (№ 23-43-00017 and 19-73-20087).

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Stacking in Organic and Organometallic Chemistry

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The past years have seen a precipitous growth in the number of publications related to various aspects of weak intermolecular interactions. Despite the low energy of noncovalent interactions (NCIs), in many cases they act collectively and the sum of their actions can play a significant role in various transformations of chemical compounds, synthesis and catalysis, including noncovalent organic catalysis. Crystal engineering makes extensive use of interactions between multiple noncovalent bonds, allowing the design and production of associates, clusters, extended supramolecular systems and ultimately functional materials.

A special emphasis will be put on stacking interactions involving multicenter contacts between any planar π systems. The stacking is characterized by the presence of net attractive interactions between at least two planar π-systems – organic, organometallic, or mixed organic–inorganic. These NCIs are actively studied thank to their significance in the design of functional materials (including liquid crystals) and pharmaceutically useful compounds, and also due to their applications in catalysis, molecular and ion recognition. It is currently well established that the double helical structure of DNA occurs mainly due to the combined binding action of stacking and hydrogen bond interactions of planar nucleic acid bases.

In the talk, types of NCIs will be examined and classified along with the digested data on intermolecular stacking – all obtained in the group of authors.

Acknowledgements

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Organic fluorine in crystal engineering

Giuseppe Resnati[1]

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Prof. Resnati is full professor of Chemical Basis of Technologies at the Department of Chemistry, Materials and Chemical Engineering “Giulio Natta” of the Politecnico di Milano since 2001. Before that, he was associate professor at the same university (since 1997) and Team Leader at the Institute of Molecular Science and Technology of the National Research Council in Milano.

The research interests of Prof. Resnati are in the field of supramolecular chemistry with a particular attention to the role of chalcogen and halogen atoms in recognition and self-assembly phenomena. Late nineties he introduced the concept and the use of halogen bond, namely the non-covalent interaction wherein halogen atoms work as the positive site (electron acceptor site, Lewis acid). The concept is now receiving attention worldwide in the chemical community, and it is increasingly of interest also to other scientist, e.g. biologists, pharmacologists, materials scientists. More recently he extended the mindset developed in relation to the halogen bond to elements of other groups of p block of the Periodic Table focusing on the tetrel and chalcogen bonds, the interactions where the electrophilic site is an element of group 14 and 16, respectively. Notably, Prof. Resnati coordinated the IUPAC projects which resulted in the IUPAC definitions of the halogen bond (2013) and chalcogen bond (2019) and the impact of the corresponding papers is measured by the obtained citations which were 916 and 63, respectively. Prof. Resnati developed reliable heuristic principles for the construction of one-, two-, and three-dimensional architectures. As a part of his interest in solid systems, he studied various molecular materials and the way to control and tune their functional properties via the control of their structure and the intermolecular interactions determining the solid state. In particular, he has been studying self-assembled and fluorinated liquid crystals, non-linear optical materials, organic porous networks. He is also interested in fluorine chemistry, encompassing new synthetic approaches based on perfluorinated catalyst, reagents, and solvents and the asymmetric synthesis of bioactive fluoroorganic compounds.

He is author of more than three hundred and fifty original papers on high impact journals, of several reviews, chapters in books, entries in technical encyclopedias. He is the inventor of seven patents valid in most WTO countries.

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Non-covalent interactions and catalytic amine-boranes dehydrogenation

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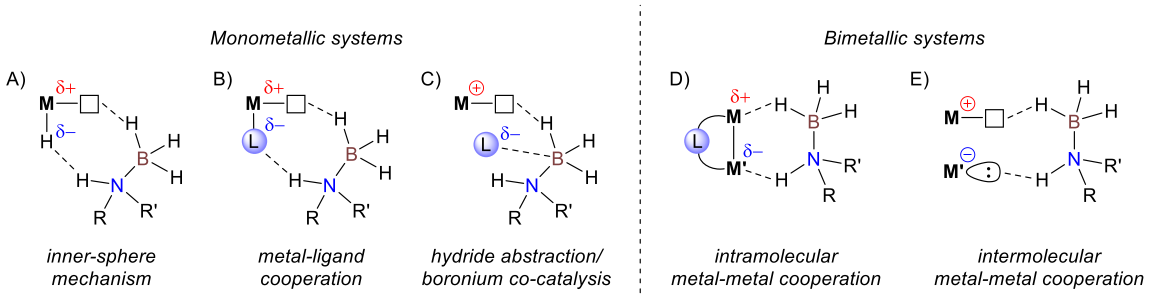
Amine-boranes are considered as promising materials for hydrogen storage systems due to their availability, easy handling and elevated hydrogen content. Formation of dihydrogen bonded (DHB) adduct NH…HB promotes H_2 evolution for amine-boranes. Several types of mechanisms for NH and BH bonds activation by TM complexes are known leading to amine-boranes dehydrogenation (Scheme 1) and will be considered in the lecture. Non-covalent interactions are the driving force in these processes. Particular attention will be paid to intermolecular cooperative activation of amine-boranes.

DHB between two transition metal hydrides also results in H_2 evolution and formation of bimetallic complexes $[LM(CO)_2(\mu\text{-}CO)\cdots M'(PCP)]$.[1] In these complexes two transition metal-based building units do not interact directly but act as a Lewis acid and a Lewis base, cooperatively splitting the N–H and B–H bond in amine-boranes without changing the metals' oxidation state (Scheme 1E).[2] In the case of manganese(I) complexes the intermolecular activation of amine-boranes is realised through novel cooperative action of [MnH] base and $[Mn]^+$ Lewis acid.[3] At that the Lewis acid and base can be generated from one precursor - $L_2Mn(CO)_3X$, yielding the record catalytic activity for BH_3NHMe_2 when L_2 = bis(NHC).[3]



Scheme 1. Known mechanisms for NH and BH bonds activation by TM complexes

Acknowledgements

The financial support by RSF project № 24-13-00283 is gratefully acknowledged

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Self-organisation of tetrapyrrolic compounds: a design of novel biomimetic materials

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Prof. Yulia Germanovna Gorbunova is a Russian chemist, a specialist in the field of coordination and supramolecular chemistry, the author of more than 150 scientific articles, 13 reviews and book chapters and 4 Russian patents.

Her scientific interests are related to the development of fundamental principles for the preparation of coordination compounds and the development of new functional materials based on them. Head researcher of the Institute of General Economy and Chemistry of the Russian Academy of Sciences and the Institute of Physical Chemistry of the Russian Academy of Sciences, Doctor of Chemical Sciences, Professor, Professor of the Russian Academy of Sciences, Academician of the Russian Academy of Sciences (2022).

Her scientific works propose i) methods for the targeted synthesis of a wide range of coordination compounds based on tetrapyrrole ligands; ii) fundamental principles for obtaining new functional materials based on macrocyclic compounds and supramolecular architectures have been developed as the basis for multifunctional devices of a new generation; iii) new thin-film systems have been created for devices for recording, processing and storing information, molecular switches, optical tomography, nonlinear optics, solar energy converters, magnetic materials and photosensitizers with world-class characteristics; iv) materials developed for the near-infrared range for use in optical computers.

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Specific recognition between beta-octamolybdate and onium cations

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The specific molecular recognition is involved in a great number of processes spanning from supramolecular chemistry to biology and medicinal chemistry. The recognition parameters between “partners” such as geometry, size, type of interactions and their number, are the main points to achieve favorable conditions for the supramolecular assembly. A special attention, in this context, has been drawn to the utilization of polynuclear transition metal oxocomplexes (polyoxometalates, POM) as building blocks for the design of new smart materials for energy conversion, storage and transfer systems.

In this research a new approach to the tunable design of supramolecular associates based on the specific recognition between beta-octamolybdate (β-$[Mo_8O_{26}]^{4-}$) and onium cations has been demonstrated (Fig. 1). The specific structure of the current molybdate backbone gives an electronic pool localized around two pseudo cavities. This situation is preferential to generate any noncovalent interactions especially with good σ-hole donors. The formation of corresponding R_2I^+ iodonium salts (containing hypervalent iodine(III)) is simple and can be directed by the electronic effects of R. The electronic competition between n-Bu_4N^+ and R_2I^+ can produce mixed $(R_2I)^+$/n-Bu_4N^+ salts which should be taken into consideration. On the other side these two electronic pools interact with a series of R_3Q^+ chalconium cations (which contain hypervalent chalcogen(IV)) producing $(R_3Q)_2(TBA)_2[Mo_8O_{26}]$ and $[R_3Q]_4[Mo_8O_{26}]$ associates.

This strategy opens a general method to functionalize beta-octamolybdate platform in a wide range of perspectives directed by onium functional groups.

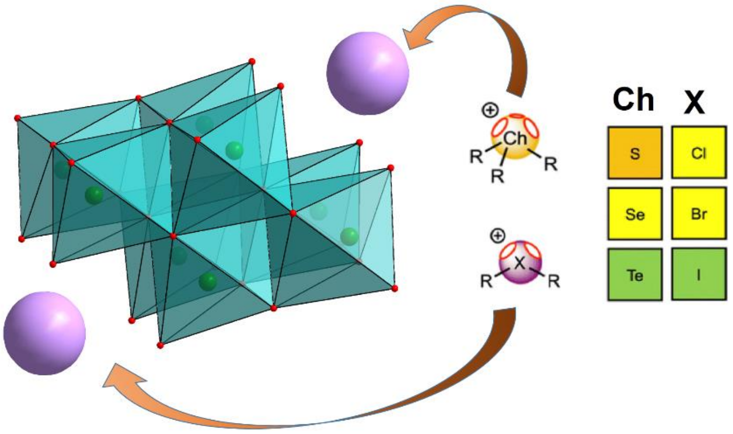

Figure 1. Representation of beta-octamolybdate and onium cations interactions

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Molecular and Supramolecular Design of Luminescent Systems

Andrey A. Karasik,[1] Igor D. Strelnik,[1] Elvira I. Musina,[1] Asia R. Mustafina[1]

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Within the last decade an effective strategy of design of biocompatible luminescent systems based on transition metal complexes of tailor made P,N-heterocyclic ligands have been developed. On the first stage P,N-ligands with exocyclic chromophoric pyridyl-, pyridylethyl-, thienyl-, thienylethyl- and biphenyl-groups on phosphorus atoms have been obtained. On the second stage wide range of luminescent mono-, bi-, tetra- and hexa-, homo- and heteronuclear complexes of gold (I) and copper (I) based on novel heterocyclic phosphines has been designed. In order to enhance luminescent properties, the halide anions of transition metal salts were substituted by alkynyl groups or cluster hexarhenium or -molibdenium anions exhibiting their own photoluminescence. For these compounds, stimuli-responsive phosphorescence is observed in a wide range of wavelengths, including the infrared range[1] and a rare two-band white emission[2]. So, the obtained complexes could be regarded as promising sensors for pH, temperature, presence of organic solvents.[3,4,5]

For biomedical applications the stability of complexes in bioenvironment and cytotoxicity should be improved. Biocompatible luminescent systems have been created by immobilization of their nano-sized collloids on a polyelectrolyte matrix. The obtained materials were successfully used as contrasting agents in confocal microscopy and for the generation of active oxygen species in cancer cells.[6,7] So, the presented luminescent systems are rather perspective for biomedical application.

Acknowledgements

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Non-covalent self-assembly of hybrid materials for heterogeneous photocatalysis

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Heterogeneous photocatalysis is one of the most important and rapidly growing areas of research in modern chemistry. This kind of light-driven processes provides a platform for innovative chemical technologies that utilize sunlight as an energy source. The progress of this field will depend on advancing the development of hybrid materials combining organic chromophores and inorganic semiconductors. These hybrid nanostructures are capable of converting the light energy absorbed by the material into chemical work to produce active particles that initiate chemical reactions. Supramolecular self-assembly based on non-covalent interactions and coordination bonds is a convenient tool for creating such hybrid materials, allowing manipulation of their composition and resulting functionalities, avoiding pre-modification of the inorganic component. This type of supramolecular assembly is particularly useful for the combinatorial design of materials based on macro- and polycyclic chromophores (e.g. zinc porphyrinates or bis-imide perylene derivatives) and two-dimensional inorganic matrices such as graphene oxide, molybdenum sulfide or layered anion-exchange matrices based on rare-earth metal hydroxides. Combinatorial strategy provides an opportunity for tuning the functional response of the resulting photocatalytic systems by simple changing combinations of components integrated through the same non-covalent binding motive.[1-3] The lecture will discuss various examples of photosensitive hybrid systems obtained through combinatorial self-assembly, their most distinguishing structural features and the methods to control photocatalytic pathways by using such hybrid photocatalysts.

Acknowledgements

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KEYNOTE LECTURES

Weak Bonds, Strong Effects: Way to Application of Halogen Bond in Chemical Engineering

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To date, the phenomenon of halogen bonding can be considered as one of the most investigated across the whole universe of noncovalent interactions.[1-3] Despite the significant contributions in this field, the application of halogen bonding in chemical engineering is still far from reality.

To the best of our knowledge, there are two main opportunities to introduce the halogen bonding phenomenon to chemical engineering. First, this is the design of novel stable porous materials that provide the alternative to traditional covalent organic or metal-organic frameworks based on donors of charge-supported σ-holes.[4] Another opportunity is the introduction of iodine to the ligand in the structure of metal-organic frameworks containing terephthalate-based linkers.[5] The developed approach consumes the utilization of waste polyethylene terephthalate as a feedstock, providing fascinating opportunities for the upcycling of wastes with the formation of metrist products. The developed UiO-66-I framework is able to selectively entrap chloroarenes in the presence of unchlorinated analogues. Last but not least, UiO-66-based metal-organic frameworks bearing iodine as an σ-holes donor can be used as a recognition layer for the selective detection of chloroarenes by surface-enhanced Raman spectroscopy in combination with porous noble metal nanostructures.

Thus, the application of halogen bond donors presents bright opportunities for the design of novel materials demonstrating fascinating technological properties.

Acknowledgements

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The intriguing world of noncovalent interactions

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Noncovalent interactions are widespread in nature and contribute to the bonding of chemical systems. Compared to covalent bonds, intra- and intermolecular noncovalent interactions are usually weak and have much lower energy and directionality, which is reflected in the term "noncovalent". Due to the active development of these topics during recent years, most achievements in chemistry in the 21st century already is and will continue to be largely determined by noncovalent interactions.

Our achievements in this area include diverse acid-base interactions of transition metal and main group element hydrides, which ultimately determine their activity in stoichiometric and catalytic processes such as (de)hydrogenation, dehydrocoupling, alkene isomerization, and could be used for fine-tuning of metal hydride properties[1-4].

Application of the concept of noncovalent interactions to Mn(I) phosphine and NHC complexes allowed us to find a new type of metal-ligand cooperation,[2,3] to determine the possibilities of competition of deprotonation and dehydrogenation of hydride complexes.[4] Notably “simple” hydride transfer process proceeds via thermodynamically unfavorable but kinetically reactive *mer* isomer of (L^L)Mn(CO)$_3$H complex (L=P or NHC).[5] Strikingly, the coplanarity of the two NHC rings within the Mn(I) complex with Janus-type bis(NHC) ligand, [Mn(η^5-C$_5$H$_5$)(CO)$_2$]$_2$(μ-bis(IMes)), favored by steric hindrance along with stabilizing intramolecularC-H···π interactions, allows the alignment of the π-systems and, as a direct consequence, significant electron communication through the bis(carbene) scaffold.[6]

It will be a fascinating journey into an intriguing world of noncovalent interactions.

Acknowledgements

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Strong Hydrogen Bonds with Charge Relay

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The control of nucleophilicity of atoms in molecules using non-covalent interactions is employed both in synthetic organic chemistry and biomolecular chemistry. Here we consider – more as a general principle than a practical tool – systems with coupled H-bonds, which demonstrate high charge cooperativity, *i.e.* the ability to shift atomic charges with minimal energy costs. Such systems are created when one of the H-bonds in the chain becomes short and its bridging proton moves in a broad shallow (virtually barrierless) potential between two heavy atoms. In this case, even small geometric adjustment of the neighboring weak H-bond is able to cause significant shift of the bridging proton in the short H-bond, leading to considerable changes in nucleophilicity of its heavy atoms. We discuss four causes for proton displacement in strong H-bonds a) fluctuations of H-bonded solvent (FHF^- anion; Figure 1a),[1] b) disruption of tertiary structure in proteins (OHO bonds in photoactive yellow protein active site models; Figure 1b),[2] c) protein-substrate interactions (OHN bonds in trypsin active site models; Figure 1c),[3] d) H-bonding with counterion (OHO bonds in homoconjugated anions of phosphinic acids; Figure 1d). We also address the problem of interpretation of NMR parameters that are sensitive to geometries of two coupled H-bonds simultaneously[4] and NMR effects of quantum-chemical delocalization of bridging proton in low-barrier H-bonds.[5]

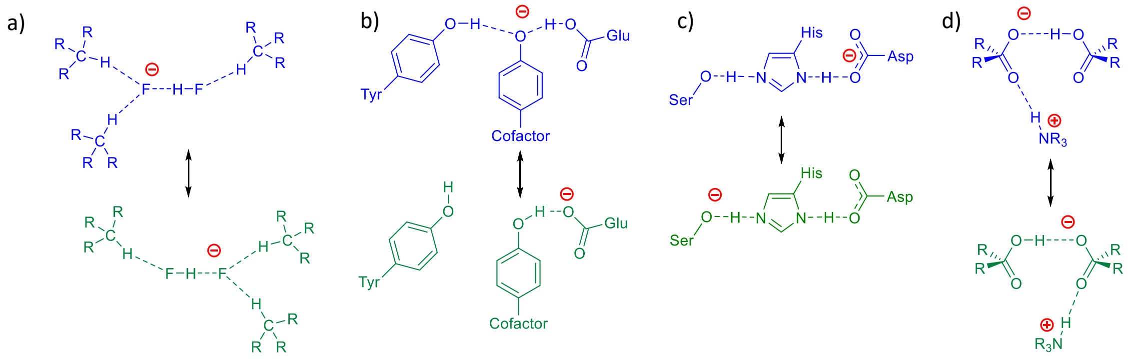

Figure 1. Examples of charge relay H-bonded systems considered in this work.

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Chiral Metal-Templated Hydrogen Bond Donor Catalysts

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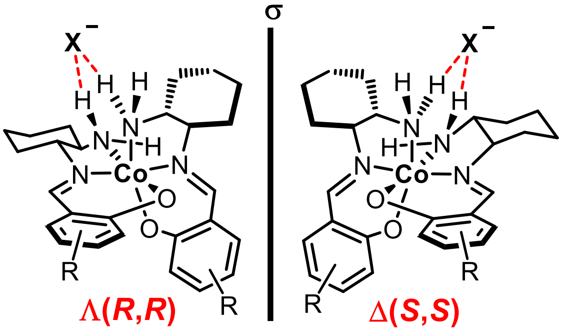
The development of new chiral catalytic systems based on the metal-templated approach is a promising area of research today.[1] It is worth noting that these catalysts activate substrates through the ligand sphere via well-orchestrated non-covalent interactions, rather than the coordination metal centre.[1] These metal complexes exhibit extremely high catalytic activity and excellent stereoselectivity at low catalyst concentrations.[1]

We have developed a novel class of chiral octahedral cobalt(III) complexes that are based on commercially available chiral diamines and various salicylic aldehydes (Figure).[2-6] In these complexes, the amino groups act as effective hydrogen bond donors due to their coordination with the metal ion. These complexes effectively catalyze asymmetric reactions, producing bioactive molecules with up to 96% enantioselectivity.[2-6] In addition, they have been shown to be efficient selectors in chiral sensors for the recognition of enantiomers of bioactive compounds in real systems.[7]



X = Cl, I

Figure. Structures of enantiomeric Co(III) complexes.

Acknowledgements

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Halogen Bond Promoting Self-Arrangement of Exchange-Coupled Paramagnetic Systems

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Nitroxides are actively used as building blocks in the design of molecule-based magnets. In this field, a special attention has been paid to the targeted solid-state assembly of functionalized nitroxides into exchange-coupled clusters.[1] Herewith, metal binding or noncovalent intermolecular interactions (e.g., hydrogen bonds or π–π stacking) are effectively utilized for the directed self-assembly of nitroxide-based building blocks into multispin architectures. The closest analogues to hydrogen bonds are halogen bonds (abbreviated as HaB), in which the role of the H-atom, which functions as a Lewis acid, is played by a halogen.

In this lecture, it will be shown that the exceptional directionality of HaB is an attractive feature that promotes the assembly and self-assembly of stable nitroxides into exchange-coupled paramagnetic systems.[2,3] Furthermore, experimental evidences for the involvement of HaB in enhancing exchange interactions between unpaired electrons of paramagnetic centers will be presented in the context of this study.

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Complexes of molecular iodine with Lewis acids and Lewis bases

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The donor-acceptor interactions span a very large range from weakly bound species in the gas phase to the strong molecular complexes, existing in vapors at elevated temperatures.[1] Molecular iodine is capable to serve both as Lewis acid and as Lewis base, which earned it’s comparison with two-faced Janus from Roald Hoffmann.[2] In recent years, molecular iodine attracted attention as catalyst in metal-free catalysis.[3]

In the present report, results of computational (optimized geometries, stability of isomers, bonding analysis, thermodynamics, reaction pathways)[4,5] and experimental (synthesis, structural features, tensimetry measurements) studies of molecular and ionic complexes of iodine with nitrogen-containing Lewis bases and group 13 Lewis acids with perfluorinated substituents $B(C_6F_5)_3$ and $Al(C_6F_5)_3$ will be reported.

The influence of the Lewis acids and Lewis bases on the heterolytic splitting of molecular iodine (Figure 1) will be presented and discussed. Reactivity of iodine will be compared with those of molecular chlorine and iodine monochloride.

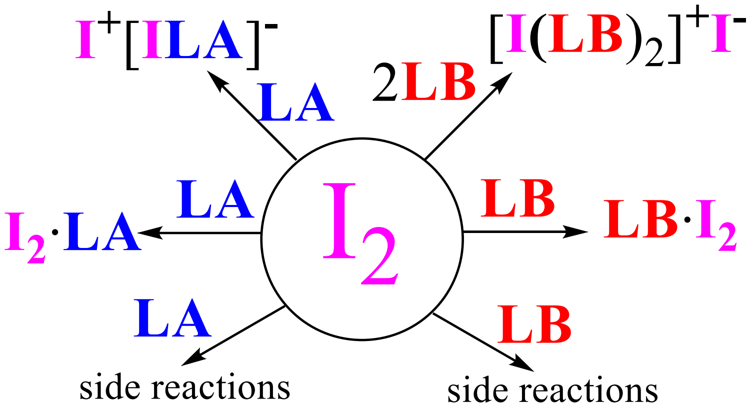

Figure 1. Schematic representation of reactivity of molecular iodine.

Acknowledgements

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Phosphorescent Mn(II) complexes: the recent progress

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In the last decade, there has been a renaissance in the chemistry of phosphorescent Mn^{II} complexes because of their remarkable emission properties, eco-friendless, cheapness and elementary earth-abundance (manganese, 0.1% of the Earth's crust). Recently, a number of emissive Mn^{II} complexes have been highlighted as efficient phosphors, triplet dopants for OLEDs, stable X-ray scintillators, optical sensors, triboluminescent materials, anti-counterfeiting dyes, etc.

Our research group is focused on designing highly emissive Mn^{II}-organic compounds based on P=O-functionalized and halido ligands. We have developed new approaches to the design of effective Mn^{II}-based emitters featuring bright room temperature phosphorescence, dual phosphorescence, triboluminescence, vapor-/solvatochromic emission as well as X-ray radioluminescence and circular polarized luminescence.

In the report, it will be discussed:

- chiral Mn^{II} complexes with strong X-ray radioluminescence and circular polarized luminescence [1];
- dual emissive of “two-in-one” $Mn^{II}(O_h)$-$Mn^{II}(T_d)$ and Mn^{II}-Cu^{I} complexes [2, 3];
- photo- and triboluminescence of Mn^{II} polymers based on *m*-carborane-derived ligands [4];
- polymorphic luminescence of Mn^{II} halide complexes with P,P’-dioxide of Xantphos [5];
- first observation of luminescence from Mn^{II} ion in a square-pyramidal ligand field [6].

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The role of molecular and supramolecular structures in the design of efficient lanthanide 1,3-diketonate-based luminophores

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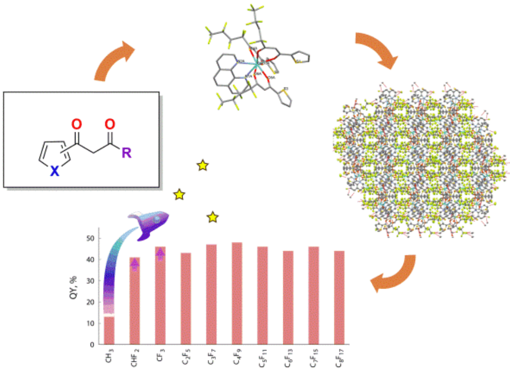

The rational design of efficient luminophores based on lanthanide complexes represents an urgent task in the fields of modern coordination chemistry and chemical materials science. One such approach is based on the optimization of the energy transfer pathways between the organic ligand and the central emitter ion.

The introduction of halogen or other heavy heteroatoms into various fragments of 1,3-diketonate ligands has been demonstrated to have a significant effect on several factors that determine the efficiency of the ligands, including factors that determine the efficiency of energy transfer and electronic excitation. In particular, this modification of the structure allows for the flexible tuning of the energies of the corresponding singlet and triplet levels of the ligand. It also suppresses undesirable processes of nonradiative relaxation of excited states, and in some cases, it is possible to completely "switch" the pathways of excitation energy transfer between the ligand and the ion.

The communication will discuss in detail the different types of structural modification of 1,3-diketonate ligands and their influence on the photophysical properties of the resulting ligands. It will also discuss the influence of these modifications on the luminescent properties of the neutral coordination compounds of selected trivalent lanthanides.

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The key role of the hydrogen bonding with the second coordination sphere in complexes with hydrogen peroxide

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Hydrogen peroxide metal complexes are important in catalysis, materials science and biotechnology. But the nature of the interaction of H_2O_2 with metal cations remains unclear and controversial. This is explained by the extremely weak coordinating ability of H_2O_2,[1] which makes it difficult to characterize and understand the specifics of these interactions. The only one complex of H_2O_2 with a metal cation has been isolated and structurally characterized, namely a hydrogen peroxide complex with zinc(II).[2] However, the isomorphic substitution of H_2O_2 with H_2O (in a 50:50 occupancy ratio) preventing the positions of the H_2O_2 protons being determined objectively. Herein, we present a new approach to obtain H_2O_2–metal complexes using pure H_2O_2 as both solvent and ligand. Coordinatively unsaturated Lewis acids $SnCl_4$ and $InCl_3$ do not catalyze the decomposition of hydrogen peroxide, so they are suitable for obtaining hydrogen peroxide complexes. Indeed, $SnCl_4$ was shown to effectively bind H_2O_2, forming a $SnCl_4(H_2O_2)_2$ complex, as confirmed by ^{119}Sn and ^{17}O NMR spectroscopy. Crystalline adducts, $SnCl_4(H_2O_2)_2$•H_2O_2•18-crown-6 (**1**) 2[$SnCl_4(H_2O_2)(H_2O)$]•18-crown-6 (**2**) and $InCl_3(H_2O_2)(H_2O)_2$•18-crown-6 were isolated and characterized by scXRD, providing the complete characterization of the hydrogen bonding of H_2O_2 ligands.

DFT calculations revealed a synergy between the coordination bond of H_2O_2 with the metal cation and its hydrogen bond with the second coordination sphere. This synergism of primary and secondary interactions might be a key to understanding H_2O_2 reactivity in biological systems.

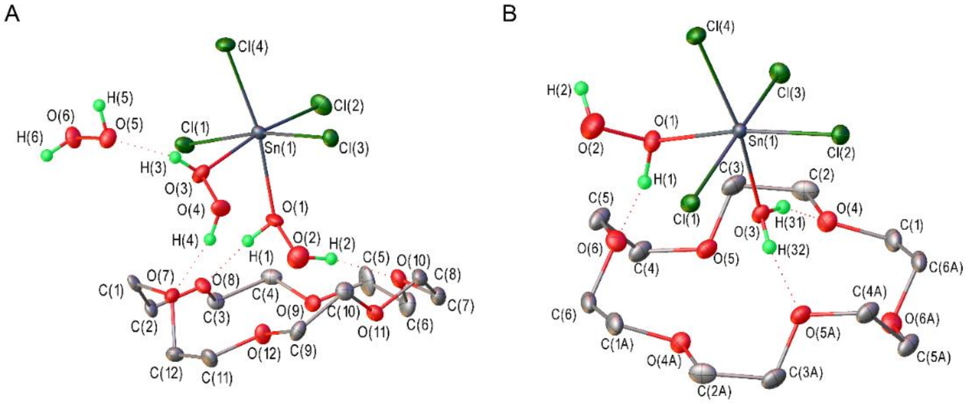

Figure 1. Asymmetric unit in **1** (A) and 2 (**B**).

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Noncovalent interactions in isolated molecules of sandwich complexes: A combined quantum chemical / laser spectroscopic study

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Metallocenes and related compounds are archetypical organometallics relevant to many areas of basic and applied chemistry including studies of the metal–ligand bonding, catalysis, nanoelectronics, and biomedicine. Both covalent and noncovalent intramolecular interactions are responsible for the specific structures and properties of sandwich systems. The role of covalent and ionic contributions to metal-ligand bonding, as well as weak noncovalent interactions between ligands, can be analyzed on the basis of DFT calculations coupled with high-resolution mass-analyzed threshold ionization (MATI) laser spectroscopy.

Ionic contributions appear to be responsible for unexpected structural transformations of some sandwich complexes upon ionization. For instance, DFT calculations predict a noticeable contraction of the interligand distance caused by a detachment of the nonbonding d_{z2} electron from the “17-electron” $(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5H_5)Ti$ molecule (**1**), in contrast to isoelectronic $(\eta^6\text{-}C_6H_6)_2V$ or “18-electron” $(\eta^6\text{-}C_6H_6)_2Cr$. Accordingly, the MATI spectrum of **1** shows a long vibrational progression on the metal-ligand symmetric stretch.[1] Electron density analysis reveals the higher ionic character of molecule **1** compared to other mixed sandwich systems.

Weak noncovalent interactions between Me substituents in methylated sandwich complexes lead to slightly different ionization energies of rotational conformers. Traditional photoelectron spectroscopy is unable to detect such differences. However, high-resolution threshold ionization spectra show well-resolved peaks corresponding to different rotamers of methylated bis(η^6-benzene)chromium.[2-4] This gives an unprecedented opportunity to study noncovalent interactions between substituents and their influence on ionization properties of sandwich systems. Recently, new data have been obtained from the DFT/MATI study of methylated cobaltocenes. The influence of Me-Me interactions on the ionization energy of $(\eta^5\text{-}C_5H_4Me)_2Co$ appears to differ from that in $(\eta^6\text{-}C_6H_5Me)_2Cr$. DFT calculations unveil the mechanisms responsible for such effects.

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Functional metallasilsesquioxanes: (non)covalent mechanisms of self-assembly

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Cagelike metallasilsesquioxanes is a growing class of metallacomplexes with attractive (supra)molecular architectures and different applications.[1, 2] Noncovalent mechanisms (metallocene, stacking, C-H…π or crown ether interactions) are non-trivial but influential effects governing the self-assembly of of metallasilsesquioxane cages/coordination polymers. Lecture will present recent results of our group in molecular design of metallasilsesquioxanes and investigation of their functionality.

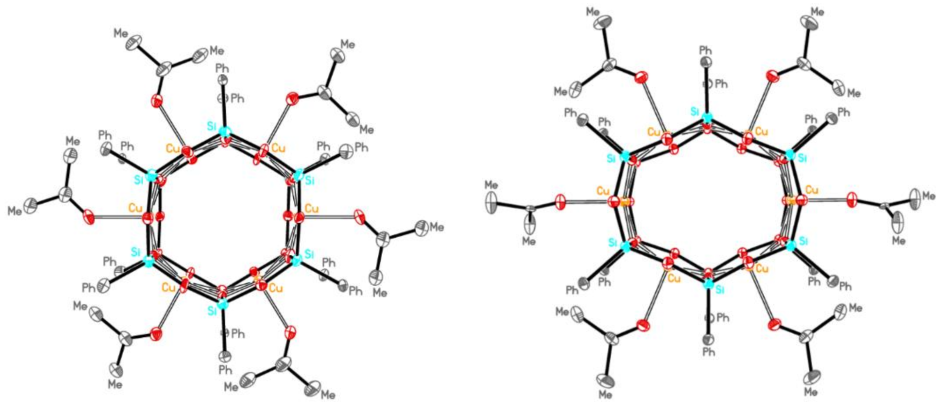

Figure 1. Top views of $[(Ph_6Si_6O_{12})_2Cu_6(acetone)_6]$ cages of regular (left) and ellipsoid (right) forms, governed by the localization of acetone solvates.[3]

Acknowledgements

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Non-covalent Interactions in Coordination Compounds with P,N- and related Ligands bearing Heterocyclic Luminophores

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Within the last few years our work was focused on the synthesis and study of coordination chemistry of novel N,N- and N,P-donor ligands bearing such well-known luminophore fragments as 2,1,3-benzothiadiazoles and 1,3-benzothiazole.[1-4] Compounds of the types shown in Figure 1 were found to be appealing ligands in neutral or anionic deprotonated form towards different kinds of metals both of main and neighboring groups of Periodic Table of the Elements. All the ligands as well as coordination compounds display interesting luminescent properties. In this report we present the first attempt to analyze correlation between the luminescence and the structures of the new compounds from the point of view of non-covalent inter- and intramolecular interactions existing in the crystal structures.

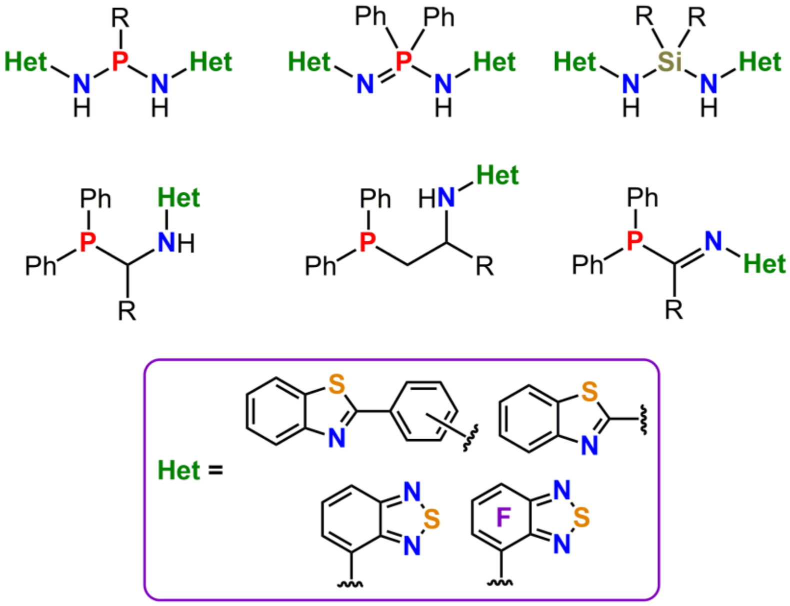

Figure 1. The major types of compounds used as ligands or proligands in this work.

Acknowledgements

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Structural-molecular plasticization of polymers: the role of non-covalent interactions and application limits for controlling the conformational structure in an elementary unit, the packing of macromolecules and the physicochemical properties of films

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Classical plasticization of polymers is divided into two types, which are opposite in thermodynamics, mechanism and manifestation effects: structural plasticization and molecular plasticization. *Structural plasticization* assumes that the additive and the polymer form a thermodynamically incompatible system[1]. In such systems, a structural plasticizer is introduced in small quantities (1–3 wt.%, "small additives") and increases the mobility of intermacromolecular structures due to adsorption (the "lubrication" effect), which leads to a decrease in the glass transition temperature of the polymers. *Molecular plasticization* implies a thermodynamically compatible polymer-solvent system, in which the solvent (molecular plasticizer) content can reach up to 50 wt. %, and the plasticization effect is achieved by reducing intermacromolecular interaction: non-polar in the case of a diluent (entropic process) or polar in the case of solvation (energetic nature of the interaction)[2].

Nature abhors a vacuum, and between two opposing concepts of the types of plasticizers, there must be an intermediate type. We proposed the concept of "*structural-molecular plasticization*", in which molecules of a low-molecular substance (which can also be solvent molecules) through non-covalent interactions initiate conformational ordering in the elementary unit of the polymer[3]. The implementation of hydrogen bonds with a binding energy > 20 kJ/mol under certain conditions can become comparable to the energy of covalent binding along the chain, which leads to a change in the packing of macromolecules in a polymer object (film) and contributes to a change in the physicochemical properties of this film.

For a number of aromatic polyetherimides, we have found a structural criterion that allows the most effective use of structural-molecular plasticization to control the gas separation characteristics of films: increasing the selectivity of gas separation without loss of gas permeability.

For polymers based on substituted cyclooctenes, we have found the limits of application of the structural criterion, in which structural-molecular plasticization has a limit for controlling the physicochemical properties of polymer films, which we can register spectrally and through the values of the dispersion component of the specific free surface energy.

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Exploring Reactions of Ambiphilic Selenyl Reagents with Unsaturated Substrates: Synthesis, Structures, and Non-covalent Interactions

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Small molecules, such as N_2O, N_2, CO_2, CH_4, simple nitriles, alkenes, isocyanides, and others, have the potential to become alternative cheap and readily available raw materials for the synthesis of more complex compounds (1). Throughout the past century, the activation of the small molecules has almost exclusively been associated with the use of transition metals. Catalytic transformations involving transition metals, developed over recent decades, have, without exaggeration, transformed both the chemical industry and human activity as a whole. Despite the appeal of transition metals, their use comes with several drawbacks, such as the high cost and toxicity of some derivatives. In 2006, Stephan made a groundbreaking discovery: he demonstrated that an effective system exists that does not contain transition metals and is capable of reversibly activating a small molecule like hydrogen (2). This discovery served as a starting point, after which the concept of using frustrated Lewis pairs for the activation of small molecules has been developed by many leading chemical centers worldwide.

In this report, our progress towards the application of another system—ambiphilic selenyl platforms—for the activation of unsaturated substrates will be highlighted. It will be shown that they are capable of forming covalent adducts with a number of unsaturated substrates, such as nitriles, isocyanates, isothiocyanates, isoselenocyanates, ketones and others. It will be demonstrated that these reactions are reversible. Furthermore, it will be shown that the aforementioned new reactions allow the synthesis of selenium-containing compounds that are inaccessible through other known methods. Many new electron-deficient selenium heterocycles are donors of the so-called chalcogen bond. The types of supramolecular organization of the new selenazoles in the solid phase, as well as their potential for directed construction of supramolecular assemblies, will be discussed in the report (3).

Acknowledgements

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Towards the criteria for distinguishing the covalent and noncovalent bonds

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It is important to establish whether there is a recognizable boundary between the typical noncovalent and covalent bonds. The problem related with the categorization of the type for strong Tetrel Bonds (TtB) is particularly interesting. As a rule, the TtBs are relatively weak or have to be assisted by charges. Relatively strong bonding in five-coordinated structures is usually classified as the donor-acceptor or covalent bonds. At that, the σ-holes of a Tt-atom undergo the steric hindrances. We revealed the physically sound picture of tetrel chemical bonds using the tools based on the orbital-free quantum crystallography[1]. The profiles of some one-electron functions along bond line are very informative[2]. We focused on the electrostatic, exchange-correlation and total static potentials along the bond lines. The 230 strong and weak TtBs were examined. We concentrated on the Cl-Tt/Cl…Tt and N-Tt/N…Tt (Tt = C, Si, Ge) bonds in molecular complexes, silanyls and germanyls, silatranes and germatranes, the systems at the reaction path of bimolecular nucleophilic substitution. Our observations show, that the difference between displacements of the electrostatic and total static potential’s extremes from the boundary of atomic basins highlights the information about the bond type. The qualitative differences between the weakened covalent and noncovalent bonds we observed using the behavior of the Fermi hole, the strong covalent interaction index (SCI), as well as the profiles of the Pauli potential along the bond line. All these descriptors lead to full agreement with the suggested criterion[2] based on the superposition of the total static and electrostatic potentials.

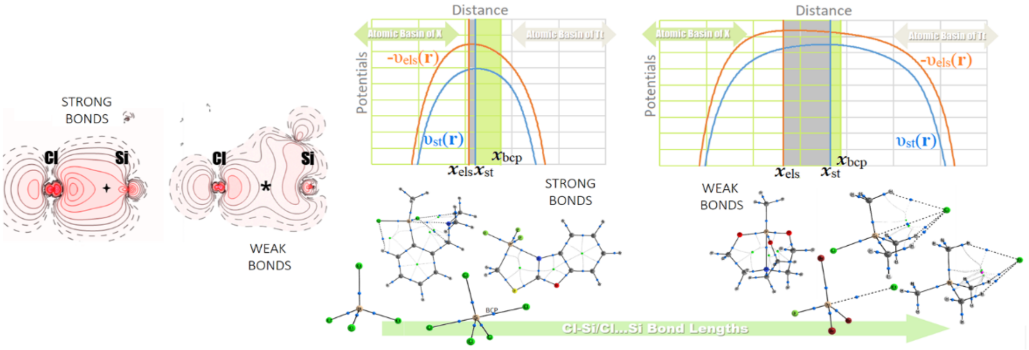

Figure 1. The Fermi holes and superposition of potentials along the Cl-Si/Cl…Si bond lines

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Research is supported by the Russian Science Foundation, grant № 22-13-00170.

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Diversity of Noncovalent Interactions of Cyclic Copper(I) and Silver(I) Pyrazolate Complexes

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Cyclic trinuclear copper(I) and silver(I) complexes (CTCs) with anionic pyrazolate ligands form a wide class of compounds with a planar structure. These complexes exhibit a variety of coordination chemistry, and their planar structure leads to metalophilic interactions in the solid state, determining their photophysical behavior through the formation of excimers. As Lewis acids, these compounds can form noncovalent intermolecular complexes with various bases. This opens up opportunities for designing new aggregates with predictable structures and properties. One popular strategy for creating new coordination compounds involves intermolecular forces, such as metal-metal or metal-π interactions.[1-4] On the other hand, the use of P- or N-containing ligands can lead to the rearrangement of the metal-pyrazolate core, opening up new possibilities for noncovalent complexes formation.

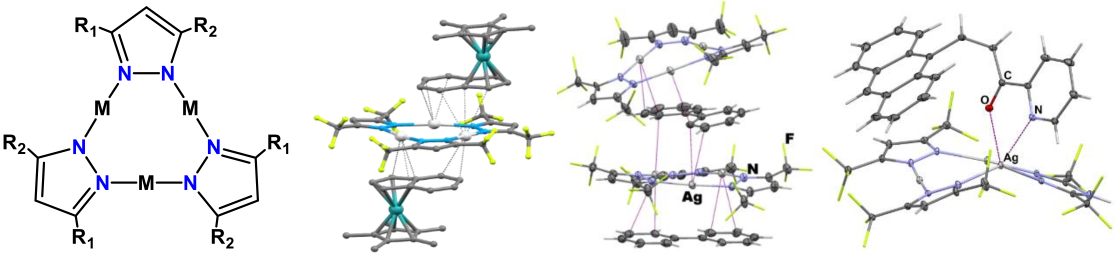

Figure 1. Chemical structure of CTCs and examples of their intermolecular complexes

The talk covers our findings on the investigation of the intermolecular interactions between trinuclear pyrazolate complexes and bases of various types and structures.

Acknowledgements

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Supramolecular polyhalogen-halometalates

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Ability of halide complexes (hetero- or, more commonly, homoleptic) to form inclusion compounds with di- or polyhalogens via halogen bonding (XB) was noticed decades ago. Surprisingly, this feature was not systematically studied for years; after a long pause, this area experiences revival nowadays.

The talk covers the results obtained by our group[1-7] within the last few years: the family of structurally diverse polyhalide-halometalates of bismuth, antimony, tellurium, tin, lead and some other elements, as well as their physical properties relevant to modern materials science.

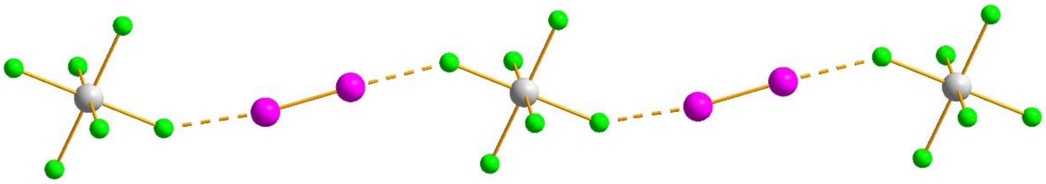

Figure 1. Example of polyhalogeno-halometalate: $\{[TeCl_6](I_2)\}$

Acknowledgements

This work is supported by Russian Science Foundation (23-73-10054).

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Ionic Liquids: Self-Organization at Nanoscale studied by EPR techniques

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Ionic liquids (ILs) draw an increasing attention in different fields of science due to their unusual physicochemical properties that give promise of various applications,[1] including new direction of porous liquids.[2] In particular, self-organization driven by non-covalent interactions and formation of nanostructures/heterogeneities are important properties of ILs. However, the detection and characterization of such nanostructures is often challenging; thus, the development of new experimental approaches for such studies is highly needed.

In a recent series of works, we developed and applied Electron Paramagnetic Resonance (EPR) methodology to study and characterize nanostructuring in ILs in a wide range of systems and conditions.[3] Since ILs are naturally diamagnetic, various spin probes (including directly spin-labeled ILs[4]) and corresponding techniques have been used. We demonstrate that complex application of continuous wave, pulse and time-resolved EPR allows obtaining unique information on nanostructures formed in ILs,[5] IL-water mixtures[6] and composites that include ILs.[7] This report summarizes our recent developments on EPR of ILs and provides perspective for future research.

Acknowledgements

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INVITED LECTURES

Adding a dimension: crystal engineering of iodonium-based 1D and 2D assemblies

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Halogen bonding as tool of crystal engineering is widely used in various fields of chemistry, including mechanochemistry, catalysis and the design of new materials. Particularly interesting is design of porous materials based on noncovalent interaction to achieve the simpler regeneration of such materials after sorption. However, the design of noncovalent bonding framework is still complicated due to low predictability of crystal structure. Moreover, weak noncovalent interactions do not allow designing a stable framework structure.

In our work, we propose utilization of iodonium salts as charged halogen bond donors. We displayed fundamental possibility of targeted design of various supramolecular architectures (0D, 1D and 2D) depending on the charge of the anion and cation structures. [1,2]

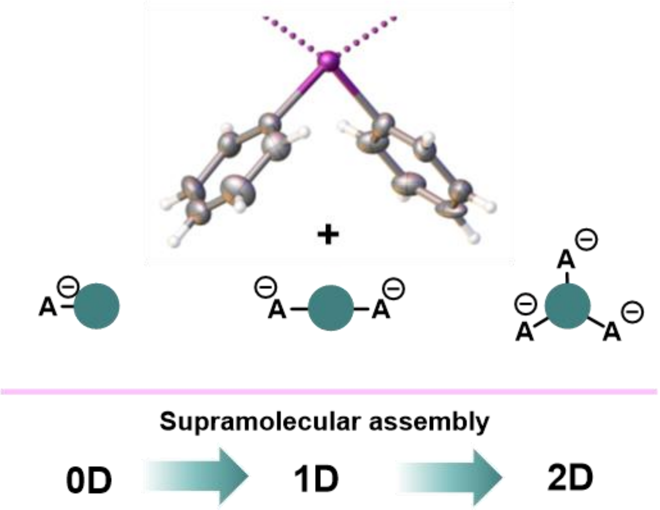

Figure 1. Adding a dimension to supramolecular assembly of iodonium salt

Acknowledgements

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Hydrogen Bonding and Anticancer Properties of Palladium(II) Acyclic Diaminocarbene Complexes

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Noncovalent interactions, in particular hydrogen bonds, play a pivotal role in biological molecular recognition and binding. Hydrogen bonding, hydrophobic and electrostatic interactions can effectively enhance site- and base-recognition, not only of nucleic acids but also of proteins and enzymes. The presence of hydrogen bonding can also enhance the solubility of the resulting drugs in biological media.

In this context, transition metal complexes with acyclic diaminocarbene (ADC) ligands offer significant advantages for biological applications [1]. The electrophilicity and Bronsted acidity of NH hydrogens, as well as the presence of a lone pair of electrons on the nitrogen atoms of the deprotonated ADC species, ensure the involvement of the N(H) groups in intra- and intermolecular hydrogen bonds with biomolecules. The flexibility of the open structure of acyclic diaminocarbene ligands not only leads to different metal-carbene interactions, but also results in the adaptation to biological targets for efficient binding.

This talk will report the discovery of a novel classes of hydrolytically stable Pd^{II} and Pt^{II} species with *C,N*-chelated acyclic diaminocarbene ligands, which exhibit excellent antiproliferative activity for cancer cells in vitro (IC_{50} up to 0.07 μM) together with effective inhibition of tumor growth model in mice [2]. Hydrogen-bond interactions seem to be a key factor in the observed their biological activity.

Acknowledgements

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Noncovalent Catalysis with Organic Lewis Acids

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Organocatalysis is an attractive alternative to metal complex catalysis due to the significantly lower harmful effects on the environment and the low sensitivity of organocatalysts toward atmospheric oxygen and moisture. One of the directions in the development of the field of electrophilic organocatalysis is the preparation of analogues of metal complex catalysts featuring a nonmetal element with a kinetically labile coordination vacancy as the central atom. Such catalysts combine high activating ability, environmental friendliness, and high stability toward oxygen and water.

The report will discuss the latest experimental data on the kinetics of reactions in the presence of cationic organochalcogen and organohalogen compounds (Figure 1). Special attention will be paid to the creation of tandem catalytic systems involving a new type of organocatalyst and untypical patterns of the reactivity of the organocatalysts.[1-4]

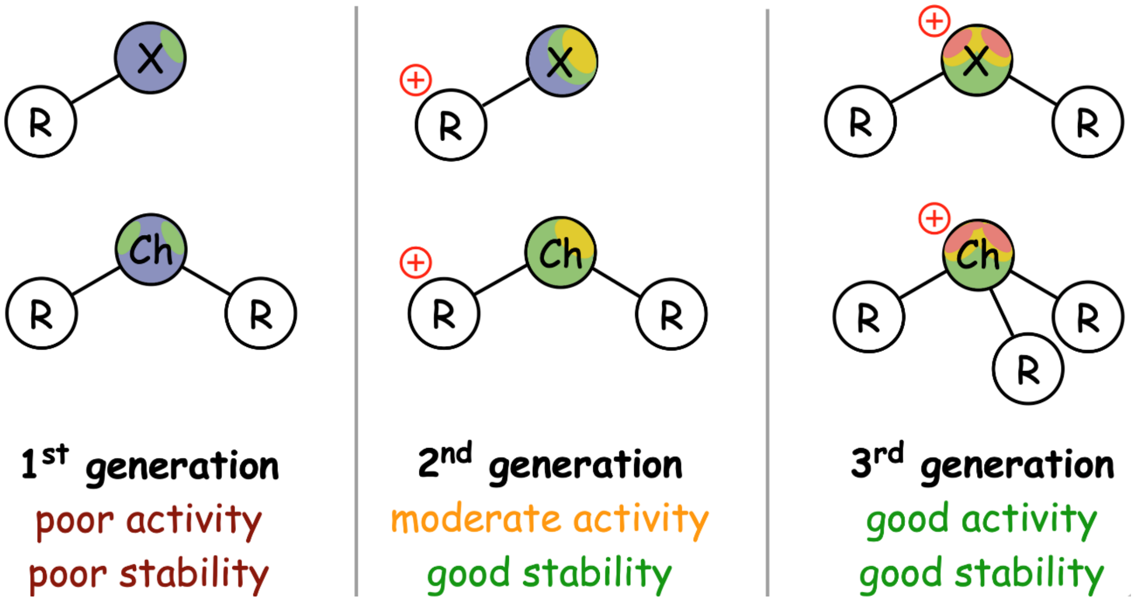

Figure 1. Schematic representation of the catalysts structures.

Acknowledgements

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Bis((9H-(diazafluoren)-9-ylidene)methyl)arylenes: Structure, Optoelectronic Properties and Sensorics

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Fluorene derivatives are widely used in active layers of semiconductor and light-emitting devices.[1] Their wide structural variability allows one to obtain materials with tunable functionalities for organic optoelectronics and sensorics. Particularly, 9H-fluorene-9-ylidene derivatives possess aggregation-induced emission, mechano- and thermochromism due to conformational rearrangements in solid state.[2] Additionally, introduction of nitrogen atoms in fluorene moiety allows one to improve electron-withdrawing effect, stability and brings N,N’-chelating ability.

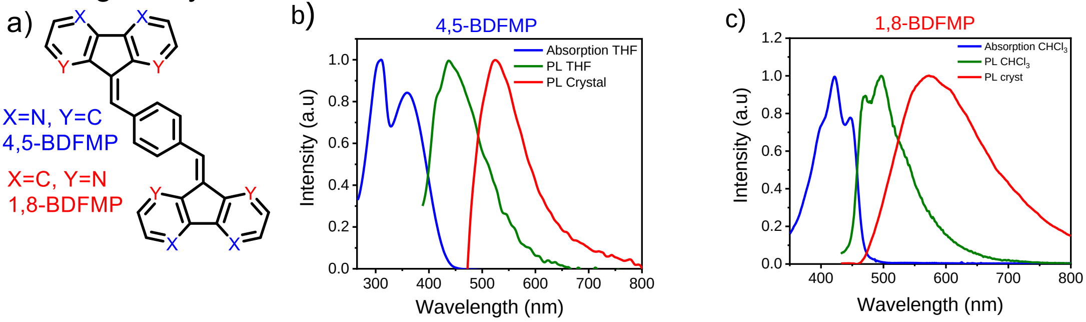

Figure 1. Structures of 1,4-bis((9H-(diazafluoren)-9-ylidene)methyl)phenylenes (4,5- and 1,8-BDFMP) (a), absorption and photoluminescence spectra of 4,5-BDFMP (b) and 1,8-BDFMP (c) in solutions and crystals.

Here, we studied molecular/crystal structure and optoelectronic properties of bis((9H-(diazafluorene)-9-ylidene)methyl)arylenes (Fig. 1). Two polymorphic forms with different types of aggregation and photoluminescent characteristics were obtained for 4,5-BDFMP. Addition of metal cations was shown to increase photoluminescence intensity of 4,5-BDFMP solution. 4,5-BDFMP forms emissive coordination polymers with a porous structure, which allows its application as sensors and security inks. 1,8-BDFMP demonstrated highly rigid and planar structure due to non-covalent N…H intramolecular interactions. High electron-accepting character of diazafluorene moiety results in a π-π-stacked crystal packing for both derivatives. Despite the rigid and planar structure and strong H-aggregation behavior, 1,8-BDFMP possessed aggregation-induced emission with photoluminescence quantum yield of 0.04% in solution and 10% in single crystals. Therefore, introduction of diazafluorene moieties is a powerful tool for design of conjugated materials with tunable functionalities for organic optoelectronics.

Acknowledgements

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Iodides of heavy *p*-elements as halogen bond donors

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The halogen bonding defined in 2013[1] is still actively investigating type of noncovalent σ-hole interactions. In most cases, iodine atoms bound to electron withdrawing substituent through nonmetal atom are electrophilic centers in the formation of halogen bonds. In this work we show that heavy *p*-element iodides including electropositive Ge, Sn and Sb atoms can also be halogen bond donors toward iodide ligands, which was demonstrated in their cocrystals with *trans*-$[PtI_2(NCNR_2)_2]$ (R_2 = Me_2, $(CH_2)_4$) (Figure 1). The single-crystal XRD data revealed the M–I···I–Pt interactions, which can be treated as halogen bonds due to their geometric parameters and further theoretical calculations, performed in models with periodic boundary conditions.

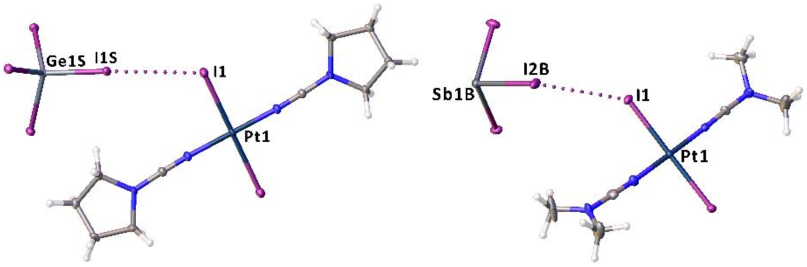

Figure 1. Views of the Ge–I···I–Pt (left) and Sb–I···I–Pt (right) interactions.

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Halogen Bonding on Serve of Nitronyl-Nitroxides

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Stable organic radicals are one of the promising building blocks for design of qubits, organic memory devices and magnetic materials. In all abovementioned applications control of inter- and intramolecular exchange interactions are the key factors influenced on final properties of materials. For example, symmetrical triradical reported by us early[1] despite equal linkers and radical moieties has five-fold differenced J values specified by solid-phase organization. Typically, hydrogen bonds significantly determined intermolecular short contacts but, in our research, we focused on more directional and energy efficient halogen bonding.

We found that addition of halogen bonding donor as 1,4-diiodotetrafluorobenzene to pyridine-containing nitronyl-nitroxides lead to formation of family of new phases depending on component ratio.[2] In all cases unique architectures of intermolecular short contacts were observed leading new materials from the same starting compounds.

In another case[3] we demonstrated that addition of halogen bond to non-crystallize nitronyl-nitroxide allowed to obtain suitable for single crystal XRD and homogeneous samples. Thus, halogen bonding could be possessed as new tool for control and changing of solid phase organization and as a result magnetic properties.

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Cyclic and macrocyclic polyhydroxylamine ligands for coordination chemistry and design of H-bonded networks

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Cyclic polyamines and aza-crowns have tremendously impacted many areas, including coordination chemistry, catalysis, nanotechnology, medicine, and materials chemistry. The ability of these ligands to serve as multiple H-bond donors/acceptors provides vast opportunities for application in crystal design, recognition, and sensing of small molecules.

Replacing the N–H moiety with an N–OH group enables the alteration of the coordination and hydrogen bonding properties of amines. With this idea in mind, we designed and synthesized (macro)cyclic poly-*N*-hydroxylamines that incorporate up to five N–OH units within one molecule.[1,2] The structures of these ligands and their complexes with d-metal ions and small molecules are governed by the formation of multiple intra- and intermolecular hydrogen bonds involving hydroxylamine motifs.

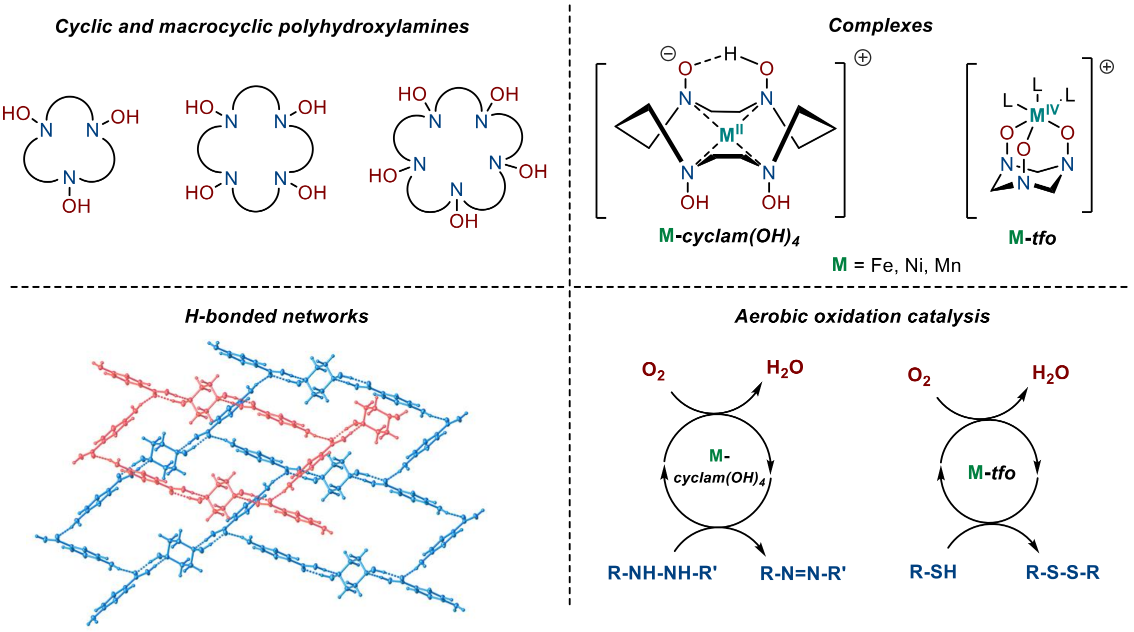

Figure 1. Cyclic and macrocyclic polyhydroxylamine ligands

Acknowledgements

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The key role of hydrogen bonds of hydroperoxo groups in the formation of functional materials from peroxide containing sols

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The sol gel process in peroxide systems is based on a number of unique properties of hydrogen peroxide. Firstly, hydrogen peroxide has acidic properties. Secondly, hydrogen peroxide in its molecular form is a weak ligand and does not form the corresponding coordination compounds in the presence of coordinating solvents. In basic media, H_2O_2 is deprotonated and forms peroxo- and hydroperoxo complexes.[1, 2] In addition, hydrogen peroxide forms strong hydrogen bonds, while the H_2O_2 molecule always participates in the formation of two H-bonds as a proton donor, which, due to the acidic properties of hydrogen peroxide, are higher in energy than those of water molecules in isostructural hydrates.[3]

Addition of H_2O_2 to systems of hydroxo compounds of p-block elements results in competing reactions of polycondensation and coordination of peroxo ligands, which, under certain concentration conditions, makes it possible to obtain and stabilize sol particles with high activity on the surface of the substrate material due to the presence of terminal hydroperoxo groups capable of forming strong H-bonds. Such sol particles are a building block for the production of composite materials of various morphologies. The deposition of a sol on the surface makes it possible to obtain composite 2D materials in which nanoparticles of the oxide of the corresponding element form continuous thin films.[4] In addition, the presence of peroxo groups in sol particles makes it easy to modify films through interaction with various oxidizing or reducing agents. Thus, treatment of a film of nanoparticles of peroxo complexes of tin, antimony, zinc and other elements with gaseous hydrogen sulfide followed by heat treatment makes it possible to obtain sulfides of the corresponding elements in the form of continuous uniform nanocrystalline coatings on the surface of the substrate material.[5,6]

Acknowledgements

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Metallophilic interactions in the chemistry of gold complexes bearing N-heterocyclic ligands

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Metallophilic interactions impart important properties to functional materials such as luminescence, polychromism, magnetism, or one-dimensional electrical conductivity. This phenomenon is generally considered as weak attractive interactions between adjacent metal centers due to the overlapping of their d_{z2} and p_z orbitals and it has been intensively studied in recent years. Most reports in this area are related to the solid state, where structural parameters obtained by X-ray diffraction provide precise information on metal···metal contacts. In the structures of gold complexes, intra- and intermolecular weak bonding Au···Au interactions (aurophilic interactions) are often realized, as a result of relativistic and correlation effects. Such specific noncovalent interactions are manifested in all areas of gold chemistry, especially in catalysis and photoluminescence.

In this work, we report the synthesis and properties of a series of gold complexes based on N-heterocyclic ligands displaying aurophilic and other weak interactions. These are Au(I) complexes with aromatic acceptor diimines, such as 1,10-phenanthrolines, 2,2’-bipyridines, bis(arylimino)acenaphthenes (BIAN) and others, as well as complexes Au(III) complexes with macrocyclic tetraarylporphyrins (TPP) (Figure 1).[1-4]

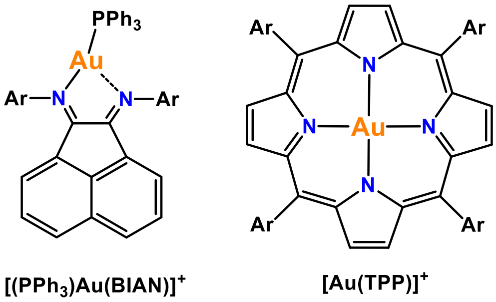

Figure 1. Examples of studied gold complexes.

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Noncovalent interactions of aromatic fragments as a factor of the formation of new structures

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When analyzing the molecular and crystal structure of compounds, increasing attention is being paid to the role of non-covalent interactions. An urgent task for targeted use of them as a structure-forming factor, is to study systems in which the results of these interactions are quite evident. The combination of aromatic fragments with strong electron-withdrawing substituents and various aromatic ligands can lead to the formation of unusual structures or the formation of atypical reaction products. To study the structure-forming effects manifested in such combinations, we synthesized and studied pentafluoro- and tetrafluorobenzoate complexes of Cd, Ln, and 3d metals with heterocyclic N-donor ligands. Structure-forming effects in these systems are provided by a combination of π-π, C-F-π, C-H-F, F- π and other types of non-covalent interactions. For compounds of Cd and Ln there was a strong tendency to form 1D coordination polymers with compositions typical of molecular carboxylate complexes; for 3d metals the formation of new types of carboxylate complexes or atypical reaction products was observed. As in arene-perfluoroarene cocrystals, the crystals of coordination compounds formed stacks in which pentafluoro- or tetrafluorophenyl substituents of carboxylate anions alternated with various other aromatic moieties.

To obtain a more complete picture of possible chemical transformations, it was advisable to focus on aromatic fragments with other types of substituents. The nitro group belongs to the strongest electron-withdrawing substituents, and analogs of pentafluorobenzoate were obtained with anions of 2,4- and 3,5-dinitrobenzoic acid.

Using several different anions made it possible to significantly expand the structural diversity of new carboxylate complexes, obtain them as actual chemical compounds and structurally characterize almost all types of complexes that were considred as hypothetical intermediates of quantum chemical calculations.

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ORAL COMMUNICATION

[$NiL_2(ROH)_2$] low-temperature ferromagnets: intermolecular contacts and magnetic properties

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One of the main problems in the field of molecular magnetism is the synthesis of magnetically active compounds that are stable under environmental conditions and have reproducible properties. This is due to the fact that the structural fragments forming the crystals of these compounds are connected by weak intermolecular interactions, including those between paramagnetic centers. The latter are highly sensitive to their mutual arrangement, which is reflected in the magnetic properties of the compounds.

The results of studying a series of layered-polymer complexes of Ni(II) with trifluoro-derivative of 3-imidazoline nitroxide radical by alcohols [$NiL_2(ROH)_2$] are discussed. The influence of changing intra- and intermolecular contacts on their magnetic properties is demonstrated.

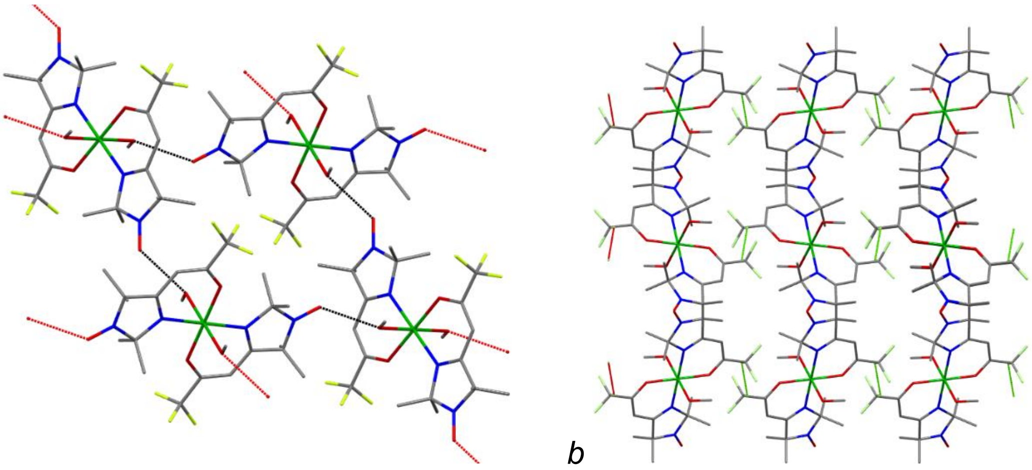

Figure 1. (a) Intralayer H-bonds OH…O_{NO} (red dot lines) and (b) interlayer F…F contacts (green dot lines) in the crystal structure of [$NiL_2(MeOH)_2$]

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Supramolecular strategy in the synthesis of graphite-like carbon nitride for photocatalytic applications

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The global trend towards decarbonization of economies and energy systems requires the development of new energy sources. The areas of alternative energy based on the use of solar energy have paramount scientific significance and practical prospects. The process of photocatalytic production of H_2, as well as CO_2 reduction, under visible light is considered to be especially attractive in this area, since in this case the transformation of solar energy into the energy of chemical bonds is carried out.[1,2] The main factor hindering the practical use of photocatalytic processes such as hydrogen production and CO_2 reduction is the lack of efficient and at the same time stable heterogeneous photocatalysts functioning under the visible light irradiation, which makes up about 43% of the solar spectrum. Recently, more attention of researchers has been attracted by the graphitic carbon nitride g-C_3N_4. It has the properties of a semiconductor with a band gap of 2.7 eV, and the positions of the valence and conduction bands are suitable for water splitting and CO_2 reduction.[3]

However, bulk g-C_3N_4 synthesized via traditional thermal polymerization methods usually suffers from low surface areas, short lifetimes of photogenerated charge carriers caused by the π–π conjugated electronic system and unsuitable photo-redox potential. Architecting of materials with the framework predesigned for the target application is the general tendency of modern material science. Recently, a two-component N-rich precursor, melamine-cyanuric acid supramolecular complex was used as starting material to synthesize C_3N_4.[4] This supramolecular complex contains two components, which are linked to each other by hydrogen bonds to form a planar structure that is similar to that of bulk g-C_3N_4. It has been shown that the use of this supramolecular structure in the synthesis leads to the materials with enhanced photocatalytic properties. This report will describe the use of supramolecular strategy in the synthesis of g-C_3N_4-based photocatalysts. The relationship between the characteristics of synthesizing g-C_3N_4 and its activity in the targeted processes of hydrogen production and carbon dioxide reduction will be discussed.

Acknowledgements

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Supramolecular organization and intermolecular interactions in novel peroxosolvates of highly-energetic compounds.

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At the beginning of the 21st century, multicomponent highly-energetic materials (cocrystals and salts) become the objects of intensive research due to their enhanced physicochemical properties.[1] Quite recently, peroxosolvates (crystalline adducts of hydrogen peroxide[2]) of highly-energetic organic compounds attracted particular interest. Cocrystallized hydrogen peroxide, being a source of additional oxygen, can correct negative oxygen balance of most energetic materials and thus improve their detonation properties.[3]

Crystalline hydrogen peroxide adducts of (nitropyrazolyl)furazans $C_6H_5N_5O_3{\bullet}H_2O_2$ (**1**$\bullet H_2O_2$), $C_6H_4N_6O_5{\bullet}H_2O_2$ (**2**$\bullet H_2O_2$) and $5(C_5H_2N_6O_5){\bullet}H_2O_2$ (**3**), were prepared from highly concentrated hydrogen peroxide and their structures were determined by X-ray crystallography. All three crystal packings are based on the same supramolecular synthon built by peroxide molecule and three adjacent coformers. All H_2O_2 molecules forms three hydrogen bonds. Compound **3** is the rare example of hydrogen bonding between H_2O_2 molecule and nitro group and besides that showing medium strength.

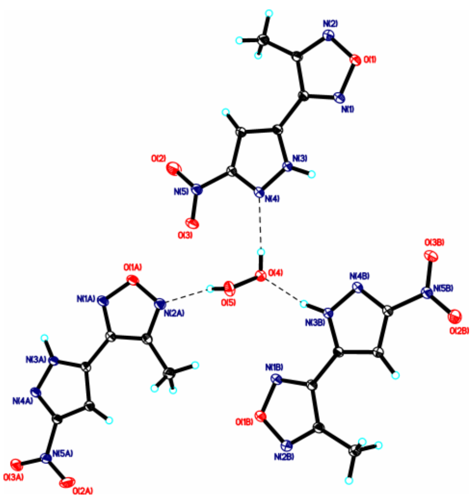

Figure 1. Hydrogen bonded motif in the structure **1**$\bullet H_2O_2$.

First peroxosolvate of zwitterionic diazo compound $^{-}O_3S\text{-}C_6H_4\text{-}N_2^{+}{\bullet}2(H_2O_2)$ (**4**$\bullet H_2O_2$) was obtained from solution in 98% hydrogen peroxide. X-ray diffraction study showed that both independent H_2O_2 molecules are involved in almost linear short hydrogen bonds HOOH…$^{-}O_3S$-C, HOOH…O_2H_2, and strong electrostatic C-N_2^{+}…O_2H_2 interactions perpendicular to C-N≡N^{+} direction with short N^{+}…O separations around 2.8 Å.

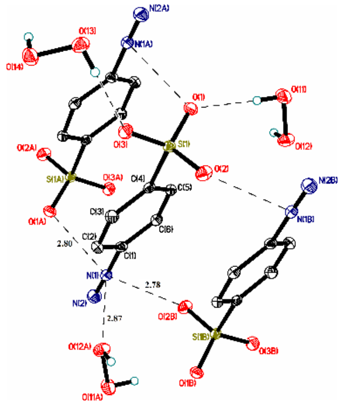

Figure 2. Supramolecular aggregation in crystal **4**$\bullet 2H_2O_2$.

Acknowledgements

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Unraveling the luminescent sensing mechanisms of metal-organic frameworks through MOF-analyte interaction analysis

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Luminescent metal-organic frameworks (MOFs) are of interest primarily in connection with the possibility of their use as sensors, since when different analytes (gases, metal cations, small organic molecules) interact with the surface of the frameworks, its photophysical properties – wavelength and emission intensity may vary significantly. The mechanisms of interactions between the analyte and MOF, leading to the luminescent sensing response, in most cases are very complex and practically unexplored.

Two selected cases are discussed in the presentation. One of them is related to luminescent zirconium-organic framework assembled from $[Zr_6O_4(OH)_4]^{12-}$ oxo-clusters and 4,4'-(2,1,3-benzooxadiazole-4,7-diyl)dibenzoate anions, which demonstrates a highly sensitive emission enhancement response to ammonia and amines in water with part-per-billion limits of detection (LOD).[1] The luminescence enhancement mechanism was rationalized on the basis of DFT analysis of the interaction between ammonia molecule and 2,1,3-benzooxadiazole fragment which revealed a non-covalent N-H···N interaction leading to strong symmetry disruption of the electronic density distribution in the excited state, resulting in emission enhancement.

The second case describes the luminescence quenching response of terbium(III)-based MOF with a flexible tetracarboxylate ligand towards sulfadiazine (SDI) antibiotic with extremely high sensitivity (LOD 0.48 nM) and high selectivity (antibiotics of three other groups demonstrated no strong quenching). In our previous works the luminescence quenching was in good correlation with relative HOMO/LUMO orbital energies of MOF models and analytes – if the photoinduced electron transfer (PET) process was possible, strong quenching was observed.[2] However, in the discussed case, we have found that two different antibiotics, ciprofloxacin (CIP) and SDI, which have similar HOMO/LUMO levels and for both of which the PET process is possible, demonstrate quite different luminescence behavior. To the best of our knowledge, for the first time we propose a new approach to analyze the PET in MOF-analyte supramolecular complexes based on the extended analysis of electron density distribution in the excited state by TD-DFT calculations. As a result, peculiarities of non-covalent interactions between the analytes (CIP and SDI) and MOF model were revealed; the calculations of analyte-MOF supramolecular complexes allowed to highlight the difference in charge transfer between the analyte (CIP and SDI) and MOF in the excited state.

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Role of Noncovalent Interactions in Structure and Properties of New Metal Complexes with N-Substituted Imidazoles

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N-Substituted imidazoles (benzimidazoles) and their metal complexes are among the most promising compounds for medicinal chemistry; based on them, numerous drugs with a range of useful properties have been obtained.[1, 2] New 13 imidazole (benzimidazole) complexes of zinc(II), cobalt(II), nickel(II) and cuprum(II) were synthesized and studied by X-ray analysis, NMR, FTIR spectroscopy and quantum chemical calculations methods (AIM analysis, molecular docking)[3].

The antimicrobial activity of compounds was tested against to *E. durans*, *B. subtilis* and *E. coli*. The complex of cobalt chloride with allylbenzimidazole (Fig.) showed antimicrobial activity in relation to *E. durans* and *E. coli* several times higher than gentamicin. AIM analysis and molecular docking made it possible to investigate the features of noncovalent interactions (hydrogen bonding, π-stacking) of the resulting compounds in the crystal and with biological targets.

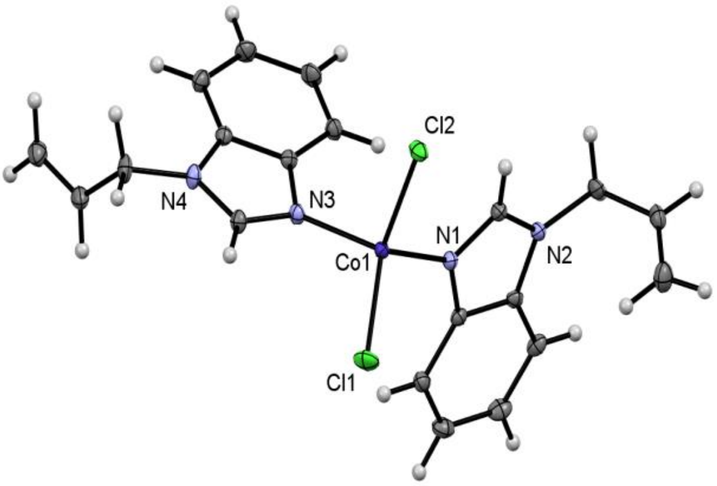

Figure. Molecular structure of cobalt chloride with allylbenzimidazole ligands

Acknowledgements

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ROK$^+$-η^n-arene coordination as substrate preorganization and activation for superbasic metalation and intermolecular hydroamination

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Non-covalent intermolecular interactions in systems containing s-block metals play an important role in many biological, chemical processes and can be fruitfully employed in catalysis. In this work, we synthesized a series of potassium alkoxides with a super bulky carbinolate ligand.[1] Due to coordination unsaturation, potassium ions coordinate various aromatic and heteroaromatic substrates. Coordinated benzene and toluene within the potassium coordination sphere can undergo metalation into the core and side chain, respectively, upon interaction with *n*-BuLi and Me_3SiCH_2Li (Fig. 1).

In this work, unprecedented results were obtained on the intermolecular hydroamination of olefins, catalyzed by the ROK$^+$-BnK binary system. It is assumed that the pronounced electrophilic nature of potassium alkoxide promotes precoordination of olefinic substrates and the amide anion, allowing rapid and efficient hydroamination.[2]

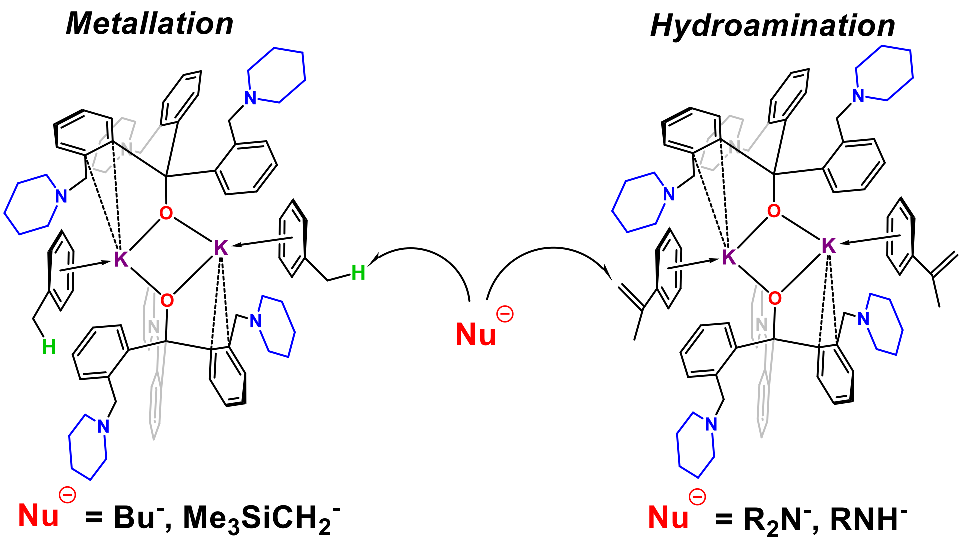

Figure 1.

Acknowledgements

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The role of intermolecular interactions and crystal structure in photoisomerization and mechanical response of solid pentaamminenitrocobalt(III) complexes

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Crystals exhibiting various mechanical effects during phase transitions and chemical reactions, such as jumping, twisting, bending, shape and size change attract much attention. The reason of this is the fact that such crystals are promising for creation of various micro- and nanodevices such as sensors, displays, movers, switches. A number of papers on this topic has been published, these contributions are mainly devoted either to studies of new substances with these effects, or to shedding light on the nature and a detailed study of the mechanical response phenomenon itself[1,2].

Chemical reactions generate mechanical response of a crystal. Therefore, *in situ* crystallographic studies of products and reactants are often helpful to explain this phenomenon. At the same time these studies do not provide information on the effect of mechanical loading on selected intermolecular interactions. In this case studying the influence of external action on reactant and product crystal structures even without photochemical reaction can be helpful. The study of the effect of deformation on the isomerization was carried out earlier under uniaxial loading of a crystal with its simultaneous irradiation, however, this approach significantly limits the area of the samples. It requires a specific crystal habit, like needles or rods, that cannot be obtained for all compounds of interest. This approach in fact was applied to a single compound $[Co(NH_3)_5NO_2]ClNO_3$ only.

This contribution will present the results of using a new approach to create a load on the crystal using external hydrostatic compression, cooling and changing the size of outer-sphere anions of coordination compounds (“internal pressure”). Cobalt nitropentaammine complexes with various outer-sphere anions undergoing nitro-nitrito linkage isomerization accompanied with mechanical response were chosen as objects of studies. The contribution is intended to show how comparison of the anisotropy of structural strain caused by the photochemical reaction itself, hydrostatic compression, temperature change, and anion substitution can help to establish the relationship between mechanical response, photochemical transformation and intermolecular interactions in crystal structure that is important for the practical use of mechanically responsive crystals in materials and devices[3-5].

Acknowledgements

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Coordination-Supported Chalcogen Bonding for Molecular Design and Enhanced Properties

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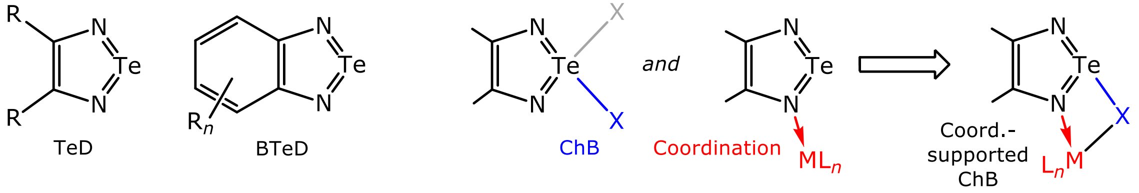
Tellurium-based chalcogen bonds (ChB) are among the most appealing non-covalent interactions that include heavy elements. These ChBs are noticeably stronger as compared to those with sulfur or selenium, and can allow for much more versatile structural chemistry to be studied. In 1,2,5-telluradiazoles (TeD) and benzo-fused derivatives, the Te atom can form one or two chalcogen bonds, thus leading to oligomers or polymeric structures. Energies of these Te–X ChBs (calculated at 1–10 kcal/mol)[1] make it possible to form stable complexes with- different types of donors (*e. g.* X = halogenides, chalcogenolates, neutral N- or C-donors), possessing molecular or polymeric structures.[2] Nitrogen atoms of the TeD ring can also form „classical“ coordination bonds with acceptors (such as BPh_3). One of consequences is the $[Te_2N_2]$ secondary bonding units in free TeDs, that result in their low solubility.

We propose simultaneous use of donor and acceptor interactions of the TeD ring by forming 4-membered [TeN···MX] secondary bonding units, which include *both* coordination with a N atom and ChB with the Te atom of the ring (M = metal centre, X = donor atom). Complexes of benzotelluradiazole (BTeD) with AlX_3 (X = Cl, Br) were first to demonstrate the viability of such an approach: in various ratios, oligo- or polymeric chains with alternating BTeD and AlX_3 units are formed, with the direct N to Al coordination and Te···X distances characteristic for a ChB (2.92–3.22 Å for Cl, 3.02–3.30 Å for Br). Mutual orientation of the fragments is determined by these bonds. Complexation with copper(I) halides (PPh_3CuX, X = Cl, Br, I) leads to a series of molecular and polymeric structures, which include Cu–N coordination and Te···X ChBs. Influence of bonding in this series on molecular geometry and spectroscopic properties is discussed.



Acknowledgements

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Binary Co-crystals of Functionalized Polyhalogenarenes with Macrocyclic Ethers: Structure and Self-assembly Regularities

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The report considers a systematic study of a family of objects (~60) for crystal engineering – molecular co-crystals of polyhalogenated arenes containing H-donor functions with crown ethers.[1-5] Variable parameters in the structure of co-formers are: crown ether size (18-, 15-, 12-membered), aromatic framework (benzene, pyridine, naphthalene, quinoline, biphenyl), acceptor fragment (CF_3, CN, NO_2, N_{het}), kind and number of hydrogen bond donors (NH_2, OH, COOH) and halogens (F, Cl). There are characterized the types and competition of the main structure-forming interactions (hydrogen bonds X-H…Y, where X = C, N, O, Y = O_{cr}, O_{nitro}, N_{cyano}, N_{het}, N_{amino}, Hlg; p…π and π…π electron contacts), motifs and dimensions of the supramolecular structure. The role of the structural elements in co-formers as factors controlling the selectivity and stoichiometry of co-crystallization, common features and peculiarities of the supramolecular structure, thermodynamic and photophysical characteristics of co-crystals is evaluated.

(TD-)DFT calculations and QTAIM, NBO, NCI analyses are used to describe at a quantitative level criteria of the co-crystallization behavior, efficiency of various supramolecular synthons and photophysical effects upon co-crystallization. Tools are proposed for designing crystals with demanded structure and characteristics.

The first example of 18-crown-6–promoted self-assembly of the co-crystals with helical chirality ($P6_1$, $P6_5$) based on the achiral octafluorobenzidine molecule has been discovered.

The molecular recognition effect, based on the linear correlation between the supramolecular and thermodynamic parameters of the co-crystals, was used to isolate high-purity diamine monomers for polycondensation. The detected change in the fluorescent characteristics of polyhalogenaromatic amines upon co-crystallization simulates the operating principle of solid-state supramolecular thermal and chemoindicators.

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SHORT COMMUNICATION

Interaction of iodide cluster complexes $[\{M_6I_8\}I_6]^{2-}$ (M = Mo, W) with dimethyl sulfoxide

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There are less explored areas in the chemistry of octahedral cluster complexes of molybdenum and tungsten. For example, cationic complexes, which can be obtained by replacing the terminal ligands with neutral molecules (e.g. coordinating solvents). Even less studied heteroleptic cluster complexes (with several types of terminal ligands) can be obtained by gradual ligand substitution. Such compounds exhibit a unique set of properties with significant practical potential (X-ray contrast, luminescence, photocatalytic activity, etc.); they are also interesting from the point of view of coordination chemistry due to the presence of labile ligands.

In this work the interaction of iodide cluster complexes of molybdenum and tungsten with dimethyl sulfoxide (DMSO) has been studied, mono- and disubstituted products have been obtained and structurally characterized. The 1H-NMR and SC-XRD methods were used to compare the observed signals with specific substitution products, allowing the substitution route to be defined.

The addition of molecular iodine shifted the equilibrium of the reaction towards more substituted forms up to homoleptic hexasubstituted products. Based on this study, a method for the synthesis of cluster complexes with triiodide counterions $[\{M_6I_8\}(DMSO)_6](I_3)_4$ (M = Mo , W) was developed.[1] Analysis of the structures of these compounds revealed the presence of non-covalent I-I interactions between inner iodine ligands and triiodide anions (Mo: 3.647-3.952 Å; W: 3.868-3.991 Å). The literature describes the same cluster complexes but with nitrate counterions,[2] so it was possible to evaluate the effect of the counterion on the optical properties and solubility of such compounds.

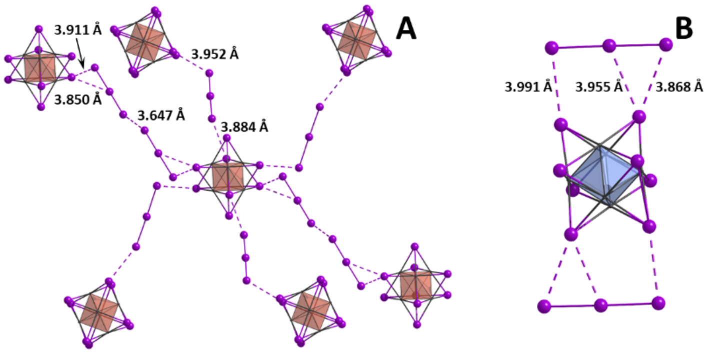

Figure 1. I-I contacts in the structure of $[\{Mo_6I_8\}(DMSO)_6](I_3)_4$ (A) and $[\{W_6I_8\}(DMSO)_6](I_3)_4 \cdot 4DMSO$ (B).

Acknowledgements

This work was supported by the Russian Science Foundation (№22-73-10174).

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Ionic and supramolecular approaches in the design of smart emissive hybrid materials based on octahedral cluster complexes

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Luminescent organic, inorganic and hybrid materials are the subject of active investigation by a large number of groups in the world scientific community. One of the most promising classes of compounds for the preparation of such materials are the octahedral cluster complexes of molybdenum and rhenium, whose general formula can be expressed as $[\{M_6X_8\}L_6]^n$, where M is the metal and X and L are the ligands of the inner and outer spheres of the complex. Complexes of this composition have strong absorption in the ultraviolet and visible spectral range, up to 550 nm. Their combination with compounds luminescing in this range can lead to a significant modification of the spectroscopic and photophysical properties of the resulting material, not only due to the combination of the emission spectra, but also due to the energy transfer between the two emission centres. One of the suitable candidates for such a combination may be blue organic fluorophores, of which there are many examples.

In this work we have combined several octahedral cluster complexes of molybdenum and rhenium with anthracene and tetraphenylethylene derivatives using ionic, based on the interaction of anionic cluster fragments with cations of organic derivatives, and supramolecular approaches, based on the formation of hydrogen bonds between complementary fragments. The hybrid compounds obtained show efficient energy transfer and, in some cases, a significant change in emission colour (Figure 1). To obtain a material with exciting luminescent properties, some of them have been incorporated into a polymer matrix.

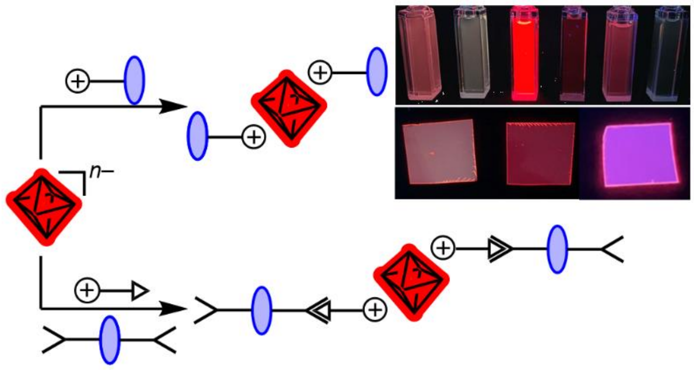

Figure 1. Schematic representation of the approaches used in this work, as well as the emission of some of the hybrids obtained under UV irradiation.

Acknowledgements

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Hydrogen bonding in crystalline organotin(IV) and antimony(V) hydroperoxo complexes

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Hydroperoxo complexes, which are coordination compounds with directly bound hydroperoxo ligands, are encountered and applied in various fields, including catalytic oxygenations and functional material precursors. Hydroperoxide complexes also are recognized as intermediates in numerous biological processes, including cellular oxygen transport and the catalytic oxidation of diverse substrates.[1] According to the CSD and the ICSD, reliable crystal structures of hydroperoxo complexes account for 24 out of 1500 structurally characterized peroxo complexes. The relatively small number of characterized OOH complexes is attributed to their high chemical activity due to coordination of the hydroperoxo ligand with the Lewis acid center rather than simple covalent binding to the organic moiety.

Two conditions must be met for the successful preparation of hydroperoxide complexes: first, a base must be present to facilitate the deprotonation of hydrogen peroxide or organic hydroperoxides; second, a large excess of hydrogen peroxide is necessary to prevent the formation of peroxo-bridged or hydroxo complexes by shifting the equilibrium of the reaction.[2-3]

In this work hydroperoxocomplexes of tryphenyltin(IV) Ph_3SnOOH and dihydroperoxo complexes of antimony ($Ph_3Sb(OOH)_2$, p-$Tol_3Sb(OOH)_2$, p-$Tol_3Sb(OOH)_2{\cdot}THF$, $Me_3Sb(OOH)_2$, $Me_3Sb(OOH)_2{\cdot}H_2O$) were obtained and structurally characterized for the first time.[4] In the structures OOH ligand participate in hydrogen bonding with adjacent phenyl fragment (Ph_3SnOOH) or with OOH ligands and solvent molecules in antimony(V) hydroperoxocomplexes. The implemented hydrogen-bonded motifs (HBMs) can be classified based on the number of hydroperoxo ligands engaged in hydrogen bonding with each other, neighboring ligands, solvent molecules, and anions. The representatives of dihydroperoxo (2OOH), trihydroperoxo (3OOH) and polyhydroperoxo (n-OOH) HBMs are found in the considered structures of p-$Tol_3Sb(OOH)_2$, $Ph_3Sb(OOH)_2$ and $Me_3Sb(OOH)_2$, respectively.

Acknowledgements

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A new rearrangement in the series of racemic thiazolo[3,2-*a*]pyrimidines: stereochemical aspects and chiral discrimination in the crystalline phase

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Thiazolopyrimidine derivatives are promising in the field of organic stereochemistry due to the presence of asymmetric carbon atoms. 2,3-Disubstituted-2,3-dihydrothiazolo[3,2-*a*]pyrimidine derivatives belong to such structures. However, methods for obtaining these structures are unknown in the literature. Therefore, microwave irradiation, one of the effective alternative activation method [1], was applied. This method made it possible to carry out the methanolysis reaction of 2-arylmethylidentiazolo[3,2-*a*]pyrimidine derivatives with the formation of the target compounds in almost quantitative yields. It was found that only one pair of stereoisomers is formed during the reaction: *S*-,*R*-,*R*- and *R*-,*S*-,*S*-isomers with trans-orientation between substituents at asymmetric carbon atoms [2].

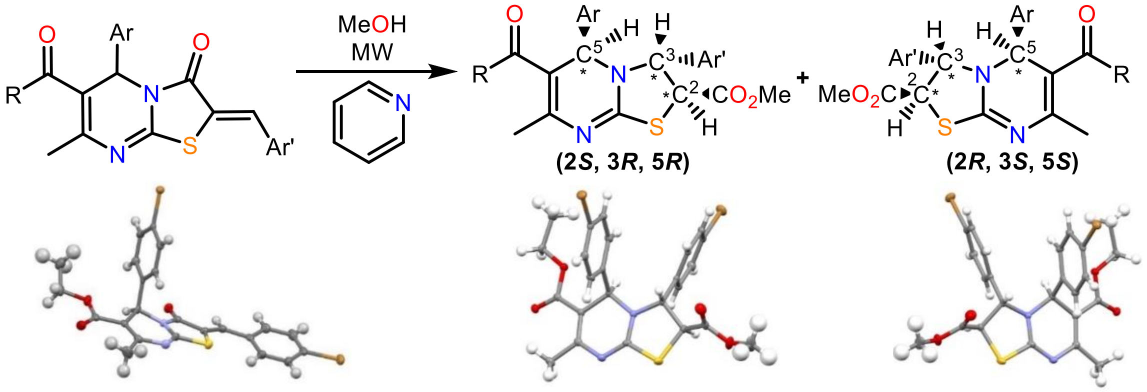

Figure 1. Diastereoselective synthesis of 2,3-disubstituted-2,3-dihydrothiazolo[3,2-*a*]pyrimidine derivatives.

This work is devoted to the selective synthesis of 2,3-disubstituted-2,3-dihydrothiazolo[3,2-*a*]pyrimidine derivatives and the study of their supramolecular organization in the crystalline phase.

Acknowledgements

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Supramolecular organization of noval salicylic thiazolo[3,2-*a*]pyrimidine derivatives: development of a hierarchical approach to realize chiral discrimination

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Most compounds actively used in medicine contain chiral centers in their structure. It turned out that in most cases only one of the isomers has the necessary biological activity. Thiazolo[3,2-*a*]pyrimidine derivatives containing an asymmetric carbon atom are promising structural fragments for the development of drugs, including antitumor ones [1]. In this regard, this work is devoted to the synthesis and study of supramolecular organization of new salicylic derivatives of thiazolo[3,2-*a*]pyrimidine in the crystal phase (Fig. 1) [2-4].

The structural factors of new salicylic derivatives of thiazolo[3,2-*a*]pyrimidine that influence self-organization in the solid phase have been revealed: the formation of racemic dimers, homo- and heterochiral chains of hydrogen-bonded molecules, including those leading to conglomerate crystallization.

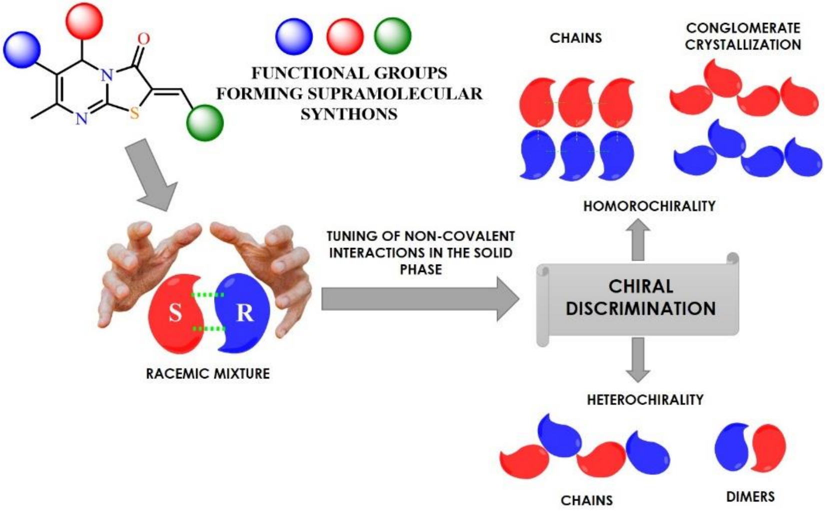

Figure 1. Supramolecular organization of thiazolo[3,2-*a*]pyrimidine derivatives

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4-Nitro-5-thio(seleno)cyanatophthalonitriles as supramolecular tectons

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Previously we demonstrated that 4-nitro-5-halophthalonitriles are prominent halogen bond donors and can be used as supramolecular tectons for the preparation of cocrystals with organic and metalorganic acceptors of noncovalent interactions. [1–3]

In continuation of our studies we synthesized 4-nitro-5-thiocyanatophthalonitrile and 4-nitro-5-selenocyanatophthalonitrile by nucleophilic substitution of halogen atoms in 4-nitro-5-halophthalonitriles with potassium thioc- or selenocyanate. Their potential as donors of noncovalent interactions was evaluated by cocrystalization with various organic and metalorganic species and several cocrystals series were obtained. In most cases stacking interactions were recognized as the structure-directing force that is responsible for the cocrystal formation.

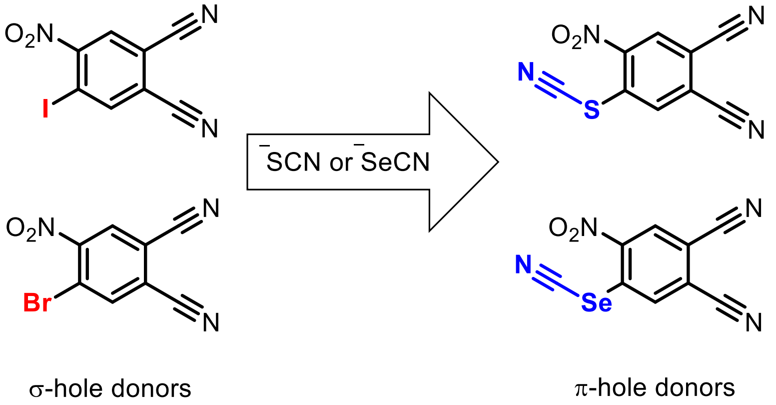

Figure 1. Transformation of 4-nitro-5-halophthalonitriles to 4-nitro-5-thio(seleno)cyanatophthalonitriles.

Acknowledgements

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Supramolecular self-assemblies of metal clusters with cyclodextrins: from interaction to functional materials

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Octahedral cluster complexes of molybdenum and rhenium $[M_6X_8L_6]^n$ (M = Mo, Re; X = S, Se, Te, Cl, Br, I; L = organic or inorganic ligands) are of great interest due to the combination of useful physicochemical properties (luminescence, X-ray contrast and redox properties), promising for applications in different fields such as biology, medicine, catalysis, etc. Many works in the literature are devoted to the study of properties of the obtained compounds, the possibility of their variation depending on the ligand environment and the obtaining of functional materials with incorporated cluster complexes. In this work, a supramolecular approach has been implemented, which allows the modification of the properties of cluster compounds and opens up the possibility of creating new functional materials.

A detailed study of the formation of host-guest type supramolecular compounds in both solid (single crystal X-ray diffraction analysis) and aqueous solution (NMR spectroscopy, etc.) will be presented. The main drivers of adduct formation and the influence of these processes on the properties of cluster complexes will be outlined. Finally, the prospects of this approach and its possible application to the formation of three-component (cluster, cyclodextrin and polyoxometalates) systems with anionic or cationic polyoxometalates for the creation of new functional materials will be discussed.

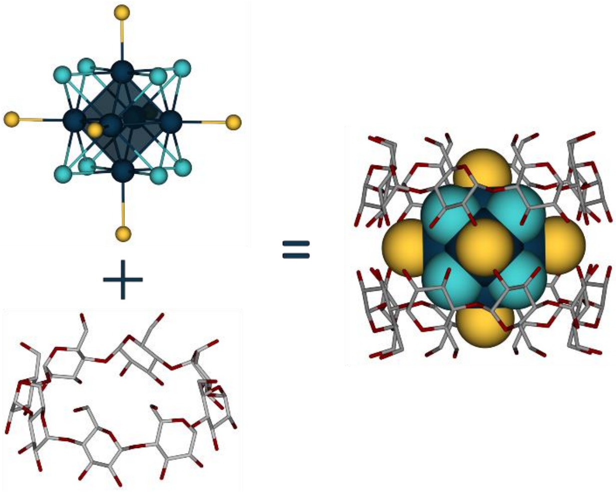

Figure 1. Illustration of the object of study: octahedral metal cluster complexes $[M_6X_8L_6]^n$, cyclodextrin and host-guest complexes.

Acknowledgements

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Hydrogen Bonds in Controlling the Reaction at the Phase Boundary

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A systematic study of the influence of hydrogen bonds on the reactivity of a complex acyl chloride–hydroxyl-containing compound system allows us to take a fresh view at the reaction mechanism from modern positions.[1–3] Hydrogen bonds are extremely important because they can change the free energy of activation $\Delta G^{\neq}$, exhibiting a cooperative nature of action. Interest in studying the reaction mechanism is associated with catalysis by hydrogen bonds and the search for ways to control a chemical reaction at the level of individual reacting molecules. At a more advanced level, the reaction is best controlled by having data on the $\Delta G^{\neq}$ and its significance in the efficiency of the process.[4]

We have taken a step forward towards in understanding the control of the reaction through hydrogen bonds. A new principle of the influence of a nonplanar adsorbent on a reaction system has been proposed and implemented.[5] It has been shown that the geometry of the reactant can be influenced even in the ground state. In the force field of a nonplanar macroporous silica adsorbent with hydroxyl groups on the surface, the resulting hydrogen bonds and dispersion forces change the geometry of the aromatic molecule, which can significantly increase the efficiency of the process. It has been shown that the direct inclusion of silica in the process helps oxygen and chlorine atoms move out of the plane of the benzene ring and activates the trimolecular mechanism. The selectivity of the reaction is determined by the catalytic effect of hydrogen bonds at the phase boundary.

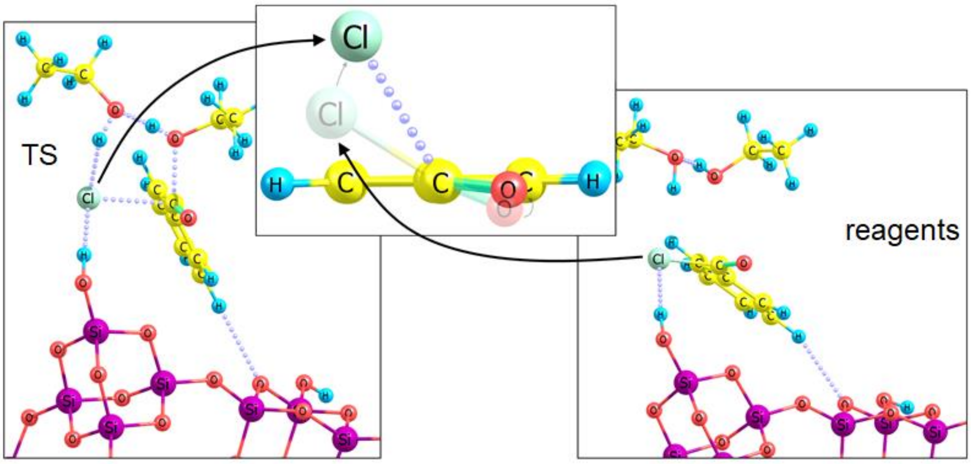

Figure 1. Transition and ground states in trimolecular reactions at the phase boundary

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Mechanistic insights into dehydrogenation and hydrosylilation reactions involving bimetallic FLP analogue

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The dehydrogenation of formic acid to produce hydrogen and carbon dioxide is of significant interest in catalysis, with applications in hydrogen storage and clean energy technologies. Formic acid, a liquid at room temperature, is a promising source of molecular hydrogen for on-board storage in fuel cell-powered vehicles.[1] The CO_2 released can be utilized in hydrosilylation, transforming it into formate ion, formaldehyde or methanol using silanes as reducing agents.[2]

In this report we present the synthesis of a series bimetallic complexes ($(^{tBu}PZCZP)Pd(OC)M(CO)_2L$ (Z = CH_2, O; M = Mo, W; L = Cp, Tp) and the study of their reactivity in formic acid dehydrogenation and carbon dioxide hydrosilylation reactions by variable temperature IR and NMR spectroscopy. Kinetic and spectroscopic data analysis revealed a HCOOH dehydrogenation mechanism where hydride migration and CO_2 release are facilitated by −OCHO···HA hydrogen bond. Catalytic activity of bimetallic complexes was estimated; and effect of ligands, metal atom and temperature on the reaction rate was demonstrated.[3] For CO_2 reduction, it was shown that catalytic CO_2 hydrosilylation with bimetallic complexes could be stopped at the formate level, whereas the use of sole (^{tBu}PCP)PdH leads to more extensive reduction. The diffusion-controlled step involves CO_2 insertion into the Pd-H bond, making Si-H bond activation by bimetallic complex in the FLP-fashion the rate-determining step. The crucial role of non-covalent interactions and the potential of transition metal-based FLPs in catalytic reactions were also demonstrated.[4]

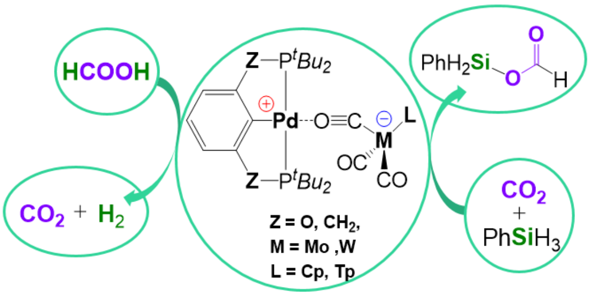

Figure 1.

Acknowledgements

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Complex compounds based on the structural fragment {Mo_2O_4} with azole ligands

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One of the well-studied and widely presented in the literature are polyoxometallates – polynuclear oxo-compounds of transition metals in higher oxidation degrees [1]. However, a lot of attention is attracted to hybrid polyoxometallates – compounds covalently bonded to organic ligands. Such compounds may have an efficient catalytic property [2,3] or biology and medicine [4], as well as demonstrate higher stability in solutions over a wide pH range compare to classical POMs.

This work aims to obtain and characterize new representatives of hybrid polyoxometallates, $(NH_4)_4[Mo_{12}O_{28}L_8]$, where L = pyrazolate, 1,2,3-triazolate or 1,2,4-triazolate ion (Figure 1). Polyoxometallates were prepared by the interaction of the binuclear cluster $(NH_4)_2[Mo_2O_4(C_2O_4)_2]$ with an excess of organic ligand in sealed glass ampoules at 200°C [5]. The compounds have a similar anionic motif, where binuclear {Mo_2O_4} clusters are linked to each other by bridging oxygen atoms and pyrazolate or triazolate ligands. The packing of the obtained POMs occurs due to hydrogen bonds between ammonium cations, solvated water molecules and azole ligands. All the obtained compounds were characterized by various physicochemical methods (e.g., X-ray diffraction and elemental analysis, NMR spectroscopy and mass spectrometry). In addition to the detailed characterization in solid state and in aqueous solution, the biological properties of the compounds on healthy and cancer cells were investigated, as well as antiviral activity against influenza A virus (subtype H5N1) was demonstrated.

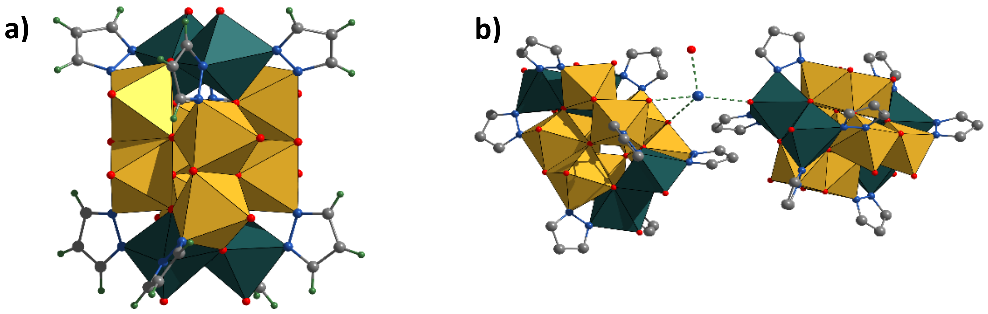

Figure 1. a) anionic motif of compound $(NH_4)_4[Mo_{12}O_{28}(L)_8]$, b) hydrogen bonds observed in the crystal structure $(NH_4)_4[Mo_{12}O_{28}(pz)_8]$.

Acknowledgements

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Transition metals complexes containing 2,1,3-benzothiadiazole-5,6-dithiolate

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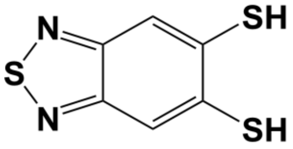

Figure 1. Structures of **H_2btdas**

2,1,3-benzothadiazoles (btd) are one of the subclasses of heteroaromatic compounds. Due to their photophysical and electron-withdrawing properties, btd derivatives are promising for creating sensors, OLEDs, solar cells and OFET which are actively used in contemporary microelectronics. For these applications, both organic btd derivatives and their coordination compounds are of interest.

In this work, 2,1,3-benzothiadiazole-5,6-dithiol (H2btdas, Fig. 1) was chosen as the object of study. H2btdas can be doubly deprotonated, with the corresponding 2,1,3-benzothiadiazole-5,6-dithiolate (btdas2-) acting as a ligand. However, only a few examples of such complexes are known in the literature and there is no information about their luminescent properties, so some new organic derivatives of H2btdas and a series of complexes of Zn, Pt and Pd with (btdas2-) were obtained. The structure of the obtained compounds was determined by X-ray diffraction. Crystal structure of transition metal complexes with o-aryldithiolate ligands often features intra- or intermolecular π-π stacking interactions. These noncovalent interactions are of great influence on the stability and properties of coordination compounds. In our case, π-π interactions affect both the intramolecular structure of the resulting compounds and their packing in the crystal (Fig. 2).

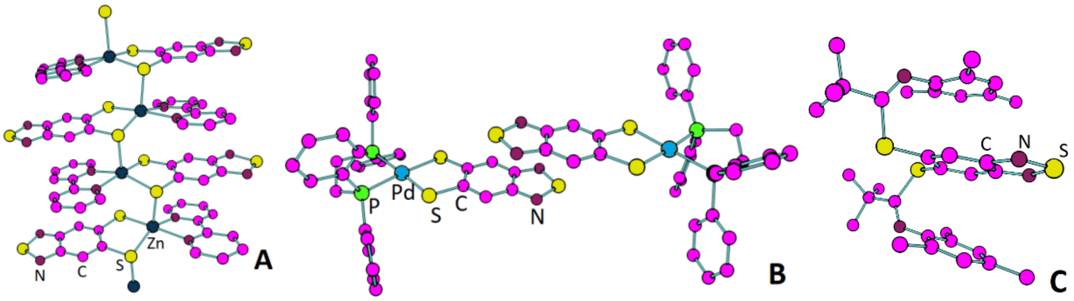

Figure 2. Structures of **[Zn(bpy)(btdas)]** (A), **[Pd(dppe)(btdas)]** (B), **PivN$^{Mes}{}_2$btdas** (C).

Additionally, the photoluminescent properties of the resulting compounds were studied. Experimental absorption spectra were interpreted using dft calculations.

Chiral-at-cobalt(III) complexes as asymmetric hydrogen bond donor catalysts

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Non-covalent interactions play a crucial role in asymmetric catalysis, providing unparalleled control over the stereochemistry of reactions. Organocatalysts, for example, bind to substrates via weak intermolecular interactions such as hydrogen bonding, ionic interactions, and π-stacking interactions. The development of asymmetric catalysts has led to the discovery of a new class of chiral organocatalysts that provide high stereoselectivity through non-covalent bonding. One promising example of this type of catalyst is the octahedral positively charged Co(III) complex with a chiral NNO-donor ligands. The ligands coordinate with the metal ion through the amino groups, acting as hydrogen bond donors, while the positive charge of the complex makes the catalyst bifunctional.[1-3] We believe that the ability of these chiral-at-metal complexes to form non-covalent bonds makes them well suited for the creation of supramolecular assemblies, which could pave the way for new approaches to asymmetric catalysis.

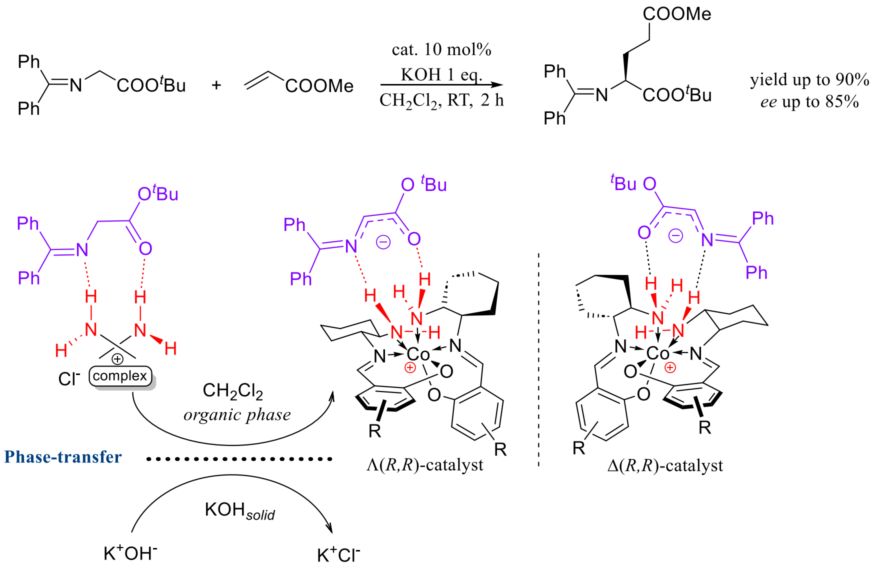

Figure 1. Asymmetric Michael addition of O'Donnell's substrate to methyl acrylate catalyzed by chiral-at-metal Co(III) complexes

Acknowledgements

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Diversity of Transformation of Heteroallenes on Acenaphthene-1,2-diimine Aluminum Compounds

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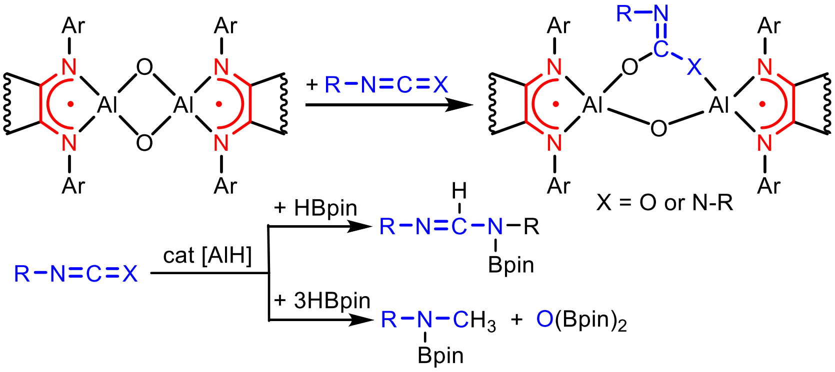
Heteroallenes – carbon dioxide, isocyanates, carbodiimides, etc. – could be listed as one of the most important unsaturated organic compounds that are widely utilized in organic synthesis. The hydroelementation of heteroallenes provides a convenient route for the preparation of amines, formamidines, methanol derivatives, organic amides and other useful products. This work is devoted to the catalytic and stoichiometric transformations of heteroallenes by various acenaphthene-1,2-diimine aluminum derivatives (hydrides, oxides).[1-4] Some compounds obtained during the study have the intermolecular *π…π* interactions in solid state (Figure 1).[2]



Scheme 1. Various ways of binding and transformation heteroallenes by acenaphthenediimine aluminum compounds

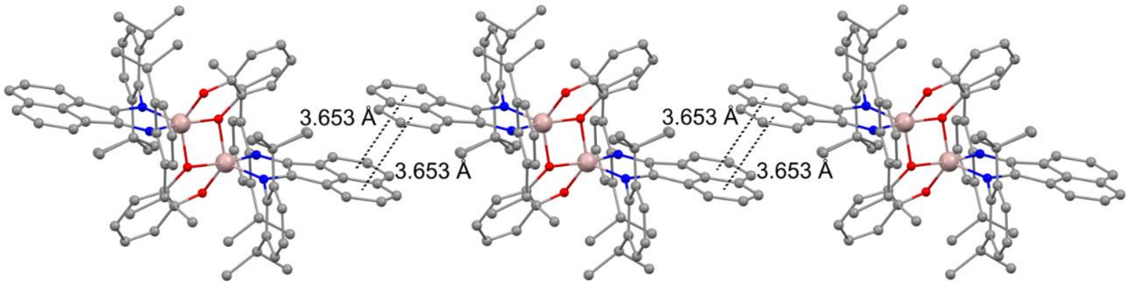


Figure 1. Fragment of crystal packing of complex [{(dpp-bian)Al(μ-Cat)}$_2$]

Acknowledgements

This work was supported by the Russian Science Foundation (Projects No. 20-13-00052).

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Study of structure-forming non-covalent interactions in the structure of perhalobenzoate complexes of cadmium and lanthanides

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The synthesis of the heteroanionic benzoate(bnz)-pentafluorobenzoate(pfb) complex with 1,10-phenanthroline (phen) [Eu_2(phen)$_2$(pfb)$_4$(bnz)$_2$] was carried out in MeCN. According to X-ray diffraction data, the synthesis with different initial ratios of reagents resulted in obtaining a series of compounds with non-integer occupancy of four out of six positions of carboxylate anions, thus creating solid solutions of [Eu_2(phen)$_2$(pfb)$_{4-x}$(bnz)$_{2+x}$].

Stacking interactions between phen and the C_6F_5 fragment occur in the equatorial position of the molecules. The formation of such compositions allows to combine in a crystal the molecules [Eu_2(phen)$_2$(pfb)$_4$(bnz)$_2$] and [Eu_2(phen)$_2$(pfb)$_2$(bnz)$_4$], which do not crystallize as individual compounds in MeCN. Recrystallization of solid solutions in chloroform or aromatic hydrocarbons leads to the formation of another isomer of the complex [Eu_2(phen)$_2$(pfb)$_4$(bnz)$_2$]·Solv. In this isomer, phen is the axial ligand, and the stacking interactions between phenyl and pentafluorophenyl substituents of the carboxylate anions are observed in the equatorial position. Recrystallization of stoichiometric products in MeCN revealed the reversibility of the isomerization reaction.

Using bathophenanthroline (bphen) instead of 1,10-phenanthroline resulted in a co-crystal, in which molecules [Eu_2(bphen)$_2$(pfb)$_4$(bnz)$_2$] and [Eu_2(bphen)$_2$(pfb)$_2$(bnz)$_4$] combined in ratio 1:1. The composition is similar to the molecules forming the solid solution, but is in the form of isomers with axial N-donor ligands. The compounds [Eu_2(phen)$_2$(pfb)$_4$(1-naph)$_2$] and [Eu_2(phen)$_2$(pfb)$_2$(1-naph)$_4$] were obtained in the 1-naphthoate(1-naph)-pentafluorobenzoate system. This compounds are structural analogues of molecules with bphen, as well as [Eu_4(phen)$_4$(pfb)$_{11}$(1-naph)]$_n$·n[Eu_2(phen)$_2$(pfb)$_4$(1-naph)$_2$] is a co-crystal of a heteroanionic coordination polymer and a heteroanionic bimetallic complex.

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Solid-state Photodimerization of Fluorinated 2-Quinolinones

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Crystal engineering is a field within supramolecular chemistry that focuses on harnessing intermolecular interactions to create frameworks with desired physical or chemical properties. The photoreactions in crystals are primarily controlled by the crystal packing. For example, the solid-state [2π+2π] photodimerization often leads to the products that are unattainable in solution. These solid-state reactions are in alignment with the principles of green chemistry.

The solid-state photodimerization of coumarin derivatives in crystals and inclusion complexes is extensively researched and is of interest for various applications, e. g. smart photoresponsive materials.[1] Several topochemical rules were revealed, as well as potential "steering groups" such as halogen atoms that are necessary for achieving the desired crystal packing.[2] There is a lack of information regarding the solid-state dimerization of the coumarin analogue - 2-quinolinone. Earlier studies have only shown its ability to dimerize in solution,[3] while remaining non-dimerizable in inclusion complexes.[4]

We have previously obtained anti-hh dimers of fluorinated 2-quinolinones in solution.[5] In this work the solid-state photodimerization of fluorinated 2-quinolinones, resulting in the formation of syn-hh dimers, is demonstrated for the first time. The intermolecular interactions inside crystals of halogenated 2-quinolinones that facilitate their solid-state photodimerization are discussed.

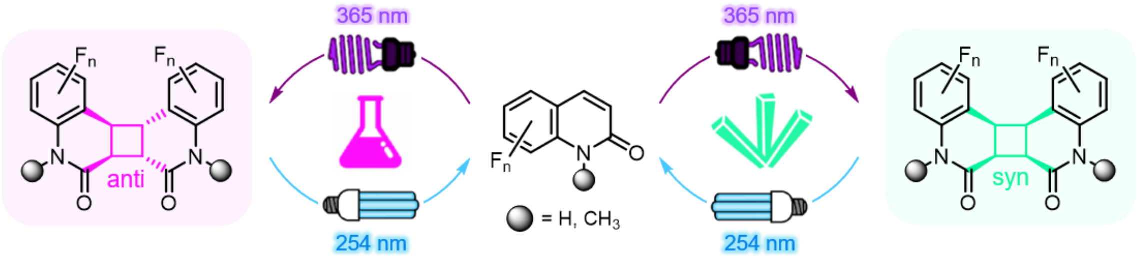

Figure 1. Reversible photodimerization of fluorinated 2-quinolones in solid state and solution

Acknowledgements

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Synthesis and structure of tungsten bromide complexes with the metal cluster {FeW$_5$}

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Cluster complexes are defined by the presence of covalent bonds between metal atoms. Well-known octahedral cluster complexes have the formula [{M_6X_8}X_6]$^{n-}$, where M is a metal atom, X is a ligand, and n is a charge. They represent an octahedron of 6 metal atoms, surrounded by 14 ligands. These include eight inner sphere (μ_3-) ligands and six outer ligands.

Such cluster complexes are frequently reported in the literature because of their potential as agents in photodynamic therapy[1]. There are also heterometallic examples of compounds based on molybdenum combined with other transition metals such as osmium and rhenium[2,3]. Heterometallic cluster complexes are promising for the creation of materials with specific functionalities, since changes in the composition of the cluster core can modify the redox and spectroscopic properties of the compounds.[3]. However, no examples of heterometallic cluster complexes involving 3d-row transition metals have yet been reported in the existing literature.

This research presents a synthesis method for a new class of compounds – tungsten-iron bromide cluster complexes with {FeW$_5$} core. In addition, in the work presents crystal structures of compounds obtained under different conditions, evaluates their stability and reactivity with different solvents, and discusses the nature of the bonds in the heterometallic cluster complex based on the results obtained.

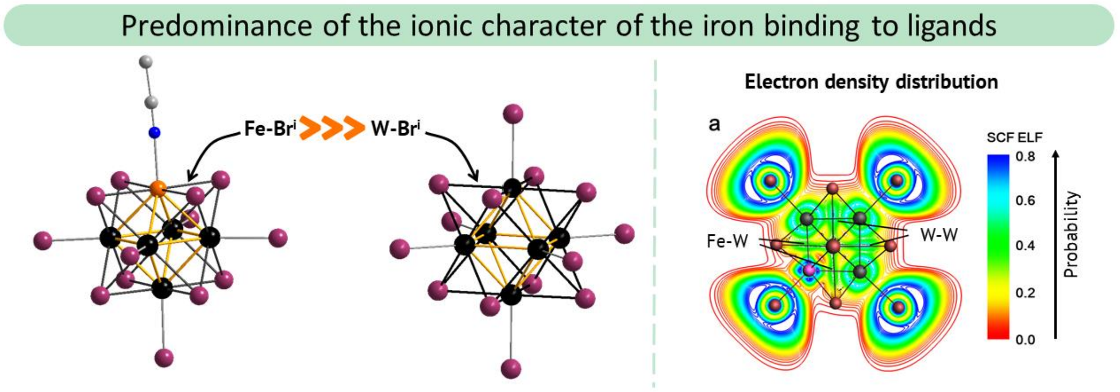

Figure 1. Description of the structure of the cluster complex.

Acknowledgements

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Non-covalent interactions in compounds with phenylphosphonium cations

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Non-covalent interactions play a crucial role in determining the structure, stability, and properties of ionic compounds, particularly those containing phenylphosphonium cations. The commonly used tetraphenylphosphonium moieties as cations in various compounds engage in a wide range of non-covalent interactions, including but not limited to hydrogen bonding, π-π stacking, and electrostatic interactions. These interactions can also occur with triphenylphosphonium cations involving P-H or PO-H bonds. However, the Ph_3P-H or Ph_3PO-H bonds are more labile than the Ph_3P-Ph bonds, allowing the formation of complex compounds with unique behaviors, such as proton transfer between different fragments.

The non-covalent interactions of triphenylphosphonium cations (HL) were investigated using novel tetrahalozincate(II) compounds $[HL]_2[ZnX_4]$ [X = Cl, Br] as examples. It is noteworthy that these compounds exhibit strong ultraviolet (UV-B) fluorescence and blue-green phosphorescence in the solid state. The tetrachlorozincate(II) compound mentioned displays an unexpected up-conversion luminescence, possibly induced by proton-coupled electron transfer. Quantum-chemical calculations were performed to deeper investigate the optical and luminescence properties of the aforementioned compounds and the role of non-covalent interactions in the observed phenomena.

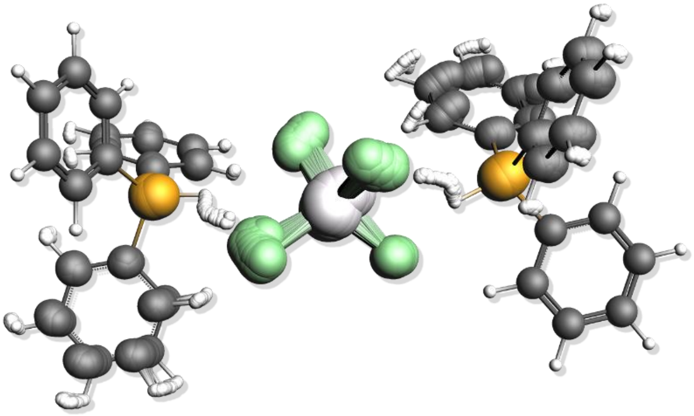

Figure 1. Calculated atomic position change due to $\{P_1H_1..Cl_1\}$ and $\{P_2H_2..Cl_2\}$ proton transfers of the cut out $\{[Ph_3PH]_2[ZnCl_4]\}$ moiety

Acknowledgements

This research was funded by the Russian Science Foundation for the funding project № 23-73-01102.

[{Mo_6I_8}$(H_2O)_6$][$SiW_{12}O_{40}$] hybrid salt and its activity in photocatalyzed hydrogen evolution reaction

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Polyoxometalates (POMs) are a large class of polymeric ionic compounds formed by three or more transition metal oxoanions linked together by bridging oxygen atoms. POMs are currently under active research, as they exhibit a wide range of properties, mainly ox-red, which makes them promising for photocatalysis, electrocatalysis, energy storage, biomedicine, etc. Due to the high oxidation states of the metals, POMs are considered to be electron-poor compounds. Their combination with other electron-rich active components can result in synergistic effects or the appearance of unpredictable properties. Octahedral halide cluster complexes of transition metals – [{M_6X_8}L_6]^n (M = Mo(II), W(II), X = Cl, Br, I, L is inorganic or organic ligand) – represent an optimal class of compounds for use as electron-rich components. In addition to exhibiting such properties as high absorption and bright emission, these compounds have pronounced photocatalytic properties. Since most POMs are anionic, one of the easiest methods to combine these compounds is to obtain hybrid salts with cationic clusters.

In this work, by simple mixing of Keggin-type POM H_4[$SiW_{12}O_{40}$] and cationic cluster [{Mo_6I_8}$(H_2O)_6$]$(NO_3)_4$ hybrid salt [{Mo_6I_8}$(H_2O)_6$][$SiW_{12}O_{40}$] was obtained. The compound was characterized in detail by a set of modern analytical methods including single crystal (Fig. 1) and powder XRD, elemental analyses, thermogravimetric analysis, and cyclic voltammetry. Flat band potential was determined using Mott-Schottky plot and open-circuit potential method. The hybrid salt was also tested in the process of photocatalytic generation of molecular hydrogen from water (Fig. 1).

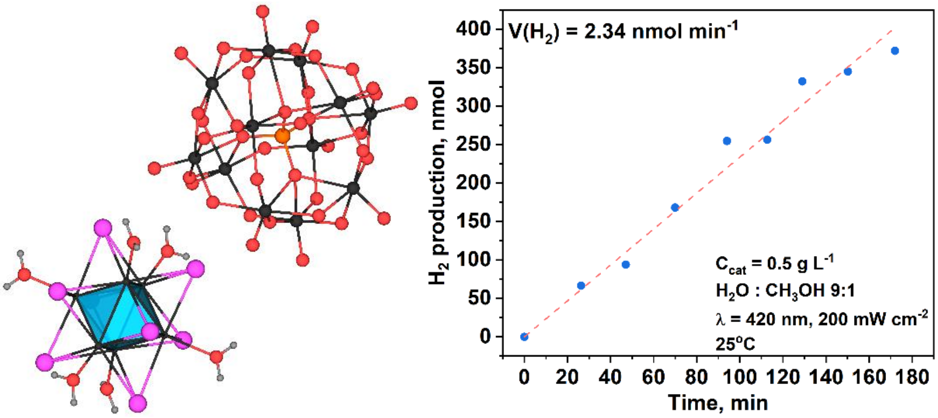

Figure 1. Structure of [{Mo_6I_8}$(H_2O)_6$][$SiW_{12}O_{40}$] (left) and its activity in photocatalytic hydrogen production from water (right)

Acknowledgements

This work was supported by Russian Science Foundation (grant number 22-73-10174).

Photoactive hydrogels based on gelatin and octahedral molybdenum iodide clusters

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Hydrogels as a separate field started its development in 1960-1980, but only recently have they been the subject of active investigation in a number of biomedicine areas. These include the development of medical dressing, drug delivery systems, and techniques for repairing bone tissue. The high biocompatibility and biodegradability of hydrogels are the key factors in driving this research. Hydrogels are distinguished by their capacity to absorb significant quantities of water (the mass of water can be several thousand times more than the mass of dry material) and the formation of an extensive network of ionic and weak interactions. A moist and warm environment is conducive to accelerated wound healing and the proliferation of pathogenic microorganisms. Therefore, it is crucial to impart anti-pathogenic properties to the materials. The octahedral molybdenum cluster complexes with the general formula $[\{Mo_6I_8\}L_6]^n$ (L - apical ligand, n is a charge) were selected as agents capable of imparting such properties. The cluster complexes exhibit pronounced photoluminescence in the red and near-IR regions. One of the prevailing mechanisms of luminescence quenching is energy transfer to oxygen with the transition to the excited singlet form. Singlet oxygen is employed in a variety of applications, including the development of antibacterial coatings and the treatment of various diseases through photodynamic therapy.

In this study, a series of materials based on gelatin and the cluster complexes $[\{Mo_6I_8\}(DMSO)_6](NO_3)_4$ (**1**), $Na_2[\{Mo_6I_8\}(OMe)_6]$ (**2**) and $Na_2[\{Mo_6I_8\}(OOCCH_2OH)_6]$ (**3**) were prepared using glutaric aldehyde as a cross-linker. The amount of cluster complexes was varied in materials $\mathbf{X}^m$@gelatin (**X** – the number of cluster, m = 0.3, 0.6 and 0.8 w/w in %), but this had no apparent effect on material binding. The luminescence spectra of the materials were found to be similar, suggesting that the external ligand environment is substituted with H_2O and/or OH groups. For all materials, the luminescence spectra were studied both with drying/swelling cycles and when stored in a refrigerator for several months. It was demonstrated that the cluster luminescence persists in prolonged contact with water. In contrast, being solubilized in water, $Na_2[\{Mo_6I_8\}(OOCCH_2OH)_6]$, precipitates after 3-5 days with the disappearing of luminescence. The gelatin matrix serves to stabilize the cluster in aqueous conditions. The obtained hydrogels absorb approximately 9 parts of water relative to the mass of dry material when swelling. Materials $\mathbf{1}^n$@gelatin were found to demonstrate the anti-mould effect under sunlight.

Acknowledgements

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Dicarbonyl manganese(I) complexes: reactivity in hydride ion transfer processes

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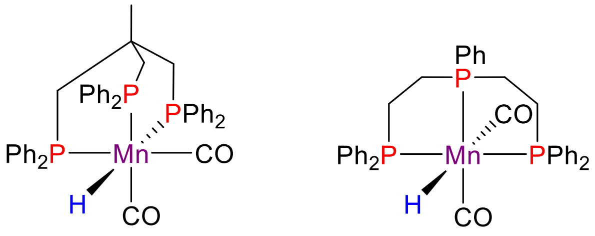
In the last twenty years, catalytic systems based on 3d metals have been actively developed as alternatives to noble metals derivatives. In particular, carbonyl-containing manganese(I) complexes have proven themselves to be good catalysts for (de)hydrogenation and hydrosilylation reactions of organic substrates.[1] Generally, non-covalent adducts of metal hydrides adducts with substrates represent the key intermediates in these catalytic transformations.

Our previous work was devoted to the study of the reactivity and kinetic hydricity ($\Delta G^{\neq}$) of tricarbonyl manganese(I) complexes with phosphite, phosphine and phosphine-carbene ligands.[2, 3] In this report we present recent results on the reactivity of dicarbonyl manganese complexes (**1**, **2**) with pincer-type and tripodal phosphine ligands (Figure 1) in hydride ion transfer processes to Lewis acid using IR (ν_{CO}) and NMR (^{1}H, ^{31}P) spectroscopic methods in a wide temperature range (160-298 K). This investigation allowed to identify reaction mechanism, determine structure of the reaction intermediates and experimentally estimate the values of the kinetic hydricity, which is higher for tripodal structure **2**. These data were in agreement with catalytic activity of triphosphine manganese(I) complexes in the hydrosilylation of benzyl benzoate with phenylsilane.



1^{H} **2^{H}**

Figure 1. Objects of investigation

Acknowledgements

The work was supported by the Russian Science Foundation (project № 24-13-00283).

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Effect of crystal packing on the optical properties of cyclometalated rhodium(III) and iridium(III) complexes with 1,3-diketones

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Cyclometalated iridium complexes demonstrate good optical characteristics, which ensures their use in OLED and other areas, while similar rhodium complexes do not have such properties. Since luminescent at room temperature rhodium(III) complexes are still rare[1], their careful investigation, in a comparative analysis with similar iridium(III) complexes, becomes the issue of interest. Moreover, in optoelectronic and photovoltaic devices such complexes are in the solid (in some cases, aggregated) state, it is necessary to establish relationships between the optical characteristics of compounds and the features of their organization in solid form.

In line with this, the aim of the work was to disclose how weak intermolecular interactions affect the optical properties of iridium(III) and rhodium(III) complexes.

For this purpose, two similar series of cyclometalated rhodium(III) and iridium(III) complexes with 2-phenylpyridine and various aromatic β-diketones were synthesized. The resulting compounds were characterized by ^{1}H NMR, high-resolution mass spectrometry, powder and single-crystal XRD. Although the prepared rhodium(III) cyclometalates are isostructural with iridium(III) analogues, different types of π–π interactions are responsible for the aggregation-induced emission (AIE) of the complexes depending on the metal ion. Enabled by phenyl–pyridyl interactions partially blocking the population of non-emissive *d*–*d* states, solid-state phosphorescence enhancement is successfully achieved in a rhodium(III) complex with ancillary benzoyltrifluoroacetone, which is the first example of a rhodium complex exhibiting AIE[2].

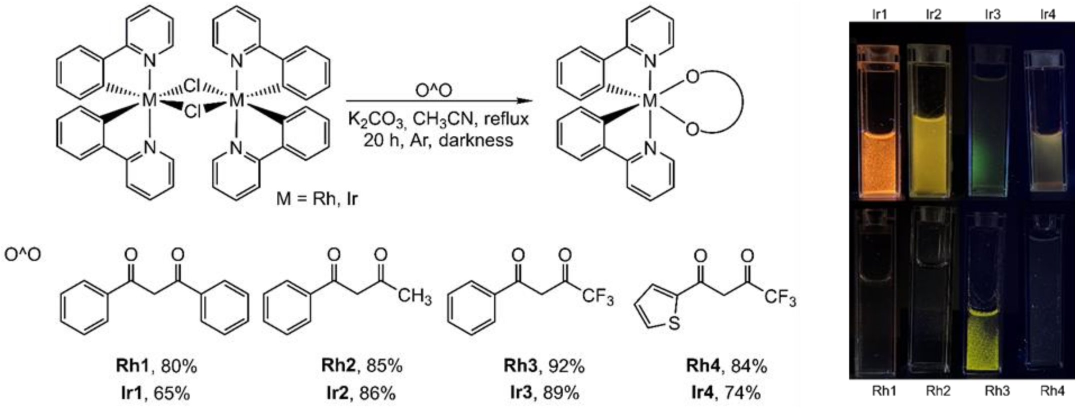

Figure 1. Synthesis of rhodium(III) and iridium(III) complexes (left) and luminescence photographs of the complexes in CH_3CN/H_2O (1/3) solution at 298 K (λ_{ex} = 365 nm).

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2-(2-aminophenyl)benzothiazole derivatives: a new class of visible-light organic photosensitizers

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The chemistry of heterocyclic compounds is one of the most developing fields in modern material sciences. Such organic compounds serve as important building blocks in OLED technology, sensors, dyes, and solar cells. Among them, 2-phenylbenzothiazole (pbt) and its derivatives are a particularly interesting class of fluorophores, which are actively employed in coordination chemistry, biochemistry and sensors research. Introducing donor substituents (-SH, -OH, -NHR) at the 2-position of the phenyl group leads to intriguing photophysical properties involving Aggregation Induced Emission[1] or Excited State Intramolecular Proton Transfer (ESIPT)[2].

Herein, we present the first application of 2-(2-aminophenyl)-benzothiazole derivatives (NHR-pbt) as photosensitizers (PS) in [2+2] photocycloaddition reactions. By varying the substituents on the amino-group, we have demonstrated that the catalytic efficiency depends on the compound’s light-absorbing properties and its tendency to undergo the ESIPT process. Using NMR spectroscopy, time-resolved luminescence studies, and DFT calculations, we have shown that photocatalysis proceeds through the noncovalent interaction and triplet-triplet energy transfer between PS and substrate. A range of cyclobutene products with different functional groups were obtained in moderate to good yields, indicating that NHR-pbt are a promising class of organic photosensitizers.

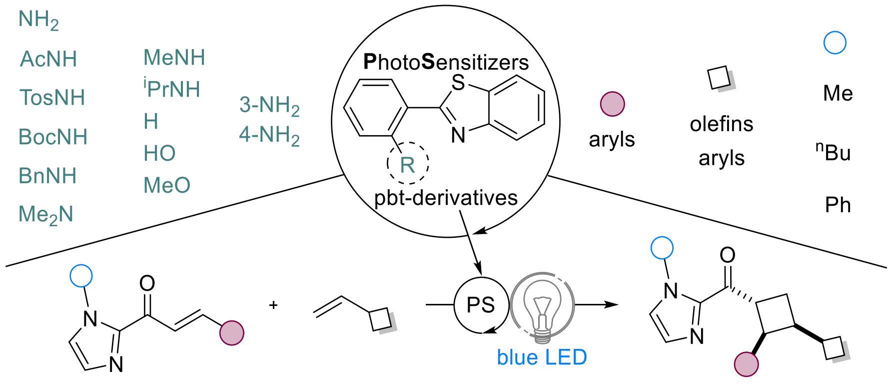

Figure 1. Application of pbt derivatives as a photosensitizer in [2+2] photocycloaddition

Acknowledgements

E.K.P. thanks the French Embassy in Russia for a Vernadski PhD scholarship.

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Crystal structure, thermal properties, and photostability of potassium sorbate

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The crystal structure of the potassium salt of sorbic acid is still unknown, though the compound is a widely used food additive. Even its thermal behavior has been studied for the first time only some years ago, revealing a phase transition in the solid state. Since most foods are exposed to heat during manufacturing or cooking, the thermal behavior of additive should be studied comprehensively, while the crystal structure may shed light on the phase change. In this work, the crystal structure of potassium sorbate was determined by single-crystal X-ray diffraction. The salt forms a 2D-coordination polymer. The crystal packing is characterized by alternating metal-oxygen and loose aliphatic regions (Fig. 1). We noted that the potassium cation interacts with one double bond of the sorbic fragment, and this seems to play an important role in the phase transition. At 156°C, potassium sorbate undergoes a phase transition associated with the disappearance of the cation-π interaction, which leads to a destruction of translational symmetry perpendicular to the layers and a sharp increase in the distance between layers in the aliphatic region. We followed this process by DSC, termomicroscopy and variable-temperature powder XRD. Additionally, the effect of UV-light on the crystalline powder of potassium sorbate was studied. Apparently, the UV-light exposure induces [2+2] photocycloaddition reactions, resulting in partial amorphization of the powder. For additional insights, a comparative study of sodium, calcium and ammonium sorbates was also carried out.

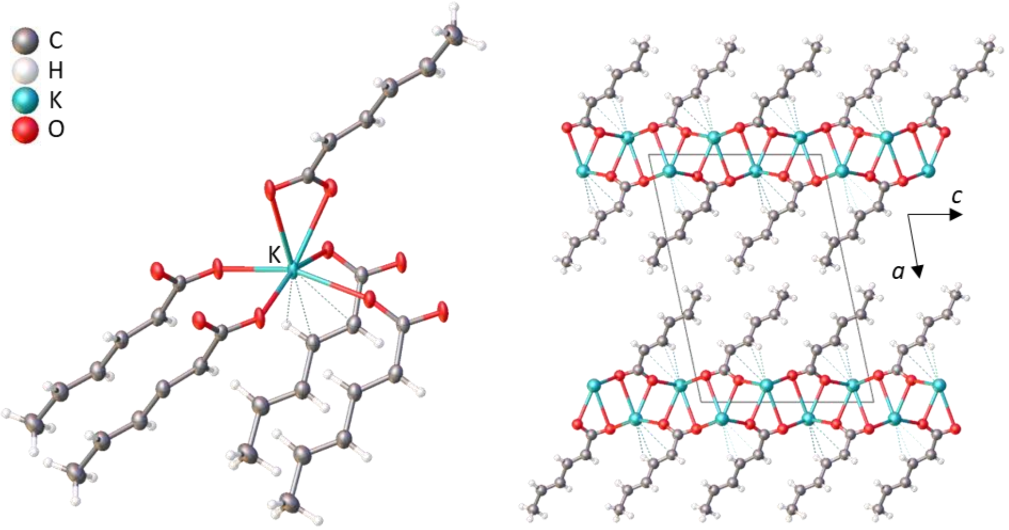

Figure 1. Coordination environment of potassium in potassium sorbate (*left*). Fragment of the crystal packing of potassium sorbate (*right*).

Acknowledgements

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Enhancing the stability of water-soluble octahedral tungsten cluster complexes using gamma-cyclodextrin

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Octahedral cluster complexes $[\{M_6X_8\}L_6]^{m-}$ (M = Re, Mo, W; X = Cl, Br, I, S, Se, Te; L = organic or inorganic ligand, m – charge) have demonstrated potential in a range of fields, including biology and medicine. They can be utilized as radiocontrast agents and as active components of photodynamic therapy systems [1]. These complexes, comprising six metal atoms linked by metal-metal bonds and stabilized by internal X and external L ligands, effectively absorb X-rays due to their high concentration of heavy atoms. They also exhibit red luminescence under light and X-ray exposure and can generate reactive singlet oxygen in the presence of molecular oxygen.

However, their application is limited by low solubility or instability in aqueous media, spurring interest in finding water-soluble forms or stabilizing them in various organic [2] and inorganic polymer matrices [3].

Compared to similar molybdenum and rhenium complexes, tungsten cluster complexes have been less studied, largely due to the more labor-intensive synthesis methods required. This research introduces a novel synthesis method for the tungsten bromide octahedral cluster complex $[\{W_6Br_8\}Br_6]^{2-}$ using accessible starting materials. It also covers the preparation and characterization of tungsten bromide and iodide complexes with various substituted external ligands. Moreover, the synthesis of water-soluble complexes $[W_6X_8Y_6]^{2-}$ (X = Br, I; Y = Cl, Br) is described in detail, including their stabilization in aqueous solutions using gamma-cyclodextrin. The binding of the complexes to gamma-cyclodextrin is primarily achieved through hydrogen bonding, which enhances the solubility and stability of the complexes.

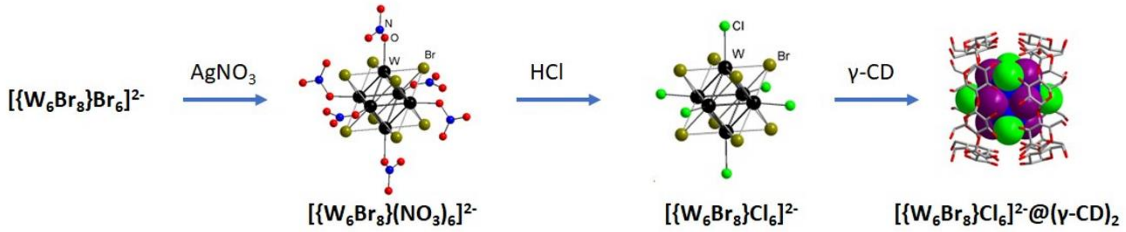

Figure 1. Schematic representation of preparing the inclusion compound $[\{W_6Br_8\}Cl_6]^{2-}@(\gamma\text{-}CD)_2$.

Acknowledgements

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Template-Induced Crystallization of 9,10-Diphenylanthracene

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Polymorphism of organic conjugated materials attracted a great interest due to the possibility of structure and optoelectronic properties tuning for next-generation optoelectronic devices. Template-induced crystallization is one of the intriguing crystallization control approaches allowing heterogeneous nucleation of solute on template surfaces. [1]

Here, we studied template-induced crystallization of organic luminophore 9,10-diphenylantracene (DPA) on the following crystals: pyrene, perylene, anthracene, and rubrene. Crystallization of DPA in the presence of pyrene and perylene resulted in the formation of their co-crystals, whereas crystallization with anthracene and triclinic rubrene crystals revealed no effect on DPA polymorphism. We found that in the presence of orthorhombic rubrene (Orth-RUB) as a template novel orthorhombic DPA polymorph (δ-DPA) crystallized. δ-DPA was demonstrated to have herringbone packing similar to that of the used template (Fig. 1). δ-DPA crystals demonstrated blue emission with photoluminescence (PL) quantum yield of 52% and needle-like morphology (Fig. 1). The work shows that, when choosing a template for crystallization of a polycyclic aromatic hydrocarbon crystalline form, one should consider the similarity of crystal system, molecular inclination, type of crystal packing and both the energy and the nature of intermolecular interactions. The results obtained could be used for crystallization control and engineering of high-performance functional materials.

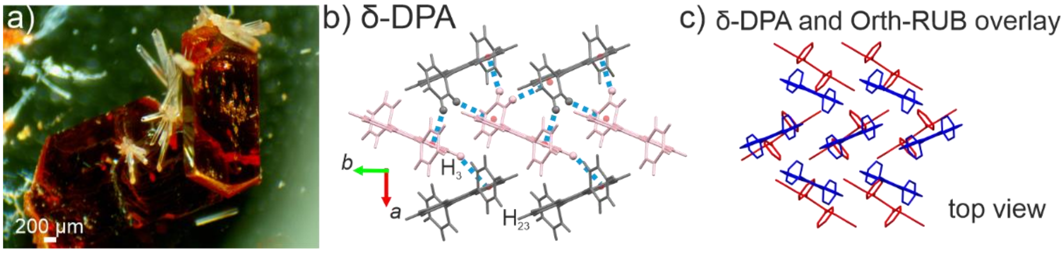

Figure 1. Optical images of needle-like δ-DPA crystals in the presence of red plate of Orth-RUB in reflected light (a); herringbone packing of δ-DPA (b); δ-DPA and Orth-Rub crystal structure overlay (c).

Acknowledgements

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The key role of catalytically active molecules in hydrogen transfer reactions of atmospheric aldehydes

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The transformations of atmospheric carbonyl compounds in an aqueous medium are the key reactions in the formation of secondary organic aerosols.[1] In this work, we proposed, for the first time to our knowledge, to distinguish two factors (the number of members in the TS cycle and the nature of the catalytically active species) that affect the energy barriers of aldehyde reactions in the atmosphere.[2] The contribution of each factor to the energy barriers of the ammonization and amination stages, dehydration, and intramolecular hydrogen transfer is studied using the example of the acetaldehyde and glyoxal interactions with ammonia in aqueous solution. The effect of different number of molecules of water, methanol and ethanol, formic and acetic acids, and ammonia on the energy barriers of all reaction stages was considered.

A regular decrease in energy barriers is observed in a series of 4-, 6-, and 8-membered transition states (TSs) regardless of the nature of the catalytically active species and their numbers. The 8-membered TSs of ammonization, amination, and dehydration reactions are the most efficient catalytic systems. The role of the nature of catalytically active species is secondary and is expressed in different cases through the influence of entropy and different acidity/basicity of catalytically active species and their structures.

The regularities for the stage of intramolecular hydrogen transfer stand out from those for the ammonization, amination, and dehydration stages. The intramolecular hydrogen transfer is organized by three atoms in TSs without the participation of catalytically active species, while the 5- and 7-membered TSs are formed with the participation of such species. A proportional decrease in energy barrier with a sequential increase in the number of TS sites (3-, 5-, and 7-) is not observed. A sharp decrease in the barriers occurs only during the formation of the 7-membered TSs, while the 5-membered structures lie above the 3-membered catalytically inactive structures on the potential energy surface regardless of the nature of the species forming these structures.

When modeling the reactions of small carbonyl compounds in atmospheric aerosols to develop ways to prevent SOA formation, it is necessary to take into account the fact that the resulting effect of the catalytically active species will depend, to a large extent, on the number of members in the organized TS, and, to a lesser extent, on their nature.

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Thiazolo[3,2-*a*]pyrimidine derivatives: new rearrangements, chiral supramolecular architectures in the crystalline phase and antitumor activity

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In modern supramolecular chemistry, interest in non-covalent interactions is manifested in the exponential growth of articles containing the term “non-covalent interactions” published over the past few decades. The report will discuss methods for obtaining previously unavailable heterocyclic derivatives of thiazolo[3,2-*a*]pyrimidine, as well as successes in creating a hierarchical approach for tuning supramolecular synthons in order to implement chiral discrimination of potential biologically active heterocyclic derivatives [1-4].

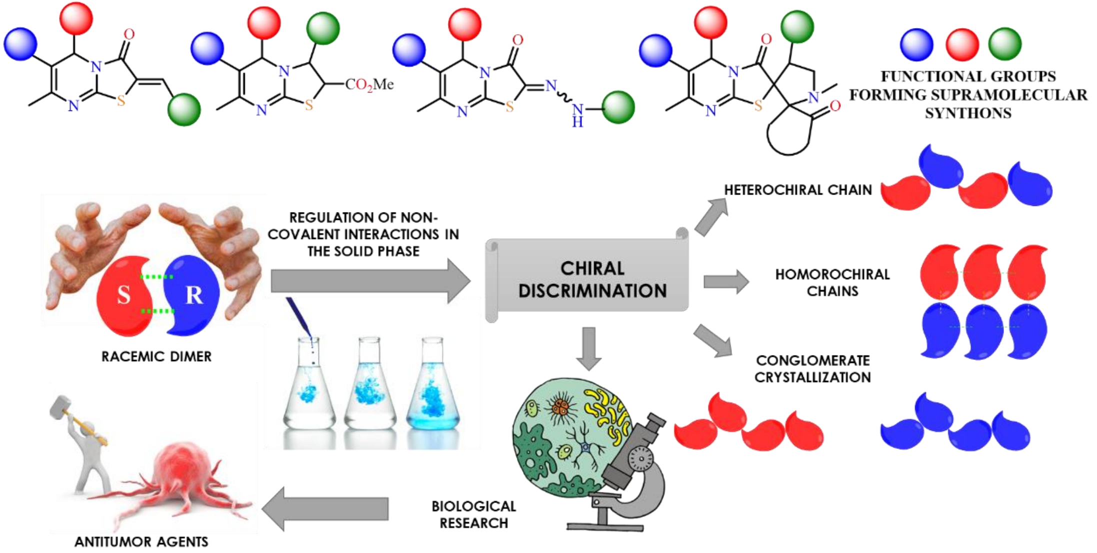

Figure 1. Rearrangements in the thiazolo[3,2-*a*]pyrimidine series

Acknowledgements

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Noncovalent Interactions in Design of Volatile MOCVD Precursors: A Case of Magnesium β-Diketonate Complexes

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Volatile magnesium complexes are in demand for producing emissive Mg-O-F thin films to improve modern electron multipliers via metal-organic chemical vapor deposition (MOCVD). Creating a library of such precursors is important not only in terms of controlling film composition and deposition conditions, but also for selecting compatible combinations to obtain of composite materials, for example, doped with a resistive component. MOCVD precursors must possess a certain set of thermochemical properties while the presence of fluorine in the ligands will make it possible to obtain Mg-O-F without aggressive co-reagents.

Thus, fluorinated β-diketonate ($R^FCOCHCOR^-$) complexes are promising for target library development because their properties can be tunable through terminal substituents (R^F, R). In the case of magnesium, a neutral ligand should also be introduced to prevent oligomerization, and this is another tuning tool. Important precursor properties such as volatility and melting point are largely determined by non-covalent interactions in the crystal lattice. Such relationships are usually explained at a qualitative level, whereas quantitative understanding is required for effective precursor design.

To identify the effects of the ligand environment on the features of non-covalent interactions, in this work we consider a series of magnesium β-diketonate complexes with gradual changes in both types of ligands (Fig. 1). As a basis for correlations, various levels of analysis of crystal structures were used, namely (a) the shortest intermolecular interactions (b) % total contacts according to Hirschfeld surfaces (c) estimation of the energies of contacts and crystal lattice using Crystal Explorer ("cluster" approach, basis set B3LYP/6-31G(d,p). An attempt was made to correlate the obtained values with the thermodynamic parameters of fusion and sublimation.

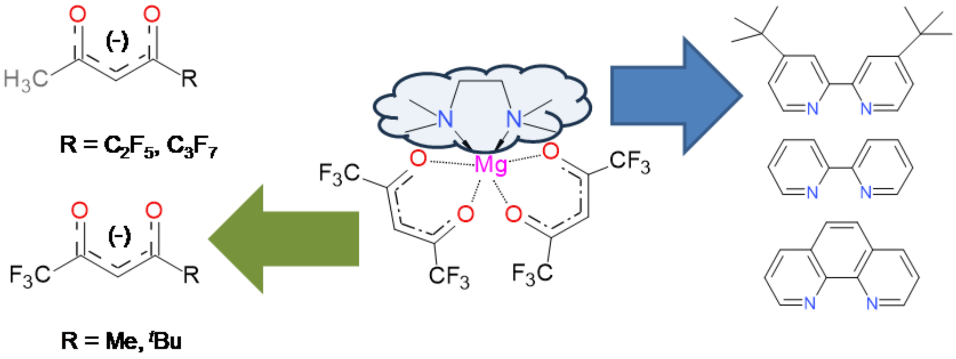

Figure 1. A seria of selected magnesium complexes

Acknowledgements

The study was supported by the Russian Science Foundation grant No. 24-79-10272, https://rscf.ru/project/24-79-10272/

STEREOCHEMICAL TRANSFORMATIONS OF 16-S-DIHYDRO- AND 15-EN-STEVIOLS DURING CRYSTALLIZATION

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Within the framework of the developing field of supramolecular dynamic stereochemistry, the ability of two derivatives of the natural compound steviol to form two stereochemically different types of homochiral dimers in crystals – asymmetric and symmetric – was studied. A dimer of the first type is formed by molecules of two different supramolecular diastereomers, while a dimer of the second type is formed by two identical ones. Diastereomerization of steviol molecules occurs at the stage of formation of hydrogen bonds with the participation of stereochemically identical or different lone pairs of the hydroxyl oxygen atom. The analysis of the electron density Laplacian function, performed on the optimized geometry of dimers of both types, made it possible to carry out an evidence-based correlation, as well as visualize the participation of one or another Lp in a specific intradimeric hydrogen bond (Fig. 1). Controlled conditions for obtaining phases containing a dimer of a particular configuration as a building block and terms of their mutual transitions were revealed.

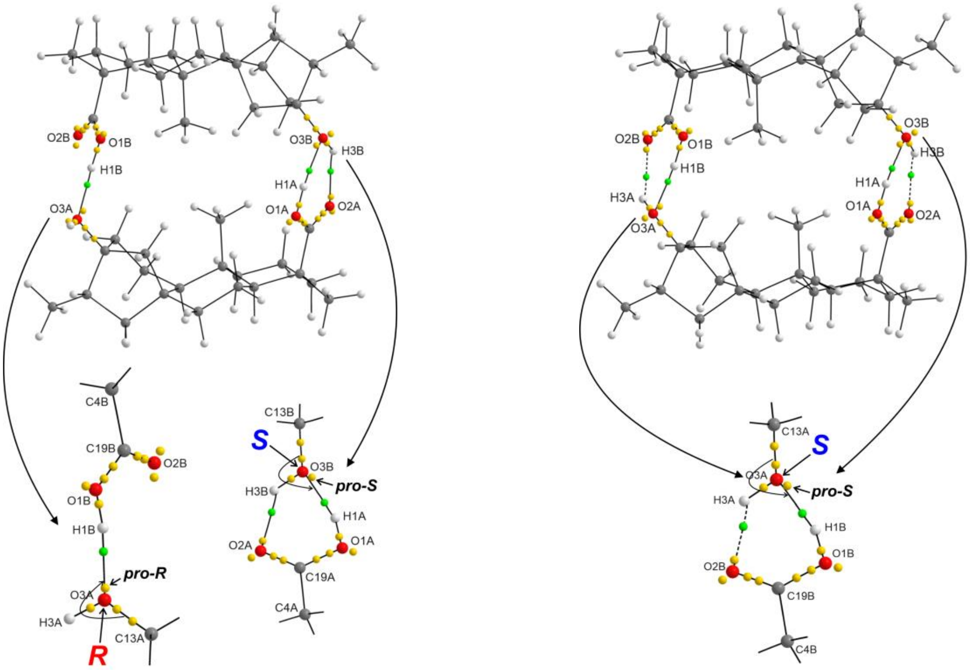

Figure 1. Asymmetric (left) and symmetric (right) homochiral dimers.

Acknowledgements

This work was financially supported by RSF, grant 22-13-00284.

Noncovalent Interactions Underlying the Mechanism of the Chemiresistive Sensor Response of Metal Phthalocyanines Thin Films to Ammonia

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Thin films of phthalocyanines of various metals are used to create chemiresistive sensors for different gases, including ammonia.[1,2] However, the question of the mechanism of the sensor response of these materials remains open. The most common point of view is that most phthalocyanines thin films are *p*-semiconductors and, consequently, the majority charge carriers in them are holes. When electron-donating molecules, such as NH_3, for example, are adsorbed on the surface the hole concentration decreases, and, as a result, the electrical conductivity of the films decreases as well, the measurement of which makes it possible to determine the magnitude of the sensor response.

Using quantum-chemical DFT calculations, we have shown that the most likely sites of ammonia molecules adsorption in the case of tetrahalogen-substituted cobalt ($CoPcHal_4$) and vanadyl ($VOPcHal_4$) phthalocyanines are the side atoms, including the bridging nitrogen atoms (Figure 1). Topological analysis of the electron density distribution, carried out within the framework of QTAIM, shows that the interaction of gas molecules with macrocycles is noncovalent, based on the formation of hydrogen and van der Waals bonds. In this case, the values of interaction energy and electron density parameters at the corresponding bond critical points (BCPs) correlate with the magnitude of the sensor response of thin films, which in turn depends on the nature of the central metal atom and side substituents (chlorine or fluorine atoms) of phthalocyanine.

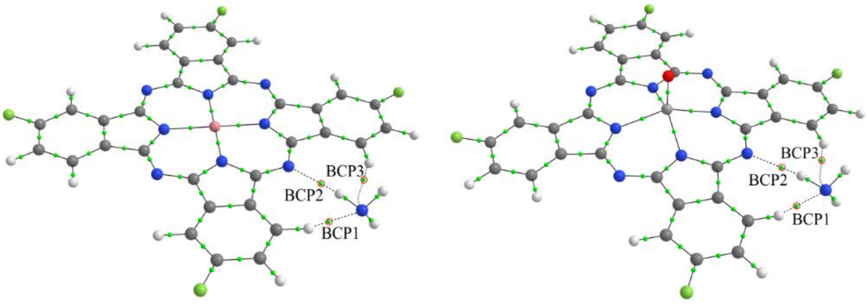

Figure 1. Structures of $CoPcF_4/NH_3$ (left) and $VOPcF_4/NH_3$ (right) aggregates and bond critical points (BCP) in them. Red circles indicate BCPs characterizing the interaction of the ammonia molecule with phthalocyanine atoms

Acknowledgements

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Polymorphic multicomponent crystals of riluzole with hydroxyl derivatives of benzoic acid

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A combined theoretical and experimental approach using virtual screening, X-ray diffraction, thermal analysis and periodic DFT computations was conducted to study the influence of the mutual arrangement of OH groups within the counterion on the packing of riluzole[1] multicomponent crystals with hydroxybenzoic acids, ionization state of the components and the aptness to form multiple crystal forms.

From the performed CSD survey of riluzole multicomponent crystals, we found that salicylic acid derivatives with $pK_a < 3.8$ form salts with riluzole, while benzoic acid derivatives not containing hydroxyl groups in ortho position form cocrystals. A number of multicomponent crystals of riluzole with benzoic, 2-, 3-, 4-hydroxybenzoic, 2,3-, 2,4- and 2,6-dihydroxybenzoic acid were obtained and structurally characterized. Variation of experimental conditions allowed us to isolate the samples of metastable polymorphic forms of the salts with benzoic, salicylic, 2,4- and 2,6-dihydroxybenzoic acids. For the RLZ + 2,6-dihydroxybenzoic acid salt Form II, the crystal structure was solved from powder diffraction data of high-energy synchrotron radiation. The hydrogen bond network was found to be identical in Form I and Form II, and the packing difference is caused by variable mutual orientation of hydrogen-bonded layers. The metastable form was found to undergo an irreversible phase transition, indicating the monotropic relationship between polymorphs. For the salicylic acid salt, two polymorphic modifications were discovered in addition to the form known in the literature[2], and their order of stability was determined based on thermal and dissolution studies. A common trend in supersaturation affecting the solid form stability was observed both in salts and in pure RLZ. In addition, solvated crystals were found in the systems with 2,4- and 2,6-dihydroxybenzoic acids when water, dioxane, THF or DMSO were used as solvents.

For the obtained phases and pure components, the dissolution parameters were determined in aqueous buffer solutions and organic solvents, and salt formation enthalpies and free energies were determined from the solution thermodynamic cycle in acetonitrile.

Acknowledgements

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Polyfluorinated nitronyl-nitroxide as a supramolecular synthon

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Halogen bonding (XB) was found to be a useful crystal engineering tool because of its high directionality. This type of noncovalent interaction can be used, *inter alia*, in supramolecular architectures with nitronyl-nitroxide (NN) radicals where XB has a role of structure-directing force. Using this approach, we can obtain a new class of self-assembling magnetic materials based on molecular magnets which can potentially be useful in such fields as organic electronics and quantum computing.

We have investigated the phenomenon of halogen bonding formation between NN with 4-iodotetrafluorophenyl fragment **1** (FIB-NN) and this radical represents unusual supramolecular properties. In solid-state of pure FIB-NN there is O···I halogen bonding where the oxygen atom is a nucleophile for two halogen atoms (fig. 1, a) and this supramolecular motif is unknown for any other NN in crystalline phase.

On the other hand, FIB-NN can form heterodimer with another NN (fig. 1, b) where halogen bonding links iodine and nitrogen atoms and by this example for the first time we have demonstrated the possibility of supramolecular heteroradical architecture design using XB.

The crystal of FIB-NN and DABCO (fig. 1, c) is the most noticeable since it is insoluble in acetone, dimethyl sulfoxide or N-methyl-2-pyrrolidone at room temperature and the cocrystal dissolves only upon heating to 50 °C.

Thus, we have demonstrated supramolecular features of a new radical **1** and these results will be the foundation for the design of more complex supramolecular systems with spin-labeled synthons bound via noncovalent interactions.

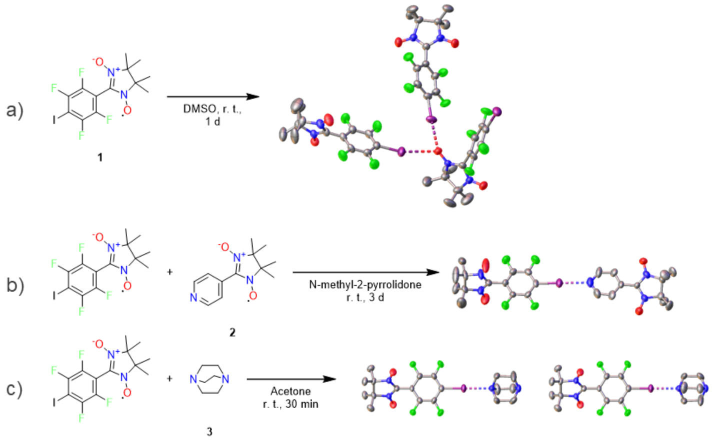

Figure 1. New crystals containing FIB-NN

Acknowledgements

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Noncolavent Interactions in the Tellurium Complexes with Redox-Active Ligands

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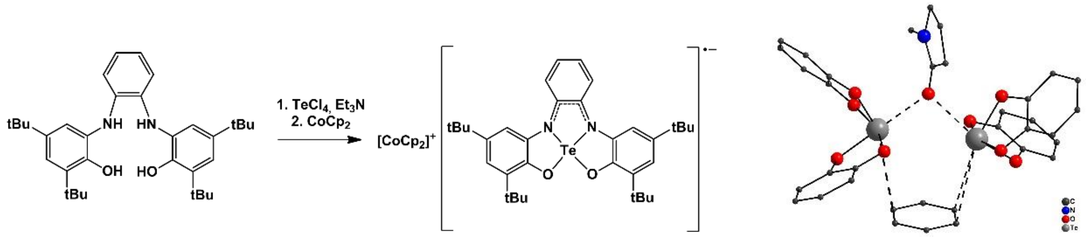
Radical-anionic derivatives of 2,1,3-benzatelluradiazoles are regarded as precursors of perspective magnetic materials, but suffer from both instability and tendency to oligomerize leading to complete spin coupling. We have succeeded in building a 2,1,3-benzatelluradiazole-like fragment by reacting $TeCl_4$ with a sterically hindered bis(aminophenol) (Fig. 1a). Reduction of the product with $CoCp_2$ revealed radical-anionic complex which remains monomeric both in solution and in solid state thus representing rare example of Te-centered radical.[1]

Tellurium 3,6-di-*tert*-butylcatecholate $Te(Cat^{36})_2$ was synthesized from Te and 3,6-di-*tert*-butyl-o-benzoquinone and was found to form the adducts with a variety of O- and N-donor ligands.[2,3] NMR study of the series of adducts with substituted pyridines revealed that their $\delta(^{125}Te)$ depends linearly on ligand's pK_b. A series of arene adducts of formulae $[\{Te(Cat^{36})_2\}_2(\mu\text{-NMP})(\mu\text{-arene})]$ (NMP = N-Methyl-2-pyrrolidone, arene = C_6H_6, C_6H_5Me, C_6H_5I) was isolated (Fig. 1b). The ease of arene binding makes the Te(IV) catecholates attractive precursors for selective arene sorption and separation. According to DFT calculations, the Te···O, Te···N, and Te···C contacts in the adducts are purely attractive with estimated energies not exceeding 6 kcal/mol.



(*a*) (*b*)

Figure 1. (*a*) Synthesis of radical-anionic tellurium complex. (*b*) Structure of adduct $[\{Te(Cat^{36})_2\}_2(\mu\text{-NMP})(\mu\text{-}C_6H_6)]$ (*tert*-butyl groups not shown).

Acknowledgements

Dr. Taisiya S. Sukhikh is acknowledged for X-ray diffraction data collection. Prof. Nina P. Gritsan, Dr. Alexey A. Dmitriev and Dr. Alexander S. Novikov are acknowledged for quantum chemical calculations.

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Investigation of the luminescent properties of the pH-sensitive family of $\{Mo_6I_8\}$ complexes with H_2O and OH ligands

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Octahedral molybdenum iodide cluster complexes $[\{Mo_6I_8\}L_6]^n$ (L is an external ligand of organic/inorganic nature) have a set of remarkable properties, such as X-ray contrast, luminescence in the red and near-IR regions, as well as promoting the process of singlet oxygen generation. However, the exact mechanism of luminescence of these compounds is still unclear. Literature notes that both the ligands in a cluster complex and the distances between cluster cores can affect luminescence, but the influence of these factors has only been studied on relatively small groups of compounds. Cluster complexes $[\{Mo_6I_8\}(H_2O)_x(OH)_{6-x}]^{x-2}$ (x = 0, 2, 4, 6) are suitable for studying the influence of these parameters on luminescence, as their ligands can be varied by altering the pH of the environment, and they exhibit different intercluster distances.

In this work, complexes of the composition $[\{Mo_6I_8\}(H_2O)_4(OH)_2](An)_2{\cdot}nH_2O$ (An = $NO_3^–$, n = 3; An = $OTs^–$, n = 2), $[\{Mo_6I_8\}(H_2O)_4(OH)_2]((PhO)_2PO_2)_2{\cdot}6H_2O{\cdot}2EtOH{\cdot}2(PhO)_2PO_2H$; $[\{Mo_6I_8\}(H_2O)_2(OH)_4]{\cdot}12H_2O$; $[\{Mo_6I_8\}(H_2O)_6](An)_4{\cdot}nH_2O$ (An = $NO_3^–$, $ClO_4^–$, $SO_3CF_3^–$, n = 2; An = $OTs^–$, n = 0) were obtained. For all the obtained compounds in the solid, luminescence spectra were recorded and then these spectra were resolved into components using the Gaussian function. At room temperature, an increase in the crystal packing density and the presence of direct hydrogen bonds between the external ligands of the complexes lead to a decrease in the quantum yield, luminescence lifetime, and the contribution of the two components of the luminescence spectrum. A decrease in temperature, in turn, leads to a redistribution of the intensities of the Gaussian components and, accordingly, a hypsochromic shift of the emission maxima.

Analysis of the electronic absorption spectra of aqueous solutions established that a decrease in pH value leads to the protonation of apical ligands and the formation the $[\{Mo_6I_8\}(H_2O)_6]^{4+}$ cation. Such protonation results in an increase in luminescence intensity, accompanied by a hypsochromic shift of the emission maximum. At the same time, decomposition of the obtained spectra showed that as pH decreases, the contribution of high-energy components increases.

Acknowledgements

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FLASH PRESENTATIONS

Magnetic bistability in fluorinated wolmershauser radical

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S.V. Cherepanova,[4] I.G. Irtegova,[1] A.Yu. Makarov,[1] V.A. Morozov,[3]
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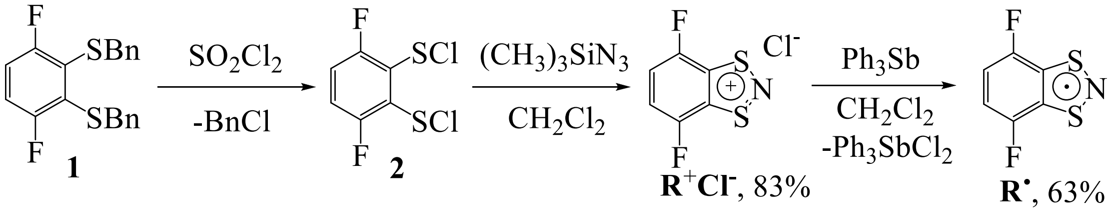
Magnetically bistable materials hold great promise in the field of organic electronics, particularly for the development of molecular switches and sensors. Among these materials, 1,3,2-benzodithiazoles stand out for their potential applications.



4,7-Difluoro-1,3,2-benzodithiazolyl **R**$^\cdot$ is generated via a chemical reduction of the corresponding 1,3,2-benzodithiazolium salt **R**$^+$Cl$^-$. Its properties are thoroughly investigated using various methods including ESR spectroscopy in solution, solid-state ESR, SQUID-magnetometry, TG-DSC, and XRD.

Within the temperature range of 310-325 K, a reversible phase transition from a diamagnetic to paramagnetic state occurs, accompanied by a hysteresis loop of approximately 10 K. XRD analysis reveals distinct structural differences between the low and high-temperature phases. The low-temperature phase consists of weakly linked π-dimers, while the high-temperature phase is characterized by equidistant stacks of monomers. Notably, the low-temperature modification displays shortened N...H, S...F, and H...F contacts, which are absent in the high-temperature modification.

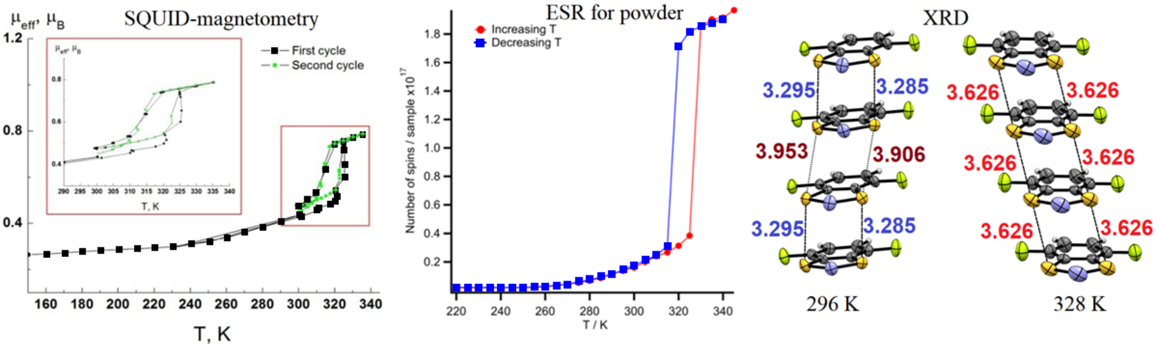


Figure 1. Results of SQUID magnetometry, solid-state ESR, and XRD for **R**$^\cdot$.

The influence of stereoelectronic effects on the values of hfc constants on γ- and δ-hydrogen atoms in EPR spectra of nitroxides

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It has long been known that additional splitting constants may be observed in the EPR spectra of some sterically hindered nitroxides. This results in complex spectral hyperfine structure and/or inhomogeneous line broadening, which complicates the analysis of spectral line shapes and makes these radicals unsuitable for some biophysical applications. These constants have been attributed to the hfc with γ-hydrogen atoms of the alkyl moieties in the side chains1. It was also shown that the presence of substituents at the 3 and/or 4 positions of the five-membered heterocycle is necessary for the appearance of a large hfc constant in the EPR spectra2. The exact assignment of HFC splits to specific hydrogen atom(s) has not yet been made, and the reasons for their occurrence are still not clear, which makes it difficult to create radicals with the desired spectral characteristics.

In order to study the factors influencing hfc constants on distant hydrogen atoms, a series of pyrrolidine-1-oxyls were synthesised and their EPR spectrum parameters were measured.

The analysis of quantum-chemical calculations conducted using the NBO method indicates that the occurrence of hfc constants on γ-hydrogen atoms results from the significant spin polarization of the s-orbital of the hydrogen atom. This is a consequence of the interaction of the σ-orbital of the C-H bond with the π*-orbital of the N-O bond in the β-spin space, due to direct overlapping. This results in the transfer of β-electron density from the C-H bond, in particular from the hydrogen atom, to the N-O bond.

The potential for the emergence of significant hfc constants on δ-hydrogen atoms was also empirically demonstrated in the case of nitroxide with a spirocyclic substituent. The mechanism by which hfc constants arise on the δ-hydrogen atom is associated with the transfer of spin polarisation from the nitroxyl fragment to the (γ-C)-(δ-H) bond through the intermediate (α-C)-(β-C) bond via hyperconjugation.

Acknowledgements

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Effect of temperature, hydrostatic pressure and irradiation on photosensitive complexes [Co(NH$_3$)$_5$NO$_2$]XY

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Noncovalent interactions have a significant impact on chemical transformations in solids. By influencing noncovalent interactions one can control the structure and reactivity of a substance. Noncovalent interactions are sensitive to external influences, such as heating, cooling and pressure. They determine the crystal structure, anisotropy of crystal deformation and possibility of phase transitions and solid-state chemical reactions. Information about impact of external influences on the crystal structure allows understanding how changes in external conditions affect the course of chemical reactions. Also this information helps to understand relationships between anisotropy of deformation of the structures and noncovalent interactions.

Convenient objects for studying such solid-state transformations are cobalt coordination compounds [Co(NH$_3$)$_5$NO$_2$]XY. In such compounds a mechanical response during the photoisomerisation reaction [Co(NH$_3$)$_5$NO$_2$]XY → [Co(NH$_3$)$_5$ONO]XY is observed[1-3]. The convenience of using such cobalt complexes for studying the relationship «composition-structure-properties» arises from the fact that in most of them no destruction of the crystal is observed during the photoisomerisation reaction. This allows solving their crystal structure and geometry of intermolecular interactions using X-ray diffraction analysis and also comparing changes arising from the photoisomerisation reaction and from external influences for both irradiated and non-irradiated compounds.

In this work previously unknown cobalt complexes [Co(NH$_3$)$_5$NO$_2$]XY, XY = BrNO$_3$, INO$_3$, C$_3$H$_4$O$_4$, (NO$_3$)$_2$ and [Co(NH$_3$)$_5$NO$_2$]$_2$I$_3$Cl were studied. The goal of this work is establishing the relationship between the possibility of photoisomerisation reaction, the outer-sphere anion, crystal structure and anisotropy of its deformation under external influences. In this work crystallochemical analysis was performed: structural changes during photoisomerisation reaction for studied complexes were compared and main structural factors influencing the course of photoisomerisation reaction and the presence of photomechanical response were revealed. It was shown that all studied compounds react differently to irradiation, all of them show anisotropic deformation upon cooling and increasing pressure. The phase transitions were also observed for several compounds under the influence of hydrostatic pressure.

Acknowledgements

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Effect of mineral acid strength on the kinetic parameters of the reaction of allantoin synthesis

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The class of imidazolidinone compounds has a wide application sphere as pharmacy, medicine and organic synthesis[1]. The condensation reaction between nitrogen-containing and carbonyl compounds is the most used way to heterocyclic compounds synthesis with imidazolidinone cycle. One of them is allantoin. It is actively used in cosmetology due to its antioxidant, anti-inflammatory and restorative properties[2]. In industry allantoin is produced by a condensation reaction between glyoxalic acid, urea with acid catalysts[3]. Glyoxalic acid can be autocatalyst in the reaction.

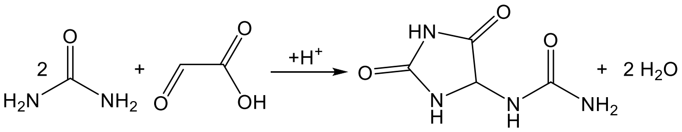

Figure 1. Condensation between glyoxalic acid and urea

The formation process of imidazolidinone cycle is not studied well. Thus, the aim of the work was determination kinetic parameters of allantoin synthesis reaction by Raman spectroscopy (Horiba Scientific, Japan) *in situ* and the effect of strength of the acid catalyst on its.

As a result of this study, it was determined that increasing reaction-rate constants and decreasing activation energy for temperature range of 30-40 °C indicate the dependance between strength of acid catalysts effects and kinetic parameters of reaction (Fig. 2).

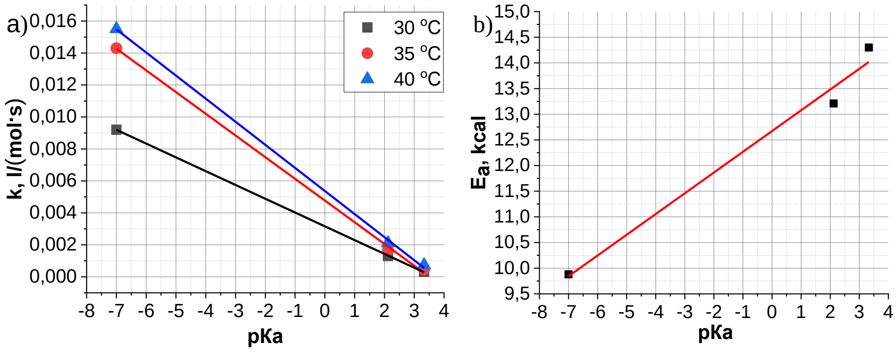

Figure 2. Correlation of the reaction rate constant (a) and activation energy (b) with the pKa of the acid catalyst at temperatures of 30, 35 and 40 °C

Acknowledgements

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Synthesis, structure, and properties of a tungsten bromide complex featuring a $\{NiW_5\}$ metal cluster

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A cluster complex is defined by covalent bonds between metal atoms. Octahedral cluster complexes are represented structurally as $[M_6X_{14}]^q$, where 'M' is the metal atom, 'X' is the ligand, and 'q' is the charge. These complexes form an octahedron surrounded by fourteen ligands.

Octahedral cluster complexes have been extensively studied due to their remarkable luminescence and redox properties [1]. Heterometallic complexes, typically involving molybdenum combined with niobium or rhenium, remain underexplored due to the challenges in their synthesis [2,3]. To date, the literature lacks examples of heterometallic octahedral complexes with third-row metals such as nickel. The study of new cluster complexes enhances the understanding of metal-metal and metal-ligand bonding, and variations in metal composition can significantly affect their redox and spectroscopic properties.

This study presents a synthesis method for a novel complex, $(NBu_4)_2[NiW_5Br_{14}]$, with an octahedral $\{NiW_5\}$ core. The work delves into the crystal structure and redox properties of the complex and includes quantum chemical analyses to elucidate the bonding nature within the heterometallic complex. Comparative analysis with the established $(NBu_4)_2[W_6Br_{14}]$ highlights differences in bonding and reactivity and sheds light on the unique aspects of the new complex.

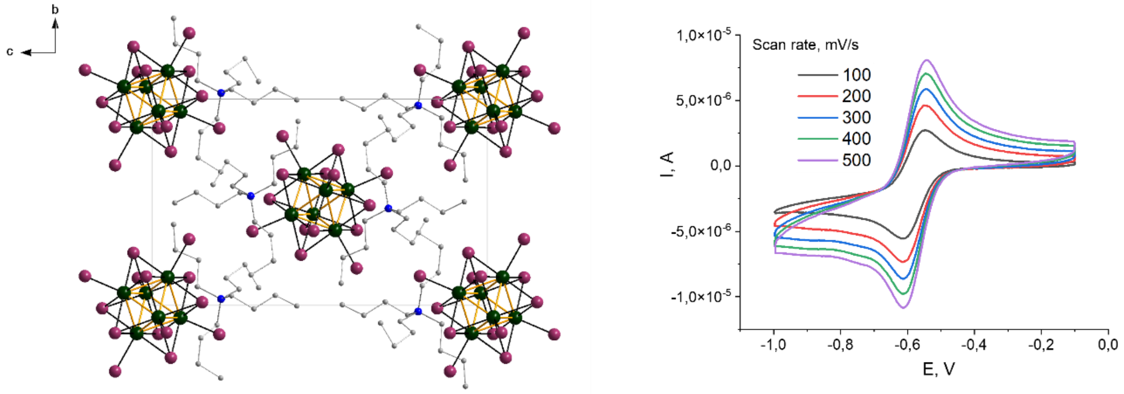

Figure 1. Crystal structure of $(TBA)_2[NiW_5Br_{14}]$ (*left*), CV curves of compound $(TBA)_2[NiW_5Br_{14}]$ in acetonitrile at different scan rates (*right*).

Acknowledgements

Authors thank Dr. Vasiliy N. Yudin and Dr. Yakov M. Gayfulin for helpful discussions.

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Organocatalysis by diaryliodonium salts

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Halogen-bond donors have been used as effective non-covalent organocatalysts in a series of model processes, though the scope of reactions explored remains very scarce. In the previous work, we expanded the scope of transformations catalyzed by halogen bond donors and demonstrated that donor-acceptor cyclopropanes can be successfully activated toward reaction with aromatic nucleophiles by cyclic iodonium salts. It was found that the combination of non-coordinating anions such as bistriflimide and aromatic solvent was crucial to the success of reaction.

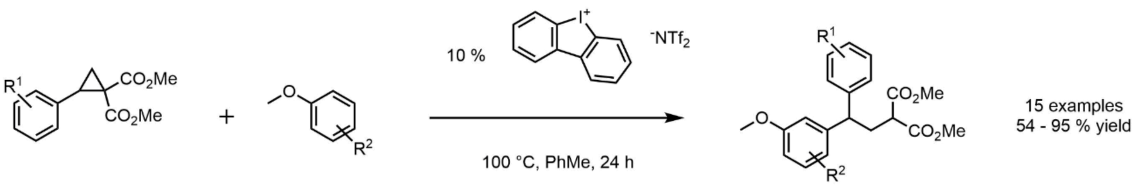

Figure 1. Nucleophilic ring-opening of donor-acceptor cyclopropanes.

To better understand the influence of various structural modifications in the structure of halogen bond donors on their catalytic activity, we prepared a series of cyclic diaryliodonium salts, containing various anionic and cationic species, including previously unexplored fluorinated iodonium cations. Next, we evaluated catalytic activity of obtained compounds in the benchmark Michael addition reaction.

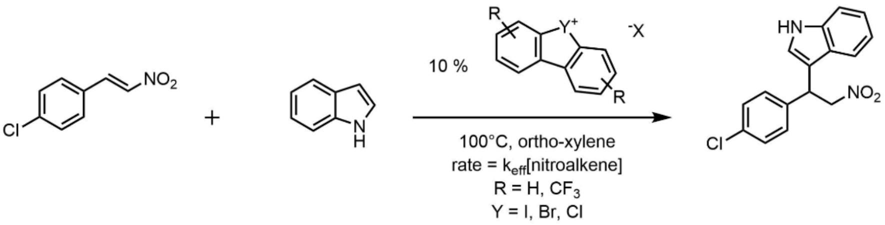

Figure 2. Michael addition to nitroalkenes as benchmark reaction.

We discovered that the coordinating ability of the counterion and the presence of electron-withdrawing groups in the structure of diaryliodonium cation are most significant factors affecting catalytic activity of studied halogen bond donors. Obtained experimental data are in agreement with computed ESP functions for ion pairs and reflect the impact of anion coordination and aromatic system electronic structure on the iodonium center Lewis acidity.

Acknowledgements

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Investigation of Relative Stability of Diene Rhodium Complexes

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Information about bond strength between metal and ligand in complexes of transition metals is essential for homogenous catalysis. Activity of the catalyst and selectivity of the reaction depend on it. Diene rhodium complexes is one of the most widely used in different catalytic transformations class of organometallic compounds.[1] However diene ligands bind metal more weakly than phosphine ligands, for example. For this reason, it is important to know how bond strength depends on structure of the diene ligand for pointed catalyst design. So, our main purpose was to suggest a method of quantitative evaluation of metal-ligand bond strength in diene complexes of rhodium.

To reach our goal, we investigated the equilibrium in reactions of diene ligand exchange in complexes [(diene)Rh(acac)] with NMR spectroscopy. Equilibrium constants of corresponding reactions were chosen as a measure of their relative stability. We investigated broad range of different dienes to have a possibility to make a conclusion about dependence of bond strength on their structure. So, we obtained an experimental row of relative stability of diene rhodium complexes (Fig. 1). Also we adjusted quantum calculation method in accordance with experimental data, which allows us to predict stability of complexes with newly invented diene ligands.

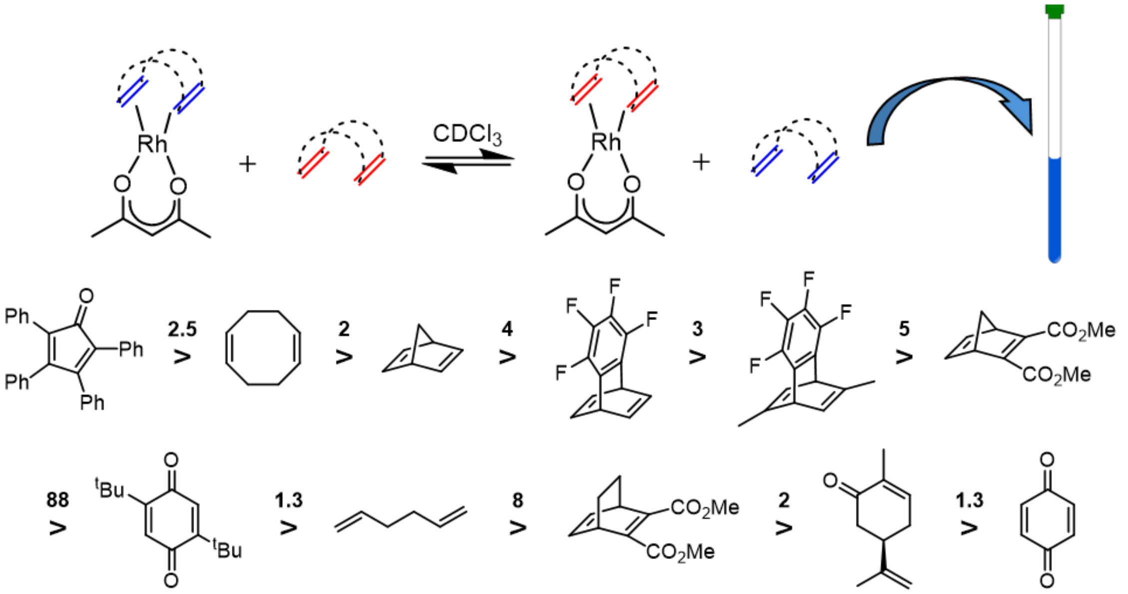

Figure 1. Row of relative stability of diene rhodium complexes.

Acknowledgements

This work was supported by the Russian Science Foundation (grant №23-13-00345).

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Features of Calculations of Structural and Energy Characteristics in Complex Reaction Systems with Non-Covalent Interactions

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This work examines the methodological aspects of choosing computational methods that allow adequate assessment of the structural and energy characteristics of reaction systems, the properties of which are significantly influenced by weak non-covalent interactions.

The complexity of the problem is due to the need to determine the optimal method that has acceptable performance and allows one to take into account with quantitative accuracy the features of systems with:

- flexible molecules, for which an energy change of several kJ/mol can lead to significant structural changes;
- similar free energies of various conformational states of reagents and products (the accuracy of free energy values affects the possibility of thermodynamic control of the reaction);
- the possibility of implementing various mechanisms[1] (direct and reverse reactions; mono-, bi- and trimolecular interactions; one-stage and two-stage reactions);
- with free energy of activation close to the reaction threshold (the accuracy of activation free energy values affects the possibility of kinetic control of the reaction).

When calculating such systems, the task becomes more complicated if the molecules fall into the force field of the adsorbent. Dispersion interactions, weak and medium hydrogen bonds can significantly influence changes in the structure and reactivity of adsorbed molecules.[2–4]

The need to accurately take into account non-covalent interactions determines the requirements for the calculation method. The significant number of non-hydrogen atoms does not allow the use of precision computational methods. As a result of comparing the values obtained by various calculation methods and experimental data, the preferred methods of density functional theory were determined. Along with relatively new methods, the B3LYP functionality shows sufficient reliability. Its versatility and performance are suitable for the systems under consideration and allow reliable energy characterization values to be obtained even for proton transfer reactions.

The suitability and limits of applicability of various basis sets are considered depending on the assigned tasks. When calculating the structural and energy characteristics on the surface of the adsorbent, we had to abandon the inclusion of diffuse functions. However, the systematic nature of the errors makes it possible to find correlations with experiment even when using small basis sets.

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Crystallization of chiral thioureas with a 1-phenylethylamine fragment: transfer of stable motifs from racemic to homochiral environments

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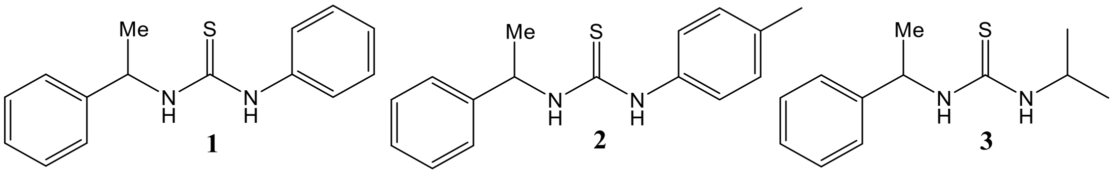
Chirality of molecular compounds is of great importance for medicinal chemistry. Due to the chirality of the living organism environment, the required physiological effect is usually provided by only one enantiomer of a chiral drug. The different effects of enantiomers are based on differences in homo- and heterochiral binding types, which are most conveniently studied in crystals, according to PCA data.

In this work, we perform a comparative analysis of intermolecular interactions in racemic and homochiral crystals of 1-(1-phenylethyl)thiourea derivatives in order to reveal the fundamental differences between hetero- and homochiral binding.

The studied thioureas in racemic crystals form classical heterochiral associates - a dimer symmetric about the center or a chain on the plane of sliding reflection, while the formation of homochiral crystals occurs by transfer of stable motifs from the racemic environment to the homochiral one. In this case, the symmetry element - center or plane - changes its status from crystallographic to noncrystallographic, acting locally on hydrogen-bonded achiral fragments of molecules. The cost of this motif transfer is an increase in the number of independent molecules and significant differences in their conformations.[1]



1 2 3

Figure 1. Structural formulas of the examined compounds **1-3.**

Acknowledgements

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Bidentate Lewis base receptors based on triazole-linked (aza)benzochalcogenadiazoles

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1,2,5-chalcogenadiazoles are 6π-electron heteroarenes that are able to form chalcogen bonds – net attractive interactions between an electrophilic chalcogen atom and a Lewis base.[1] Chalcogen bond-based complexes binding strength depends on receptor structure, Lewis base nature and solvent properties. Chalcogen bond formation is accompanied by occurrence of the new charge-transfer band in Vis spectra that comes a precondition for selective Lewis base recognition.[2] However, relatively simple molecules containing one chalcogenadiazole moiety are not able to achieve significant binding selectivity. Recognition selectivity can be increased by chelating receptors containing two chalcogenadiazole moieties simultaneously binding a Lewis base.

Compounds **1** and **2** are the first chalcogenadiazole-based chelating Lewis base receptors, and Se-receptor **2** is supposed to be better chalcogen bond donor. XRD experiment showed a non-planar structure of compound **2**. Low solubility of compound **2** is caused by strong crystal packaging due to formation of intermolecular chalcogen bonds. The distance between selenium atoms in compound **2** is 7.25 Å, that prohibits monoatomic Lewis base chelating. Hypothetically, polyatomic Lewis bases such as carboxylates, sulfonates, etc, are more suitable for chelating recognition.

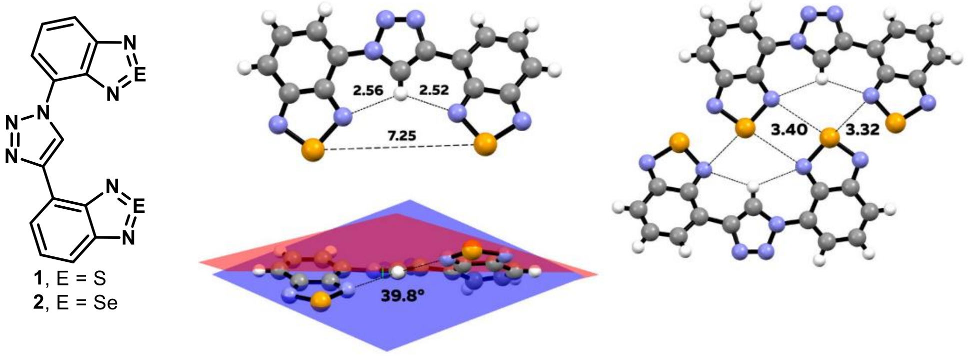

Figure 1. Structure formulas of compounds **1** and **2** and XRD structure of compound **2**.

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The influence of crystal packing on the optical properties of cyclometalated iridium(III) complexes

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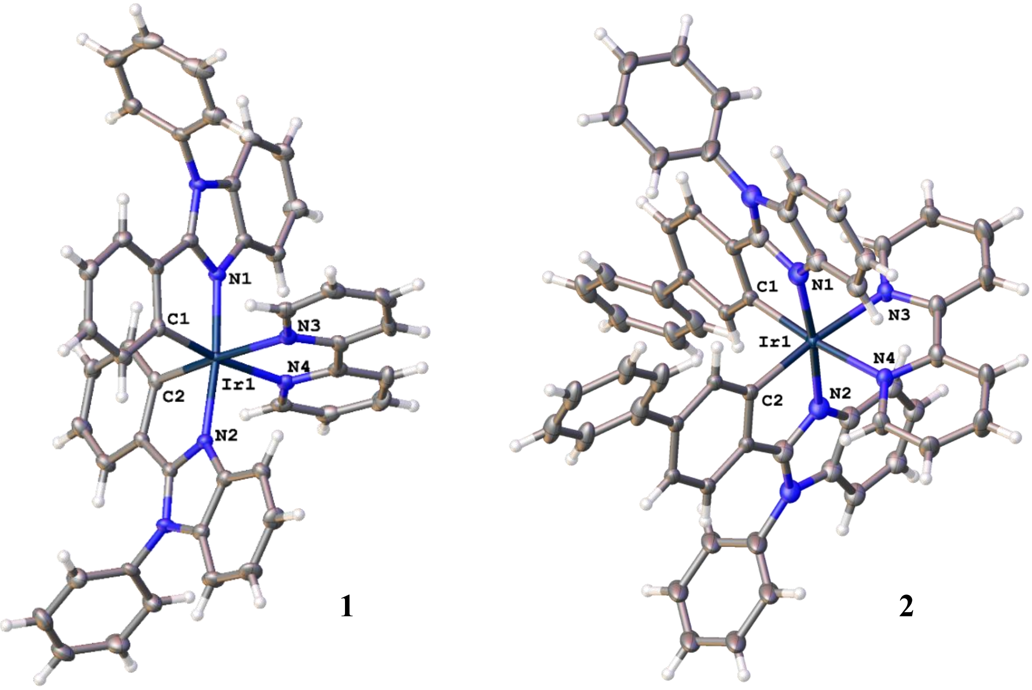
Some of the brightest and most promising phosphors for OLEDs are cyclometalated iridium(III) complexes. Because in these devices such complexes can be in the solid (aggregated) state, it is important and relevant to study relationships between the optical characteristics of the complexes and their crystal packings.

In this work, two cationic iridium(III) complexes were synthesized (yield > 90%) and characterized by ^{1}H and ^{13}C NMR, HRMS, single-crystal and powder X-ray diffraction. For both complexes, the counterions were chloride or PF_6^- anions, thus, 4 salts were prepared and studied. The octahedral geometry around the Ir(III) ion is formed by two cyclometalated 2-arylbenzimidazoles and 2,2′-bipyridine. The counterion affects the crystal packing of complex **1** (C–H···π contacts and π–π stacking between the benzimidazole units), while complex **2** is packed only by C–H···π interactions irrespective to the counterion.

According to cyclic voltammetry data, both complexes show reversible redox behavior with E_{ox} of ca. 0.9 V and E_{red} of ca. –1.9 V vs. the Fc+/Fc couple. For the complexes **1** and **2** both in solution and in the solid phase, UV-vis and luminescence spectra were measured to probe the role of crystal packing on the optical properties. The influence of π–π stacking on emission of the complexes is discussed.



1

2

Figure 1. Molecular structures of the complex cations. Displacement ellipsoids are drawn at 50% probability level.

Parametrization of Electrostatic Interactions in Molecular Mechanics Based on Electron Density Descriptors

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Molecular mechanics is a valuable tool widely used in biology and materials science, as it provides possibility to model systems of hundreds and thousands of atoms[1-2]. Noncovalent (electrostatic and dispersion) interactions are of a great importance for most systems of interest.

Common way to describe electrostatic interactions is to use Coulomb law with point charges, located at the atomic positions. This representation is computationally effective, but sometimes is unable to reproduce charge distribution around an atom, the most common example being halogen atoms[3]. The so-called sigma hole at line connecting carbon atom and heavy heteroatom can be described by an additional virtual charge, improving the quality of approximation. The positions for such virtual sites are usually chosen based on chemical intuition or quantum mechanical data. It is also important to choose correct values of atomic charges as they are not a measurable in quantum mechanics.

This work suggests analyzing the electron density topology to locate virtual sites positions. The method helps to make virtual sites localization automatic and provides physical argumentation for their positions. We also describe electron density descriptors, which can be used to improve charge fitting. It is shown that virtual sites fitted using our procedure improve the description of noncovalent interactions in biological molecules and halogenated molecules.

Acknowledgements

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POSTER SESSION

Electronic and crystal packing effects within binding approach: picolinic acid N‑oxide and methimazole

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We experimentally obtained and studied the inner-crystal scalar potential fields and the respective vector force fields of kinetic and static nature in picolinic acid N-oxide and methimazole. The “through-bond” and “through-space” electronic effects were defined and distinguished via the vector fields and concurred with the penetration of the electron contributor’s electrostatic and kinetic force field pseudoatoms into the occupier’s chemical atom. The experimental electric and kinetic force fields in the molecular crystals were compared to the theoretical ones for the free molecules and hydrogen-bonded associates, which helped figure out the natural consequences of the crystal packing effect. As expected, the appearance of neighboring attractors in a dense crystal packing requires zero-flux surfaces emerging in the vector fields and the compression of the outer force field pseudoatoms of a molecule. We proposed to consider a zero-flux surface in the kinetic force field to be a turning surface for electrons in the sense that an electron passed through the boundary is immediately affected by the redirected force attributed to another attractor.

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Experimental evaluation of the energy of interactions determining the crystal chemical design of chiral compounds based on the thermochemical parameters of crystal forms and their solubility in alkane

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The method of crystallization of a chiral compounds (pseudoracemate, racemic compound or racemic conglomerate - in classical stereochemistry; crystallization-induced stereochemical transformations of chiral organic molecules - in supramolecular dynamic stereochemistry) is determined primarily by the ratio of the thermodynamic potentials of the corresponding crystalline forms. In this context, it seems important to identify systematic trends in changes in energy relationships between the phases of various compounds when the structure is varied. Detection of such trends may enable targeted changes in structure to control the thermodynamic preference for crystallization of such a system in the desired configuration. To identify them, it is proposed to use data on solubility in an alkane (cyclohexane) and thermochemical parameters of melting of crystalline forms with systematic variation of the structure[1]. We used this approach to compare the energy characteristics of the crystal structures of derivatives of the natural compound steviol. It should be noted that this makes it possible to construct thermodynamic cycles to assess the energy of intermolecular interactions in metastable phases, for which direct experimental determination is impossible.

Acknowledgements

This work was financially supported by RSF, grant 22-13-00284.

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Crystal structure of optically active sulphones based on 4-aminophenol and 5-menthyloxy- and 5-bornyloxy-2(5H)furanones: stereochemical features

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Based on 4-aminothiophenol and 5-menthyloxy- and 5-bornyloxy-2(5H)-furanones sulfones are interesting objects as systems, containing on the one hand a chiral fragment (menthyl- or bornyloxy-2(5H)-furanone) carrying all stereogenic centers of the molecule, and on the other hand an achiral substituent bearing functional groups, which is capable of hydrogen bonding: an amino group and a sulfonyl group as a potential donor and acceptor of hydrogen bonds. It is interesting what kind of supramolecular associates are realized in crystals, what kind is the symmetry of the formed associates -truly chiral or pseudo-racemic.

Within the developing area of supramolecular stereochemistry, we have studied the crystal structure of two chiral compounds of the furanone series. In both crystals, the substance is represented by independent molecules A and B, which have significant differences in conformations and hydrogen bonds system.

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Electronic force field based binding approach: Appel’s salt

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We present a binding approach based on the electrostatic and kinetic force density fields, which is proposed to elucidate interatomic interactions, structures, and chemical reactions. It consists in the understanding of (*i*) the arrangement of pseudoatomic zero-flux surfaces (ZFSs), (*ii*) the mutual compression of force-field pseudoatoms of the same type, (*iii*) the penetration of a bonded atom into neighboring force-field pseudoatoms, (*iv*) the distortion of the force fields, and (*v*) the occurrence of a binding path connecting two force-field attractors as the inherent consequences of the emergence and existence of any many-electron multinuclear system. Herein, the interatomic charge transfer and the reciprocal quantum-chemical response accompanying the covalent and noncovalent bond formation were studied using the abovementioned penetration, exemplified by Appel’s salt. It was found that the three-center chalcogen bonding $\mathrm{Cl}^{-}\cdots\mathrm{S{-}S}$ and tetrel bonding $\mathrm{Cl}^{-}\cdots\mathrm{C}\cdots\mathrm{Cl}^{-}$ in the crystal of Appel’s salt resemble the initial and transition states of bimolecular nucleophilic substitution reactions, respectively. Being extracted from the crystal structure, the corresponding ion pairs undergo chemical rearrangement: forming the covalent bonds Cl–S and Cl–C leads to the collapse of the pseudoatomic ZFSs and the alignment of the bond and binding paths in the internuclear regions.

Acknowledgements

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Study of two different crystallization pathways of pyridinoyl-hydrazone derivatives of isosteviol: true and pseudosymmetric homochiral motifs

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The coexistence of two fragments, a chiral isosteviol moiety and an achiral pyridinoyl-hydrazone moiety, in the molecules of pyridinoyl-hydrazone derivatives of isosteviol results in the realization of two distinct supramolecular motifs in their crystals, namely, a true homochiral motif and a pseudosymmetric homochiral motif.[1] A common feature among them is the propensity to form helices around axis 2_1 through hydrogen bonds of the carboxyl group with different acceptors.

In the “double helix” packing, the direction of all classical hydrogen bonds is the same, and their joint realization results in forming a 1D-associate representing two interweaved helices. In the pseudosymmetric homochiral packing, helices exhibit opposite directions, and an element of local pseudosymmetry is formed at the points of their joining in the crystal.

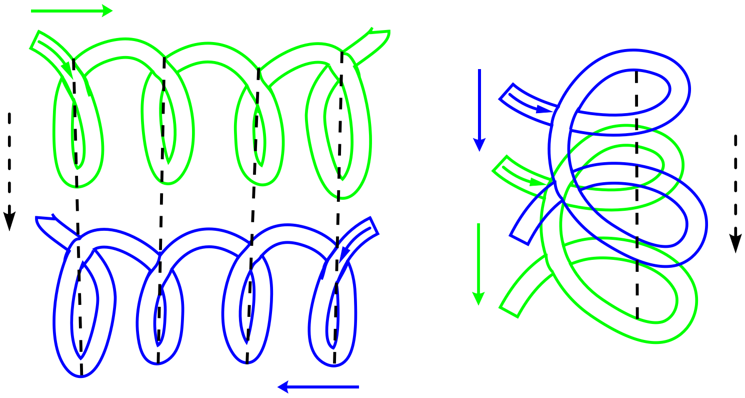

Figure 1. Pseudosymmetric (left) and “double helix” true (right) homochiral packings.

Acknowledgements

The work was supported by the Russian Science Foundation (grant No 22-13-00284).

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Planar chiral arene complexes of Ruthenium. Synthesis and catalysis

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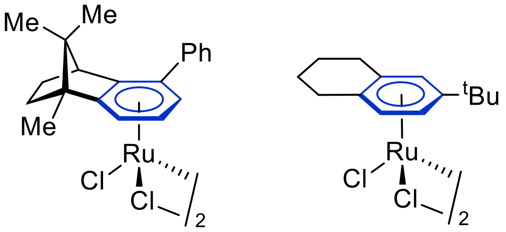
Activation of C-H bonds in aromatic compounds containing directing groups is a very active field of research, which has revolutionised the synthesis of heterocycles. The most common catalysts for such reactions are the cyclopentadienyl rhodium complex $[(C_5Me_5)RhCl_2]_2$ and its arene ruthenium congener $[(p\text{-cymene})RuCl_2]_2$. Ruthenium complexes with chiral arene ligands are scarce, and their use as catalysts for C-H activation reactions have been reported only a year ago.

Our group has synthesised the ruthenium complex **1** with the arene ligand derived from chiral natural camphor, but unfortunately it turned out to be too hindered and susceptible to replacement of arene in C–H activation reactions.[1] At the same time, Wang et al.[2] reported the synthesis of the ruthenium complex with the chiral arene ligand derived from paracyclophane, which successfully catalysed asymmetric C-H activation of N-methoxybenzamides and their annulation with alkynes providing axially chiral isoquinolones (up to 99 % yield and 96 % ee). Based on these results, we proposed a concise approach to ruthenium complexes with planar chiral arene ligands via resolution of racemates as diastereomeric adducts with a chiral phosphine[3]. The obtained chiral complex **2** catalysed the annulation of N-methoxybenzamides with N-vinylamides, giving dihydroisoquinolones in 50-90% yields and 70:30-90:10 e.r. Taking into account the complexity of the synthesis of ruthenium complexes from chiral arenes, we hope that our approach will be useful for further development of such catalysts for asymmetric transformations.



1 **2**

Figure 1. Ruthenium complexes were synthesised our group

Acknowledgements

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Non-covalent interactions in crystals of silver complexes with 3-arylidene-1-pyrrolines and nitrate anions

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In the last couple of decades, the study of non-covalent interactions with the participation of silver ions is one of the most rapidly growing fields in crystal engineering and supramolecular chemistry.

New silver complexes with 3-arylidene-1-pyrroline derivatives as N-donor ligands and external nitrate anions were obtained as part of the study of new coordination compounds with potentially biologically active properties.

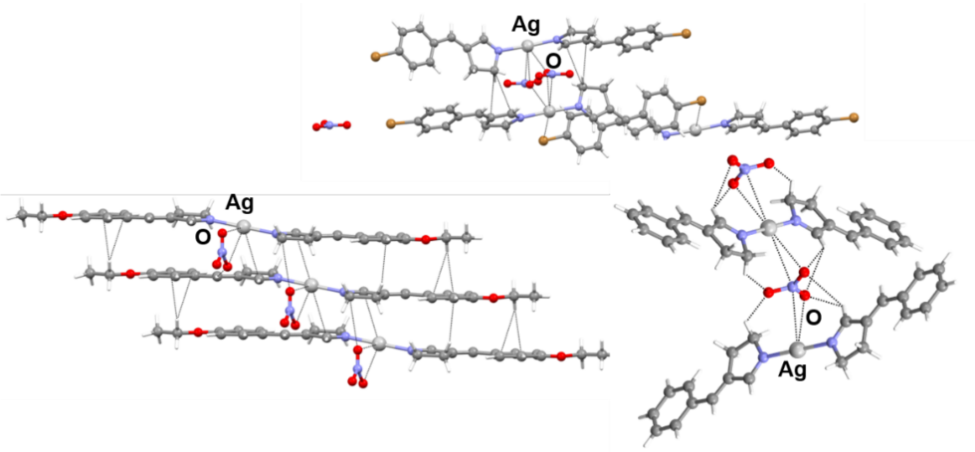

Figure 1. Non-covalent interactions in crystals of investigated complexes.

The presence of a large number of functional groups in the composition of molecules leads to the realization of a variety of weak intermolecular interactions. Thus, in the crystals of all obtained complexes, the interaction between the silver atom and the nitrate anion is realized, but the topology of these interactions differs. In some cases, it can be described as a bifurcate one with the participation of one oxygen atom and two silver atoms (including those bound to each other by the argentophilic interaction), in others – as a bifurcate with the participation of one silver atom and two oxygen atoms of the nitrate anion. In addition, Ag...π interactions involving pyrroline fragment are realized in the crystals of some complexes. As a result of the study, all the described interactions were analyzed within the framework of the geometric and quantum-topological approach, the energy was estimated and the dependences of the crystal structure and non-covalent interactions on the substituent in the *para*-position of the benzene ring of the arylidenepyrroline ligand were revealed.

Acknowledgements

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Intermolecular interactions in the structures of gold(III) tetraarylporphyrinates

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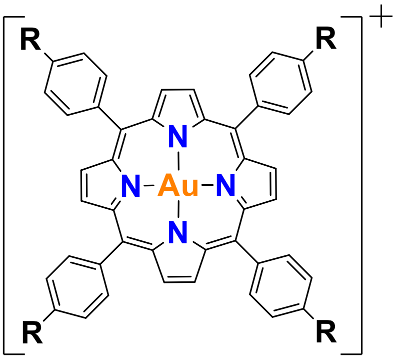
Metallophilic interactions are of great interest in chemistry because they can contribute to the emergence of unusual properties of materials, such as luminescence, magnetism, sensing, thermochromism, solvatochromism, and electrical conductivity. The beginning of the study of metallophilic interactions lies in gold-gold contacts, i.e. aurophilic interactions. Such interactions are widely used in gold chemistry due to the steric accessibility of the gold center and the strength of aurophilic contacts. Until the last decade the term “aurophilicity” was almost synonymous with Au(I) ··· Au(I) interactions. However, in the 2000s, it was theoretically proven that Au(III) can also promote aurophilic attraction. Since then, various gold complexes with Au(III) ··· Au(III) interactions have been synthesized and characterized[1]. However, such interactions are still quite rare.

In this work, new gold(III) porphyrinates were obtained and characterized[2] (Fig. 1). It was shown that the structures are characterized by non-covalent interactions of various types including aurophilic interactions.



R = oBu iPr
tBu Ph

Figure 1. Structure of the synthesized gold(III) porphyrinates.

Acknowledgements

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Volatilization Thermodynamics of Magnesium(II) β-Diketonates for Revealing Noncovalent Interactions

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The basic application of β-diketonate metal complexes is as precursors for the formation of film materials in gas-phase chemical deposition. Quantitative data on volatilization (temperature dependences of saturated vapor pressure, thermodynamic characteristics of enthalpy and entropy) as well as thermal behaviour in the condensed phase (phase transitions) of the precursors used are of great importance for efficiency of these processes. As a matter of fact, the data available in the literature tend to have a significant scatter.[1, 2] Zherikova K.V. and co. began developing a technique for diagnosing the quality of thermodynamic data, which is based on the structure-property correlations and group additivity principles in the series of various metals with β-diketonates.[3] Such a tool is intended not only to diagnose the quality of available or as-obtained data but also to assess lacking properties. However, metal β-diketonates turned out to be the compounds that have many non-covalent interactions that apparently do not obey the laws of additivity.[4] In order to assess the level of these interactions, it is first necessary to obtain a number of standardized values on a series of compounds carefully selected.

The focus of this work is a set of heteroligand magnesium(II) complexes, $[\mathrm{Mg(Q)(\beta\text{-}diketonate)_2}]$, where Q = N,N,N’,N’-tetramethylethylenediamine, 2,2’-bipyridine, 1,10-phenantroline, 4,4’-di^{t}Bu-2,2’-bipyridine, β-diketonate = ligand with CF_3, C_2F_5, CH_3, ^{t}Bu, and Ph terminal substituents. The thermodynamic properties of the compounds (sublimation, vaporization, fusion) have been investigated for the first time by using $p(T)$ and calorimetric measurements (DSC, static and flow methods). As a result of the procedure developed by Zherikova K.V. et al. all the thermodynamic characteristics of enthalpy and entropy have been standardized and could be used as basis for identifying any structure-property correlations.

Acknowledgements

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Synthesis and optical properties of ((9H-diazafluoren)-9-ylidene)methyl)arylenes

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Fluorenylidene derivatives, such as 2,5-bis((9*H*-fluoren-9-ylidene)methyl)arylenes, exhibit high conformational lability, polymorphism, and aggregation-induced emission.[1] Such materials are used in light-emitting devices, sensors, bioimaging, etc. Replacement of some carbon atoms in the fluorene fragment with more electron-withdrawing nitrogen atoms leads to changings in physico-chemical properties. For example, 4,5-diazafluorenylidene derivatives may have chelating ability, which is necessary for the preparation of coordination compounds based on them.[2] 1,8-Diazafluorenylidene derivatives can form planar structures due to intramolecular non-covalent interactions.

In this work, approaches to the synthesis of ((9*H*-diazafluoren)-9-ylidene)methyl)arylenes have been developed, and their optical properties have also been studied. The target compounds were prepared using a combination of cross-coupling and condensation reactions. It was shown that 4,5-diazafluorenylidene derivatives have a non-planar and conformationally flexible molecular structure, while 1,8-diazafluorenylidene derivatives have a planar structure due to intramolecular N…H bonds. It was also shown that some of the obtained compounds possess aggregation-induced emission. The quantum yield in the crystalline state and in solution reaches 25%.

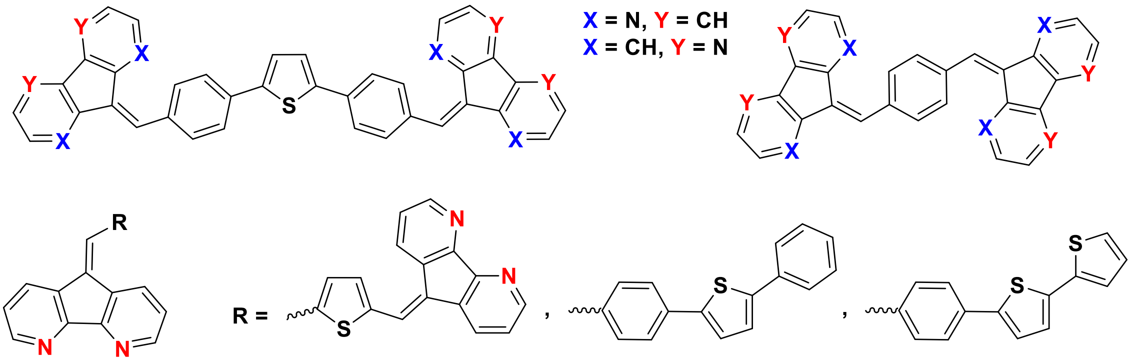

Figure 1. Chemical structures of ((9*H*-diazafluoren)-9-ylidene)methyl)arylenes.

Acknowledgements

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Diaryliodonium dichloroiodates(I): synthesis and structure

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Halogen bonding is a subject of growing interest in crystal engineering, biomedical science, ion and molecular recognition, noncovalent catalysis, and other fields. Examples of supramolecular aggregates of diaryliodonium cations with various halides,[1] pseudohalides,[2] and complex anions[3] can be found in the literature. This study mainly focuses on XBs in diaryliodonium dichloroiodates(I) (Fig. 1). Three diaryliodonium dichloroiodates(I) were synthesized in two ways: 1) through the decomposition reaction of diaryliodonium tetrachloroiodate(III); 2) in the reaction between diaryliodonium chloride and iodine monochloride. Single-crystal X-ray diffraction analysis was performed for all compounds. The C–I···Cl XBs were detected in all structures. It was demonstrated that diaryliodonium dichloroiodates(I) exhibit heterotetrameric and polymeric organization types. The presence of XBs, as well as the nature of the contact participants were confirmed by theoretical calculations. The calculations were performed under periodic boundary conditions (crystal models) in the CP2K-8.1 program.

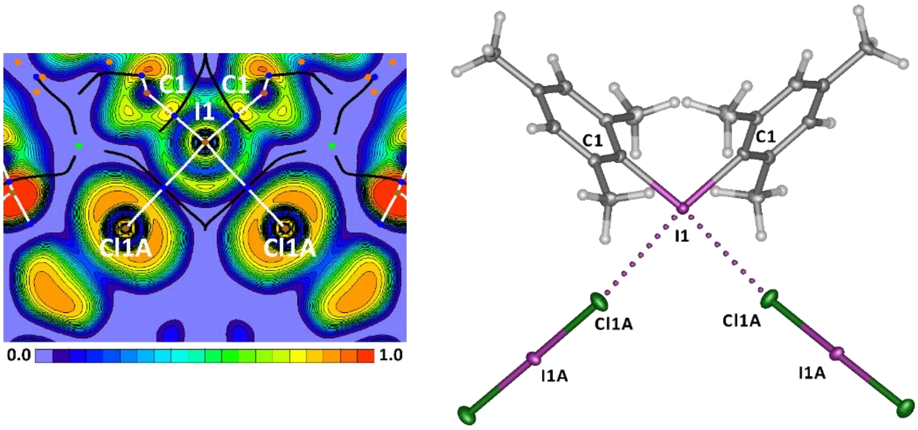

Figure 1. Diaryliodonium dichloroiodates(I) (Ar = Ph, Mes)

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Application of different calculation schemes for sublimation enthalpies and Gibbs energies of amino- and hydroxypyridines

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The saturated vapor pressures of 2-, 3-, and 4-aminopyridine and 3-hydroxypyridine were determined at different temperatures by the transpiration method. The thermodynamic calculations provided the sublimation standard molar enthalpies, entropies, and Gibbs energies for the studied substituted pyridines.

A detailed insight into the nature of packing forces in the crystals of isomeric aminopyridines with the help of the Hirshfeld surface analysis revealed the close nature of the intermolecular interactions. The packing energetics in the considered crystals was studied based on periodic DFT computations, and lattice enthalpies and Gibbs energies were calculated for structures optimized using five different functionals, namely, PBE, PBE0, B3LYP, HSE06 and CAM-B3LYP. The effect of functional and unit cell optimization on hydrogen bond and cell parameters, hydrogen bond properties and packing energetics. The most accurate lattice enthalpies were obtained at PBE0-D3/pob-TZVP_rev2 level of theory. HSE06 and CAM-B3LYP functionals also demonstrated satisfactory agreement with the experimental data, while PBE and B3LYP were found to systematically overestimate the experimental sublimation enthalpy. Contrary to the expected, the full relaxation of the crystal structure led to decrease in lattice enthalpy caused by BSSE correction increase by 15-35 $kJ\cdot mol^{-1}$ that comes from denser packing of molecules in fully relaxed structures. Compared to DFT-D3, the results of lattice sum methods based on force fields and QTAIMC were found to be less reliable, as none of them could predict the sublimation enthalpy within chemical accuracy for all four compounds. It is worth noting that the QTAIMC scheme for lattice energy calculation is relatively independent on the functional used.

The calculated values of sublimation free Gibbs energies were found to be in a good agreement with the experiment only for 3- and 4-aminopyridine with fixed unit cell parameters. In this case, the cancellation of different errors takes place, as the overestimated entropy term is subtracted from the overestimated lattice enthalpy.

Based on the experimental thermodynamic sublimation parameters from this study and those for the structurally related compounds from the sublimation thermodynamics database for molecular crystals (taking into account the Tanimoto similarity indices) the correlation equations well describing the experimental values were proposed. The virtual screening of hypothetical two-component crystals was successfully carried out taking the most popular drugs for which the sublimation thermodynamic characteristics are available.

Acknowledgements

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The study of the mechanism of the allantoin formation by quantum-chemical calculations

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Allantoin is a biologically active component that is widely used in cosmetics and the pharmaceutical industry. It is used in the manufacture of moisturizers and sunscreens. Allantoin is an effective product in treating wounds, ulcers, burns due to its antioxidant and healing properties. Allantoin is a keratolytic compound, for what reason it is used for treatment of scars.[1,2]

The synthetic method of production allantoin is the condensation reaction between glyoxalic acid and carbamide in presence of mineral acids (Fig. 1).[3]

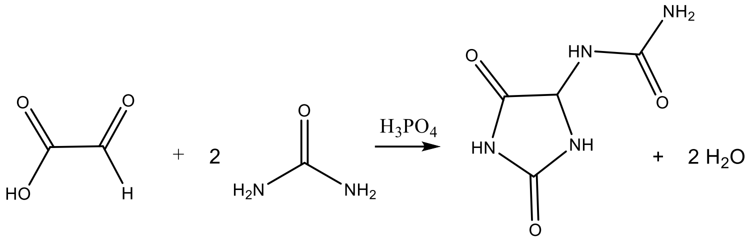

Figure 1. The reaction of allantoin formation

However, the mechanism of reaction between these compounds is not fully understood. The regularities of the allantoin synthesis determined will help to control the conditions for the production of macrocyclic compounds of this type.

In present work, for the first time the mechanism of allantoin formation was proposed and the thermodynamic and kinetic characteristics of the mechanism of the allantoin formations were studied. The catalytic role of water molecules and the influence of protonation were investigated.

The energies in terms of Gibbs free energy of the optimized structures and transition states in the solution were used to construct the potential energy surface. The Gibbs free energy calculations for each structure in an solution consisted in the optimization of the geometry and calculation of the frequencies of this structure at the B3LYP-D3/6-311G(d,p) level of theory taking into account the PCM solvation and correction the obtained thermochemical data using composite method CBS-QB3 taking into account the CPCM solvation. Calculations were performed using the Gaussian’09 program package installed at the SKIF “Cyberia” supercomputer of Tomsk State University.

Acknowledgements

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