



The 3rd STRUCHKOV MEETING

International Workshop on Chemical Crystallography and Structural Biology

dedicated to the 95th Birth Anniversary of Yuri T. Struchkov

Book of Abstracts

November 15-19, 2021

Moscow, RUDN University

*The event was financially supported by the
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**International Workshop on Chemical Crystallography and Structural Biology
“The 3rd Struchkov Meeting”**: Book of Abstracts. Moscow, November 15-19, 2021 – Moscow,
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The Book of Abstracts of The International Workshop on Chemical Crystallography and Structural Biology “*The 3rd Struchkov Meeting*”, which was held in November 15-19, 2021 based on Chemical Departments of Faculty of Science of RUDN University, includes summaries of Plenary and Keynote lecturers, Oral speakers, and the Laureates of Struchkov Prize-2020. The present publication was designed to popularize scientific research activity in the field of chemistry and to discuss modern chemical problems on the international level.

The digest is intended for scientists, students, postgraduates and for wide range of readers interested in problems in chemistry.

Dear Colleagues,

Let me start with the words of welcome to the participants of the 3rd International Workshop on Chemical Crystallography and Structural Biology, dedicated to the memory of Prof. Yuri T. Struchkov. This is the second time when the RUDN University gets the honor of hosting this vibrant and diverse scientific community, which took its roots from the remarkable achievements of Prof. Struchkov's laboratory in the decades around the turn of the last century and was since diversified both in scientific and geographical sense thanks to the work and enthusiasm of Struchkov's lab alumni as well as their colleagues and students. We are very happy that members of this community will present within our workshop their interesting results in various fields ranging from nanomaterials and supramolecular chemistry to green chemistry and proteins.

It gives me special pleasure to mention that just as during our 2nd Workshop, we will also be hosting a dedicated session which will give the opportunity to present their newest results to the laureates of the Struchkov Prize. It is always interesting to follow the scientific careers of the scientists many of whom were first introduced to broad crystallographic community as winners and participants of the Struchkov Prize competition.


I'd like to stress that this conference comes in the year which happens to carry two important dates, the 95th anniversary of Prof. Yu.T. Struchkov's birthday, as well as the 70th birthday of Prof. M.Yu. Antipin, who took over the helm of the leader of the laboratory from Prof. Struchkov in 1995 and was heading it up to his untimely death in 2013. It was prof. Antipin, who, in 1997, took initiative along with other former colleagues of Prof Struchkov, organized the first Struchkov Prize Competition thus setting up the annual tradition and initializing the community, which formed around it and which we are welcoming today as participants of our Workshop.

Since our 2nd Struchkov Workshop in November 2018, Struchkov Prize and competition has undergone significant changes. In 2020 it joined the growing circle of prestigious scientific prizes which are administered and awarded by the International Union of Crystallography. Beginning in Melbourne in 2023, the Struchkov Prize will be bestowed by the IUCr every triennium at the IUCr Congress and General Assembly. The Prize will be awarded to up to three young scientists for outstanding achievements in small-molecule X-ray diffraction methods application in the fields of chemistry, crystal chemistry, or material science.

The decision to approach the leadership of the IUCr with the request to accept Struchkov Prize under their auspices did not come lightly to those of us who were involved in Prize administration before. While the Prize was established in 1997 to recognize young Russian small-molecule crystallographers and researchers working in related fields, we felt that as a global award Struchkov Prize would more adequately reflect Professor Struchkov's life-long belief that crystallography, just as any other science, should represent joint international effort. Throughout his life he persistently fought for universal integration and openness of science in the Soviet Union. We strongly believe that Professor Struchkov himself would have approved the decision to seek acceptance of the Struchkov Prize as one of the IUCr awards.

The details on the submission of nominations for the first Struchkov Prize can be found on the IUCr website. We are hoping that participants of the Workshop will become major champions of the now global Struchkov Prize and will nominate their friends and colleagues for the Prize. I'm sure we will eventually see many of them in our future Struchkov Workshops as participants of its traditionally most lively and diverse section, which presents the achievements of Struchkov Prize laureates. And let us also hope we will then see and warmly hug all our old and new friends, live and in person, on the premises of our great RUDN University in our beautiful city of Moscow.

Conference Chair,



Prof. Dr. Victor N. Khrustalev



**International Workshop
on Chemical Crystallography and Structural Biology
*“The Third Struchkov Meeting”***

dedicated to the 95th Birth Anniversary of Yuri T. Struchkov

Moscow • November 15-19, 2021

**Scientific Program
(*online*)**

<https://struchkovprizeassociation.org/2021-struchkov-society-meeting/>

Moscow Time • JCT+6 • CST+5 • GMT+3 • IST+2.30 • CET+1 • EST-8
JCT – Japan; CST – China; GMT – Portugal; IST – India; CET – France; EST – New York

Monday • November 15, 2021

/ Moscow – 10:00 / London – 07:00 / New York – 02:00 / Tokyo – 16:00 /

10 00–11 00	Workshop Opening • Moscow Time
10 00–10 20	<i>Victor N. Khrustalev</i> (Conference Chair)
10 20–10 30	<i>Igor L. Eremenko</i> (Chair of Program Committee)
10 30–10 40	<i>Leonid G. Voskressensky</i> (Dean of Faculty of Science, RUDN University)
10 40–10 50	<i>Tatiana V. Timofeeva</i> (Member of Program Committee)
10 50–11 00	<i>Leonid A. Aslanov</i> (Member of <i>Struchkov Prize</i> Association)
Session A	Chair: Victor N. Khrustalev; Working language – <i>Russian/English • Moscow Time</i>
11 00–11 45	Plenary – Commemorative <i>Yuri Timofeevich Struchkov: Commemorating 95th Birthday</i> <i>Yuri L. Slovokhotov</i> Institute of Control Science RAS (Moscow, Russia)
11 45–12 30	Plenary <i>Fluoride-phosphates with the KTP-type structure as perspective cathode materials for metal-ion batteries</i> <i>Evgeny V. Antipov</i> Lomonosov Moscow State University (Moscow, Russia)
12 30–13 15	Plenary <i>Pushing the Limits: Orbital-Free Quantum Crystallography</i> <i>Vladimir G. Tsirelson</i> Mendeleev University of Chemical Technology (Moscow, Russia)
13 15–14 00	Plenary <i>Proton transfer in 3d metal carboxylates</i> <i>Sergei E. Nefedov</i> Kurnakov Institute of General and Inorganic Chemistry RAS (Moscow, Russia)
14 00–15 00	LUNCH
Session B	Chair: Igor A. Litvinov; Working language – <i>Russian/English • Moscow Time</i>
Struchkov Prize-2020 Session	
15 00–15 30	Keynote <i>X-ray diffraction study of structural organization of the unsubstituted and substituted phthalocyanine thin films</i> <i>Alexander S. Sukhikh</i> Nikolaev Institute of Inorganic Chemistry SB RAS (Novosibirsk, Russia)
15 30–16 00	Keynote <i>(Thia)calix[4]arenes and their functional derivatives as versatile molecular building blocks for rational design of crystalline materials</i> <i>Alexander S. Ovsyannikov</i> Arbuzov Institute of Organic and Physical Chemistry RAS (Kazan, Russia)
16 00–16 30	Keynote <i>Structural diversity of rhenium(I) complexes: approaches to fine-tuning photophysical behavior</i> <i>Kristina S. Kisel</i> Saint Petersburg State University (Saint Petersburg, Russia)
16 30–17 00	Keynote <i>Synthesis of Novel Cationic 1,2,4-Selenadiazoles via Addition of 2-Pyridylselenyl Halides to Unactivated Nitriles</i> <i>Alexander G. Tskhovrebov</i> RUDN University (Moscow, Russia)
17 00–19 00	Round Table “Advances in the Modern X-Ray Structural Analysis” dedicated to the 70th Birth Anniversary of Mikhail Yu. Antipin <i>Anna V. Vologzhanina</i> Nesmeyanov Institute of Organoelement Compounds RAS (Moscow, Russia)

Tuesday • November 16, 2021

/ Moscow – 10:00 / London – 07:00 / New York – 02:00 / Tokyo – 16:00 /

Session C	
Chair: Yan V. Zubavichus; Working language – English • Moscow Time	
10 00–10 45	Plenary <i>Crystal Engineering in Chemistry and Society</i> Gautam R. Desiraju Indian Institute of Science (India)
10 45–11 30	Plenary <i>Silver Nanoclusters</i> Di Sun Shandong University (China)
11 30–12 15	Plenary <i>Iron oxide nanoparticles and nanocomposites: their biosafety and applications</i> Yannick Guari University of Montpellier (France)
12 15–13 00	Plenary <i>Metal Coordination Catalysis of Selected Small Molecules towards Sustainability</i> Armando J. L. Pombeiro University of Lisbon (Portugal)
13 00–13 45	Plenary <i>Receptor Tyrosine Kinase KIT: A New Look for an Old Receptor</i> Luba Tchertanov Centre Borelli, CNRS – ENS Paris-Saclay (France)
13 45–14 15	Keynote <i>Titanium phenoxides and phosphonates as molecular models and molecular precursors of hybrid oxide materials</i> Vadim G. Kessler Swedish University of Agricultural Sciences (Sweden)
14 15–15 15	LUNCH
Session D	
Chair: Alexander G. Tskhovrebov; Working language – English • Moscow Time	
15 15–16 00	Plenary <i>Synthetic Chemistry with Laughing Gas</i> Kay Severin Ecole Polytechnique Fédérale de Lausanne – EPFL (Switzerland)
16 00–16 45	Plenary <i>Supramolecular crystallography</i> Kari Rissanen University of Jyväskylä (Finland)
16 45–17 30	Plenary <i>Accessing micro- and macroscopic pictures of gas adsorption by in situ powder diffraction</i> Yaroslav Filinchuk Université catholique de Louvain (Belgium)
17 30–18 00	Keynote <i>Some examples of Co(II), Zn(II), Cd(II) and Cu(I) coordination polymers with inclusion and luminescent properties</i> Marina S. Fonari Institute of Applied Physics (Moldova)
18 00–18 30	Keynote <i>Back to the Roots – Dress Chemistry in Green</i> Adam Slabon Stockholm University (Sweden)
18 30–19 00	Keynote <i>Structural Chemistry of Azulenes</i> Nick Gerasimchuk Missouri State University (USA)

Wednesday • November 17, 2021

/ Moscow – 10:00 / London – 07:00 / New York – 02:00 / Tokyo – 16:00 /

Session E	Chair: Andrey S. Kritchenkov; Working language – English • Moscow Time
10 00–10 45	Plenary <i>Prussian blue type nano-objects: new opportunities for old materials</i> Jouliia Larionova University of Montpellier (France)
10 45–11 30	Plenary <i>Well-defined silsesquioxanes with novel structures</i> Masafumi Unno Gunma University (Japan)
11 30–12 15	Plenary <i>4th Generation Synchrotron Radiation Facility SKIF: New Prospects for Small-Molecule and Macromolecular Crystallography in Russia</i> Yan V. Zubavichus Boreskov Institute of Catalysis SB RAS (Novosibirsk, Russia)
12 15–13 00	Plenary <i>Functional Metal-Organic Architectures: from Self-Assembly in Water to Applications</i> Alexander M. Kirillov University of Lisbon (Portugal)
13 00–13 45	Plenary <i>Many Faces of a Cuboctahedron: A Journey of an Intermetallic Fragment from Simple structures to Complex Arrangements</i> Alexey N. Kuznetsov Lomonosov Moscow State University (Moscow, Russia)
13 45–14 30	Plenary <i>Structural chemistry of polynuclear complexes of transition metals</i> Dmytro S. Nesterov University of Lisbon (Portugal)
14 30–15 30	LUNCH
Session F	Chair: Igor S. Antipin; Working language – Russian/English • Moscow Time
15 30–16 15	Plenary <i>Structure and reactivity of transition metal tetrahydroborates and their dihydrogen bonded complexes</i> Natalia V. Belkova Nesmeyanov Institute of Organoelement Compounds RAS (Moscow, Russia)
16 15–17 00	Plenary <i>Supramolecular Interactions in the Condensed State on the Example of Bispidines</i> Sergey Z. Vatsadze Zelinsky Institute of Organic Chemistry RAS (Moscow, Russia)
17 00–17 45	Plenary <i>Statistical and local structure of large-sized multifunctional single crystals</i> Galina M. Kuzmicheva MIREA – Russian Technological University (Moscow, Russia)
17 45–18 30	Plenary <i>Charge density distribution of APIs in crystals and ligand-receptor complexes</i> Alexander A. Korlyukov Nesmeyanov Institute of Organoelement Compounds RAS (Moscow, Russia)
18 30–19 00	Keynote <i>Molecular and supramolecular design of cage-like metallacomplexes based on sil- and germesquioxane ligands. Synthesis, structure, properties</i> Alexey N. Bilyachenko Nesmeyanov Institute of Organoelement Compounds RAS (Moscow, Russia)

Thursday • November 18, 2021

/ Moscow – 10:00 / London – 07:00 / New York – 02:00 / Tokyo – 16:00 /

Session G	
Chair: Vladimir A. Larionov; Working language – Russian/English • Moscow Time	
Young scientist Session	
10 00–10 20	Oral <i>The tetranuclear lanthanide-based silsesquioxanes: synthesis, structure and properties</i> Alena N. Kulakova RUDN University (Moscow, Russia)
10 20–10 40	Oral <i>High-resolution powder diffraction with the scanning 2D detector at the «XSA» beamline of Kurchatov synchrotron radiation source</i> Roman D. Svetogorov National Research Centre “Kurchatov Institute” (Moscow, Russia)
10 40–11 00	Oral <i>Crystal structure of low-melting organoelement compounds</i> Alexander D. Volodin Nesmeyanov Institute of Organoelement Compounds RAS (Moscow, Russia)
11 00–11 15	Oral <i>Salts of nucleobases and alkali metals: preparation and structural study at broad range of T, P</i> Anna A. Gaydamaka Novosibirsk State University (Novosibirsk, Russia)
11 15–11 30	Oral <i>The influence of experimental setup on the thermal expansion of glycinium phosphite</i> Nikita E. Bogdanov Boreskov Institute of Catalysis SB RAS (Novosibirsk, Russia)
11 30–11 45	Oral <i>The crystal structure elucidation of a tetrapeptide analogue of somatostatin DOTA-Phe-D-Trp-Lys-Thr-OMe</i> Sabina E. Diusenova Boreskov Institute of Catalysis SB RAS (Novosibirsk, Russia)
11 45–12 00	Oral <i>Structure investigation of bismuth-containing binary apatite system</i> Evgeny N. Bulanov Lobachevsky University (Nizhny Novgorod, Russia)
12 00–12 15	Oral <i>Distribution of electron density in luminescent and magnetic coordination compounds. Molecular and crystal invariom approaches</i> Roman V. Rumyantsev Razuvaev Institute of Organometallic Chemistry RAS (Nizhny Novgorod, Russia)
12 15–12 30	Oral <i>Computer Modeling in Chemistry: Reactivity and Non-Covalent Interactions</i> Alexander S. Novikov Saint Petersburg State University (Saint Petersburg, Russia)
12 30–12 45	Oral <i>Novel heterocyclic chitosan derivatives and their derived nanoparticles</i> Niyaz Z. Yagafarov RUDN University (Moscow, Russia)
12 45–13 00	Oral <i>Structural studies of chitosan and its composites with iron (II) hydroxide and sulfate</i> Yana V. Sultanova RUDN University (Moscow, Russia)

13 00–13 15	Oral <i>Synthesis and structural investigation of new aryl- and heteroaryl gold(I) isocyanide complexes</i> Maria V. Grudova RUDN University (Moscow, Russia)
13 15–13 30	Oral <i>Features of supramolecular organization in the crystals of benzimidazolone derivatives</i> Aida I. Samigullina Nesmeyanov Institute of Organoelement Compounds RAS (Moscow, Russia)
13 30–14 30	LUNCH
Session H	Chair: Yuri L. Slovokhotov; Working language – English • Moscow Time
14 30–15 00	Keynote <i>Chiral metal-templated Co(III) complexes as a powerful class of catalysts</i> Vladimir A. Larionov Nesmeyanov Institute of Organoelement Compounds RAS (Moscow, Russia)
15 00–15 30	Keynote <i>Structure-driven possibilities and challenges: from heterogeneous catalysis to extracellular matrix glycation</i> Alexey V. Klitskov RUDN University (Moscow, Russia)
15 30–15 45	Oral <i>Palladium-based reagents for protein bioconjugation</i> Ivan V. Buslov RUDN University (Moscow, Russia)
15 45–16 00	Oral <i>Ultrasound-mediated synthesis of Co/Al layered double hydroxide</i> Nbutsu D. Sikaona Shared with RUDN University (Zambia)
16 00–19 00	Master Class on OLEX2 “A complete structure solution and analysis program” Ilia A. Guzei University of Wisconsin-Madison (USA)

Friday • November 19, 2021

/ Moscow – 10:00 / London – 07:00 / New York – 02:00 / Tokyo – 16:00 /

Session I	
10 00–10 30	Keynote <i>High-pressure X-ray diffraction experiments and data reduction: the difference from ambient pressure studies and factors influencing the data quality</i> Boris A. Zakharov Boreskov Institute of Catalysis SB RAS (Novosibirsk, Russia)
10 30–11 00	Keynote <i>Ultrasound-mediated polymer-analogous reactions in the chitin and chitosan chemistry</i> Andrei S. Kritchenkov Institute of Technical Acoustics NASB (Belarus)
11 00–11 30	Keynote <i>Platinum and palladium-based heterometallic carboxylic complexes. New approaches to the synthesis and X-ray synchrotron radiation crystallography studies</i> Ilia A. Yakushev Kurnakov Institute of General and Inorganic Chemistry RAS (Moscow, Russia)
11 30–11 50	Oral <i>Synthesis and crystal structure of the zinc complex of sildenafil citrate (Viagra®)</i> Vakhob Kh. Sabirov Tashkent State Technical University (Uzbekistan)
11 50–12 10	Oral <i>NMR spectroscopy and X-Ray crystallography at the investigations of conformationally non-rigid molecules</i> Ibrahim G. Mamedov Baku State University (Azerbaijan)
12 10–12 30	Oral <i>Fuzzy sets in chemical crystallography</i> Yuri L. Slovokhotov Institute of Control Science RAS (Moscow, Russia)
12 30–13 30	Workshop Closing • Moscow Time
	Concluding remarks of Chairmen and Members of the Program and Organizing Committees

Plenary Lectures

Yuri Timofeevich Struchkov: Commemorating 95th Birthday

Slovokhotov Y.L., Yanovsky A.I.

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Photo: Victor N. Khrustalev, People's Friendship University of Russia, Moscow

Yuri Timofeevich Struchkov was one of the most prominent Russian crystallographers in XXth century. His single crystal X-ray studies of almost all types of small-molecule compounds obtained in the USSR – Russian Federation substantially accelerated the development of organic, organoelement, and organometallic chemistry both in national scale and worldwide. We present a brief personal and scientific biography of Yuri T. Struchkov together with some recollections on life and science in his laboratory during the years of 1970th – 1990th.

Reference

Slovokhotov Y., Yanovsky A., *IUCr Newsletter* (2021), 29 (2),
<https://www.iucr.org/news/newsletter/volume-29/number-2/yuri-t.-struchkov-commemorating-his-95th-birthday>

Fluoride-phosphates with the KTP-type structure as perspective cathode materials for metal-ion batteries

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The rapid progress in mass-market applications of metal-ion batteries intensifies the research of electrode materials for Na-ion and K-ion batteries as a possible alternative to the already matured Li-ion technology. Similar to the Li-ion intercalation systems, the Na and K-based mixed oxides and polyanion materials are extensively scrutinized as potential cathodes with the aim to enhance the specific energy, durability and rate capability. Whereas the layered oxides are characterized by greater volumetric energy density, the polyanion materials usually exhibit better cycling and thermal stability and higher C-rate capability due to covalently bonded structural frameworks in these compounds. The polyanion compounds also demonstrate an extra dimension in their crystal chemistry which significantly expands the search space for the materials with better electrochemical performance. Further advantages are expected from combining different anions (such as $(\text{XO}_4)^{p-}$ and F^-) in the anion sublattice.

The fluoride-phosphates AMPO_4F ($\text{A}=\text{Li}, \text{Na}, \text{K}; \text{M}=\text{V}$ and Ti) with the KTP-type structure are considered now as perspective cathode materials for the metal-ion batteries. The “ VPO_4F ” framework featured outstanding rate capability and capacity retention. Another quality of this framework is supporting reversible Na^+ , K^+ and even Rb^+ ions de/insertion sustaining the host structure. The ion diffusion coefficients obtained by PITT were the lowest for Li^+ and the highest for K^+ , with the latter anticipating high-power applications of KVPO_4F in K-ion batteries. Moreover, the titanium redox activity traditionally considered as “reducing” can be upshifted to near-4V electrode potentials in the “ TiPO_4F ” framework thus providing a playground to design sustainable and cost-effective titanium-containing positive electrode materials with promising electrochemical characteristics.

An overview of the research on these fluoride-phosphates will be presented with a special emphasis on the interrelation between chemical composition, synthesis conditions, crystal structure peculiarities and their electrochemical properties.

This work was supported by the Russian Science Foundation (grant No. 17-73-30006).

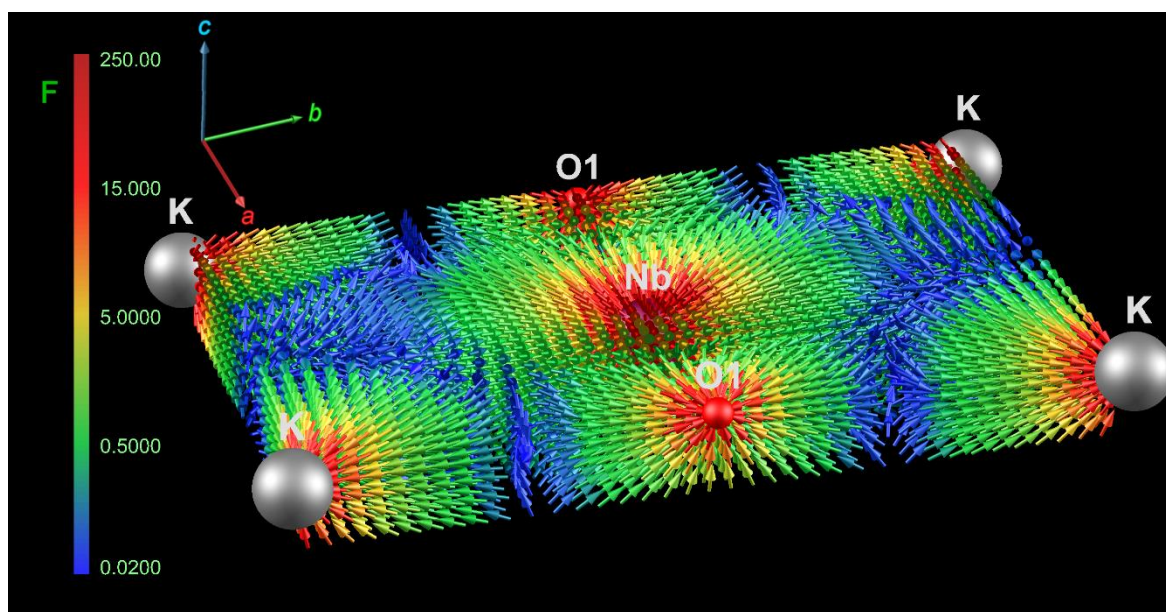
Pushing the Limits: Orbital-Free Quantum Crystallography

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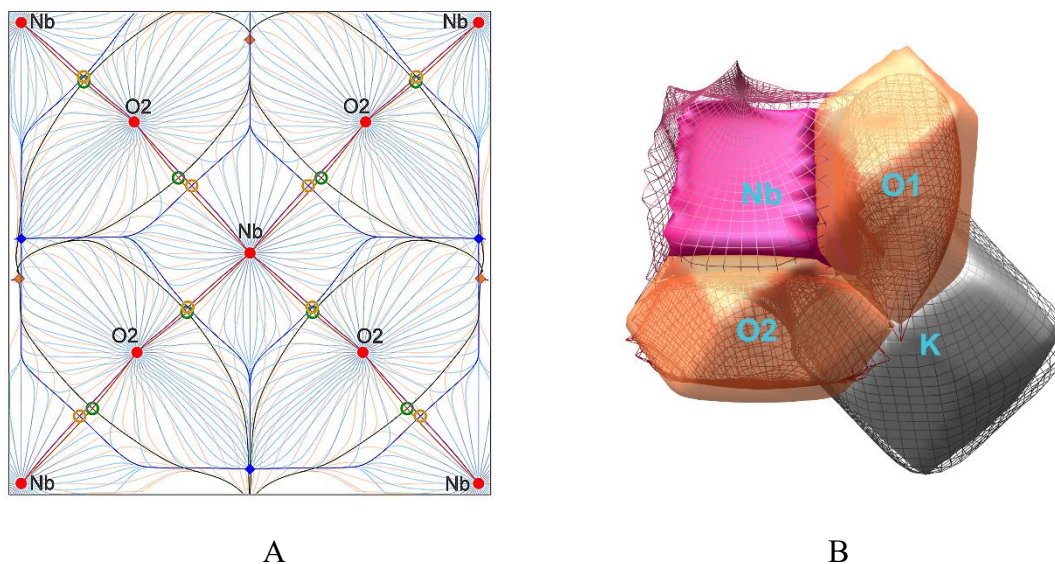
Email: vtsirelson@yandex.ru

We present the approach which combines the orbital-free density functional theory and X-ray diffraction crystallography to study the spatial distribution of electrostatic and quantum electronic potentials and associated forces in a stable crystal. The electron distribution is determined by electrostatic electron repulsion corrected for exchange and correlation, their attraction to nuclei and by electron kinetic energy. The latter defines the dispersion of the electron momenta resulting from the de Broglie relationship and uncertainty principle, as well as from the limitations of Pauli principle and from specific crystal structure. We express kinetic and static potentials as well as related inner-crystal forces via the experimental electron density and its derivatives using orbital-free DFT. The net force acting on any electron in a crystal at equilibrium is zero everywhere, presenting balance of the kinetic and potential forces, $\mathbf{F}_{kin}(\mathbf{r})$ and $\mathbf{F}_{pot}(\mathbf{r})$, respectively. The points at which these forces separately are zero are identified as the Lagrange points, which are analogues of the Bader critical points in electron density. The positions of the Lagrange points in a crystal are described according to Wyckoff notations, while their types depend on the considered scalar potential field. We found that $\mathbf{F}_{pot}(\mathbf{r})$ force pushes electrons to the atomic nuclei favoring electron density *homotropy*, while the kinetic force $\mathbf{F}_{kin}(\mathbf{r})$ is *heterotropic* and draws electrons from nuclei. This expresses the opposing trends, which determine the structure and properties of substances at all levels of their spatial organization and favors formation of the electron concentration bridges between some of the nearest atoms.



Static vector field $\mathbf{F}_{pot}(\mathbf{r})$ in layer with height of 0.6 Å, in ab plane of orthorhombic cell of KNbO_3 . The arrows indicate the direction of the forces at each point, while the colour reflects their magnitude.

The force-field approach and quantum topological theory of atoms in molecules are compared and their distinctions are clarified. Important finding is that a crystal at equilibrium, only kinetic potential $v_{kin}(\mathbf{r})$ and corresponding force exhibit the electronic shells and atomic-like zero-flux basins enveloped the nuclear attractors. The general observation is that kinetic electronic forces, arising in the v_{kin} -basins of cations and directed to their boundaries, penetrate through the surface of the ρ -basins of anions and press the cations to anions. It is concluded that the formation of the actual structure of a crystal with the participation of both static and kinetic factors, both are of a quantum nature.



A) Superpositions of atomic basins, gradient fields, bond paths in the distributions $\rho(\mathbf{r})$ (blue gradient lines) and $v_{kin}(\mathbf{r})$ (orange gradient lines) and critical points observed in these fields. (a) (011) plane; (b) (101) plane. BCPs in $\rho(\mathbf{r})$ are marked by orange and dark green circles for $v_{kin}(\mathbf{r})$; ring CPs in $v_{kin}(\mathbf{r})$ are indicated by green triangles; cage CPs are labeled by blue and orange rhombs for $\rho(\mathbf{r})$ and $v_{kin}(\mathbf{r})$ correspondingly. The traces of ED basin boundaries are blue-coloured and those for $v_{kin}(\mathbf{r})$ are of burgundy colour.

B) Orthorhombic KNbO_3 : spatial arrangement of ρ -basins (solid coloured surfaces) and v_{kin} basins (mesh surfaces).

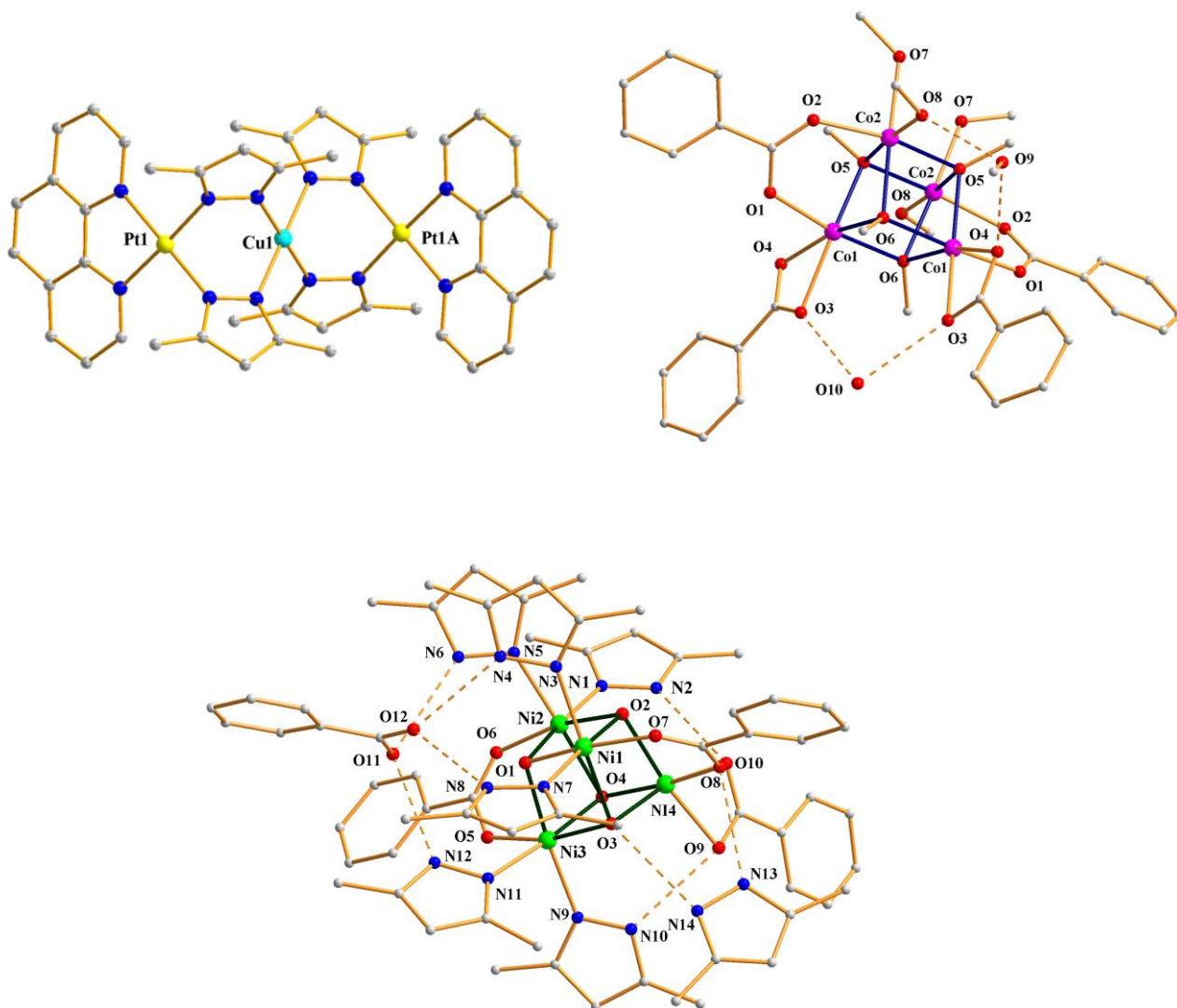
This work was supported by the Russian Foundation for Basic Research (grant № 19-03-00141)

Proton transfer in 3-d metal carboxylates

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Based on X-ray diffraction data, the report examines the features of the coordination and deprotonation of H-N (pyrazole and its analogs) H-O (alcohols) depending on the nature of the transition metal, the R substituent in the carboxylate anion, the nature of the organic molecule, leading to the formation of homo-, heterometallic binuclear complexes, clusters and polynuclear compounds.

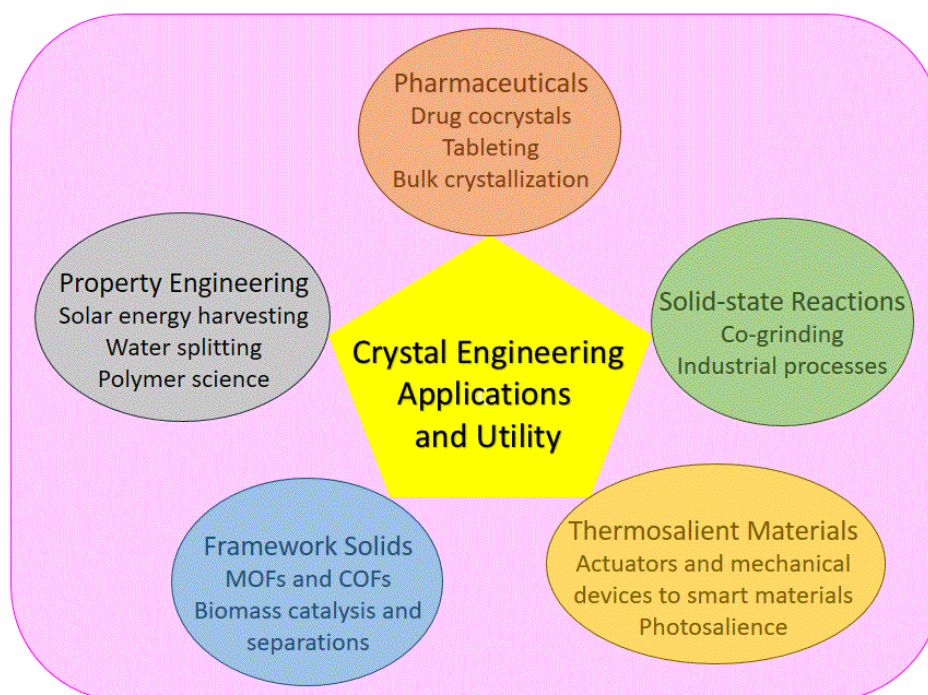


Crystal Engineering in Chemistry and Society

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A field that was defined 30 years ago as “the understanding of intermolecular interactions in the context of crystal packing and in the utilisation of such understanding in the design of new solids with desired physical and chemical properties”[1] and which identified as the central issue in structure design the lack of a direct correspondence between molecular and crystal structure in the sequence “One → Few → Many → Nucleus → Crystal” [2] has now evolved into “in an area of virtually unlimited scope where science funding and translation efforts could be directed in the current climate of a society that increasingly expects applications and utility products from science and technology”[3]. Certain current concerns will be addressed in this talk [4].



References

- [1] Desiraju, G. R. *Crystal Engineering. The Design of Organic Solids*, Elsevier 1989.
- [2] Desiraju, G. R. *J. Am. Chem. Soc.*, 2013, 135, 9952.
- [3] Nangia, A. K., Desiraju, G. R. *Angew. Chem. Int. Ed.* 2019, 58, 4100.
- [4] YouTube channel: Gautam Desiraju
https://www.youtube.com/channel/UCdA81RtmW1MYZoTQMe7Hk_g

Silver Nanoclusters

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Over recent years, research on the ligand-protected silver clusters have gained significant interest owing to their unique potential applications in catalysis, organic optoelectronics, and luminescent materials. However, the synthesis of structurally precise silver nanoclusters and their assembly mechanism are still challenging and become one of the prime interests of chemists. The controllable synthesis of high-nuclearity silver nanoclusters involves the ingenious use of capping ligands or/and templating agents. Thereinto, the main role of the templating agents is to promote the order arrangement of silver ions around them to form discrete molecules. Our lab has performed comprehensive studies on the ligand-protected silver clusters including silver(I) clusters and silver(I/0) clusters in the past eight years. Furthermore, some interesting photo- and electrochemical properties revealed by silver clusters including luminescent thermochromism and electrical conductivity are quite interesting.

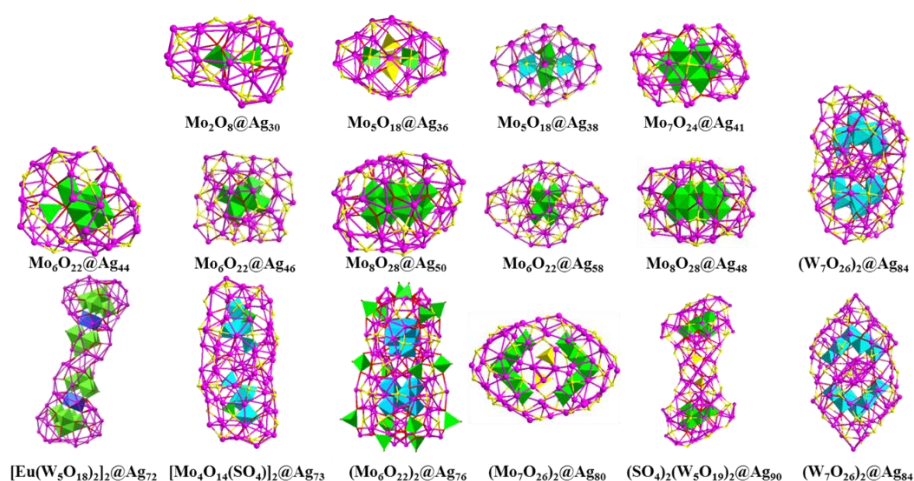


Fig.1 The family of POMs templated silver nanoclusters.

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Iron oxide nanoparticles and nanocomposites: their biosafety and applications

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The role of nanoscience is currently of primary importance in the development of innovative strategies in the fields of nanomedicine and personalized medicine. Several in vitro studies and preclinical trials have been undertaken on a great variety of nanostructures: among these, magnetic nanoparticles represent the core of several advanced biomedical applications. Magnetic nanoparticles of novel synthesis can improve the capabilities of already existing and widely used clinical diagnostic and therapeutic techniques, like, for example, molecular imaging, magnetic fluid hyperthermia, and magnetofection, acting as contrast agents, markers, and carriers, respectively. Moreover, the possibility of new approaches to synthesize a single nanostructure with more than one function through post-functionalisation or its combination with other materials gives the opportunity to overcome the limitations of standard medicine. During this presentation, we will discuss different aspects related to the use of iron oxides magnetic nanoparticles for biomedical applications through the functionalization of these nanoparticles for magnetic resonance imaging and magneto-induced hyperthermia; the development of mesoporous iron oxide-silica core-shell nanoparticles as part of a study on the biosafety of silica nanoparticles; and the development of biocompatible polymer composites and iron oxide nanoparticles as imageable postoperative implants [1-5].

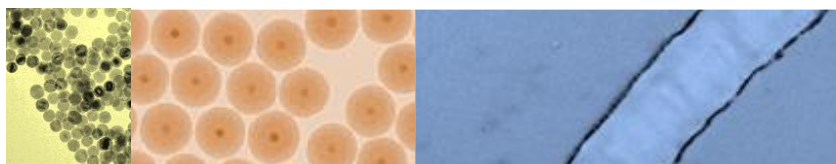


Figure: From left to right: iron oxide nanoparticles, iron oxide-mesoporous silica core-shell nanoparticles and PLA-iron

Keywords: Nanoparticles, Nanocomposites, Iron oxide, Silica, PLA, MRI, Biosafety, Implants

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Metal Coordination Catalysis of Selected Small Molecules towards Sustainability

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Catalysis *per se* provides a major general contribution of Chemistry towards sustainability, namely within some of the UN Sustainable Development Goals, fostering, *e.g.*, sustainable industrialization, consumption/production and energy. However, in order to fulfil this broad aim, the application of Catalysis should satisfy appropriate criteria which often are not easy to achieve.

Various approaches followed in the author's research Group are discussed, concerning the development of simple one-pot processes under environmentally tolerable conditions, such as the use of (i) microwave irradiation or mechanochemical energy input, (ii) water or a biomass derived solvent, (iii) ionic liquids, (iv) solvent-free processes, or (v) catalyst heterogenization on a carbon matrix. Catalysts include single- and multinuclear complexes and MOFs with earth abundant and non-toxic first row transition metals. The following areas and prospects are illustrated:

Functionalization of inert alkanes to added value organic products; oxidation of volatile organic compounds; CO₂ utilization; aldehydes cyanosilylation; and azide-alkyne cycloaddition.

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Receptor Tyrosine Kinase KIT: A New Look for an Old Receptor

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Receptor tyrosine kinases (RTKs) control various signalling pathways in cells. Their remarkable conformational plasticity enables the specific recognition of many molecules such as ligands, substrates or proteins. In solution, RTKs are in equilibrium between different conformations ranging from an inactive auto-inhibited state to a fully active state. Ligand-induced activation of RTKs leads to the recruitment and activation of multiple downstream signalling proteins carrying the signal to the nucleus, where it alters the transcription patterns of genes that govern various aspects of cell physiology [1]. The explicit elucidation of signalling events is an important and unresolved problem in cell biology. The initiation of these cascade-like processes involves different domains of RTK, each of them performs its own specific actions, which are finely concerted by a tightly regulated allosteric mechanism that controls all functional processes [2]. Aberrant regulation of RTKs signalling networks is associated with the progression of many diseases.

Focusing on the RTK KIT, an important target in oncology (leukaemia, mastocytosis, melanoma, gastrointestinal stromal tumour, and stomach cancers) [3], we first explain its physiological and mutation-induced activation [4]. Next, we will discuss KIT as a key starter/regulator of intracellular signalling which is mediated by regions possessing multiple phosphorylation sites. Since these regions are very flexible or disordered, they are not well understood yet. We present the first structural model of the full-length cytoplasmic domain of KIT, which contains all regions involved in post-transduction processes, phosphorylation and binding of intracellular protein [5] (Figure 1).

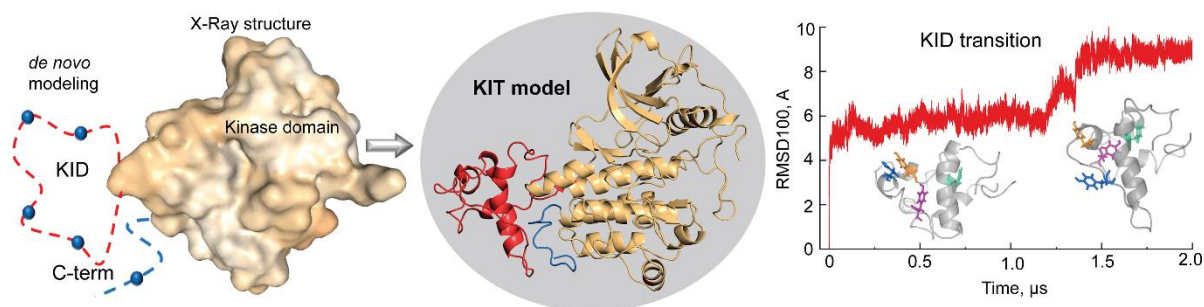


Figure 1. Modelling of the cytoplasmic domain of the RTK KIT. *Ab initio* models of KID and C-term were integrated into the X-ray structure (left); the KIT model (middle) with kinase domain (yellow), KID (red) and C-terminal (blue) was refined by molecular dynamics simulation. The KID conformational transition (right) is illustrated by RMSDs and two conformations selected before and after the transition (at $t = 0.8$ and $2 \mu\text{s}$).

Rigorous analysis of the structure and dynamics of KIT, carried out using advanced mathematical methods, has led to a new vision of KIT as a multidomain protein made up of structurally ordered and disordered regions which together constitute a mutually and tightly driven engine [6,7]. This atomistic model of an allosterically regulated KIT is the first step for the reconstruction of its INTERACTOME, which consists of a set of KIT complexes with its signalling

proteins, and DYNASOME, which constitutes an ensemble of intermediate conformations of KIT before, over and after the post-transduction processes. The practical delivery of such modelling consists in defining targets for the development of modulators/inhibitors capable of regulating or blocking several steps of KIT activation or its post-transduction processes in cells.

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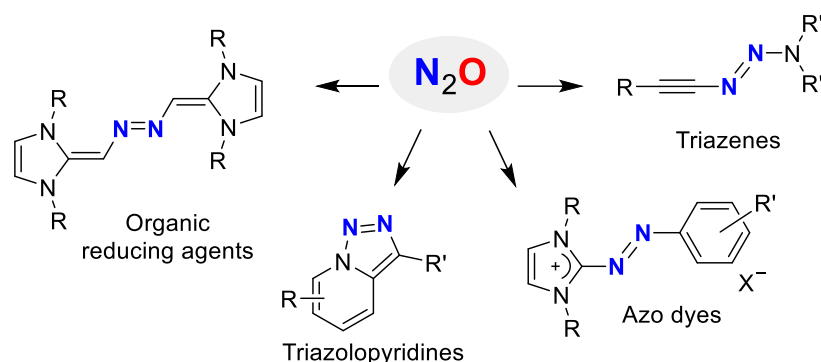
Synthetic Chemistry with Laughing Gas

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Nitrous oxide (N_2O , ‘laughing gas’) is rarely used as a reagent in synthetic chemistry. On the contrary, industrially produced N_2O is destroyed by catalytic decomposition into the elements, because release of N_2O is problematic from an environmental point of view. In the lecture, I will show that N_2O can be used as a nitrogen-atom donor for the synthesis of interesting azo compounds such as organic reducing agents, triazenes, azo dyes, and triazolopyridines [1–6].



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Supramolecular crystallography

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An exciting research challenge in supramolecular chemistry is to design, synthesize, and characterize nano-sized architectures with applications in biology, chemistry, and materials science [1]. Predicting and designing non-covalently bound supramolecular complexes and assemblies is difficult because of the weakness of the interactions involved, thus the resulting superstructure is often a compromise between the geometrical constraints of the building blocks and the competing weak intermolecular interactions [2].

Our research interest has been focused on the studies of weak non-covalent intermolecular, *viz.* supramolecular interactions as the driving force in self-assembly and molecular recognition, especially in the solid state by single crystal X-ray diffraction. The lecture will highlight some of our recent studies on halogen bonded systems [3], anion... π interactions [4] and metal ion coordination [5] in molecular self-assembly and molecular recognition in various systems such as rotaxanes, M_4L_6 tetrahedra, M_8L_6 cube, spheres, knots, etc.

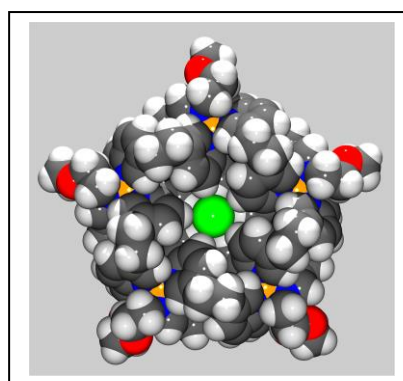


Fig. 1. The X-ray structure of the

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Accessing micro- and macroscopic pictures of gas adsorption by in situ powder diffraction

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Two methods are traditionally used to characterize gas adsorption properties in porous solids: volumetric and gravimetric. They have a number of limitations, but most importantly, they yield a macroscopic picture of interactions (*properties*), without access to a microscopic picture (mechanisms on an atomic level). Diffraction is commonly used as a complementary technique to explain these properties, giving insight into structure and thus revealing the underlying guest-host and guest-guest interactions. Various anomalies (deviations from a typical behaviour) detected by the macroscopic methods require an in situ diffraction experiment, aiming to identify the responsible phenomena like a guest rearrangement / repacking, framework deformation etc. Thus, a separate diffraction experiment is usually providing a microscopic picture for the properties found by other physico-chemical methods.

In this presentation we will show examples of using in situ powder diffraction to simultaneously access the structure and adsorption properties of a small pore crystalline solid. (Quasi)-equilibrium isotherms and isobars can be built directly from sequential Rietveld refinements, both on adsorption and desorption, thus addressing the hysteresis and kinetics of gas adsorption/desorption. Detailed picture of guest reorganization with an increasing uptake can be obtained. Note that the reorganization of the individual guest sites is not accessible to volumetric and gravimetric methods, as they give only total amounts of gas uptake.

Interestingly, the adsorption isobars and isotherms obtained directly from diffraction data can be fitted by known equations, such as a logistic function (isobars) or a Langmuir equation (isotherms). Thermodynamic properties, such as enthalpy and entropy of gas adsorption can be extracted from these curves. The limitations of this technique are very different from traditional methods, thus making it highly complementary.

Lastly, the adsorption kinetics can be followed by in situ powder diffraction at given P,T conditions versus time. The guest uptake extracted by a sequential Rietveld refinement can be fitted and analysed in terms of Arrhenius theory giving access to the activation energies for gas diffusion. Thanks to the microscopic picture these barriers can be tentatively attributed to various diffusion paths inside the solid.

This talk will be illustrated by examples of noble gas adsorption in a porous hydride, γ -Mg(BH₄)₂ [1], featuring 1D channels suitable to distinguish and likely separate some of these gases. Besides published results [2,3], a lot of unpublished data will be shown.

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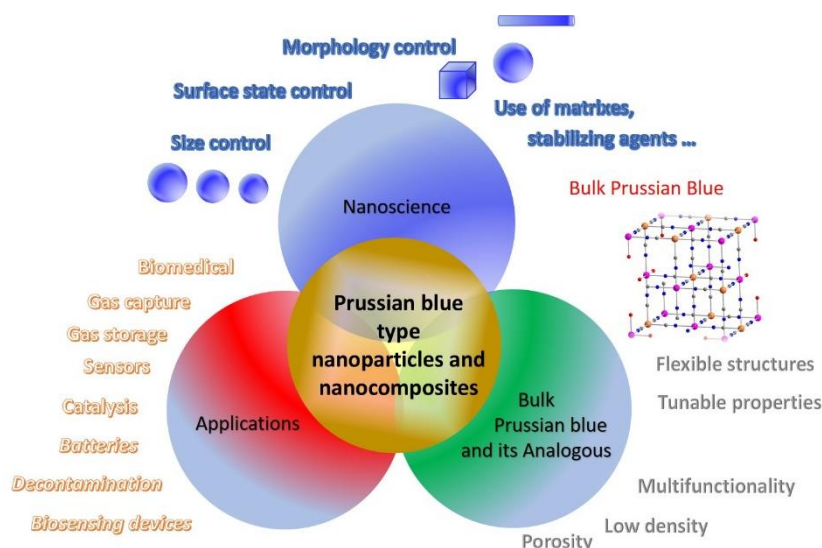
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Prussian blue type nano-objects: new opportunities for old materials

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Prussian Blue type nanoparticles are exciting nano-objects that combine the advantages of molecule-based materials and nanochemistry (see Figure below). They are made by transition metal ions or lanthanides assembled through cyano-bridged ligand into nano-sized architectures of the general formula $A_xM_y^{II}[M^{III}(CN)_6]_z$ (where A is a monovalent cation, M^{II} and M^{III} are transition metal ions or lanthanides). These nano-objects attracted a great deal of interest during the last ten years due to their specific molecule-based nature that is different compared to other inorganic nanoparticles. This lecture will provide a brief critical look on the recent advancement in this field of research focalising on the design of PB type nano-objects and their nanocomposites promising as nanoprobe for imaging, as therapeutic agents for photothermal therapy, as well as agents for Cs^+ decontamination.



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Well-defined silsesquioxanes with novel structures

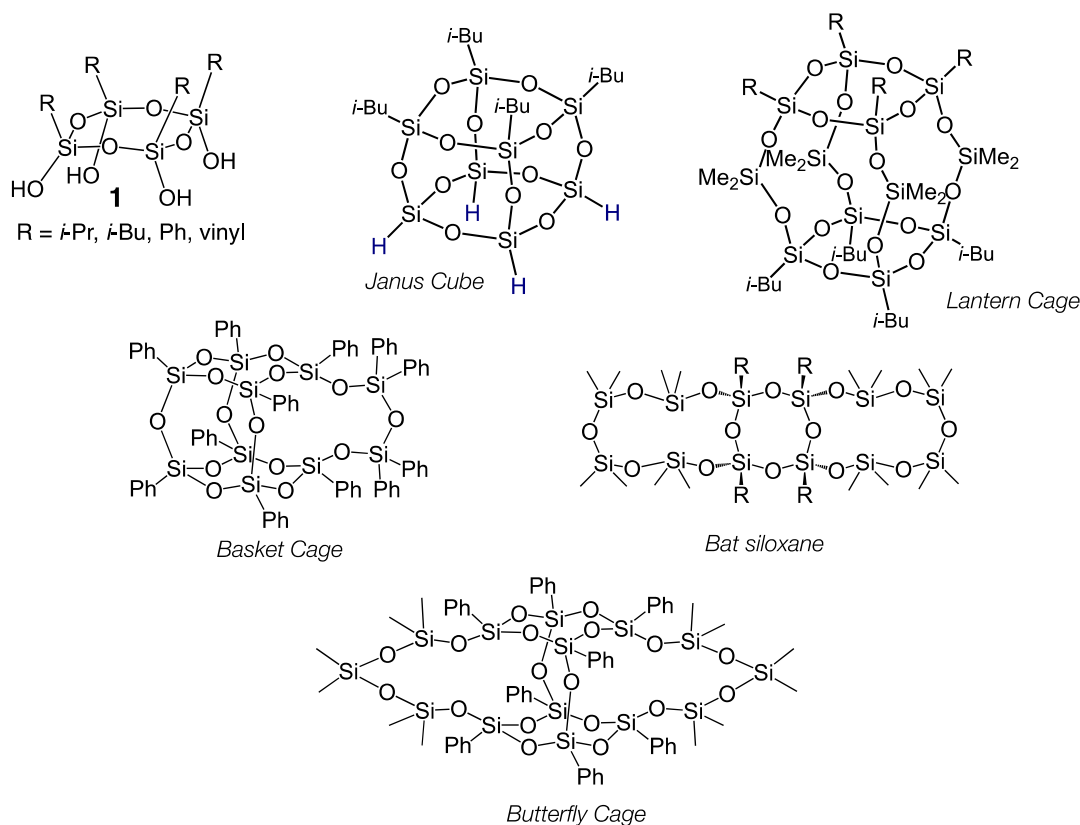
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The synthesis of well-defined silsesquioxanes is now strongly desired, especially from the industry because of recent high demanding to materials. Usually, these unique compounds can not be obtained by simple conventional methods, and new approach like starting from well-defined precursors, development of new synthetic methods, or effective and selective preparation is necessary. Recently, we control the structure of starting materials for the selective construction of unique structures also by applying new synthetic methods.

Cyclic silanol (**1**) possesses multiple hydroxyl groups in the molecule, and potential precursors to well-defined silsesquioxanes. We prepared many novel cyclic silanols [1], and prepared cage, partial-cage, and ladder silsesquioxanes [2]. More recently we reported Janus cube (1st [3] and 2nd generation [4]), Octopus Cage [5], Lantern Cage [6], Butterfly Cage [7], Basket Cage [8], and Bat siloxane [9]. Notably these silsesquioxanes show the expected high stability (thermal and photo- and radiochemical) as well as some unusual properties.

Detailed synthesis and properties of these silsesquioxanes shown below based on our fundamental research in the last two decades, and recent results are summarized in the presentation.



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Organosilicon Functional Materials” project (PL: K. Sato) from the New Energy and Industrial Technology Development Organization (NEDO).

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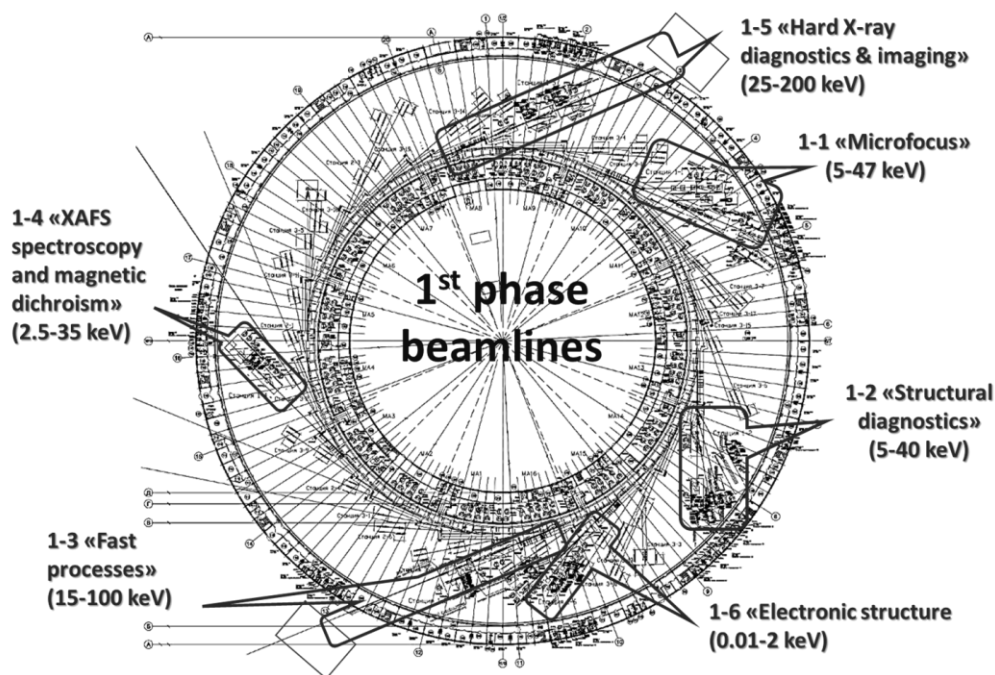
4th Generation Synchrotron Radiation Facility SKIF: New Prospects for Small-Molecule and Macromolecular Crystallography in Russia

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Synchrotron Radiation Facility SKIF is a new large-scale research infrastructure project currently underway in Novosibirsk region in Russia. The 3 GeV electron storage ring designed by specialists from the Budker Institute of Nuclear Physics SB RAS will provide the record low emittance of 75 pm·rad by the date of scheduled commissioning in December, 2024.

At the first phase of the project implementation, the research infrastructure of the synchrotron radiation facility will include six beamlines, dedicated to diverse techniques and X-ray spectral ranges (see Figure).



Key directions of the scientific program to be deployed at the SRF SKIF will encompass biomedicine, green technologies in chemistry and energetics, advanced engineering materials and mechanical engineering technologies. The present contribution surveys essential details of the SRF SKIF project, including functionality of the first-phase beamlines. The emphasis in discussion will be placed on crystallography-oriented techniques, research capabilities, and instrumentation. In particular, these will concern a side-branch 1-1-3 of the 1-1 Microfocus beamline devoted to Macromolecular crystallography and 1-2 Structural diagnostics beamline comprehensively devoted to X-ray diffraction.

Preliminary plans for the second-phase beamlines will be also outlined.

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Functional Metal-Organic Architectures: from Self-Assembly in Water to Applications

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This lecture will highlight our recent research on the self-assembly synthesis, crystallization methods, structural features and applications of a wide diversity of functional metal-organic architectures, including metal-organic frameworks (MOFs), coordination polymers (CPs), and multinuclear metal complexes.

The following topics will be discussed:

(1) Aqueous medium self-assembly generation and structural diversity of Cu(II) CPs driven by aminoalcoholate and carboxylate ligands. Application of these compounds as efficient catalysts in mild oxidative functionalization of alkanes and other substrates [1,2].

(2) Crystal engineering of MOFs & CPs assembled from multifunctional polycarboxylic acids with biphenyl or phenyl-pyridine cores and various metal nodes (Fe, Co, Cu, Mn, Ni, Zn, Cd, Ln). Examples of their applications as heterogeneous catalysts, adsorbents, or luminescent probes [3,4].

(3) Design of bioactive Ag and Cu-based metal-organic architectures toward applications as topical antimicrobial agents and functional biomaterials [5].

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Many Faces of a Cuboctahedron: A Journey of an Intermetallic Fragment from Simple structures to Complex Arrangements

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Ordered intermetallic compounds are one of the most fascinating objects in inorganic chemistry, their very existence challenging classical concepts of metallic bond and its directionality, or lack thereof. The variety of crystal structures arising from different combinations of metals is simply amazing, with 2166 structure types and just under 21000 unique ordered intermetallics (excluding solid solutions and statistical alloys) characterized by 2015 [1], and yet the field is still considered practically unexplored. The range of unconventional and potentially useful properties that intermetallics exhibit is only matched by their structural variety.

One of the most common structure types among intermetallics is the AuCu₃ type. It is derived from the copper structure type and is a primitive cubic structure with coordination number of 12 for each metal. Thus, the structural unit in AuCu₃ is a cuboctahedron, e.g. gold-centered copper cuboctahedron [Cu₁₂Au]. In our work, we try to use cuboctahedra based on Group 10 metals (Ni, Pd, Pt) as building blocks for the structures of varying complexity, either by diluting 3D metallic system with a nonmetal (such as chalcogens or pnictogens), or by specifically designing new linear intergrowth structures. In this report we showcase several structure types and motifs arising from such approach (see Fig.1) [2].

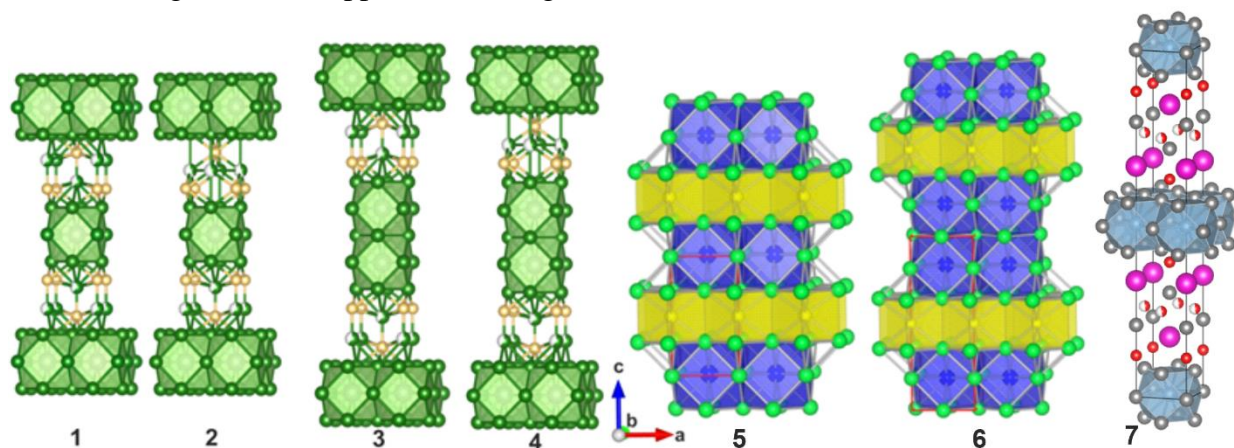


Figure 1. Main AuCu₃-based structure motifs for Group 10 – p-block metal chalcogenides and pnictides.

The simplest, perhaps, naturally after its parent intermetallic, is the Pd₅TlAs structure type (5, see Fig.1), where layers of face-sharing [Pd₁₂M] or [Pt₁₂M] cuboctahedra are separated by pnictogen or chalcogen layers. Its variation is the Pd₈In₂Se type (6), where cuboctahedra are double-stacked. These structures are not adopted in the case of nickel, which shows a tendency to form intergrowth structures where single- or double-stacked [Ni₁₂M] cuboctahedra alternate with either a combination of Li₂O / Cu₂Sb nickel-chalcogen blocks (2, 4) or simply Cu₂Sb-type blocks (1,3). The structure of 1 is also adopted by two mixed palladium-tin and palladium-indium tellurides, but so far this is the only proven crossover between ternary Ni and Pd/Pt compounds of

this type. To complicate things further, we tried to produce intergrowth structures between AuCu₃-type fragments and ternary blocks with the CaBe₂Ge₂-type structure, which resulted in obtaining the family of different compounds with the Eu₂Pt₇AlP_{4-x}-type structure (7). The potential to vary the elements in the CaBe₂Ge₂-type fragment might make this class particularly interesting in terms of tunable properties.

In our studies we pay particular attention to the electronic structure and chemical bonding in intermetallics and derived compounds, which are analyzed using DFT calculations and state-of-the-art bonding indicators. The key common feature of all the compounds in question is multi-centered heterometallic bonds within cuboctahedra. Key differences in the bonding patterns of different compounds will also be discussed.

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Structural chemistry of polynuclear complexes of transition metals

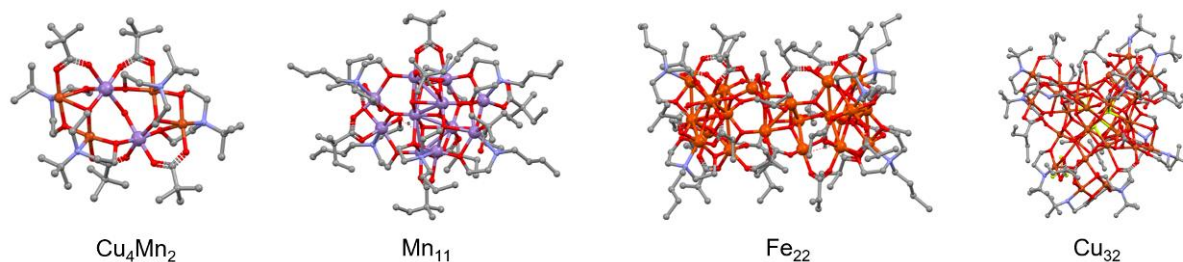
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Discrete polynuclear homo- and heterometallic complexes of transition metals constitute a class of compounds with recognized magnetic and catalytic effects, appearing from synergic interactions of a few metal centres within one complex molecule [1]. The presence of closely located spin carriers provides a useful model for studying the exchange coupling interactions and may lead to secondary effects such as single molecule magnetism (SMM). The cooperative interaction of a few redox-active metal centres enhances the catalytic activity of polynuclear species, as observed in some natural enzymes as well as in numerous artificial catalytic systems.

The importance of single-crystal X-ray diffraction (SCXD) analysis in the chemistry of polynuclear coordination compounds cannot be overestimated. Precise knowledge of the topology and geometry of coordination cores is crucial for understanding their physical properties and establishing structure-properties correlations, whereas the SCXD analysis is practically the only technique allowing to get such kind of structural information.

In our work, the synthetic strategy known as spontaneous self-assembly (SSA) is employed. The SSA approach foresees the one-step interaction of flexible polydentate ligand(s) with metal source(s) under thermodynamically driven conditions. Although the SSA method can lead to incredibly sophisticated compounds, its low predictability makes the use of SCXD mandatory for determination of the final structure of a product. The use of simple aminoalcohol aliphatic and Schiff base ligands allowed us to obtain a series of homo- and heterometallic transition metal compounds of 3d metals of various nuclearity, from simple Cu_2 or Mn_4 complexes to large Fe_{22} and Cu_{32} ones.



Our recent efforts have been concentrated on the use of combination of aminoalcohol and carboxylate ligands having bulky inert (aliphatic or aromatic) substituents [2-5]. The role of these groups is to sterically isolate polynuclear species preventing their fuse into coordination polymers. Also, this approach allows better magnetic isolation of discrete metal cores due to longer distance between them. Through our work, we employ the SCXD analysis not only to determine crystal structures of novel coordination compounds, but also to characterize catalytic reaction products and intermediates, as well as to understand the equilibria that occur in the crystallization processes.

This lecture will be focused on the synthesis, crystal chemistry and applications of homo- and heterometallic polynuclear coordination compounds of transition metals, with special attention to the structure-property relationships.

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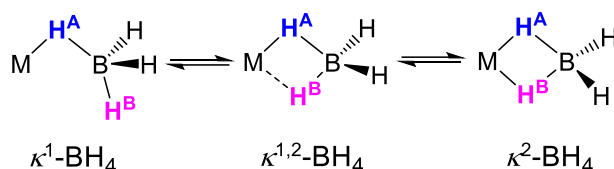
Structure and reactivity of transition metal tetrahydroborates and their dihydrogen bonded complexes

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Transition metal borohydride complexes are widely used as selective reducing agents, building blocks for the synthesis of new organometallic derivatives, precursors for the production of borides, hydrides, and other inorganic materials, and as hydrogenation catalysts. Still, the question of the BH_4^- ligand coordination mode and the criteria for its determination remains one of the “damned questions” in the chemistry of metal tetrahydroborates. In this lecture, we inspect the known structures of d-block metal tetrahydroborate complexes and their spectral properties obtained experimentally along with DFT calculations to elaborate the criteria for $\kappa^{1,2}$ - BH_4 complexes demarcation as a particular class between κ^1 - and κ^2 -coordinated BH_4 ligands.



Besides a variety of the BH_4^- ligand coordination modes another peculiarity of transition metal tetrahydroborate complexes is the presence of several types of hydride ligands (MH , BH^{term} , BH^{br}). That leads to a variety of mono-, bi-, and trifurcate dihydrogen bonded complexes, but only a few of them are the proton transfer reaction intermediates [1-5]. Our investigations on the reactivity of $[\text{BH}_4]^-$ and transition metals (Cu, Ru, Pd) tetrahydroborate and hydrido-tetrahydroborate complexes in the presence of alcohols by variable-temperature IR, UV-vis, and NMR spectroscopies in combination with DFT calculations revealed that the nature (Lewis acidity/basicity) of transition metal in borohydride complexes is the major determinant for the overall mechanism of the borohydride fragment activation.

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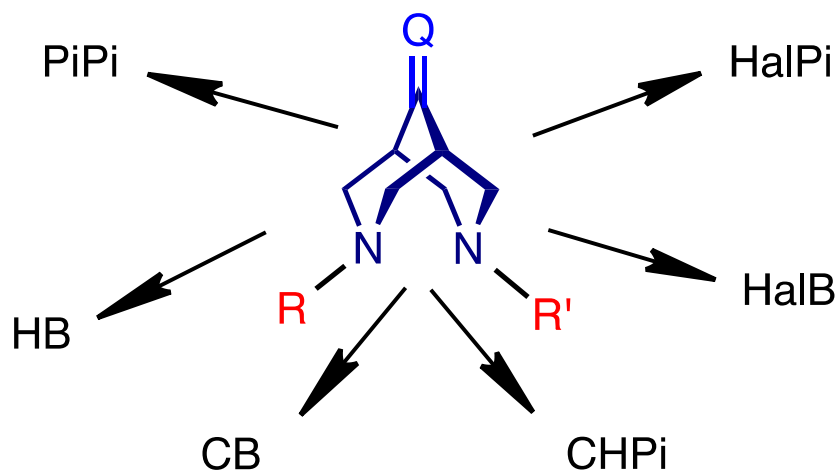
Supramolecular Interactions in the Condensed State on the Example of Bispidines

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This report describes the whole palette of the supramolecular interactions, including the coordination bonds (CB), hydrogen bonds (HB), halogen bonds (HalB), halogen...pi interactions (HalPi), C-H...Pi interactions (CHPi), pi-pi stacking interactions (PiPi), and some other less energetic but nonetheless important types of intermolecular bonds, which could be found in the solid state and gel state chemistry.

All the examples are illustrated by the author's works on 3,7-diazabicyclo[3.3.1]nonanes (aka *bispidines*) and their structural analogues (Scheme).



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Statistical and local structure of large-sized multifunctional single crystals

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Due to the fine tuning of the physical and chemical properties of single crystals through the correct choice of composition and structure, they are successfully used in many fields of science and technology, but their potential has not yet been exhausted. The creation or improvement of materials for known or new devices is impossible without understanding the fundamental relationship "composition-structure-method (conditions) of synthesis-properties", the establishment of which is the main goal of modern materials science. Knowledge of all the links of this chain makes it possible to purposefully obtain compounds and materials based on them with desired characteristics and parameters, to control their functional properties, to simulate new crystalline systems taking into account the conditions of their growth and behavior in different conditions, including extreme ones.

Determination of the actual composition and real structure of large-sized single crystals obtained by melt or solution methods and having a commercial focus is a non-trivial task that differs significantly from the study of the same single-crystal objects, but with small sizes. It is necessary to know *a priori* phase diagrams to determine the melting parameters and the distribution coefficients of the components along the length and cross-section of the crystal, to take into account the directions of growth and possible growth defects (facet effect, growth banding), the potential influence of the growth conditions (composition of the initial charge, method of introduction of impurity, growth atmosphere, post-growth processing), etc. However, even the provision of all the above factors does not guarantee the growth of single crystals of uniform composition within a specific structure: in the overwhelming majority of cases, the composition of the synthesized crystals (the actual composition, taking into account all types of point defects and main associates), which should be associated with the parameters of functional properties, differs significantly from composition of the initial charge. This does not allow establishing the correct composition-property relationship and directionally growing crystals with the required set of properties. On the other hand, the synthesis conditions can change the statistical structure, which is determined by the methods (techniques) of structural analysis, and the local environment of the components, revealed by X-ray absorption spectroscopy. It is the local structure that is the forerunner of the crystal structure and its stability. Further, the examples show the efficiency of either one or both methods in the study of single crystals of different compositions and structures. The obtained details of the crystal and local structures made it possible to explain the functional properties of the objects under investigation and to find important correlations.

1. For a long time, it was believed that compounds of the huntite family with the general composition $RESc_3(BO_3)_4$ with $RE = La - Gd$, obtained by melt methods, crystallize in space group $R32$, which was due to widespread survey on laboratory diffractometers or rejection of weak

reflections in the analysis of diffraction patterns. A detailed structural study of single crystals and the same powdered crystals using synchrotron radiation revealed a decrease in the symmetry caused by the order-disorder structural transition accompanied by the distribution of Sc (*RE*) ions over two (space group *P321*) rather than one (space group *R32*) crystallographic sites of the huntite structure.

2. Different coordination environments of Na^{1+} and Gd^{3+} ions was established in the structures of single crystals of the scheelite family with the initial compositions $(\text{Na}_{1/2}\text{Gd}_{1/2})\text{MoO}_4$ and $(\text{Na}_{2/7}\text{Gd}_{4/7}\square_{1/7})\text{MoO}_4$ and, respectively, refined (actual) compositions $(\text{Na}_{0.498(2)}\text{Gd}_{0.502})(\text{Mo}_{0.999(4)}\square_{0.001})\text{O}_4$ and $(\text{Na}_{0.348(8)}\text{Gd}_{0.528}\square_{0.124})(\text{Mo}_{0.996(3)}\square_{0.004})\text{O}_4$ (\square -vacancies). This seemed obvious from the crystal-chemical point of view due to the difference in the formal charges of the Na^{1+} and Gd^{3+} ions, but it was proved for the first time, which made it possible to explain the observed kinetic processes in this family of crystals.

3. The method of introducing activators affects their content, formal charge, and structural location in the host crystal. Thus, Mn activator ions introduced over stoichiometry (up to 1.0 wt%) into a crystal melt with a whitlockite-like structure $\text{Ca}_3(\text{VO}_4)_2$ (CVO:Mn) or by high-temperature diffusion annealing of $\text{Ca}_3(\text{VO}_4)_2$ in the presence of a Mn_2O_3 solid phase (CVO: Mn_2O_3) showed different structural behavior. A higher content of manganese was found in CVO: Mn_2O_3 . In addition, different formal charges (Mn^{3+} and $\text{Mn}^{(2+\delta)+}$, respectively, in CVO:Mn and CVO: Mn_2O_3) and different coordination environments (elongated Jahn-Teller octahedron and tetrahedron, respectively, in CVO:Mn and CVO: Mn_2O_3) were revealed. It should be noted that, according to the structural analysis, manganese ions occupy coordination polyhedra unusual for them (mono- and two-capped trigonal prisms). Only the use of X-ray absorption spectroscopy made it possible to remove this contradiction.

4. The most interesting effect is "homeopathic", which we first observed: a significant difference in the local structure of single crystals doped with ions of rare earth or transition metals in small ($< \sim 5$ wt%) or relatively large (~ 5 wt%) amounts over stoichiometry. Thus, in the structure of Dy^{3+} -doped sillenite crystals $\text{Bi}_4\text{Ge}_3\text{O}_{12}:\text{Dy}$ (BGO:Dy) with actual compositions $(\text{Bi}^{3+}_{3.972(5)}\text{Dy}_{0.028})\text{Ge}_3\text{O}_{12}$ (BGO:1.0%Dy) and $(\text{Bi}^{3+}_{3.993(5)}\text{Dy}_{0.007})\text{Ge}_3\text{O}_{12}$ (BGO:0.1%Dy), different polyhedra are formed: DyO_5 (derivative of a trigonal prism) and BiO_6 (distorted octahedron), DyO_7 (derivative of an octahedron) and BiO_5 (defective octahedron), respectively.

Numerous studies on single crystals of the garnet, perovskite, scheelite, huntite, whitlockite and many other families have shown that structural analysis and X-ray absorption spectroscopy are a powerful tandem for applied and fundamental materials science.

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Charge density distribution of APIs in crystals and ligand-receptor complexes

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The analysis of charge density in crystal is very useful for evaluating the strength of intermolecular binding in crystals of organic compounds. The term “charge density analysis” encapsulates a group of methods related to qualitative and quantitative description of the charge density distribution and the functions derived from it. Quantum theory “Atoms in molecules” (QTAIM) is the most essential approximation for description of chemical bonds and weak interatomic interactions. Being applied to the study of crystals of active pharmaceutical ingredients (API) the QTAIM allows one to estimate their lattice energy and evaluate the stability of polymorphs. Also, important information can be obtained using qualitative approach through the NCI method and the molecular electrostatic potential. The results of charge density analysis cannot be directly compared with the results of the studies of receptor-ligand complexes. Fortunately, such a problem can be solved using Voronoi partitioning and computational charge density studies of simplified models described ligand bonded to an active center.

Herein we present the results of experimental charge density studies, quantum chemical calculations and Voronoi partitioning for several APIs (abiraterone acetate [1], bicalutamide [2] lamivudine, favipiravir [3] and several other APIs) used in common practice for medication of tumors, HIV and COVID-19 infections. As result the energies of individual interatomic interactions were evaluated for single crystals of API and simplified models describing ligand-receptor interaction constructed using PDB data as starting points. The characterization of intermolecular interactions was carried out with a variety of theoretical approaches including deformation electron density, QTAIM theory, NCI method, molecular electrostatic potential and solid bond angles (Fig. 1). The data on intermolecular interaction obtained for single crystals and models of ligand-receptor binding demonstrated the similarity of lattice energy values with those for the energies of interactions between API and receptor despite of conformational changes.

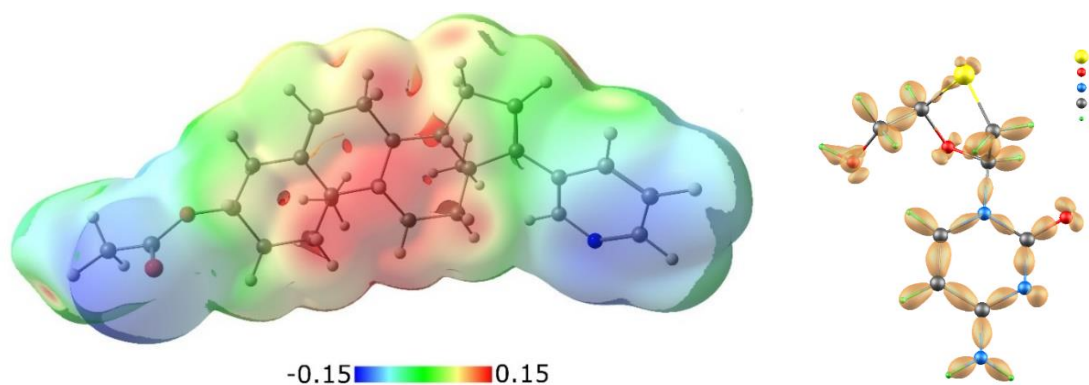


Figure 1. Molecular electrostatic potential of abiraterone acetate (left), 3D surface of experimental deformation electron density of lamivudine (right).

The work was financially supported by the Russian Science Foundation (project 20-13-00241).

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Keynote Lectures

X-ray diffraction study of structural organization of the unsubstituted and substituted phthalocyanine thin films

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Metal phthalocyanines (**MPc**) belong to the class of complex compounds with organic ligands and are close analogs of porphyrins. Many of the MPc are capable of sublimation in vacuum or in an atmosphere of inert gases, which makes it possible to obtain thin uniform MPc films on the substrate surface by physical vapor deposition (**PVD**). One of the important advantages of MPc is their semiconducting properties. Presently, organic light-emitting diodes, solar cells, field-effect transistors and gas sensors based on MPc thin films have been created. Molecular structure of MPc makes it possible to synthesize a wide class of so-called substituted MPc by purposefully varying the end groups, which allows to change semiconducting properties of obtained thin films.

The common feature of unsubstituted and substituted MPc is a tendency to form multiple polymorphic modifications. Another feature is related to the fact that MPc usually form oriented polycrystalline layers when deposited on smooth surfaces, which creates additional difficulties when performing X-ray phase analysis. Diffraction patterns of oriented MPc thin films obtained in the classic Bragg-Brentano scheme often contain single diffraction peak corresponding to the plane of preferred orientation. X-ray phase analysis of such samples can be very difficult due to the presence of several polymorphic modifications with close 2θ positions of the diffraction peaks. To solve this problem, a 2D Grazing Incidence X-ray Diffraction (**2D GIXD**) technique for studying oriented thin films was implemented on the basis of a laboratory single-crystal diffractometer. MPc thin film sample in the shape of a narrow (2-3 mm wide) strip is attached to the goniometer head using a special adapter and oriented in such a way, that the angle of incidence of the primary beam is within $0.1 \div 1^\circ$ range. The resulting diffraction pattern is then recorded using 2D detector. Figure 1 shows the difference between the data obtained using standard powder diffraction (a) and 2D GIXD (b) on the example of tetra-fluorinated palladium phthalocyanine thin films. Because the additional diffraction reflections are observed, the amount of diffraction data obtained is greatly increased. By measuring the azimuthal width of the observed diffraction arcs/spots it is possible to estimate the degree of preferential orientation, while the azimuthal position of the observed diffraction reflections is related to the angle between the corresponding crystallographic plane and the substrate plane. Combined with the measured interplanar distances, this information can be used to roughly estimate the unit cell parameters of the crystalline phase in case it can not be obtained in the form of a bulk polycrystalline powder.

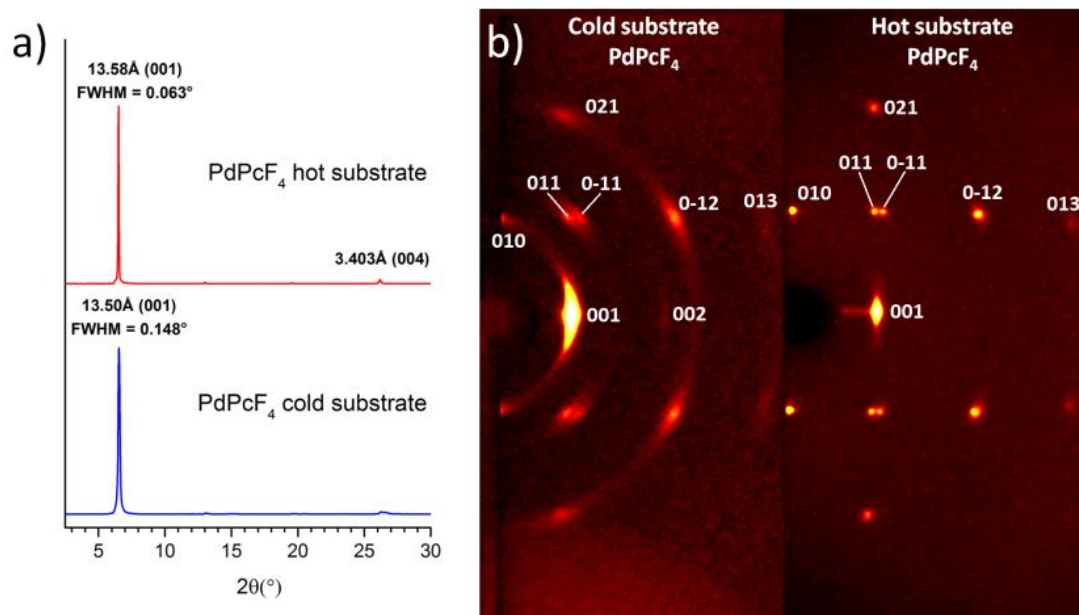


Fig. 1. Standard XRD patterns (a) and 2D GIXD patterns (b) obtained from the same tetra-fluorinated palladium phthalocyanine thin film samples.

In this work, the crystal structures of 14 polymorphic phases of unsubstituted (MPc) and fluorine-substituted (**MPcF_x**) metal phthalocyanines (α -PdPc, γ -PdPc, β -CrPc, CuPcF₄, CoPcF₄, ZnPcF₄, FePcF₄, PdPcF₄, PbPcF₄, VOPcF₄, β -PdPcF₁₆, β -VOPcF₁₆, γ -VOPcF₁₆, PbPcF₁₆) were determined. Several structural features of thin films of these compounds, such as the inclination of the molecules relative to the substrate surface, the mutual arrangement of the molecules and the degree of preferential orientation were analyzed using combination of conventional XRD and 2D GIXD. The revealed influence of PVD conditions on the phase composition and structure of oriented phthalocyanine thin films can be used in the future for creating functional layers with desired properties.

(Thia)calix[4]arenes and their functional derivatives as versatile molecular building blocks for rational design of crystalline materials

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(Thia)calix[4]arenes represent versatile molecular platform especially adopted for generation of various crystal state coordination compounds displaying various dimensionalities (0D-3D) and functions [1-5]. Depending of the conformation of macrocyclic platform (*cone* or *1,3-alternate*) their interaction with *d* or *f* cations may afford the formation of either discrete metal-organic clusters or extended coordination polymers in the crystalline phase exhibiting tunable luminescence and single molecule magnet behavior (Figure 1) [6]. Moreover, it was shown that the shape of resulting solid-state supramolecular architectures can be controlled also up by the proper choice of the used auxiliary ligands bearing N/O-donor atoms. Here we report the approaches for controlled design of crystalline materials exhibiting different smart properties such as tunable porosity, single molecule magnetism or/and luminescence using (thia)calix[4]arene based molecular building blocks upon their coordination with *d* and *f* metal ions.

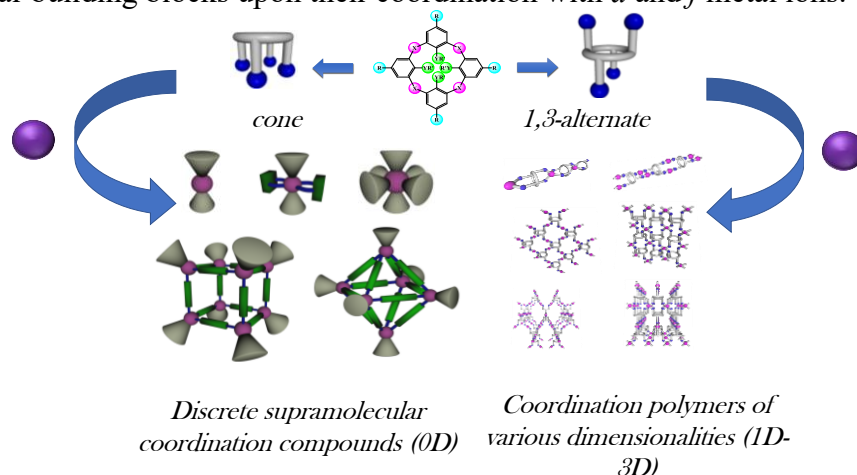


Figure 1. (Thia)calix[4]arenes in *cone* and *1,3-alternate* conformations as molecular building blocks for discrete supramolecular complexes as well as 1D-3D coordination polymers formation.

This work was financially supported by Russian Science Foundation (grant № 19-73-20035).

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Structural diversity of rhenium(I) complexes: approaches to fine-tuning photophysical behavior

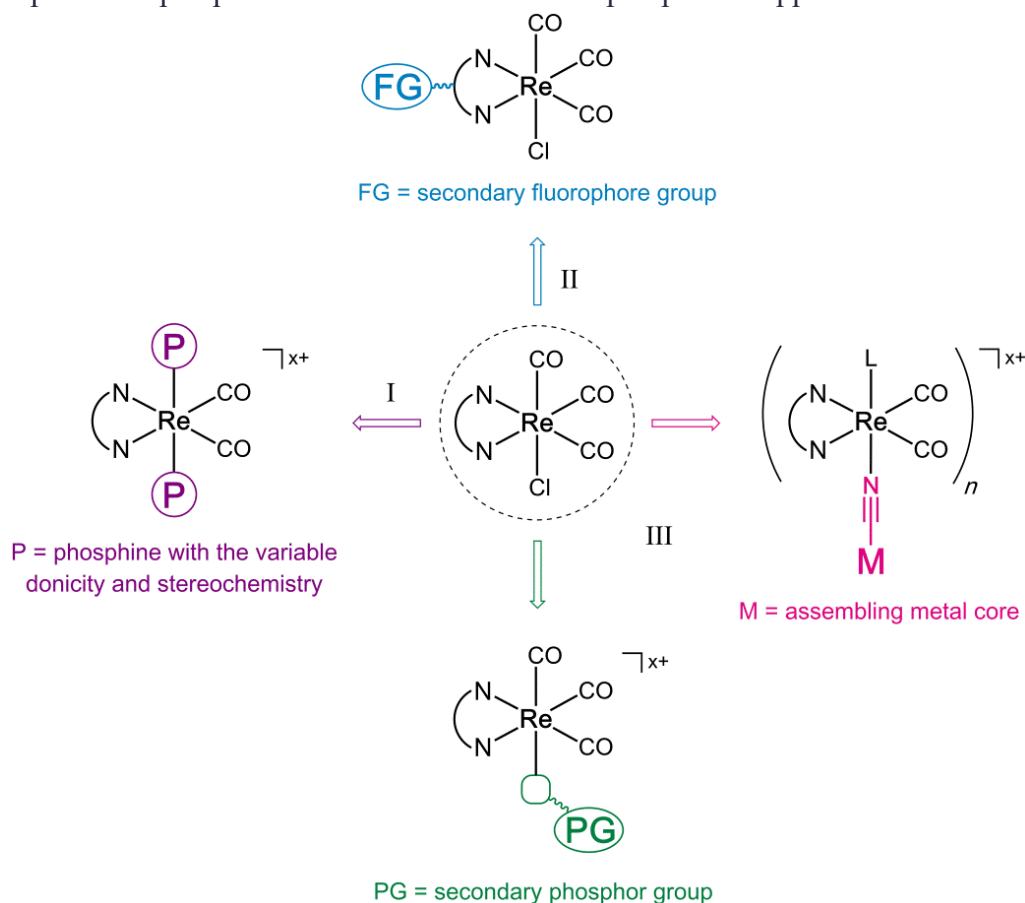
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The development of versatile optically active compounds and materials is crucial in various technological fields including photodynamic therapy, bio-imaging, sensing, photocatalysis, high-performance solar cells, and optoelectronic devices. Much of the research to date has focused on transition metal complexes, due to the variety of their molecular configurations that allows significant freedom in molecular design to attain unique photophysical characteristics [1].

Among the transition and rare earth metal light-emitting compounds, the rhenium(I) luminophores, displayed remarkable stability, low toxicity, and appealing physical properties [2], have attracted ever-increasing interest from both academic and industrial researchers. Rhenium(I) derivatives of the general formula $[\text{Re}(\text{NN})(\text{CO})_3\text{L}]$, where $\text{NN} = \pi$ -conjugated diimine ligand and $\text{L} =$ ancillary ligand, illustrate the archetypal emitters, which have been studied over the past several decades. The optical characteristics of the rhenium(I) complexes can be altered through the modification of the coordination sphere of the metal center by means of the diimine and auxiliary ligands, and the introduction of secondary chromophore units to the parent rhenium motif.

This project is devoted to the design of a new generation of rhenium(I)-based chromophores (Scheme 1) and to a more comprehensive understanding of the structure-property relationships for the perspective modifications towards prospective applications.



Scheme 1. Illustration of the research directions.

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(I) The first strategy is based on the incorporation of the auxiliary ligands into the {Re(phen)(CO)₂} structural fragment. A series of alkynylphosphines served as peripheral ancillary ligands with different donor ability and stereochemistry.

(II) The second approach to the efficient photofunctional Re(I) materials involves the use a pyridyl-phenanthroimidazole fragment as chelating diimine. The integration of the secondary chromophore moieties into the pyridyl-phenanthroimidazole system led to extending the range of luminescence colors to the whole visible spectrum.

(III) The third feasible way to manipulate the photophysical behavior relies on the construction of homo- and heterometallic rhenium-containing coordination assemblies through merging two or more metal chromophores. The binding of the metal centers was implemented by means of a) flexible aminopyridine bridging ligands, b) rigid cyanide linkers, that assumed the preparation of the target polynuclear compounds with various degrees of conjugation between luminescent units.

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Synthesis of Novel Cationic 1,2,4-Selenadiazoles via Addition of 2-Pyridylselenenyl Halides to Unactivated Nitriles

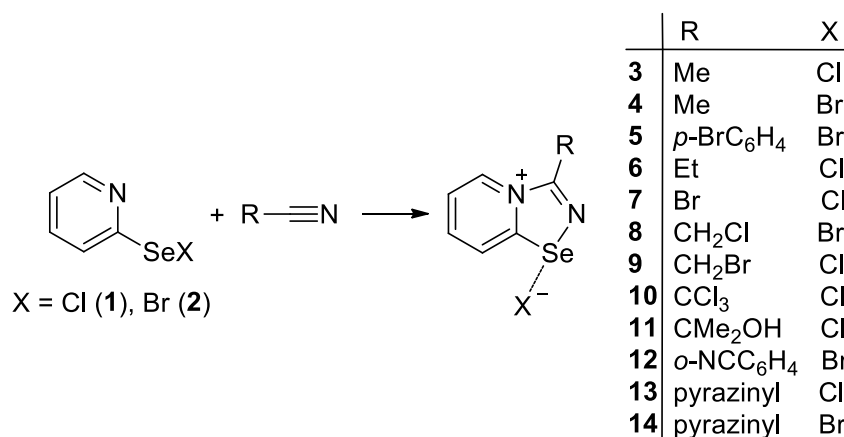
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Nitriles are important building blocks that are widely employed both in the laboratory and industry. Electrophilic or nucleophilic additions or asymmetric dipolar cycloaddition to the triple bond of nitriles often serve as indispensable tool for the creation of various functionalities. However, utilization of nitriles in organic synthesis is often hampered by their inert nature, which even allows application of some of their congeners as media for the synthesis.

Activation of nitriles by organometaloid compounds could be beneficial due to the fact that activator of CN triple bond is already present in the substrate, and a synthesis of organometaloid derivatives, which involve reactions with nitriles, potentially could be performed in a catalyst-free fashion.

Organoselenium compounds are of considerable pharmacological importance. Therefore, preparation of novel selenium-containing building blocks is of substantial interest. Recently, it was demonstrated that 2-pyridylchalcogenyl halides react with alkenes or alkynes resulting in the formation of corresponding five-membered heterocycles. Here we showcase that 2-pyridylselenenyl halides undergo facile coupling with unactivated nitriles, which allows the preparation of novel cationic 1,2,4-selenadiazoles in remarkably high yields. Novel heterocyclic compounds feature unusual attractive interactions via four-center $\text{Se} \cdots \text{N}$ chalcogen bonding in the crystal [1].



Scheme. Synthesis of 3–14.

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Titanium phenoxides and phosphonates as molecular models and molecular precursors of hybrid oxide materials

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Grafting of organic functions exploiting phenoxide and phosphonate anchoring has become a powerful tool in synthesis of organic-inorganic hybrid materials via post-functionalization [1, 2]. Phosphonate groups are attractive also as complex-building functions in creation of hybrid nano adsorbents [1, 2]. The mode of attachment of phosphonate-bound ligands to metal oxide surfaces remains a topic of vivid debate. Also, the reactivity of alkoxide phosphonate and phenoxide complexes has become a topic of strong interest as they were proposed as molecular photocatalysts in the investigation of molecular mechanisms of reactivity of titanium dioxide nanoparticles. Titanium (oxo-)alkoxide phenoxide and phosphonate complexes were synthesized using different titanium precursors and selected ligands to produce molecular models for interaction between phosphonates and titania surfaces and to investigate the solution stability of these species. The obtained compounds were characterized by X-ray single crystal studies, revealing possible grafting modes of these ligands on oxide surfaces [3, 4]. Crystals of these complexes, when immersed into water, undergo topotactic transformation into complex oxide nanostructures, characterized by TEM and AFM techniques. The molecular transformation mechanisms have been outlined. The structure data were used for interpretation and prediction of behavior of titania nanoparticles as drug carriers in skin drug delivery applications.

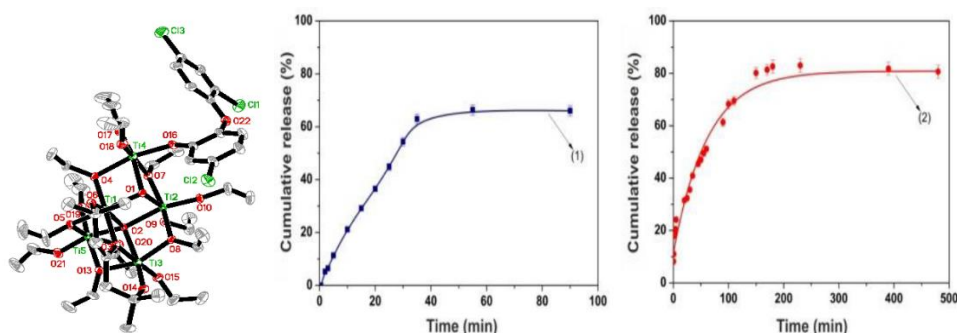


Figure 1. Molecular structure of a paperbag model and release profiles of phenoxide drugs.

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Some examples of Co(II), Zn(II), Cd(II) and Cu(I) coordination polymers with inclusion and luminescent properties

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Coordination polymers (CP) being coordination compounds with repeating coordination entities extending in 1, 2, or 3 dimensions nowadays demonstrate their significance as materials for luminescence, catalysis, magnetism, optics, electric conductivity etc. The pore regulation by design explains an advantage of CPs compared to traditional porous materials such as zeolites and activated carbons. Alongside the rigid 3D MOFs, interest to low-dimensional 1D and 2D CPs is originated from their diversity, flexibility of coordination skeleton and impressive adsorption properties accompanied by the guest selectivity.

This contribution reports some recent results obtained in Laboratory of Physical Methods of Solid State Investigation ‘Tadeusz Malinowski’ IAP in the frameworks of national and international cooperation and focused on crystallography of mixed-ligand CPs with useful properties.

For Co(II), Zn(II) and Cd(II) the examples are given for: isomorphic, and isostructural 1D and 2D coordination arrays; n-fold interpenetration in 2D and 3D coordination grids; guests accommodation in the pores that act as templates and determine the shapes and sizes of pores [1-3]; reversible and irreversible SC-SC transformations with retention or transformation of 1D, 2D or 3D coordination arrays [4-7]; lack of crystal color as an indicator for lack of conjugation in the bridging azine ligands [3].

On the way to Cu(I) iodide CPs with specific luminescent properties, the *in situ* reduction of Cu(II) in the presence of bidentate and tridentate N-heteroatomic ligands, resulted in unique coordination networks including $[\text{CuI}(\text{pyz})]_n$ (pyz=pyrazine) as the missing member in the row of 2D CPs with general formula $[\text{CuX}(\text{pyz})]_n$ (X=Cl, Br, I) and 3D $\{[\text{Cu}(\text{pyz})_2]_2\text{I}_5\}_n$ and $\{[\text{Cu}_3(\text{triimidazole})_4] (\text{I})_3\}_n$ with interesting topologies and impressive void volumes [8,9].

This work was supported by the National Agency for Research and Development (NARD) (project number 20.80009.5007.15).

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Back to the Roots – Dress Chemistry in Green

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A naive comparison between nature and chemists on production capacities, e.g. biopolymers and plastics productions, respectively, marks nature as clear winner. The same accounts for the required feedstocks, because nature uses CO₂ directly from air whereas the chemist relies on crude oil. Although both parties have been independent actors for such a long time, the development of Green Chemistry has helped chemists to learn nature's biodegradation strategies in materials design and to synthesize novel bio-inspired materials. Within this respect, I will demonstrate how the chemist can dress chemistry in green on examples covering metal-free catalysts [1-2], sustainable methods for Li-ion batteries recycling (Figure 1) [3-4], functional lignin-based coatings [5-6], electrocatalytic denitrification [7], and bio-inspired fibres [8].

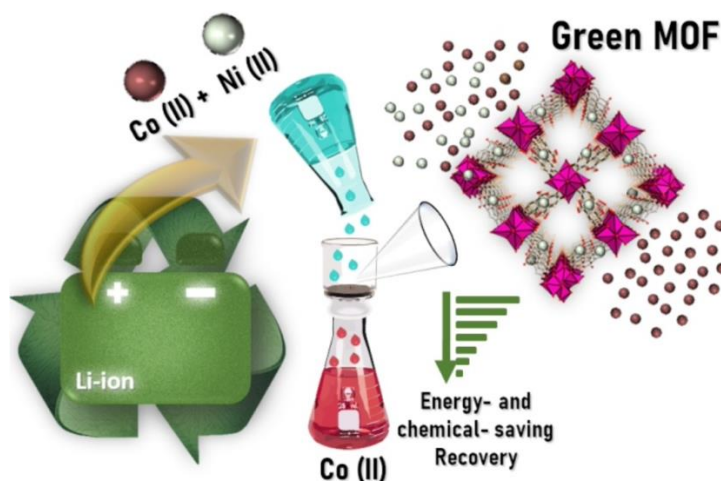


Figure 1. Green MOF for sustainable separation of cobalt and nickel from leaching solutions.

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Structural Chemistry of Azulenes

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Azulene is a dark-blue, polar, bicyclic aromatic hydrocarbon (Figure 1) that is a non-benzenoid isomer of naphthalene. In addition to its long-standing medicinal and pharmaceutical relevance, the polar non-benzenoid aromatic framework of azulene constitutes an attractive building block in the design of redox-addressable, optoelectronic, and conductive materials [1]. This presentation will highlight our recent developments in the chemistry of hybrid metal / azulene platforms featuring isocyanide and thiolate junctions (**X**) along their molecular axis (Figure 2) [2].

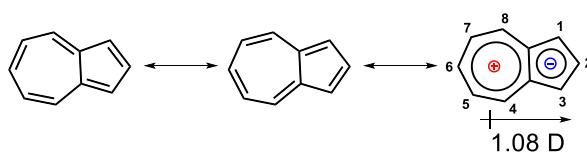


Fig 1.

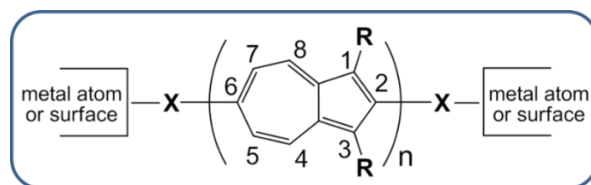


Fig 2.

Single crystal X-ray structural analysis of a series of novel 2,6-functionalized azulenes will be presented [3]. In particular, heterobimetallic ensembles that incorporate the first examples of a conjugated \square -bridge equipped with both isocyanide and thiol junction groups in the same molecular linker will be discussed (e.g., Figure 3B).

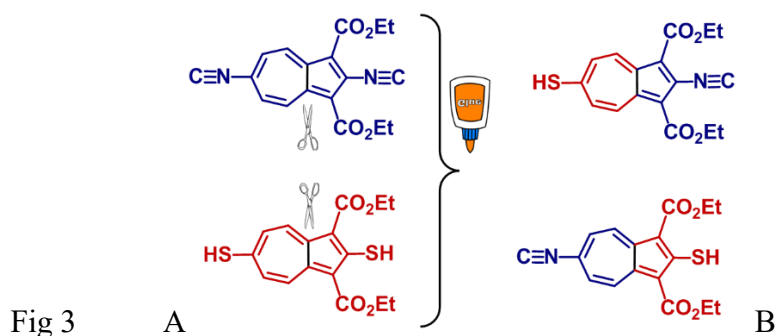


Fig 3

A

B

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Molecular and supramolecular design of cage-like metallacomplexes based on sil- and germsesquioxane ligands. Synthesis, structure, properties

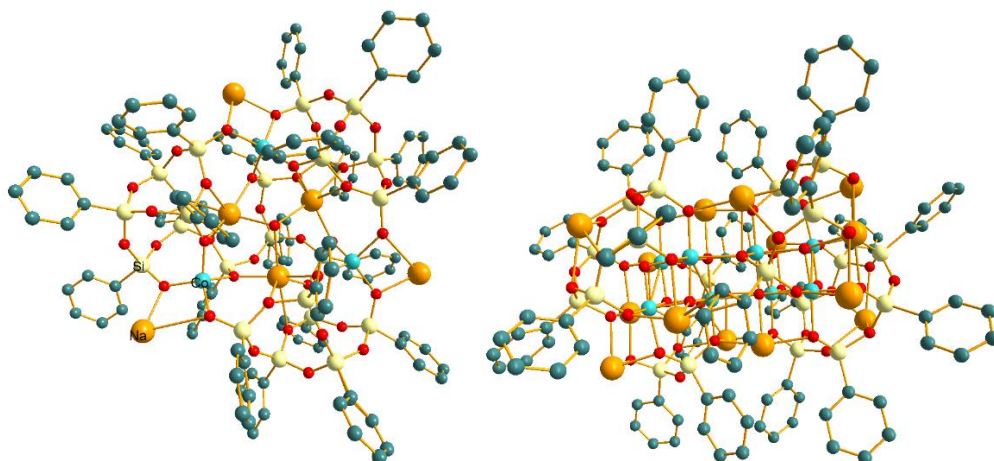
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Cage-like sil-[1] and germsesquioxanes [2] are in the research focus of many scientific teams worldwide. Diverse forms of sesquioxane ($\text{REO}_{1.5}$, E = Si or Ge) ligands – from monomeric to polycyclic – provide numerous types of metallacomplexes. Particularly efficient synthetic approach implies use of different auxiliary organic (N,N-, P,P-, N,O-, O,O-) ligands [3]. Plenty of structural forms endows metallasesquioxanes with practically important properties, e.g. catalytic [4], magnetic [5], photophysical [6] ones. Lecture will discuss main results of our group in synthesis of cage-like metallasesquioxanes as well as features of their catalytic activity, magnetic effects and luminescent behavior.



This work was supported by the RUDN University Strategic Academic Leadership Program

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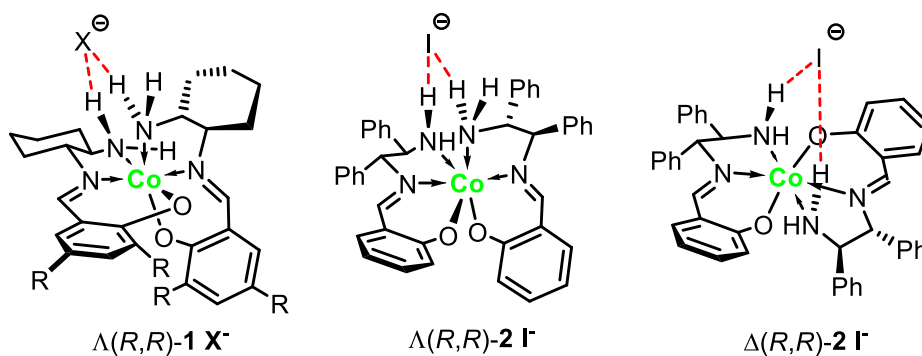
Chiral metal-templated Co(III) complexes as a powerful class of catalysts

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Chiral metal-templated complexes have broadly applied as powerful catalysts for many asymmetric transformations [1]. Among them, the chiral-at-metal Co(III) complexes have a great potential [2,3]. For instance, our group introduced a novel class of chiral coordinatively saturated positively charged Co(III) complexes, featuring chirality centered both at metal and ligands (Figure) [2-7]. In those complexes the metal center activates the NH₂ groups of the ligands, doing them hydrogen bond donors and serves, mainly, a structural role as a "scaffold" for the ligands, keeping them in space and providing a proper chiral environment.

As a result, we demonstrated that the obtained complexes efficiently catalyze many asymmetric reactions such as asymmetric alkylation, Michael addition, epoxidation, trimethylsilylation and etc [2-7].



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Structure-driven possibilities and challenges: from heterogeneous catalysis to extracellular matrix glycation

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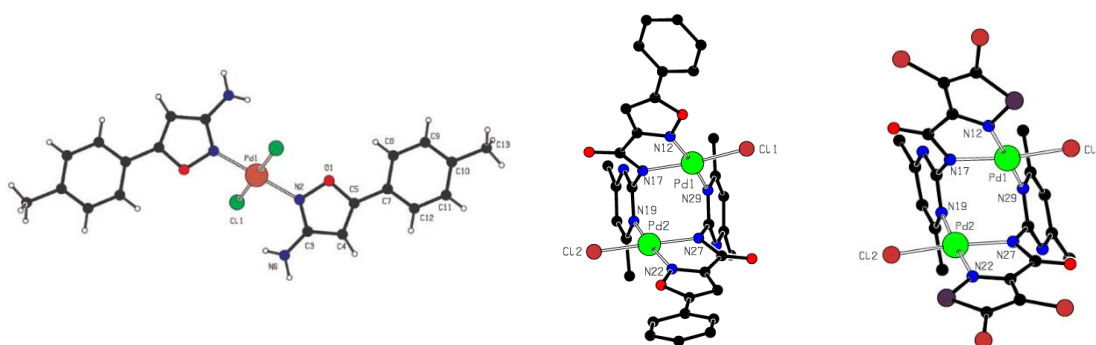
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Modern achievements of structural chemistry provided not only a broad basis for numerous new materials but also highlighted the roads for further studies in both theoretical and practical fields of chemistry. The studies within both fields are intertwined, as new structural characteristics are able to provide new ideas for a different kind of research, and vice versa.

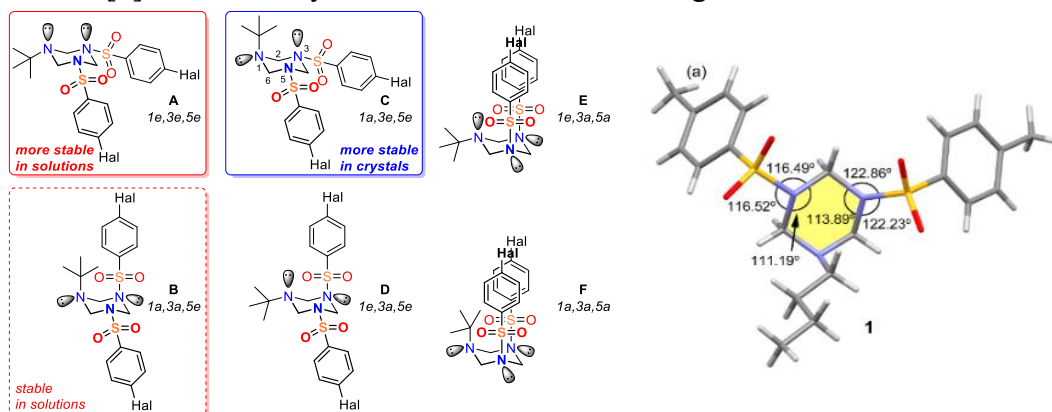
Such studies, for example, could be represented by the research in the domain of palladium metal complexes of azolic row, which were developed for high-efficient cross-coupling reactions catalysis under “green chemistry” conditions – by themselves and in immobilized forms [1]. Among the latter, an unusual structure of “pincer ligands mimics” was observed that allowed obtaining binuclear metal complexes that were stable enough to be detected using HPLC-MS [2].



The pathways of such types of structures implementation beyond catalysis are yet to be discovered, most likely in the domain of nanochemistry, through joint international collaboration.

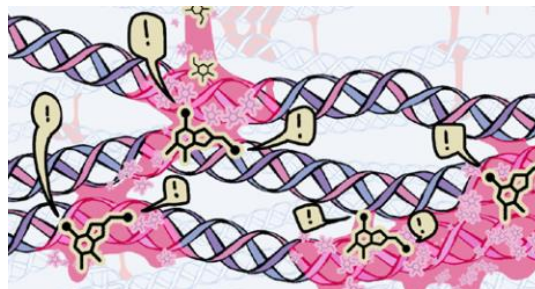
Another example that provides important facts that could be used for new materials design and engineering is represented by substituted 1,3,5-triazinanes, which were studied both in solid and liquid phase. Structural elucidation of the latter allowed to observe a row of unusual facts and

effects, including a *tert*-butyl group in axial position of triazinane heterocycle [3] and sp^2 - sp^3 deequalization [4] of chemically identical sulfonamide nitrogens in the solid state.



The potential of the practical applicability of the aforementioned phenomena are yet to be fully uncovered in the process of various new materials design, and for sure will be useful in the development of new types of bioactive substances.

Many challenges for structural chemistry in the biological domain remain unsolved. The description of some complex macromolecular objects of biological nature remains a somehow elusive yet important task for modern structural chemistry. Among the latter, the precise observation of structures formed through non-enzymatic glycation (and other chemical modifications) of proteins remains an important task. The information on the structure of glycated collagen could provide insight on the ways of preventing this process and the possible role of metal ions in this process. The detailed information on intercellular matrix structure is also a desirable goal.



This, as well as many other challenges, pushes modern structural chemistry towards the development of new methods and the application of already existing techniques, both for structural elucidation of matter and for the design and creation of new materials and biologically active molecules.

The work was supported by Russian Foundation for Basic Research (18-58-00013-Bel_a, 20-58-00005-Bel_a, 20-53-00028-Bel_a) and the Belarusian Republican Foundation for Fundamental Research (X18P-010, X20P-017, X20P-056).

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High-pressure X-ray diffraction experiments and data reduction: the difference from ambient pressure studies and factors influencing the data quality

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High pressures can influence the structure of different materials leading to a number of interesting phenomena like phase transitions, changes in conductivity, amorphisation, metallisation *etc.* Pressures can also be used for chemical synthesis and often lead to formation of previously unknown solvates and clathrates. In order to understand all these phenomena one needs to know exact structure changes caused by high pressures. X-ray diffraction with diamond anvil cells (DACs) is widely used to determine crystal structures for most organic, inorganic and biological crystalline samples. The quality of diffraction data is critically important for obtaining reliable information on atomic coordinates and intermolecular distances. The recent improvements in high-pressure X-ray diffraction were related not only to technical aspects of diffraction experiment (new DAC designs, fast and sensitive detectors, brilliant X-ray sources), but also to development of a new software for sample centering, absorption correction, recognizing and excluding unwanted reflections that do not belong to the sample, data reduction, finding the orientation matrices for several crystallites in the same diamond anvil cell. The recent developments in instrumentation and software allowed even determination of electron charge density distribution for such a samples.

All types of high-pressure studies require rigorous experimental planning and special methods of X-ray diffraction data treatment since the crystal is not “free” but located in confined environment in hydrostatic liquid inside DAC with certain construction with limited opening windows for X-ray probe. A lot of questions can arise on planning the experiment: which pressure transmitting media to choose? how fast the pressure should be increased? Is not it better to perform all the experiments at synchrotron rather than at lab source if I have this opportunity? which factors should be taken into account on data collection and reduction? This list of issues is quite far from being complete. *The aim* of my contribution is to give a brief overview of the most interesting and useful generally arising questions and try to answer them. I would also like to highlight the importance of considering some “hidden” factors like choice of pressure transmitting media, pressure variation protocol and diffraction equipment while planning and performing the diffraction measurements to obtain the most reliable results of high-pressure experiment.

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Ultrasound-mediated polymer-analogous reactions in the chitin and chitosan chemistry

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Treatment of chitin and chitosan with ultrasound in the frequency, power and time in the range 70–80 kHz 250 W, 5–20 min, or 100 kHz, 280–300 W, 5–10 min, or 200 kHz 120 W 10 min does not lead to the polymers degradation. This fact was used for the ultrasonic promotion of polymer-analogous transformations (1).

In particular, we found that the alkylation of chitosan with alkyl halides, the aza-Michael reaction with chitosan, and the Ad_N-E reaction of chitosan with aldehydes are effectively promoted by ultrasonic irradiation. It was also revealed that the treatment of chitin with 1-azido-3-chloropropan-2-ol under the action of ultrasonic irradiation in water (as well as the treatment of chitin with 2-azidomethyloxirane in a DMAA solution with the addition of lithium chloride) are convenient one-step methods for introduction of azido group into the chitin macromolecule.

We show that phenol-yne and thiol-yne click-reactions are effectively promoted by ultrasonic irradiation, proceeding by a radical mechanism. This fact was used to obtain new derivatives of chitosan. Chitosan derivatives with phenolic and thiolic functions have been involved in ultrasound-promoted click reactions with betaine propargyl ether as an alkyne component to form new cationic chitosan derivatives.

Moreover, ultrasound makes it possible to effectively use the Cu(0)/Cu(II) system for the click reaction of azide-alkyne cycloaddition in the chemistry of chitin and chitosan under aerobic conditions.

Cycloaddition of ketonitrons to nitrile substrates, which is not feasible in the absence of a metal center, is effectively promoted by platinum(II), while ketonitrones are more reactive than the corresponding aldonitrones. The cycloaddition is reversible, and is the first example of reversibility of metal-mediated 1,3-dipolar cycloadditions. This reaction is effectively accelerated by ultrasound and it is a convenient method for introducing the dihydrooxadiazole ring into the chitosan chain.

In all the cases described above, the optimization of acoustic parameters makes it possible to significantly increase the reaction rate (tenfold), achieve high selectivity, and save the integrity of the polysaccharide chain. However, this is not always the case. Thus, for example, we revealed that the metal-promoted 1,3-dipolar cycloaddition of the azide ion to cyanoethyl derivatives of chitosan and chitin is a convenient and effective way to obtain tetrazole derivatives of chitin and chitosan. The most suitable metal centers for promoting this reaction are Zn(II) and Al(III). However, ultrasonic treatment of the reaction mixtures in this case, on the contrary, significantly reduces the product yield.

As a result of the study, it was also established that the interaction of isonitriles coordinated to palladium(II) center with ketonitrones proceeds as nucleophilic oxygenation to give imine-isonitrile palladium(II) complexes. However, in this case, ultrasonic irradiation also does not contribute to this reaction. Based on the complexes obtained using the traditional (without

ultrasound) approach, palladium(II) complexes based on one of the chitin derivatives and its nanoparticles were obtained.

The interaction of chitin with acrylonitrile in a DMAA solution leads to the selective formation of cyanoethyl derivatives of chitin, and in this case, ultrasound is also unsuitable for promoting polymer-analogous transformation.

On the basis of the synthesized highly substituted derivatives of chitin and chitosan we obtained nanoparticles by ionic gelation with sodium tripolyphosphate (TPP). The nanoparticles are characterized by a spherical shape and unimodal size distribution. Thus, particles with a hydrodynamic diameter of about 100, 200, 300, 500, and 800 nm and a positive zeta potential of 18–68 mV were obtained.

This work was supported by RUDN Priority 2030 Program, RFBR (№20-53-04027, №20-316-90026 u №20-53-00009) u BRFR (T20P-375 u X21PM-081), RFBR and Vietnam Foundation №20-53-54006, RFBR №19-016-00077, 19-33-60039 and №20-04-60014.

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Platinum and palladium-based heterometallic carboxylic complexes. New approaches to the synthesis and X-ray synchrotron radiation crystallography studies

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Today, the bimetallic palladium-based carboxylic complexes showed the chemical properties as efficient catalysts for homogeneous hydrogenation of unsaturated hydrocarbons, as well as precursors of supported heterogeneous bimetallic catalysts with improved activity and selectivity. However, single-molecular precursors of the supported catalysts, platinum carboxylates were not available until recently because of inaccessibility and low reactivity of the platinum acetate $[\text{Pt}_4(\text{OOCMe})_8]$, and until recently the iron-containing acetate-bridged complexes with palladium were not known.

In this work, we synthesized and characterized by single crystal XRD more than 30 new homo- and heterometallic acetate complexes of platinum and a number of palladium-based complexes, which were useful precursors of supported catalysts. Three synthetic approaches were suggested, two for platinum-containing species (Fig. 1) based on platinum acetate blue (PAB, $\text{Pt}(\text{OOCMe})_{2.25-2.75}$ [1] and potassium hexahydroxoplatinate (Fig. 2) [2,3].

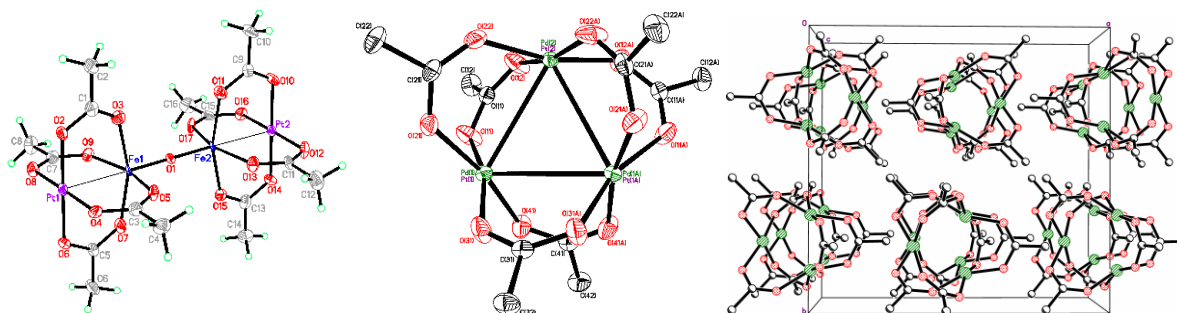


Fig. 1. Molecular structure of Pt(II)-based complexes obtained by reaction of PAB.

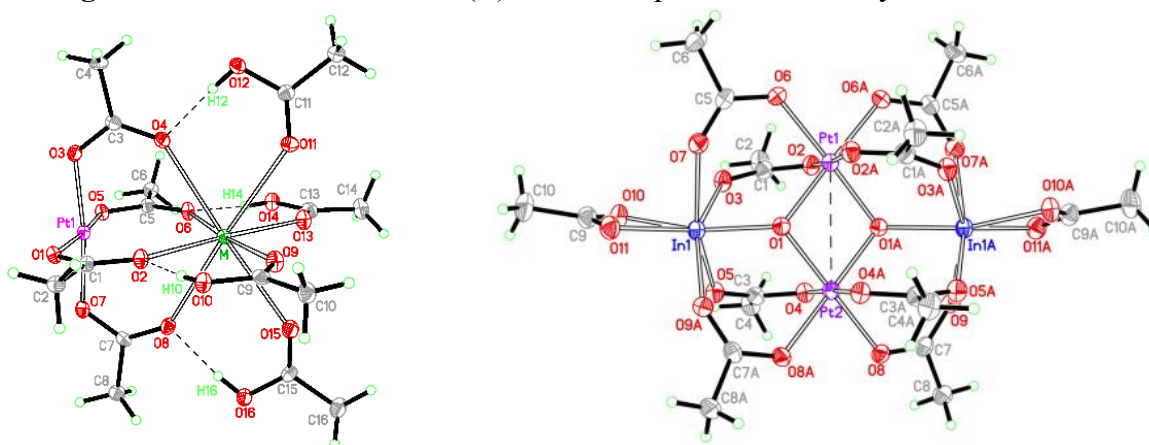


Fig. 2. Molecular structure of Pt(II)-based complexes obtained with using $\text{K}_2[\text{Pt}(\text{OH})_6]$.

The third approach to heterometallic's molecular design in this work consist in using metal-containing carboxylic acids, in particular in using of ferrocenecarboxylic acid as the second metal

source. The developed synthetic methods for bimetallic Pd-Fe systems made it possible to obtain palladium and iron mixed-metal compounds in high yields (Fig. 3).

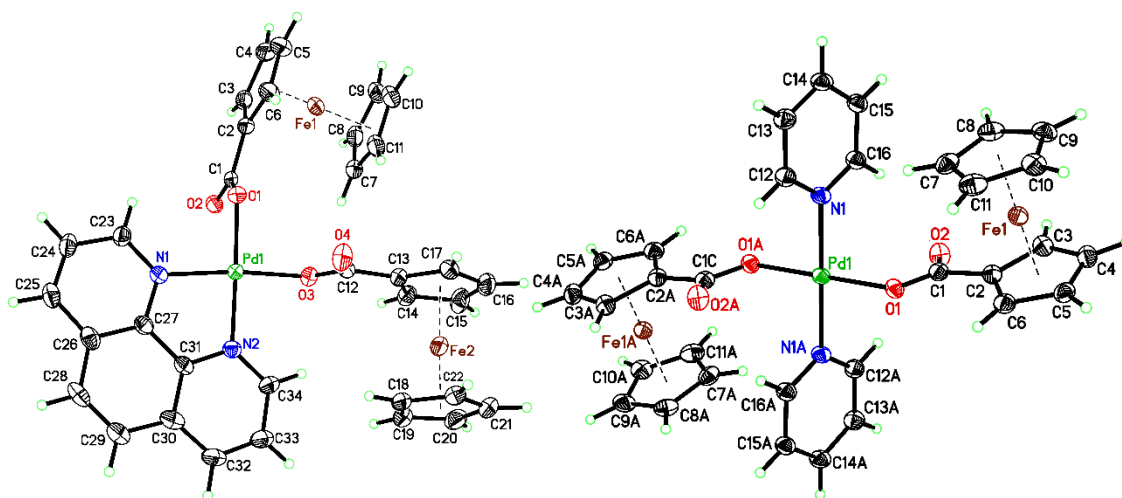


Fig. 3. Molecular structure of Pd-based complexes.

The structures of the complexes were investigated by conventional single-crystal X-ray diffraction technique and also using synchrotron radiation single crystal XRD methods. («Belok» beamline of the specialized source of synchrotron radiation "KISI-Kurchatov", National Research Center «Kurchatov Institute», Moscow, Russian Federation) [4].

This work was supported by the Russian Science Foundation (grant № 18-73-10206).

This research was performed using the equipment of the JRC PMR IGIC RAS.

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Oral Reports

Molecular models for structural insight into TiO₂ phospholipid interactions

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In order to understand better the anchoring interaction between inorganic compounds and biomolecules, single crystals of titanium complexes with boronic acids as well as with phosphoric acids are to be produced in this project. The structural insight from these structures in addition to further investigations with methods such as NMR and MS are planned to lead to molecular dynamics measurements, this to provide semi-quantitative estimations of interaction energies on the surface of living cells.

In our previous work we have used molecular models to understand the mechanism of complexation on the surface of nanomaterials. Ligand grafting and estimation of potential maximal capacity of hybrid organic–inorganic adsorbents bearing phosphonate ligands [1], as well as titanium oxo complexes as models for oxide surfaces are some examples of these type of activities [2].

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Novel supramolecular building blocks based on adducts of 2-pyridylselenenyl halides and nitriles: synthesis and self-assembly study

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Supramolecular chemistry of chalcogen diazoles attracts attention due to its applications in materials chemistry. Chalcogen bonding allows a fine tuning of the self-assembly and, therefore, modulation of physical properties when these compounds are employed. Here we report a facile preparation of the broad scope of 1,2,4-selenadiazoles via coupling of 2-pyridylselenenyl halides with unactivated nitriles with excellent yields (Figure 1).

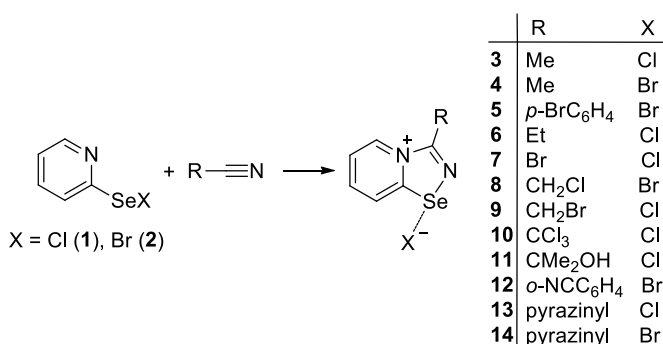
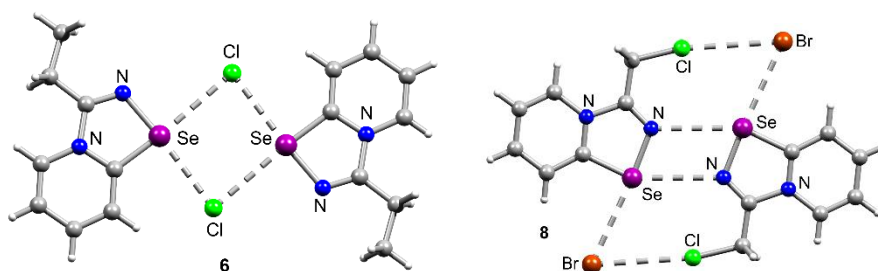


Figure 1. Synthesis of 3–14.

These adducts represent a novel type of supramolecular synthons which eagerly engage in a variety of chalcogen bonding interactions. Some of these novel selenadiazoles can form the four-center Se···N chalcogen bonding. Besides, other weak interactions, which in some cases outcompete the formation of 2Se–2N squares were investigated.



Moreover, the adducts obtained from α -halogenated nitriles can form robust dimers featuring a specific combination of 2Se–2N square, two Hal···Hal and two Se···Hal non-covalent interactions.

This work has been supported by the RUDN University Strategic Academic Leadership Program. Funding for this research was provided by RFBR and BRFR (project number 20-53-00006).

The tetranuclear lanthanide-based silsesquioxanes: synthesis, structure and properties

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Polynuclear compounds based on lanthanide ions are attracting great attention of scientific groups due to their exceptional optical and magnetic properties. The photophysical properties of such compounds are promising for the development of new types of displays, sensors, etc. [1]

We report here the synthesis, structure, luminescence of new cage-like tetranuclear silsesquioxanes Tb^{3+} , Eu^{3+} and $\text{Eu}^{3+} / \text{Tb}^{3+}$ (fig. 1). They present an unusual prism-like topology of cage architectures and lanthanide-characteristic emission, which makes them the first luminescent cage-like lanthanide silsesquioxanes. The mixed $\text{Eu}^{3+} / \text{Tb}^{3+}$ -containing silsesquioxanes were studied as self-regulating temperature sensors based on LIR transitions Tb^{3+} and Eu^{3+} ($^5\text{D}_4 \rightarrow ^7\text{F}_5$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$). The sensor showed excellent linearity over a temperature range of 41-100 °C and a maximum relative thermal sensitivity of 0.63% °C⁻¹ at 68 °C, indicating successful operation. This work opens up great prospects for the creation of a new class of temperature sensors based on cage-like lanthanide silsesquioxanes.

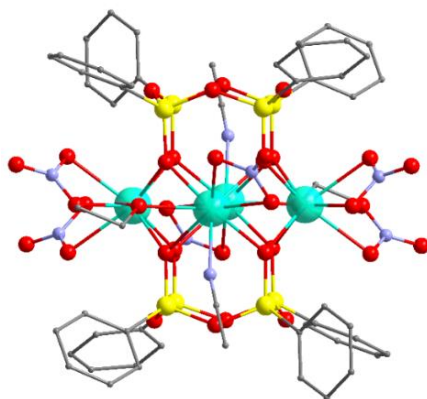


Figure 1. Molecular structure Ln^{3+} -containing silsesquioxanes.

This work was supported by the PRC2287 Premium 2019–2021 program.

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High-resolution powder diffraction with the scanning 2D detector at the «XSA» beamline of Kurchatov synchrotron radiation source

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The use of a two-dimensional position-sensitive detector in a powder diffraction experiment makes it possible to study small (up to $\sim 10\text{-}100\ \mu\text{m}$) samples, methodically eliminating both line asymmetry and intensity distortion at small and very wide diffraction angles. In addition, the registration of complete diffraction rings makes it possible to reduce the influence of coarse grain and texturing on the quality of the obtained diffraction patterns. Together with the design of the optical system of the beamline, which additionally focuses the beam of synchrotron radiation (due to the sagittal bending of the second crystal-monochromator) and significantly increases the photon flux on the sample, this makes it possible to reduce the experiment time by several orders of magnitude and significantly improve the statistics of diffraction patterns, making it possible to estimate very low concentration of impurity phases that are not visible on a laboratory device.

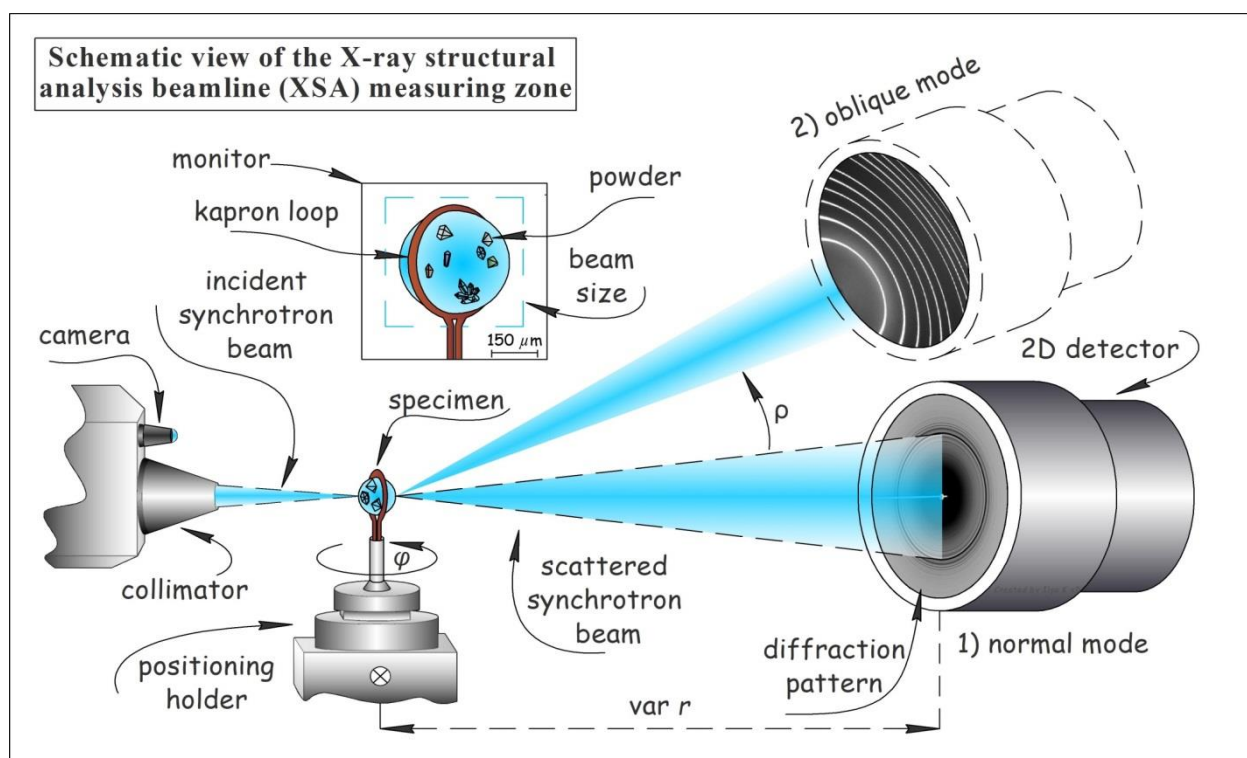


Fig. 1. Schematic view of the powder diffraction experiment at the XSA beamline

The main disadvantage of this approach is the relatively small size of the two-dimensional detector, which leads to a limitation of the angular scale of the diffraction pattern. In case of measurement of good powder samples, it makes sense to measure only part of the diffraction ring (arc) by directing the synchrotron beam towards the bottom of the detector. In this case, it is possible to obtain a larger angular range with the same resolution of the diffraction pattern, or, conversely, a significant improvement in resolution while obtaining the same angular range. At the

"XSA" beamline, this geometry is achieved by rotating a two-dimensional detector around the sample along the 2θ axis.

The maximum tilt angle of the detector is 29.5° , which in the standard experimental mode with the distance between the sample and the detector 150 mm (this value is chosen based on considerations that at maximum tilt the shadow from the direct beam falls on the lowest edge of the detector) provides an angular range of $2\theta = 2 - 56^\circ$. Due to the possibility of varying the distance between the sample and the detector, it is possible to increase the angular range to $\sim 85-87^\circ$, which at the standard used wavelength of incident radiation - 0.74 \AA gives a range for the transmitted vector (q) more than 11.4 \AA^{-1} . For a high-precision experiment with maximum resolution, an experimental mode is implemented with the maximum distance between the sample and the detector, obtained using our diffractometer (380 mm). In this case, the full width at half maximum (FWHM) of the peaks of a standard reference sample LaB_6 NIST SRM 660a, placed in a capillary with a diameter of $300 \text{ }\mu\text{m}$ and a beam size of $400 \times 400 \text{ }\mu\text{m}$, gives a value of 0.039° , which is practically the maximum realizable resolution for diffraction experiments with a two-dimensional detector. A further decrease in the instrumental contribution to the broadening of reflections is possible only when using analyzer crystals. Diffraction experiments with this resolution make it possible to clearly separate closely spaced peaks, which is extremely important for accurate determination of the crystal space group and for the highest quality phase and structural analysis.

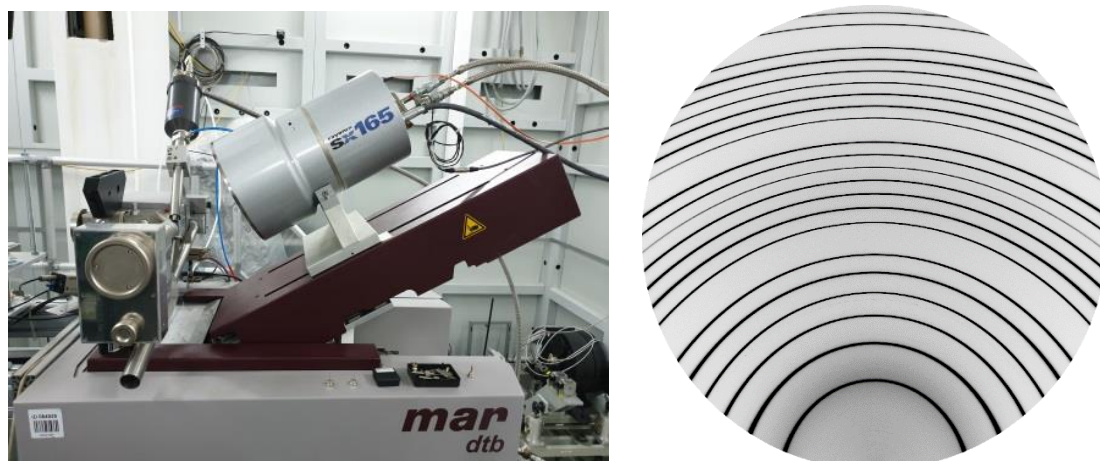


Fig. 2. Diffractometer of the "XSA" beamline in an oblique geometry experiment and an example of the obtained two-dimensional diffraction pattern

Beamline characteristics:

- an angular range of up to 85° in 2θ ($q = 11.4 \text{ \AA}^{-1}$ at standard wavelength of 0.74 \AA and up to 23 \AA^{-1} at highest photon energy)
- instrumental contribution to the peak broadening from 0.039°
- operating temperature range $80-480 \text{ K}$
- the accuracy of determining the intensities of the Bragg peaks of the standard – 0.5%
- the range of recorded intensities of the Bragg peaks – $I_{\text{max}}/I_{\text{min}} = 10^4$

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Crystal structure of low-melting organoelement compounds

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Establishing the crystal structure is the most reliable way to establish the structure of a substance. The most popular and accessible method for establishing the crystal structure is X-ray diffraction analysis. X-ray structural analysis has a number of requirements for the sample under study. One of these requirements is usually the physical and chemical stability of the crystalline phase at room temperature. Crystalline phases of low-melting compounds are thermodynamically unstable at temperatures above the melting point. It is the study of the structure of low-melting organic element compounds that is the purpose of this work.

To achieve this goal, we mastered, and later modified, the method of crystal growth in situ. This technique consists in the growth of a crystal in a thin-walled capillary mounted on the head-holder of the diffractometer. For crystal growth, the zone melting method is used, which is performed either by pushing out a part of the capillary from the flow of cold nitrogen (the diffractometer cooling system), or by a third-party heating element (nichrome filament, focused light or IR laser).

We have developed and constructed an in situ crystallization unit and written control software. Studies have shown that zone melting is excellent for crystallizing low viscosity compounds, but for highly viscous compounds, this approach usually results in sample amorphization. For viscous compounds, a separate in situ crystallization procedure has been developed. It consists in carrying out non-equilibrium crystallization: namely, crystal growth occurs in a rotating capillary.

On the basis of 56 crystal structures of organoelement compounds from the literature, crystallized in situ, many dependences were considered based on the melting temperature, the size and shape of the molecular Hirschfeld surfaces in the crystal, as well as the nature and forces of intermolecular interactions [1]. As a result, the features inherent in compounds with a low melting point, forming crystalline phases, were revealed, for example, the possibility of separating compounds into groups based on the ratio of the melting point to the energy of the crystal lattice (Fig. 1).

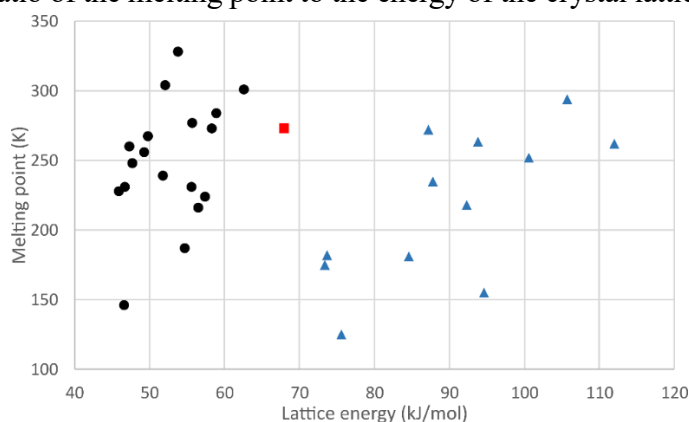


Figure 1. Graph of the dependence of the melting temperature on the energy of the crystal lattice. Allows you to divide the connections into two groups (black dots and blue triangles). Also shown is a compound that does not obey this division (red square).

The structure of the crystalline phases of 15 organoelement compounds was established

using the in situ crystallization method (Fig. 2). For octamethylcyclotetrasiloxane (D4), a crystal-crystal phase transition mechanism was proposed. This phase transition belongs to the "shift" type, and during the phase transition the molecules assume an almost flat conformation (6-7 atoms of the 8-membered ring lie in the same plane). For bromodifluoromethyltrimethylsilane, the activation energies of dissociation were calculated, as well as the reaction paths for obtaining difluorocarbene with and without Lewis base (HMPA) [2].

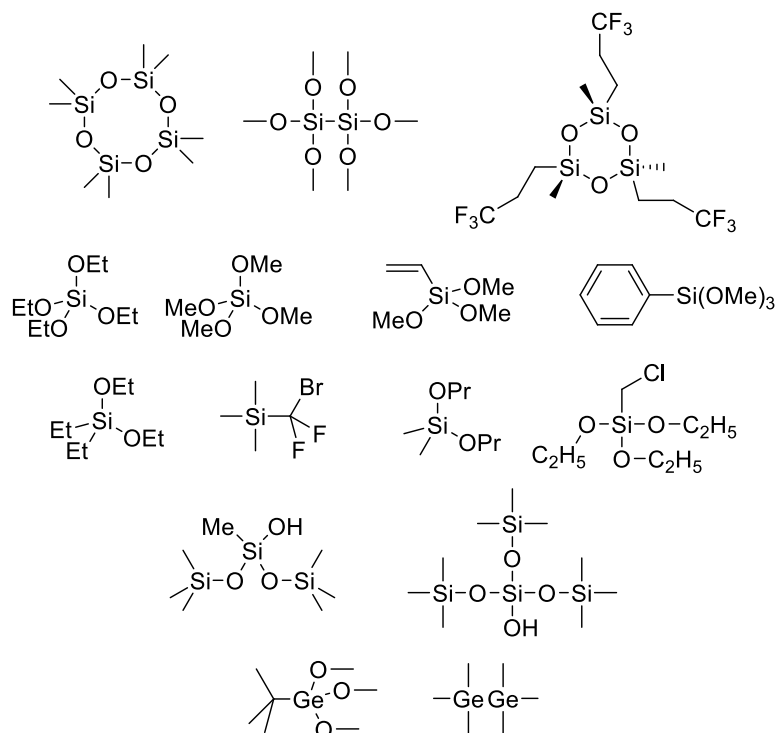


Figure 2. Compounds identified using the in situ crystallization technique.

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Salts of nucleobases and alkali metals: preparation and structural study at broad range of T, P

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High pressure is a powerful tool to study experimentally the response of selected hydrogen bonds to mechanical stress. Cooling is an alternative method to compress a structure. A comparison of compression on cooling and increasing pressure gives an insight into intermolecular interactions. Crystals made of small RNA or DNA fragments can serve as models of the effect of pressure on nucleic acids and oligonucleotides, similar to how the crystals of amino acids are used to model proteins. Crystal structures containing guanine, metal ions and water molecules can also be used, to shed more light on the interactions between the guanine anions, metal cations and water molecules. Potassium cations are of special biological importance because they form natural quadruplexes, which are present in telomeric parts of the chromosome.

The crystals of two salts of guanine were obtained and investigated by single-crystal X-ray diffraction at broad range of temperature and pressure, namely, $2\text{Na}^+ \cdot \text{C}_5\text{H}_3\text{N}_5\text{O}^{2-} \cdot 7\text{H}_2\text{O}$ (100 K - 300 K; 1 atm- 2.5 GPa [1]) and $\text{K}^+ \cdot \text{C}_5\text{H}_4\text{N}_5\text{O}^- \cdot \text{H}_2\text{O}$ (100 K - 300 K). The cation coordination, the tautomeric form of the guanine anions, as well as the role of water molecules in the crystal structure are different for the two salt hydrates. In the potassium salt hydrate, there are two tautomeric forms of guanine anions and two types of potassium ions with different coordination. It is interesting to note, that though no “true” guanine quadruplexes could be found in the crystal structure of the potassium salt of guanine hydrate the “quartets” of guanine connected via hydrogen bonds with each other and two water molecules are present in this crystal structure. ThetaToTensor software was used to calculate the coefficients of thermal expansion tensor and create a graphical representation of the characteristic surface [2]. The anisotropy of strain on temperature variation was compared for the two salt hydrates, the similarities and the differences are discussed concerning the intermolecular interactions [3].

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The influence of experimental setup on the thermal expansion of glycinium phosphite

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The ferroelectric phase transition at 225 K in single crystals of glycinium phosphite has been confirmed experimentally in the literature by a wide range of different methods. However, the structural data obtained by single crystal X-ray diffraction in a wide temperature range (87 - 265 K) in order to characterize the structural changes during the phase transition were presented for the first time. Two separated series of experiments were carried out using synchrotron radiation at the Swiss-Norwegian BM01A line of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and also by a similar experiment with a laboratory STOE IPDS X-ray diffractometer. The obtained results are drastically different for synchrotron and laboratory data (Fig. 1). The data collected with synchrotron beam show an abnormal non-linear increase in volume on cooling whereas laboratory data confirm the overall structure compression upon cooling. We link the resulting difference in structural data to a radiation damage accumulated during consecutive data collections. The increase in volume as a result of radiation damage to the sample compensates for the compression of the structure upon cooling in such a way that the total change in volume remains positive [1].

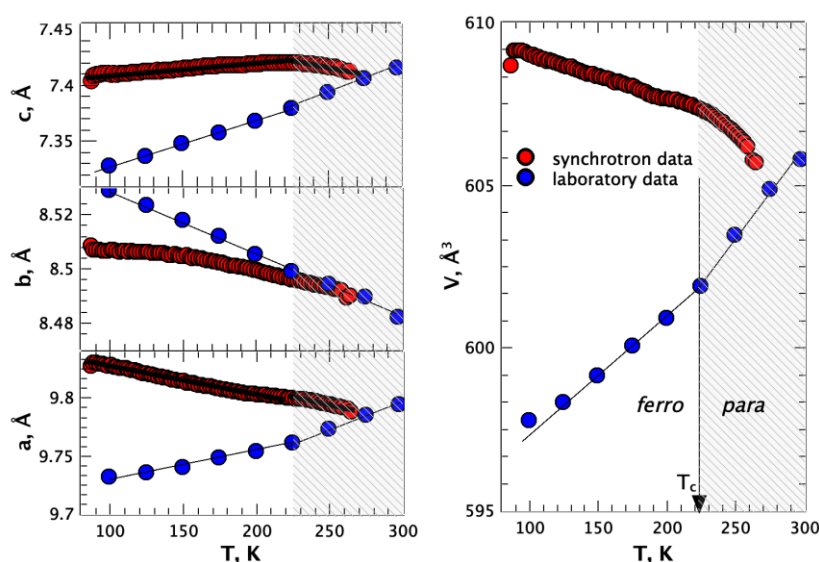


Figure 1. The unit cell parameters and volume vs. temperature from the synchrotron and laboratory data, the error bars are smaller than the symbols. Shaded zone indicates the temperature domain for the paraelectric phase.

Radiation damage of GPI results in a significant volume increase, but does not prevent the temperature induced phase transition from paraelectric to ferroelectric state. It does, however,

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affect the temperature dependence of the lattice constants and static disorder of the entire molecular structure. The radiation damage may therefore be considered not only as a negative effect reducing the resolution power of the diffraction experiment, but also as a tool to prepare an organic ferroelectric in the polar state with enlarged volume and potentially new properties [2].

The laboratory experiments were carried out using the equipment of Research and Education Center "Molecular design and ecologically safe technologies" (NSU). NEB, BAZ, EVB acknowledge support by the Ministry of Science and Higher Education of Russia; the project was carried out jointly by Boreskov Institute of Catalysis (governmental order AAAA-A21-121011390011-4) and Novosibirsk State University.

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The crystal structure elucidation of a tetrapeptide analogue of somatostatin DOTA-Phe-D-Trp-Lys-Thr-OMe

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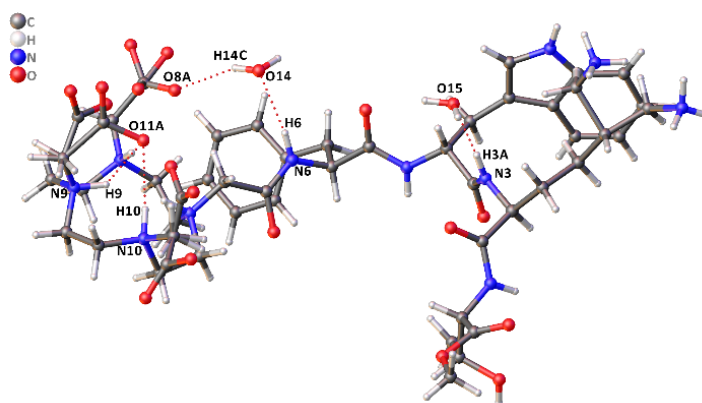
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Herewith, we report for the very first time the crystal structure of tetrapeptide FwKT (Phe-D-Trp-Lys-Thr), which is considered to represent an epitope for biomedically relevant hormone somatostatin. This peptide is interesting because all drugs based on somatostatin analogs have been developed on the basis of its pharmacophore sequence Phe-Trp-Lys-Thr which is responsible for their binding to somatostatin receptors (sstr), the overexpression of which is observed in tumor cells.

The target molecule was successfully crystallized, solved and refined as a conjugate of the tetrapeptide moiety bearing a protective group DOTA (1,4,7,10-tetraazacyclododecane - 1,4,7,10-tetraacetic acid) at the N-terminus and methylated at the O-terminus. The combination of a hormone active site and a powerful chelator make the substance a highly prospective targeted drug delivery system.



The conjugate was synthesized according to the previously described method [1]. The tetrapeptide was crystallized by the “hanging drop” vapor diffusion method in 24-well plates. The crystals were needle-shaped, 30 x 100 x 200 μm in size. Single-crystal diffraction datasets were acquired at the BELOK beamline of the Kurchatov Synchrotron Radiation Source (NRC “Kurchatov Institute”, Moscow) under 100(2) K [2]. The frames were indexed, integrated and scaled, the apparent resolution is 0.78 Å, $R_{int} = 15.8\%$.

The structure was solved in $P4_32_12$ space group ($a = 20.335$ (3), $c = 27.105$ (5) Å) by the intrinsic phasing modification of direct methods and refined by the full-matrix least-squares refinement against F^2 . The positions of two water molecules were determined unambiguously in difference Fourier maps. The remaining hydrate water molecules were strongly disordered and

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couldn't be localized and refined using difference Fourier maps. They were taken into account in the refinement procedure using the Solvate Mask function of OLEX2 [3]. The Solvent Mask procedure identified the total volume of solvent accessible voids of 3269 Å³ and 520 e⁻ per unit cell, which amounts approximately 29% of the unit cell volume. The final estimate for hydrate water content was approximately 8.5 molecules per tetrapeptide molecule. The figure shows the tetrapeptide model, the quality parameters of the model: $R1 = 9.6$ and $wR = 19.8\%$.

The search for structures containing the FwKT sequence was carried out using the CCDC [4] and PDB [5] databases. The structure data were found for 6 somatostatin analogues, which were the octreotides: 2 in CCDC [6, 7], 4 in PDB [8-10]. Only 3 of them [6-8] were determined by X-ray diffraction analysis, the rest were determined by NMR. The sequences of the remaining somatostatin analogues didn't contain the FwKT sequence. Thus, the somatostatin analogue consisting of four amino acid residues FwKT was successfully crystallized, its crystal structure was solved, refined and described at this work for the first time.

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Structure investigation of bismuth-containing binary apatite system

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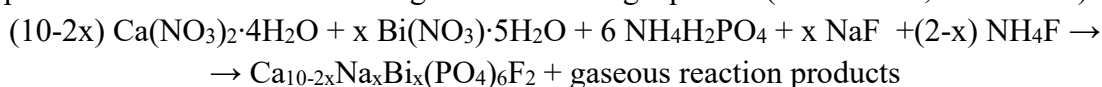
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The progressive loss of bone mineral density leads to changes in bone architecture and an increased likelihood of fractures. Unfortunately, the human body has only a limited ability to auto-regenerate its main tissues and organs in the case when the integrity of the tissue has been deeply disturbed. Because of this, there is a need for materials with stimulating properties that can enhance tissue regeneration and are the next generation of biomaterials. Despite the emergence of new types of implants, along with the increase in the number of operations, the number of complications after them, in particular the appearance of infection, also increases. The best solution to the problem is to prevent infection, not cure it. This can be achieved by imparting antibacterial properties to bioceramic materials, for example, by isomorphic incorporation of bismuth ions into the apatite matrix.

Samples of the composition $\text{Ca}_{10-2x}\text{Bi}_x\text{Na}_x(\text{PO}_4)_6\text{F}_2$ ($x = 1, 2, 3, 4, 5$) were prepared by the solid-phase reaction method according to the following equation ($T = 1223 \text{ K}$, $t = 8 \text{ hours}$):



An analysis of the dependences of the parameters of the unit cells allows us to conclude that they have insignificant positive deviations from the Vegard and Retgers rules, which indicates a lower strength of chemical bonds in solid solutions in comparison with the extreme terms of the considered series of solid solutions - $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and $\text{Bi}_5\text{Na}_5(\text{PO}_4)_6\text{F}_2$.

The ratios of the cations of calcium, sodium, bismuth and phosphate ions in the obtained compounds for further refinement by the crystalline Rietveld method based on powder X-ray diffraction data. the structures were established using probe microanalysis.

Table 1. Some results of refinement of the crystal structure of compounds with the composition $\text{Ca}_{10-2x}\text{Na}_x\text{Bi}_x(\text{PO}_4)_6\text{F}_2$ ($x = 1,2,3,4,5$)

Composition (theory)	Na_5Bi_5	$\text{Ca}_2\text{Na}_4\text{Bi}_4$	$\text{Ca}_4\text{Na}_3\text{Bi}_3$	$\text{Ca}_6\text{Na}_2\text{Bi}_2$	Ca_8NaBi
Composition (real)	$\text{Na}_{4.4}\text{Bi}_{5.6}$	$\text{Ca}_{1.9}\text{Na}_{4.0}\text{Bi}_{3.9}$	$\text{Ca}_{3.9}\text{Na}_{3.0}\text{Bi}_{3.0}$	$\text{Ca}_{5.8}\text{Na}_{2.0}\text{Bi}_{1.9}$	$\text{Ca}_{7.8}\text{Na}_{0.9}\text{Bi}_{1.0}$
R-Bragg (%)	4,354	8,975	4,078	4,688	5,940
a (Å)	9,48866(32)	9,49099(39)	9,46909(21)	9,43303(26)	9,39000(22)
c (Å)	7,00083(26)	6,98414(34)	6,95860(19)	6,93606(20)	6,90159(18)
V (Å ³)	545,871(43)	544,837(52)	540,343(28)	534,497(34)	527,000(28)

The crystal structure of apatite is characterized by two cationic positions $4f$ and $6h$, which differ in the multiplicity and symmetry of the cation polyhedra, which are located in them (Fig.1).

In the compounds under study, calcium, bismuth, and sodium ions are distributed between these positions for cations. The refinement of the structure showed that the bismuth atoms are located predominantly in the tunneling position of the $6h$ structure, which is characterized by lower coordination numbers (7) compared to the $4f$ position (9), which is more typical for bismuth. Moreover, an increase in sodium content enhances the localization of bismuth ions.

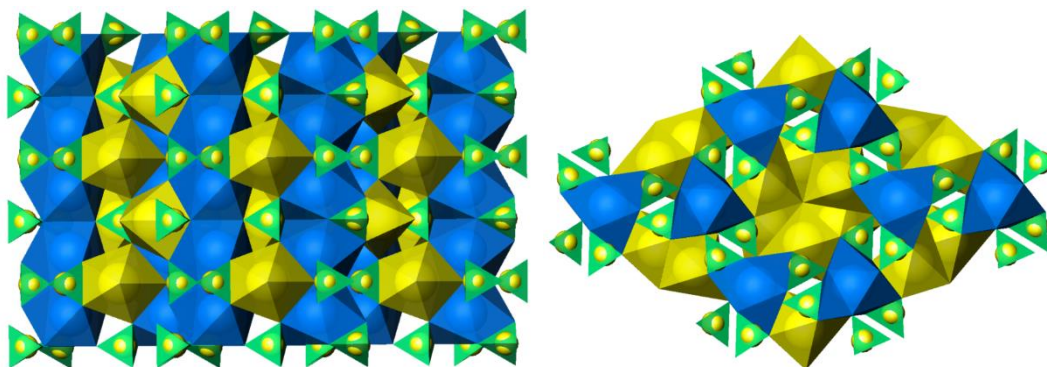


Figure 1. Crystal structure of $\text{Ca}_{10-2x}\text{Bi}_x\text{Na}_x(\text{PO}_4)_6\text{F}_2$ compounds (yellow polyhedra – atoms in $6h$ position, blue polyhedra – atoms in $4f$ position, green polyhedra – PO_4 groups) along a -axis (left) and along c -axis (right).

Since the obtained compounds are considered as potential materials for the manufacture of bioceramics, we conducted studies of their cytotoxicity. To assess the cytotoxicity of solid solutions ($x = 1, 2, 3, 4$), a standard MTT test was used. As a test culture, a culture of human dermal fibroblasts of 4-5 passages was used. The results showed the absence of cytotoxicity in all samples at extraction times of 1 and 7 days. In addition, for samples $x = 1$ and 2, an increased relative intensity of cell growth was observed, which can be associated with the localization of bismuth in the position $6h$, which is more acceptable from the point of view of the coordination capabilities of the atom, whereas for compositions $x = 3$ and 4, the level of intensity of cell growth can be preserved. be associated with the washing out of bismuth from position $4f$.

Distribution of electron density in luminescent and magnetic coordination compounds. Molecular and crystal invariom approaches

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Organic derivatives of lanthanides (Ln) find their application as luminophores [1], magnetic materials [2], and also as catalysts for various processes [3]. The replacement of hydrogen atoms in the ligand with fluorine leads to an improvement in the luminescent properties of the complexes [4]. As a result, understudied interactions with the participation of fluorine atoms (F...F, C-F→Ln) can be realized in the complexes [5]. Therefore, the study of the electronic structure of such compounds is of certain scientific interest. Obtaining rare-earth crystals for precision X-ray structural analysis is a difficult task. An alternative to carry out a precision X-ray structural analysis is quantum chemical calculations or an experimental-theoretical invariom approach [6]. For organometallic and coordination compounds, it is more convenient to use the whole-molecule aspherical scattering factor (molecular invariom) [7].

We have selected the optimal procedure for calculating molecular invarioms for complexes of lanthanides with fluorinated ligands (single point calculation, B3LYP/dzp[8] functional/basis set, strategy that takes into account simultaneously the valence f- and s-electrons of the ytterbium atom). A complex of divalent ytterbium with perfluorinated 2-mercaptobenzothiazolate ligands ($\text{Yb}^{2+}(\text{mbt}^{\text{F}})_2(\text{DME})_2$) was chosen as a model system (Fig. 1).

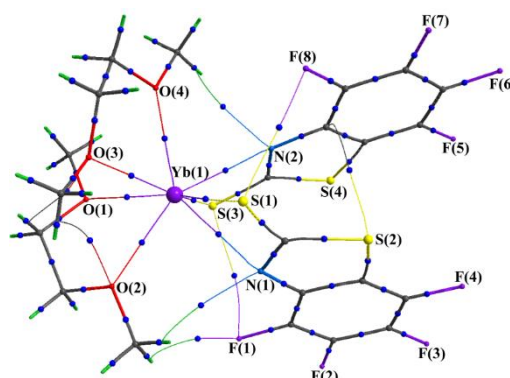


Fig. 1. Molecular graph of complex $\text{Yb}^{2+}(\text{mbt}^{\text{F}})_2(\text{DME})_2$.

According to the chosen strategy, 5 molecular invarioms of dimeric complexes of lanthanides with hexafluoroisopropoxide ligands $\{\text{Ln}^{3+}_2(\mu_2\text{-OCH}(\text{CF}_3)_2)_2(\text{OCH}(\text{CF}_3)_2)_4(\text{Sol})_2\}$ (Ln = Ce, Sm, Tm, Yb; Sol = DME or Phen) were obtained. For all studied compounds, good convergence was observed in the values of the main topological characteristics of electron density (ED) when compared with the DFT calculations.

Note that even the obtaining of crystals, the quality of which is suitable for precision X-ray diffraction analysis, does not guarantee obtaining information on the topology of the electron density. The experience of conducting such experiments shows that for complexes of atoms with atomic numbers >50 , during refinement, a high residual density is often observed without any chemical sense. As a result, the electronic parameters of the metal atoms (P_{val} , P_{lm} , k , k') in the multipole refinement may assume unrealistic values and the topological characteristics of the ED in the coordination sphere of a metal atom may be incorrect. We have compared the topological characteristics of the ED in the coordination sphere of the metal atom of complex $[\text{Tb}(\text{Tpm})\text{Cl}_3] \cdot 2\text{MeCN}$; Tpm = tris(3,5-dimethyl-pyrazolyl)methane, Fig. 2), obtained in a

precision experiment and experimentally-theoretically.

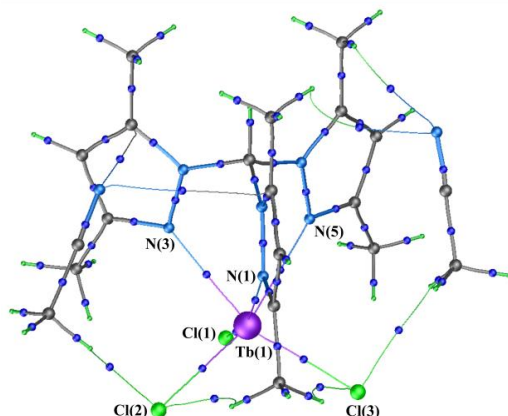


Fig. 2. Molecular graph of complex $[\text{Tb}(\text{Tpm})\text{Cl}_3]\cdot 2\text{MeCN}$.

The atomic invariom of terbium was calculated using the CRYSTAL14 program [9] taking into account the crystal packing of the complex. The replacement of the experimental electron density by the theoretical one on the terbium atom has no the significant effect on the topological characteristics of the ED in the coordination sphere and the intermolecular interactions energy.

Thus, the use of an invariom approach can be a good solution for investigation the distribution of electron density in complexes for which a precision experiment is impossible or leads to an abnormally high residual density.

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Computer Modeling in Chemistry: Reactivity and Non-Covalent Interactions

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I am a computational chemist and have a lot of experience in application of advanced quantum chemical methods as well as some special techniques (e.g., QTAIM, NCI, NBO, CDA, HSAB principle theoretical model, Hirshfeld surface analysis, etc.). Previously, I was involved in studies of catalytic reactions and organic transformations assisted by metal complexes, e.g. oxidation of hydrocarbons, nucleophilic addition and cycloaddition processes (mechanisms, driving forces, kinetics and thermodynamics), as well as properties of coordination and organometallic compounds (e.g. conformational isomerism and rotational barriers, properties of chemical bonds, orbital and charge factors). My current research interests are mainly focused on supramolecular chemistry (in particular, involving coordination and organometallic compounds) and theoretical studies of unusual non-covalent interactions (e.g., hydrogen, halogen and chalcogen bonding, stacking, anagostic and metallophilic interactions, etc.). The obtained results are potentially useful for biochemistry, medicine, and chemical industry/technology.

In this report, I will focus on discussing some of the results of my research in 2018-2021. For some recent representative publication, see [1–10].

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Novel heterocyclic chitosan derivatives and their derived nanoparticles

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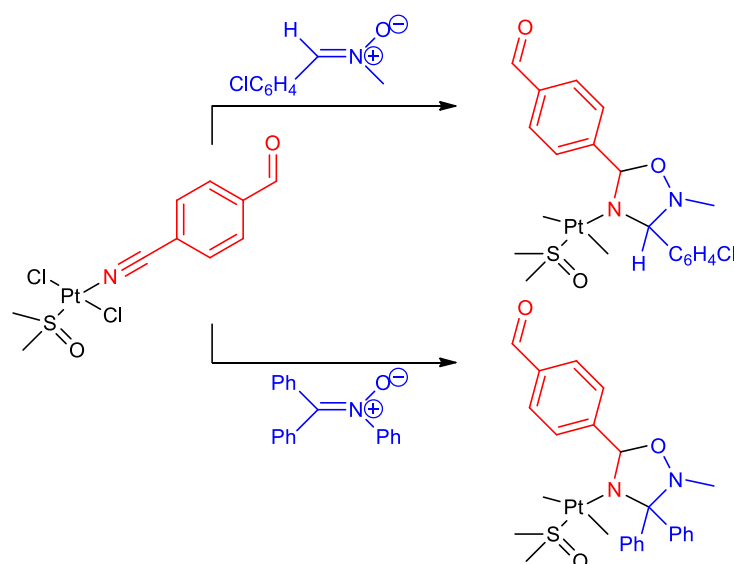
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Heterocyclic chitosan derivatives are of increasing interest since grafting of a heterocyclic moiety to the chitosan chain provides new attractive mechanical, physicochemical, and biological properties of the polymer formed [1,2].

Preparation of heterocyclic chitosan derivatives directly with native chitosan matrix via the [3 + 2] cycloaddition is an attractive synthetic route and it is well developed especially for the synthesis of triazole chitosan derivatives by Cu(I) catalyzed click cycloaddition involving azido (or alkyne) chitosan derivatives and alkynes (or azides). Meanwhile, nitrile chitosan derivatives are much less studied in their polymer [3+2] cycloaddition, and the scarce examples available in the literature have been focused so far only on the preparation of tetrazole heterocyclic chitosan derivatives via the [3+2] cycloaddition between nitrile chitosan derivatives and sodium azide.

We intended to adapt the Pt(II)-mediated and ultrasound-assisted cycloaddition of nitrones to a C`N function of nitrile chitosan derivatives into chitosan chemistry. The scenario of this work was thus as follows: a) to study the activation effect of ultrasound on model Pt(II)-mediated cycloaddition of nitrones $\text{ClC}_6\text{H}_4\text{C}=\text{N}(\text{O})\text{CH}_3$ and $\text{Ph}_2\text{C}=\text{N}(\text{O})\text{Ph}$ to nitrile ligands in the complex $[\text{PtCl}_2(\text{HOCC}_6\text{H}_4\text{CN})(\text{DMSO})]$; b) to synthesize a nitrile chitosan derivative and its Pt(II) complexes with the coordinated nitrile group to involve it in the ultrasound-assisted Pt(II)-mediated cycloaddition with nitrones; c) to study antibacterial and catalytic activity of the obtained new heterocyclic chitosan derivatives and their derived nanoparticles in the monoglyceride synthesis via the epoxide ring opening.



This work demonstrated that ultrasonic irradiation (80 kHz and 250W) efficiently accelerates Pt(II)-mediated cycloaddition of nitrones to nitrile chitosan derivatives affording new heterocyclic (1,2,4-oxadiazoline) chitosan derivatives and avoiding ultrasonic degradation of the chitosan backbone. Involvement of aldonitrones in this reaction furnishes in water-soluble chitosan derivatives, while the cycloaddition ketonitrones leads to toluene-soluble polymers. Water-soluble chitosan derivatives and their nanoparticles possess high antibacterial activity coupled with low toxicity.

The reported study was funded by RFBR (project number 19-33-60039)

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Structural studies of chitosan and its composites with iron(II) hydroxide and sulfate

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Chitosan is a promising material for the manufacture of edible films and medicine, but this biopolymer has a low solubility and brittleness, so there is a need of chemical modification of chitosan for the creation on its basis of the composites with novel properties [1].

In this work, we studied the initial samples of chitosan and composites based on it with iron (II) hydroxide and sulfate, as well as samples of the same materials subjected to various types of treatment: ultrasound, low temperature, followed by defrosting and microwave activation.

X-ray phase analysis of chitosan samples was performed on an automatic X-ray diffractometer for polycrystalline materials DRON-7 in the step-by-step scanning mode using copper radiation. Some diffractograms of the studied samples are shown in Fig. 1-2.

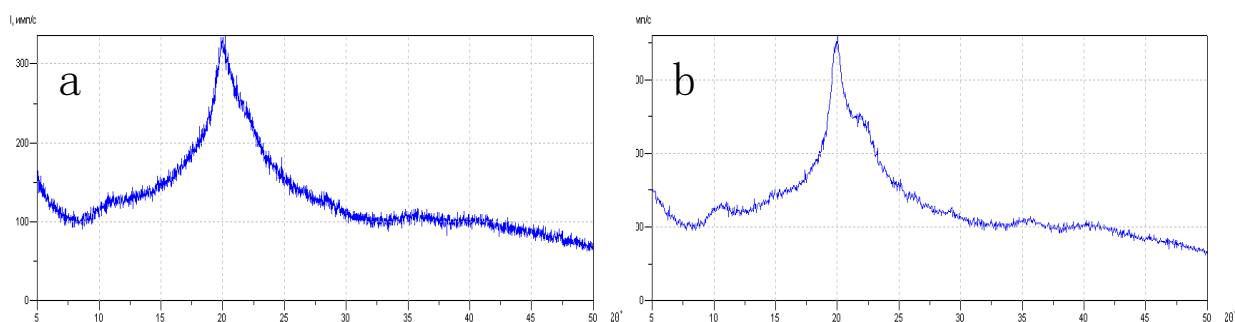


Figure 1. Diffractograms of the initial chitosan sample (a) and the chitosan sample after microwave activation (b).

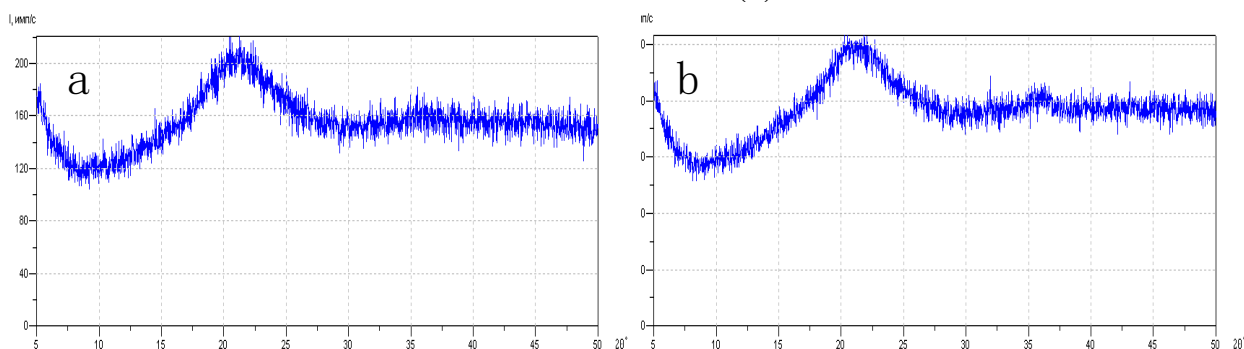


Figure 2. Diffractograms of the initial sample of a chitosan composite with iron (II) sulfate and a sample of a chitosan composite with iron (II) sulfate after microwave activation.

The profiles of single diffraction reflections of hkl samples are studied. The parameters of the elementary cells are calculated.

With the help of profile analysis, the average sizes of OCD and the values of microdeformations in the studied samples were calculated. The influence of the effects on the microstructure of samples of chitosan and its complexes with iron (II) hydroxide and sulfate was found.

It is shown that the processing of samples after exposure to various temperatures and microwave activation leads to an improvement in the crystal structure. Treatment in a microwave reactor has the most noticeable effect on improving the structure of chitosan. Ultrasonic treatment leads to some deterioration of the crystal structure of chitosan. Similar changes occur in chitosan composites with iron (II) hydroxide and sulfate. The crystal structure of chitosan composites with iron (II) hydroxide and sulfate is best improved by microwave activation and low temperature exposure to samples with subsequent defrosting. Ultrasound treatment somewhat worsens the structure of composites.

Synthesis and structural investigation of new aryl- and heteroaryl gold(I) isocyanide complexes

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Recently, isocyanide gold (I) complexes excite extremely interest due to the wide possibilities of their potential application. For example, solid compounds whose properties depend on mechanical stimulation represent an interesting class of "smart" materials: recording and storage devices, sensors, probes [1]. Also, isocyanide gold (I) complexes are of particular interest for the study of their use for catalytic purposes.

Here we present a facile and efficient method for the preparation of gold(I) isocyanide compounds in high yields under mild conditions. In previous works, similar isocyanide gold complexes were prepared from organometallic Mg [1] or Li [2] precursors under inert atmosphere and subzero temperatures. Here we describe a more convenient procedure: all reactions were performed at room temperature under air. In most cases, target gold(I) isocyanide complex was easily isolated by slow crystallization in excellent yields (Figure 1).

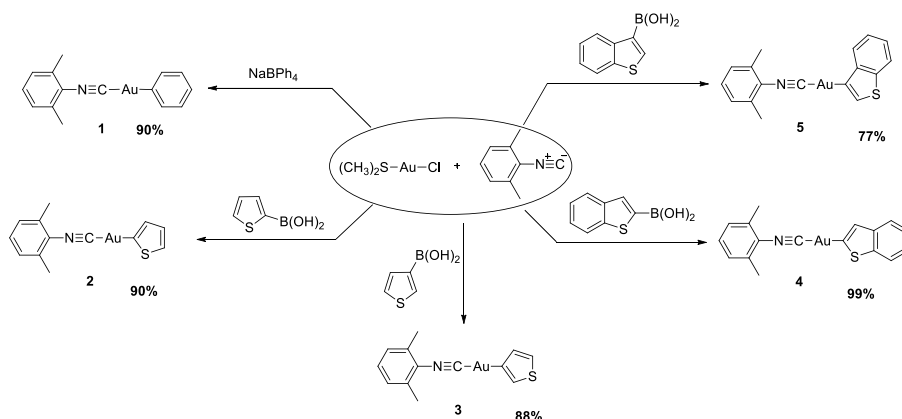


Figure 1. Preparation of gold(I) isocyanide complexes.

Novel approach allowed us to prepare several new aryl- and heteroaryl gold(I) isocyanide complexes. Interestingly, the latter organogold(I) isocyanide complexes were found to exist in several polymorphic modifications in the solid state. Crystallization of complexes under various conditions afforded different polymorphs. Self-assembly in the solid state was driven by the aurophilic interactions between gold(I) centers. Besides, $\text{Au}\cdots\text{S}$ contacts in isocyanide gold (I) complexes with 2-thiophenyl and 2-benzothiophenyl fragment promote increase of the nuclearity of clusters in the solid state.

This work was supported by the Russian Foundation for Basic Research (project number 20-53-00006) and Belarusian Foundation for Fundamental Research (grant X20P-066). Funding for this research was provided by Ministry of Science and Higher Education of the Russian Federation (award no. 075-03-2020-223 (FSSF-2020-0017)) and the RUDN University Strategic Academic Leadership Program.

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Features of supramolecular organization in the crystals of benzimidazolone derivatives

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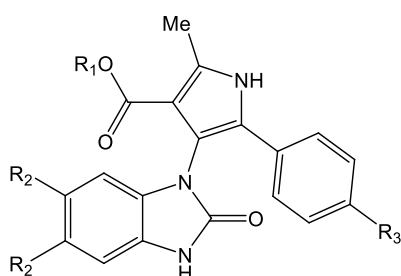
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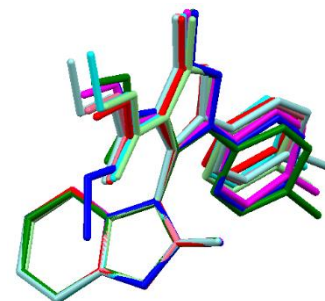
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The establishment of correlations between the molecular structure of organic compounds, the nature of intermolecular interactions, the supramolecular structures in crystals, and the properties of materials expands opportunities for the directed design of new compounds with desired physicochemical properties. Recently we established the empirical correlations between the supramolecular structure and its orientation in the crystals of terminal ethers of glycerol and benzodiazepines derivatives [1-2] which suggest that 1D and 2D- supramolecular structures preferably oriented along the shortest parameters of the unit cell.

In this work we attempted to expand this approach to the supramolecular structure analysis of heterocyclic compounds of another type. The results of X-ray analysis of a series of synthesized N-(pyrrol-3yl)benzimidazolone derivatives containing additional aromatic fragments and several proton-donor and proton-acceptor groups are presented [3].



	R1	R2	R3
1	Me	H	H
2	Me	H	F
3	Me	H	Cl
4	Et	H	Cl
5	Et	Me	H



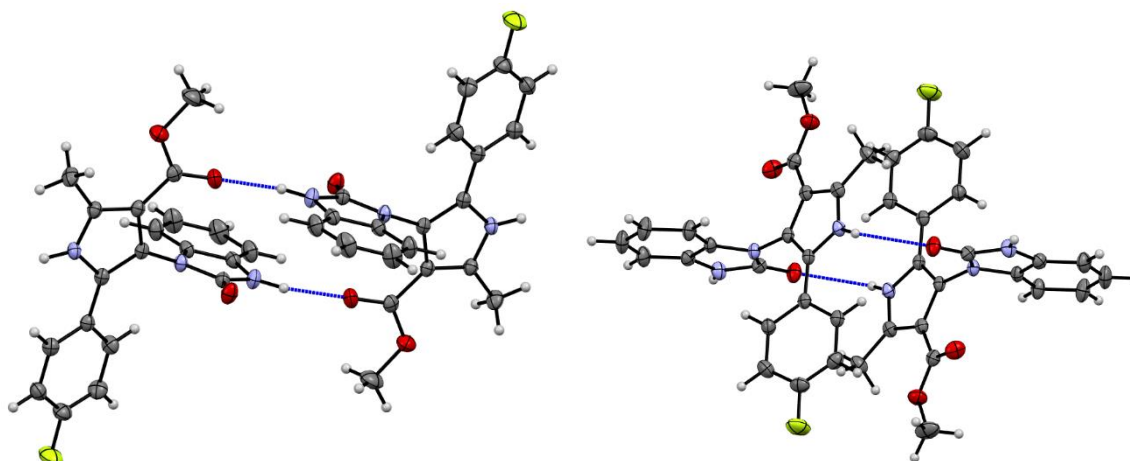
According to the X-ray analysis the main molecule skeleton is not subject to changes in the crystals. It was showed that the differences in the geometry of the molecules of the studied compounds are associated only with different relative position of pyrrole substituent and benzimidazolone system.

Despite the several proton-donor and proton-acceptor centers, the realization of the same types of primary supramolecular structures could be pointed out in the crystals. For this series of compounds realises two types of centrosymmetric dimers. The first type H-dimer with participation the hydrogen atom of pyrrole cycle is observed for compounds 1–4. The second type dimer with participation in H-bonding the hydrogen atom of benzimidazolone system is observed for compound 2, 5. It should be noted that crystallization with the solvent molecule (in the case of compound 2, acetic acid in the ratio 1:1) does not prevent the formation of such dimers in crystal.

Analysis of the supramolecular structure within the framework of the proposed approach shows that the realization of classical hydrogen bonds in the crystals of majority studied compounds leads to the binding of primary H-synthons into supramolecular structures, the

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orientation of which obeys this empirical rule. But, the dimensionality of supramolecular structures formed by the classical hydrogen bonds N–H...O depends on the number of independent molecules (Z') in the unit cell. In the case of crystallization with two independent molecules ($Z'= 2$) the supramolecular structure is represented by infinite layers. During reduction of the number of independent molecules to $Z'= 1$ the basic supramolecular structure is a stack of H-bonded molecules, but oriented along the lowest parameter of the unit cell. The conditions of realization of empirical correlation in the crystals of investigated benzimidazoles are explained basing on the calculation of the energy of various types of interactions.



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Palladium-based reagents for protein bioconjugation

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Existing methods for covalent conjugation of proteins have several synthetic limitations and the resulting conjugates often demonstrate limited stability.

We show that palladium complexes with dialkylbiaryl phosphine ligands can be used as stable reagents for highly selective arylation of biomolecules of varying complexity under biocompatible reaction conditions.

The robustness of the developed method was illustrated by the preparation of site-specific protein-protein conjugates, formed as a result of sequential cross-coupling of cysteine residues on two different proteins [1]. The method involves the synthesis of stable palladium-protein oxidative complexes, which converts nucleophilic cysteine residues into an electrophilic S-aryl-Pd-X motif using an intramolecular oxidative addition strategy. The resulting Pd-protein complexes can react with other thiol-containing proteins to obtain homogeneous protein-protein bioconjugates.

The resulting products have increased stability against acids, bases and thiol nucleophiles compared to commonly used bioconjugation reagents. In addition, the oxidative stability of arylated proteins can be easily controlled by varying the substitution pattern in the aromatic ring. The practical significance of this bioconjugation method is further emphasized by the synthesis of new classes of biotherapeutic agents [2].

Author is grateful to the RUDN University Strategic Academic Leadership Program for financial support.

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Ultrasound-mediated synthesis of Co/Al layered double hydroxide

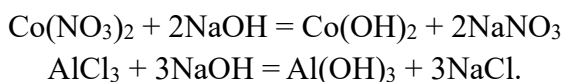
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Layered double hydroxides are a class of inorganic compounds consisting of positively charged layers formed by divalent and trivalent metal ions and hydroxide ions, separated by mobile anions and water molecules in the interlayer space. Like organometallic polymers, layered double hydroxides can be used for storage of various gases, water purification, targeted drug delivery, and sustained release systems with predetermined kinetics. Layered double hydroxides are characterized by pronounced anion exchange properties, which have recently attracted more and more attention of specialists in the field of inorganic chemistry and materials science. An especially urgent task is the development of anion exchange systems based on layered double hydroxides for the sorption of organic anions [1, 2]. This task is directly related to the development of systems for prolonged release of pharmaceutical substances, since many pharmacologically active compounds are organic anions by their nature.

The purpose of this work was to synthesize, identify and study the anion-exchange properties of Co/Al layered double hydroxide, including when exposed to ultrasonic vibrations. The Co/Al layered double hydroxide was prepared by coprecipitation using cobalt (II) nitrate and aluminum chloride as the cation sources, and sodium hydroxide as the precipitating reagent. The formation of cobalt (II) and aluminum hydroxides proceeds in accordance with the reaction equations:



With prolonged exposure at a temperature of 80 °C, the layered Co / Al double hydroxide matures with the formation of a characteristic layered structure. The resulting layered double hydroxide was characterized using a set of instrumental analysis methods, including infrared spectroscopy, X-ray diffraction analysis (powder diffraction), complex thermal analysis (thermogravimetry and differential scanning calorimetry), and scanning electron microscopy. The following vibration bands were found in the infrared spectra: $\nu(\text{OH}) = 3366.89 \text{ cm}^{-1}$, $\delta(\text{OH}) = 1637.99 \text{ cm}^{-1}$, $\nu(\text{NO}_3^-) = 1345.57 \text{ cm}^{-1}$, $\delta(\text{NO}_3^-) = 817.87 \text{ cm}^{-1}$. Vibrations in the range of $580.72 - 423.31 \text{ cm}^{-1}$ refer to vibrations M–O and M–O–M, where M is Co, Al. X-ray diffraction and complex thermal analysis data are also consistent with the proposed composition of the layered double hydroxide.

The resulting Co/Al layered double hydroxide was tested for its anion exchange properties with respect to 2-mercaptobenzimidazole in its anionic form. The anion exchange properties of the obtained layered double hydroxide were compared with those of cobalt(II) hydroxide and aluminum hydroxide. As a result, it was revealed that when treating a solution of 2-mercaptobenzimidazole in its anionic form with Co/Al layered double hydroxide, the concentration of the organic anion decreases by 46%, while when using cobalt (II) hydroxide and aluminum hydroxide - by 4%.

We also studied the possibility of using ultrasonic vibrations (USV) to accelerate and

reduce the number of stages in the synthesis of Co/Al layered double hydroxide. The suspension obtained after the standard coprecipitation procedure was subjected to ultrasonic treatment, bypassing the stage of prolonged exposure at 80 °C. Ultrasonic treatment of the suspension was carried out using a submersible waveguide on an UZDN-2T disperser in a cavitation mode at a frequency of 22 and 44 kHz for 1, 2, 5, 15, and 30 minutes. The data of X-ray diffraction and complex thermal analyzes completely corresponded to the layered Co/Al double hydroxide obtained by the standard method. The observed significant reduction in the time of crystallization and homogenization of crystallites is due to acoustic cavitation in the suspension due to ultrasonic action.

Thus, as a result of the work performed, a Co/Al layered double hydroxide was obtained and characterized, and its high anion exchange capacity for 2-mercaptobenzimidazole in its anionic form was revealed, which is many times higher than the anion exchange capacity of cobalt(II) hydroxide and aluminum hydroxide. It is shown that ultrasonic treatment of a suspension of layered double hydroxide Co / Al at the crystallization stage can significantly reduce the duration of the process of its synthesis. The results of this study are consistent with the results of studies [3,4], which also established a high efficiency of the use of ultrasonic vibrations at the stage of crystallization and anion exchange of the process of obtaining a layered double hydroxide Co/Al.

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Synthesis and crystal structure of the zinc complex of sildenafil citrate (Viagra®)

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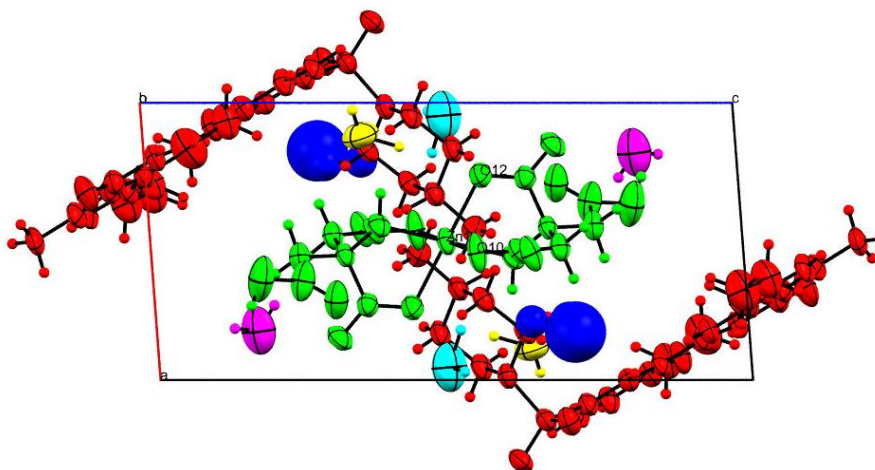
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Sildenafil, 5-[2-ethoxy-5-(4-methylpiperazin-1-yl)sulfonylphenyl]-1-methyl-3-propyl-6H-pyrazolo[4,3-d]pyrimidin-7-one 2-hydroxypropane-1,2,3-tricarboxylic acid, (S) (see Figure), is an orally bioavailable pyrazolopyrimidine derivative structurally related to zaprinast, with vasodilating and potential anti-inflammatory activities. The drug was synthesized in the search for a medicine to improve blood flow in the myocardium, treatment of angina pectoris and coronary heart disease. The missing of the aimed firstly medicinal properties of sildenafil can be replenished by complexation of sildenafil with zinc.

Crystals of the complex $[\text{Zn}(\text{Cit-3H})_2] \cdot (\text{H}_2\text{S})_2 \cdot 2\text{EtOH} \cdot 6\text{H}_2\text{O}$ (1) (where Cit-2H – a triple protonated cation of the citric acid) were prepared by slowly evaporation at room temperature of hydroalcohol solution containing of the $\text{HS} \cdot \text{Cit} \cdot \text{H}_2\text{O}$ and HNO_3 in molar relation 1:1. The crystal structure is built from one $[\text{Zn}(\text{Cit-2H})_2]^{4+}$ anion, two a double protonated H_2S cation, two ethanol solvate molecules and six molecule of crystallization. The C19 and C20 atoms of the propyl group are disordered over two positions (A and B) and C1-C18-C19-C20 torsion angles involved these atoms equal to $-63(1)$ (A) and $116.6(8)^\circ$ (B) and differ from values found in other related structures. The EtOH solvate molecule is also disordered over two positions.

The Zn-O bond lengths are 2.047(5), 2.090(4) and 2.127(4) , that are close to the values found in the crystal structure of $\text{K}_4[\text{Zn}(\text{Citrate})_2]$, where these bond lengths equal to 2.041(2), 2.093(2) and 2.135(2) Å [1]. One of the bonds angles, O7-Zn-O12, is smaller than others and equal to $76.51(14)^\circ$.



It was shown that coordination of the Zn atom by sildenafil citrate occurs through tridentate citrate anion.

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NMR and X-Ray crystallography at the investigations of conformationally mobile molecules

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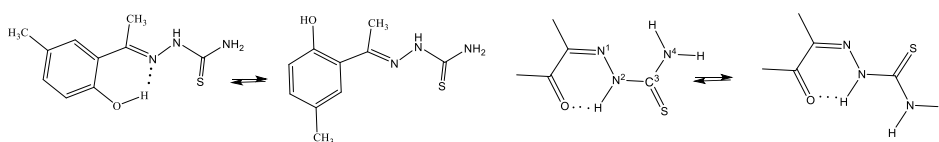
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For studying weak inter-, intramolecular interactions, molecular mobility in solutions and solid-state systems various physical methods are intensively used. Among these methods, NMR and X-Ray have a significant role. As it is known, the use of various physical methods at investigations of different types of interactions and their obtained data are complementary [1, 2].

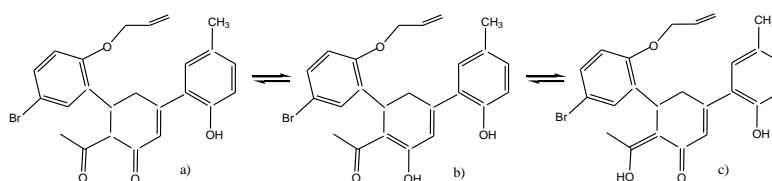
In the presented work is reported the applying of NMR, X-Ray methods at studying the conformational mobile molecules in solutions and solid-state systems.

Thiosemicarbazones are used in medicine as anticancer chemotherapeutic agents, in the treatment of tuberculosis, etc. As is noted in the literature, two types of preferred rotations are present in these molecules: rotation around the C-Ar [3] and N²-C³ bonds [4].

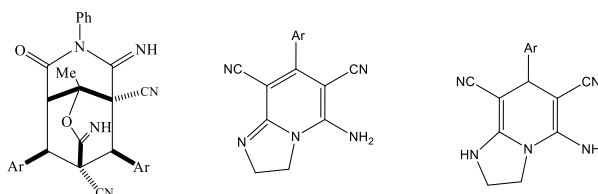


Considering it, (*E*)-4-bromoacetophenone- and (*E*)-2-hydroxy-5-methylacetophenone thiosemicarbazones have been investigated by NMR [5].

The chalcones and their derivatives are important intermediates in organic synthesis and in drugs chemistry. New chalcone derivative investigated by NMR and X-Ray, biological activity against microorganisms tested by disc diffusion method [6].



Pyridine ring, an important structural fragment in heterocyclic chemistry, is present in many natural products such as nicotinic acid, nicotinamide, vitamin B₆ which play key roles in metabolism. The structural properties of the tricyclic pyranopyridines, bicyclic cyanopyridines were investigated by X-Ray, NMR, and tested their biological activity [7].



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Fuzzy sets in chemical crystallography

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Fuzzy sets, first introduced by Lotfi Asker-zade in 1965 [1], are now widely used to formalize uncertain relations. A *fuzzy set* $A = \{x, \mu_A(x) | x \in U\}$ is composed of elements of the reference *universe set* $\{x_i\} \subset U = \text{supp}A$ augmented with *membership function* $0 \leq \mu_A(x) \leq 1$ that corresponds to a grade of membership $x \in U$ in A . In 1D case, membership function (e.g. linear one) on $a \leq x \leq b$ segment, corresponds to probability. If $\mu_A(x) = 1$ for $x \in [a, b]$ and $\mu_A(x) = 0$ for $x \notin [a, b]$, we go back to ordinary (or ‘*crisp*’) set of $x \in [a, b]$ points (Figure).

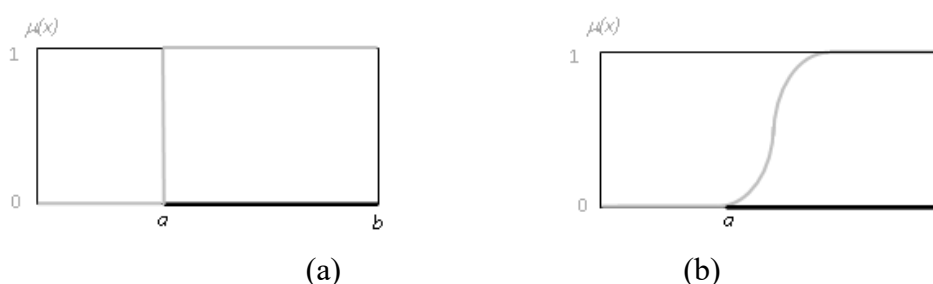


Figure (a) crisp and (b) fuzzy sets with membership functions (in grey)

Fuzzy sets allow to express loosely formulated relations by means of a natural language, or *linguistic values*, such as ‘on average more’, ‘generally smaller’, ‘approximately the same’, etc. *Fuzzy logic* developed on this basis, differs from the classic Boolean logic. Thus, for combining sets

$A \cup B: \mu = \max(\mu_A, \mu_B)$, so if A and \bar{A} («non- A ») $\subset U$, then $A \cup \bar{A} \neq U$
(no *exclusion of the third*), and for intersection of sets

$A \cap B: \mu = \min(\mu_A, \mu_B)$, so for $A, \bar{A} \subset U$ the intersection $A \cap \bar{A} \neq \emptyset$
(no *law of contradiction*), etc. [2].

Fuzzy sets are a powerful tool for convolution of information in pattern recognition, robotics, applied artificial intelligence, and other fields. In chemistry and crystallography, loosely determined relations are used to classify experimental data (e.g. subdivide metals from non-metals basing on their electronegativity). In particular, *Hirshfeld surfaces* [3] as conditional borders of multi-atomic fragments or molecules in a crystal, are determined by weight function

$$w(\mathbf{r}) = \frac{\sum_{\text{мол}} \rho_i^{\text{at}}(\mathbf{r})}{\sum_{\text{крист}} \rho_i^{\text{at}}(\mathbf{r})},$$

with electron density of ‘promolecule’ at \mathbf{r} point of the unit cell in numerator and the sum of all atoms’ electron densities $\rho^{\text{at}}(\mathbf{r})$ at the same point in denominator. The weight function $0 \leq w(\mathbf{r}) \leq 1$ is close to 1 inside a molecule and quickly tends to zero outside it. Therefore $w(\mathbf{r})$ is a membership function showing for all points within the unit cell a grade to belong to a fuzzy set of a molecule or atomic fragment in 3D space.

Assignment of substances to fuzzy or conditional classes basing of numerical data, is a general problem in chemistry and other natural sciences. Several crystallographic examples like van der Waals radii, coordination polyhedra, and packing motifs, will be discussed.

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