HRVATSKA AKADEMIJA ZNANOSTI I UMJETNOSTI
HRVATSKA KRISTALOGRAFSKA ZAJEDNICA

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CROATIAN ACADEMY OF SCIENCES AND ARTS
CROATIAN CRYSTALLOGRAPHIC ASSOCIATION

FACULTY OF CHEMISTRY AND CHEMICAL TECHNOLOGY,
UNIVERSITY OF LJUBLJANA

The Twenty-eighth Croatian-Slovenian Crystallographic Meeting

Poreč, Croatia, September 7 - 11, 2022

Book of Abstracts

CROATIAN CRYSTALLOGRAPHIC ASSOCIATION
FACULTY OF CHEMISTRY AND CHEMICAL TECHNOLOGY,
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The twenty-eighth Croatian-Slovenian Crystallographic Meeting – CSCM28

Poreč, Croatia, September 7 – 11, 2022

Programme book

The twenty-eighth Croatian-Slovenian Crystallographic Meeting

will be held in the HOTEL VALAMAR DIAMANT, POREČ, CROATIA,

from Wednesday to Sunday, September 7 – 11, 2022.
The opening of the Meeting will take place on Thursday at 8:30.

Honorary Chair
Ivan Leban, Ljubljana

Chair of the Scientific and Organizing Committee
Dubravka Matković-Čalogović, Zagreb
Anton Meden, Ljubljana

Chair of the Scientific and Organizing Committee
Marijana Đaković, Zagreb

Scientific and Organizing Committee Members
Amalija Golobič, Ljubljana
Mariusz Jaskólski, Poland
Matic Lozinšek, Ljubljana
Luka Pavić, Zagreb
Andrej Pevec, Ljubljana
Marta Počkaj, Ljubljana
Željko Skoko, Zagreb
Darko Vušak, Zagreb

The Meeting is organized jointly by the Croatian Crystallographic Association and the *Faculty of Chemistry and Chemical Technology, University of Ljubljana*

Wednesday, September 7, 2022

16^{30}-18^{30}	Registration of participants
18^{30}	Welcome drink

Thursday, September 8, 2022

8^{00}-8^{30}	Registration of participants	
8^{30}-8^{40}	Opening of the Meeting	M. Đaković, D. Matković-Čalogović, A. Meden

SHORT ORAL CONTRIBUTIONS

CHAIRS: D.Matković-Čalogović, Z. Štefanić

8^{40}-8^{50}	Anton Meden *Is thinking a good idea? Example of structure solution from powder diffraction data*
8^{50}-9^{05}	Ivana Brekalo, David E. Deliz, Leonard J. Barbour, Michael D. Ward, Tomislav Friščić, K. Travis Holman *The single crystal-to-single crystal transformations and porosity of guanidinium 1,4-benzenedisulfonate*
9^{05} -9^{15}	Ivana Kekez, Sara Matić, Sanja Tomić, Dubravka Matković-Čalogović *Binding of peptide mimicking the ETGE loop of dipeptidyl peptidase III to the Kelch domain of Keap1*
9^{15}-9^{30}	Mirela Dragomir, Adam W. Phelan, Lucas Presley, Patrick J. Clancy, John E. Greedan, *Revisiting the Structure and Magnetism of the Quasi-One-Dimensional* La_3MoO_7*: A Single Crystal Study*
9^{30}-9^{45}	Vladimir Stilinović, Luka Fotović, Nikola Bedeković *Halogen bonding in an isostructural series of N-(4-halogenobenzyl)-3-halogenopyridinium halogenides*
9^{45}-10^{00}	Matic Lozinšek, Dominique Cahard, Andrej Emanuel Cotman *Mechanically flexible crystals of homochiral β-*CF_3*, β-*SCF_3*, and β-*OCF_3 *benzylic alcohols*

10^{00} -10^{30} Coffee break

PLENARY LECTURE

CHAIR: M. Đaković

10^{30}-11^{30}	**Alessia Bacchi** ***Smart materials for the release of liquid ingredients***

SHORT ORAL CONTRIBUTIONS

CHAIRS: V. Stilinović, A. Meden

11^{30}-11^{45}	Jasminka Popović, Željko Skoko, Juraj Ovčar, Luca Grisanti, Martina Vrankić, Ivor Lončarić, Aleksandra Djurišić *Mixed halides – a way to stabilize Ruddlesden-Popper structures*
11^{45}-12^{00}	Yizhi Xu, Joseph M. Marrett, Hatem M. Titi, James P. Darby, Andrew J. Morris, Tomislav Friščić, Mihails Arhangelskis *Experimentally-validated ab initio crystal structure prediction of novel metal-organic framework materials*
12^{00}-12^{15}	Teodoro Klaser, Jasminka Popović, Ana Šantić, Luka Pavić, Željko Skoko *Some relevant results from electrical analysis of thermosalient crystals of 1,2,4,5-tetrabromobenzene and 1,2,4,5-tetraclorobenzene*
12^{15}-12^{30}	A. El Hachmi, B. Manoun, M. Sajieddine, Y. Tamraoui, S. El Ouahbi *Structural and optical properties of perovskites:* $Sr_3Fe_{2+x}Mo_{1-x}O_{9-3x/2}$ $(0.3 \leq x \leq 1)$

12^{30}-13^{40} Vladyslav Ievtukhov, Małgorzata Rybczyńska, Karol Krzymiński
Unique structural features of new acridan aryl esters – promising indicators in luminescence analysis

12^{40}-13^{00} Vernon Smith, Mirko Giansella
Structure determination on challenging samples – how modern X-ray instrumentation can help

13^{10}-15^{00} Lunch break

WORKSHOP

CHAIRS: A. Bjelopetrović, L. Pavić

15^{00}-17^{00} CCDC Workshop

17^{00}-17^{30} Coffee break

PLENARY LECTURE

CHAIR: I. Brekalo

17^{30}-18^{30} Dominik Cinčić
Crystal engineering of organic and metal-organic multicomponent halogen bonded solids

SHORT ORAL CONTRIBUTIONS

CHAIRS I. Kekez, M. Dragomir

18^{30}-18^{40} Valentina Martinez, Bahar Karadeniz, Nikola Biliškov, Ivor Lončarić, Alexey A. Popov, Krunoslav Užarević
Mechanochemical strategy for controllable encapsulation of Buckminsterfullerene for preparation of fulleretic ZIF materials

18^{40}-18^{50} Katarina Ležaić, Mia Jurković, Darko Vušak, Biserka Prugovečki
A new copper(II) metal–organic frameworks constructed from N-alkyl glycinates and 3,3'-bipyridine: synthesis, structure and thermal behavior

18^{50}-19^{00} Nea Baus Topić, Dominik Cinčić
Perhalogenated amines as bifunctional donor molecules in cocrystals with nitrogen-containing acceptors

19^{00}-19^{10} Mia Jurković, Katarina Ležaić, Darko Vušak, Biserka Prugovečki
Syntheses and structures of copper(II) coordination polymers with N-methylglycinate and 4,4'-bipyridine

19^{10}-19^{20} Soufiane Zerraf, Malika Tridane, Said Belaauad
Structural and vibrational study of single crystal $(C_6H_9N_2)_2H_2P_2O_7$

19^{20}-19^{30} Thomas Kendall
Problem solving with co-crystals: Screening and single crystal

Friday, September 9, 2022

SHORT ORAL CONTRIBUTIONS

CHAIRS: D. VUŠAK, K. KRANJC

8^{30}-8^{45} M. Kušter, Z. Samardžija, A. Meden, B. Markoli, M. Vončina, P. Boulet, E. Gaudry, J.-M. Dubois, S. Šturm
TEM studies of a Newly Discovered Ternary Phase in the Al-Cr-Sc system

8^{45}-8^{55} Matjaž Kristl, Ivana Goričan, Brina Dojer, Amalija Golobič
Crystal structures of three 2,6-diaminopyridine compounds

8^{55}-9^{05} Lidija Posavec, Dominik Cinčić
Building ternary halogen bonded cocrystals with Werner coordination compound and perhalogenated benzenes

9^{05}-9^{15} Filip Kučas, Vinko Nemec, Dominik Cinčić
Methylated isatin derivatives as halogen bond acceptors in multicomponent crystals

9^{15}-9^{30} Lavanya Kumar, Katarina Leko, Vinko Nemec, Nikola Bregović, Dominik Cinčić, Mihails Arhangelskis
Inspiring mechanochemical interconversions of halogen-bonded cocrystals by periodic DFT calculations

9^{30}-9^{45} Valentina Milašinović, Vedran Vuković, Anna Krawczuk[3] Krešimir Molčanov, Christoph Hennig, Michael Bodensteiner
A novel π-hole interaction between an iodide anion and a quinoid ring involving an $n\rightarrow\pi^*$ charge transfer

9^{45}-10^{00} Khai-Nghi Truong
Rigaku Advances in X-ray and Electron Crystallography

10^{00}-10^{30} Coffee break

PLENARY LECTURE

CHAIR: J. POPOVIĆ

10^{30}-11^{30} Anna Moliterni
Crystallography, a powerful lens for Materials Science

SHORT ORAL CONTRIBUTIONS

CHAIRS: O. MIŠURA, S. PETRIČEK

11^{30}-11^{40} Krištof Kranjc, Amadej Juranovič, Marijan Kočevar, Franc Perdih
Cycloaddition of vinyl-moiety-containing dienophiles on 2H-pyran-2-one derivatives: A surprising diversity of possible products

11^{40}-11^{50} Dominik Fendre, Bor Lucijan Turek, Marijan Kočevar, Franc Perdih, Krištof Kranjc
Synthesis of linked double 2H-pyran-2-one derivative: A possible precursor to double Diels–Alder cycloadducts and various macrocycles

11^{50}-12^{00} Bor Kolar Bačnik, Luka Jamšek, Franc Perdih, Krištof Kranjc
Use of derivatization with hydrazine to determine the correct stereostructure of maleic anhydride-double cycloadducts with substituted 2H-pyran-2-ones

12^{00}-12^{15} Darko Vušak, Silvija Štriga, Biserka Prugovečki
Crystallization and structural transformations of ternary copper(II) coordination compounds with 1,10-phenanthroline and glycine

12^{15}-12^{25} Boris Gomaz, Zoran Štefanić
Oligomeric symmetry of purine nucleoside phosphorylases

12^{25}-12^{35} Bogdan Kotur, Volodymyr Babizhetskyy, Chong Zheng
New ternary scandium cobalt silicide $Sc_{38}Co_{144}Si_{97}$: crystal and electronic structures

12^{35}-12^{45}	Antonio Magnabosco, Vinko Nemec, Dominik Cinčić *Cocrystallization of the Schiff base derived from ethylenediamine and pyridine-2-carbaldehyde with perfluorinated halogen bond donors*
12^{45}-12^{55}	Mario Cetina, Silvija Maračić, Jasmina Lapić, Senka Djaković, Silvana Raić-Malić *Conformation and supramolecular architecture of novel 1,1’-disubstituted ferrocene–quinoline hybrids*

Afternoon - Excursion

Saturday, September 11, 2022

SHORT ORAL CONTRIBUTIONS

CHAIRS: T. Klaser, M. Cetina

8^{30}-8^{45}	Krunoslav Užarević, Dijana Žilić, Senada Muratović, Valentina Martinez, Bahar Karadeniz, Teodoro Klaser, Željko Skoko, Damir Pajić, Ivana Brekalo *The magnetism of solvatomorphic copper(II)-intermediates in the synthesis of mixed-metal MOF-74 materials*
8^{45}-8^{55}	Ana Lozančić, Krešimir Molčanov, Sanja Renka, Sanja Burazer, Marijana Jurić *High proton conductivity in 2D oxalate* $[\mathrm{Mn^{II}Cr^{III}}]$ *polymer with alkyl ammonium cations and its oxide-related usage*
8^{55}-9^{05}	Alen Bjelopetrović, Marina Juribašić Kulcsár, Manda Ćurić *Mechanosynthesis of Pd(II) photosensitizers under solvent-free conditions in a ball mill*
9^{05}-9^{15}	Klemen Motaln, Kristian Radan, Matic Lozinšek *Structures of the* XeF_2–MnF_4 *adducts*
9^{15}-9^{25}	Nina Podjed, Barbara Modec *An interesting case of polymorphism involving acetamide*
9^{25}-9^{35}	Marin Liović, Nikola Bedeković, Vladimir Stilinović, Dominik Cinčić *Crystal structures of 2,4,6-collidinium and 3,5-lutidinium halogenides' cocrystals with 1,4-diiodotetrafluorobenzene*
9^{35}-9^{45}	Lidija Molčanov, Dario Barišić, Pavla Šenjug, Damir Pajić, Krešimir Molčanov, Marijana Jurić *Anion-directed synthesis of oxalate-based [CuM] (M = Cr or Fe) complexes containing a tridentate ligand: Structural and magnetic properties*
9^{45}-10^{00}	Zoran Štefanić, Aleksandra Maršavelski, Boris Gomaz *Search for Allostery in Purine Nucleoside Phosphorylases via Database of Molecular Interactions*

10^{00} -10^{30} Coffee break

PLENARY LECTURE

CHAIR: K. Molčanov

10^{30}–11^{30}	**Mariana Klementová** ***Structure determination of nanomaterials from electron diffraction data***

SHORT ORAL CONTRIBUTIONS

CHAIRS: K. Užarević, K. Motaln

11^{30}-11^{40}	Vinko Nemec, Dominik Cinčić *A bromine-containing imine and its copper(II) and nickel(II) coordination compounds in cocrystals with perhalogenated aromates*
11^{40}-11^{50}	Patryk Nowak, Artur Sikorski *Review of the CSD crystallographic database for selected structures containing acridine and benzoic acid derivatives*
11^{50}-12^{00}	Saša Petriček *Pyridin-2-one in a manganese(II) complex, cocrystals and an ionic liquid*
12^{00}-12^{10}	Nikola Jakupec, Vladimir Stilinović, Krešimir Molčanov *Charge density study of a halogen bonded salt of 2-chloropyridine and hexacyanocobaltate(III) acid*
12^{10}-12^{20}	Marko Dunatov, Andreas Puškarić, Zoran Štefanić, Lidija Androš Dubraja *Reversible single-crystal-to-single-crystal transformations in the pleochroic complex salt of the bis(oxalato)chromium(III) anion*

12^{20}-12^{30} Amalija Golobič, Srečo D. Škapin
Structural characterization of $LaNbTiO_6$–$La_4Ti_9O_{24}$ based solid solution

12^{30}-12^{40} Simona Gričar, Matija Uršič, Jakob Kljun, Iztok Turel
Structure of ruthenium(II) diketonato complexes designed as potential anticancer agents

12^{40}-12^{50} Erik Uran, Mirela Dragomir, Kristian Radan, Matic Lozinšek
Exploring the XeF_2–TaF_5 system with mechanochemistry

12^{50}-13^{00} Miha Virant, Kristian Radan, Matic Lozinšek
Metal(II) salts of $[MoOF_5]^-$ and $[Mo_2O_2F_9]^-$ and their HF complexes

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13^{00}-15^{00} Lunch break

SHORT ORAL CONTRIBUTIONS

CHAIRS: V. Nemec, S. Gričar

15^{00}-15^{10} Ozana Mišura, Marijana Đaković
Variability of mechanical responsiveness of crystals of copper(II) halides with a family of pyridine-based ligands

15^{10}-15^{20} Anja Pečkaj, Marta Počkaj
Reactions between $Co(NO_3)_2\cdot 6H_2O$ and 2-(hydroxymethyl)pyridine

15^{20}-15^{30} Kristian Radan, Juan Forero Saboya, Alexandre Ponrouch, Matic Lozinšek
Novel BF_3 adducts of organic carbonates: Syntheses and crystal structures

15^{30}-15^{40} Uroš Rapuš, Mihaela Rebernik, Jakob Kljun, Iztok Turel
p-Cymene ruthenium pyrithionato complexes with triphenylphosphine and triphenylarsine

15^{40}-15^{50} Małgorzata Rybczyńska, Artur Sikorski
Structural characterization of multicomponent crystals formed from nimesulide and quaternary ammonium compounds

15^{50}-16^{00} Lia Šibav, Denis Arčon, Zvonko Jagličić, Graham King, Mirela Dragomir
Doping effects on the structural and magnetic properties of $SrCu_2(BO_3)_2$

16^{00}-16^{10} Sara Cerovski, Ruđer Sušanj, Vinko Nemec, Dominik Cinčić
Competition of different halogen bond acceptors in oxazole derivatives for halogen bonding with perhalogenated benzenes

16^{10}-16^{20} Viktoriia Drushliak and Marek Szafrański
Modification of crystal structure and optical absorption edge in compressed perovskite-like $CsPb_2Br_5$

16^{20}-16^{30} Petra Stanić, Krešimir Molčanov
π-stacking and multicentric bonding of TMPD (Wurster's blue) in charge-transfer complexes with different quinones

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16^{30}-17^{00} Coffee break

PLENARY LECTURE

CHAIR: A. Golobič

17^{00}–18^{00} **Jakob Kljun**
Development of bioactive metal compounds: structural insights into design and molecular modes of action

SHORT ORAL CONTRIBUTIONS

CHAIRS: L. Molčanov, M. Počkaj

18^{00}-18^{10} Matic Belak Vivod, Matic Lozinšek, Mirela Dragomir
Single-crystal growth and structure determination of $BaAgF_4$ and $(BaF)_2AgF_4$

18^{10}-18^{20} Petar Štrbac, Valentina Milašinović, Krešimir Molčanov
Salts of 1,1,2,3,3-pentacyanopropenide carbanion with aromatic cations

18^{20}-18^{30} Ruđer Sušanj, Vinko Nemec, Nikola Bedeković and Dominik Cinčić
Halogen bond motifs in cocrystals of Schiff bases that contain a morpholine or piperazine moiety

18^{30}-18^{40} Mišel Hozjan, Franc Perdih
Sodium salt with zinc dipicolinato anionic complex

18^{40}-18^{50} Leon Poljanić, Nea Baus Topić, Nikola Bedeković, Vladimir Stilinović, Dominik Cinčić
Cocrystallization of perhalogenated halogen bond donors with imines derived from 2-nitrobenzaldehyde and 4-haloanilines

18^{50}-19^{00} Valentina Milašinović, Krešimir Molčanov, Petar Štrbac
Multicentre bonding in dimers of tetracyanoethylene (TCNE) radical anions

19^{00}-19^{10} Marijana Đaković
Crystals' adaptability to external mechanical stimuli: Structural causes and consequences

19^{10} Closing remarks A. Meden, D. Matković-Čalogović

20^{00} Meeting dinner

The twenty-eighth Croatian-Slovenian Crystallographic Meeting – CSCM28

s financially supported by

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PLENARY LECTURES

Smart materials for the release of liquid ingredients

Alessia Bacchi
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We here present a rational design of crystalline materials, such as cocrystals and MOFs, capable to store and release liquid active ingredients (L-AI) (Figure 1). We show that the release profile can be related to the solid state arrangement of the material, offering a strong and rational tool to afford a vast range of materials for a controlled delivery of L-AI.

Widely known examples of compounds relevant to human health and nutrition which are liquid at ambient conditions are propofol, vitamin E, nicotine, and terpenoids and phenolic derivatives used as natural antioxidants such as carvacrol, eugenol , eucalyptol, and valproic acid. The thermodynamic requisites to embed liquid ingredients in a crystalline form have been discussed [1]. Recently, cocrystallization has proven to be a powerful method to control the release of such liquid ingredients in the environment, thanks to the engineering of ad hoc intermolecular interactions which strengthen or weaken the tendency of the ingredient to be retained inside the solid matrix [2-3]. Similarly, L-AI have been encapsulated within adaptable cavities of Metal Organic Frameworks purposedly designed to uptake such guests; the evolution in time of the supramolecular arrangement of the nano-confined guests in the cavities has been monitored by SCXRD and related to the observed selectivity of the material towards different liquid guests [4–5].

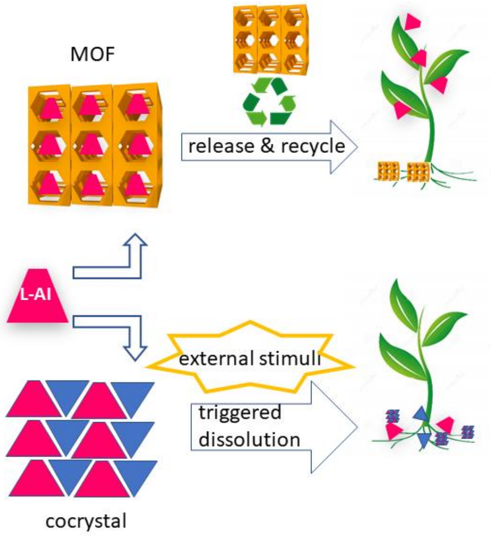

Figure 1: Smart materials, MOFs and cocrystals, for the release of L-AI.

References

[1] A.J. Cruz-Cabeza, S.E. Wright, A. Bacchi, *Chem. Comm.*, **56** (2020) 5127–5130.
[2] A. Bacchi, et al., *Cryst. Growth Des*. **16** (2016) 6547–6555.
[3] P.P. Mazzeo, et al., *ACS Sustainable Chem. Eng*. **7** (2019) 17929–17940.
[4] D. Balestri, et al., *Angew. Chem. Int. Ed*. **58** (2019) 17342–17350.
[5] D. Balestri, et al., *Angew. Chem. Int. Ed*. **60** (2021) 10194–10202.

Crystal engineering of organic and metal-organic multicomponent halogen bonded solids

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Over the past 20 years, research into halogen bonding has been intensified in all fields of chemistry, especially in crystal engineering [1]. Studies on halogen-bonded cocrystals have mostly focused on organic systems with perfluorinated compounds as halogen bond donors, and a variety of organic acceptors involving nitrogen and oxygen atoms [2]. The use of halogen bonding to direct the assembly of coordination compounds or building blocks containing heavier elements of Groups 15 and 16 as acceptors in cocrystals remains largely unexplored. Our group is focusing on developing halogen bonding as a tool in crystal engineering of multi-component solids through the involvement of new acceptor [3-5] and donor types [6], notably the incorporation of metals into halogen-bonded structures [7-9]. This presentation will provide an overview of some of the work related to the study of halogen bonding synthons in organic cocrystals as well as metal-based halogen-bonded cocrystals that we have pursued recently – the potential of chelating and anionic ligands as halogen bond acceptors in crystal engineering based on coordination compounds [10].

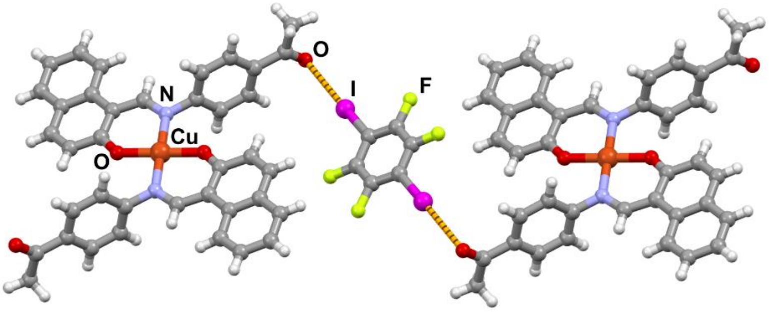

Figure 1: Fragment of the crystal structure of a halogen-bonded metal-organic cocrystal.

References

[1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* **116** (2016) 2478–2601.
[2] C. R. Groom, I. J. Bruno, M.P. Lightfoot, S.C. Ward, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* **72** (2016) 171–179.
[3] M. Zbačnik, M. Vitković, V. Vulić, I. Nogalo, D. Cinčić, *Cryst. Growth Des.* **16** (2016) 6381−6389.
[4] V. Nemec, D. Cinčić, *CrystEngComm.,* **18** (2016) 7425−7429.
[5] K. Lisac, F. Topić, M. Arhangelskis, S. Cepić, P.A. Julien, C.W. Nickels, A.J. Morris, T. Friščić i D. Cinčić, *Nature Communications* **10** (2019) no. 61.
[6] M. Eraković, V. Nemec, T. Lež, I. Porupski, V. Stilinović, D. Cinčić, *Cryst. Growth Des.* **18** (2018) 1182−1190.
[7] V. Nemec, L. Fotović, T. Friščić, D. Cinčić, *Cryst. Growth Des.* **17** (2017) 6169−6173.
[8] K. Lisac, D. Cinčić, *CrystEngComm* **20** (2018) 5955–5963.
[9] V. Stilinović, T. Grgurić, T. Piteša, V. Nemec, D. Cinčić, *Cryst. Growth Des.* **19** (2019) 1245–1256.
[10] V. Nemec, K. Lisac, N. Bedeković, L. Fotović, V. Stilinović, D. Cinčić, *CrystEngComm* **23** (2021) 3063−3083.

Crystallography, a powerful lens for Materials Science

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The humain evolution has been always favoured by the discovery of new materials. In the last decades, special materials with unique and amazing optoelectronic properties like, for example, perovskites, attracted a growing scientific interest and revealed themselves promising and appealing candidates for technological applications (*e.g.*, solar cells, LEDs, lasers, photodetector devices,..). Among them, the hybrid organic-inorganic perovskites, consisting of alternating layers of organic cations and inorganic corner-sharing octahedra, offer a great potential, relying on the large tunability of their optoelectronic properties: *e.g.*, by changing the type of organic cations and/or the number of layers in the inorganic slabs, strong differences in the emitted wavelength can be observed.

To optimize and tune the optoelectronic properties of new crystalline materials Crystallography plays a fundamental guiding role: a successful structure determination process gives precious insights into the structure-property relationships of the investigated compounds.

The *ab-initio* structure solution process of crystalline materials is not always straightforward, it can be hampered by their small size and/or their low crystallinity and weak diffraction power; for example, in the case of a few-μm-thick laminar single crystals, a crystallographic study based on conventional laboratory X-ray sources usually fails. The access to non-conventional high-brilliance X-ray sources (*i.e.*, the use of synchrotron radiation) allows to reduce the size of the single crystals that can be successfully characterized and to increase the complexity of the crystal structures that can be determined by X-ray diffraction data.

To enhance the power of Crystallography, making it an effective lens for studying also challenging cases, the use of synchrotron radiation is fundamental and can reveal itself an obliged choice, as proved by some recent cases of successful *ab-initio* structure solution of new hybrid organic-inorganic perovskites [1–4], *via* powder diffraction [1] and single crystal diffraction [2–4].

Very recently, the use of synchrotron radiation opened the door also to the structural investigation of metal chalcohalides nanocrystalline materials by powder diffraction: *e.g.*, the *ab-initio* structure solution of bismuth chalcohalides [5] that belong to a still poorly explored world of new materials of interest for applied nanotechnology and that, similarly to perovskites, show appealing optoelectronic properties.

The latest outcomes of the structural characterization by synchrotron X-ray diffraction data in the case of challenging compounds of interest for Materials Science (*i.e.*, new hybrid organic-inorganic perovskites [1–4] and metal chalcohalides [5,6]) will be presented.

References

[1] A. Ray *et al.*, *Adv. Mater*. **34** (2022) Article Number: 2106160.
[2] L. Polimeno *et al.*, *Nat. Nanotechnol.* **16** (2021) 1349–1354.
[3] M. Cinquino *et al.*, *Adv. Mater*. **33** (2021) Article Number: 2102326.
[4] B. Dhanabalan *et al., Adv. Mater*. **33** (2021) 2008004.
[5] D. Quarta *et al., Angew. Chem. Int. Ed.* (2022) Article Number: e202201747.
[6] S. Toso *et al., Nat. Commun*. **13** (2022) Article Number: 3976.

Structure determination of nanomaterials from electron diffraction data

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Electron diffraction is a powerful technique for the study of nanomaterials [1]. Because of the strong interaction of electrons with matter, diffraction from individual nanocrystals can be exploited for structure solution and differences among individual nanocrystals within a sample can be studied. However, the strong interaction also leads to multiple diffraction of electrons and violations of the kinematical approximation. Therefore, electron diffraction data require a dedicated data reduction and especially refinement. Our group at FZU now offers a complete software support for 3D electron diffraction (3DED) structural analysis including the analysis of modulated structures.

The PETS software for the processing of electron diffraction data [2] offers a number of features unique to electron diffraction *e.g.* treatment of precession electron diffraction data. In addition to dealing with periodic structures, the data processing of modulated structures is also available including the definition of modulation wave vectors and data integration. For the structure solution, the program Superflip has been long available for X-rays [3] but it can be also applied to 3DED data. Jana2020 software is then well known as a versatile and very powerful tool for the analysis of challenging crystal structures, and it now fully supports structure analysis from 3DED data, including advanced features as the combination of several datasets from different crystals or refinement against data from twinned crystals [4]. Last but not least, the structures, including incommensurately modulated structures, can be refined by the dynamical approach using the program Dyngo [5]. This approach uses the full dynamical diffraction theory in the calculation of model intensities and provides refinement quality and accuracy of structure models that is superior to other approaches in 3DED. Several examples will be presented to illustrate the above described procedure [6,7].

References

[1] M. Gemmi et al., ACS Cent. Sci. **5** (2019) 1315–1329.
[2] L. Palatinus et al., *Acta Cryst.* **B75** (2019) 512–522.
[3] L. Palatinus and G. Chapuis, *J. Appl. Cryst.* **40** (2007) 786–790.
[4] V. Petricek, M. Dusek, L. Platinus, *Z. Krist* **229-5** (2014) 345–352.
[5] L. Palatinus, V. Petricek, C.A. Correa, *Acta Crystallogr.* **A71** (2015) 235–244.
[6] M. Klementova et al., *Intermetallics* **85** (2017) 110–116.
[7] M. Klementova et al., *Cryst. Growth Des.* **17** (2017) 6762–6769.

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Development of bioactive metal compounds: structural insights into design and molecular modes of action

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In the first part of the lecture we will discuss the importance of 8-hydroxyquinoline (8hq) as a chemical scaffold in medicinal chemistry. Several compounds containing this structural fragment are or have been in clinical use, and the fragment is often incorporated into new molecules to give them chelating properties. On the other hand, these molecules can be used for the development of new metallodrugs. By synthesizing ruthenium compounds bearing the clinical drugs clioquinol and nitroxoline, as well as a number of their derivatives, we have shown that organoruthenation of the 8hq lead scaffold is a viable strategy to obtain highly toxic compounds and specific inhibit catB activity, as demonstrated by enzyme kinetics and microscale thermophoresis. The new metallodrugs significantly impair tumor progression by inhibiting catB in cell-based *in vitro* functional assays at low, non-cytotoxic concentrations [1].

Our group has developed ester-substituted 2,2'-bipyridine analogs in the recent years. In the second part of the talk, we will discuss how the choice of appropriate metal precursors in the synthesis of antimicrobial silver(I) [2], copper(II) [3], and zinc(II) [4] complexes affects the stoichiometry, coordination geometry and nuclearity of the complexes formed. All these factors influence the antibacterial and antifungal properties of these complexes, which have great potential for the treatment of mastitis-associated pathogens and Candida infections.

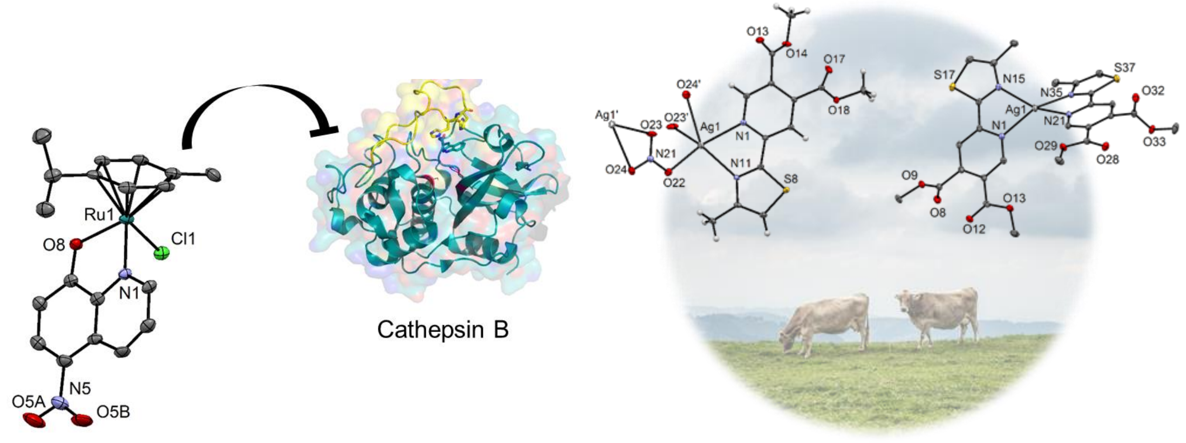

Figure 1: Left – Anticancer ruthenium-nitroxoline complex, right – antibacterial silver complexes.

References

[1] a) A. Mitrović and J. Kljun, I. Sosič., M. Uršič, A. Meden, S. Gobec, J. Kos and I. Turel, *Inorg. Chem.* **58** (2019) 12334–12347; b) J. Kljun, I. E. Leon, Š. Peršič, J. F. Cadavid-Vargas, S. B. Etcheverry, W. J. He, Y. Bai and I. Turel, *J. Inorg. Biochem.* **186** (2018) 187–196; c) M. C. Ruiz, J. Kljun, I. Turel, A. L. Di Virgilio and I. E. Leon, *Metallomics* **11** (2019) 666–675.

[2] T. P. Andrejević, D. Milivojević, B. Đ. Glišić, J. Kljun, N. L. Stevanović, S. Vojnović, S. Medić, J. Nikodinović-Runić, I. Turel and M. Djuran, *Dalton Trans.* **49** (2020) 4084–6096.

[3] T. P. Andrejević, I. Aleksić, M. Počkaj, J. Kljun, D. Milivojević, N. L. Stevanović, J. Nikodinović-Runić, I. Turel, M. Djuran and B. Đ. Glišić, *Dalton Trans.* **50** (2021) 2627–2638.

[4] T. P. Andrejević, I. Aleksić, J. Kljun, B. V. Pantović, D. Milivojević, S. Vojnović, I. Turel, M. Djuran and B. Đ. Glišić, *Inorganics* **10** (2022), atr. No. 71

SHORT ORAL CONTRUBUTIONS

Is thinking a good idea?
Example of structure solution from powder diffraction data

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Structure solution form powder diffraction data (SDPD) relies heavily on computer programs. Each step, from indexing and space group determination, through finding and completing a structural model, to final refinement, requires a computer program. Some model-finding methods, in particular, are very computationally intensive. Thus, one might get the impression that success in SDPD depends more or less on the skillful use of a number of good programs, but they can be integrated into a suite with a single user interface.

The title I have chosen for this talk refers to an anecdote that I will explain in the talk, along with a case of successful SDPD where the "brute force" computational approach failed and the intervention of the human mind was necessary to achieve success – taking into account, of course, the results of computer programs - in this case, indexing in particular.

The example is a layered structure of $Mg(BHIm_3)_2$ (Im is imidazolate $C_3H_3N_2^-$). The powder pattern was recorded during heating with a synchrotron, and the crystallinity of the sample was not very good. This was probably the reason why various methods of structure solution failed, although the indexing was correct (trigonal/hexagonal a = 8.7338(9) Å, c = 17.621(2) Å). Because of the high symmetry and knowledge of the structure of the starting material, it was possible to deduce what the building block might be and how the building blocks might be arranged in the unit cell. The building block was then simply constructed "by hand" in the form of a Z-matrix and inserted into the unit cell at a logical special position. The structure is shown in Figure 1 and will be described in more detail in the lecture, together with the details of "structure solution by thinking" and an attempt to generalize this example and illustrate circumstances in which the human mind and crystallographic knowledge can make a crucial complementary contribution to the performance of computer programs.

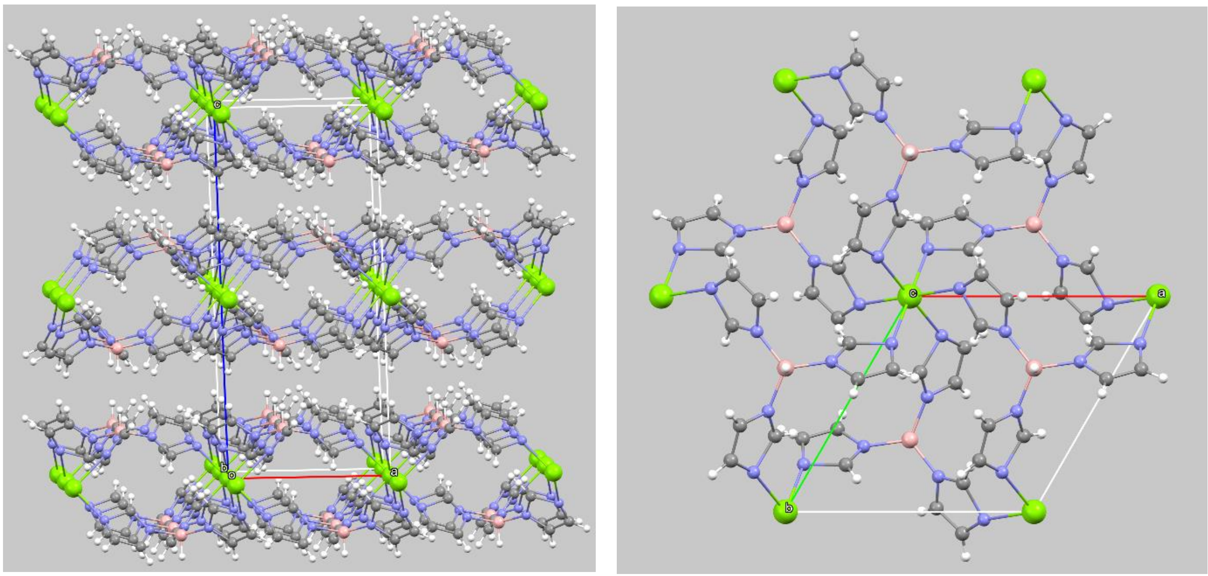

Figure 1: Packing of $Mg(BHIm_3)_2$ layers (left) and projection of a single layer along c axis (right).

The single crystal-to-single crystal transformations and porosity of guanidinium 1,4-benzenedisulfonate

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With the recent emphasis on the importance of porous materials, so called porous hydrogen bonded organic frameworks (**HOF**s) [1] have started gaining attention. A well-known class of **HOF**s are bisguanidinium organodisulfonates (**GS**), extensively explored due to their diverse host-guest chemistry and inclination towards architectural isomerism [2]. Especially interesting is the persistence of the 2D hydrogen bonded sheet motif, allowing the targeted synthesis of a multitude of different pillared architectures (such as the bilayer or brick structure) where the type of architecture depends on the size of the guest and the pillar type. Most importantly, these materials have been shown to exchange guest molecules in a single crystal-to-single crystal fashion [3].

Surprisingly, despite the stability of these frameworks, the desolvation of **GS** has not been extensively studied, and the structures of their empty forms - either 'collapsed' or 'open/porous' - have gone unreported. As a result, the formal existence of microporosity in the **GS** class of compounds has not yet been established. In this work we study the desolvation of guanidinium 1,4-benzenedisulfonate materials and their absorption of gases *via* Single Crystal-to-Single Crystal transformations, demonstrating their formal microporosity [4].

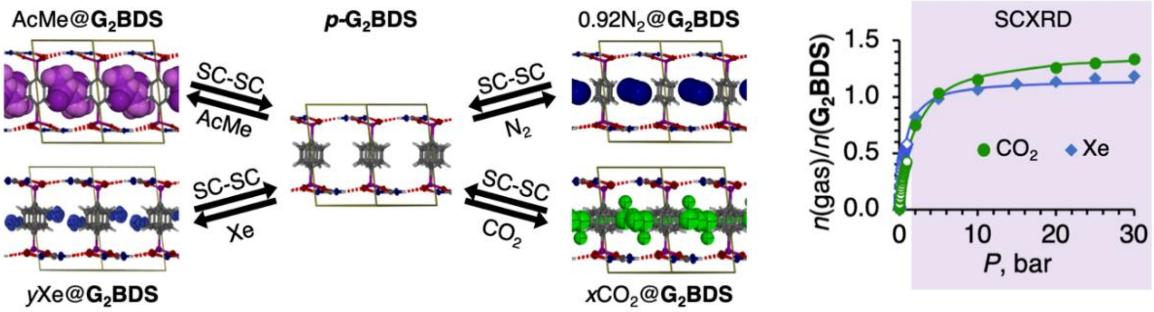

Figure 1: A summary of Single Cristal-to-Single Crystal transformations described here. Combined bulk (low pressure) and single crystal (high pressure) Xe and CO_2 sorption isotherms of **G_2BDS**.

References

[1] P. Brunet, M. Simard and J. D. Wuest, *J. Am. Chem. Soc.* **119** (1997) 2737–2738.
[2] K.T. Holman, A.M. Pivovar, J.A. Swift and M. D. Ward, *Acc. Chem. Res.* **34** (2001) 107–118.
[3] W. Xiao, C. Hu and M. D. Ward, *J. Am. Chem. Soc.* **136** (2014) 14200–14206.
[4] I. Brekalo, D.E. Deliz, L.J. Barbour, M.D. Ward, T. Friščić and K.T. Holman, *Angew. Chem. Int. Ed.* **59** (2020) 1997–2002.

Binding of peptide mimicking the ETGE loop of dipeptidyl peptidase III to the Kelch domain of Keap1

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Signaling pathway of the NRF2–KEAP1 factor 2 (nuclear factor erythroid 2-related–Kelch like ECH-associated protein 1) is important for cell protection. However, it is impaired in many cancer cells where NRF2 target gene expression leads to resistance to chemotherapeutic drugs [1–2]. Dipeptidyl peptidase III (DPP III) competitively binds to KEAP1 in the conditions of oxidative stress and induces release of NRF2 and its translocation into nucleus. The binding is established mainly through the ETGE motif located on the flexible loop of DPP III and the Kelch domain of KEAP1. To better understand interactions between DPP III and the Kelch domain of the KEAP1 protein we solved its crystal structure at a resolution of 2.70 Å (Figure 1A). The asymmetric unit contains one protein molecule, one 11-mer peptide molecule mimicking the ETGE loop of the DPP III peptide, nine water molecules, and one sodium ion. The final model was refined to R_{work} = 18.1% and R_{free} = 25.8%. Clear electron density (Figure 1B) was observed in the difference map near the region involved in the interactions with the ETGE motif, allowing proper fitting of the peptide and determination of the main interactions between the peptide and the Kelch domain of the KEAP1 protein. We found that ETGE itself is firmly attached to the peptide by strong hydrogen bonds in the same way as in the crystal structure of the Kelch–NRF2 complex. The backbone of the 11 AA peptide makes five hydrogen bonds with the Kelch domain, in four of them the peptide residues (P479, E480, T481 and Q484) are hydrogen bond acceptors, and donor in one (Q484).

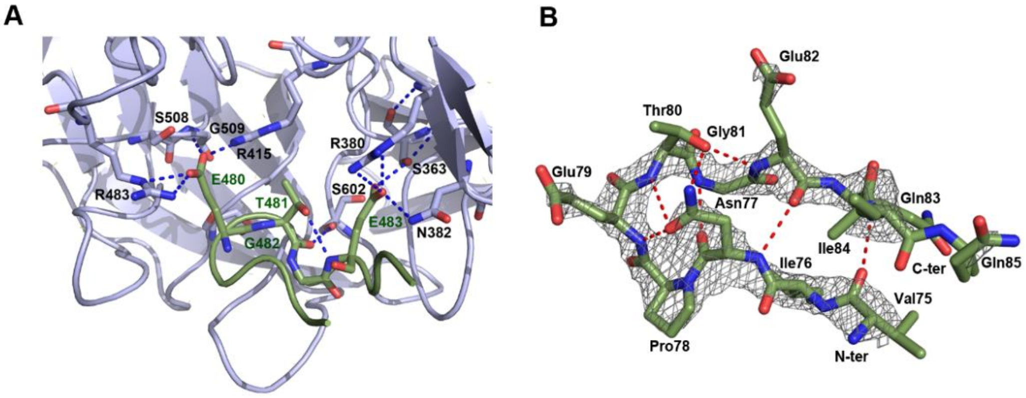

Figure 1: A. Polar interactions between the Kelch domain and ETGE motif residues of the 11 AA peptide. B. The $2F_o$–F_c electron density map contoured at a 1.6 σ level is shown as grey mesh.

References

[1] N. Wakabayashi, K. Itoh, J. Wakabayashi, H. Motohashi, S. Noda, S. Takahashi, S. Imakado, T. Kotsuji, F. Otsuka, D.R. Roop, T. Harada, J.D. Engel and M. Yamamoto, *Nature Genetics* **35 (3)** (2003) 238–245.
[2] A. Kobayashi, M.I. Kang, H. Okawa, M. Ohtsuji, Y. Zenke, T. Chiba, K. Igarashi and M. Yamamoto, *Molecular and Cellular Biology* **24 (16)** (2004) 7130–7139.

Revisiting the Structure and Magnetism of the Quasi-One-Dimensional La_3MoO_7: A Single Crystal Study

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The family of compounds with the $Ln_3^{3+}M^{5+}O_7$ composition adopt two main structure types: cubic and orthorhombic (weberite). In the weberite-type structure, the MO_6 octahedra share opposite corners to form well-isolated zig-zag chains with *M*–O–*M* angles of about 145°−155° along the chain axis. Due to this feature, the electrons are localized on the *M* cation and thus weberites constitute prime candidates for one-dimensional magnetism with electron configurations ranging from d^1 to d^3. Examples include La_3MoO_7, La_3ReO_7, La_3OsO_7 or La_3RuO_7.

The magnetic properties of d^1 La_3MoO_7 are yet unclear and have been only studied on powders so far [1,2]. Here, the structural and magnetic properties of La_3MoO_7 are revisited on a large single crystal. At room temperature, La_3MoO_7 adopts an orthorhombic structure, space group $P2_12_12_1$, while at ~500 K it undergoes a continuous phase transition to *Pnma* as shown by *in-situ* powder X-ray diffraction. Differential scanning calorimetry data showed two phase transitions at ~370 K and 500 K, in reasonable agreement with the two previous studies. Magnetization data showed a transition near 370 K with a strong hysteresis with the applied field along the *b*-axis. A broad susceptibility maximum occurs near 550 K which is taken as evidence for one dimensional spin correlations while Curie-Weiss behavior is seen only above 650 K. Attempts are currently being made to observe magnetic reflections in neutron diffraction data.

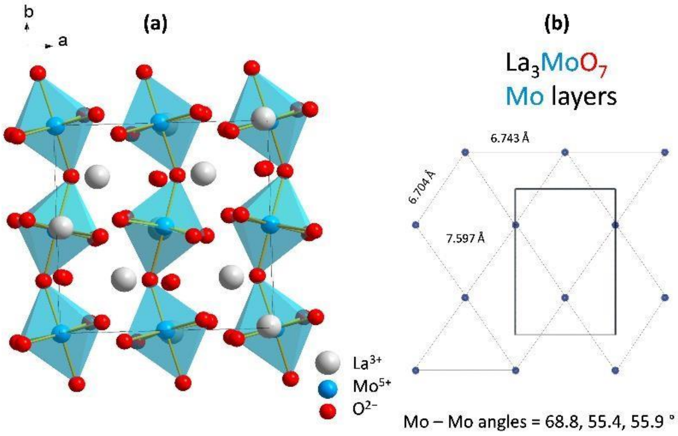

Figure 1: (a) Projection of the La_3MoO_7 weberite structure in the *ab* plane and the corner sharing octahedral chains along *b* axis. (b) The Mo forms an edge-sharing triangular net which could inhibit inter-chain couplings.

References

[1] J.E. Greedan, N.P. Raju, A. Wagner, P. Gougeon and J. Padiou. *J. Solid State Chem*. **129** (1997) 320–327.
[2] H. Nishimine, M. Wakeshima and Y. Hinatsu, *J. Solid State Chem*. **178** (2005) 1221–1229.

Halogen bonding in an isostructural series of *N*-(4-halogenobenzyl)-3-halogenopyridinium halogenides

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Isostructurality – the occurrence of different substances adopting very similar (or almost identical) crystal structures – has over previous decades shown to be a particularly useful phenomenon for study of minute differences in crystal structures and properties, as in isostructural materials the majority of various contributions of the overall crystal packing can be taken to be equivalent within an isostructural series. One field of supramolecular chemistry which has particularly benefited from the study of isostructural systems, is the study of halogen bonded materials, since replacing one halogen atom with another in a molecule generally has only a minute effect on molecular geometry. As halogen bond energy greatly increases with the donor atom size, the only significant difference between two crystals within an isostructural series comprising different halogens, will be the strength of the halogen bond.

In this contribution, we shall present a study of a series of *N*-(4-halogenobenzyl)-3-halogenopyridinium halogenides. The cation was selected as a potential donor of two inequivalent halogen bonds – one through the halogen on the pyridine ring (on which the majority of the charge is expectedly located) and the other through the halogen on the *N*-benzyl substituent. Sixteen compounds were obtained; two crystallized as hydrates and 14 as solvent free salts, 11 of which belonged to one isostructural series and 3 to another. The halogen bonds with the pyridine halogen show a linear correlation between the relative halogen bond length and angle, which in turn primarily depend on the donor halogen. The parameters of the other halogen bond vary with all three halogens, indicating that the former halogen bond is the dominant interaction. This is also in accord with the calculated electrostatic potential in the σ-holes of the halogens, as well as the measured thermal properties of the solids. The second isostructural group comprises combinations of best halogen bond donors and acceptors, and features a more favourable halogen bond geometry of the dominant halogen bond, reaffirming its significance as the main factor in determining the crystal structure.

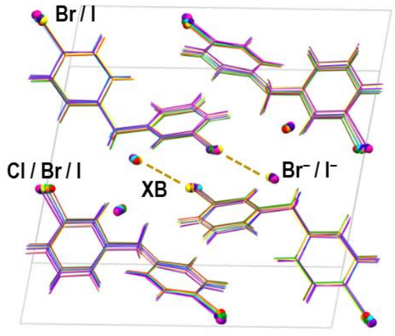

Figure 1: Overlay of unit cells of 11 isostructural *N*-(4-halogenobenzyl)-3-halogenopyridinium halogenides.

References

[1] L. Fotović, N. Bedeković, and V. Stilinović, *Cryst. Growth Des*. **22** (2022) 1333−1344.

Mechanically flexible crystals of homochiral β-CF_3, β-SCF_3, and β-OCF_3 benzylic alcohols

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The study of interesting crystalline materials that exhibit compliant mechanical properties as opposed to typical brittleness is a growing field of research [1,2].

In this work, dynamic kinetic resolution based on Ru(II)-catalyzed Noyori–Ikariya asymmetric transfer hydrogenation [3] was employed for the stereoconvergent synthesis of homochiral β-CF_3, β-SCF_3, and β-OCF_3 benzylic alcohols [4]. The absolute configurations of products with two contiguous stereogenic carbon atoms were determined by single-crystal X-ray diffraction analysis. Several novel enantiopure compounds that crystallize as needle-shaped crystals were found to exhibit elastic or plastic flexibility. The studied crystal structures feature a short crystal axis (~5 Å), anisotropic packing, and a prominent unidirectional intermolecular interaction with much weaker interactions in the perpendicular directions. The same characteristics were previously identified in other reported examples of mechanically responsive organic crystals [5]. These enantiomerically pure trifluoromethyl-substituted benzo-fused secondary alcohols represent an unprecedented class of enantiopure small organic molecules, which crystallize as homochiral single-component mechanically responsive crystals.

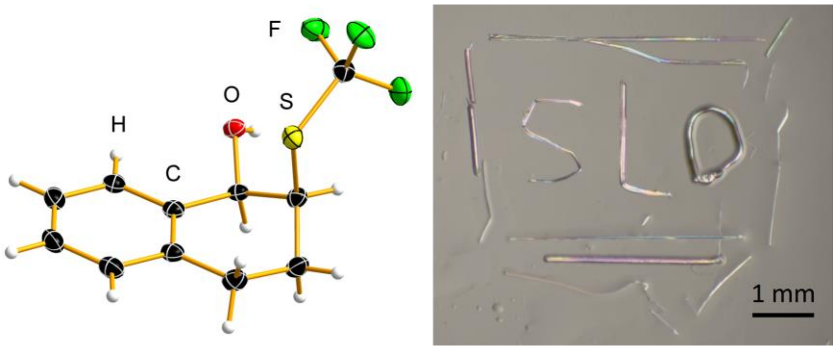

Figure 1: (1*R*,2*S*)-2-(trifluoromethylthio)-1-tetralol forms plastically flexible crystals [4].

References

[1] S. Saha, M.K. Mishra, C.M. Reddy and G.R. Desiraju, *Accounts of Chemical Research* **51** (2018) 2957−2967.
[2] M. Pisačić, I. Biljan, I. Kodrin, N. Popov, Ž. Soldin and M. Đaković, *Chemistry of Materials* **33** (2021) 3660–3668,
[3] A.E. Cotman, M. Lozinšek, B. Wang, M. Stephan and B. Mohar, *Organic Letters* **21** (2019) 3644–3648.
[4] A.E. Cotman, P.A. Dub, M. Sterle, M. Lozinšek, J. Dernovšek, Ž. Zajec, A. Zega, T. Tomašič and D. Cahard, *ACS Organic & Inorganic Au* **2** (2022)
[5] C.M. Reddy, R.C. Gundakaram, S. Basavoju, M.T. Kirchner, K. A. Padmanabhan and G. R. Desiraju, *Chemical Communications* (2005) 3945–3947.

Mixed halides – a way to stabilize Ruddlesden-Popper structures

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Hybrid inorganic-organic lead halide perovskites are impressing the semiconductor community with their astounding physical properties and optoelectronic applications as solar cells and light-emitting diodes that outperform many other materials. Low dimensional perovskites are attracted attention due to their improved properties compared to 3D perovskites, such as higher exciton binding energy and improved environmental stability due to the presence of spacer cations capable of locking the octahedral framework and preventing the penetration of water molecules. While there are no restrictions on organic spacer length, there is still a requirement for the width; cation must fit into an inorganic pocket defined by the axial halide anions of four adjacent corner-shared octahedra. Given these requirements imposed by the dimensions of the inorganic pocket, it is obvious that the shape of the spacer cation, especially but not limited to the shape of its amino head, plays an important role in the dimensionality of the perovskites. Reduced dimensionality becomes even more expected when bulky size is additionally accompanied by the limited flexibility of ammonium head. Considering the effects that both the size and the shape of the ammonium head have on the (de)stabilization of the 2D layered structure, one might expect that the branching of the spacer cation (in the vicinity of the ammonium head) could also have a significant impact on the dimensionality of the perovskite and the resulting properties. In this work, we report the effects of branching on the dimensionality of the perovskite and show that neither bromides nor iodides with t-BA spacer can form the 2D RP structure while new approach, utilizing mixed halide inorganic slab, results in the formation of desired RP assembly [1]. This work was supported by the PZS-2019-02-2068 project financed by the "Research Cooperability" Program of the Croatian Science Foundation and European Union from the European Social Fund under the Operational Programme Efficient Human Resources 2014-2020.

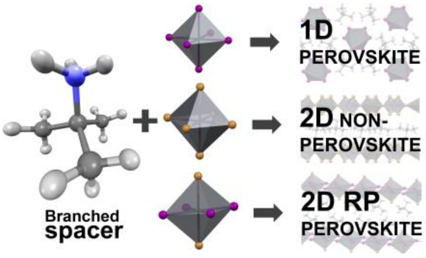

Figure 1: Perovskite dimensionality as a function of halide anions.

References

[1] J. Ovčar, T.L. Leung, L. Grisanti, Ž. Skoko, M. Vrankić, K-H. Low, S. Wang, P-Y. You, H. Ahn, I. Lončarić, A. Djurišić and J. Popović, *Chemistry of Materials* **34** (2022) 4286–4297.

Experimentally-validated *ab initio* crystal structure prediction of novel metal-organic framework materials

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Metal-organic frameworks (MOFs) are microporous materials being developed for a wide range of applications, including gas storage and separation, catalysis, artificial photosynthesis, energetic materials[1,2]. The diversity of MOF applications stems from their modular node-and-linker composition, where different combinations of building blocks yield materials with different crystal structures and, consequently, properties. Currently, MOF design is principally based on empirical experimental approaches based on considerations of geometry and chemical intuition. In that context, the development of *ab initio* methods for predicting structures and properties of MOFs could provide new, unexpected opportunities for a more general design and synthesis of such microporous materials.

We have recently [3] reported the first-principles crystal structure prediction (CSP) method for MOFs, based on the *ab initio* random structure searching (AIRSS) [4] and Wyckoff Alignment of Molecules (WAM) algorithms. Several classes of existing MOFs have been tested by our CSP method and their structures were successfully being reproduced. Here, I will present the first examples for predicting three new energetic Cu^{2+} ion nodes with imidazolate linkers zeolitic imidazolate frameworks (ZIFs). The subsequent experimental screening provided materials whose structures matched our computationally low-energy predictions, validating this MOF CSP approach for new materials discovery.

Moreover, our specific focus on the unsaturated substituted imidazolate linkers with vinyl and acetylene moieties yield ZIFs exhibit hypergolic behavior [5,6]. The experimentally-observed ZIFs demonstrated excellent hypergolic ignition properties, coupled with high energy densities derived from CSP calculations. Overall, our *ab initio* MOF design can potentially lead to a major advance in MOF design as well as improve our understanding of their structure-property relationships.

References

[1] P. Silva, S.M.F. Vilela, J.P.C. Tomé and F.A. Almeida Paz, *Chem. Soc. Rev.* **44** (2015) 6774–6803.
[2] J. Zhang, Y. Du, K. Dong, H. Su, S. Zhang, S. Li and S. Pang, *Chem. Mater.* **28** (2016) 1472–1480.
[3] J.P. Darby, M. Arhangelskis, A D. Katsenis, J.M. Marrett, T. Friščić and A. J. Morris, *Chem. Mater.* **32** (2020) 5835–5844.
[4] C.J. Pickard and R.J. Needs, *J. Phys. Condens. Matter* **23** (2011) 53201.
[5] H.M. Titi, J.M. Marrett, G. Dayaker, M. Arhangelskis, C. Mottillo, A.J. Morris, G.P. Rachiero, T. Friščić and R.D. Rogers, *Sci. Adv*. **5** (2019) 1–9.
[6] Y. Xu, J.M. Marrett, H.M. Titi, J.P. Darby, A.J. Morris, T. Friščić and M. Arhangelskis, *ChemRxiv* (2022).

Some relevant results from electrical analysis of thermosalient crystals of 1,2,4,5-tetrabromobenzene and 1,2,4,5-tetraclorobenzene

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Thermosalient materials, or more colloquially called jumping crystals, are a class of materials that exhibit mechanical motion as a response to the thermal stimulus. Such materials, which are capable of extremely fast and, more important, controllable energy conversion are extremely important candidates for active actuating elements, such as flexible electronic switches, displays, artificial muscles, microfluidic valves and gates, heat sensors etc.

Synthetized crystals of molecular alloys, with different concentrations of 1,2,4,5-tetrabromobenzene and 1,2,4,5-tetraclorobenzene, were studied with hot stage microscope to characterize the thermosalient behavior of these mixed crystals. Resulting analysis shows that a threshold concentration for the activation of the jumping of crystals is present and that there is a dependency of the temperature, at which phase transition occurs, on the concentration of the mixture. The temperature of the thermosalient phase transition can be fine-tuned in the interval of 10 K which presents a giant step towards the practical utilization of this effect.

On this system a preliminary spectroscopic impedance analysis was performed, and several interesting new information emerged about electric properties of thermosalient materials, showing that this kind of analysis could provide new important information about crystal jumping and how to electrically control the activation of "jumping".

Structural and optical properties of perovskites: $Sr_3Fe_{2+x}Mo_{1-x}O_{9-3x/2}$ (0.3 ≤x≤ 1)

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Perovskites-type oxides $Sr_3Fe_{2+x}Mo_{1-x}O_{9-3x/2}$ (x= 0.30, 0.45, 0.60, 0.75, and 1.00) [1] were synthesized in polycrystalline form using solid-state reaction, in air. These oxides have been studied at room temperature using of XRD, Mössbauer and UV-vis spectrophotometry. The crystal structures were refined by Rietveld's method, and revealed that this series adopts two phase transitions from a tetragonal *I*4/*mcm* (x= 0.30, 0.45, and 0.60) to a simple cubic *Pm*3*m* (x= 0.75) to another tetragonal *P*4/*mmm* (x= 1.00) phase. The values of the isomer shift (IS) and quadrupole splitting (QS) confirm that the formal oxidation state of iron containing our compounds consist of the mixed valence of the Fe 3+ and Fe4+ cations for octahedral environment. The Mössbauer spectrum of the sample (x= 0.75) $SrFe_{0.917}Mo_{0.083}O_{3-\delta}$ is consistent with Fe in a cubic lattice site. The direct bandgap energy increases from 1.70 to 2.25 eV with increasing x.

Spectral dependence of optical parameters such as; absorption coefficient, refractive index, extinction coefficient, optical conductivity, real and imaginary parts of the complex dielectric function, complex electric modulus and complex impedance were performed in the range 1.54 - 4.94 eV using UV- spectroscopy experiments.

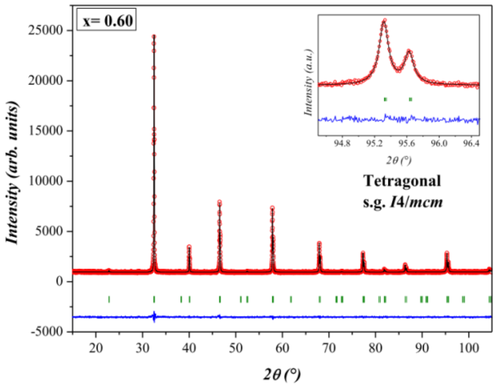

Figure 1: Final Rietveld refinement plot of tetragonal compound.

References

[1] A. El Hachmi, B. Manoun, M. Sajieddine, Y. Tamraoui, S. El Ouahbi, *Polyhedron* **200** (2021) 115133.

Unique structural features of new acridan aryl esters – promising indicators in luminescence analysis

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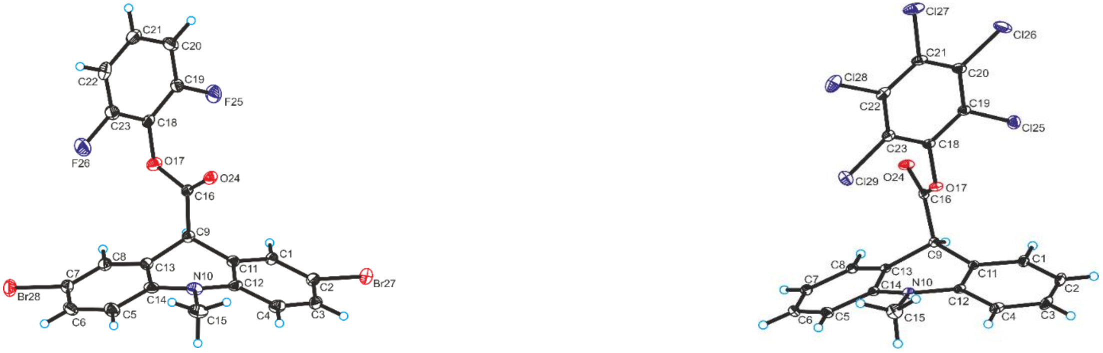
Bioimmunodiagnostics expresses a key role in modern medical diagnostics. It requires specific chemical indicators, that can enable to detect and assay the concentration of biological analytes such as peptide pathogens, viruses or infections in complex matrices originated from humans and animals. That is why in our work we focused on the synthesis and structural investigations of original compounds, that can be used in medical diagnostics.

Original compounds are not represented in crystallographic database (The Cambridge Structural Database). In this paper, we present original compounds with potential biomedical use. The systems are not aromatic and have a bend around the N10-C9 axis (butterfly-like structure). Researched structures are represented on the (Fig. 1). The crystals of synthetized compounds were obtained by the crystallization from ethanol-H_2O mixtures. Diffraction data were collected, employing Oxford Diffraction Gemini R ULTRA Ruby CCD diffractometer with MoKa radiation.

The new compounds, being the reduced forms of acridinium salts, are very susceptible to oxidation by oxidizing enzymes, e.g., horseradish peroxidase (HRP). After oxidation with HRP, compounds of this type are transformed into chemiluminogenic substrate, that can efficiently emit radiation in the visible range of the electromagnetic spectrum [1]. The susceptibility to effective emission depends on the structure of given compound - particular on the presence, type, and localization of substituents - as well as environmental conditions, such as the proportion of reagents, solvent type, presence of signal enhancer, surfactants, etc. [2].



1 2

Figure 1: Crystallographic structures of two original compounds with potential biomedical use.

1 - 2,6-difluorophenyl 2,7-dibromo-10-methyl-9,10-dihydroacridine-9-carboxylate

2 - pentachlorophenyl 10-methyl-9,10-dihydroacridine-9-carboxylate;

References

[1] H. Akhavan-Tafti, R. DeSilva. Z. Arghavani, R. A. Eickholt, R. S. Handley, B. A. Schoenfelner, K. Sugioka, Y. Sugioka, A. P. Schaap, *J. Org. Chem*. **63** (1998) 930–937.

[2] A. Niziołek, B. Zadykowicz, D. Trzybinski, A. Sikorski, K. Krzyminski, J. Błazejowski, *J. Mol. Struct*. 920 (2009) 231–237.

Structure determination on challenging samples – how modern X-ray instrumentation can help

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Although new methods, such as cryo-EM and electron diffraction, expand the spectrum of methods for 3D structure investigations, X-ray diffraction remains the gold standard for obtaining precise models within reasonable time and efforts. Highly integrated platforms such as Bruker's D8 QUEST and D8 VENTURE make it easier to work effectively on today's ever more complex crystallographic targets. At the same time these platforms provide a comprehensive range of programs to obtain accurate structures from even the most difficult datasets. New features in both automation hardware and software design have emerged and are at the scientist's service for challenging projects. Instant access, often with fewer time restrictions are another important point to mention in advantage of in-house solution.

The presentation will begin with an overview of key technologies, such as the goniometer, the IμS DIAMOND II and the METALJET D2 PLUS X-ray sources and the PHOTON III detectors. We will discuss these technologies contribute to advancing structure determination from more challenging samples in the D8 VENTURE platform complete high-performance system. We will show how the latest software advances in APEX make data collection more efficient and provide newly added features. Using selected application examples we will demonstrate the integration of accessories, such for high pressure research or automated sample handling.

Figure 1: D8 VENTURE X-ray diffraction solution featuring two IμS 3.0 microfocus sources and a PHOTON III 14 detector.

Mechanochemical strategy for controllable encapsulation of Buckminsterfullerene for preparation of fulleretic ZIF materials

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Fullerene and fullerene derivatives show tremendous application potential due to their unique physico-chemical properties. Functional materials with fullerene embedded in their structure are researched due to their increased stability, conductivity, or catalytic activity compared to their constitutional components. Metal-organic frameworks (MOFs) are a class of porous crystalline materials extensively studied for their applicability. Enclosing the fullerenes inside the pores of MOFs produces fulleretic materials with unique properties.[1] Guest encapsulation into MOFs is mainly done by solution post-synthetic methods, which depend on the solubility, MOFs aperture size and competition with the solvent.[2] Here, a fast and green mechanochemical approach, in which a framework is formed around the guest, arose as a suitable solution because it requires only traces of solvents. Ball milling allowed stoichiometrically controlled encapsulation into sodalite ZIF (zeolitic-imidazolate framework) and provided C_{60}@ZIF crystalline materials containing various amounts of fullerene entrapped in the available pores of the ZIF while solution-based strategies resulted in minimal load. The aforementioned approach is highly efficient, and fullerenes are immobilized within the ZIF with the precise spatial arrangement inside the framework matrix which gives them single-molecule-like properties.[3] Therefore, we expect it can be used to confine other rigid nanoguests in suitable MOFs to achieve new and advanced MOF materials.

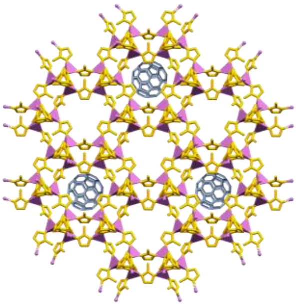

Figure 1: Schematic representation of fulleretic ZIF material.

References

[1] A.M. Rice, E. A. Dolgopolova, N.B. Shustova, *Chem. Mater.* **29** (2017) 7054–7061.
[2] S.B.T. Sadjadi, *Organic Nanoreactors*, Elsevier: Boston, 2016.
[3] V. Martinez, B. Karadeniz, N. Biliškov, I. Lončarić, S. Muratović, D. Žilić, S.M. Avdoshenko, M. Roslova, A.A. Popov, K. Užarević, *Chem. Mater.* **32** (2020) 10628–10640.

A new copper(II) metal–organic frameworks constructed from *N*-alkyl glycinates and 3,3'-bipyridine: synthesis, structure and thermal behavior

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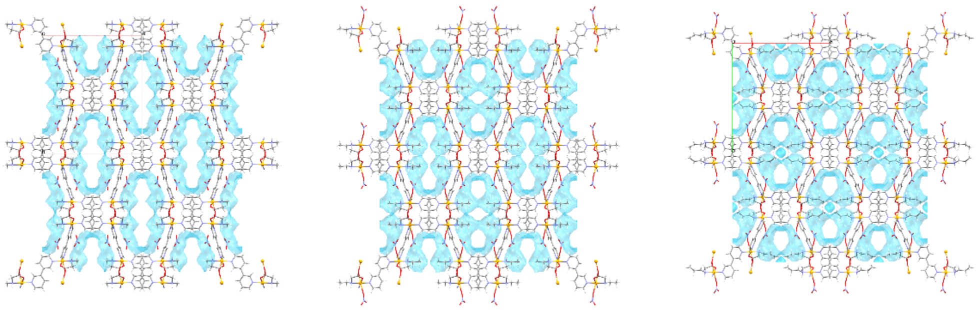
Metal–organic frameworks (MOFs) are coordination compounds that include metal ions or metal clusters connected with organic ligands, linkers, in their structure. MOFs are porous materials and have potential applications in gas or solvent sorption, gas storage and separation, water harvesting, purification, homogeneous and asymmetric catalysis and drug delivery [1–3]. In MOF design, it is possible to control the intermolecular interactions, the size of MOF pores, and MOF shape by choosing the organic ligands [2,4]. Amino acids are interesting ligands because of their chelating nature, diversity in types and lengths of sidechains, and potential for functionalization, such as *N*-alkylation.

In this work, we report synthesis and structural characterization of four novel copper(II) metal–organic frameworks with *N*-alkyl glycinates (*N*-methyl- (MeGly), *N*-ethyl- (EtGly) and *N*-propylglycinate (PrGly)) and 3,3'-bipyridine: $\{[\mathrm{Cu(NO_3)(MeGly)(3,3'\text{-}bpy)}]\cdot\mathrm{DMF}\cdot\mathrm{H_2O}\}_n$ (**1a**), $\{[\mathrm{Cu(NO_3)(EtGly)(3,3'\text{-}bpy)}]\cdot\mathrm{DMF}\cdot\mathrm{H_2O}\}_n$ (**2a**), $\{[\mathrm{Cu(NO_3)(EtGly)(3,3'\text{-}bpy)}]\cdot\text{(unidentified solvate)}\}_n$ (**2b**), $\{[\mathrm{Cu(NO_3)(PrGly)(3,3'\text{-}bpy)}]\cdot\mathrm{DMF}\}_n$ (**3a**). These three-dimensional MOFs were obtained by solution synthesis under mild conditions. Additionally, compound **1a** was synthesized by a mechanochemical method. The influence of the alkyl chain length of *N*-alkylglycine on crystal packing, as well as the shape and the size of pores was investigated. In compounds **1a**, **2a** and **3a** the volume fraction of voids range from 27.1% to 31.6% (Figure 1). The topologies of all crystal structures were determined. The thermal behavior of selected compounds has been investigated by powder X-ray diffraction and thermogravimetric analysis.



1a **2a** **3a**

Figure 1: Crystal packing of compounds **1a**, **2a** and **3a**. Blue surfaces represent 1D channels filled with solvent molecules. All structures are shown along the crystallographic *c* axis.

References

[1] S.R. Batten, N.R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M.P. Suh and J. Reedijk, *Pure Appl. Chem.* **85** (2013) 1715–1724.

[2] A.Y. Tsivadze, O. E. Aksyutin, A. G. Ishkov, M.K. Knyazeva, O.V. Solovtsova, I.E. Men'shchikov, A.A. Fomkin, A.V. Shkolin, E.V. Khozina and V. A. Grachev, *Russ. Chem. Rev.* **88** (2019) 925–978.

[3] W. Xu and O.M. Yaghi, *ACS Cent. Sci.* **6** (2020) 1348–1354.

[4] C.-X. Ren, M. Ji, Q.-X. Yao, L.-X. Cai, B. Tan and J. Zhang, *Chem. Eur. J.* **20** (2014) 14846–14852.

Perhalogenated amines as bifunctional donor molecules in cocrystals with nitrogen-containing acceptors

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Investigating directional intermolecular interactions as predictable and efficient tools in supramolecular synthesis has been in the focal interest of crystal engineering of multi-component systems, including cocrystals [1]. While the majority of research is focused on either hydrogen (HB) or halogen bonding (XB), the examination of competition and cooperation of the two whenever they are present within the same system is gaining importance [2].

In this work, to investigate the structure-directing balance between halogen and hydrogen bonds in cocrystals, we used two perhalogenated amines, 4-bromo-2,3,5,6-tetrafluoroaniline (**btfa**) and 4-iodo-2,3,5,6-tetrafluoroaniline (**itfa**), as bifunctional donor molecules containing XB donor (iodine or bromine atom) and HB donor (amino group) on the same perfluorinated aromatic backbone. Using three different ditopic nitrogen-containing acceptors 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane and 1,4-diazabicyclo[2.2.2]octane, we have prepared seven cocrystals by grinding and crystallization from solution. Prepared compounds were characterized by diffraction methods (single-crystal X-ray diffraction and X-ray powder diffraction), and their thermal stability was determined by differential scanning calorimetry. Structure analysis revealed that in four cocrystals both N···I or N···Br halogen and N–H···N hydrogen bonds were formed, in two cocrystals with **btfa** only N–H···N hydrogen bond was formed, while in one cocrystal with **itfa** only N···I halogen bond was formed. Based on our results, **btfa** is more likely to form only hydrogen bonds, while **itfa** has a great potential as a bifunctional donor. Utilizing **itfa** in crystal engineering of cocrystals could lead to the formation of supramolecular chains based on halogen and hydrogen bonds in a predictable and reliable matter.

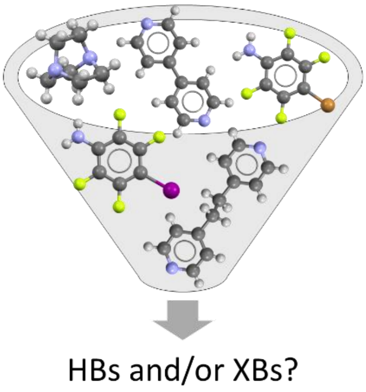

Figure 1: Donors and acceptors used for cocrystals preparation.

References

[1] G.R. Desiraju, *J. Am. Chem. Soc.* **135** (2013) 9952–9967.
[2] C.B. Aakeröy, S. Panikkattu, P. D. Chopade and J. Desper, *CrystEngComm* **15** (2013) 3125–3136.

Syntheses and structures of copper(II) coordination polymers with *N*-methylglycinate and 4,4’-bipyridine

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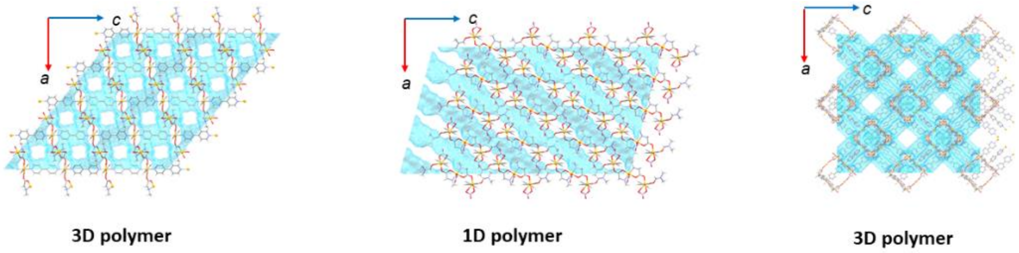
Metal–organic frameworks are porous polymeric materials built from metal ions or clusters linked by organic ligands [1,2]. They have attracted a high interest due to their specific properties (porosity, stability, low density, large specific surface area, susceptibility to functionalization) [3,4] and potential for application in various fields, such as gas storage [2], water harvesting [5], air purification [2], drug delivery [4] and many others. Great significance is given to the design of three-dimensional, highly porous structures with predictable topologies and properties controlled mainly by the chemical nature of the individual components, but also by other factors such as temperature, type of solvent and pH-value [1,2].

In this work we report synthesis and structural characterization of four new copper(II) coordination polymers with *N*-methylglycinate (MeGly) and 4,4’-bipyridine (4,4’-bpy). Three of them are 3D coordination polymers, while the fourth compound is 1D coordination polymer. The topological analysis revealed that one of the compounds has completely new topological type, which has not been stored in the Reticular Chemistry Structure Resource database so far. We investigated the influence of crystallization conditions on the crystal packing, as well as on the shape and size of channels. Channels in these metal–organic frameworks occupy from 29.2% to 61.8% of the unit cell volume. For one of reported compounds, stability at different relative atmospheric humidity and biological activity against human hepatocellular carcinoma cells and acute monocyte leukemia cells *in vitro* were also tested.



3D polymer **1D polymer** **3D polymer**

Figure 1: Crystal packing of compounds with copper(II) ion, *N*-methylglycinate and 4,4’-bipyridine: $\{[\mathrm{Cu(MeGly)(H_2O)(4,4'\text{-}bpy)}]\mathrm{NO_3}\cdot(\text{unidentified solvate})\}_n$ (left), $\{[\mathrm{Cu_3(NO_3)_3(MeGly)_2(H_2O)(4,4'\text{-}bpy)_2(DMF)_2}]\mathrm{NO_3}\cdot 2\mathrm{DMF}\cdot 2\mathrm{H_2O}\}_n$ (middle), $\{[\mathrm{Cu_3(NO_3)_{4-\mathit{x}}(MeGly)_2(4,4'\text{-}bpy)_4}](\mathrm{NO_3})_x\cdot(\text{unidentified solvate})\}_n$ (right). Infinite channels are shown in blue.

References

[1] S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O’Keeffe, M. Paik Suh and J. Reedijk, *Pure Appl. Chem.* **85** (2013) 1715–1724.
[2] A. U. Czaja, N. Trukhan and U. Müller, *Chem. Soc. Rev.* **38** (2009) 1284–1293.
[3] S. L. James, *Chem. Soc. Rev.* **32** (2003) 276–288.
[4] A. Y. Tsivadze, O. E. Aksyutin, A. G. Ishkov, M.K. Knyazeva, O.V. Solovtsova, I.E. Men’shchikov, A.A. Fomkin, A. V. Shkolin, E.V. Khozina and V.A. Grachev, *Russ. Chem. Rev.* **88** (2019) 925–978.
[5] M. J. Kalmutzki, C. S. Diercks and O. M. Yaghi, *Adv. Mater.* **30** (2018) 1704304.

Structural and vibrational study of single crystal $(C_6H_9N_2)_2H_2P_2O_7$

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Chemical preparation, crystal structure and vibrational study are reported for a new diphenyl hydrazine dihydrogen phosphate monocrystal DPHDP $(C_6H_9N_2)_2H_2P_2O_7$.This organic cationic diphosphate $(C_6H_9N_2)_2H_2P_2O_7$ was synthesized by the method of ion exchange resin**.** $(C_6H_9N_2)_2H_2P_2O_7$ crystallizes in the monoclinic system, with a merit factor of 0.0285, space group $P2_1/c$, a = 7,1991 (2) Å, b = 8,0209 (4) Å, c =31,2070(2) Å, β = 93,577(1)°, Z = 4, V = 1798.5 (1) $Å^{3.}$ The crystal structure was refined down to R = 0.027, R = 0.069 for 1830 reflections satisfying criterion $I \geq 2\sigma$ (I). The structural resolution shows the existence of $H_2P_2O_7^{2-}$ ion chains linked together by hydrogen bonds. The organic cations $C_6H_9N_2^+$ and the phosphate chains are linked together by hydrogen bonds. Diphosphate group adopt an eclipsed configuration. A network of O-H... O hydrogen bonds reinforce the cohesion of the structure. The vibrational study by IR absorption spectroscopy of the title compound reveals the presence of three bands and confirms the existence of non-equivalent positions of water molecules in the structure.

$(C_6H_9N_2)_2H_2P_2O_7$ is a nonlinear optical NLO product as it is not centrosymmetric.

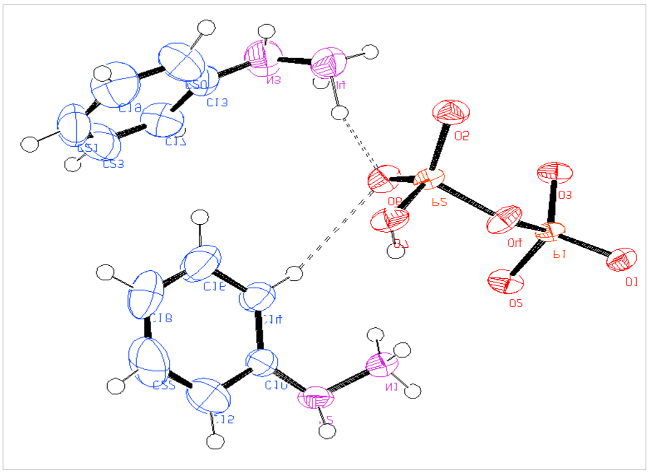

Figure 1: ORTEP representation of $(C_6H_9N_2)_2H_2P_2O_7$

References

[1] A. Jouini, J.C. Gacon , M. Ferid and M. Trabelsi-Ayadi, *Opt. Mat.* **24** (2003) 175–180.
[2] H.Y.-P. Hong, *Mat. Res. Bull.* **10** (1975) 1105–1110.
[3] H. Koizumi, *Acta Cryst.* **B32** (1976) 266–268.
[4] J.H. Cambell and T.I. Suratwala, *J. Non Cryst. Sol.* **263-264** (2000) 318–341.

Problem solving with co-crystals: Screening and single crystal

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The most common form of administering active pharmaceutical ingredients (API) is through solid dosage, therefore selecting an appropriate solid form is of great importance as they can have a wide range of physicochemical properties such as stability, bioavailability and solubility. A relatively new solid form that is gaining a growing amount of interest is co-crystals. This can be seen in the increase in patients and papers on co-crystals over several years.

Co-crystals offer a unique ability to modify the properties of API's though selection of co-former such as permeability, bioavailability and taste. Screening for co-crystals can be a hit and miss exercise where co-crystals are not formed, this can be related to incorrect stoichiometry of components. Presented in this talk is a solubility-based approach to screening for co-crystals.

Single crystal has also been shown to be the only definitive way of differentiating between a co-crystal and a salt, which is important for regulatory bodies and patient protection. Therefore, this talk will also cover how modifications to single crystal experiments can be used to improve the probability of single crystal generation.

TEM studies of a newly discovered ternary phase in the Al-Cr-Sc system

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The transmission electron microscope is a powerful method for characterizing the structure of materials, including crystals and defect structures. The advantage of electron diffraction and imaging is a short wavelength of the incident electrons, strong atomic scattering and the ability to examine very small volumes of matter down to individual atomic columns. The focus of the research was on the crystal structure of a newly discovered phase in the Al-Cr-Sc system with a composition of $Al_{52}Cr_{14}Sc_{34}$ (at.%). The observed phase belongs to the Laves-phases family with a $P6_3/mmc$ hexagonal crystal structure and is prototypic to $MgZn_2$. With Single crystal and powder X-ray diffraction (PXRD) combined with the Rietveld refinement method, we confirmed the full occupancy of Sc on the 4f Wyckoff site and mixed occupancy of Al/Cr on sites 2a and 6h. High-angle annular dark-field scanning transmission electron microscopy mode (HAADF-STEM) was performed to validate the crystal structure of the Al-Cr-Sc ternary phase and to confirm or invalidate structural homogeneity on the atomic scale. In agreement with the predicted model, the maximal intensity spots correspond to a pair of Sc (Z=21) columns, intercalated with a mixed Al (13) – Cr (24) column. A fraction of 47 % of the Al sites is replaced by Cr atoms (2a site), which is in fair agreement with the observed intensity variations. The intensity variation within the flat plane shows a periodic exchange of maximal intensity spots with spots of very low intensity due to Al-Cr mixed with 11.4% of Al exchanged by Cr atoms on the 6h-site, which is not directly evident from the experimental observation. This can be interpreted by the fact that the projected atomic density within the individual Al-Cr mixed atomic columns is different, which has a straight impact on the observed signal intensity. Within a unit cell, the 6h sites are characterised by a single-atom site, especially, the projected atomic density within the flat planes periodically oscillating between neighbouring columns, thus explaining the observed intensity oscillations.

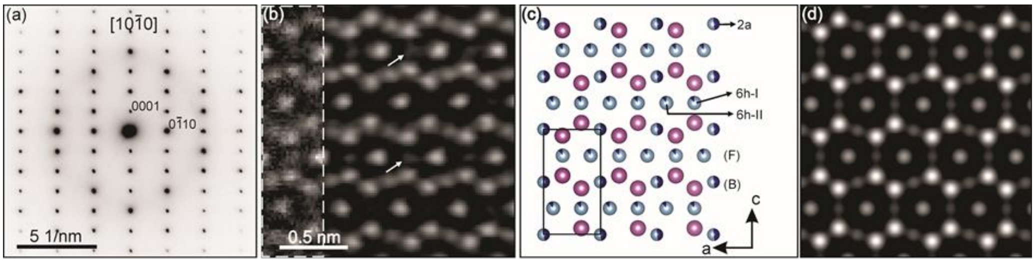

Figure 1: TEM studies of the ternary phase: (a) SEAD pattern analysis with the corresponding (b) atomically-resolved HAADF-STEM image. (c) Projected atomic model of the ternary phase, viewed in $[10\bar{1}0]$ zone-axis with the related (d) calculated HAADF-STEM image.

Acknowledgements

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Reference

M. Kušter, A. Meden, B. Markoli, Z. Samardžija, M. Vončina, P. Boulet, E. Gaudry, J.-M. Dubois and S. Šturm, *Crystals* **11** (2021)

Crystal structures of three 2,6-diaminopyridine compounds

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Diaminopyridines are of particular interest in coordination chemistry, acting either in protonated form as cations, or as neutral ligands, which can bind in a variety of ways due to their two types of donor sites, i.e. the nitrogen atom of the aromatic ring and nitrogen atoms of both amine groups, yielding compounds with unusual structural and magnetic properties. Complexes of transition metals with 2,6-diaminopyridines have been studied as anti-static agents for polyethylene [1–2].

Dark blue crystals of a new coordination compound, (2,6-dapyH$^+$)$_2$[Co(NCS)$_4$], have been prepared by the reaction of 2,6-diaminopyridine and cobalt thiocyanate under reflux in methanol. Crystals were monoclinic with $P2_1/m$ space group. The compound was further investigated by FTIR and thermal analysis including powder diffraction measurements of the residue after thermal decomposition. Furthermore, new structures of 2,6-diaminopyridinium bromide monohydrate (triclinic, P-1), and 2,6-diaminopyridinium sulfate monohydrate (orthorhombic, $Pna2_1$ space group), were determined and will be reported.

The unit cell of (2,6-dapyH$^+$)$_2$[Co(NCS)$_4$] consists of two complex anions containing Co(II), tetrahedrally coordinated by four NCS$^-$ ions *via* the nitrogen atom, and four protonated 2,6-diaminopyridine cations. The complex anion is symmetric – Co(II) and two thiocyanate ligands lie on mirror plane. Cations and anions are connected via N-H…S and N-H…N hydrogen bonds.

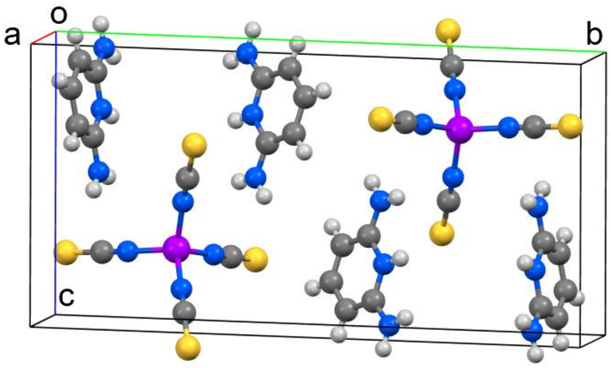

Figure 1. Unit cell of (2,6-dapyH$^+$)$_2$[Co(NCS)$_4$]

References

[1] J.R. Allan, A.R. Gardner, B. McCloy and W.E. Smith, *Thermochim. Acta* **208** (1992) 125–131.
[2] D.P. Singh and V.B. Rana, *Polyhedron* **14** (1995) 2901–2906.

Building ternary halogen bonded cocrystals with Werner coordination compound and perhalogenated benzenes

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In recent years, the design strategy of binary cocrystals has been established by utilizing specific intermolecular interactions and using the knowledge of supramolecular synthons. However, the synthesis of ternary or quaternary cocrystals remains a challenging task, since balancing more components and controlling specific interactions in a crystal is difficult [1-3]. Obtaining ternary cocrystals bind together exclusively by halogen bonds presents a significant challenge in crystal engineering. To the best of our knowledge, around 200 fully characterized ternary cocrystals can be found in literature and only 4 of them are halogen bonded cocrystals [4]. Those cocrystals are based on a small organic molecule or π-system which served as a halogen bond acceptor and two perhalogenated molecules as donor moieties.

Our approach to this topic was focused on using the metal complex as the main building block for obtaining ternary cocrystals. We synthetized the Werner coordination compound, $Ni(CH_3C_5H_5N)_4(NCS)_2$ - **K1**, containing two *trans*- isothiocyanate groups, which are flexible and sterically unhindered. This way we designed a ditopic metal-organic acceptor which can interact with perhalogenated benzenes to form halogen bonds. To build cocrystals, we used combination of selected donors: 1,2-diiodotetrafluorobenzene (**12tfib**), 1,3-diiodotetrafluorobenzene (**13tfib**), 1,4-diiodotetrafluorobenzene (**14tfib**), 1,3,5-trifluoro-2,4,6-triiodobenzene (**135tfib**) and 1,4-dibromotetrafluorobenzene (**14tfbb**). A series of 7 ternary cocrystals was obtained, of which 5 were structurally characterized by single-crystal X-ray diffraction: (**K1**)(**135tfib**)(**13tfib**), (**K1**)(**135tfib**)(**12tfib**), (**K1**)(**13tfib**)$_3$(**14tfib**) and 2 polymorphs of (**K1**)(**135tfib**)(**14tfib**). Cocrystals were also prepared by mechanochemical synthesis using two possible routes: either by milling binary cocrystals with donor molecule or by one-pot synthesis. Isothiocyanate sulfur in **K1** proved to be a very good and dependable halogen bond acceptor capable of forming multiple halogen bonds, which then enabled shape-size mimicry of donor molecules and formation of ternary cocrystals.

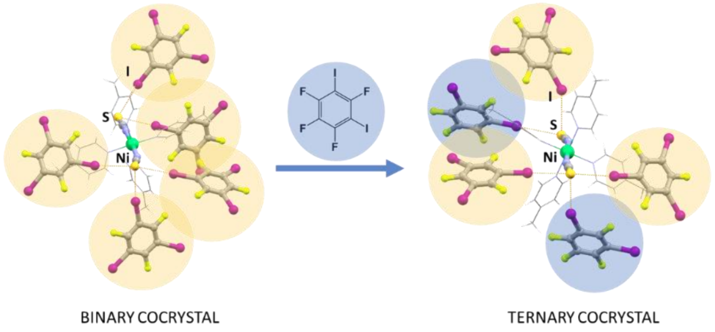

Figure 1: Structures of (**K1**)(**135tfib**)$_2$ (binary) and (**K1**)(**135tfib**)(**13tfib**) (ternary cocrystal).

References

[1] C.B. Akeröy, P.D. Chopade and J. Desper, *Cryst. Growth Des.* **11** (2011) 5333–5336.
[2] S. Tothadi and G. R. Desiraju, *Chem. Commun.* **49** (2013) 7791–7793.
[3] F. Topić and K. Rissanen, *J. Am. Chem. Soc.* **138** (2016) 6610–6616.
[4] H. Jain, D. Sutradhar, S. Roy and G.R. Desiraju, *Angew. Chem. Int. Ed.* **60** (2021) 12841–12846.

Methylated isatin derivatives as halogen bond acceptors in multicomponent crystals

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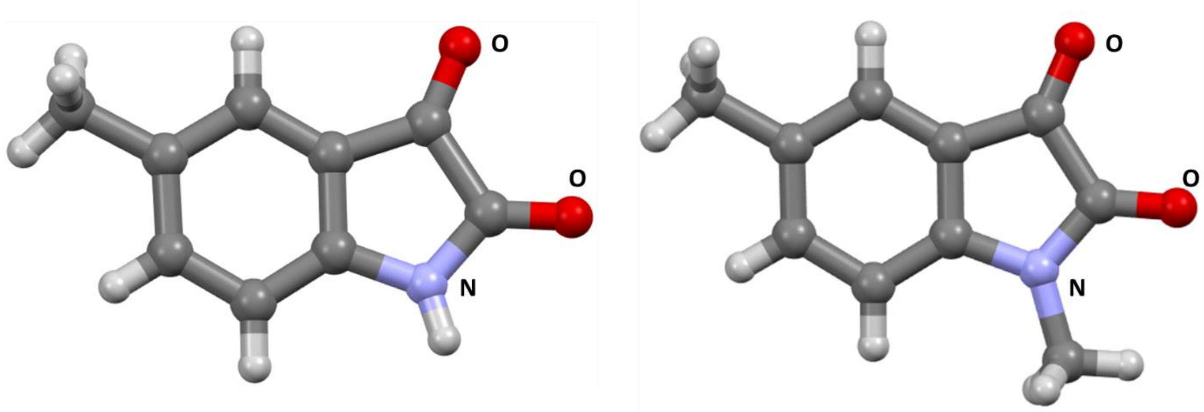
Isatin (1*H*-indole-2,3-dione) and its derivatives have been extensively used as substrates in syntheses of a large variety of heterocyclic compounds [1]. Due to the presence of several functional groups it can undergo many different types of chemical transformations and its derivatives are used for synthesizing many bioactive compounds [2]. From a crystal engineering point of view, isatin and its derivatives represent interesting moieties because they are asymmetrical dicarbonyl compounds. The usage of isatin and its derivatives as halogen bond acceptors has not been studied so far. In this work, we explored how alkyl substituents on isatin affect halogen bond formation by using different perfluorinated halobenzenes as donor molecules. Two methylated derivatives of isatin, 5-methylisatin (**5-Meis**) and *N*-methyl-5-methylisatin (**NMe5Meis**) have been cocrystallized with four different halogen bond donors: 1,2-, 1,3- and 1,4-diiodotetrafluorobenzene (**1,2-tfib**, **1,3-tfib** and **1,4-tfib**) and 1,3,5-triiodo-2,4,6-trifluorobenzene (**1,3,5-tfib**). Cocrystallization experiments were performed both mechanochemically, using liquid-assisted grinding and solution-wise, using crystallization techniques. A series of five cocrystals was obtained, which were all characterized by X-ray powder diffraction, single crystal X-ray diffraction and differential scanning calorimetry. Dominant interactions in cocrystals obtained with **5-Meis** are C–H···O and N–H···O hydrogen bonds and I···O halogen bonds, while with **NMe5Meis** the dominant interactions are C–H···O hydrogen and I···O halogen bonds.



5-Meis **NMe5Meis**

Figure 1: Methylated isatin derivatives used in this work.

References
[1] J.F.M. da Silva, S.J. Garden and A.C. Pinto, *J. Braz. Chem. Soc.* **12** (2001) 273–324.
[2] F.A. Khan and A. Maalik, *Trop. J. Pharm. Res.* **14** (2015) 1937–1942.

Inspiring mechanochemical interconversions of halogen-bonded cocrystals by periodic DFT calculations

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Design and synthesis of new type of multicomponent molecular crystals (cocrystals), as a means to target materials with desired properties, relies on detailed understanding of non-covalent interactions such as hydrogen bonding, halogen bonding and π-π stacking. In particular, halogen bonding, as an interaction arising from the positive region of electrostatic potential (σ-hole) on the halogen atom and a negative region of electrostatic potential on the acceptor species, including π-systems lighter acceptor atoms (N, O, S), and, more recently, heavier elements such as As and Sb, offers a method for building unprecedented supramolecular architectures and yield materials with unusual luminescent, optical behavior, and pharmaceutical bioavailability [1].

Reliable design of halogen-bonded cocrystals with desired properties relies on good understanding of the effects controlling halogen bond formation, insights into which can be gained from theoretical calculations [2]. In this presentation I will describe our work on mechanochemical synthesis and interconversion of a series of halogen-bonded cocrystals inspired by previously conducted periodic density-functional theory (DFT) calculations. Here we have chosen co-crystals sharing either an identical donor or acceptor and experimentally introduced the co-former to a co-crystal system, resulting in a competition between two cocrystals. By conducting the calculations prior to experiment, we can judge the likelihood of solid-state transformations occurring, and adjust our experimental strategies accordingly. One excellent way of validating the theoretical thermodynamic predictions from periodic DFT is via dissolution calorimetry measurements, which will be presented herein, as one of an early benchmark of this sort for the study of halogen-bonded materials.

In all cases examined herein, reactions which DFT predicted to be thermodynamically favorable, occurred under a variety of experimental conditions, including ball milling with several liquid additives (LAG) [3], as well as slurry experiments. Reactions with strongly positive calculated enthalpies (i.e., unfavorable) were found not to occur under any of the experimental conditions. Moreover, in one inconclusive example, where the calculated reaction enthalpy is close to zero, we detect the coexistence of two cocrystals in an equilibrium fashion, regardless of the direction of the attempted transformation.

References

[1] Y. Lu, T. Shi, Y. Wang, H. Yang, X. Yan, X. Luo, H. Jiang and W. Zhu, *J. Med. Chem.* **52(9)** (2009) 2854–2862.
[2] M. Arhangelskis, F. Topić, P. Hindle, R. Tran, A.J. Morris, D. Cinčić and T. Friščić, *Chem. Commun.* **56(59)** (2020) 8293–8296.
[3] T. Friščić and L. Fábián, *CrystEngComm* **11(5)** (2009) 743–745.

A novel π-hole interaction between an iodide anion and a quinoid ring involving an *n*→π* charge transfer

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π-hole interaction between an iodide anion and a quinoid ring in a co crystal of 3-chloro-*N*-methylpyridinium iodide with tetrabromoquinone (3-Cl-*N*-MePy·I·Br_4Q) involves a sandwich-like $I^-\cdots$quinone$\cdots I^-$ moiety with close contacts between the iodide anion and carbon skeleton of the quinoid ring (Fig. 1). Distance between the iodide and the ring mean plane is 3.73 Å, which is slightly shorter than the sum of van der Waals radii for C and I. This close contact forms because the quinoid ring with four electron-withdrawing substituents is severely electron-depleted, resulting in a large π-hole at the carbonyl C atom [1-2]. In the studied case there is also a partial electron transfer between the iodide and the quinone which is noted by a change of colour: the neutral quinone is yellow, while the co-crystals and the semiquinone crystals are black.

This unusual interaction is studied by quantum crystallography, combining X-ray charge density with quantum chemical modelling. It involves an *n*→π* charge transfer, so the quinoid ring has a partial negative charge (estimated to 0.08 - 0.11 e) and a partial radical character. A detailed X-ray charge density study revealed two symmetry-independent bonding critical points between the iodide and carbon atoms of the ring with maximum electron density of 0.065 e $Å^{-3}$, which were reproduced by quantum chemical modelling. Energy of the interaction is estimated to −13 kcal mol^{-1}, which is comparable to hydrogen bonding; it is dominantly of electrostatic nature, with a considerable dispersion component.

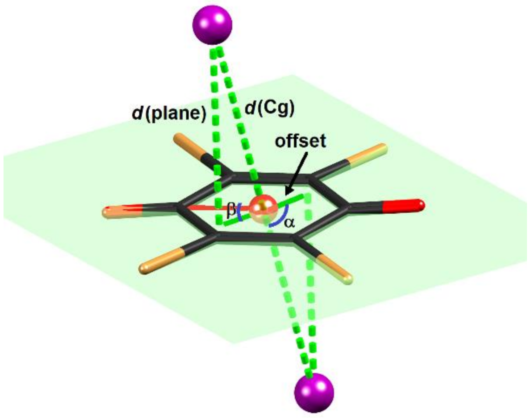

Figure 1: A sandwich-like $I^-\cdots Br_4Q\cdots I^-$ unit with geometric parameters indicated.

References

[1] K. Molčanov, G. Mali, J. Grdadolnik, J. Stare, V. Stilinović and B. Kojić-Prodić, *Cryst. Growth Des.* **18** (2018) 5182–5193.
[2] V. Milašinović and K. Molčanov, *CrystEngComm* **23** (2021) 8209–8214.

Rigaku Advances in X-ray and Electron Crystallography

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The latest range of Rigaku Oxford Diffraction instrument configurations will be summarized and illustrated with a number of particular examples in application.

The XtaLAB Synergy-ED is a new and fully integrated electron diffractometer, creating a seamless workflow from data collection to structure determination of three-dimensional molecular structures. The XtaLAB Synergy-ED is the result of an innovative collaboration to synergistically combine our core technologies: Rigaku's high-speed, high-sensitivity photon-counting detector (HyPix-ED), state-of-the-art instrument control, single crystal analysis software platform (CrysAlis^{Pro} for ED), and JEOL's long-term expertise and market leadership in designing and producing transmission electron microscopes.

Furthermore, our X-ray diffraction instruments will be presented. The XtaLAB Synergy platform with microfocus or rotating anode sources on one side and a series of Hybrid Photon Counting (HPC) X-ray area detectors on the other side of the four-circle goniometer allows for versatile configurations perfectly adapted to the researcher's needs. These systems can be further equipped with the sample changing robot (XtaLAB Synergy Flow), an Intelligent Goniometer Head (IGH) for automated crystal centering, the plate scanning device XtalCheck-S and/or a high-pressure unit.

Figure 1: XtaLAB Synergy-S (left), XtaLAB Synergy-R (middle), and XtaLAB Synergy-ED (right).

Cycloaddition of vinyl-moiety-containing dienophiles on 2*H*-pyran-2-one derivatives: A surprising diversity of possible products

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Cycloaddition is a well-established method for constructing new complex compounds. In this regard 2*H*-pyran-2-one derivatives **1** (Figure 1) represent versatile dienes reacting with a variety of alkynes and alkenes towards highly substituted (fused) aromatic compounds [1], isoindoles [2], indoles [3] and bicyclo[2.2.2]octenes that are appropriate for further transformations [4,5]. Vinyl-moiety-containing dienophiles **2** (such as ethyl vinyl ether (**2a**), cyclohexyl vinyl ether (**2b**), 1-vinyl-2-pyrrolidone (**2c**)) have already shown great potential in forming various cycloadducts [6,7], however the initially formed CO_2-bridged systems **3** and **4** cannot be isolated when conventional thermal reaction conditions are applied; on the other hand, when such cycloadditions [7] are carried out under high pressure (around 15 kbar) at ambient temperature compounds **3** and **4** are formed, isolated and their structures elucidated with the help of single crystal X-ray diffraction (in combination with other analytical and spectroscopic methods). All products were (as expected) obtained as racemates, but the regioselectivity and diastereoselectivity was complete in all cases. Due to the presence of amide NH (classical hydrogen bond donor) groups in all products combined with many C–H···O and C–H···π interactions interesting supramolecular architectures were observed in the crystal forms.

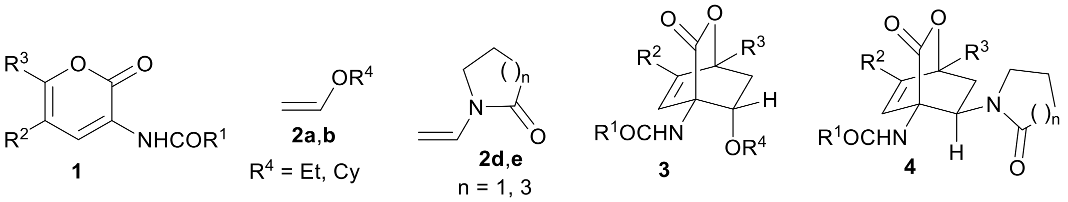

Figure 1: 2*H*-pyran-2-one derivatives, dienophiles and possible cycloadducts

References

[1] J. Suljagić, A. Juranovič, M. Krivec, K. Kranjc, M. Kočevar, *J. Heterocycl. Chem*. **54** (2017) 457–464.
[2] M. Krivec, M. Gazvoda, K. Kranjc, S. Polanc, M. Kočevar, *J. Org. Chem*. **77** (2012) 2857–2864.
[3] K. Kranjc, M. Kočevar, *Tetrahedron* **64** (2008) 45–52.
[4] J. Ekar, K. Kranjc, *Synthesis* **53** (2021) 1112–1120.
[5] B. Herlah, A. Hoivik, L. Jamšek, K. Valjavec, N. Yamamoto, T. Hoshino, K. Kranjc, A. Perdih, *Pharmaceuticals* **15** (2022) art. number 539.
[6] K. Kranjc, M. Kočevar, *Synlett* **17** (2008) 2613–2616.
[7] K. Kranjc, A. Juranovič, M. Kočevar, F. Perdih, *Symmetry* **12** (2020) art. number 1714.

Synthesis of linked double 2*H*-pyran-2-one derivative: A possible precursor to double Diels–Alder cycloadducts and various macrocycles

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For some time now, 2*H*-pyran-2-ones **1** have been used as dienes for [4+2] Diels–Alder cycloadditions with various dienophiles, such as maleic anhydride or its derivatives, for the synthesis of bicyclo[2.2.2]octenes [1]. To this day there have been just a few studies that focus on the synthesis of more complex cycloadducts, such as a macrocycle previously reported by us [2]. In this case a double maleimide was used and *via* [4+2] cycloaddition the desired product was obtained; its structure was determined by single crystal X-ray diffraction analysis. Recently, we succeeded to synthesize a double 2*H*-pyran-2-one **2** connected by a diamide linker. We successfully applied it in a cycloaddition with maleic anhydride yielding a linear double cycloadduct **3**. Cycloadditions of 2*H*-pyran-2-ones sometimes yield aromatized products as well [3]; thus, if a double maleimide (described in [1]) could be used in such controlled aromatization reaction with the novel double 2*H*-pyran-2-one **2** the formation of various macrocycles, such as **4**, might be achieved.

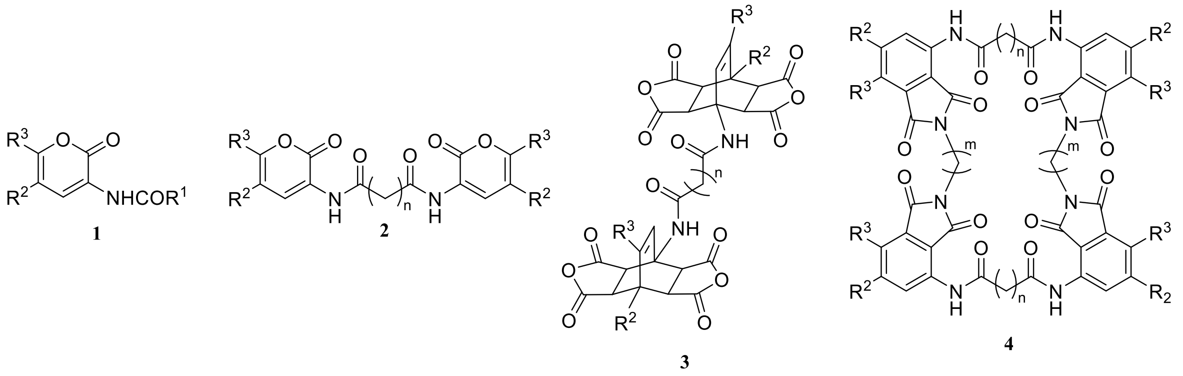

Figure 1: 2*H*-pyran-2-ones and corresponding possible cyclodducts.

References

[1] K. Kranjc, M. Kočevar, *Curr. Org. Chem.* **17** (2013) 448–456.
[2] B.L. Turek, M. Kočevar, K. Kranjc, F. Perdih, *Acta Chim. Slov.* **64** (2017) 737–746.
[3] M. Krivec, M. Gazvoda, K. Kranjc, S. Polanc, M. Kočevar, *J. Org. Chem*. **77** (2012) 457–464.

Use of derivatization with hydrazine to determine the correct stereostructure of maleic anhydride-double cycloadducts with substituted 2*H*-pyran-2-ones

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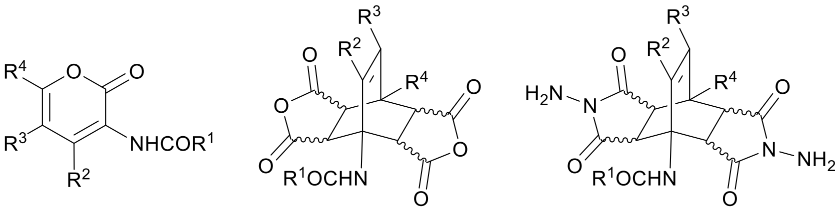
The Diels–Alder reaction between substituted 2*H*-pyran-2-ones **1** (Figure 1) acting as dienes and two molecules of maleic anhydride having the role of dienophile yields bicyclo[2.2.2]octenes **2** which are appropriate for further transformations [1,2]. These double cycloadducts can be formed as four stereoisomers: two *meso* adducts containing a plane of symmetry (*exo,exo* and *endo,endo*) and a pair of enantiomeric asymmetric products (*endo,exo* and *exo,endo*) [3]. NMR analyses of the bicyclo[2.2.2]octenes formed with maleic anhydride show that only one stereoisomer is obtained (having a plane of symmetry). As the products of the Diels–Alder reaction do not always crystallize it is not possible to determine which of the two *meso* stereoisomers was obtained. However, upon derivatization of the maleic anhydride-double cycloadducts with hydrazine, crystalline products **3** are formed and they are appropriate for single-crystal X-ray diffraction analysis. The configuration of the bicyclo[2.2.2]octenes **3** was determined as *exo*,*exo* and thus the configuration of the initial cycloadduct was of the same type. This example clearly demonstrates the importance of single-crystal X-ray diffraction for organic synthesis and structural characterization.



1 **2** **3**

Figure 1: 2*H*-pyran-2-one, its maleic anhydride-double cycloadducts and their hydrazine derivatives

References

[1] J. Ekar, K. Kranjc, *Synthesis* **53** (2021) 1112–1120.
[2] B. Herlah, A. Hoivik, L. Jamšek, K. Valjavec, N. Yamamoto, T. Hoshino, K. Kranjc, A. Perdih, *Pharmaceuticals* **15** (2022) art. number 539.
[3] K. Kranjc, M. Kočevar, *Arkivoc* **i** (2013) 333–363.

Crystallization and structural transformations of ternary copper(II) coordination compounds with 1,10-phenanthroline and glycine

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Ternary coordination compounds of copper(II) with amino acids and chelating heterocyclic bases have been investigated for several decades due to their pronounced antitumor activity [1]. These compounds are interesting in crystal engineering since they have the ability to form predictive supramolecular motifs through non-covalent interactions, such as π-interactions and hydrogen bonds. However, systematic research of different solvatomorphs has been reported only in a few research articles [2–4]. Our group is also interested in exploring the properties of such compounds, *i.e.* stability of crystals in the solid state and their ability to absorb water molecules or other solvents [2,3].

As a part of our research, we report the solution-based and mechanochemical syntheses and crystal structures of five ternary coordination compounds of copper(II), 1,10-phenanthroline (phen) and glycine (HGly) with water and methanol as solvent. Different crystallization experiments with a very small difference in the amount of water (less than 1% of volume fraction) resulted in different solvatomorphs crystallizing. Water content in reactants was crucial for the formation of certain solvatomorphs in mechanochemical syntheses. All compounds contain crystallization solvent molecules forming pockets and/or infinite channels (1D or 2D). Stability and solid-state transformations in atmospheres of methanol vapors or different relative humidity were also investigated (Figure 1).

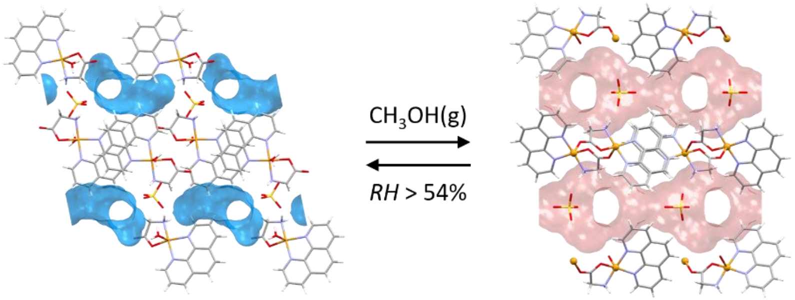

Figure 1: Structural transformations of compounds $[Cu(Gly)(H_2O)(phen)]_2SO_4\cdot 6H_2O$ (left) and $\{[Cu(\mu\text{-}Gly)(phen)]_2SO_4\cdot H_2O\cdot 4CH_3OH\}_n$ (right) in the solid state.

References

[1] J.C. García-Ramos, R. Galindo-Murillo, A. Tovar-Tovar, A. L. Alonso-Saenz, V. Gómez-Vidales, M. Flores-Álamo, L. Ortiz-Frade, F. Cortes-Guzmán, R. Moreno-Esparza, A. Campero, L. Ruiz-Azuara, *Chem. Eur. J.* **20** (2014) 13730–13741.
[2] D. Vušak, B. Prugovečki, D. Milić, M. Marković, I. Petković, M. Kralj, D. Matković-Čalogović, *Cryst. Growth Des*. **17** (2017) 6049–6061.
[3] D. Vušak, K. Ležaić, J. Jurec, D. Žilić, B. Prugovečki, *Heliyon* **8** (2022) e09556.
[4] W.C. Zhang, X. Tang, X. Lu, *J. Inorg. Biochem*. **156** (2016) 105–112.

Oligomeric symmetry of purine nucleoside phosphorylases

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Many enzymes are composed of several identical subunits which are arranged in some regular fashion and usually comply with some definite symmetry. [1] This symmetry may be approximate or exact and may or may not coincide with the symmetry of crystallographic packing. Purine nucleoside phosphorylases (PNP) are one class of oligomeric enzymes that show interesting properties connected with the interplay of symmetry. [2] There are two main classes of this enzyme: trimeric PNP or "low molecular mass" protein which can be found mostly in eukaryotic organisms, and hexameric PNP or "high molecular mass" protein which can mostly be found in prokaryotic organisms (Figure 1). [3] Interestingly, these two enzyme classes share only 20-30% sequence identity, but the overall fold of the single monomer is similar, and yet this similar monomeric building block makes a different quaternary structure.

As part of the ALOKOMP project (alokomp.irb.hr) which tries to understand the allosteric communication between these monomeric subunits, the relational database of PNPs is constructed. As a special subset of this database, an all-to-all overlap of these structures is also made, which makes possible the assessment of symmetry relations in these enzymes using programmatic methods.

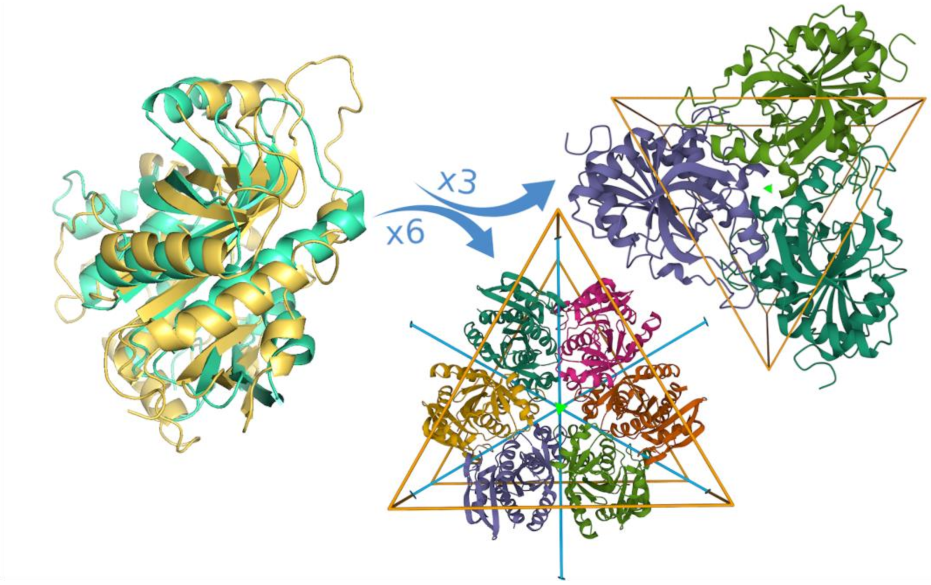

Figure 1: Monomeric units from trimeric PNP and hexameric PNP show similar overall fold but form different quaternary structures.

References

[1] B. Kojić-Prodić i Z. Štefanić, *Symmetry* **2(2)** (2010) 884–906.
[2] M. Luić, Z. Štefanić, *Croat. Chem. Acta* **89(2)** (2016) 197–202.
[3] M. Narczyk, B. Bertoša, L. Papa, V. Vuković, I. Leščić Ašler, B. Wielgus-Kutrowska, A. Bzowska, M. Luić i Z. Štefanić, *FEBS J.* **285(7)** (2018) 1305–1325.

New ternary scandium cobalt silicide $Sc_{38}Co_{144}Si_{97}$: crystal and electronic structures

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Scandium alloys exhibit interesting properties from a materials viewpoint and have been intensively investigated. The isothermal section of the Sc–Co–Si system at 800 °C (and a part of it at 700 °C) have been reported [1]. Twelve ternary compounds have been synthesized: $ScCo_2Si_2$, $Sc_6Co_{16}Si_7$, $Sc_2Co_3Si_5$, $ScCo_{1.52-1.46}Si_{0.48-0.54}$, $ScCo_{0.25}Si_{1.75}$, ScCoSi, $Sc_2Co_{0.85}Si_{0.15}$, $Sc_3Co_2Si_3$, Sc_2CoSi_2, $Sc_6Co_{30}Si_{19}$, $Sc_5Co_4Si_{10}$, $Sc_{12}Co_{41.8}Si_{30.2}$. In [1] and later publications they were characterized structurally. The latter silicide $Sc_{12}Co_{41.8}Si_{30.2}$ has been reported recently [2] and was assumed to be the last unknown ternary compound in the Sc–Co–Si system. However, further explorations of the phase equilibria revealed presence of another unknown compound nearby.

$Sc_{38}Co_{144}Si_{97}$ was prepared from the elements by arc melting under argon and subsequent annealing at 800 °C for 350 h. Single-crystal X-ray diffraction revealed $Sc_{38}Co_{144}Si_{97}$ to crystallize in a new hexagonal structure type: Pearson's symbol *hP*279, space group $P6_3/m$, a=33.624(7), c=3.639(1) Å. The crystal structure of $Sc_{38}Co_{144}Si_{97}$ can be considered as an 2D intergrowth of three kinds of fragments of simpler hexagonal structure types: hexagons (fragment I) and quadrilaterals (fragment II) with the arrangements of $Sc_6Co_{30}Si_{19}$-type and triangulars (fragment III) with the arrangement of $Gd_4Co_{13}(Si,P)_9$-type (see Figure 1). Quantum chemical calculations have been performed to analyze the electronic structure and provide deeper insight into the structure-property relationships. The EH calculation indicates that Co in the $Sc_{38}Co_{144}Si_{97}$ is close to a d^{10} configuration owing to the covalent interaction with Si. The Co–Si bonds provide the highest contribution to the total orbital interactions.

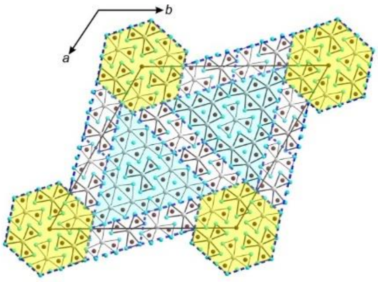

Figure 1: The structure is presented in projection along [001]. Linking of the trigonal prisms of metal atoms that surround the Si atoms are shown. Prisms drawn by thin and thick lines are shifted by half the translation period *z*. The Si atoms are drawn with black circles and Sc and Co atoms with large grey and small blue circles, respectively (online). The relative boundaries of structure fragments I, II and III are indicated by dashed lines.

References

[1] B.Ya. Kotur and E. Gratz, *Scandium Alloy Systems and Intermetallics*, in: K.A. Gshchneidner Jr. and L. Eyring (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, vol. 27, North-Holland, 1999, Amsterdam; pp: 339–533.

[2] B. Kotur, V. Babizhetskyy, V. Smetana, C. Zheng and A.-V. Mudring, *J. Solid State Chem.* **302** (2021) 122373 (11 p.).

Cocrystallization of the Schiff base derived from ethylenediamine and pyridine-2-carbaldehyde with perfluorinated halogen bond donors

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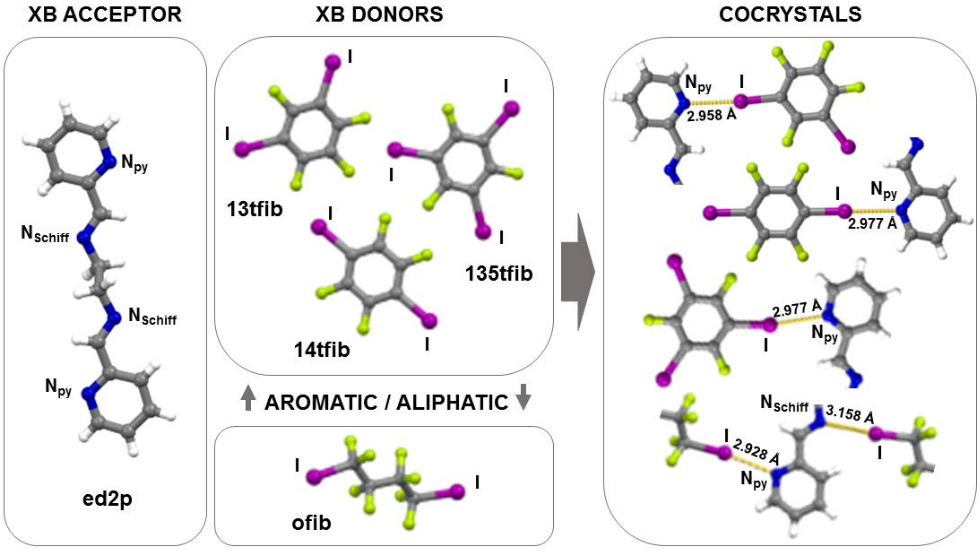
The halogen bond [1] is a growing part of supramolecular chemistry and crystal engineering research in the last few decades, due to the tuneability of its strength and higher directionality than other supramolecular interactions. Some of the most studied and reliable acceptor species are cyclic nitrogen atoms, specifically pyridine nitrogen atoms [2]. Therefore, it's reasonable to assume that Schiff bases with multiple peripherally located pyridine nitrogen atoms will also be reliable halogen bond acceptors and form cocrystals with a variety of halogen bond donors.

In this work, a Schiff base (**ed2p**) was synthesized from ethylenediamine and pyridine-2-carbaldehyde by a condensation reaction in hot methanol. Using the obtained Schiff base and perhalogenated halogen bond donors with different donor atom dispositions: tetrafluoro-1,3-diiodobenzene (**13tfib**), tetrafluoro-1,4-diiodobenzene (**14tfib**), trifluoro-1,3,5-triiodobenzene (**135tfib**) and octafluoro-1,4-diiodobutane (**ofib**), four novel halogen bonded cocrystals were prepared by crystallization from solution. Molecular and crystal structures of (**ed2p**)(**13tfib**)$_2$, (**ed2p**)(**14tfib**), (**ed2p**)(**135tfib**) and (**ed2p**)(**ofib**)$_2$ were determined by single-crystal X-ray diffraction. In all obtained cocrystals the dominant supramolecular interactions are I···N halogen bonds between both pyridine nitrogen atoms in **ed2p** and donor iodine atoms. In the (**ed2p**)(**ofib**)$_2$ cocrystal I···N halogen bonds are formed even with imine nitrogen atoms. All herein observed halogen bonds are linear and short with relative shortening between 10.8 % and 17.3 % and angles between 168.3° and 175.9°.



References
[1] G. Desiraju *et al.*, *Pure and Applied Chemistry* **85(8)** (2013) 1711−1713.
[2] G. Cavallo *et al.*, *Chemical Reviews*, **116(4)** (2016) 2478−2601.

Conformation and supramolecular architecture of novel 1,1'-disubstituted ferrocene–quinoline hybrids

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Ferrocenes conjugated with biologically active heterocycles, such as those that have a triazole ring, have shown promising cytostatic activities [1]. Besides, quinoline derivatives containing additional aromatic rings have been also reported to possess potent anticancer properties [2]. In this contribution, we present the conformation and supramolecular structures of two 1,1'-disubstituted *O*-alkylated ferrocene-quinoline hybrids containing triazole rings (Figure 1).

X-ray structural studies of both compounds show that the Fe atom of the ferrocene skeleton is positioned on a symmetry element (a 2-fold axis in **1** and an inversion centre in **2**), so that the asymmetric unit contains one half of the molecule. Besides, structure of **1** crystallised as a solvate with two dichloromethane molecules per one molecule of ferrocene-quinoline hybrid. Cyclopentadienyl (Cp) rings in **1** deviate by about 10° from an eclipsed conformation, while the conformation of Cp rings in **2** is staggered. The molecules of **1** are self-assembled by only one intermolecular interaction, a C–H···N hydrogen bond, while three additional C–H···N hydrogen bonds link the molecules of the ferrocene-quinoline derivative to chloroform molecules, forming a two-dimensional network. The same type of network is also built in **2** by one C–H···N and one C–H···F hydrogen bond. Interestingly, although aromatic rings are present in both structures, neither C–H···π nor π···π interactions participate in the construction of supramolecular architectures.

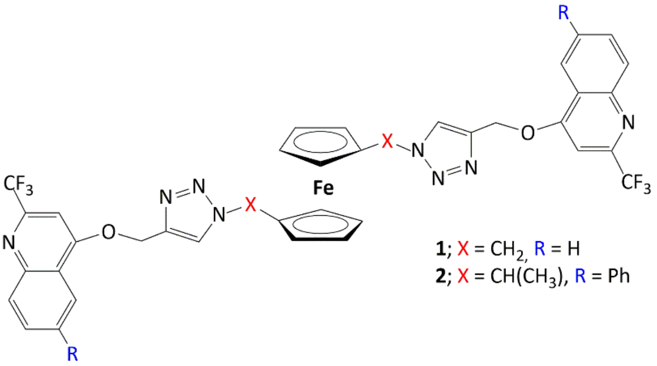

Figure 1: Chemical structures of ferrocene-quinoline hybrids.

References

[1] S.B. Deepthi, R. Trivedi, L. Giribabu, P. Sujitha and C.G. Kumar, *Dalton Trans*. **42** (2013) 1180–1190.

[2] L.B. de Freitas, T.F. Borgati, R.P. de Freitas, A.L.T.G. Ruiz, G.M. Marchetti, J.E. de Carvalho, E.F.F. da Cunha, T.C. Ramalho and R.B. Alves, *Eur. J. Med. Chem*. **84** (2014) 595–604.

The magnetism of solvatomorphic copper(II)-intermediates in the synthesis of mixed-metal MOF-74 materials

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Mixed-metal MOF-74 materials (MM-MOF-74) [1] based on the 2,5-dihydroxyterephthalic acid (H_4dhta) with controlled stoichiometry and distribution of metal nodes are much-sought materials due to their advanced properties for catalysis and magnetism[2]. Still, that level of control is hard to achieve in a solution. Recently, mechanochemistry provided a unique templated pathway toward bimetallic MOF-74 materials with 1:1 stoichiometry and ordered distribution of the metal nodes.[1] This approach relies on solid 1:1 metal:H_2dhta coordination compounds that react with the other metal by milling, resulting in the porous mixed-metal MOF-74 framework. In the synthesis of CuM-MOF-74 from copper(II)-intermediate, we observed that the Cu-int changes color from blue to green when subjected to low pressure. Time-resolved low-temperature PXRD monitoring revealed the rapid transformation of the Cu-int to the new phase that slowly transforms into CU-int by standing on the bench. The two phases display interesting and different magnetic properties and electron-spin resonance (ESR) spectra stemming from the altered connectivity among the copper centers that rise upon the phase transformation.

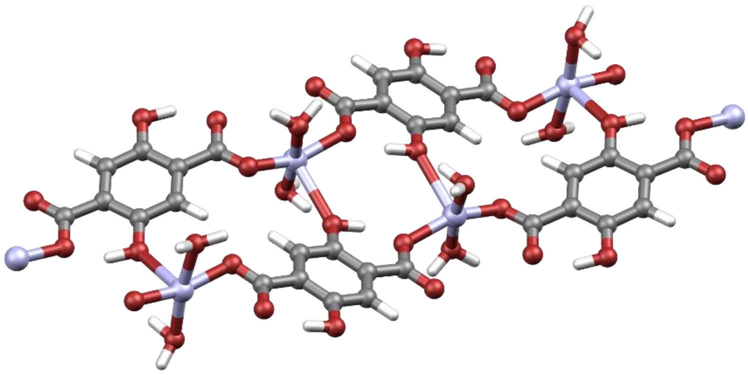

Figure 1: The laddered structure of the Cu-int.

References

[1] G. Ayoub et al., *Chem. Mater.* **31** (2019) 5494−5501.
[2] T. Stolar et al., *Appl. Mater. Interfaces* **13** (2021) 3070−3077.

High proton conductivity in 2D oxalate [$Mn^{II}Cr^{III}$] polymer with alkyl ammonium cations and its oxide-related usage

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It is well known that the oxalate group, $C_2O_4^{2-}$, used in the preparation of metal-organic coordination compounds, is one of the most versatile ligands with different coordination modes towards metal centres which likewise has ability to mediate magnetic interactions between paramagnetic metal ions. One of the synthetic strategy for preparation of (hetero)polynuclear species is "building block chemistry" in which a molecular anionic ligand, very often the tris(oxalato)metalate anion, $[M^{III}(C_2O_4)_3]^{3-}$, is used as a ligand towards other metal cations. The topology of these compounds is controlled by a templating counterion. Combining the intrinsic properties of the host, especially the magnetic ones, with additional functionalities originating from the selected guest molecules, very interesting multifunctional properties can be obtained. Proton conductivity as a new functionality of metal-organic compounds can be achieved by incorporating a counterion such as hydronium (H_3O^+), ammonium [NH_4^+, $(CH_3)_2NH_2^+$,...] or an anion (SO_4^{2-}) into the anionic network. The counterions form the hydrogen bonds with the guest water or other components of compound and create proton-conducting pathways consisting of hydrogen bonding networks [1]. In addition, heterometallic complexes as single-source precursors provide simplified synthetic routes through one-step thermal decomposition to form mixed metal oxide materials. The advantage of a solid phase transition is the retention of the elemental composition defined by the molecular precursor with only a loss of volatile decomposition products, which allows excellent stoichiometric control of the intermetallic ratio in the oxide products [2].

Motivated by our previous results [1], we investigated the proton conduction behaviour of the novel oxalate-bridged coordination polymer $\{[NH(CH_3)_2(C_2H_5)]_8[Mn_4Cl_4Cr_4(C_2O_4)_{12}]\}_n$ (**1**) obtained using an aqueous solution of $[NH(CH_3)_2(C_2H_5)]_3[Cr(C_2O_4)_3]$ as ^{a} building block in reaction with Mn^{2+} ions. Compound **1**, consisting of 2D anionic $[Mn_4Cl_4Cr_4(C_2O_4)_{12}]_n^{8n-}$ networks and hydrogen-bonded $[NH(CH_3)_2(C_2H_5)]^+$ cations between these networks, exhibits remarkable humidity-sensing properties and very high proton conductivity at room temperature [1.60×10^{-3} $(\Omega\cdot cm)^{-1}$ at 298 K under 90% relative humidity]. Moreover, this heterometallic compound was tested as a single molecular precursor for the preparation of $MnCrO_4$ oxide in one step, due to its suitable metal ratio. The oxalate group, $C_2O_4^{2-}$, easily decomposes at low temperatures into gaseous CO_2 and CO, and thus the oxalate-based solids can serve as suitable precursors for the preparation of mixed metal oxides. In addition to powder and single crystal X-ray diffraction, the obtained compound has been characterized by thermal analysis, IR and impedance spectroscopy.

References

[1] S. Burazer, K. Molčanov, A. Šantić, T. Klaser, E. Wenger, D. Pajić, Z. Jagličić, J. Popović, M. Jurić, *Materials* **14** (2021) 5543.

[2] H. Lu, D.S. Wright and S. D. Pike, *Chem. Commun.* **56** (2020) 854–871.

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Mechanosynthesis of Pd(II) photosensitizers under solvent-free conditions in a ball mill

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Cyclopalladated complexes and their derivatives have been successfully used in many areas of materials science and biological chemistry [1,2]. Although these compounds' reactivity and optical properties depend primarily on the cyclopalladated substrate, such features can also be tuned by an appropriate choice of ancillary ligands [3].

Their preparation and modification are usually carried out in solution, but the number of reports on the solid-state synthesis of these organometallic complexes is steadily increasing.

To improve the optical properties of dipalladated azobenzenes, $[\{(\mathrm{DMF})\mathrm{PdCl}\}_2(\mu\text{-AZB-2H})]$, their derivatives were prepared with 4-styrylpyridine and 1,10-phenanthroline by the solvent-free ball-milling method.

Reactions with 4-styrylpyridine gave planar complexes, while substitution of DMF ligands in dipalladated azobenzenes by 1,10-phenanthroline led to the breaking of one Pd–N bond, allowing the rotation of a phenyl ring and the positioning of both Pd atoms on the same side of the azobenzene ligand. Two Pd atoms in phenanthroline products are linked by the azobenzene ligand and additionally by the Cl-bridge. Ball milling has been shown to be a clean and highly efficient method for the solid-state synthesis of derivatives of dipalladated azobenzenes, although the formation of phenanthroline derivatives requires very complex intramolecular transformations.

References

[1] J. Dupont, C.S. Consorti, J. Spencer, The Potential of Palladacycles: More than Just Precatalysts. Chem. Rev. **105** (2005) 2527–2572.

[2] Palladacycles: Synthesis, Characterization and Applications. (Eds. Dupont, J.; Pfeffer, M.), Wiley-VCH, Weinheim, 2008.

[3] M. Ghedini, I. Aiello, A. Crispini, A. Golemme, M. La Deda, D. Pucci, *Coord. Chem. Rev.* **290** (2006) 1373–1390.

Structures of the XeF_2–MnF_4 adducts

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The study of the catalytic effect of MnF_3 on the rate of reaction between Xe and F_2 revealed the existence of a solid phase, which was later identified as $XeF_2 \cdot MnF_4$ (*abbr.* as the 1:1 adduct) [1]. Subsequent investigations of the XeF_2–MnF_4 system also revealed the existence of two other compounds, namely $3XeF_2 \cdot 2MnF_4$ and $XeF_2 \cdot 2MnF_4$, and led to the successful crystal structure determination of the 3:2 and 1:1 adducts, albeit with relatively low precision [2, 3]. The crystal structure determination of the compounds belonging to the XeF_2–MnF_4 family is of particular interest, since these compounds may be structurally related to their platinum analogues, thus helping to elucidate the structure of the first noble-gas compound "$XePtF_6$", which remains unknown more than 60 years after its discovery [4, 5].

In this work, the crystal structures of $3XeF_2 \cdot 2MnF_4$ and $XeF_2 \cdot MnF_4$ have been redetermined with improved precision and figures of merit and the crystal structure of $XeF_2 \cdot 2MnF_4$ has been determined for the first time. A common feature of the structures is the coordination of XeF_2 ligands to Mn(IV) centres, leading to formation of [MnF_6]-octahedra. Such octahedra link together via fluoride bridges to form oligomeric or polymeric species, specifically forming 1-D *zigzag* chains in the case of $3XeF_2 \cdot 2MnF_4$, discrete tetrameric rings in the case of $XeF_2 \cdot MnF_4$, and 1-D corrugated ladder in the case of $XeF_2 \cdot 2MnF_4$. The aforementioned compounds were characterised by low-temperature single-crystal X-ray diffraction, powder X-ray diffraction, Raman spectroscopy and infrared spectroscopy.

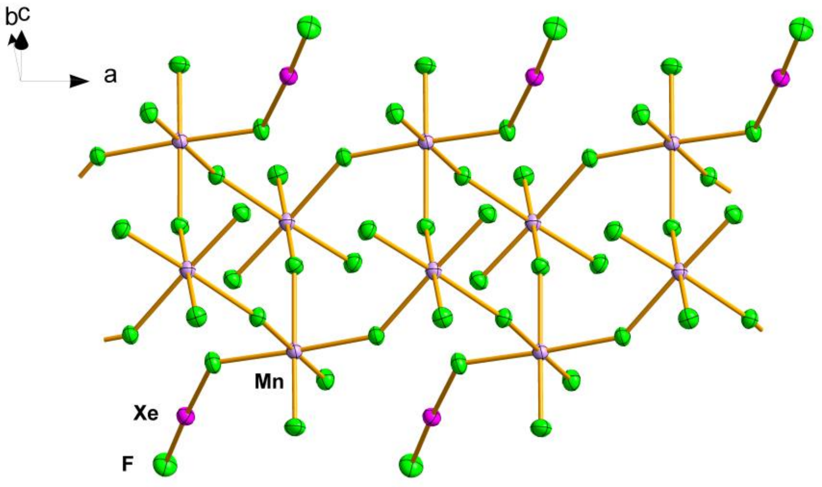

Figure 1: Crystal structure of $XeF_2 \cdot 2MnF_4$ (50% probability ellipsoids).

References

[1] B. Žemva, J. Zupan and J. Slivnik, *J. Inorg. Nucl. Chem.* **33** (1971) 3953–3955.
[2] M. Bohinc, J. Grannec, J. Slivnik and B. Žemva, *J. Inorg. Nucl. Chem.* **38** (1976) 75–76.
[3] M. Lozinšek, *Diploma Thesis*, University of Ljubljana (2008).
[4] N. Bartlett, *Proc. Chem. Soc.* (1962) 218.
[5] L. Graham, O. Graudejus, N. K. Jha and N. Bartlett, *Coord. Chem. Rev.* **197** (2000) 321–334.

An interesting case of polymorphism involving acetamide

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The coordination chemistry of zinc(II) is extensively studied because of the need for a deeper understanding of the biological role of zinc(II), an essential trace element [1]. Our previous research has shown that zinc(II) can catalyze the conversion of organic ligands. Systems with quinaldinate (anion of quinoline-2-carboxylic acid, abbreviated as quin$^-$) and secondary cyclic amines revealed the formation of amidines [2]. To broaden the understanding of these systems, study was continued with analogues of piperazine, where amidine formation was also confirmed. Interestingly, the system with 1-phenylpiperazine also yielded two polymorphs with acetamide, [Zn(quin)$_2$(1-phenylpiperazine)$_2$]·2acetamide, triclinic and monoclinic. Both contain a six-coordinate zinc(II) complex with two *N*,*O*-bidentate chelating quinaldinates and two monodentate 1-phenylpiperazine ligands in *trans* orientation and two acetamide molecules per formula unit. The polymorphs differ markedly in their hydrogen bonds and consequently in their connectivity motifs (Fig. 1). In the triclinic modification, both amine hydrogens of acetamide participate in hydrogen bonding. The characteristic acetamide···acetamide homosynthon is observed [3]. In the monoclinic modification, on the other hand, the amine group of acetamide is not involved in hydrogen bonding. Instead, an interaction is observed between the amine group of the 1-phenylpiperazine and the carbonyl oxygen linking the complex species and the two acetamide molecules.

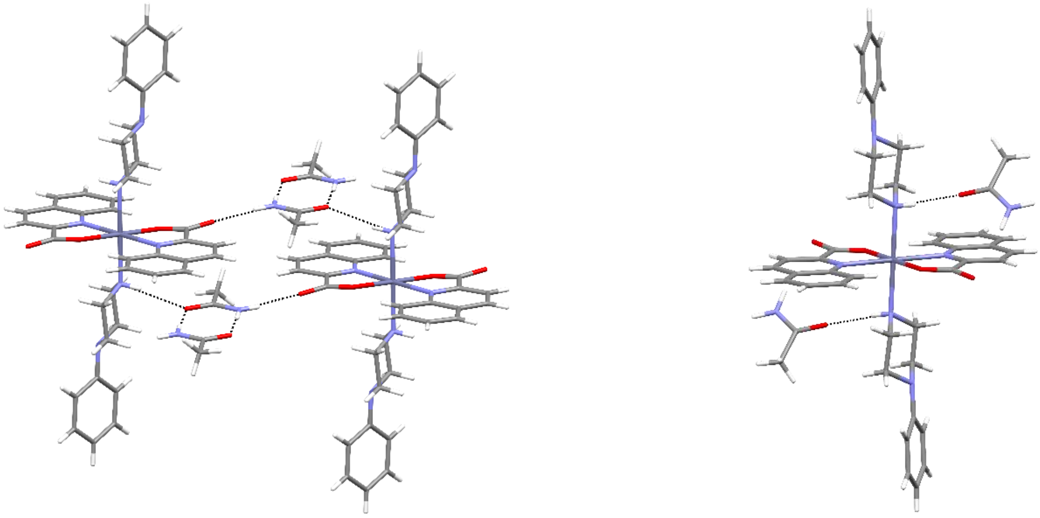

Figure 1: Triclinic (left) and monoclinic (right) polymorphs of [Zn(quin)$_2$(1-phenylpiperazine)$_2$]·2acetamide. For triclinic polymorph, a short section of supramolecular layer is shown.

References

[1] A. Krężel and W. Maret, *Arch. Biochem. Biophys.* **611** (2016) 3–19.
[2] N. Podjed, B. Modec, M.M. Alcaide and J. López-Serrano, *RSC Adv.* **10** (2020) 18200–18221.
[3] G.R. Desiraju, *Angew. Chem., Int. Ed. Engl.* **34** (1995) 2311–2327.

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Crystal structures of 2,4,6-collidinium and 3,5-lutidinium halogenides' cocrystals with 1,4-diiodotetrafluorobenzene

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Halogen and hydrogen bonds are attractive non-covalent interactions between the Lewis base (acceptor) and the Lewis acid region of covalently bonded halogen and hydrogen atoms (donors). Among neutral acceptors (oxygen, nitrogen, halogen, π-electrons, etc.), halogenide anions stand out with their negative charge and sphericity, making them better acceptors with no sterical hinderance which would disrupt the approach of one or more donors of same or different interactions. Although halogen and hydrogen bonds with halogenides were excessively investigated separately in solid state [1,2], joint research remains scarce. Halogenopyridinium halogenides are an example of simplest systems that encompass the aformentioned [3], followed by their cocrystals with halogen bond donors [4]. However, to the best of our knowledge, no systematic research on systems with neutral molecules as the only donors of halogen bond, cations as the only donors of hydrogen bonds, and halogenides as the only acceptors has been performed to date.

In order to examine the potential of halogenide anions to act simlultaneously as acceptors of halogen and hydrogen bonds, we prepared cocrystals of 2,4,6-collidinium and 3,5-lutidinium halogenides with 1,4-diiodotetrafluorobenzene (**14tfib**). Each halogenide salt (X = F, Cl, Br, I) and **14tfib** were dissolved in ethanol in 1:1 ratio. All crystallization experiments yielded single crystals with the exception of the 3,5-lutidinium fluoride cocrystal. The obtained single crystals were suitable for X-ray diffraction experiments, which enabled the determination of their molecular and crystal structures. In all the prepared solids, the halogenide anion forms two C−I⋯X^- halogen bonds with two **14tfib** molecules, and one N−H⋯X^- hydrogen bond with a cation. The halogen bonding between **14tfib** (a ditopic donor) and halogenides acting as a ditopic acceptors results in infinite chains. Additionally, **14tfib** molecules form C−H⋯F−C contacts with cations. Although the cations and halogenides differ, halogen and hydrogen bonded motifs are preserved in spite of the changes in the crystal packing.

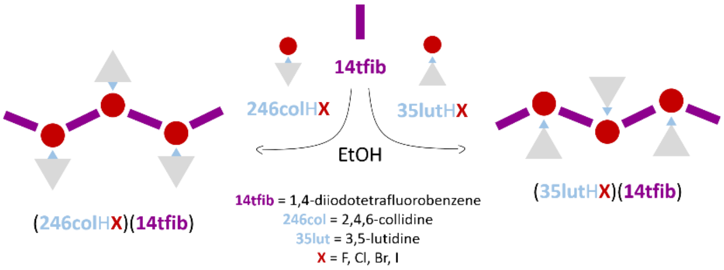

Figure 1: Schematic representation of cocrystal synthesis and resulting motifs.

References

[1] G. Gilli and P. Gilli, *The Nature of the Hydrogen Bond*, Oxford University Press, Oxford, 2009.
[2] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati and G. Terraneo, *Chem. Rev.* **116** (2016) 2478–2601.
[3] L. Fotović and V. Stilinović, *CrystEngComm* **22** (2020) 4039–4046.
[4] L. Posavec, V. Nemec, V. Stilinović and D. Cinčić, *Cryst. Growth. Des.* **21** (2021) 6044–6050.

Anion-directed synthesis of oxalate-based [CuM] (M = Cr or Fe) complexes containing a tridentate ligand: Structural and magnetic properties

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Heteropolynuclear metal complexes have been extensively studied for their ability to form various architectures and topologies, from discrete polynuclear metal compounds to polymeric one- (1D), two- (2D) or threedimensional (3D) assemblies, featuring a range of distinct magnetic properties. In recent decades, the chemistry of oxalate-containing complexes has become an active area of research – the oxalate moiety, $C_2O_4^{2-}$, acts as a linker between metal centres with various possibilities of bridiging modes and has the ability to mediate magnetic interactions between paramagnetic metal centres. Stable mononuclear anionic oxalate complexes such as tris(oxalato)metalate anions, $[M^{III}(C_2O_4)_3]^{3-}$ (M^{III} = Mn, Cr, Fe, V), are often used as ligands toward another metal ion for the preparation of extended multifunctional systems. Also, the introduction of organic ligands containing *N*-donors into the metal–oxalate systems also influences the nuclearity of the metal centres and additionally stabilizes their solid-state structures.

Applying the layering technique, crystals of the tetranuclear chloride-bridged compounds $[Cu_4(terpy)_4Cl_5][M(C_2O_4)_3]\cdot nH_2O$ [M = Cr^{3+}; n = 9 (**1**) and M = Fe^{3+} n = 10 (**2**)] grew from the reaction of an aqueous solution of $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ or $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$, respectively, methanol solution containing $CuCl_2\cdot 2H_2O$ and a tridentate ligand 2,2′:6′,2′′-terpyridine (terpy). When $Cu(NO_3)_2\cdot 3H_2O$ was used instead of the chloride salt, unexpected change in type of the bridge, oxalate *versus* chloride, was achieved and crystals of the 1D oxalate-bridged coordination polymers $\{[Cu_4Cr_2^{III}(H_2O)_2(terpy)_4(C_2O_4)_7]\cdot 10H_2O\}_n$ (**3**) and $\{[Cu^{II}_2Fe^{III}(H_2O)(terpy)_2(C_2O_4)_{7/2}]\cdot 6H_2O\}_n$ (**4**) together with compound $[Cu^{II}_2(H_2O)_2(terpy)_2(C_2O_4)][Cu^{II}Fe^{III}(CH_3OH)(terpy)(C_2O_4)_3]_2$ (**5**), respectively, have been formed. Further, two polymorphs of 3D coordination polymer $[Cu^{II}Fe^{II}_2(H_2O)(terpy)(C_2O_4)_3]_n$ (**6a** and **6b**), crystallizing in the triclinic (a) and monoclinic (b) space groups, were formed hydrothermally, depending on whether $CuCl_2\cdot 2H_2O$ or $Cu(NO_3)_2\cdot 3H_2O$ was added to the water, besides $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ and terpy, respectively. Compounds **1** and **2** exhibit a ground-state spin of 1, which is due to antiferromagnetic and ferromagnetic interactions of Cu^{2+} ions across the chloride bridges in the tetramers; ferromagnetic coupling transferred through the oxalate bridge was found between Cu^{2+} ions in **3**, as well as strong antiferromagnetic coupling of the Cu^{2+} ions mediated by the oxalate ligand in cation moiety, and weak ones between Cu^{2+} and Fe^{3+} ions through oxalate bridge in the anion of compound **5**. Polymer **6** exhibits an antiferromagnetic phase transition at 25 K [1].

Reference

[1] L. Kanižaj, D. Barišić, F. Torić, D. Pajić, K. Molčanov, A. Šantić, I. Lončarić and M. Jurić, *Inorg. Chem.* **59** (2020) 18078–18089.

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Search for Allostery in Purine Nucleoside Phosphorylases via Database of Molecular Interactions

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Allostery is a phenomenon where the information is transmitted from one part of the enzyme to the other. The means by which this is achieved is still to be understood in many proteins. One class of enzymes where allostery plays an intriguing role are Purine Nucleoside Phosphorylases (PNPs) [1]. Since allostery is a fundamentally dynamical phenomenon, the static structures provided by X-ray crystallography only are not able to reveal it. It is necessary to somehow include the dynamics by leveraging the molecular dynamics simulations. Adding a time dimension in form of molecular simulations to the static picture is essential for following the changes in molecular contacts and tracing the signatures of allosteric communication between different parts of the protein.

To facilitate the information retrieval from this complex data, specially designed molecular interaction databases have been applied in search for allosteric pathways in PNPs, as part of the project *Allosteric communication pathways in oligomeric enzymes* (ALOKOMP, https://alokomp.irb.hr/). By enhancing the static information obtained from X-ray crystallography with dynamic time evolution obtained via molecular dynamics simulations and combining both in form of specially designed databases to which automated machine learning algorithms can be applied, it is hoped that elusive allosteric pathways can be identified in this class of enzymes.

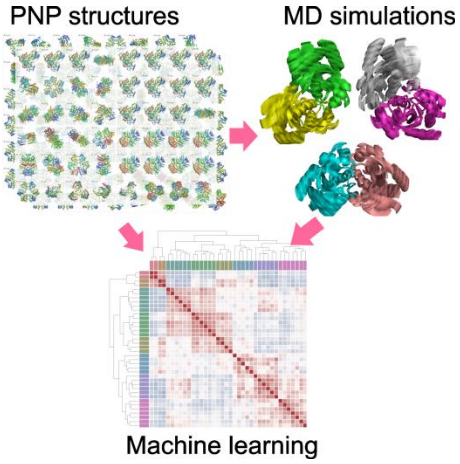

Figure 1: The workflow for combining static and dynamic data for programmatic discovery of allosteric communication in oligomeric enzymes.

References

[1] M. Narczyk, M.I. Wojtyś, I. Leščić Ašler, B. Žinić, M. Luić, E.K. Jagusztyn-Krynicka, Z. Štefanić and A. Bzowska, Journal of Enzyme Inhibition and Medicinal Chemistry, 37:1 (2022)1083-1097.

A bromine-containing imine and its copper(II) and nickel(II) coordination compounds in cocrystals with perhalogenated aromates

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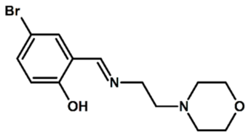
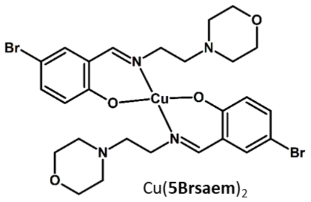
In our past work on crystal engineering of multi-component solids using halogen bonds [1,2], we have established the viability of a strategy utilizing acceptor functional groups that are peripherally located on a coordination compound [3,4]. More specifically, we used imines derived from 2-hydroxy-1-naphthaldehyde and either 4'-aminoacetophenone [3] or *N*-aminomorpholine [4].

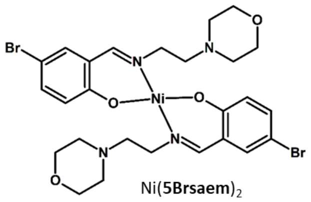
To study the effects that a ligand with an additional functional group which could potentially compete for halogen bonding would have, we have synthesized a bromine-containing imine from 5-bromosalicylaldehyde and *N*-(2-aminoethyl)morpholine, **5Brsaem**, and its copper(II) and nickel(II) coordination compounds, Cu(**5Brsaem**)$_2$ and Ni(**5Brsaem**)$_2$. The viability of the ligand itself as a halogen bond acceptor has been tested by cocrystallization experiments with perhalogenated aromatic halogen bond donors: 1,4-diiodotetrafluorobenzene (**14tfib**), 1,3,5-triiodotrifluorobenzene (**135tfib**) and 1,3-diiodotetrafluorobenzene (**13tfib**) and confirmed by the successful synthesis and structural characterization of two cocrystals, (**5Brsaem**)$_2$(**14tfib**) and (**5Brsaem**)(**135tfib**). These experiments were then followed by the synthesis of Cu(**5Brsaem**)$_2$(**14tfib**), Ni(**5Brsaem**)$_2$(**14tfib**) and Cu(**5Brsaem**)$_2$(**13tfib**)$_2$ cocrystals. In both imine cocrystals, the morpholine oxygen atom participates in I···O halogen bonding, and the bromine atom does not compete for halogen bonding. Additionally, in the (**5Brsaem**)(**135tfib**) cocrystal the morpholine nitrogen also participates in I···N halogen bonding as a result of a combination of imine flexibility and difference in the disposition of iodine atoms between **14tfib** and **135tfib**. Structural characterization of the Cu(**5Brsaem**)$_2$(**14tfib**) and Ni(**5Brsaem**)$_2$(**14tfib**) has shown that they are isostructural, yet the only established halogen bonds are those with the morpholine nitrogen atoms. Morpholine oxygen atoms participate in C–H···O hydrogen bonding. On the other hand, in the Cu(**5Brsaem**)$_2$(**13tfib**)$_2$ cocrystal both the morpholine nitrogen and oxygen atoms participate in halogen bonding, with the oxygen atom also an acceptor of a Br···O halogen bond.



5Brsaem



Cu(5Brsaem)$_2$



Ni(5Brsaem)$_2$

References

[1] R. Bertani, P. Sgarbossa, A. Venzo, F. Lelj, M. Amati, G. Resnati, T. Pilati, P. Metrangolo and G. Terraneo, *Coord. Chem. Rev.* **254** (2010) 677–695.

[2] V. Nemec, K. Lisac, N. Bedeković, L. Fotović, V. Stilinović and D. Cinčić, *CrystEngComm* **23** (2021) 3063–3083.

[3] V. Nemec, L. Fotović, T. Friščić and D. Cinčić, *Cryst. Growth Des.* **17** (2017) 6169–6173.

[4] V. Nemec, T. Piteša, T. Friščić and D. Cinčić, *Cryst. Growth Des.* **20** (2020) 3617–3624.

Review of the CSD crystallographic database for selected structures containing acridine and benzoic acid derivatives

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Multicomponent crystals are an intriguing object of research from the viewpoint of chemistry and pharmaceutics. The preparation of multicomponent crystals, in which at least one of the components is a pharmaceutically active substance, can improve the solubility and absorption of a drug, solve problems of its hygroscopicity and instability, as well as poor tabletability and improve its palatability. This makes such crystals applicable as alternative forms of drugs with more favourable physicochemical and pharmacokinetic properties [1].

Acridines are a group of organic compounds with a broad spectrum of therapeutic properties, including anticancer, antibacterial and antiviral activity, as they are able to intercalate, i.e. interact specifically with DNA [2]. Benzoic acid derivatives, on the other hand, are good, non-toxic coformers that not only enable the formation of stable multicomponent crystals, but also constitute biologically active substances [3].

In this presentation, the structures of multicomponent crystals derived from acridine and benzoic acid derivatives found in the Cambridge Structural Data (CSD) crystallographic database will be presented and briefly discussed.

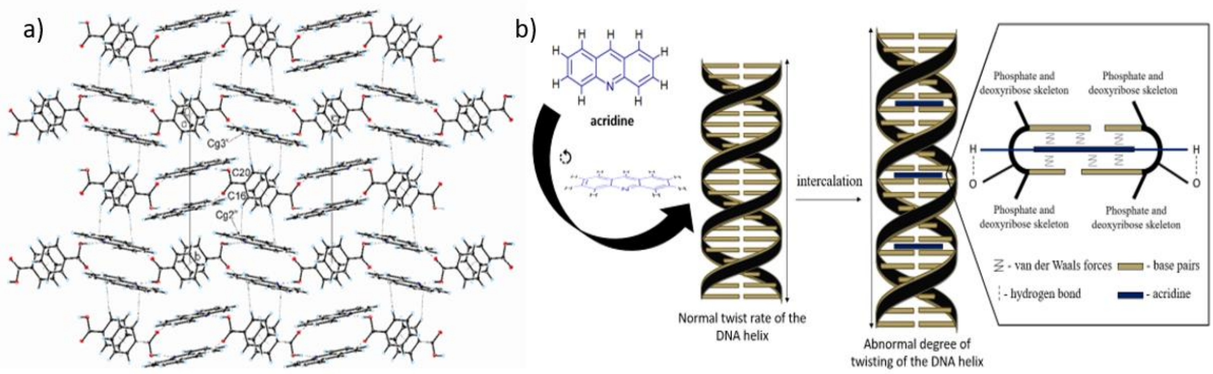

Figure 1: (a) Crystal packing of acridine · benzoic acid co-crystal with intermolecular interactions between heterotetramers [4]. (b) The process of acridine intercalation with intermolecular interactions forming [5].

References
[1] S. Aitipamula, R. Banerjee, A. Bansal et al., *Crystal Growth & Design*, **12** (2012) 2147−2152.
[2] P. Belmont, J. Bosson, T. Godet, *Anti-cancer agents in medicinal chemistry* **7** (2007) 139−169.
[3] Ch. Kent, A. Alfarsi, J. Kruse et al., *Crystal Growth & Design* **18** (2018) 6528−6537.
[4] K. Kowalska, D. Trzybiński, A. Sikorski, *CrystEngComm* **17** (2015) 7199−7212.
[5] P. Graham, *An Introduction to Medicinal Chemistry*, Oxford University Press, London, 2017.

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Pyridin-2-one in a manganese(II) complex, cocrystals and an ionic liquid

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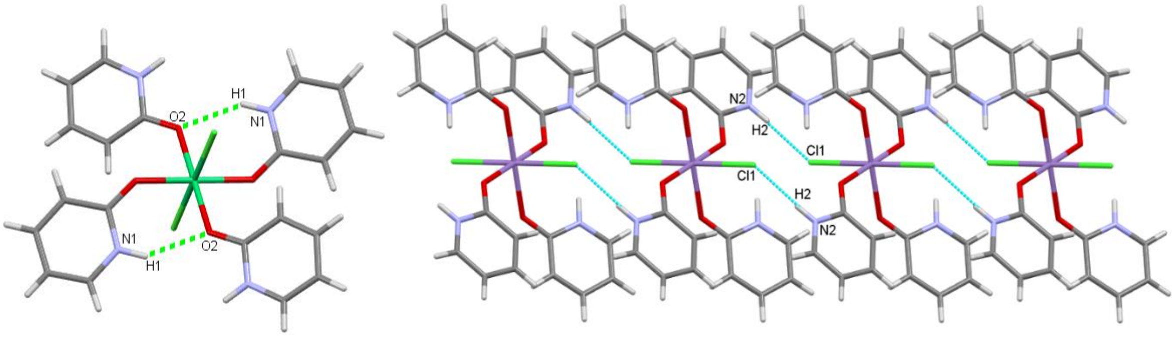
Pyridin-2-one (Hhp) and its anionic form (hp^-) are bound as ligands in many transition metal compounds. The diverse coordination modes of these ligands, stabilization of the complexes by hydrogen bonds and other weak intermolecular interactions lead to different structural motifs for a plethora of compounds with interesting magnetic, catalytic and biochemical properties. Structural diversity has been demonstrated for nickel(II) and copper(II) chloride complexes with Hhp [1, 2], while only one type of simple either molecular or ionic complex has been described for some of the first row transition metals such as vanadium(III), chromium(III) and zinc(II) [3]. In several experiments focused on the preparation of manganese(II) compounds with Hhp, only the complex $[MnCl_2(Hhp)_4]$ was isolated. If the water in the starting compound $MnCl_2{\cdot}4H_2O$ was not removed in the reaction with chlorotrimethylsilane, cocrystals $[MnCl_2(H_2O)_2]_n{\cdot}2nHhp$ were obtained. In the strongly acidic environment caused by the addition of chlorotrimethylsilane to $MnCl_2{\cdot}4H_2O$ and Hhp in THF, protonation of Hhp occurred, followed by crystallization of H_2hpCl. Based on the low melting point of H_2hpCl revealed by thermal analysis, the new compound can be classified as an ionic liquid.

Hydrogen bonds and parallel stacking arrangements of Hhp molecules determine the connectivity patterns in the crystals, resulting in 1D structures in $[MnCl_2(Hhp)_4]$ and H_2hpCl or in wavy layers in $[MnCl_2(H_2O)_2]_n{\cdot}2nHhp$. The different supramolecular architectures will be discussed in detail.



a) b)

Figure 1: a) Intramolecular b) intermolecular hydrogen bonds in a section of a chain in $[MnCl_2(Hhp)_4]$.

References

[1] S. Petriček, *Molecules* **25** (2020) 846–869.

[2] K.C. Shortsleeves, M.M. Turnbull, C.B. Seith, E.N. Tripodakis, F. Xiao, C.P. Landee, L.N. Dawe, D. Garrett, G.D. de Delgado, B.M. Foxman, *Polyhedron* **64** (2013) 110–121.

[3] S. Petriček, *24th Croatian-Slovenian Crystallographic Meeting*, Bol, Croatia, 2016.

Charge density study of a halogen bonded salt of 2-chloropyridine and hexacyanocobaltate(III) acid

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Cyanometallates are a family of transition metal coordination compounds with the most well-known representative being Prussian blue. Due to them being good Lewis bases cyanometallate anions, most notably hexacyanoferrates, have been used as hydrogen [1] and halogen bond acceptors [2]. It has also been shown that protonated hexacyanoferrates are good hydrogen bond donors, with the resulting compounds exhibiting a wide range of supramolecular motifs[3]. More recently, they have also been used as halogen bond acceptors [4]. Protonated hexacyanocobaltates however, remain largely unexplored in this regard.

In this work we have synthesized and analyzed a halogen bonded 2-chloropyridinium hexacyanocobaltate(III) salt; (H_5O_2)(**2-ClpyH**)$_2$[Co(CN)$_6$]. Analysis of the crystalline structure of the compound revealed the presence of O_{Zundel}-H···N and N_{py}-H···N hydrogen as well as Cl_{py}···N halogen bonds which were further studied by experimental charge density methods. Deformation electron density of the **2-ClpyH**$^+$ cation reveals the presence of a σ-hole on the chlorine atom which is necessary for the establishment of a halogen bond. The energy of the Cl···N halogen bond (15.8 kJ/mol) is much lower than the N-H···N hydrogen bond (44.5 kJ/mol) making the latter the prevalent intermolecular interaction between the **2-ClpyH**$^+$ cation and the $[Co(CN)_6]^{3-}$ anion. However, the dominant intermolecular interaction is the O-H···N hydrogen between the anion and the Zundel ($H_5O_2^+$) cation (81.8 kJ/mol).

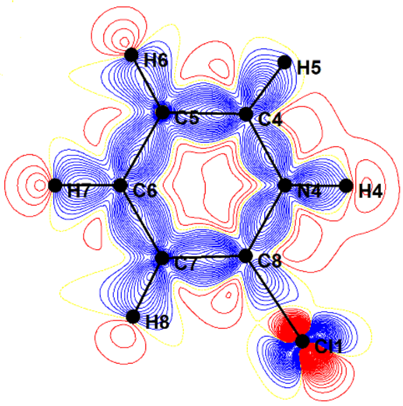

Figure 1: Deformation electron density of 2-chloropyridinium cation present in (H_5O_2)(**2-ClpyH**)$_2$[Co(CN)$_6$].

References

[1] B. Yan, H. D. Wang, Z.D. Chen, *J. Mol. Struct.*, **569** (2001) 65–70.
[2] J.E. Ormond-Prout, P. Smart, L. Brammer, *Cryst. Growth. Des.*, **12** (2012) 205–216.
[3] I. Cvrtila, V. Stilinović, *Cryst. Growth Des.*, **17** (2017) 6793–6800.
[4] N. Jakupec, L. Fotović, V. Stilinović, *CrystEngComm*, **22** (2020) 8142–8150.

Reversible single-crystal-to-single-crystal transformations in the pleochroic complex salt of the bis(oxalato)chromium(III) anion

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Reversible structural transformations related to the changes in environmental conditions are attracting considerable attention due to their potential use in functional devices, such as molecular sensors.[1] Different stimuli (e.g., humidity, vapour exposure, temperature) can trigger a phase transformation in the solid state, resulting in a small displacement of atoms in the crystal lattice, which leads to a change in material properties.[2] Herein we report on the synthesis and structural, as well as electrical characterization of metal-organic complex salt containing a bicyclic amine cation $(CH_3–DABCO)^+$ (1-methyl-4-aza-1-azoniabicyclo[2.2.2]octan-1-ium) and a bis(oxalato)chromium(III) anion $[Cr(bpy)(C_2O_4)_2]^-$ (bpy = 2,2'-bipyridine). Following the principles of green chemistry and due to the low solubility of the chromium(III) precursor, the complex salts were prepared by mechanochemical synthesis. Single crystals were subsequently grown from the methanol-acetonitrile solution of the prepared complex salt as methanol solvate $(CH_3–DABCO)[Cr(bpy)(C_2O_4)_2]\cdot MeOH$ (**1_{MeOH}**) The interesting optical phenomenon of pleochroism was observed in these crystals, where they change color from dark orange to purplish red if rotated under the plane-polarized light. When exposed to the air with low relative humidity, these crystals transform to the dry form $(CH_3–DABCO)[Cr(bpy)(C_2O_4)_2]$ (**1**). In a humid atmosphere with RH > 90%, the dry form is converted to the pentahydrate form $(CH_3–DABCO)[Cr(bpy)(C_2O_4)_2]\cdot 5H_2O$ (**1_{H2O}**). The structural and electrical properties along with the dynamics of the transformation between the different forms were investigated by a combination of single crystal and powder X-ray diffraction, thermal analysis, infrared spectroscopy and chronoamperometric measurements.

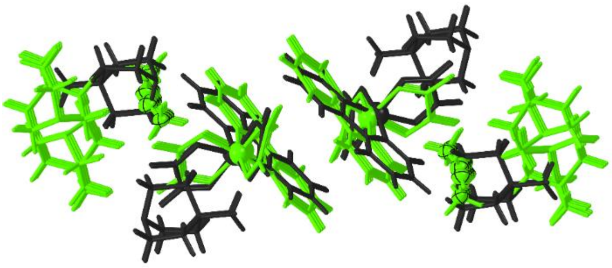

Figure 1: Comparison of crystal structures of $(CH_3–DABCO)[Cr(bpy)(C_2O_4)_2]\cdot MeOH$ (green) and $(CH_3–DABCO)[Cr(bpy)(C_2O_4)_2]$ (black). It can be seen that small variations in crystal composition have a significant effect on complex geometry.

References

[1] M. Dunatov, A. Puškarić, L. Pavić, Z. Stefanić, L. Androš Dubraja, *J. Mater. Chem. C* **10** (2022) 8024–8033.
[2] A. Aslani, A. Morsali, *Chem. Commun*. **29** (2008) 3402–3404.

Structural characterization of $LaNbTiO_6$–$La_4Ti_9O_{24}$ based solid solution

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The ceramics based on ternary system La_2O_3–Nb_2O_5–TiO_2 has the interesting microwave dielectric properties [1]. We have already reported the structural characterization of ternary compounds from the $LaNbTiO_6$–$La_{1/3}NbO_3$ tie line in this system at 1300 °C and determined the crystal structure of monoclinic modification of $LaNbTiO_6$ with *C*2/*c* symmetry [2]. Recently we confirmed that the compound $LaNbTiO_6$ forms a solid solution along the join $LaTiNbO_6$- $La_4Ti_9O_{24}$ according to the scheme (1-x) $LaTiNbO_6$: x $La_4Ti_9O_{24}$, resulting in the general formula $La_{1+3x}Nb_{1-x}Ti_{1+8x}O_{6+18x}$. The solid solution is stable within the compositional range $0 \leq x \leq 0.065$. The structures of solid solutions for x = 0.015, 0.030, 0.05 and 0.065 (samples **1**, **2**, **3** and **4**, respectively) were determined by X-ray powder diffraction using the structure of monoclinic $LaNbTiO_6$ as a model. In this structure Nb^{5+} and Ti^{4+} are randomly distributed over the same site with the same, 50% occupancy. They are coordinated by six O^{2-} forming distorted octahedron. By sharing edges Nb/TiO_6 octahedra form layers (shown in Fig. 1) parallel to (100) plane. Below and above each such layer there are layers of La^{3+}. In solid solutions the Nb/Ti site remains to be fully occupied, with increasing occupancy of Ti^{4+} and decreasing occupancy of Nb^{5+} with the increase of x. The sites of La and O atoms are partially occupied. Their occupancy decreases with increase of Ti content. The volume of the unit cell of the solid solution decreases with the increase of x, i.e., with the increase of Ti content, which is consistent with the smaller ionic radius of Ti^{4+} (0.605 Å) compared to Nb^{5+} (0.64 Å) and with a decrease in the occupancies of La^{3+} and O^{2-}.

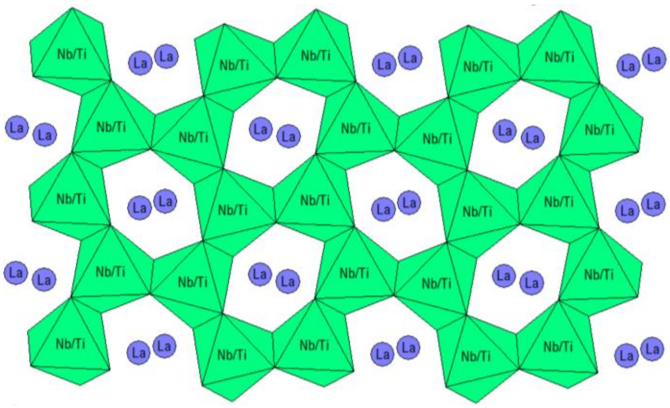

Figure 1: One layer of edge sharing Nb/TiO_6 octahedra and surrounding La atoms in the structure **4** with formula $La_{0.487}Nb_{0.381}Ti_{0.619}O_{2.921}$

References

[1] J. Zhang and R. Zhuo, Mat. Res. Bull. **83** (2016) 568–572.
[2] A. Golobič, S.D. Škapin, D. Suvorov, A. Meden, Croat. Chem. Acta **77** **(3)** (2004) 435–446.

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Structure of ruthenium(II) diketonato complexes designed as potential anticancer agents

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The anticancer activity of ruthenium complexes has been studied for 30 years. They have been the focus of interest because of their ligand exchange kinetics, which is comparable to those of clinically used platinum agents, and because they have a greater number of accessible coordination geometries. The most promising ruthenium complexes discovered to this day, were those bearing imidazole ligands and half-sandwich complexes with diamine or amphiphilic pta (1,3,5-triaza-7-phospphaadamantane) ligands [1]. Interesting ligands for the synthesis of metal complexes with potential anticancer activity are also *β*-diketonates, which are used as bidentate ligands by many research groups around the world. Different substituents, such as trifluoromethyl and phenyl groups, have been added to the diketonate scaffold to enhance lipophilicity and improve cellular uptake [2].

In recent years, our group has focused on ruthenium(II) complexes with *β*-diketonates as *O*,*O*-ligands [3,4]. We synthesized 1-(3-(dimethylamino)phenyl)-4,4,4-trifluorobutane-1,3-dione and used it as a ligand to obtain new ruthenium(II) complexes $[(\eta^6\text{-}p\text{-cym})\mathrm{Ru}(\kappa^2\text{-}O,O\text{-}\mathrm{F_3CCOCHCOPhN(CH_3)_2})\mathrm{Cl}]$ (**1**) and its pta derivative (**2**). The synthesized diketone and the two complexes were characterized with NMR, mass spectrometry, IR and UV-Vis spectroscopy. Crystals for both complexes were obtained, and X-ray structural analysis confirmed the pseudo-octahedral geometry of the half-sandwich complexes with typical ˝piano stool˝ conformation, similar to those of previously published complexes with diketonate ligands [3].

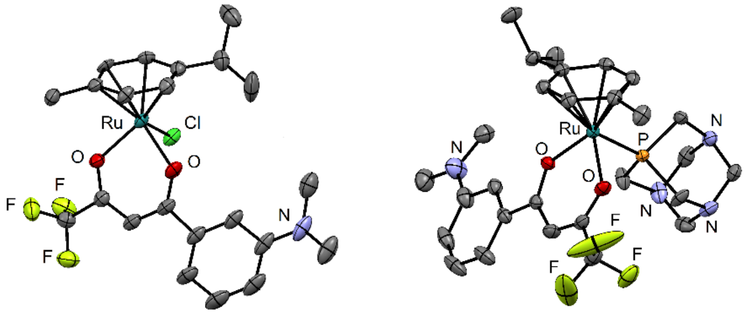

Figure 1: Crystal structures of complexes **1** and **2**.

References

[1] J.P.C. Coverdale, T. Laroiya-McCarron and I. Romero-Canelón, *Inorganics* **7** (2019) 31.
[2] J. Kljun and I. Turel, *Eur. J. Inorg. Chem.* (2017) 1655–1666.
[3] S. Seršen, J. Kljun, K. Kryeziu, R. Panchuk, B. Alte, W. Körner, P. Heffeter, W. Berger and I. Turel, *J. Med. Chem.* **58** (2015) 3984–3996.
[4] M. Uršič, T. Lipec, A. Meden and I. Turel, *Molecules* **22** (2017) 326.

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Exploring the XeF_2–TaF_5 system with mechanochemistry

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The property of XeF_2 to act as fluoride ion donor is perhaps most evident in its acid-base reactions with strong Lewis acids such as AsF_5, SbF_5, TaF_5, RuF_5, IrF_5 etc., in which either $[XeF]^+$ or the $[Xe_2F_3]^+$ cation is formed [1–3]. Since all reagents are strong oxidizers and strong fluorinating agents, the synthesis of such compounds is carried out under inert conditions, employing custom-built vacuum line, non-classical solvents (anhydrous HF or bromine(V) fluoride), and vessels constructed from inert materials. Not surprisingly, the special conditions for the synthesis and handling of such compounds greatly hinder their study in non-specialized laboratories.

In this work, we demonstrated that mechanochemistry [4] can be implemented as a fast, easy, and technically not demanding synthetic method for noble-gas compounds. In the XeF_2–TaF_5 system, selective mechanosynthesis of all three known species [3], $[XeF][Ta_2F_{11}]$, $[XeF][TaF_6]$, and $[Xe_2F_3][TaF_6]$, was developed. All reaction products were characterized by vibrational spectroscopy (Raman, ATR-FTIR) and by powder X-ray diffraction. The reactions were also carried out at elevated temperatures and in anhydrous HF to determine how well the new synthetic method compares with “classical” approaches in terms of selectivity and purity. In addition, crystal structures of all three compounds were elucidated, making this only the second fully structurally characterized XeF_2–MF_5 system after the XeF_2–SbF_5 family of compounds.

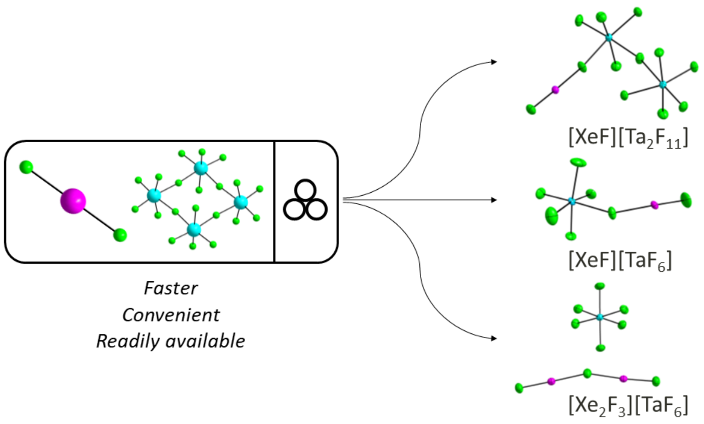

Figure 1: Mechanosynthesis of $[XeF][Ta_2F_{11}]$, $[XeF][TaF_6]$, and $[Xe_2F_3][TaF_6]$ and their crystal structures.

References

[1] H.S.A. Elliot, J.F. Lehmann, H.P.A. Mercier, H.D.B. Jenkins and G.J. Schrobilgen, *Inorganic Chemistry* **49** (2010) 8504–8523.

[2] F.O. Sladky, P.A. Bulliner and N. Bartlett, *Journal of the Chemical Society A: Inorganic, Physical, Theoretical* (1969) 2179–2188.

[3] B. Frlec and J.H. Holloway, *Journal of Chemical Society, Dalton Transactions* **6** (1975) 535–540.

[4] T. Friščić, C. Mottillo and H.M. Titi, *Angewandte Chemie International Edition* **59** (2020) 1018–1029.

Metal(II) salts of $[MoOF_5]^-$ and $[Mo_2O_2F_9]^-$ and their HF complexes

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An important part of material science entails the exploration of novel anionic species. The accumulation of knowledge in this field is based on the development of synthetic methods, structural characterization, and computational modelling. This, in turn, enables the design of novel materials with superior functionalities [1].

The field of fluoridooxidomolybdates(VI) is relatively underexplored with only a handful of reported structurally characterized compounds [2–4]. These were synthesized by utilizing the weak Lewis acidity and weak fluoride-ion accepting properties of precursor $MoOF_4$ to prepare neutral adducts with NgF_2 (Ng = Xe, Kr) [2] and a series of $[Mo_2O_2F_9]^-$ salts with monovalent cations [3,4]. It was also described that $[Mo_2O_2F_9]^-$ anions are in equilibrium with fluoride ions in solution and can form species with higher metal to fluorine ratio, namely $[MoOF_5]^-$ and $[MoOF_6]^{2-}$ [5].

We have investigated a new synthetic protocol towards fluoridooxidomolybdate(VI) salts. It avoids the synthesis and isolation of $MoOF_4$ by forming it in situ and immediately reacting it with metal fluoride already available in reaction mixture. We have used a series of divalent metal fluorides, namely CaF_2, SrF_2, and PbF_2 to prepare corresponding fluoridooxidomolybdate(VI) salts. In addition to preparing $[Mo_2O_2F_9]^-$ salts, employing an excess of PbF_2 enabled us to synthesize $Pb[MoOF_5]_2$. It was successfully grown in form of single crystals from a concentrated anhydrous HF solution and subsequently analyzed by X-ray diffraction and vibrational spectroscopy. In addition, Sr and Ca salts with $[Mo_2O_2F_9]^-$ crystallized in the form of HF-coordinated complexes.

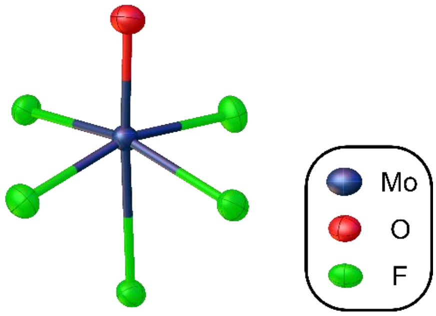

Figure 1: Crystal structure of $[MoOF_5]^-$ anion (50 % thermal ellipsoids).

References

[1] H. Kageyama, K. Hayashi, K. Maeda, J.P. Attfield, Z. Hiroi, J.M. Rondinelli and K.R. Poppelmeier, *Nature Communications* **9** (2018) 772.
[2] M.R. Bortolus, H.P.A. Mercier and G.J. Schrobilgen, *Chemistry–A European Journal* **28** (2022) e20210372.
[3] R.E. Stene, B. Scheibe, A.J. Karttunen, W. Petry and F. Kraus, *European Journal of Inorganic Chemistry* (2019) 3672–3682.
[4] D. Turnbull, P. Chaudhary, D. Leenstra, P. Hazendonk, S.D. Wetmore and M. Gerken, *Inorganic Chemistry* **59** (2020) 17544–17554.
[5] R. Bougon, T. Bui Huy and P. Charpin, *Inorganic Chemistry* **14** (1975) 1822–1830.

Variability of mechanical responsiveness of crystals of copper(II) halides with a family of pyridine-based ligands

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For a long has brittleness been ascribed to crystalline materials as the main feature that impeded the application of those highly ordered materials in advanced technologies, *e.g.* soft robotics, optical waveguides, flexible electronics, and others. [1] Only recently, phenomena of crystals' mechanical flexibility have been reported, and so far, organic crystals have been examined more extensively [2] whereas a substantially smaller number of metal-containing crystals have been reported. Yet, the exploration of mechanical flexibility on crystals of metal-organic compounds yielded new and distinctive mechanical responses, including a specific extent of elastic or plastic response inherent to a material itself as well as newly described elastic⟶plastic response. [3–5]

To shed more light on the newly observed mechanical behavior of metal-containing crystalline solids, in particular the role of small yet significant structural differences in the delivery of a variety of mechanical responses, here we opted for 1-D coordination polymers of copper(II) with a family of pyridine-based ligands. They allowed systematic exploration of the impact of selected functionalities, in particular their steric requirements and supramolecular potential, on the delivery of a variety of morphologies as well as mechanical responses. Moreover, a detailed comparison of our results with those previously reported will be brought in a systematic manner.

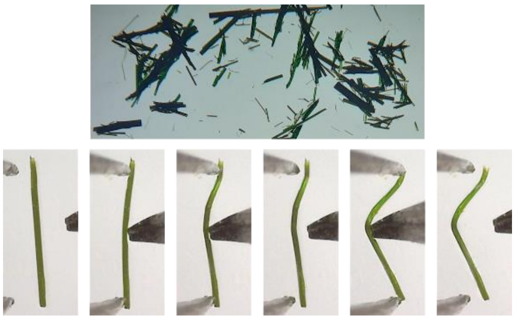

Figure 1: Mechanical flexibility of single-crystal of 1-D coordination polymer of copper(II).

Acknowledgements
This work has been fully supported by the Croatian Science Foundation under project "From form to function: Mechanically flexible crystalline materials with controllable responses" (IP-2019-04-1242).

References

[1] P. Naumov, D. P. Karothu, E. Ahmed, L. Catalano, P. Commins, J. M. Halabi, M. B. Al-Handawi, L. Li, *J. Am. Chem. Soc.* **142** (2020) 13256–13272.
[2] P. Naumov, S. Chizhik, M. K. Panda, N. K. Nath, E. Boldyreva, Chem. Rev., 2015, **115**, 12440.
[3] M. Đaković, M. Borovina, M. Pisačić, C.B. Aakeröy, Ž. Soldin, B.-M. Kukovec, I. Kodrin, *Angew. Chem. Int. Ed.* **57** (2018) 14801–14805.
[4] M. Pisačić, I. Biljan, I. Kodrin, N. Popov, Ž. Soldin, M. Đaković, *Chem.Mater.* **33** (2021) 3660–3668.
[5] M. Pisačić, I. Kodrin, A. Trninić, M. Đaković, *Chem.Mater*. **34** (2022) 2439–2448.

Reactions between $Co(NO_3)_2{\cdot}6H_2O$ and 2-(hydroxymethyl)pyridine

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Simple pyridine-alcohols are interesting group of organic ligands due to the presence of two possible coordination sites, i.e. pyridine-N and oxygen from hydroxo group that can coordinate to metal centers in different ways and thus the formation of larger architectures can be achieved. Furthermore, the obtained complexes are known to possess interesting physical properties, e.g. such as catalytic [1,2] or single molecule magnets in case of Mn(II) compounds [3] etc.

Focusing on 2-(hydroxymethyl)pyridine (2hmp, C_6H_7NO) and its reactions with $Co(NO_3)_2{\cdot}6H_2O$, the following four novel coordination compounds were obtained:

1 $[Co^{II}(2hmp)_3](NO_3)_2$,
2 $[Co^{II}(2hmp)_3](NO_3)_2{\cdot}CH_3COCH_3$,
3 $[Co^{II}(2hmp)_2(OH_2)_2](NO_3)_2$, and
4 $[Co^{III}(L)_2(NO_2)(OH_2)]$ where L=2-pyridinecarboxylate anion ($C_6H_4NO_2$).

Compound **4** was prepared when crystals of **3** were left in mother liquor for few weeks in a series of redox reactions. The detailed description of the crystal structures will be given together with their Hirshfeld surface analysis.

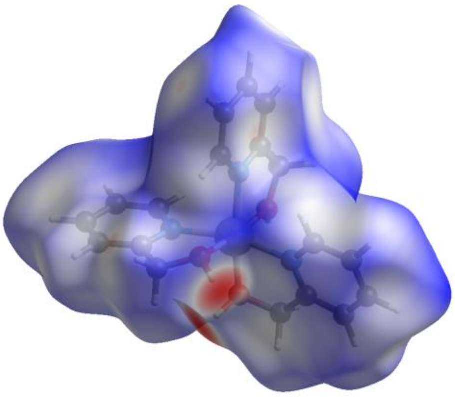

Figure 1: Hirshfeld surface of coordination cation in **1** plotted over d_{norm}.

References

[1] A. Kermagoret and P. Braunstein, *Dalton Trans.* (2008) 1564–1573.

[2] J. Zhang, T. Peilj, R. Pattacini, A. Kermagoret, R. Welter, G. Rogez, T.S.A. Hor and P. Braunstein, A*ngew. Chem. Inter. Ed.* **49** (2020) 4443–4446.

[3] H. Miyasaka, K. Nakata, L. Lecren, C. Coulon, Y. Nakazawa, T. Fujisaki, K.I. Sugiura, M. Yamashita and R. Clérac*, J. Am. Chem. Soc.* **128** (2006) 3770–3783.

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Novel BF_3 adducts of organic carbonates: Syntheses and crystal structures

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The compounds BF_3·A (A = organic carbonate) have recently been shown to be promising functional electrolyte additives for lithium-ion batteries. It was reported that these adducts increase the battery length-life, improve the electrode interphases and decrease the overall resistance of the cell [1]. The mechanism of this beneficial action has not been fully clarified yet, thus more research with similar compounds is required.

In this work, several BF_3 adducts have been synthesized employing the specialised experimental techniques that are in use in inorganic fluorine chemistry. These methods have been successfully adopted in battery electrolyte synthesis and have proven to ensure anhydrous conditions and low contaminant contents [2]. Among others, the structures of the novel adducts BF_3·dec and BF_3·gbl (where dec: diethyl carbonate and gbl: γ-butyrolactone; Figure 1) have been determined for the first time by low-temperature single-crystal X-ray diffraction analysis using a custom-developed low-temperature crystal mounting procedure [3]. The structural peculiarities of all synthesised BF_3 adducts together with their corresponding Raman spectra are presented and discussed.

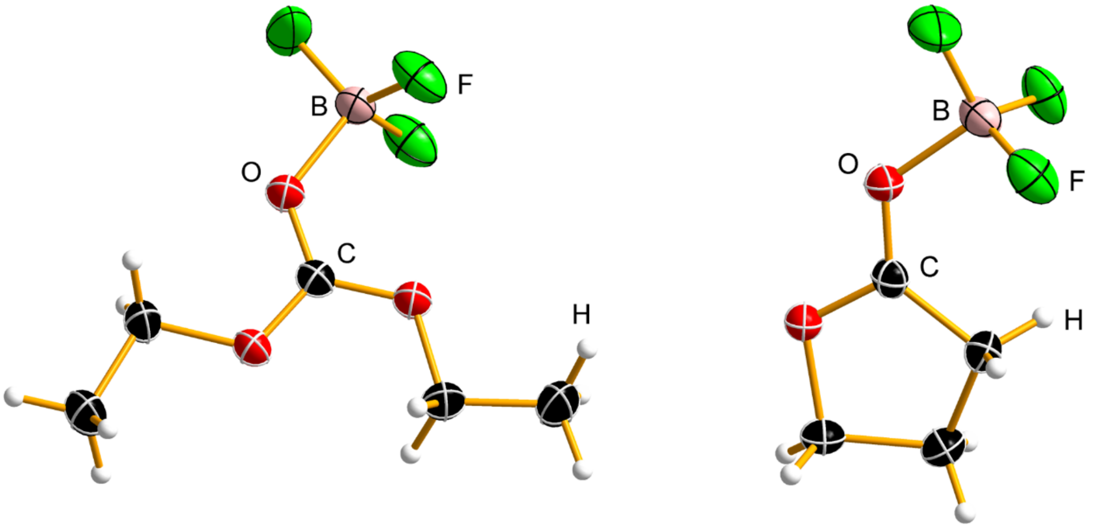

Figure 1: The asymmetric units of the compounds BF_3·dec (left) and BF_3·gbl (right). Thermal ellipsoids are drawn at the 50% probability level.

References

[1] L. Eisele, N. Laszczynski, M. Schneider, B. Lucht and I. Krossing, *Journal of The Electrochemical Society* **167** (2020) 060514.
[2] J.D. Forero-Saboya, M. Lozinšek and A. Ponrouch, *Journal of Power Sources Advances* **6** (2020) 100032.
[3] M. Lozinšek, H.P.A. Mercier and G.J. Schrobilgen, *Angewandte Chemie International Edition* **60** (2021) 8149–8156.

p-Cymene ruthenium pyrithionato complexes with triphenylphosphine and triphenylarsine

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Ruthenium based anticancer drugs have been studied for several decades. One of the best known representatives of this group is the ruthenium(II) *p*-cymene (CYM) pta (1,3,5-triaza-7-phosphaadamantane) complex (RAPTA-C [1]. In recent years, various analogues have been prepared using different ligands, replacing monodentate pta ligand and/or one or both chloride ligands. In many cases, pta and chloride ligands were replaced by ligands with *N*,*N*, *N*,*O* and *S*,*O* donor atoms [2]. In our research group, we have prepared various pyrithione (pth) analogues that are *S*,*O* type ligands and their ruthenium complexes in both chlorido and pta variants. In addition, we evaluated the structure activity relationship of the prepared compounds [3,4]. To fully understand the role of the monodentate ligand, we also decided to synthesise complexes introducing some alternatives of pta ligand in order to evaluate their biological activity and further explore the structure activity relationship.

Thus, we synthesised *p*-cymene triphenylphosphine ruthenium(II) complex with hexafluorophosphate anion (RuCYM-pth-PPh$_3$-PF$_6$) and a triphenylarsine analogue (RuCYM-pth-AsPh$_3$-PF$_6$). Both complexes were characterised by nuclear magnetic resonance spectroscopy (NMR) for ^{1}H, ^{19}F and ^{31}P atoms, mass spectrometry (HRMS) and X-ray diffraction on single crystals [5].

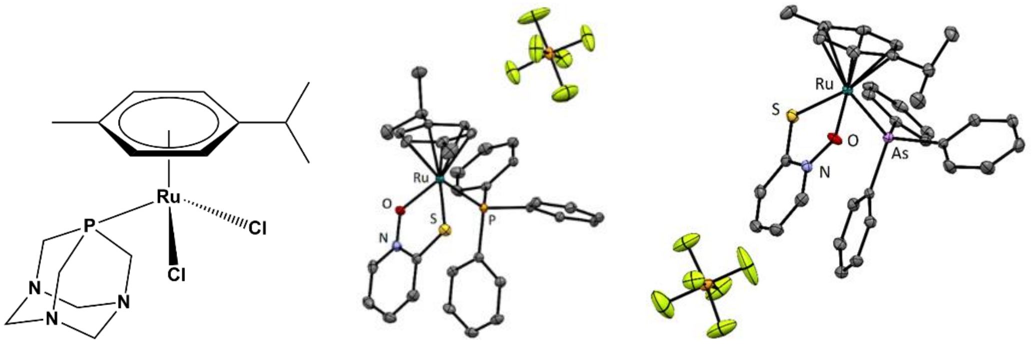

Figure 1: RAPTA-C (left), crystal structure of RuCYM-pth-PPh$_3$-PF$_6$ (middle) and RuCYM-pth-AsPh$_3$-PF$_6$ (right) complex. Thermal ellipsoids were drawn at 35% probability level and hydrogen atoms were omitted.

References

[1] J.P.C. Coverdale, T. Laroiya-McCarron, I. Romero-Canelón, *Inorganics* **7** (2019) 31.

[2] G. Gasser, I. Ott, N. Metzler-Nolte, *J. Med. Chem.* **54** (2011) 3–25.

[3] J. Kladnik, J. Kljun, H. Burmeister, I. Ott, I. Romero-Canelón, I. Turel, *Chem. Eur. J.* **25** (2019) 14169–14182.

[4] J. Kladnik, J.P.C. Coverdale, J. Kljun, H. Burmeister, P. Lippman, F.G. Ellis, A.M. Jones, I.Ott, I. Romero-Canelón, I. Turel, *Cancers* **13** (2021) 2493.

[5] J. Kljun, M. Rebernik, L. M. Balsa, J. Kladnik, U. Rapuš, T. Trobec, K. Sepčić, R. Frangež, I. Leon, I. Turel, in preparation.

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Structural characterization of multicomponent crystals formed from nimesulide and quaternary ammonium compounds.

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Synthesis new forms of crystal compounds and analyze the intermolecular interactions are few of aspects which crystal engineering is. This field of science is also use in pharmacy - to design multi-component complexes containing active pharmaceutical ingredients (API - Active Pharmaceutical Ingredient). New forms of drugs can change their narrow therapeutical index or improve some of physicochemical properties [1-2].

One of the APIs, which properties should be improved is nimesulide (4–nitro–2–phenoxymethanesulfonanilide). It is non-steroidal anti-inflammatory drug (NSAID), use in severe pain treatment [3]. Substance is poorly soluble in water [4]. What is more, crystals consist of nimesulide are barely known – only few structures are in the crystallographic database (The Cambridge Structural Database).

Due to the all of above, in my presentation I will show results of my research at newly received tetraalkylammonium nimesulide salts (Fig. 1).

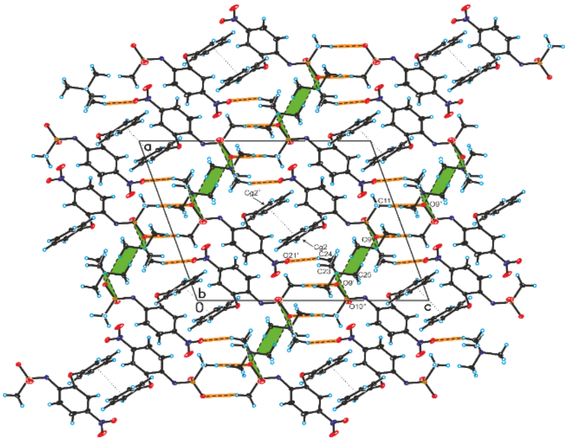

Figure 1: Intermolecular interactions in a tetramethylammonium crystal of nimesulide salt.

References

[1] S. Mirza, I. Miroshnyk, J. Heinämäki, O. Antikainen, J. Rantanen, P. Vuorela, H. Vuorela, J. Yliruusi, *AAPS PharmSciTech* **10(1)** (2009) 113–119.

[2] L.S. Taylor, D.E. Braun, J.W. Steed, *Crystal Growth & Design* **21(3)** (2021) 1375–1377.

[3] H.G. Kress, A. Baltov, A. Basiński, F. Berghea, J. Castellsague, C. Codreanu, E. Copaciu, M.A. Giamberardino, M. Hakl, L. Hrazdira, M. Kokavec, J. Lejčko, L. Nachtnebl, R. Stančík, A. Švec, T. Tóth, M.V. Vlaskovska, J Woroń, *Medical Research and Opinion* **32(1)** (2016) 23–36.

[4] S.O. Purcaru, M. Ionescu, C. Raneti, V. Anuta, I. Mircioiu, I. Belu, *Curr Health Sci J.* **36(1)** (2010) 42–49.

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Doping effects on the structural and magnetic properties of $SrCu_2(BO_3)_2$

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The two-dimensional (2D) layered oxide $SrCu_2(BO_3)_2$ or SCBO, identified as a realization of the Shastry-Sutherland model, exhibits intriguing magnetic properties due to its exchange topology and the presence of a spin gap [1,2]. The crystal structure of SCBO (space group $I\bar{4}2m$) is shown in Figure 1a. It consists of magnetic $Cu_2(BO_3)_2^{2-}$ layers and nonmagnetic Sr^{2+} layers alternating along the crystallographic *c*-axis [3]. The $S = 1/2$ of Cu^{2+} ions are arranged in the form of dimers orthogonally coupled to each other, forming a 2D network of interacting spins. This compound exhibits rich physics as a function of magnetic field and/or pressure [4]. A strong interplay between the crystal structure and magnetic properties is also characteristic of this low-dimensional magnetic material and unique ground states such as quantum spin liquid states or superconductivity are predicted to arise when the system is chemically doped. However, doping of SCBO has not been thoroughly investigated [5]. With the aim of understanding the effects of doping on the structural and magnetic properties of SCBO, various A-site and B-site doped SCBO samples were synthesized in polycrystalline form by the solid-state method, while single crystals of selected compositions were grown by the flux method (Figure 1b). A combination of techniques including synchrotron PXRD, magnetic susceptibility, EPR, DSC and Raman spectroscopy were further employed to study the structural changes and evolution of magnetic properties as a function of doping type and concentration.

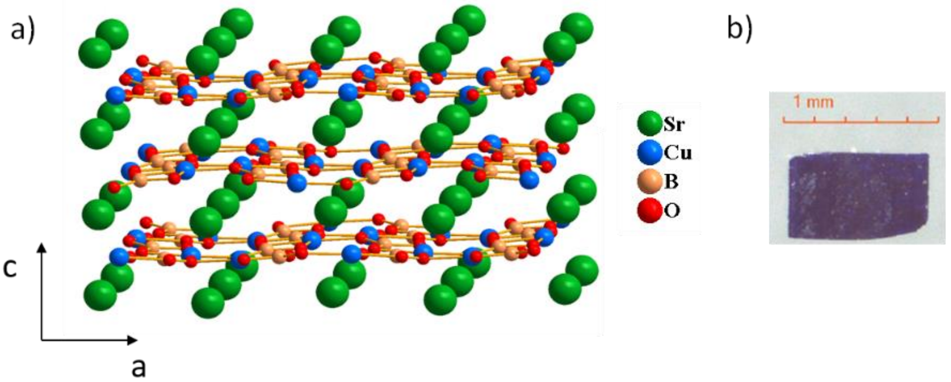

Figure 1: a) Crystal structure of SCBO along the crystallographic *b* axis. b) As-grown SCBO single crystal.

References

[1] B.S. Shastry, B. Kumar, *Prog. Theor. Phys.* **145** (2002) 1–16.
[2] H. Nojiri, H. Kageyama, K. Onizuka, Y. Ueda and M. Motokawa, *J. Phys. Soc. Jpn.* **68** (1999) 2906–2909.
[3] R.W. Smith and D. A. Keszler, *J. Solid State Chem*. **93** (1991) 430–435.
[4] S. Haravifard, D. Graf, A. E. Feiguin *et al.*, *Nat. Commun.* **7** (2016) 11956–11961.
[5] Z. Shi, W. Steinhardt, D. Graf *et al.*, *Nat. Commun*. **10** (2019) 2439–2447.

Competition of different halogen bond acceptors in oxazole derivatives for halogen bonding with perhalogenated benzenes

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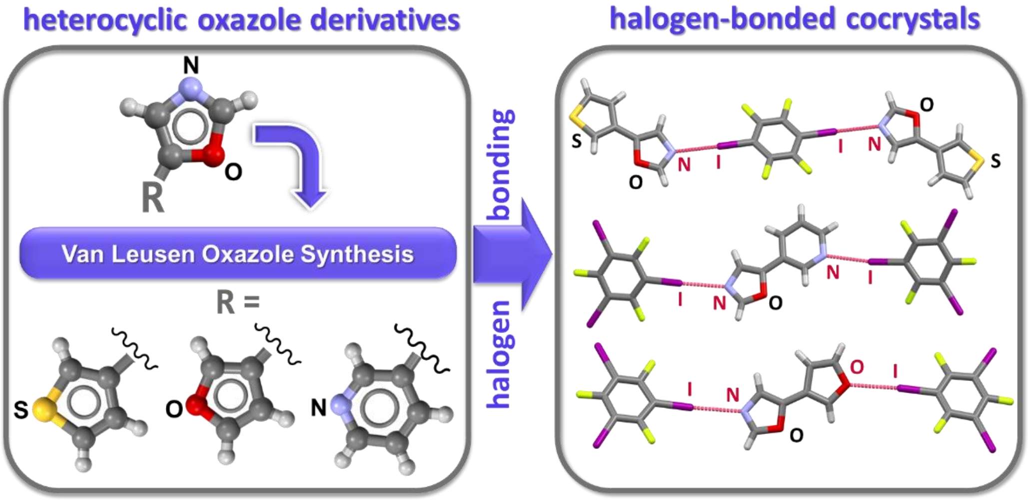
In the last three decades the halogen bond [1] has become recognized as a valuable tool in crystal engineering due to its particular directionality and tunability as compared to other noncovalent interactions. In order to study the competition of different heteroatoms as halogen bond acceptors [2], three oxazole derivatives with multiple acceptor sites were prepared in the Van Leusen synthesis. The synthesis allows for the preparation of oxazoles from different aldehydes by a reaction with tosylmethyl isocyanide in the presence of an equimolar amount of potassium carbonate in refluxing methanol. [3] The obtained derivates were 5-(4-pyridyl)-1,3-oxazole, 5-(2-thienyl)-1,3-oxazole and 5-(2-furyl)-1,3-oxazole. Cocrystals were obtained by dissolving the corresponding oxazole derivative and one from a selection of halogen bond donors, 1,4-diiodotetrafluorobenzene, 1,3-diiodotetrafluorobenzene, 1,3,5-triiodotrifluorobenzene or 1,2-diiodotetrafluorobenzene, in an appropriate solvent. The crystallization experiments yielded eight cocrystals and were characterized by single crystal X-ray diffraction. Structural analysis revealed that the nitrogen atom in oxazole is the dominant halogen bond acceptor in eight cocrystals, featuring I···N halogen bonds with the most prominent relative shortening values that are comparable to ones between iodine atoms and pyridine nitrogen. As expected, cocrystallization with 5-(4-pyridyl)-1,3-oxazole resulted in a larger amount of cocrystals featuring diverse supramolecular motifs with the pyridine nitrogen atom participating in halogen bonding in three of four obtained cocrystals. On the other hand, the sulfur and oxazole oxygen atoms did not participate in any halogen bonds.



References

[1] P. Metrangolo, *Acta Crystallogr. A.* **73** (2017) C309–C309.
[2] D. Cinčić, T. Friščić and W. Jones, *Chem. Eur. J.* **14** (2008) 747–753.
[3] H. Saikachi, T. Kitagawa, H. Sasaki, A. M. van Leusen, *Chem. Pharm. Bull.* **27** (1979) 793–796.

Modification of crystal structure and optical absorption edge in compressed perovskite-like $CsPb_2Br_5$

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Recently, cesium lead halide perovskite-related compounds have emerged as promising functional materials for optoelectronic applications owing to their remarkable spectroscopic and electronic properties [1-2]. Here, we focus on $CsPb_2Br_5$, which structure has a two-dimensional character. In this crystal, the face-connected $PbBr_8$ polyhedrons form layers which are sandwiched between the layers composed of Cs^+ cations (see Figure 1). As recently reported, $CsPb_2Br_5$ exhibits strong green photoluminescence, which opens prospects for applications in light-emitting diodes, lasers, and photodetectors [2-3].

To clarify the literature inconsistencies regarding the physical properties of this material, we performed systematic structural and spectroscopic high-pressure studies. The diamond anvil cell technique was employed to generate pressure up to 6 GPa. Isopropanol and Daphne oil 7575 were used as hydrostatic media. Crystallographic data were collected by the single-crystal X-ray diffraction method. No anomalies were observed in the lattice parameters and unit-cell volume, which proves that the crystal does not undergo any phase transition in the studied pressure range, as opposed to the previously published data [4]. These results are in accordance with our spectroscopic studies. We also show that $CsPb_2Br_5$ does not emit light in the visible range and its absorption edge is located at 332 nm. The reasons of literature discrepancies are discussed.

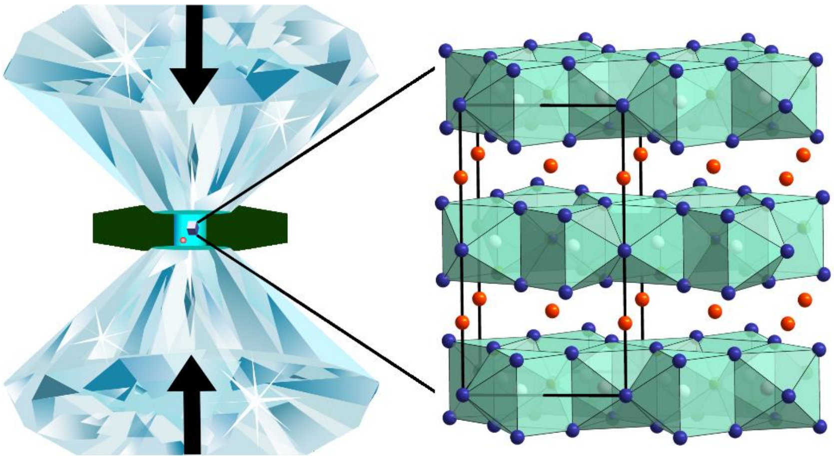

Figure 1: Scheme of the diamond anvil cell (left) and $CsPb_2Br_5$ crystal structure (right).

References

[1] P. Tonui, S.O. Oseni, G. Sharma, Q. Yan and G.T. Mola, *Renew. Sustain. Energy Rev.* **91** (2018) 1025–1044.
[2] Q.A. Akkerman, A.L. Abdelhady and L. Manna, *J. Phys. Chem. Lett.* **9** (2018) 2326–2337.
[3] K.H. Wang, L. Wu, L. Li, H.B. Yao, H.S. Qian and S.H. Yu, *Angew. Chem.* **128** (2016) 8468–8472.
[4] Z. Ma, F. Li, G. Qi, L. Wang, C. Liu, K. Wang, G. Xiao and B. Zou, *Nanoscale* **11** (2019) 820–825.

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π-stacking and multicentric bonding of TMPD (Wurster's blue) in charge-transfer complexes with different quinones

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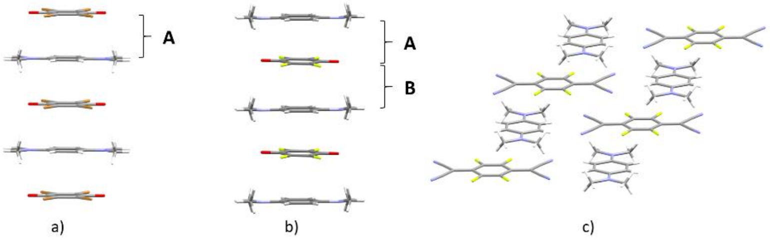
N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine (TMPD or Wurster's blue) is a well-known electron-donor [1]. It can form charge-transfer complexes with electronegative quinones [2]. Such complexes are stabilized by the electrostatic attraction between electron-rich donors and electron-deficient acceptors [3]. In two such co-crystals studied previously, π-stacks of alternating quinone and TMPD molecules are present [2].

Here we report a study on π-stacking and multicentric bonding in charge-transfer complexes with partially charged **TMPD** radical cation. We have prepared a series of co-crystals of **TMPD** and differently substituted quinones; 2,3-dicyano-5,6-dichloroquinone (**1**), tetrafluorquinone (**2**), tetrachlorquinone (**3**), tetrabromquinone (**4**), 7,7,8,8-tetracyanoquinodimethane (**5**) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (**6**). These systems were studied by means of variable-temperature crystallography (80 - 400 K) and X-ray charge density [4]. Complexes of **TMPD** with **3** and **5** have been observed previously [2].

There are three types of stacks found in this series of compounds (Figure 1.). First, in co-crystals with **1**, **3**, **4** and **5** moieties form equidistant stacks of alternating **TMPD** and quinones. The second type is *pancake-bonded* dimers of **TMPD** and quinone in complex with **2**. And in co-crystal with **6** moieties form 2D arrays of alternating **TMPD** and quinone molecules. For crystals of TMPD with **3** and **4,** polymorphic phase transitions at lower temperatures have been observed when orientations of the moieties change from parallel (at room temperature) to inclined (at low temperature).

Besides that, we studied structure and behavior of TMPD radical cation in its novel chloride salt co-crystal with 2,5-dichlorohydroquinone. In that co-crystal, TMPD radical cations stack in *pancake-bonded* dimers, so this is the first *pancake-bonding* between radical cations studied by X-ray charge density.



a) b) c)

Figure 1: Three types of stacking in co-crystals of **TMPD** and a) **1**, **3**, **4**, **5**, b) **2** and c) **6**.

References

[1] C. Wurster, E. Schobig, *Ber. Dtsch. Chem. Ges.* **12** (1879) 1807–1813.
[2] J.L. de Boer, A. Vos, *Acta Crystallogr. B*, **B24** (1968) 720–725; A.W. Hanson *Acta Crystallogr. B*, **B24** (1968) 768–778.
[3] H. J. Wörner, C. A. Arrell, N. Banerji, et al., *Struct. Dyn.* **4** (2017) 061508.
[4] V. Milašinović, K. Molčanov, A. Krawczuk, N.E. Bogdanov, B.A. Zakharov, E.V. Boldyreva, C. Jelsch, B. Kojić-Prodić, *IUCrJ,* **8** (2021) 644–654.

Single-crystal growth and structure determination of $BaAgF_4$ and $(BaF)_2AgF_4$

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Barium layered fluorides with the Ba*M*F_4 chemical formula are interesting materials with ferroelectric behaviour at room temperature for the *M* = Mg, Co, Ni, and Zn, and antiferromagnetic ordering with T_N ~20–80 K for *M* = Mn, Fe, Co, and Ni [1]. All these compounds adopt the orthorhombic structure with the polar space group $Cmc2_1$ with layers of corner-shared *M*F_6 octahedra that are separated by Ba sheets stacked along the *c*-axis. The $BaCuF_4$ member is a magnetoelectric candidate with an ideal direct coupling between the polarization and the magnetization [2]. Interestingly, the Ag^{2+} analogues have been the least investigated compounds from this series. They were first reported by Odenthal in 1970's together with structures derived from powder X-ray diffraction data [2,3]. However, a complete investigation of these phases is still missing due to a lack of single-crystal data as these compounds are changeling to synthesise and grow in large-enough single crystals. This work reports on the first single-crystal growth of $BaAgF_4$. The single crystals were grown by a solid-state method from the metal fluorides at 500 °C under an argon atmosphere. We found that $BaAgF_4$ adopts a centrosymmetric tetragonal structure with the *I*4/*mcm* space group and with unit cell parameters in good agreement with the values reported by Odenthal from powder data. The Ag atoms are coordinated by four F atoms forming square planar $[AgF_4]^{2-}$ anions, whereas Ba^{2+} are located between the Ag-F layers (Figure 1).

In addition, single crystals of the $(BaF)_2AgF_4$ phase were also grown and its crystal structure determined for the first time using single-crystal X-ray diffraction.

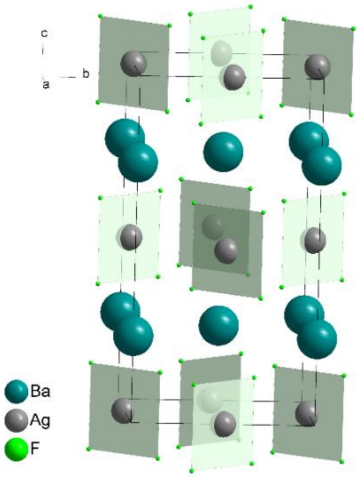

Figure 1: The $BaAgF_4$ crystal structure is composed of square-planar $[AgF_4]^{2-}$ and Ba^{2+} layers.

References

[1] S.W. Kim, H. Y. Chang, and P. S. Halasyamani, *J. Am. Chem. Soc*. **132** (2010) 17684–17685.

[2] A.C. Garcia-Castro, W. Ibarra-Hernandez, E. Bousquet, and A. H. Romero, *Phys. Rev. Lett*. **121** (2018) 117601–5.

[3] R.-H. Odenthal and R. Hoppe, *Z. Anorg. Allg. Chem*. **385** (1971) 92–101.

[4] R.-H. Odenthal and R. Hoppe, *Naturwissenchaften* **57** (1970) 305–306.

Salts of 1,1,2,3,3-pentacyanopropenide carbanion with aromatic cations

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1,1,2,3,3-Pentacyanopropenide (Fig.1 left) is one of the most stable carbanions, whose salts are easily crystallised. The reason of its high stability is inductive effect of its five electron-withdrawing cyano-substituents. As a result, a negative charge is delocalised over the central propenide fragment. Up-to-date over 50 crystal structures with pentacyanopropenide have been published [1]; these involve various salts of a free carbanion [2] and its transition metal complexes [3].

In this work we present three novel salts of pentacyanopropenide with three analogous organic cations, 2-methyl-*N*-pyridinium, 3-chloro-*N*-pyridinium and 4-methyl-*N*-pyridinium (Fig. 1 right). It is known that geometry of the pentacyanopropenide carbanion is easily affected by crystal field effects, so it often deviates from its calculated minimum-energy configuration, which has a molecular symmetry C_{2v}. Therefore, we studied in detail effect of crystal packing and intermolecular interactions on geometry of the carbanion three salts with similar cations.

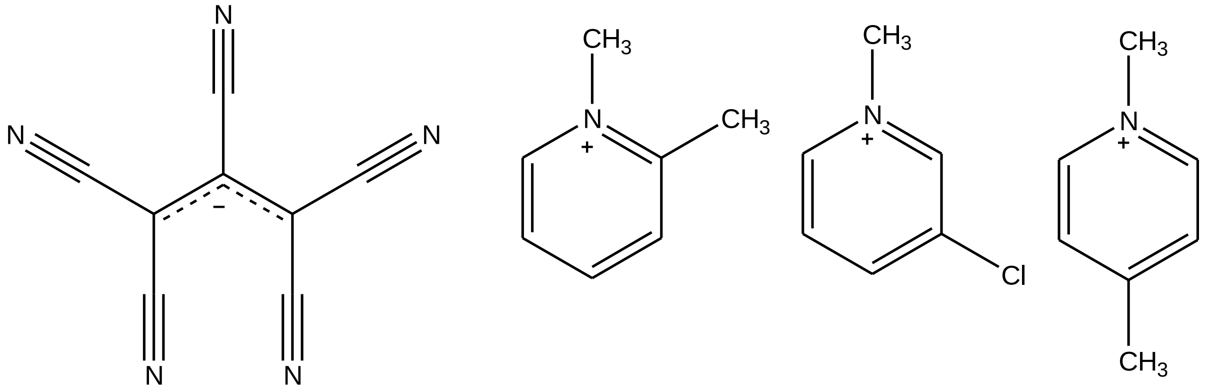

Figure 1: Pentacyanopropenide and three cations used in this work.

References

[1] C.R. Groom, I.J. Bruno, M.P. Lightfoot and S.C. Ward, *Acta Crystallogr. B* **B72** (2016) 171–179.

[2] T.J. Johnson, K.W. Hipps and R.D. Willet, *J. Am. Chem. Soc.* **92** (1988) 6892–6899.

[3] S. Duclos, F. Conan, S. Triki, Y. Le Mest, M. L. Gonzalez and J. Sala Pala, *Polyhedron*, **18** (1999) 1935–1939; Q. Zhu, A. M. Arif, L. Öhrströhm and J. S. Miller, *J. Mol. Struct.* **890** (2008) 41–47.

Halogen bond motifs in cocrystals of Schiff bases that contain a morpholine or piperazine moiety

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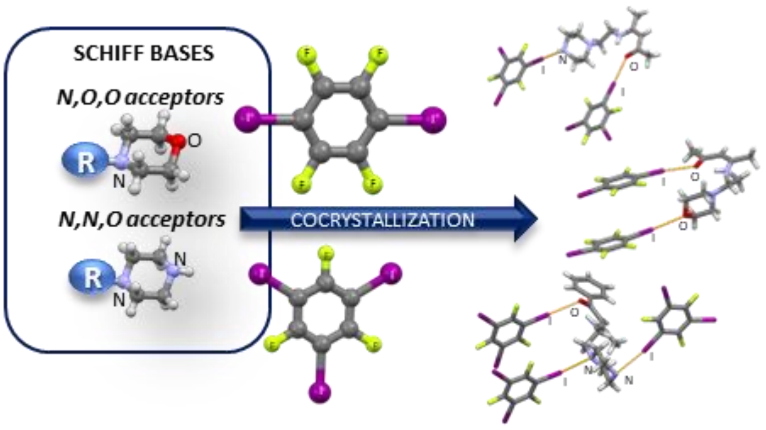
In the past few decades halogen bonding has become a focus of research of many organic, supramolecular and solid-state chemists. It has been shown that it can be a powerful tool in crystal engineering for the design of organic, metal-organic and ionic materials [1,2]. In the course of this research we have investigated the halogen bond acceptor potential of oxygen and nitrogen atoms of morpholine and piperazine fragments when located peripherally on tritopic *N,O,O* or *N,N,O* acceptor molecules. For this purpose, four Schiff bases with peripherally located piperazine and morpholine moieties, derived from acetylacetone and 1-benzoylacetone, have been cocrystallized with 1,4-diiodo- and 1,3,5-triiodotrifluorobenzene. This has resulted in eight halogen-bonded cocrystals featuring different topicities and geometric dispositions of donor atoms. The obtained cocrystals have been structurally characterised by X-ray diffraction (SCXRD, PXRD) and thermal (TG-DSC) methods. From the crystallographic data it was possible to infer that the morpholine oxygen and terminal piperazine nitrogen atoms participate in all cases as acceptors in halogen bonding, thus confirming our hypothesis and previous research indicating that these fragments could be used in crystal engineering of various halogen-bonded solids [3,4]. Contrary to our expectations, the $\mathrm{I\cdots O_{morpholine}}$ halogen bonds feature lower relative shortening values than $\mathrm{I\cdots N_{terminal}}$, $\mathrm{I\cdots O_{carbonyl}}$ and $\mathrm{I\cdots N_{proximal}}$ halogen bonds. The N and O halogen bond acceptor sites were additionally evaluated through calculations of molecular electrostatic potential (MEP) values.



References

[1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati and G. Terraneo, *Chem. Rev.* **116** (2016) 2478–2601.

[2] V. Nemec, K. Lisac, N. Bedeković, L. Fotović, V. Stilinović and D. Cinčić, *CrystEngComn,* **23** (2021) 3063–3083.

[3] D. Cinčić, T. Friščić and W. Jones, *Chem. Eur. J.* **14** (2008) 747–753.

[4] V. Nemec, T. Piteša, T. Friščić and D. Cinčić, *Cryst. Growth Des.* **20** (2020) 3617–3624.

Sodium salt with zinc dipicolinato anionic complex

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Metal complexes have been known for decades for their potent and versatile biological activities. Their application in medicine and pharmacy is fundamental, as they are used as antidiabetica, anticancer agents, antimicrobials and SOD mimetics, as well as for the treatment of Alzheimer's disease. One of the diseases that is increasing at an alarming rate in the 21st century is believed to be diabetes mellitus (DM). In recent decades, it has been reported that several metal ions such as Cr, Mn, Mo, W, V and Zn exhibit insulin-like effects. An ideal substitute for insulin should meet several criteria, such as favorable absorption properties, stability in body fluids, high specificity and low toxicity, etc. In addition, unlike insulin, it should be preferable to be administered orally. Zinc and vanadium-containing compounds have proved to be among the most efficient regarding insulin-enhancing properties and anti-diabetic effects both in vivo and in vitro [1]. Zinc complexes with picolinic acid (pyridine-2-carboxylic acid) and its derivatives have shown promising insulin-mimetic activity [2], and we have also extended our research to the close analog dipicolinic acid (pyridine-2,6-dicarboxylic acid) and its derivatives.

We have successfully prepared a Zn complex that crystallizes as a sodium salt in the monoclinic space group C2/c with the formula $[Na_4(H_2O)_{16}Zn(dipic)_2][Zn(dipic)_2]\cdot 5H_2O$, consisting of two crystallographically independent $[Zn(dipic)_2]^{2-}$ complex anions. Both Zn atoms are octahedrally coordinated by two dipicolinato ligands. The sodium cations are penta- and hexacoordinated by water molecules and by the carbonyl group of the $[Zn(dipic)_2]^{2-}$ complex.

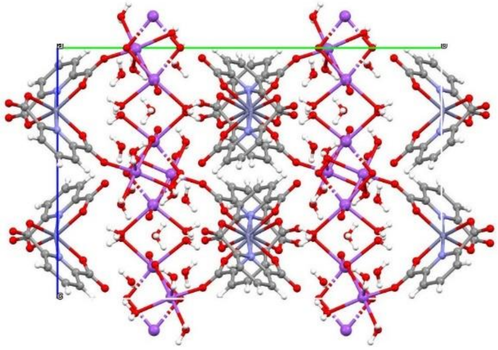

Figure 1: Packing diagram of $[Na_4(H_2O)_{16}Zn(dipic)_2][Zn(dipic)_2]\cdot 5H_2O$.

References

[1] Y. Yoshikawa, M. Kondo, H. Sakurai and Y. Kojima, *J. Inorg. Biochem*. **99** (2005) 1497–1503.
[2] T. Koleša-Dobravc, K. Maejima, Y. Yoshikawa, A. Meden, H. Yasui and F. Perdih, *New J. Chem*. **41** (2017) 735–746.

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Cocrystallization of perhalogenated halogen bond donors with imines derived from 2-nitrobenzaldehyde and 4-haloanilines

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The study of halogen bond and other σ-hole interactions, such as pnicogen bond, in multicomponent systems is one of the most developing areas in crystal engineering and supramolecular chemistry [1,2]. In crystal structures, different σ-hole interactions can be achieved simultaneously. In such cases, there is requited influence to interaction geometries, strength and linearity [3]. One of the functional groups that has the potential to form both halogen and pnicogen bonds is nitro group [4,5].

In this work, three imines were prepared by condensation of 2-nitrobenzaldehyde and 4-haloaniline (halogen = Cl, Br, I). The prepared imines were cocrystalized with selected perhalogenated halogen bond donors in order to investigate the potential of different functional groups located on imines that can act as halogen bond acceptors. Six novel cocrystals were prepared using liquid assisted mechanochemical synthesis, *one-pot* mechanochemical synthesis and by crystallization from solution. The obtained products were characterized by both powder and single-crystal X-ray diffraction, thermal analysis and computational methods. Structure analysis reported N···I halogen bond between halogen bond donor and imine as the dominant supramolecular interaction in all six cocrystals, while in five of them acceptor moleculues are additionally connected *via* N···O pnicogen bonds and pi-nitro group interactions.

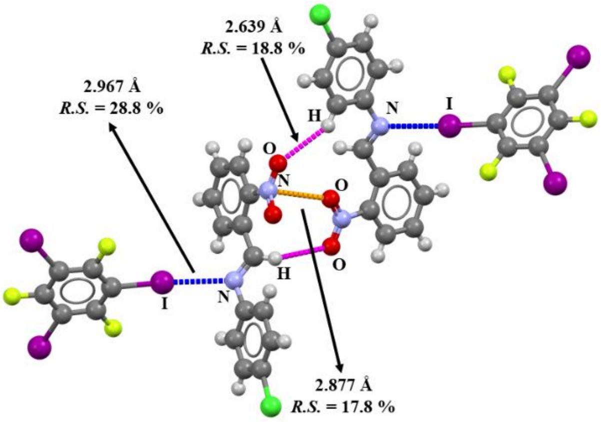

Figure 1: Halogen, pnictogen and hydrogen bonds in (**nba4Clan**)(**135tfib**).

References

[1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* **116** (2016) 2478–2601.
[2] J.S. Murray, P. La Ne, T. Clark, P. Politzer, *J. Mol. Model.* **13** (2007) 1033–1038.
[3] V. Kumar, P. Scilabra, P. Politzer, G. Terraneo, A. Daolio, F. Fernandez-Palacio, J.S. Murray, G. Resnati, *Cryst. Growth Des.* **21** (2021) 642–652.
[4] V. Nemec, D. Cinčić, *CrystEngComm* **18** (2016) 7425–7429.
[5] A. Bauza, A.V. Sharko, G.A. Senchyk, E.B. Rusanov, A. Frontera, K.V. Domasevitch, *CrystEngComm* **19** (2017) 1933–1937.

Multicentre bonding in dimers of tetracyanoethylene (TCNE) radical anions

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π-stacking interactions are responsible for unique properties of organic materials. Stacking of planar organic radicals involves some of the closest interplanar and intermolecular C–C contacts, of *ca*. 2.9 Å [1]. Quantum chemical models indicate a considerable covalent component in the total interaction, and this type of weak multicentric covalent bonding has been dubbed '*pancake bonding*'. The strongest interaction of this type is found in pancake bonded dimers of radicals, and its energy can exceed 15 kcal mol^{-1} [2].

The simplest and also one of the most thoroughly studied case of pancake bonding is two-electron four-centre covalent bond between tetracyanoethylene (TCNE$^-$) radicals [3]. The π-bonded tetracyanoethylene dimer has been investigated for the first time by the experimental X-ray charge density. This system involves two-electron four-centre covalent bonding which is between localised, single bonds and pancake bonding, and this study will thus serve as a standard for comparison with other types of multicentre bonding. A detailed X-ray charge density study of TCNE radicals with a short separation distance of 2.81 Å revealed two symmetry-independent bonding critical points (3, −1) between the TCNE$^-$ radical rings with maximum electron density of 0.17 e Å^{-3}, and one ring critical point (3, +1), showed in Figure 1.

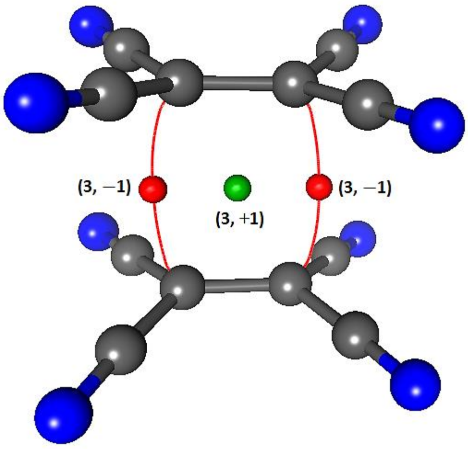

Figure 1: Critical points in a stack of TCNE$^-$ radical anions. Bond paths are shown as red lines, bond (3,−1) critical points are shown as red spheres, and ring (3,+1) critical points are green.

References

[1] K. Molčanov, B. Kojić-Prodić, *IUCrJ* **6** (2019) 156–166.
[2] K. Molčanov, V. Milašinović, and B. Kojić-Prodić, *Cryst. Growth Des*. **19** (2019) 5967–5980.
[3] Z.-H. Cui, H. Lischka, T. Mueller, F. Plasser, M. Kertesz, *ChemPhysChem* **15** (2014) 165–176.

Crystals' adaptability to external mechanical stimuli: Structural causes and consequences

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Adaptability to external stimuli is a highly desired property of crystalline matter as it enables their application in emerging technologies [1]. Unfortunately, most synthetic crystalline materials are largely incapable of mobility and dynamic behaviour, and coordination polymers (CPs), as typical crystalline solids, tend to be brittle and inelastic. Recently, it has been shown that some families of CPs are capable to respond to applied external mechanical force and present flexible responses [2-5].

Herein, a variety of unprecedented adaptabilities of several families of crystalline coordination polymers to external mechanical force will be demonstrated. Moreover, crystals' mobilities observed on the macroscopic scale will be rationalized within the context of structural features, in particular the intermolecular interactions as well as the arrangement of molecular building blocks with respect to bending faces, and mobilities on the microscopic scale.

Acknowledgment
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References

[1] D. P. Karothu, R. Ferreira, G. Dushaq, E. Ahmed, L. Catalano, J. M. Halabi, Z. Alhaddad, I. Tahir, L. Li, S. Mohamed, M. Rasras, and P. Naumov, *Nature Chem*., 2022, **13**, 2823.
[2] M. Đaković, M. Borovina, M. Pisačić, C. B. Aakeröy, Ž. Soldin, B.-M. Kukovec, I. Kodrin, Angew. Chem. Int. Ed. 2018, **57**, 14801–14805.
[3] M. Pisačić, I. Biljan, I. Kodrin, N. Popov, Ž. Soldin, M. Đaković, *Chem. Mater*. 2021, **33**, 3660–3668.
[4] M. Pisačić, I. Kodrin, I. Biljan, M. Đaković, *CrystEngComm*, 2021, **23**, 7072–7080.
[5] M. Pisačić, I. Kodrin, A. Trninić, M. Đaković, Chem. Mater. 2022, **34**, 2439–2448.

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