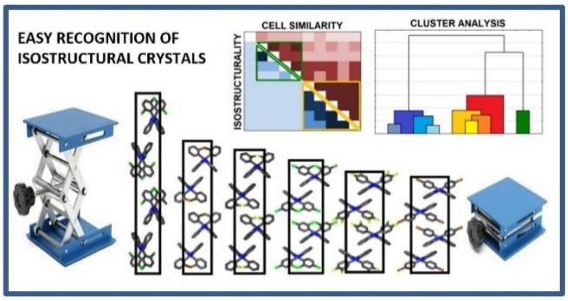
Closing report of OTKA K124544 (01.10.2017 - 31.12.2022)

Principles in crystal engineering: supramolecular interactions, polymorphy, temperature and pressure

The research project was performed to increase our knowledge on the principles of organic and inorganic crystal engineering investigating supramolecular chemistry and symmetry of one and more component systems of organic molecules and of metal coordination complexes. The main emphasis was made on the relationship of secondary interactions and crystal architecture, on the sterical and electrostatical aspects, on their effect on the molecular conformation and the packing arrangement. The outcome of the work contributes to the understanding and efficiency of crystal engineering. The overall aim of the research project was to reveal structure – property relationships, to enrich the knowledge on the aspects, which play role in the development of materials with specific new properties used as pharmaceutics, catalysts, ferroelectrics, non-linear optical materials or energetic materials, etc.

Systematic studies on the principles of crystal engineering:

The compound family of the homologous series of benzimidazole derivatives proved to be a very fortunately selected model system in the research of principles of crystal engineering, its supramolecular aspects and of polymorphism. Several compounds were synthetized, and if they were available, data were imported from the Cambridge Structural Database to complete the series for structural analysis. The structures show isostructurality for a long while but reaching a – very broad – limit, different packing arrangement appears. The likeness of the structures is quantified by different kinds of similarity and isostructurality calculations. **Correlations** of the substituents' types and positions, secondary interactions and the crystallographic parameters, as well as the electrostatic and sterical aspects of the packing arrangements are revealed [1].

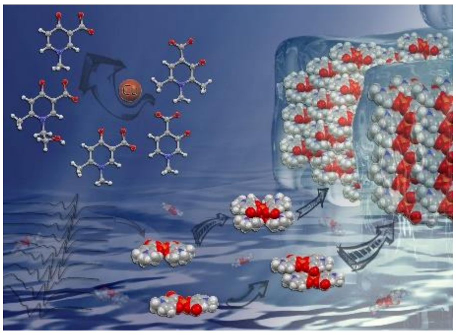


Cover graphics, CrystEngComm

In general, the recognition of isostructurality is not necessarily straightforward. It requires the deep understanding of supramolecular aspects of crystal packing principles and also polymorphism. We have developed a **technique on how to recognize isostructurality** step by step [1, invited, cover page], how the relationship between the molecular and supramolecular properties with the structural features can be revealed and characterized. The technique contains two main modules. 1. The correlations of the crystallographic parameters, the substituent positions and secondary interactions are possible to uncover by statistical methods without prior structural analyses. **Multivariate data analysis** proves that the cluster analysis is a quick and easy-to-use tool to discover isostructurality before performing a thorough structure analysis to filter isostructural crystals out from the abundance of structures with similar cell parameters or even similar internal arrangements. 2. The **software** 'ISOS' [2] for calculation of numerical descriptors of similarities of isostructural crystals based on the atomic parameters determined by single crystal diffraction has been completed. The software has already been distributed by request to nine universities in seven countries on three continents.

Years of experience during our work with isostructural crystals converged to the conclusion that the **definition of isostructurality** needs a revision and improvement [3]. On the one hand it is necessary to define the criteria for the limits of isostructurality: what the extent of differences we do still consider similar. On the other hand the definition of isostructurality needs to be completed with the internal criteria which is now missing from the definition.

The design of efficient chelating drugs for the treatment of metal overloading conditions demands the fine tuning of the affinity of chelators to the different metal ions. In the ligand compound family of β-hydroxypyridine-carboxylate derivatives (3-hydroxy-4-pyridine- (3HPC) and 4-hydroxy-3-pyridine-carboxylic acids (4HPC) with different pyridine ring substituents) [4] the proton position correlates with the aromaticity of the pyridine ring described by the Bird-index, while the packing arrangements and the main hydrogen bonding schemes are characterised by Hirshfeld surface analysis. The electron donating effect of the different substituents modify the **electron distribution in the aromatic ring**, resulting in a gradual shift between the keto and enol forms. The 3HPC and 4HPC molecular pairs with highly similar molecular shapes provided the opportunity to examine how the electron distribution exclusively affects the secondary interactions and thus the arrangement of the molecules in the crystals. The fine-tuned sterical effect of the substituents resulted in the appearance of mirror symmetry or glide planes. The complexation properties of the series of HPCs have been studied with Cu(II) [5, back cover page], one of the most competing metal ion during a chelation therapy regiment. Solution and solid phase studies have been performed at different temperatures to reveal stoichiometry, stability and structure of the complexes. The different *cis* or *trans* configuration as well the different axial coordination could be explained by the different electron distribution of the ligands. The mechanism of the self-assembly and the different coordination properties of the systematically modified HPC ligands were revealed with Zn(II) cation also [6].



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As a **knowledge driven fine-tuning of crystal properties** a stepwise increase of the Z' value is achieved along with the step by step appearance of pseudo symmetries by the systematic chemical change of the 7-phenyl-6H-chromeno[4,3-b]quinoline molecule as an effect of electron donating and withdrawing properties of the phenyl substituents [7].

We succeeded to construct **ionic hydrogen bond assisted organic frameworks** (iHOF) [8, back cover page], the first ever described in the literature, from two newly synthesized Maruoka-type phase-transfer organocatalysts containing a diazadibenzo[ef,kl]heptalene skeleton. A well-orchestrated interplay of intermolecular forces, molecular inflexibility and the presence of symmetry characterize our non-covalently bonded organic frameworks. The crystal structures show polymorphism. The frameworks are constructed by charge assisted hydrogen bonds and the recently described anion…π interactions. A solvatomorph of the framework itself is also successfully prepared. The molecular rigidity as a condition of framework construction is demonstrated by the non-porous crystal structures of related more flexible molecules, where polymorphism also appears. This molecular system proved to be ideal to study supramolecular interactions, symmetries and polymorphism in the solid state. HOF chemistry belongs to the cutting-edge science. Extensive work is in progress on the labour-intensive synthesis of new series of compounds and the preparation of HOF and related MOF structures to reveal the condition of organic and metalorganic framework construction and to challenge the limits of structural variations.

Cover graphics, CrystEngComm

Previously we have collected experiences with a few series of upper and lower rim substituted calixarenes, how to fine tune the crystal architecture [P Bombicz *et al*. Fine tuning of crystal architecture by intermolecular interactions: synthon engineering. CrystEngComm, 16, 3646, 2014, invited paper, highlight paper, cover page; and references therein]. Pillararene **macrocycles** also form supramolecular complexes with various guests, as well as their versatile synthetic manipulation offers countless applications based on their tunable molecular recognition. Phenylene-substituted functionality was introduced to get pillar[5]arene derivatives. Analogously to some calix families, one of the neighbouring rings turns upside down, what makes the formation of a hydrogen bond between the substituents possible contributing to the stability of the pillararene structure [9].

Although clopamide (4-chloro-N-2,6-dimethylpiperidin-1-yl)-3-sulfamoylbenzamide) is used worldwide in the treatment of hypertension and oedema its structure has not been published earlier. We succeeded to determine the crystal structures of both clopamide anhydrate and hemihydrate. Its importance is that the pharmaceutical compounds often form hydrates during the manufacturing process, which affect many of their physicochemical properties. We presented how the **inclusion of water** contributes to the crystal perfection, how it increases the crystal symmetry. The recently defined chalcogen bond is recognised in the clopamide anhydrate crystals being in competition with the intramolecular halogen bond. **Solvatomorph and polymorph screening** of the copper complexes of Clopamide revealed the similarities and differences in the system of intermolecular interactions and molecular conformation. The isostructural series and polymorphic forms of the structural landscape provide strategies to control the molecular self-assembly. The results [10] presented at the 32nd European Crystallographic Meeting received the IUCr Structural Chemistry poster prize.

The deeper insight into the **chiral recognition** contributes to the mastery of crystal engineering. Diastereomeric salt crystallization is used to resolve the antiepileptic pregabalin, which is a racemate-forming compound with recently discovered hydrate-forming activity. The quaternary system of pregabalin enantiomers, L-tartaric acid and water was investigated by the characterization of the relevant solid forms and the measurement of solubilities and solid-liquid equilibria creating a thermodynamic model to simulate the effect of variable parameters on the resolution process [11]. It is revealed how the non-covalent interactions are responsible for the formation of diasteromeric complexes of P-stereogenic secondary phosphine oxides incorporating various aryl and alkyl groups [12]. The number of crystal structures of diastereomeric salt pairs is limited in the literature, and it is especially the case for the double salts. It is exceptional that we presented [13] the structures of two complete sets of chiral systems: two constitutional isomer double salts along with their related diastereomeric salt pairs , (S–S, R–S, SS–SR) and (R–R, S–R, SS–SR). Their thermal properties have been determined and comparatively analysed providing a detailed landscape of the effect of stereochemistry on the solid-state structures.

Exploring the structure of a compound makes possible to explain its **crystallisation properties**. It happened with a novel jatrophane diterpene which was isolated from Euphorbia dulcis having potassium ion channel inhibitory activity. We had to find the tricky way of single crystal growth: after the loss of solvent the amorphous material melts followed by crystal growth of minuscule needles. These crystals were used for seeding the saturated solution provoking a supramolecular self-assembly. Data collection was performed at the synchrotron source SOLEIL at -173 ^{o}C, and it made possible to determine the absolute configuration of the 8 chiral centres. The helical structure held together by weak C-H…O type secondary interactions is in agreement with the poor crystallisation property and with the crystal habit of long needle which easily split lengthwise [14].

The **phase transition** of bis[diamminesilver(I)] sulfate at 80°C is attributed to the change of the hydrogen bond system along with the alteration of the geometry of the complex cation. SXRD data collection is unusual above room temperature and it resulted in dynamically disordered atoms mentioning the two major challenges of the work [15]. The preparation and thermal decomposition of transition metal complexes with reducing ligands and oxygen containing anions are intensively studied areas of coordination chemistry, especially due to the **quasi-intramolecular redox reactions**, which result in various simple and mixed metal oxides. The presence of halogens (ligand or anion) can drastically change the nature of the products. The formed 3D-hydrogen bond network influences the solid-phase redox reactions between the permanganate anions and ammonia ligands [16]. A systematic study for structural characterisation of the complexes of the series of $[Ag(py)_n]XO_4$ (X=Cl, Mn, Re, n=2-4) was performed in order to explore the formation of the hydrogen and π bonds and to find their role in macroscopic properties. A few of them are isostructural. The formation of these compounds is strongly influenced by the synthetic procedure and the crystallization parameters: starting material, solvent, along with crystallization temperature and gradient [17,18,19,20]. $[Fe(urea\text{-}O)_6](MnO_4)_3$ was synthetised in order to find new reaction routes and precursors to prepare catalysts for CO_2 hydrogenation. The extended hydrogen bond interactions between the anions and the ligands serve as reaction centres and have unique role in the solid-phase redox reaction [21]. In the polymorphic and solvatomorphic structures of $(Me_2NH_2)_{10}[H_2\text{-dodecatungstate}]$ the large and rigid polytungstate cages are 'swimming' in their water of crystallization connected to alkylammonium cations capable of forming flexible network of hydrogen bonds. [22,23].

Collaborative research based on our crystallographic experience gained on the field of crystal engineering and supramolecular chemistry for applications

Exploring the crystal structures, understanding of the aspects responsible for the arrangement of the molecules in the solid phase, fine-tuning of the sterical and electostatical effects of the molecular substituents and / or the components in the crystal architecture influences the macroscopical properties and the application of the materials.

Very small changes in the structure of the molecules can have a distinct impact on their biological recognition mechanisms. The thiosemicarbazone compound class is known for their strong metal-chelating ability. Several of these compounds and their copper, iron and zinc complexes were characterized in solid state and solution to reveal the influence of the substituents on their anticancer properties [24]. The effect of the variation of the chalcogen atom on the deprotonation processes and complexation with Cu(II) and Ga(III) ions of atridentate semicarbazone-estrone hybrid molecule was described [25]. The investigations were extended to tosalicylaldehyde aminoguanidine derivatives as salicylaldehyde thiosemicarbazone analogues [26], and to the terminal N-mono- and dimethylated derivatives of an estrone-salicylaldehyde thiosemicarbazone hybrid [27] and their complexes. Estradiol-based salicylaldehyde (thio)semicarbazones and their copper complexes completed the study [28]. The differences in the secondary interactions are attributed to the rotational freedom of the thiophane ring in dihydrotestosterone derivatives (Z'>1) targeting the androgen receptor in prostate cancer [29].

The stabilization of the coordinatively labile and redox-active copper ions in biological environments is a challenge for the improved diagnostic and therapeutic strategies. The ligand ring makes the difference in the investigated series: the systematically increased ring size of the macromolecular ligand may result in a faster complexation process and reduced stability [30], which may also be influenced by the number and type of coordinating nitrogen atoms [31]. Radiopharmaceutical application is expected from the copper complexes of sulfur pendant cyclen derivatives, where the chalcogen chelation was observed contributing to the high complex stability [32]. Supramolecular interactions in two macrocyclic aminopolycarboxylate-type complexes of antimony(III) were investigated with the aim to disclose the potential of rigid ligands as chelators for future applications in targeted radiotherapy for cancer treatment [33]. Half-sandwich Ru and Rh complexes have been identified as promising alternatives to anticancer Pt compounds with improved selectivity and new mode of actions. The differences in complex geometries have been studied when the methyl group positions and the ligand rigidity was varied. Structural differences were found to influence the chloride affinity, which has a crucial role in the biological activity [34].

The pyridine-based ligands containing alanine or tyrosine moieties are also efficient copper chelators. Introduction of the phenyl ring (tyrosine moiety) enhances the copper(II) binding ability [35]., as well as the sulfonated salan ligands. [36]. The redox-inactive metal single-site molecular complexes may be the way to a new generation of electrocatalysts for oxygen evolution [37]. New Ru cyclic alkylamino carbene catalysts have been synthesized with superior olefin metathesis catalytic activity showing exceptional stability accounted for the arrangement of the ligands and the different absolute configurations of the two carbenes in the complexes. The stabilizing forces proved to be the complex system of intramolecular interactions, as well as the strong $\pi ... \pi$ and $C(H)_2$-H…π interligand interactions. [38] The light controllable solubility was exploited to affect the catalytic activity of a photoresponsive palladium complex of an azopyridyl-triazole ligand [39].

Low temperature was necessary to stabilizes the sensitive sample of the unexpectedly formed $LiP(SiMe_2CH_2SiMe_3)–P\mathit{t}Bu_2$ as a by-product. Possible reaction mechanism was elucidated [40, very important paper]. The hypercoordinated silicon compounds can be considered as complexes, where the Si atom is typically surrounded by electronegative and/or multidentate ligands. Gradual replacement of the ethoxy units by the ligand yielded different hexacoordinated products. The $\pi ... \pi$ intermolecular interactions in the neutral complex are overwritten by the C-H… π interactions in the salt [41]. The aromatic character of a series of ansymmetrical thienopentalenes was investigated experiencing aromaticity loss using destabilizing benzothiophene fusion and preserved aromaticity in the benzene unit using stabilizing fusion of thiophene [42]. Indenone derivatives were synthesized in metal-free synthesis, the methodology is suitable to access π-extended indanone and s-indacene-1,5-dione as well [43]. Avoiding the formation of the low solubility polymorph was the aim of the structural investigation of the benzyl-morpholinohydroquinone derivatives for flow battery applications [44].

Project specifications

During the project various aspects of crystal engineering were investigated: self-assembly, supramolecular interactions, sterical hindrances, isostructurality and polymorphy, phase transformation, chirality, effect of hydrate and solvate formation, symmetry and Z', influence of temperature. This knowledge contributed to the deeper understanding of structure – property relationship on some selected compound families, and to the preparation of a list of new materials for various application possibilities. New method and a software was developed to describe isostructurality.

Papers, IFs, lectures, distinctions. The results of this project are presented as articles in international journals: 19 papers are published (ΣIF=67.178) and 3 more manuscripts (ΣIF=12.348) are ready for publication all based on our systematic studies of selected compounds families, furthermore 21 articles are published in collaborations where we contributed with the structural experiences to different applications (ΣIF=106.447), it is all together ΣIF=185.973. Each of our work on the benzimidazoles (invited paper), HPCs and iHOFs received the back cover page of the issues, a paper prepared in collaboration became a very important paper. The participants of the project delivered 15 lectures at international conferences on five continents, 5 of them were invited lectures; and 22 lectures at Hungarian events, 1 was an invited talk. The research was presented on 14 posters at international conferences, Gyula Tamás Gál was awarded the prestigious IUCr Structural Chemistry Poster Prize for the Clopamide research. 131 new crystal structures were deposited in the Cambridge Structural Database. One software was developed. A PhD was made based on part of the project.

Students, employment. All together ten students were involved into the research as a trainee for half or one year period. One BSc thesis work received honourable mention. Gyula Tamás Gál was employed on the project full time as PhD student. He has successfully presented and defended his dissertation. Then Sourav De, PhD has been employed full time. In connection with the present OTKA project Tamás Holczbauer was awarded OTKA PD-128504 (2018-2022) which was evaluated “good” (8).

Finances. PC-s and a laptop were purchased both for calculations and office work and as replacement for equipment control. Software licence fee was paid. All participants have received computer accessories for on-line communication. Maintenance of the UPS and DSC equipment, as well as the analytical balance were performed. UV lamp, laboratory gas burner with cylinders, fine chemicals, solvents and laboratory utensils were purchased. N_2 supply (both gas and liquid) needed to perform the low temperature diffraction (-180 – +82°C) and DSC (-80 – +400°C) measurements, as well as hot/cooling plate (-180 – +400°C) examinations, were covered from the project. Office stationery, computer accessories and post charges were also covered.

Investment 1. Our cool/hot stage apparatus has to be upgraded because of breakdown and it is now equipped with both camera and polarizing attachment. The NISelementsD software to the computer control of the hot stage was purchased to increase the performance of imaging and documentation.

Investment 2. The acquisition of the diamond anvil cell (DAC) for high pressure (HP) diffraction measurements required careful preparation regarding crystal pressurisation, mounting and software handling. In the selection process, we relied on the experiences of two highly appreciated international research groups. Our group visited Prof. Ronald Miletich at the University of Vienna. The planned visit of Prof. Andrzej Katrusiak to Budapest could not take place because of the pandemic. The benefit brought up from the delay caused by the pandemic is that meanwhile Almax EasyLab has developed and marketed an extra thin and small Boehler-Almax design diamond anvil cell with extra large aperture, which we finally purchased. Then we could start to collect the accessories needed to the work: cell loading equipment, microdriller, micrometer, ruby for pressure measurement etc. All main equipment needed to perform a full high pressure experiment have been purchased and installed for operation by now. Fitting some minor accessories is still in progress.

During our project years we were in intense on-line communication with Prof Katrusiak who was giving invaluable advices for the establishment of our high pressure laboratory. Tamás Holczbauer attended the ‘High Pressure Science and Technology’ workshop in 2017 organised by Prof Katrusiak. As the continuation of our cooperation the travel ‘Sponsorship of the Use of International and National Research Infrastructure’ of the NRDIO (NKFIH) was awarded (2021-4.1.2-NEMZ_KI-2022-00022) for 2023-2024. The delay in the investment of the high pressure cell is compensated with the accommodation of new compound families into the research project to investigate. There are high expectations with homologous series of the organic, complex and HOF/MOFs compound families at the high pressure investigations.

The reorganisation of the Research Centre for Natural Sciences influenced our financial capabilities blocking the acquisitions in 2019, then the lockdowns in 2020 and 2021, and the related restrictions caused by the pandemic affected the progress of the research project, most seriously the investment. The pandemic had several different effects on the research: restricted the involvement of students, the lab availability during lockdowns, slowed down the investments severely, and affected the participation on meetings and conferences. Nonetheless, the expected result of this project, the deeper understanding of the principles of crystal engineering, was achieved. We are grateful for the extension of the four years timeline with extra 15 months. Overall, we are very grateful for the financial support of the NKFIH to our research project.

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PhD thesis:

Gál Gyula Tamás: **Gyógyászati jelentőségű Cu(II) és Ru(η^6-toluol) komplexek és ligandumaik szilárd fázisban – koordinációs módok és szupramolekuláris szerkezetek**, PhD dissertation, Hevesy György Doctoral School of Chemistry, Faculty of Science, Eötvös Loránd University, 2022. Supervisors: Petra Bombicz and Nóra V. May