

acid affects its coordination ability and in compound **2** the ligand only connects to the metal by the carboxylate group. In the structure it is observed a dimetallic subunit where the Zn atoms are bonded by three ligands. These units are linked by another ligand through its carboxylate fragment, rendering a disposition where the metals are bonded to four oxygen atoms in a tetrahedral geometry.

[1] I.R. Amiraslanov, G.N. Nadzhafov, B.T. Usuballiev, A.A. Musaev, E.M. Movsumov, Kh.S. Mamedov. *Zh. Strukt. Khim*, **1980** 21(3), 140. [2] A. Millward, O.M. Yaghi, *J. Am. Chem. Soc.*, **2005**, 127, 17999. [3] Jesse L.C. Rowsell, O. M. Yaghi, *Microporous and Mesoporous Materials*, **2004**, 73, 3–14.

Keywords: carboxylate, coordination, zinc

MS17.P16

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Design and crystal structures of novel lamotrigine cocrystals

Edislav Lekšić,^a Gordana Pavlović,^b Ernest Meštrović,^a *PLIVA Croatia Ltd., Research and development, Prilaz baruna Filipovića 29, 10000 Zagreb, (Croatia).* ^b*Laboratory of General Chemistry, Department of Applied Chemistry, Faculty of Textile Technology, University of Zagreb, Prilaz baruna Filipovića 28a, 10000 Zagreb, (Croatia).* E-mail: edislav.leksic@pliva.com

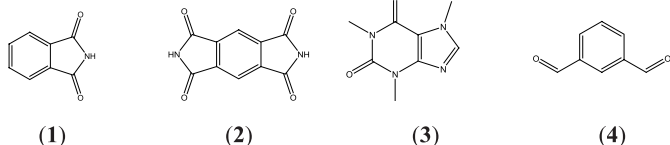
Design of cocrystals is conducted with detailed examination of selected API (Active Pharmaceutical Ingredient) molecular fragments that can be involved in supramolecular assemblies as well as with analysing similar structures available in crystallographic data bases. Exploring the potential of cocrystal formation contributes for better understanding the basic principles of supramolecular chemistry.

In this work, lamotrigine, an antiepileptic drug was chosen as a model drug to design and prepare cocrystals on the basis of the synthon types and interactions found in its crystalline structures of salts and solvates. Due to its basicity, nitrogen N2 atom of triazine ring is always protonated in lamotrigine salts.

It is well known that the N-H...N hydrogen bonds between amino groups and the N2 triazine nitrogen atom form an $R_2^2(8)$ dimer in lamotrigine structure itself [1]. These dimers are usually further connected via N-H...O hydrogen bonds between another N-H amino group and oxygen atoms of oxygen containing solvate molecules into more complex hydrogen-bonded rings.

These synthons along with the presence of chlorine atoms in lamotrigine molecule are considered as models in design of targeted lamotrigine cocrystals.

In that context, four cocrystal former molecules are chosen for lamotrigine cocrystal preparation: phthalimide (**1**) and analogous pyromellitic diimide (**2**), caffeine (**3**) and isophthalaldehyde (**4**) on the basis of their stereochemically disposable proton donors (N-H) and proton acceptors (keto groups). In cocrystal structures with (**1**), (**2**) and (**3**) molecules, the lamotrigine N-H groups and the triazine N2 atom participate into hydrogen bond formation mutually via N-H...N hydrogen bonds and with cocrystal molecule via N-H...O=C bonds. The presence of the Cl...O short contacts in (**2**), (**3**) and (**4**) structures has been confirmed.



[1] B. Sridhar and K. Ravikumar, *Acta Cryst.* **2009**, C65, o460-o464.

Keywords: cocrystal, lamotrigine, synthon

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Synthesis and structural analysis of cadmium dipicolinate coordination polymers and tetramers

Clive L. Oliver, Boris-Marko Kukovec, Centre for Supramolecular Chemistry Research, Department of Chemistry, University of Cape Town (South Africa). E-mail: clive.oliver@uct.ac.za

Metal coordination polymers constructed with multi-carboxylate ligands have been extensively studied in supramolecular chemistry and materials chemistry due to their structural diversity and application in catalysis, ion exchange, adsorption, nonlinear optics, luminescence and magnetism. [1] Dipicolinic acid, dipicH_2 , is a versatile chelating ligand which can interact with metal ions both in anionic and protonated form. It is widely used for the preparation of the various metal complexes. It displays a large number of coordination modes due to the position of its carboxylate groups and its nitrogen atom, with the potential to act as a bidentate, tridentate and/or bridging ligand [2].

Here we report the hydrothermal preparation of two cadmium dipicolinate polymers and four tetramers. The two polymers have the formula $[\text{Cd}_2(\text{H}_2\text{O})_3(\text{dipic})_2]_n$ and are polymorphs of each other. The four tetramers can be classed into two groups of general formula $[\text{Cd}_2\text{X}(\text{H}_2\text{O})_4(\text{dipic})(\text{dipicH})]_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Cd}_2\text{X}_2(\text{H}_2\text{O})_3(\text{dipicH})_2]_2 \cdot 2\text{H}_2\text{O}$, where X = Cl or Br. The structures of the compounds have been elucidated by single X-ray diffraction and their thermal behaviour characterized by thermal gravimetry and differential scanning calorimetry.

Using either the cadmium bromide or chloride salt in a 1:1 ratio with dipicolinic acid can lead to any of the above type of structures, indicating the importance of subtle differences in preparation conditions, e.g. concentration of reactants and duration of heating.

[1] [T.M. Reineke et al. *Angew. Chem. Int. Ed. Engl.* **1999**, 38, 2590. [2] M. Chatterjee et al. *J. Chem. Soc., Dalton Trans.* **1998**, 3641.

Keywords: coordination, polymer, polymorph

MS17.P18

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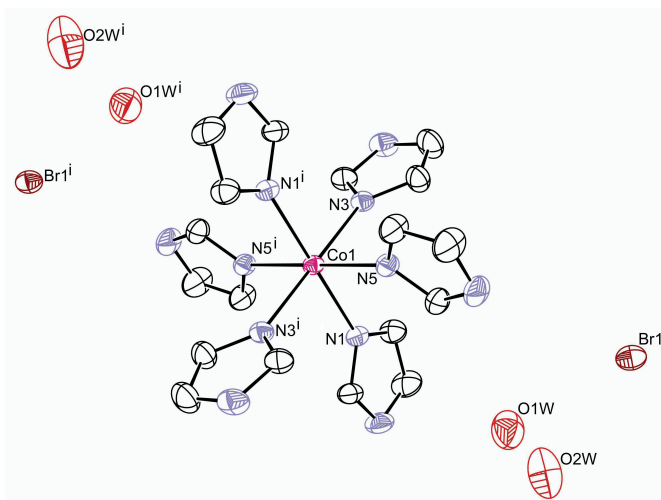
Structural analysis of hexa-imidazole cobalt (II) 2-bromide tetrahydrate

Ýlkay Yýldýrým, Bünyamin Karabulut, Orhan Büyükgüngör, *Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139, Kurupelit/Samsun, (Turkey).* E-mail: ilkayy@omu.edu.tr

Hexa-imidazole cobalt (II) 2-bromide tetrahydrate, formulated as $\text{C}_{18}\text{H}_{32}\text{Br}_2\text{CoN}_{12}\text{O}_4$ (I), was synthesized. The crystal and molecular structure of (I) have been determined by X-ray single crystal diffraction. The compound (I) crystallizes in the triclinic, space group P-1 with unit cell parameters $a=8.8660(8)\text{Å}$, $b=9.2117(9)\text{Å}$, $c=10.7641(10)\text{Å}$, $\alpha=76.356(8)^\circ$, $\beta=83.275(8)^\circ$, $\gamma=61.527(7)^\circ$, $R_1=0.431$, and $wR_2=0.0993$.

The title compound is composed of $[\text{Ni}(\text{imidazole})]^{+2}$ complex cations, Br atoms and water molecules. The cobalt atom is located at special positions. The Co atom has octahedral coordination geometry defined by imidazole rings coordinated through N atoms.

The crystal packing is achieved by strong and moderate hydrogen bonds which play an important role in the formation of the 3D network.



Keywords: X-ray_diffraction, cobalt, 4-midazole

MS17.P19

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Structural Analysis of Hexa-4-methylimidazole nickel(II) 5-aminoisophthalate tetrahydrate.

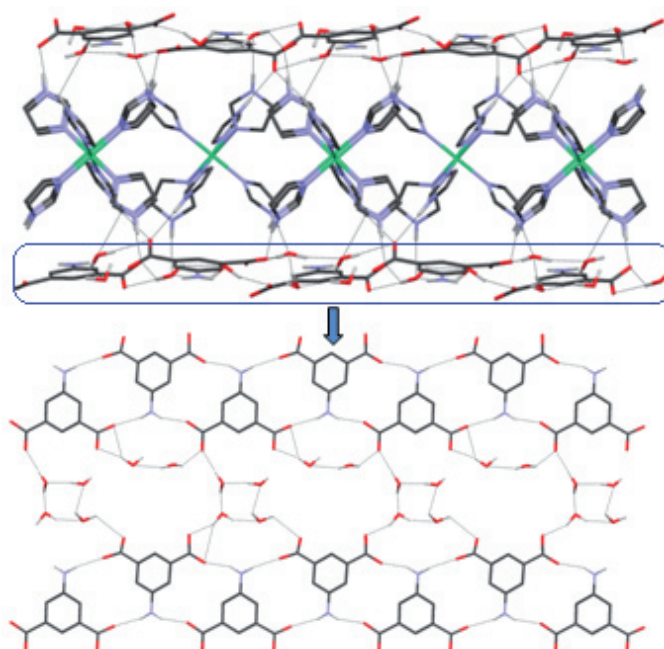
Ersin Temel,^a Alper Tolga Çolak,^b Okan Zafer Yeşilel,^c Handan Günay,^c Orhan Büyükgüngör,^a ^aDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139, Kurupelit/Samsun, (Turkey). ^bDepartment of Chemistry, Faculty of Arts and Sciences, Dumlupınar University, Kütahya, (Turkey). ^cDepartment of Chemistry, Faculty of Arts and Sciences, Eskişehir Osmangazi University, Eskişehir, (Turkey). E-mail: etemel@omu.edu.tr

The title compound is composed of $[\text{Ni}(4\text{-methyl imidazole})]^{+2}$ complex cations, 5-amino isophthalato anions and water molecules. Two nickel atoms are located at special positions. Each Ni atom has a slightly distorted octahedral coordination geometry defined by 4-methyl imidazole rings coordinated through N atoms. In the 5-amino isophthalato anions, while aniline parts are planar, carboxylate groups deviates from planarity.

The crystal packing is achieved by strong and moderate hydrogen bonds which play an important role in the formation of the 3D network. These interactions are drawn in Figure.

The packing is formed by periodic repetition of 2D A- and B-layers which are parallel to *ab*-plane. While layer A is composed of only nickel complexes, layer B is composed of the combination of 5-amino isophthalato and water molecules. In the layer A, nickel complexes with each other linked by C-H... π interaction. On the other hand, B-layers act as a bridge between nickel complexes along *c*-axis. Layers A and B are linked by N-H...O type hydrogen bonds.

It can be seen from figure that N-H...O and O-H...O hydrogen bonds construct 2D network in layer B. 5-amino isophthalato anions linked to each other by N-H...O type hydrogen bonds, generating adjacent $R_2^2(14)$ ring motifs along *a*-axis [1]. Tetrameric water clusters connect 5-amino isophthalato anions along *b*-axis. While the cyclic water tetramer is formed by O2W, O3W, O5W and O8W atoms, the dimeric clusters are formed by O1W, O4W and O6W, O7W atoms. Oxygen atoms of carboxylate groups are hydrogen bonded to dimeric and tetrameric clusters.



[1] J. Bernstein, R.E. Davis, L. Shimoni, N.L. Chang, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1555-1573.

Keywords: X-ray_diffraction, nickel, cluster

MS17.P20

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When organic and metal-organic molecules cease to crystallize?

Jan Fábry,^a Radmila Krupková,^a Miloš Kopecký^a ^aInst. Of Physics of the Academy of Sciences of the Czech Republic. Na Slovance 2, 182 21 Praha 8, Czech Republic. . E-mail: fabry@fzu.cz

The dependences of occurrences of the most frequent space-group types $P\bar{1}$, $P2_1$, $P2_1/c$, $C2/c$, $P2_12_12_1$ and $Pbca$ on reduced unit-cell volumes up to 8000 Å³ were investigated for organic and metal-organic compounds with different number of residues, *i.e.* with different number of molecular constituents (1-3). The dependences for these space-group types are similar, single-peaked; their maxima are proportional to the number of asymmetric units, affected by Z' (number of formula units *per* asymmetric unit) in the pertinent space-group types. The dependences of $Z' < 1$, $Z' = 1$, $Z' > 1$ within each space group type on reduced unit-cell volumes are also similar in shape. From these dependences it can be inferred that ability for crystallization of organic and metal-organic molecules ceases for the structures with the reduced unit-cell volumes above 8000 Å³. This volume corresponds roughly to 450 non-hydrogen atoms in a unit cell, *i.e.* to non-hydrogen 56 atoms *per* molecule [1].

The loosing ability for crystallization for large molecules is also manifested by the deviation from linearity of the Kempster-Lipson [2] rule for the structures composed from C, H, N, O at most. The present analysis has the following implications:

While a broadly shared view that the more symmetric is a molecule the more symmetric is a crystal arrangement seems to be correct [3,4] the opposite conclusion has been shown not to be quite true because the larger organic or metal-organic molecules tend to crystallize in a more symmetric space-group type such as $Pbca$. The present analysis shows influence of the molecular size on the symmetry of the crystalline state. It is known that biological macromolecules often contain huge dummy parts the function of which is unclear while active centres are surprisingly small. Can be the size of the biological