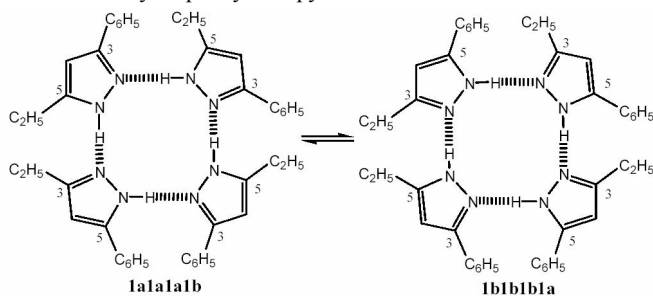


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In a systematic exploration of 3,5-disubstituted pyrazoles for crystal engineering purposes, we prepared the still unknown 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole **1**.¹ Its X-ray structure has been determined: it is a hydrogen-bonded tetramer of a new type formed by three tautomers 5-ethyl-3-phenyl-1*H*-pyrazoles of class **a**, and one tautomer 3-ethyl-5-phenyl-1*H*-pyrazole of class **b**.



The 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole tetramer.

The NH protons are disordered even at low temperature, so there are two questions that could be asked: Is the disorder static or dynamic (SSPT)? What are the proportions of both tetramers **1a1a1a1b/1b1b1b1a** (either static mixture or dynamic equilibrium)? We have tried to answer these questions by a combination of DFT calculations, analysis of the X-ray geometries and ¹³C and ¹⁵N CPMAS NMR. For this last purpose, the [¹⁵N₂]-labelled derivative of **1** was prepared.

[1] Torres V., Cornago P., Claramunt R. M., Loshkin V., Samat A., Pinilla E., Torres M. R., in progress: 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole **1**, yellow-reddish solid of m.p. 80.1 °C.

Keywords: hydrogen bonding, pyrazoles, supramolecular architectures

P.09.05.12

Acta Cryst. (2005). A61, C363

Topologic Features of Three Structures Based on I...Base Halogen Bonding

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The halogen bonding, that is the n→σ* electron donation from Lewis bases to halogen atoms (Lewis acids) is an interaction that has attracted an increasing attention, especially in haloperfluorocarbons where the heavy halogen atom (I, Br) is highly polarized¹. We have recently studied the three component structure of the cryptate K.2.2.2 with KI and 1,8-diiodo-perfluorooctane showing a very unusual borromean assembly of the superanion². We present here other three halogen-bonded supra-molecular arrays showing unusual topologic features: the assembly of tetra(4-pyridyl)pentaerythritol . 1,4-diiodo-octafluorobutane **1**, tetra(4-pyridyl)pentaerythritol . 1,8-diiodo-hexafluorooctane **2**, and tetra(4-pyridyl)pentaerythritol . tetra(4-iodo-tetrafluorophenyl)pentaerythritol **3**. The three structures present macrocyclic interpenetrate assembly. **1**, **2**, **3** show 2D 5-fold 4⁴ layers, 8-fold diamondoid class Ia, 10-fold diamondoid class IIIa topologies, respectively.

[1] Metrangolo P., Resnati G., *Enciclopedia of Supramolecular Chemistry*, ed. Steed J. W. and Atwood J. J., Marcel Decker Inc., New York, 2004, pp.1484.

[2] Liantonio R., Metrangolo P., Pilati T., Resnati G. *Crystal Growth & Design*, 2003, **3**, 355. [3] Blatov V.A., Carlucci L., Ciani G., Proserpio D.M., *CrystEngComm*, 2004, **6**, 377.

Keywords: topology, crystal engineering, halogen bonding

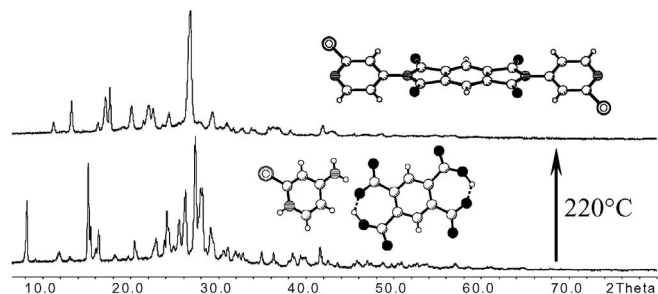
P.09.05.13

Acta Cryst. (2005). A61, C363

Inter- and Intra-solid Reactions Studied by X-ray Powder Diffraction

Antonia Neels, Déborah Gonzalez Mantero, Helen Stoeckli-Evans,

In solid state chemistry when only microcrystalline materials are obtained, X-ray powder diffraction becomes the most important tool for analysing unknown phases. *Ab-initio* structure determinations have been carried out on metal organic compounds obtained in solid state transformation processes [1,2], and on new organic materials. The latter were synthesised by solvent free reactions applying green chemistry principles. The competition of inter- and intramolecular interactions in organic crystals and co-crystals will be discussed.



[1] Neels A., Wang Y., Stoeckli-Evans H., *Z. Kristallogr.*, 2004, **219**, 892. [2] Neels A., Alfonso M., González D., Stoeckli-Evans H., *Chimia*, 2003, **57**, 619.

Keywords: green chemistry, crystal engineering, X-ray powder diffraction

P.09.05.14

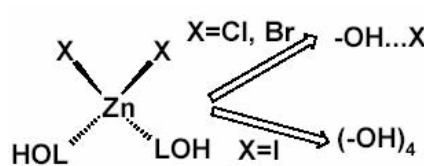
Acta Cryst. (2005). A61, C363

Anion-Dependent Switch between Sheets and Diamondoid Assembly for Zn(LOH)₂X₂

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We are currently studying the modes of solid state association of M(LOH)₂X₂ molecular building blocks built by complexation of transition metals with LOH (α-(4-pyridyl)benzhydrol), with the scope of designing organic-inorganic hybrid materials capable of uptaking/releasing small guests by solid-gas processes [1].

Here we show the abrupt change in crystal organization of Zn(LOH)₂X₂ on passing from X= Cl, Br to X=I. The smaller and more electronegative halides participate to -OH...X hydrogen bonds giving an overall arrangement of the structures in bidimensional sheets. Zinc behaves as a distorted square nodes in the network topology. The iodine atom switches the basic supramolecular synthon from -OH...X



to tetrahedral -(OH)₄ nests assembled by -OH...H hydrogen bonds, which give a non-covalent diamondoid network where the metal acts as a spacer between

tetraedra nodes.

[1] Bacchi A., Bosetti E., Carcelli M., Pelagatti P., Rogolino D., Pelizzi G., *Inorg. Chem.*, 2005, **44** (2), 431 - 442.

Keywords: crystal engineering, nonbonded interactions, diamondoid

P.09.05.15

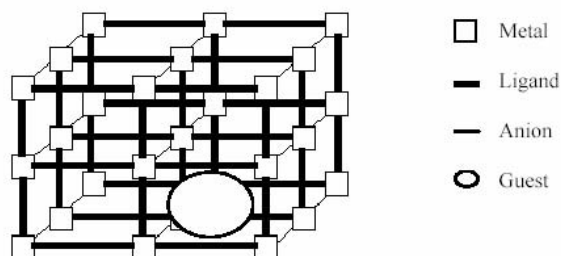
Acta Cryst. (2005). A61, C363-C364

2-D and 3-D Metal-Organic Frameworks: A Crystal Engineering Approach

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The synthesis of new metal-organic frameworks can be carried out

by rational self-assembly using the principles of crystal engineering. Metal ions are usually coordinated to two or more bridging ligands giving a final semi-rigid structure suitable for adsorption, catalysis, etc. Nano-porous materials based on new linear ligands coordinated to metallic centers are presented and have been characterized by physical and chemical methods. These compounds have the general formula $[M(L)A]_n$ where $M = Cu^{2+}, Co^{2+}, Ni^{2+}$, $L = 4,4'$ -bipyridyl, $4,4'$ -bipyridyl N,N' -dioxide and $A = S_2O_6^{2-}, SO_4^{2-}$ [1].



[1] Neels A., Montse A., González Mantero D., Stoeckli-Evans H., *Chimia*, 2003, 619-622.

Keywords: crystal engineering, nanoporous materials, physical adsorption

P.09.05.16

Acta Cryst. (2005). A61, C364

The Interplay between N-H...O Hydrogen Bonding and Cl...Cl Interactions in Arylformamides

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N-H...O hydrogen bonding occurs in both dichlorophenyl- and dimethylphenyl-formamides, regardless of the substitution pattern around the phenyl group (Fig. 1), forming infinite chains of molecules. We have found that while there are significant differences in the crystal structures of 2,6-dichlorophenyl- (1) and 2,6-dimethylphenylformamide (2) (Fig. 1), 1 undergoes a phase transformation to a phase isomorphous with that of 2,6-dimethylphenyl-formamide. The differences in these structures are rationalized in terms of the presence (2,6-dichloro) or absence (2,6-dimethyl) of Cl...Cl interactions. In addition the presence of a Me or Cl group in both phenyl ortho positions affects the conformation of the formamide group.

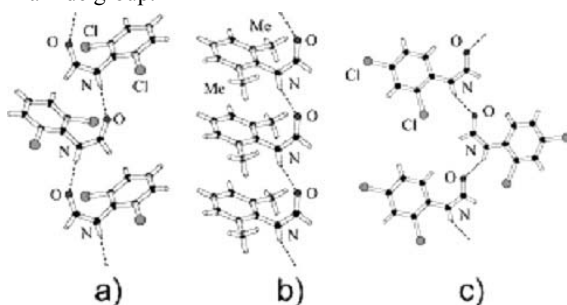


Figure 1. N-H...O hydrogen bonding patterns in (a) 1 (b) 2 (c) 2,6-dichlorophenylformamide.

Keywords: polymorph, phase transition, hydrogen bonding

P.09.06.1

Acta Cryst. (2005). A61, C364

New Helical Host System Showing True Self-Inclusion

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Crystal engineering of host/guest systems has been a major field of study for the last couple of decades. Even though recent studies appear to be focusing on coordination polymers, the organic host systems, such as the crown ethers, cavitands, cryptands and

calixarenes, have proven to be highly successful. Due to their biological relevance, helical host systems have also been developed. The urea family and the alicyclic diol family are the most well known. The compound 2,7-dimethyl-3,5-octadiyne-2,7-diol [1] was crystallized from several solvents and single crystal X-ray diffraction analysis performed to determine whether encapsulation had occurred. The host system comprises of triple helical tubes formed via hydrogen bonding. The guest is enclathrated inside these tubes. The host shows good selectivity, as it does not encapsulate most solvents. To investigate whether the host system could be porous, crystals were grown by sublimation. The sublimed material was found to have the same host helical structure but with the host compound also inside the channels. The same self-included structure was also found when no encapsulation occurred. To our knowledge this is the first example of a host system having the same basic structure when it includes itself.

[1] Leigh D.A., Moody A.E., Pritchard R.G., *Acta Cryst. C*, 1994, C50, 129.

Keywords: materials, supramolecular, self inclusion

P.09.06.2

Acta Cryst. (2005). A61, C364

Comparative Study of Framework Borates Optical Non-linearities

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One of the pressing problems of modern crystallography and crystal chemistry is construction of noncentrosymmetric crystal structures with high with second-order optical susceptibilities. Good solution to the problem may be using of the boron oxide framework matrix as a host for the high-polarizable metal cations. The recently discovered members of the known family of non-centrosymmetric halogen-pentaborates ($M_2B_5O_9Hal$, $M = Ca, Sr, Ba, Pb, Eu$, $Hal = Cl, Br$) with hilgardite-type structure are attractive due to their second harmonic generation (SHG) activity. In particular, lead derivative phases demonstrate SHG comparable with well-known BIBO (BiB_3O_6) crystal. The compounds of this family possess zeolite-like framework structures. As it was shown only metals mentioned above stabilize the structural type of hilgardite. Our attempts to obtain other representatives of this family with the same stoichiometry lead to producing another structure type of framework halogen borates – boracites stoichiometry $M_3B_7O_{13}Hal$. They are characterized by a zeolite-like 3D non-centro-symmetric structure. We report comparison of our experimental and theoretical results on SHG efficiency for hilgardite and boracite families' members. The experiments show an order less SHG efficiency for boracites relative to hilgardites. Computational methods developed by Phillips and Van Vechten and approached by Zhang to complex crystals were performed to explain corresponding difference in optical second-order nonlinearities of the crystals. Sequence of compounds in both families according to their SHG efficiencies conforms to the theoretically predicted values.

Keywords: noncentrosymmetric oxides, boron compounds, NLO

P.09.06.3

Acta Cryst. (2005). A61, C364-C365

Optical and Pyroelectric Properties and Structure of $2[K^+H(C_4H_5O_5)] \cdot C_4H_6O_5$

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The semi-organic crystal Bis (Potassium Hydrogen L-Malate) L-Malic Acid, $2[K^+H(C_4H_5O_5)] \cdot C_4H_6O_5$, shows a large spontaneous polarization (in the range 30-40mC/cm²) in the vicinity of 365K, which is one order of magnitude higher than that of TGS. The title compound also shows a second harmonic generation that is about 70% that of KDP. The crystal structure has been re-determined by single