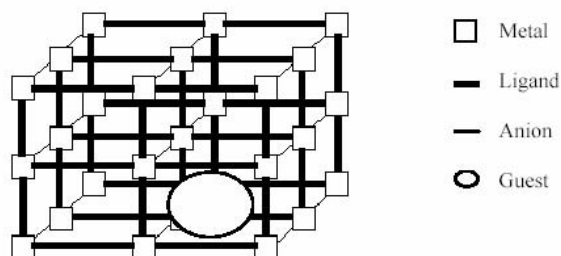


by rational self-assembly using the principles of crystal engineering. Metal ions are usually coordinated to two or more bridging ligands giving a final semi-rigid structure suitable for adsorption, catalysis, etc. Nano-porous materials based on new linear ligands coordinated to metallic centers are 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

Demi C. Levendis, M.A. Fernandes, M.S. Layh, T.S. Mkwizu, B. Omondi, *Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, Private Bag 3, PO Wits 2050, South Africa*. E-mail: demi@hobbes.gh.wits.ac.za

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.

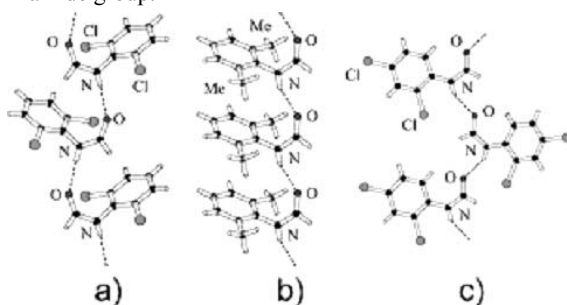


Figure 1. N-H...O hydrogen bonding patterns in (a) 1 (b) 2 (c) 2,4-dichlorophenylformamide.

**Keywords:** polymorph, phase transition, hydrogen bonding

#### P.09.06.1

*Acta Cryst.* (2005). A61, C364

#### New Helical Host System Showing True Self-Inclusion

Gareth O. Lloyd<sup>a</sup>, Leonard J. Barbour<sup>a</sup>, J. Alen, <sup>a</sup>Department of Chemistry, University of Stellenbosch, South Africa. <sup>b</sup>K.U. Leuven, Departement Chemie, Afdeling Organische Synthese, Celestijnenlaan 200F, B-3001 Leuven, Belgium. E-mail: gol@sun.ac.za

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

Pavel A. Plachinda<sup>1</sup>, V. A. Dolgikh<sup>2</sup>, S. Yu. Stefanovich<sup>2</sup>, <sup>1</sup>Department of Material Sciences. <sup>2</sup> Department of Chemistry, MSU, Moscow. E-mail: plachinda@inorg.chem.msu.ru

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 $2[K^+H(C_4H_5O_5)] \cdot C_4H_6O_5$

Maria Margarida R. Costa<sup>a</sup>, Vitor Hugo Rodrigues<sup>a</sup>, Etelvina de Matos Gomes<sup>b</sup>, Michael S. Belsley<sup>b</sup>, Arunhozi Gnanasundaram<sup>b</sup>, Alberto Criado<sup>c</sup>, <sup>a</sup>CEMDRX, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-516 Coimbra, Portugal. <sup>b</sup>Departamento de Física, Universidade do Minho, Campus de Gualtar 4710-057, Braga, Portugal. <sup>c</sup>Departamento de Física de la Matéria Condensada, Universidad de Sevilla, Apartado 423566 Sevilla, Spain. E-mail: guida@pollux.fis.uc.pt

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/cm<sup>2</sup>) 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

crystal X-ray diffraction at 270 K and the unit cell was found to be triclinic instead of orthorhombic, as reported before[1]. Hydrogen L-malate anions form infinite head-to-tail chains via O-H...O interactions and can be used as structural building blocks in solid state crystal engineering. The neutral malic acid molecules establish links between neighbouring chains. Further structural and physical properties characterization of a similar compound, in which potassium is partially substituted by rubidium, is in progress.

[1] Van Havere W.K.L., Deukrskens P.T., Lenstra T.H., *Crystall. J., Spect. Res.*, 1985, **15**, 45.

**Keywords:** pyroelectricity, crystal structure analysis, optical activity

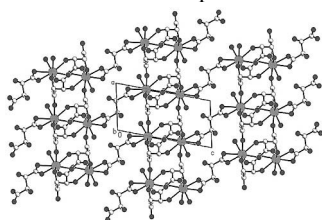
#### P.09.06.4

*Acta Cryst.* (2005). A61, C365

#### Geometric Analysis of Tartrate Coordination Modes from Crystallographic Data

Herman H.-Y. Sung, John A.K. Cha, Samadara Thushari, Ian D. Williams, *Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China*. E-mail: hermans@ust.hk

Tartaric acid is a small organic molecule [C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>] with a bewildering array of ligation (or binding) possibilities to metal centers. We are interested in using these in crystal engineering applications, especially in the formation of chiral solids. We present the results of a geometric analysis of the binding of tartrate to lanthanide metal ions. Using different stereo-chemical configurations R,R-, R,S- or R,R-/S,S- mixtures these can give different 3D arrangements incorporating a wide number of Ln-TAR binding modes. The computed minima for binding can be compared with experimental results and the energetic implications of our findings will be discussed. Finally the  $\mu$  notation set used to describe the binding modes will be introduced and explained.



Chiral Network solid [Er<sub>2</sub>(L-TAR)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] using  $\mu^4$ ,  $\kappa^6$  and  $\mu^2$ ,  $\kappa^4$  binding modes

**Keywords:** inorganic carboxylates, crystal engineering, chiral compounds

#### P.09.07.1

*Acta Cryst.* (2005). A61, C365

#### Crystal Packing: Molecular Shape and Intermolecular Interactions

Elna Pidcock, W.D. Sam Motherwell, *Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England*. E-mail: pidcock@ccdc.cam.ac.uk

The Box Model of crystal packing describes unit cells and their contents in terms of "packing patterns".[1] The packing patterns were derived from a consideration of the ways in which boxes of unequal dimensions can be stacked with faces touching and edges aligned. The resulting arrays of boxes have the same total volume but different surface areas. An examination of thousands of experimental structures contained within the Cambridge Structural Database[2] has shown that these packing patterns are a viable description of crystal structures and that molecular dimensions are related to unit cell dimensions in a systematic way. The packing patterns are not populated equally by experimental structures; packing patterns characterised by low surface area and most equal dimensions are preferred. Thus molecular shape appears to be of primary importance in crystal packing.

However, high surface area packing patterns do exist and a possible explanation is that these structures contain strong, "structure-determining" hydrogen bond interactions. Subsets of structures containing strong motifs have been examined within the context of the

Box Model. Changes in populations of packing patterns are observed and these changes can be rationalised in terms of the symmetry requirements of the motif. However, the presence of hydrogen bond motifs does not appear to greatly perturb the principal of the Box Model - that minimum surface area is preferred.

[1] Pidcock E., Motherwell W.D.S., *Crystal Growth Des.*, 2004, **4**, 611. [2] Allen F.H., *Acta Cryst.*, 2002, **B58**, 380.

**Keywords:** crystal packing, hydrogen bond, databases