

s9.m3.o1 Crystal Engineering of Metalloporphyrin Molecular Sieves and Zeolite Analogues. I. Goldberg, *School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, 69978 Tel Aviv, Israel.*
Keywords: molecular interactions, supramolecular assemblies.

The design of molecular solids with structural and functional similarity to the inorganic zeolites is an exciting challenge in materials science. We attempted in this study to crystal-engineer cross-linked open networks and stable nanoporous solids, utilizing the concepts of supramolecular self-assembly. The rigid and thermally stable metalloporphyrin building blocks, readily available in diverse functional forms, have played a major role to this aim.

A variety of new materials have been rationally designed with the aid of appropriate molecular recognition algorithms. This includes formulations of extended two-dimensional hydrogen bonded polymers with hollow architectures,¹ network structures of homogeneous as well as heterogeneous coordination polymers,² polymeric patterns sustained by external metal centers, and molecular sieves (see Figure) with different channel widths (within the range of 0.5-1.5 nm) and dimensionality.³⁻⁵ Construction of multiporphyrin networks with even larger pores (>2.2 nm) can be also realized.⁶ Representative examples will be discussed in more detail.

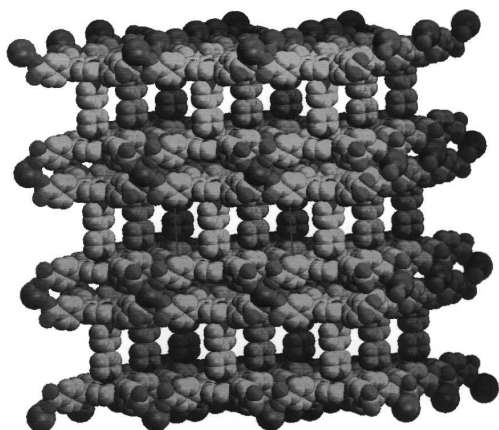


Figure. An open supramolecular array with 8x10 and 8x12.5 Å channels resembling a zeolite architecture.

[1] Diskin-Posner Y., Krishna Kumar R., Goldberg I. 'Solid-state supramolecular chemistry of porphyrins', *New J. Chem.* (1999), 23, 885-890, and references cited therein.

[2] Krishna Kumar R., Goldberg I. 'Supramolecular assembly of heterogeneous multiporphyrin arrays', *Angew. Chem. Int. Ed.* (1998), 37, 3027-3030, and references cited therein.

[3] Diskin-Posner Y., Goldberg I. 'From porphyrin sponges to porphyrin sieves', *Chem. Commun.* (1999), pp. 1961-1962.

[4] Diskin-Posner Y., Dahal S., Goldberg I. 'New effective syntheses for supramolecular self-assembly of carboxyphenyl-porphyrins', *Chem. Commun.* (2000), pp. 585-586.

[5] Diskin-Posner Y., Dahal S., Goldberg I. 'Crystal engineering of metalloporphyrin zeolite analogues', *Angew. Chem. Int. Ed.* (2000), 39 (7), in press.

[6] Dahal S., Goldberg I., 'Hydrogen-bonded networks and porous crystals of tetra(diaminotriazinophenyl)porphyrin', *J. Phys. Org. Chem.* (2000), in press.

s9.m3.o2 Crystal Engineering Low Symmetry Structures. P.D. Prince, G. S. McGrady and J.W. Steed, *Department of Chemistry, King's College London, Strand, London WC2R 2LS. E-mail jon.steed@kcl.ac.uk* Peter C. Junk *James Cook University, Townsville, Qld., Australia.*
Keywords: molecular interactions, supramolecular assemblies.

Work on an interesting series of hydrogen bonded polymers base on the unsymmetrical hydrogen bond acceptor 15-crown-5 is presented. These compounds are interesting because they all share the feature of having a large number of unique molecules in the crystallographic asymmetric unit. That is to say that there are a large number of supramolecular interactions between the molecular components that do not follow the usual "rules" of crystal packing. Particularly interesting examples include:

[UO₂Cl₂(H₂O)₃]·15-crown-5

16 unique complexes ($P3_2$, $Z = 48$, $Z' = 16$)

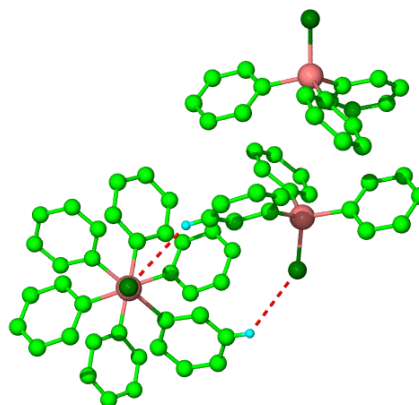
[Er(NO₃)₃(H₂O)₃]·15-crown-5·H₂O

4 unique complexes ($P1$, $Z = 8$, $Z' = 4$)

[Ni(H₂O)₆]Br₂·15-crown-5·2H₂O

4 unique half and two unique whole nickel complexes ($P1$, $Z = 8$, $Z' = 4$)

There is a remarkable number of other interesting low symmetry structures that may be still distinguished from glasses and in our own laboratory we have prepared two further entirely independent series of such compounds. In one case strongly hydrogen bonded amine complexes of mineral acids show a great deal of 'unsymmetry' arising from frustration between the conflicting driving forces towards close packing and maximisation of intermolecular interactions. One example based on diprotonated *o*-phenylenediamine contains eight unique cations and ten unique anions, [(NH₃)₂C₆H₄]₈(HSO₄)₄(SO₄)₆·8H₂O. In a completely unrelated series GePh₃Cl exhibits four independent molecules in space group $P2_1/c$ arising from the occurrence of two 'sixfold embrace' motifs of the triphenyl moieties that interact *via* weak CH...Cl hydrogen bonds (see figure). Different motifs with two independent molecules are observed for the analogous bromide and hydride compounds, all dependent on weak hydrogen bonds.



In this poster a range of such low symmetry structures will be discussed and their relevance to the control of crystalline architecture explored. Come along and browse and offer your opinions!

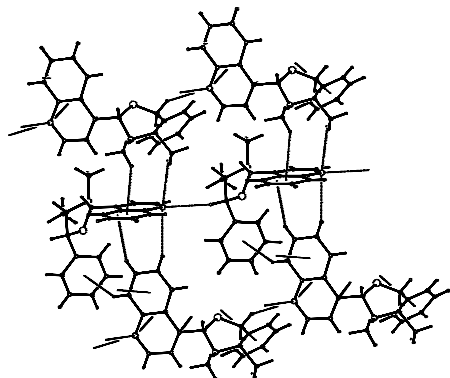
H. Hassaballa, J. W. Steed, P. C. Junk and M. R. J. Elsegood, *Inorg. Chem.*, 1998, 37, 4666-4671.

s9.m3.o3 Weak interactions in oxazolidine derivatives.

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Keywords: hydrogen bonding, weak interactions, 4-quinolinyl.

We are currently studying oxazolidine derivatives derived from (-)-ephedrine and several crystal structures will be discussed including the 4-quinolinyl derivative depicted in Figure 1 below.



(1a) $C_{20}H_{20}N_2O$, monoclinic, $P2_1$, $a = 9.0541(7)$, $b = 9.6253(7)$, $c = 9.6475(7)$ Å, $\beta = 100.969(7)^\circ$, $V = 825.40(11)$ Å³, $Z = 2$, $T = 294$ K, $D_x = 1.225$ Mg.m⁻³, $R = 0.032$ for 3692 reflections $> 2\sigma(I)$. Data were collected on an Enraf-Nonius CAD4 diffractometer.

Compound **1** crystallises with an interesting relay of C-H...N and C-H... π interactions utilising the phenyl and 4-quinolinyl groups as donors and acceptors in the solid state (Fig. 1 above). Data were also collected at 150K (using X-ray radiation) on a kappa-CCD diffractometer, **1b** and by neutron diffraction at the ISIS facility, Rutherford Appleton laboratory, **1c** in order to probe the nature of the relay of weak interactions in greater detail and for comparison with *ab initio* calculations.

These results will be compared with the crystal structure determinations of related oxazolidine derivatives¹⁻³ especially fluoro and alkoxy derivatives.

s9.m3.o4 Crystal structures and intermolecular interactions in new fullerene derivatives. I.S. Neretin,

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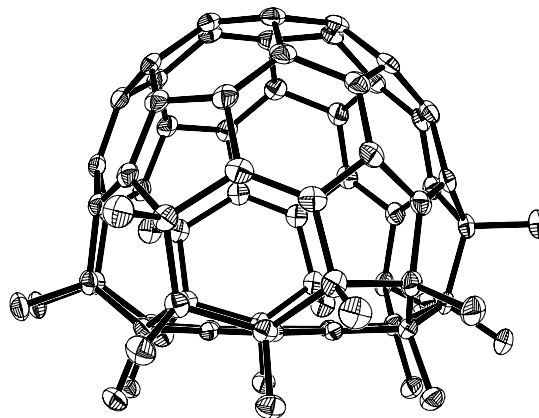
Keywords: fullerenes, disorder, molecular complexes.

Single crystal X-ray data for the six new derivatives of C_{60} and C_{70} were collected at 100-110K on SMART diffractometer in order to reveal correlations of a carbon cage disorder with intermolecular interactions.

Monoclinic structure of $C_{60} \cdot 2C_6H_5I$ with unusually short distance between C_{60} centres (9.89 Å) shows a fully ordered C_{60} moiety, whilst the previously studied $C_{60} \cdot 2C_6H_5Br$ ¹ with similar molecular packing motif have longer distances (10.00 Å) and rotationally disordered C_{60} molecules.

In a series of molecular complexes with metal tetraphenylporphyrinates (MTPP), fullerene molecules are rotationally disordered in $C_{60} \cdot 2CuTPP$, $C_{60} \cdot 2(PyZnTPP) \cdot Cp_2Fe \cdot C_6H_5CH_3$ (where Py is pyridine) and $C_{70} \cdot 2(PyZnTPP) \cdot C_6H_5CH_3$ with the normal van der Waals contacts, whereas C_{70} molecules are ordered in $C_{70} \cdot CuTPP \cdot (C_6H_5Me, C_2HCl_3)_2$ with a weak secondary Cu...C bonding at 2.88-3.03 Å. Notable is the disappearance of ferrocene molecule on a replacement of C_{60} by C_{70} in two related PyZnTPP derivatives.

In the fully ordered crystal structure of $C_{60}F_{18} \cdot C_6H_5CH_3$, carbon cage of $C_{60}F_{18}$ is strongly distorted (see Figure). C-C bond lengths vary from 1.372 Å in aromatic ring surrounded by $C(sp^3)-F$ vertices to 1.672 Å in a fluorinated belt. A high value of dipole moment (12.3 D at 3-21G* level) and strong electrostatic interactions in the crystal explain short forced C...F contacts (down to 2.75Å).



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[1] J.F.Gallagher, J.M. Briody and B.P. Cantwell, *Acta Cryst.*, C54, 1331-1334.

[2] L.M. Fitzsimons and J.F. Gallagher, *Acta Cryst.*, C55, 472-474.

[3] J.F. Gallagher and L.F. Fitzsimons, *Acta Cryst.*, C55, 1001-1003

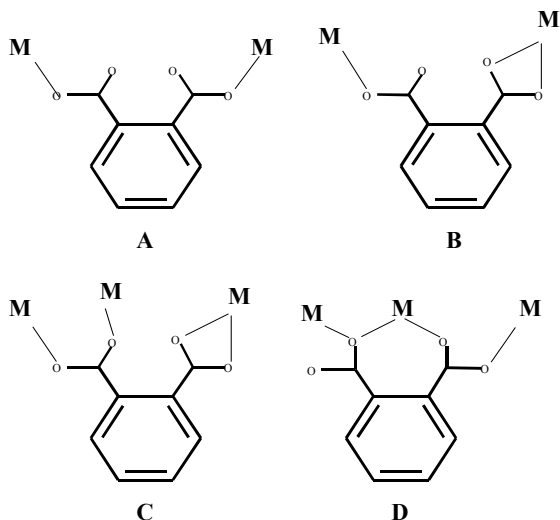
[1]. M.V.Korobov et al., *J.Phys.Chem.B* (1998), 102, 3712.

s9.m3.o5 **Structure of Copper(II), Cobalt(II) and Zinc(II) Complexes with *o*-Phthalic Acid.** Yu.A. Simonov, M. Gdaniec, P.N. Bourosh, I. Filipova, N.V. Gerbeleu, S.G. Baca, G.A. Timco, *Institute of Applied Physics, Academy of Sciences of RM, Chisinau, R. Moldova. Faculty of Chemistry, A.Mickiewicz University, Poznan, Poland. Institute of Chemistry, Academy of Sciences of RM, Chisinau, R. Moldova*
 Keywords: metallopolymers, *o*-phthalic acid, X-ray structures.

Notes

A series of new copper(II), cobalt(II) and zinc(II) complexes with *o*-phthalic acid (H_2Pht) has been prepared and structurally characterized by X-ray analysis. These compounds have the general formula $[M(Pht)A_n]$ (where $M = Cu$, $n = 2$, $A = 4$ -methylpyridine (**I**) $[Cu_2(Pht)_2A_4 \cdot H_2O]$; $M = Zn$, $n = 2$, $A =$ pyridine (**II**), 3-methylpyridine (**III**), 4-methylpyridine (**IV**); $M = Zn$, $n = 1$, $A = 4$ -methylpyridine (**V**); $M = Co$, $n = 2$, $A = 2$ -methylimidazole (**VI**) and $[M(HPht)_2A_n]$ (where $M = Cu$, $n = 2$, $A =$ pyridine (**VII**); 4-methylpyridine (**VIII**)).

In compounds **I** – **VI** the 1,6-bridging modes of *o*-phthalic acid are realized and this unambiguously gives rise to the formation of polymeric structures. However, due to the nature of metal ion and stoichiometric and geometric specific features of the nitrogen-containing ligands, the different structural functions of the phthalate ligand are carried out:



While the first two types of bridges join two neighbouring metal atoms (compounds **I** – **IV** and **VI**), **C** and **D** types of coordination (compound **V**) demand three adjacent metal atoms for their organization. Type **D** of coordination was not found in other phthalate complexes so far. The structures of **VII** and **VIII** are composed of molecular complexes in which one of the carboxylic groups is neutral and the acid residue acts as a singly charged anion $HPht^-$ giving rise to a four-membered ring. In crystals the complexes are combined by intermolecular H-bonds.