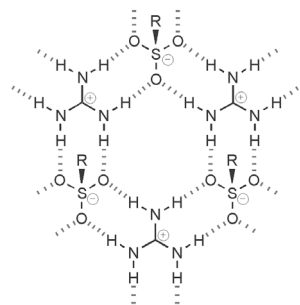


s13.m42.o1 **Structural manipulation of hydrogen-bonded networks – inclusion of metal centres and chromophores and response to loss of symmetry.** Andrew D. Burrows, Nichola J. Burke, Ross W. Harrington, Mary F. Mahon and Simon J. Teat, *Department of Chemistry, University of Bath, UK, CLRC Daresbury Laboratory, Warrington, UK. E mail: a.d.burrows@bath.ac.uk.*

Keywords: Crystal Engineering; Hydrogen Bonding; Phosphines

Crystal engineering can be defined as the synthesis of solid-state structures with predictable structures and properties. The two most commonly employed strategies for this make use of coordination bonds and hydrogen bonds. One of the most reliable hydrogen bond networks is the hexagonal sheet structure shown below which is adopted by guanidinium sulfonates, $[C(NH_2)_3][O_3SR]$ [1].



The guanidinium sulfonate (GS) structure is tolerant to wide changes in the steric demands of the substituent R, and GS layers can be bridged between using disulfonates. In this presentation the inclusion of both metal centres and chromophores into GS networks is discussed. Metal centres can be included through use of sulfonated phosphine ligands such as $PPh_2(C_6H_4SO_3-m)$ [2, 3], though in such cases the strong N–H...O hydrogen bonds of the GS array can be compromised by weaker interactions involving the phenyl rings. Chromophores can be included into GS networks through use of sulfonated indicators such as methyl orange, $Na[O_3SC_6H_4N=NC_6H_4NMe_2]$. The guanidinium derivative of methyl orange has been shown by powder X-ray diffraction and diffuse reflectance UV-visible spectroscopy to react sequentially with HCl and NH_3 . In addition, the tolerance of the GS network to substitution on the guanidinium cation has been examined. The structural impact of substituting one or two hydrogen atoms for methyl or ethyl groups has been assessed for a range of sulfonates.

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s13.m42.o2 **Crystal engineering based on mirror image recognition.** B. Calmuschi, U. Englert, *Institut of Inorganic Chemistry, RWTH Aachen University, Professor-Pirlet-Straße 1, D-52056 Aachen, Germany. E-mail: beatrice.calmuschi@ac.rwth-aachen.de*

Keywords: Crystal Engineering, Pseudosymmetry, Binary Crystals, Mirror Image Recognition

Opposite chirality offers the possibility to design binary crystals based on the favourable interaction between opposite enantiomers. We have exploited the statistical preference for heterochiral crystals [1-3] as a design tool to generate predictable molecular assemblies [4-7]. Preferred mirror image recognition in the solid extends to closely related compounds of opposite chirality, so-called quasiracemates [8,9]. The favourable interaction between “almost” enantiomeric molecules A and B may be regarded as the driving force for the formation of these latter solids. Our strategy is to design, synthesise and crystallographically characterise sets of complexes which are pseudosymmetric with respect to improper symmetry operations.

A well ordered binary solid has been obtained on purpose via cocrystallisation of two structurally related Pd(II) complexes of opposite chirality A and B. Cocrystal AB shows higher symmetry than the enantiomerically pure counterparts and a super space group of one of the components.

The following crystal data have been obtained:

Comp.	A	B	Cocrystal AB
SG	$P2_12_12_1$	$P4_3$	$P4_21'2$
<i>a</i>	4.8727(11)	12.840(2)	12.7500(15)
<i>b</i>	11.658(3)	12.840(2)	12.7500(15)
<i>c</i>	24.825(6)	37.804(8)	36.029(5)
<i>V</i>	1410.2(5)	6232.1(19)	5856.9(12)
<i>Z</i>	4	16	2

The asymmetric unit of the cocrystal contains 2 independent molecules, one A and one B, whereas the asymmetric unit of the complex B, which has the lattice constants very similar with the cocrystal but crystallises in the lower space group $P4_3$, contains 4 independent molecules related by a local pseudo two fold axis in the direction of the diagonal [10].

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