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Understanding the interactions between two different types of molecules in the complex crystal become important in the study of molecular recognition and crystal engineering. Particularly, the molecular recognition in the complex crystal is a subject of considerable interest because of its applications to separation purposes. A few years ago, it was reported [1] that an interaction between a chiral onium salt (Cinchonidinium Chloride) and racemic compound (Bis- β -naphthol) accomplishes a successful enantiomeric resolution, but many researchers are interested in exploiting economical means of resolving racemic compounds such as probable useage of a non-chiral host molecule. This is a difficult task yet to be achieved.

As an initial approach in our investigations, the crystallization of non-chiral host compound (monoalkyltrimethylammonium halides) with (R)-(+)-1,1'-Bi-2-naphthol (RBNP) and Rac-1,1'-Bi-2-naphthol (BNP) were chosen to investigate the molecular recognition between non-chiral host compound and chiral as well as racemic compound from the viewpoint of crystal structure studies in order to know the feasible interactions, molecular packing structures and space groups of such complexes. The investigations revealed that the hexyltrimethylammonium bromide (6TAB) and octyltrimethylammonium bromide (8TAB) interact with RBNP and BNP to form molecular complexes (6TAB/RBNP, 6TAB/BNP, 8TAB/RBNP and 8TAB/BNP) by crystallization or mixing of powdered samples in a mortar. Both 6TAB/RBNP and 8TAB/RBNP molecules crystallize in monoclinic space group $P2_1$, whilst 6TAB/BNP and 8TAB/BNP crystallize in triclinic space group $P\bar{1}$ and monoclinic space group $P2_1/c$, respectively. Hydrogen bonds and C-H \cdots π interactions stabilize the crystal structures and also contribute to the different packing modes observed in the complexes.

[1] Toda F., Tanaka T., *Chem. Commun.*, 1997, **12**, 1087.

Keywords: molecular recognition, crystal engineering, molecular compounds

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Spontaneous Resolution of *N*-sulfonylpyrimidine Compounds Induced by Chemical Modifications

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The title compounds belong to a novel series of pyrimidine nucleobase derivatives, some of which exhibit significant anticancer activity *in vitro*. [1] The crystal structures of 1-tosylthymine (**1**), 1-tosyluracil (**2**), α -naphthyl derivatives of thymine (**3**) and uracil (**4**) are presented. The conformational chirality was encountered in all compounds, as the consequence of the S-N single bond free rotation hindrance in solid state (*atropisomerism*). [2]

The spontaneous resolution (*à la Pasteur*) of *P* and *M* conformational enantiomers occurred during the crystallization of **2** and **4**, whereas their 5-methyl analogues, **1** and **3**, crystallized as racemic mixtures. Moreover, spontaneous resolution in the case of **2** was accompanied by a formation of racemically twinned crystals regardless of the solvent used. Obviously, substituents at C-5 position of pyrimidine base as well as in -SO₂-R group dictate the occurrence (or absence) of spontaneous resolution.

[1] Žinić B., Žinić M., Krizmanić I., *Ruđer Bošković Institute*, EP 0 877 022, 2003. [2] Cunningham I.D., Cooles S.J., Hursthouse M.B., *Chem. Comm.*, 2000, 61-62.

Keywords: conformational chirality, racemic twinning, pyrimidine nucleobases

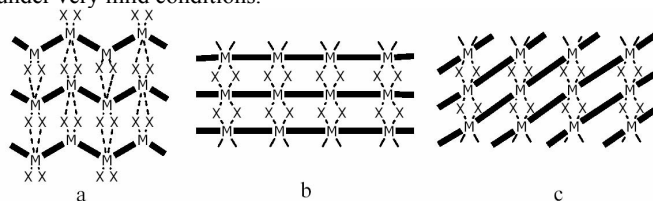
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Single-Crystal to Single-Crystal Reactions

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Single-crystal to single-crystal (SCSC) reaction represents the most fascinating field of solid-state chemistry [1-2], which in nature demands to make or break strong chemical bonds. Such transformation involves cooperative atomic movement between reactant and product (both are single crystals) in solids. In this contribution we wish to present two thermal-induced reversible SCSC reactions, in which unprecedented changes in network topology occur under very mild conditions.



1) Topotactic phase transformation between 1D tetrahedral chain polymers $[Zn(\mu-Cl)_2(4,4'-bpy)]_\infty^1$ (**1a** and **1b**, structure a) and 2D network $[Zn(\mu-Cl)_2(\mu-bpy)]_\infty^2$ (**2**, b) [3]; 2) between two 2D networks b and c on the polymer $[Pb(\mu-Cl)_2(\mu-bpy)]_\infty^2$ (**3**).

[1] Tanaka K., Toda F., *Chem. Rev.*, 2000, **100**, 1025. [2] Braga D., Grepioni F., *Angew. Chem. Int. Ed.*, 2001, **40**, 4002. [3] Hu C., Englert U. E., *Angew. Chem.*, 2005, *in press*.

Keywords: crystal engineering, topotactic phase transformations, crystal chemistry and reactions in solids

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Crystal Engineering of Metal-organic Frameworks Using 4,4'-Dipyridyl-N,N'-Dioxide

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Hybrid organic-inorganic materials provide the possibility of combining the advantages of organic and inorganic substances [1]. Schröder *et al* reported [2] that several terbium (III) coordination polymers of differing stoichiometry can be prepared by means of diffusion solvent mixtures using 4,4'-dipyridyl-N,N'-dioxide (dpdo). We have been investigating the coordination polymers of gadolinium (III) and thallium (III). Crystal structures acquired had either zigzag diamondoid or ladder shapes.

The study of metal-organic frameworks (MOF) has been extended to transition elements such as CuCl₂, ZnBr₂, Zn(NCS)₂ and PbCl₂. We have found that changing the metal geometry, while using the same spacer ligand (dpdo), has a significant effect on the type of MOF obtained. The effect of the metal salt anion is also examined. Crystal structures show that the materials we obtain are either polymeric or discrete molecules, which form a 2D or 3D network by means of supramolecular interactions.

Compounds synthesized were characterized by x-ray diffraction and thermal analysis {thermogravimetry (TG), differential scanning calorimetry (DSC) and hot stage microscopy}. Microanalysis was used to confirm the elemental composition.

[1] Mitzi D.B., *J. Chem.Soc., Dalton Trans.*, 2001, 1-12. [2] De-Liang., Blake A.J., Champness N.R., Wilson C., Schröder M., *Chem. Eur.J.*, 2002, **8**, 2026-2033.

Keywords: crystal engineering, metal-organic framework, X-ray diffraction

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MOFs of Phenylamine and Pyridine Derivatives: Structure and Thermal Analysis

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One of the aims of crystal engineering is to produce extended frameworks utilising the wide range of possible covalent and supramolecular interactions. While the most common of the latter is probably the hydrogen bond (often used to generate organic as well as inorganic frameworks) a number of other interactions exist. Changes in experimental conditions may also influence the materials produced.

We have recently prepared a series of metal-organic hybrid materials using a series of phenylamine and pyridine derivatives with transition metals and lanthanides. The same component compounds can be used to prepare network structures, inorganic-organic layered structures or even simple salts. Changes in conditions (eg. pH or temperature) are critical in determining the type of material obtained. This paper will discuss some of the well-ordered MOF networks and layered compounds we have prepared, including the MOFs formed with 4,4'-dipyridyl-N,N'-dioxide using lead(II), copper(II), zinc(II) or cobalt(II) and the layered compounds formed using the same metals with phenylamines as the organic layers. Compounds have been characterised by single crystal and powder X-ray diffraction. Their thermal stability and decomposition behaviour has been studied using Differential Scanning Calorimetry, Thermogravimetry and Hot Stage Microscopy. Kinetic parameters of the desolvation and/or decomposition reactions have also been determined in some cases.

Keywords: crystal engineering, kinetics, thermal analysis

P.09.03.4

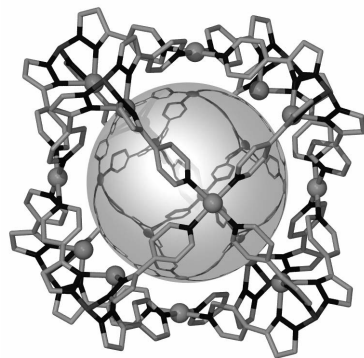
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Crystal Engineering with Scorpionate Ligands

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We have synthesized a range of new scorpionate ligands with peripheral coordination sites using pyridyl and benzonitrile substituents. These ligands have led to the formation of discrete neutral moieties, porous and non-porous coordination polymers and large supramolecules [1,2]. Of particular interest is a 'nanoball' structure shown below which was solved using synchrotron data.

The outer diameter of the nanoball is ca. 29 Å and the inner cavity of this structure is ca. 16 Å in diameter and is decorated with potential reactive sites.



[1] Adams H., Batten S. R., Davies G. M., Duriska M. B., Jeffery J. C., Jensen P., Lu J., Motson G. R., Ward M. D., *manuscript in preparation.* [2] Batten S. R., Duriska M. B., *manuscript in preparation.*

Keywords: scorpionates, supramolecular chemistry, coordination polymers

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Impact of Linkers on the Structural Diversity of 3d-4f Coordination Polymers

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3d-4f oligonuclear complexes are very attractive building blocks

in designing novel solid-state architectures because they combine the electronic and stereochemical peculiarities of both 3d and 4f metal ions. The building-blocks we use are stable bi- and trinuclear complexes [Cu^{II},Ln^{III}] (*i*=1, 2), the metal ions being held together by a Schiff base ligand derived from *o*-vanilline. The versatility of such building-blocks allows their sequential association by a selective interaction of the metal ions with various linkers, thus yielding supramolecular systems with interesting magnetic properties. The building principle is based on the employment of spacers which are able to recognize either the oxophilic rare-earth cation, or the borderline acid which is copper(II) [1].

The heterobinuclear [Cu^{II}Ln^{III}] complexes are also good candidates for the synthesis of polymetallic systems with three different spin carriers 3d-3d'-4f. The third metal ion arises from metalloligands, such as the hexacyanometallate anions [M^{III}(CN)₆]³⁻ (M^{III} = Cr, Fe_{1.s.}, Co_{1.s.}) [2].

[1] Gheorghe R., Andruh M., Müller A., Schmidtman M., *Inorg. Chem.*, 2002, **41**, 5314. [2] Gheorghe R., Andruh M., Costes J.-P., Donnadiu B., *Chem. Commun.*, 2003, 2778.

Keywords: copper, lanthanides, crystal-engineering

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Covalent Aryloxy Metal-Organic Network Materials

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Metal-organic coordination network (MOCN) materials formed from rigid organic spacers and metals of known coordination tendencies have become increasingly well known. Materials with large pores present possibilities for molecular recognition, separation and the catalytic transformation of guest molecules [1]. In addition, chiral nanoporous materials are an emerging area of research in this field. The vast majority of networks are formed from later transition metals and rigid carboxylate or pyridine based organic spacer ligands. A key feature of MOCN materials is that considerable structural predictive ability exists over traditional solid-state inorganic compounds in their design.

Here, we report results of continuing work on the synthesis and X-ray structural characterization of a unique class of early transition metal covalent metal-aryloxy network materials [2]. A prototypical example, {[Ti(OC₁₂H₈O)_{1.5}(OⁱPr)(HOⁱPr)]₂}_n, is formed by treating Ti(OⁱPr)₄ with excess 4, 4'-biphenol at 100°C in tetrahydrofuran. The three-dimensional porous network solid is derived from six 4,4'-biphenoxide linkages connecting bioctahedral dititanium cores.

Substitution of various metal precursors, solvents (pyridine, ether, etc.), and bisphenolic spacer precursors (dihydroxynaphthalene, 4,4''-dihydroxyquaterphenyl, etc.) has afforded an array of one-, two- and three-dimensional materials. We have also made use of chiral alkoxide precursors to obtain crystalline network materials. In general, coordinating solvents such as pyridine decrease network dimensionality. The effect of network dimensionality on the olefin polymerization activity of the materials has been shown to decrease in the order 3-D > 2-D > 1-D > 0-D (amorphous polymer or molecular analog).

[1] Janiak C., *Dalton Trans.*, 2003, **14**, 2781-2804. [2] Tanski J. M., Wolczanski P. T., *Inorg. Chem.*, 2001, **40**, 2026-2033.

Keywords: coordination polymers, metal-organic framework, nanostructures

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Highly Fluorinated Silver Carboxylate Layered Structures

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Previously we have reported the design and synthesis of a family of layered coordination networks based upon silver trifluoroacetate dimers linked through a variety of neutral ditopic ligands. The surfaces of these layers contain the CF₃ groups of the coordinated anions, which interdigitate with adjacent layers, [1], [2]. Here we