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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

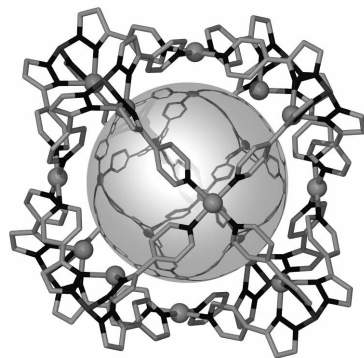
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#### Crystal Engineering with Scorpionate Ligands

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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

#### P.09.03.5

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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<sup>II</sup>,Ln<sup>III</sup>] (*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<sup>II</sup>Ln<sup>III</sup>] 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<sup>III</sup>(CN)<sub>6</sub>]<sup>3-</sup> (M<sup>III</sup> = Cr, Fe<sub>1.s.</sub>, Co<sub>1.s.</sub>) [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

#### P.09.03.6

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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(OC<sub>12</sub>H<sub>8</sub>O)<sub>1.5</sub>(O<sup>i</sup>Pr)(HO<sup>i</sup>Pr)]<sub>2</sub>}<sub>n</sub>, is formed by treating Ti(O<sup>i</sup>Pr)<sub>4</sub> 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

#### P.09.03.7

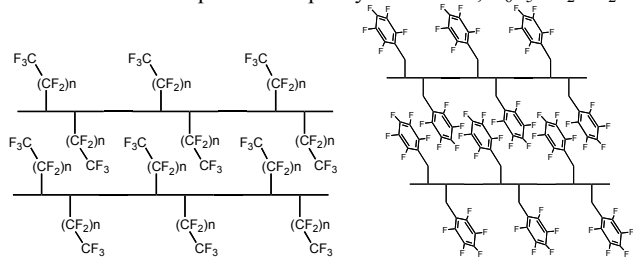
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#### Highly Fluorinated Silver Carboxylate Layered Structures

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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 CF<sub>3</sub> groups of the coordinated anions, which interdigitate with adjacent layers, [1], [2]. Here we

describe two new families of layered silver carboxylates in which the interlayer region is more highly fluorinated. The first series, of general formula  $\{\text{Ag}(\text{CF}_3(\text{CF}_2)_n\text{CO}_2)\text{Q}\}_\infty$ , where  $n = 0-3$ ,  $\text{Q} =$  quinoxaline, projects fluoroalkyl chains into the interlayer region. A family of compounds has been characterised in which interlayer spacing can be controlled. The second series employs fluoroaromatic groups through coordination of the pentafluorophenylacetate ion,  $\text{C}_6\text{F}_5\text{CH}_2\text{CO}_2^-$ .



[1] Brammer L., Burgard M. D., Rodger C. S., Swearingen J. K., Rath N. P., *Chem. Commun.*, 2001, 2468-2469. [2] Brammer L., Burgard M. D., Eddleston M. D., Rodger C. S., Rath N. P., Adams H., *CrystEngComm*, 2002, 4, 239-248.

**Keywords:** crystal engineering, coordination polymers, fluorine

### P.09.03.8

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#### Synthesis and Characterization of New Cyano-Bridged Oligonuclear Complexes

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The main synthetic route leading to heteropolynuclear cyano-bridged complexes consists in the employment of the stable cyanometallate anions as ligands toward either fully solvated metal ions, or toward metal complexes, which have at least one coordination site occupied by a weakly binding ligand that can be easily replaced.

The reaction between  $[\text{M}(\text{CN})_6]^{3-}$  ( $\text{M}^{\text{III}} = \text{Cr}, \text{Fe}, \text{Co}$ ) and  $[\text{Mn}(\text{MAC})\text{X}_2]$  ( $\text{MAC} =$  macrocyclic ligands,  $\text{X} = \text{H}_2\text{O}, \text{NCS}^-$ ) affords a series of cyano-bridged trinuclear complexes. The cryomagnetic properties of the  $\text{Cr}^{\text{III}}$  derivatives were investigated, revealing a new case of irregular spin-state structure.

A series of binuclear 3d-4f complexes  $\{(\text{H}_2\text{O})_8\text{Ln}-\text{NC}-\text{Fe}(\text{CN})_5\} \cdot n\text{hmt}$  ( $\text{Ln}(\text{III}) = \text{La}, \text{Pr}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Ho}$ ;  $\text{hmt} =$  hexamethylenetetramine;  $n = 1, 2$ ) has been synthesized and crystallographically characterized. They exhibit two structural types governed by the size of the assembling 4f cations. Such complexes are suitable models for the study of the 3d-4f exchange interactions mediated by the cyano bridge.

**Keywords:** cyanide complexes, lanthanides, magnetism

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#### Pyridine Boronic Acids as Building Blocks in Crystal Engineering

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We describe the use of different molecular tectons (building blocks), which exploit new and related synthons to generate a diverse range of crystal structures.<sup>1,2</sup> In particular salts of protonated pyridine boronic acids with anionic dithiooxalate complexes are shown to contain hydrogen-bonded supramolecular complexes which associate to form motifs of interesting dimensionality and form. Issues addressed include structural mimicry of one tecton by another, competition between alternative hydrogen bond acceptors and robustness of periodic motifs.

A series boronic acid complexes  $[\text{4-HpyB}(\text{OH})_2][\text{M}(\text{S}_2\text{C}_2\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$  ( $\text{M} = 1 \text{ Pd}, 2 \text{ Pt}, 3 \text{ Ni}$  and  $4 \text{ Cu}$ ),  $[\text{3-HpyB}(\text{OH})_2][\text{M}(\text{S}_2\text{C}_2\text{O}_2)_2]$  ( $\text{M} = 5 \text{ Pd}, 6 \text{ Pt}, 7 \text{ Ni}$  and  $8 \text{ Cu}$ ) have been prepared and

structurally characterized. The supramolecular motifs in these salts show similarities despite differences in the local position of the pyridinium NH group, the metal atom used and the incorporation of water molecules in the structures.

[1] Gillon A. L., Lewis G. R., Orpen A. G., Rotter S., Starbuck J., et al., *J. Chem. Soc. Dalton Trans.*, 2000, 3897. [2] Podesta T. J., Orpen A. G., *CrystEngComm*, 2002, 336.

**Keywords:** crystal engineering, boronic acids, supramolecular chemistry

### P.09.03.10

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#### Structural Diversity in Lead-halide Based Organic-inorganic Hybrids

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Organic-inorganic hybrids have been studied by researchers for a fair amount of time. This fascination is driven by the structural diversity exhibited by this class of compounds, and the technologically attractive opportunity to combine the desirable properties from the respective components into a single nanocomposite.

In the literature, most of compounds with the general formulae  $[\text{CH}_3(\text{CH}_2)_n\text{NH}_3]_2\text{MX}_4$ ,  $[\text{H}_3\text{N}(\text{CH}_2)_n\text{NH}_3]_2\text{MX}_4$  or  $[\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3]_2\text{MX}_4$  reported, have a layered hybrid perovskite type structure.

In our laboratory we set out to augment the body of available knowledge by a systematic investigation into the range and type of structures that can be formed by combining simple primary amines with lead halides. Although far from complete, our study to date comprises in excess of 60 new crystal structures, and has revealed a great structural diversity, particularly in terms of the nets formed by the inorganic components. To date we have observed layers of corner sharing octahedra, linear chains of face sharing octahedral as well as number of mixed intermediates. In all we have to date identified 12 distinct topologies within the inorganic sections of the class of compounds that we are investigating.

**Keywords:** organic-inorganic hybrid materials, nanocomposite, nets

### P.09.03.11

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#### High-Dimensional Structures Constructed from Alkoxo-Bridged Complexes as Nodes

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The development of crystal engineering has stimulated the search for new building-blocks able to generate extended structures with various dimensionalities. We are currently developing a research project concerning the use of binuclear complexes as nodes in designing high-dimensionality systems.

Nine new extended structures have been constructed by using alkoxo-bridged  $[\text{Cu}_2(\text{mea})_2]^{2+}$  and  $[\text{Cu}_2(\text{ap})_2]^{2+}$  ( $\text{Hmea} =$  ethanolamine,  $\text{Hap} = 3\text{-amino-1-propanol}$ ) nodes and *exo*-bidentate ligands as spacers. Bidentate aminoalcohols were chosen, in order to increase the dimensionality of the coordination networks. The binuclear cores are connected through 1,4-bis(4-pyridil)benzene, 9,10-bis(4-pyridil)anthracene and 1,2-bis(4-pyridil)ethyne resulting in 1D, 2D and 3D structures. Interesting cases of interpenetration were emphasised. The dimensionality is influenced by the presence of the different counterions ( $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$  and  $\text{CF}_3\text{SO}_3^-$ ).

**Keywords:** copper, coordination compounds, crystal engineering