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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

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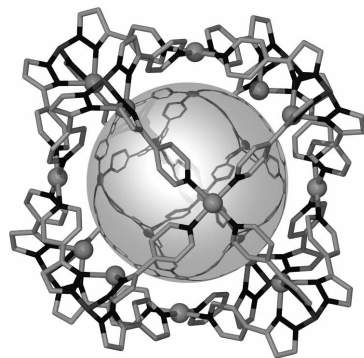
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#### Crystal Engineering with Scorpionate Ligands

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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<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 hexacyanometalate 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.

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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

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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