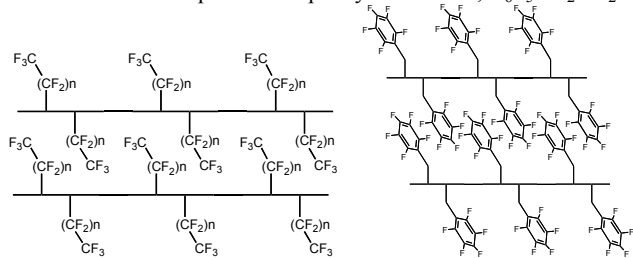


describe two new families of layered silver carboxylates in which the interlayer region is more highly fluorinated. The first series, of general formula $\{\text{Ag}(\text{CF}_3(\text{CF}_2)_n\text{CO}_2)\text{Q}\}_\infty$, where $n = 0-3$, $\text{Q} =$ quinoxaline, projects fluoroalkyl chains into the 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, $\text{C}_6\text{F}_5\text{CH}_2\text{CO}_2^-$.



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Keywords: crystal engineering, coordination polymers, fluorine

P.09.03.8

Acta Cryst. (2005). A61, C357

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 Cr^{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

P.09.03.9

Acta Cryst. (2005). A61, C357

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.^{1,2} 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 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 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.

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Keywords: crystal engineering, boronic acids, supramolecular chemistry

P.09.03.10

Acta Cryst. (2005). A61, C357

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

Acta Cryst. (2005). A61, C357

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 (NO_3^- , ClO_4^- , BF_4^- and CF_3SO_3^-).

Keywords: copper, coordination compounds, crystal engineering