Interwoven Two- and Three-dimensional Coordination Polymers Through Self-assembly of Cu^I Cations with Linear Bidentate Ligands

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The synthesis and single crystal X-ray structures are reported of two interwoven cationic frameworks that are based upon tetrahedral and trigonal Cu^I ions; the resulting architectures are diamondoid, $[Cu^I(bipy)_2(PF_6)]_\infty$ (bipy = 4,4′-bipyridyl) **1**, and honeycomb, $[(Cu^I)_2(pz)_3(SiF_6)]_\infty$ (pz = pyrazine) **2**, respectively.

That bulk solid-state properties of solids are strongly influenced by crystal packing and space group symmetry means that the ability of chemists to rationally design solid state architecture has become a particularly topical and important subject.[1] Whereas organic crystal engineering, which relies primarily upon exploitation of noncovalent interactions, has recently received a great deal of attention,[2] inorganic crystal engineering has developed more slowly.[3,4] This is surprising given the potential that exists for generating novel covalently networked materials with possible applications in catalysis, separations, magnetism and optics. Robson and Hoskins[3,5] recently outlined general principles for crystal engineering of three dimensional coordination compounds and the recent literature reveals several notable examples of interwoven networks.[5–9]

We recently reported design of interwoven diamondoid networks based on strict self-assembly[10] of $[M(CO)_3(\mu_3\text{-}OH)]_4$ (M = Mn, Re) cubane clusters with T_d symmetry and linear difunctional hydrogen bond acceptors.[11,12] We report herein the results of an attempt to extend our studies into the realm of coordination chemistry using the concepts delineated by Robson and Hoskins. We have chosen to focus initially upon Cu^I, a transition metal moiety that is well known to favour tetrahedral geometry,[13] linear bridging ligands bipy and pyrazine, pz, and noncoordinating anions. $[Cu(bipy)_2PF_6]_\infty$, **1**, was obtained as single crystals† from a hot solution of *in situ* generated $[Cu(CH_3CN)_4]PF_6$[14] and bipy in a 1:2 molar ratio. The crystal structure reveals that **1** exists as four independent concatenated diamondoid networks with Cu–Cu separations of 11.16 Å (Fig. 3). **1** is therefore the second example of an interwoven diamondoid framework based upon Cu^I since $[Cu(1,4\text{-dicyanobenzene})_2]BF_4$ crystallizes as a five-fold network.[3] The cationic adamantanoid unit that generates one of the diamondoid frameworks is illustrated in Fig. 1. The Cu^I centres occupy crystallographic $\bar{4}$ positions and hence all Cu–N bonds are identical, 2.034(11) Å. The PF_6^- counter ions occupy channels that are parallel to the *c*-axis and they sit on four-fold crystallographic axes.

Single crystals† of $[Cu_2(pz)_3SiF_6]_\infty$ **2** were obtained by a similar method to that used for **1** except that pz and a solvent mixture containing 1:1 v/v MeCN and water were used. **2** exists as enmeshed honeycomb grids rather than a diamondoid framework.[15] This is a direct consequence of the copper(I) centres adopting unusual but precedented 3-coordinate trigonal geometry.[16,17] The pz ligands bridge adjacent trigonal Cu^I centres to form honeycomb grids with bridged copper cations 6.936 and 6.685 Å apart (Fig. 2). The presence of such large hexagons and a distance of 8.405 Å between parallel grids are accommodated by enmeshing of an identical set of parallel sheets in the orthogonal direction (Fig. 4). The closest distance between copper centres in adjacent grids is 6.0335(3) Å, precluding any possibility of intergrid Cu–Cu bonding. The SiF_6^{2-} ions are located in channels parallel to the crystallographic *c*-axis (Fig. 5) and are hydrogen bonded to pyrazine hydrogen atoms, C···F distances ranging from 3.073(6) to 3.193(4) Å. The anion therefore has very low thermal motion, unlike that in **1**. This observation might represent a clue as to why **2** is so fundamentally different from **1** and other Cu^I based

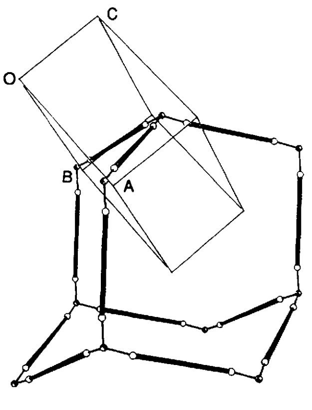

Fig. 1 The cationic adamantoid framework formed by **1**. bipy ligands are represented by rods.

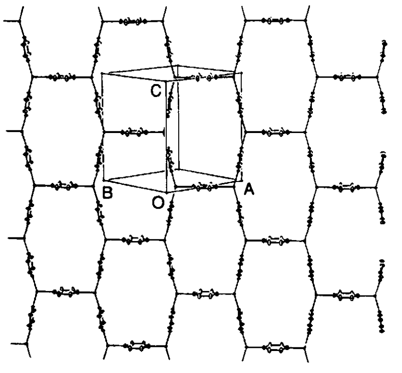

Fig. 2 An ORTEP view of one of the honeycomb networks generated by trigonal copper(I) and bridging pz ligands. Angles around Cu are 106.30(14), 106.30(14) and 147.41(21)°.

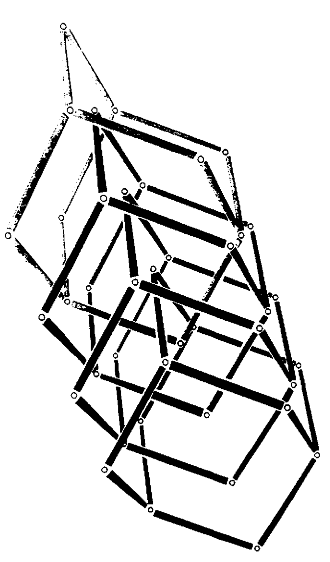

Fig. 3 Schematic representation of four independent interpenetrating adamantoid units as observed in the structure of **1**

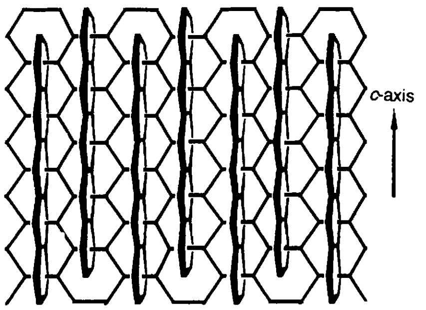

Fig. 4 Schematic representation of how the honeycomb grids in the structure of **2** are interwoven

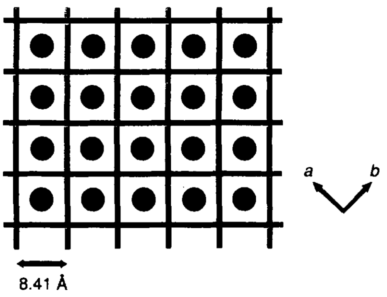

Fig. 5 Schematic representation of the *ab* plane in **2**. Circles represent the SiF_6^{2-} anions, lines represent the interwoven cationic honeycombs.

infinite frameworks, namely that the honeycomb structure packs better than the corresponding diamondoid framework for this particular combination of bridging ligand and counter ion. If **2** had adopted a diamondoid framework it would have been expected to contain a considerable amount of space based upon the observation that $[Cu(2,5\text{-}Me_2pz)_2][PF_6]$ is only a 1-fold diamondoid compound.[15]

Whereas diamondoid structures based on tetrahedral Cu^I centres were known before this study, the interwoven honeycomb framework based upon trigonal Cu^I is a novel but nevertheless predictable structure. The present study clearly indicates the important role that noncoordinating counter ions can play in crystal engineering of coordination polymers and suggests that, given the number of simple permutations of ligand and anion, Cu^I alone might have a rich and diverse role in engineered polymeric frameworks. Furthermore, interwoven solids such as those reported herein might be expected to have properties similar to classic organic host lattices such as urea[18] and trimesic acid.[19] Urea and trimesic acid are also interwoven networks when pure but, if crystallized in the presence of an appropriate guest, they can exist with lower degrees of interpenetration and possess voids for enclathration of small and medium sized guest molecules. $Cd(CN)_2$ has already been shown to exhibit such behaviour.[6] Finally, it should be noted that inorganic covalent lattices offer several possible advantages over their organic counterparts, including greater mechanical strength and the inherent presence of catalytically active transition metals.

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Footnote

[†] *Crystal data* for **1**: $[Cu(4,4'\text{-dipy})_2PF_6]$, M = 520.88, tetragonal, $P4/n$, a = 12.3251(24), c = 6.981(3) Å, U = 1060.5(5) Å^3, Z = 2, D_{cal} = 1.63 Mg m^{-3}, λ = 0.70930 Å, $F(000)$ = 524. 338 absorption corrected reflections with $I_{net} > 3\sigma$ (I_{net}) out of the 696 unique reflections measured at 293 K for a crystal of dimension 0.2 × 0.3 × 0.3 mm on an Enraf-Nonius CAD4 diffractometer using the ω-2θ scan mode ($4° \leqslant 2\theta \geqslant 45°$) on convergence gave final values of R_f = 0.077 and R_w = 0.067. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were calculated (d_{C-H} = 1.08 Å) and fixed with temperature parameters based upon the carbon atom to which they are bonded. All crystallographic calculations were carried out with the PC version of the NRCVAX programme package locally implemented on an IBM compatible 80486 computer.

For **2**: $[Cu_2(pz)_3(SiF_6)]$, M = 509.43, tetragonal $I4/mcm$, a = 11.8869(5), c = 13.0432(7) Å, U = 1842.98(13) Å^3, Z = 4, D_{cal} = 1.84 Mg m^{-3}, λ = 0.70930 Å, $F(000)$ = 1008. 414 absorption corrected reflections with $I_{net} > 3\sigma$ (I_{net}) out of the 454 unique reflections measured at 293 K for a crystal of dimension 0.3 × 0.4 × 0.5 mm on convergence gave final values of R_f = 0.034 and R_w = 0.051. Other experimental parameters were the same as those used for **1**. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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