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Assembly of 2-D inorganic/organic lamellar structures through a combination of copper(I) coordination polymers and self-complementary hydrogen bonds †

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A strategy for the deliberate assembly of lamellar inorganic/organic hybrid materials based on a combination of 1-D coordination polymers and intermolecular hydrogen bonds has been explored. Copper(I) halide coordination polymers provide infinite linear building blocks that are linked into 2-D layers by attaching a pyridine-based ligand to each metal ion. The ligand, which carries a self-complementary hydrogen-bond moiety, provides a selective non-covalent tool for connecting neighboring coordination polymers into a 2-D network. The strategy is illustrated by the crystal structures of [CuCl(6-Me-3-HO$_2$CC$_5$H$_3$N)]$_\infty$ and [CuI(6-Me-3-HO$_2$CC$_5$H$_3$N)]$_\infty$, both of which display the desired lamellar motifs.

Introduction

The reasons for incorporating metal ions into supramolecular networks are numerous, for example they give access to physical properties that are less common in organic solids *e.g.* magnetic properties, conductivity, and catalytic activity, and metal complexes with hydrogen-bonding capabilities may also be used as chemotherapeutic compounds.[1] Metal ions also display a range of coordination geometries allowing for greater flexibility in constructing materials with specific dimensions and topologies.[2] Supramolecular inorganic/organic hybrid materials have so far been constructed through two principal design philosophies.[3] First, transition-metal complexes can be assembled into coordination polymers using coordinate covalent bonds.[4] This is often achieved by employing bifunctional ligands such as 4,4′-bipyridine as linkers between adjacent metal ions.[5–7] Other examples of coordination polymers include Cu(SCN),[8] and Cu(CN)-based nets,[9] chiral silver assemblies,[10,11] interpenetrating diamondoid structures,[12] and supramolecular macrocycles.[13]

Second, weaker intermolecular forces (notably hydrogen bonding) have been used in deliberate strategies for connecting metal complexes into a wide variety of extended networks.[14–18] These results have shown that hydrogen bonds working in concert are capable of 'maneuvering' large complex ions into desirable motifs, even in the presence of competing cation–anion, solvent–metal ion, and solvent–solvent interactions.

Even though both methods have enjoyed considerable success, there have been few *systematic* attempts at using a combination of these approaches to build lamellar or 3-D hybrid materials.[19] Many coordination polymers containing hydrogen bonds (often involving solvent molecules) have been reported but those interactions are rarely part of a deliberate and predictable strategy for connecting 1-D or 2-D coordination polymers into structures of higher dimensionality. For example, it is doubtful that many practical assembly strategies can be based around versatile (and ultimately unpredictable) hydrogen-bond 'agents' such as water molecules or spherical anions; the multitude of potential hydrogen-bond geometries and interactions of these species limit the potential usefulness of such an approach.

Strategy and relevance

In crystal engineering there has been much interest in developing materials that resemble traditional inorganic zeolites[20,21] and, since selectivity is a particularly important aspect of inclusion chemistry, pore-size control is an important target. The modular approach generally employed in crystal engineering may be a particularly attractive avenue towards new porous materials since network structures can be modified by the geometric and topological characteristics of the individual building blocks. Furthermore, previous work on open-network materials has shown that the void space can occupy as much as 60–70% of the total volume and may be capable of selective guest binding or catalysis.[22]

A common problem in the design of porous inorganic/organic systems arises because most coordination polymers carry an overall positive charge, which means that anions have to be present to balance the charge. Regardless of how these anions are incorporated in the structure, *e.g.* coordinating, non-coordinating, bridging, *etc.*, they will occupy space that may hamper the construction of open channels or void space. Copper(I) halides, however, can form many neutral 1-D polymeric networks, Fig. 1, that can provide starting points for the construction of open framework inorganic–organic structures.

We recently demonstrated how the two common assembly methods for hybrid materials (the design of 1-D coordination polymers; hydrogen-bond based intermolecular synthesis) can be married into one supramolecular synthetic tool.[23] The strategy involves covalently attaching a substituted pyridine ligand to a 1-D copper(I) halide polymer whereupon self-complementary hydrogen-bond moieties on each ligand bridge neighboring coordination polymers *via* directional intermolecular hydrogen bonds. By using 1-D coordination polymers instead of discrete complexes as building blocks, the resulting network is partly 'locked' into place, which facilitates

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Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b003306p/

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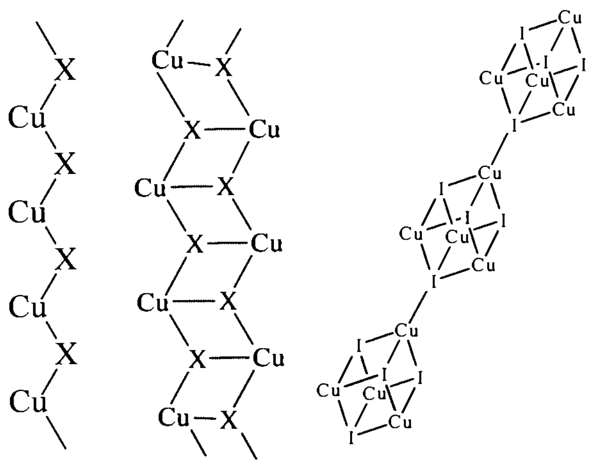

Fig. 1 Examples of coordination polymers formed by copper(I) halides.

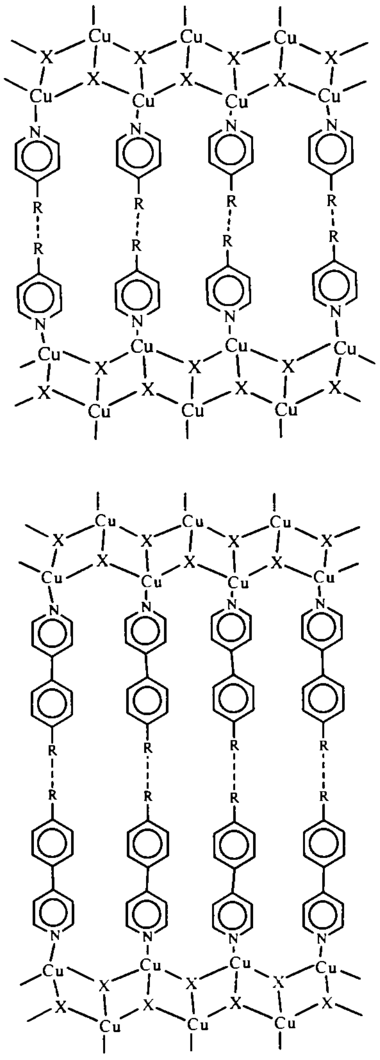

Fig. 2 Coordination polymers held together by predictable and directional hydrogen bonds (R = self-complementary hydrogen-bond moiety). The distance between adjacent chains is controlled by the ligand.

structural prediction and control. Furthermore, ligand size and shape influence the dimensionality and spatial characteristics of the extended network, thus providing a tool for fine-tuning the resulting structure, Fig. 2. In order to explore the use of this approach in the design of new lamellar structures, we report the syntheses and crystal structures of $[CuCl(6\text{-}Me\text{-}3\text{-}HO_2CC_5H_3N)]_\infty$, **1**, and $[CuI(6\text{-}Me\text{-}3\text{-}HO_2CC_5H_3N)]_\infty$, **2**.

Experimental

All starting materials were purchased from Aldrich and used as received. Melting points were determined on a Fisher–Johns melting point apparatus and are uncorrected.

Preparations

$[CuCl(6\text{-}Me\text{-}3\text{-}HO_2CC_5H_3N)]_\infty$, 1. 6-Methylnicotinic acid (0.04 g; 0.29 mmol) and copper(II) chloride dihydrate (0.05 g, 0.29 mmol) were dissolved with heating in ethanol (15 ml). An excess of ascorbic acid was added and heated until it had dissolved. The flask was then stoppered. Yellow rectangular plates crystallized after 24 h, mp >194 °C (decomp.). Yield = 43%.

$[CuI(6\text{-}Me\text{-}3\text{-}HO_2CC_5H_3N)]_\infty$, 2. Acetonitrile was carefully layered over a solution of 6-methylnicotinic acid in THF. A saturated solution of CuI was then added dropwise to the acetonitrile layer. The layered solutions were allowed to stand in ambient air. Slow diffusion produced fine, yellow needles of compound **2** after 24 h, mp >245 °C (decomp.). Yield = 70%.

X-Ray crystallography

Crystalline samples of compounds **1** and **2** were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated using a Bruker SMART 1000 system with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 173 K. The structures were solved using heavy-atom methods using SHELXS 97 and refined using SHELXL 97.[24] Non-hydrogen atoms were found by successive full matrix least squares refinement on F^2 and refined with anisotropic thermal parameters. Hydrogen atoms for **1** were located on the difference map and then refined using a riding model with fixed thermal parameters [$U_{ij} = 1.2\ U_{ij}$(eq.) for the atom to which they are bonded] for subsequent refinements. The hydrogen atoms for **2** were placed at calculated positions.

Crystal data for compound 1. $C_7H_7ClCuNO_2$, $M = 236.13$, monoclinic, space group $P2_1/c$, $a = 3.811(2)$, $b = 15.819(7)$, $c = 13.311$ Å, $\beta = 96.045(7)°$, $U = 797.9(6)$ Å^3, $Z = 4$, $T = 173(2)$ K, μ(Mo-Kα) = 3.022 mm^{-1}, $wR2 = 0.1873$ (1796 unique reflections, 1115 observed), $R = 0.0783$ [$I > 2\sigma(I)$].

Crystal data for compound 2. $C_7H_7CuINO_2$, $M = 327.58$, monoclinic, space group $P2_1/c$, $a = 4.096(1)$, $b = 13.656(5)$, $c = 16.114(5)$ Å, $\beta = 92.225(6)°$, $U = 900.7(5)$ Å^3, $Z = 4$, $T = 173(2)$ K, μ(Mo-Kα) = 5.809 mm^{-1}, $wR2 = 0.1613$ (1756 unique reflections, 1382 observed), $R = 0.0614$ [$I > 2\sigma(I)$].

CCDC reference number 186/2014.

See http://www.rsc.org/suppdata/dt/b0/b003306p/ for crystallographic files in .cif format.

Results

The crystal structure of $[CuCl(6\text{-}Me\text{-}3\text{-}HO_2CC_5H_3N)]_\infty$, **1**, contains a very simple asymmetric unit, Fig. 3(a), but the resulting extended structure is a robust lamellar solid. First, each tetrahedral copper(I) ion is coordinated to three μ_3-Cl ligands which generates a polymeric CuCl 1-D 'staircase'. The 6-methylnicotinic acid ligands are attached to the fourth coordination site of the copper ions through the pyridine nitrogen atom, [Cu(1)–N(1), 2.012(6) Å] and protrude outwards from the polymeric CuCl chain. Adjacent ligands are then hydrogen bonded to each other through acid–acid head-to-head interactions [O(7) · · · O(8), 2.631(7) Å] forming dimeric motifs. The ligand-based dimers thus act as bridges between CuCl 'staircases' and serve to propagate the 1-D polymeric chains into infinite 2-D layers, Fig. 4. The resulting sheets are non-

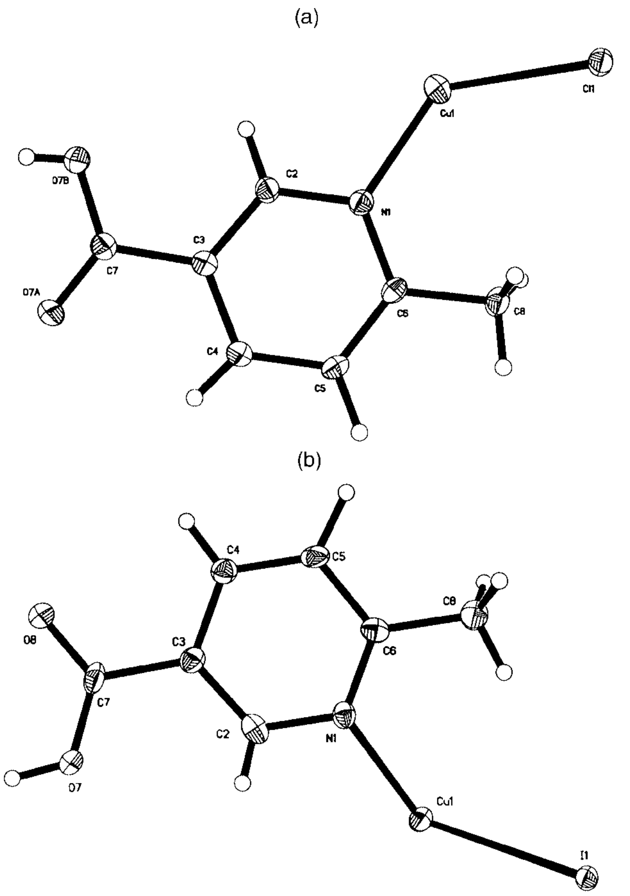

Fig. 3 Thermal ellipsoid plot (30%) and labeling schemes for compounds **1** (a) and **2** (b).

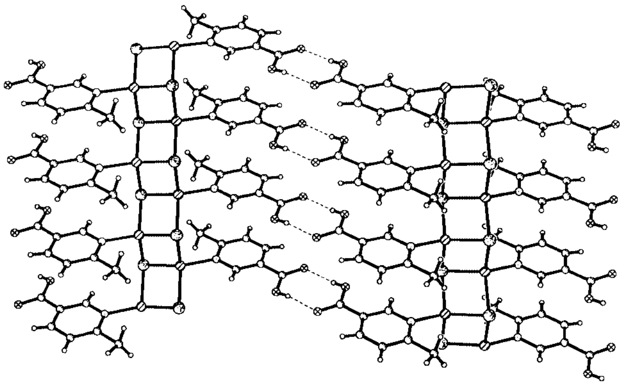

Fig. 4 Infinite 2-D sheet of $[CuCl(6\text{-}Me\text{-}3\text{-}HO_2CC_5H_3N)]_\infty$, **1**. Adjacent ligands bridge polymeric CuCl staircases *via* self-complementary O–H · · · O hydrogen bonds.

interpenetrating, slightly buckled, and stack on top of each other. The are no remarkable short contacts or noteworthy aryl–aryl interactions between adjacent sheets.

The crystal structure of $[CuI(6\text{-}Me\text{-}3\text{-}HO_2CC_5H_3N)]_\infty$, **2**, is very similar to that of **1** with an analogous asymmetric unit, Fig. 3(b). Each copper(I) ion is coordinated to three bridging iodide ligands which leads to 1-D polymeric chains arranged parallel to each other. A fourth coordination site of the metal ion is occupied by 6-methylnicotinic acid [Cu(1)–N(1), 2.06(1) Å] and all ligands protrude outwards from the 1-D CuI chain. As in **1**, the ligands form dimeric motifs through two O–H · · · O hydrogen bonds [O(7) · · · O(8), 2.64(1) Å], which subsequently bridge 1-D coordination polymers into 2-D inorganic/organic layers, Fig. 5. The buckled layers are non-interpenetrating and arranged on top of each other to yield a lamellar structure.

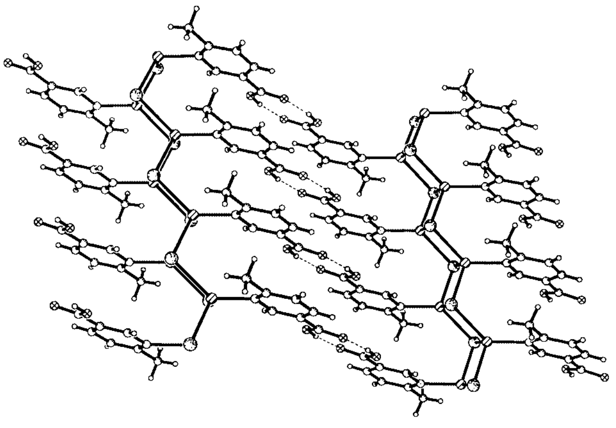

Fig. 5 Infinite 2-D sheet of $[CuI(6\text{-}Me\text{-}3\text{-}HO_2CC_5H_3N)]_\infty$, **2**. Adjacent ligands bridge polymeric CuI staircases *via* self-complementary O–H · · · O hydrogen bonds.

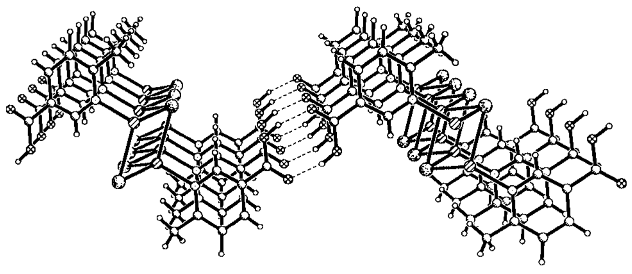

Fig. 6 Sideways view of an undulating layer in compound **2**. The layer is buckled due to the position of the hydrogen-bond moiety with respect to the pyridine nitrogen atom.

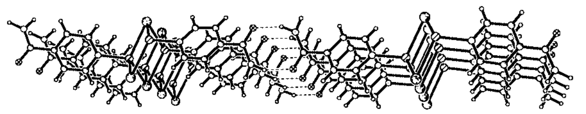

Fig. 7 Sideways view of a planar layer in $[CuI(4\text{-}H_2NCOC_5H_4N)]_\infty$.[23] The layer has a flat appearance due to the linearity of the bridging ligands.

Discussion

The structures of compounds **1** and **2** are almost identical to those of $[CuI(NC_5H_4CHNOH\text{-}3)]_\infty$, **3**,[24] $[CuI(4\text{-}H_2NCO\text{-}C_5H_4N)]_\infty$, **4**,[24] and $[CuCl(4\text{-}HO_2CC_5H_4N)]_\infty$, **5**,[25] where infinite 1-D coordination polymers are interconnected into 2-D layers through a combination of coordinate–covalent bonds and intermolecular hydrogen bonds. In each case, the short axis of the unit cell corresponds to the separation of copper ions along the staircase (3.8 Å for **1**, 3.7 Å for **5**, and 4.1 Å for **2**–**4**). In all five structures the 1-D CuX polymers are aligned parallel with each other, but the separation between them is governed by the length of the ancillary ligands and by the position of the hydrogen-bonding moiety. This family of structures is also similar to Cu^IX architectures where copper–halide staircases are interconnected through covalent bonds by bridging bidentate ligands *e.g.* pyrazine[26] and pyrimidine.[27] The precise shape of the 2-D layers in all of these cases is determined by the ligand design (angle between coordination sites) or substituent position on the intermolecular connector. Pyridine derivatives with hydrogen-bond functionalities in the *ortho* position, as well as covalent bridging ligands with an angle between N-donors, create more undulating layers, Fig. 6. On the other hand, more 'linear' ligands and *para*-substituted hydrogen-bond connectors display planar sheets, Fig. 7.

The strategy presented here for the assembly of 2-D inorganic/organic structures has shown considerable versatility and reliability: (i) three different self-complementary hydrogen-bond functionalities (oxime, amide, and carboxylic acid) have been successfully employed as directional non-covalent bridges; (ii) the layers can 'tolerate' or accommodate certain ligand modifications by changing from planar to undulating structures; and (iii) the structures are insensitive to small variations in intra-chain metal–metal separations and differences in the size of the bridging halide ligand. The structural consistency in these compounds is a result of using infinite 1-D chains as building blocks. Since the coordination polymers have a well defined geometry, they are structurally reliable and therefore reduce the task of predicting and controlling the resulting structure to a much simpler problem.

By extending this combined coordination polymer/hydrogen-bond design strategy, it is possible to envisage using a 'preformed' 2-D coordination polymer in combination with suitable organic hydrogen-bonding linkers to obtain custom-built porous solids with tunable pore sizes for a variety of host–guest applications. Further development and applications of this design principle are currently underway in our laboratories.

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