Deliberate combination of coordination polymers and hydrogen bonds in a supramolecular design strategy for inorganic/organic hybrid networks

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Received (in Columbia, MO, USA) 1st February 2000, Accepted 20th April 2000

Two crystal structures containing infinite CuI chains connected into 2-D layers by non-covalent interactions demonstrate how coordinate covalent bonds and hydrogen bonds can be combined in the design of new inorganic/organic hybrid materials.

Crystal engineering of inorganic/organic hybrid materials is typically based on a modular approach, where discrete building blocks are linked into larger networks.[1] The construction of these metal-containing networks has, so far, been achieved using two different design philosophies: adjacent transition-metal complexes are linked either through (i) coordinate covalent bonds[2] or (ii) weaker intermolecular forces (*e.g.* hydrogen bonds, aryl–aryl interactions, *etc.*).[3] Both methods have enjoyed considerable success, but there have been few *planned* attempts at using a combination of these approaches to build lamellar or 3-D architectures. Here we present two crystal structures based on copper(I) iodide and an auxiliary hydrogen-bonding ligand that demonstrate how the two philosophies can be forged into a supramolecular tool that has not yet been employed in a systematic manner.

One of the main challenges in crystal engineering is to control the assembly and solid state structures in three dimensions. This task is complicated by the fact that ionic/molecular building blocks are capable of adopting a vast number of orientations in the crystal, thus making predictions of the resulting structure very difficult. Coordination polymers, however, are typically very robust and the topology of such networks can often be predicted with the aid of well known principles of coordination chemistry.[4] Thus, by using an infinite coordination polymer with known topology instead of a discrete complex as a synthetic module, the resulting assembly process will have fewer degrees of freedom, which facilitates intermolecular synthesis. Why then use anything but coordination polymers in the design of hybrid materials? Weaker intermolecular forces can impart properties to solids that sometimes offer advantages over 'pure' coordination polymers. Materials held together by hydrogen bonds tend to be more readily soluble, which is desirable for reasons ranging from ease of synthetic modification and manipulation to crystal growth and structural characterization.[5] In addition, unlike the more rigid frameworks of coordination polymers, a network generated through hydrogen bonds[6] can 'flex' to accommodate changes in its environment, and may therefore lend itself to host–guest applications that are less accessible in a rigid framework.[7]

Copper(I) complexes with monodentate ligands, $(CuXL)_\infty$ (where L is a pyridine derivative and X is a halide), are known to form robust halogen-bridged 1-D step, stair or chain structures,[8] and several 2-D coordination polymers based on 'pre-formed' 1-D copper(I) iodide chains and cross-linking bidentate ligands have recently been reported.[9–11]

In order to change network strength and flexibility without making significant changes to the *topology* of the structure, we have replaced the bidentate bridging ligand (*e.g.* pyrazine or 4,4′-bipyridine) with a supramolecular linker capable of simultaneous metal coordination and self-complementary hydrogen bonding. To this end, we report the syntheses† and crystal structures‡ of $[CuI(3\text{-pyridinealdoxime})]_\infty$ **1** and $[CuI(\text{isonicotinamide})]_\infty$ **2**.

The crystal structure of **1** contains 3-pyridinealdoxime ligands coordinated to a polymeric 'staircase' of CuI. Each tetrahedral Cu(I) ion is coordinated to three μ_3-I ligands to generate an infinite 1-D motif. The 3-pyridinealdoxime ligand is attached to each Cu(I) ion through the pyridine nitrogen atom [Cu(1)–N(1) 2.059(3) Å], to complete the coordination sphere. The oxime ligands are staggered ($N_{py}\cdots N_{py}$ internuclear distance *ca.* 4.1 Å) along the polymeric CuI chain and protrude outward. Adjacent oxime moieties are connected *via* O–H···N hydrogen bonds [O(7)···N(7), 2.841(3) Å], in a catemer-like fashion, to propagate the 1-D polymeric chains into an infinite 2-D sheet (Fig. 1). The sheets are non-interpenetrating resulting in a lamellar structure. There are no short contacts or noteworthy aryl–aryl interactions between adjacent chains, or between neighboring sheets.

The crystal structure of **2** is very similar to **1** and also contains infinite polymeric Cu(I) chains. The isonicotinamide ligand occupies the fourth coordination site of the Cu(I) center by coordination through the pyridine nitrogen atom [Cu(1)–N(1) 2.02(2) Å].

Adjacent isonicotinamide molecules form two self-complementary N–H···O hydrogen bonds [N(8)···O(9) 2.87(3) Å] to yield a head-to-head amide–amide dimer. Through this intermolecular interaction, the carboxamide functionalities act as linear, bridging linkers between CuI 'staircases' to generate two-dimensional infinite sheets almost identical to those displayed by **1**, Fig. 2.

The structures of **1** and **2** are very similar to copper(I) iodide architectures where copper–halide staircases are interconnected through covalent bonds by bridging bidentate ligands.[10] In general, these staircases are normally aligned parallel to each other along the short axis of the unit cell. The length of this axis (which also corresponds to the Cu···Cu separation within a staircase) is *ca.* 4.1–4.4 Å for CuI,[9,10] 3.95–3.98 Å for CuBr, and 3.75–3.78 Å for CuCl containing motifs. The precise orientation and separation of neighbouring ribbons is determined by the specific geometry of the ligand(s). Variations in

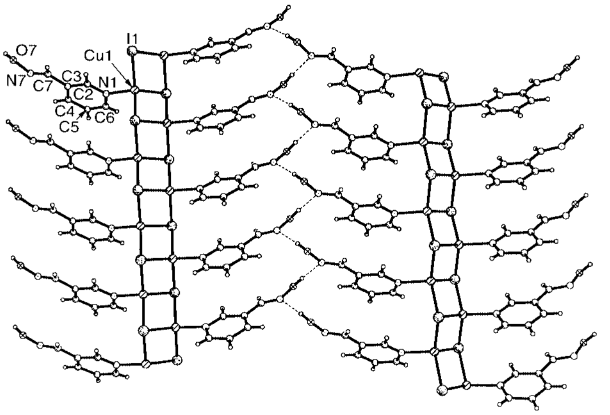

Fig. 1 Infinite 2-D sheets of $[CuI(3\text{-pyridinealdoxime})]_\infty$ **1**. Adjacent oxime moieties bridge polymeric 'staircases' of CuI *via* catemeric hydrogen bonds.

DOI: 10.1039/b001001o

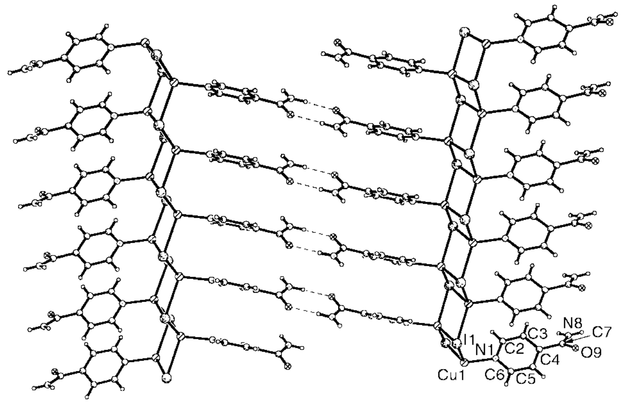

Fig. 2 Infinite 2-D sheets of [CuI(isonicotinamide)]$_\infty$ **2**. Head-to-head amide–amide interactions between isonicotinamide ligands cross-link CuI 'staircases'.

the size and substituent position(s) of the ligand also lead to modifications of the resulting layer (*e.g.* planar *vs.* undulating).

Although the chemical properties of the hydrogen-bonding moieties on the two pyridine-based ligands in **1** and **2** are different, their structural influence is very similar: network topologies and unit cell dimensions are nearly identical.[12] This, of course, is a benefit of using 1-D polymeric chains as building blocks; they are structurally reliable and therefore reduce the task of prediction and control to a much simpler problem. By extending this combined coordination polymer/hydrogen-bond design strategy, one can envisage using a 'pre-formed' 2-D coordination polymer in combination with suitable organic hydrogen-bonding linkers to obtain custom-built porous solids for host–guest applications, *e.g.* separation and catalysis. Further development and applications of this design principle are currently underway in our laboratories.

We acknowledge financial support from Kansas State University and DuPont.

Notes and references

† 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. In both cases, yields were *ca.* 70–75%.

[CuI(3-pyridinealdoxime)]$_\infty$, **1**: 3-pyridinealdoxime (0.10 g, 0.82 mmol) in the minimum amount of diethyl ether was layered on top of CuI (0.16 g, 0.84 mmol) in acetonitrile. The layered solution was covered and allowed to stand in ambient air. After 1–2 days, yellow rods of **1** were obtained. Mp > 210 °C (decomp.).

[CuI(isonicotinamide)]$_\infty$, **2**: acetonitrile was carefully layered over a solution of isonicotinamide in THF. A saturated solution of CuI in acetonitrile was then added dropwise to the acetonitrile layer. The layered solution was allowed to stand in ambient air. Slow diffusion produced yellow rods of **2** in 1–2 days. Mp > 270 °C (decomp.).

‡ *X-Ray crystallography*: crystalline samples of **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 (λ = 0.71073 Å) radiation at 173 K. The structures were solved using heavy-atom methods using SHELXS-97 and refined using SHELXL-97 (G. M. Sheldrick, University of Göttingen). 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 those for **2** were placed at calculated positions. All hydrogen atoms were 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.

Crystal data: for **1**: $C_6H_6N_2OCuI$, M = 312.57, monoclinic, space group $P2_1/c$, a = 13.544(1), b = 4.1098(4), c = 15.094(1) Å, β = 105.583(2)°, U = 809.3(1) Å^3, Z = 4, D_c = 2.565 g cm^{-3}, T = 173(2) K, μ(Mo-Kα) = 6.452 mm^{-1}, wR_2 = 0.0665 (1859 reflections collected, 1752 unique), R = 0.0253 [$I > 2\sigma(I)$].

For **2**: $C_6H_6N_2OCuI$, M = 312.57, monoclinic, space group $P2_1/c$, a = 13.459(2), b = 4.0960(6), c = 16.649(3) Å, β = 109.617(3)°, U = 864.6(2) Å^3, Z = 4, D_c = 2.401 g cm^{-3}, T = 173(2) K, μ(Mo-Kα) = 6.040 mm^{-1}, wR_2 = 0.3177 (1997 reflections collected, 1768 unique), R = 0.0868 [$I > 2\sigma(I)$].

CCDC 182/1617. See http://www.rsc.org/suppdata/cc/b0/b001001o/ for crystallographic files in .cif format.

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