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The First Triple-Layer 2-D Coordination Polymer: $[Cu_3(bpen)(IN)_6(H_2O)_2]$

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Crystal engineering of interpenetrating network structures has been a very attractive area of research in metal−organic polymers and supramolecular architecture design.[1−4] Coordination networks and interpenetrating structures have been reviewed recently.[3−5] While various fascinating open-framework coordination polymers and interpenetrating architectures have been synthesized, no structures with multiple-layer two-dimensional open frameworks have been reported. The multiple layer here is defined as two-dimensional (2-D) layer networks with more than two covalently bonded layers. Several bilayer architectures have just been reviewed by Zaworotko in which the bilayers formed by partial interdigitation.[4] One of our research interests has focused on open-framework metal−organic polymers constructed by using mixed building blocks. Bidentate organic ligands such as 4,4′-bipyridine (bpy) and *trans*-1,2-bis(4-pyridyl)ethylene (bpen) have been extensively used as single spacers to link network structures.[6] The isonicotinato (IN) ligand has recently shown interesting properties.[7] The copper(II) ions demonstrated a strong tendency to form the square pyramidal geometry in open-framework structures when coordinated by isonicotinate ligands in $\{[Cu_2(IN)_4{\cdot}3H_2O]{\cdot}[Cu_2(IN)_4{\cdot}2H_2O]\}{\cdot}3H_2O$ **1** (Figure 1), while at the same time, copper(II) ions can form the octahedral geometry as well.[7b] By replacing the water molecules in the apical position by an isonicotinate ligand in Figure 1, the square pyramidal layered network may be used to terminate extended networks at the third dimension. The bidentate ligands, such as bpen, may be used to bridge the Cu(II) octahedral centers between the square pyramidal terminal layers, thus, a multiple-layer two-dimensional open-framework structure may be self-assembled. Although this two-dimensional multiple-layer network sketch is only one of many possible choices, our initial attempt at the self-assembly of a multiple-layered two-dimensional structure under hydrothermal conditions resulted in dark blue polyhedral crystals that were later revealed, by single-crystal X-ray diffraction analysis, to have an unprecedented two-dimensional triple-layer open-framework structure stack-interlocked into a three-dimensional (3-D) polymeric coordination network; $[Cu_3(bpen)(IN)_6(H_2O)_2]$ **2**.

The reaction of $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.2326 g) with isonicotinic acid (0.1231 g), bpen (0.1842 g), and water (6.0 mL), in the mole ratio of 1:1:1:333 at 140 °C under hydrothermal conditions for 3 days, produced dark blue crystals of **2**. The dark blue crystals are suitable for single-crystal X-ray diffraction analysis.[8] The structure of **2** consists of two independent copper atoms (Figure 2). The copper atom 1 has square pyramidal geometry, while copper atom 2 is in an octahedral site (Figure 3). The octahedral copper metal centers are coordinated by two carboxylate groups of two IN units in a monodentate fashion at the axial positions, while two water molecules and two bpen spacers are at the equatorial sites (Figure 4). The axial IN units utilizing pyridyl groups occupy the apical positions of the square pyramidal copper atoms, while four equatorial positions of the square pyramidal copper atoms are coordinated by two pyridyl groups and two carboxylate groups of four IN ligands. Thus, the octahedral copper centers are bridged between two square pyramidal copper-centered networks by two connected tridentate IN units to form a triple-layer open-framework structure (Figure 5). The triple-layer structure is assembled in such a way that the Cu octahedral centers are located close to the centers of the adjacent Cu−bpen−Cu linkages. The triple-layer 2-D open frameworks propagate along

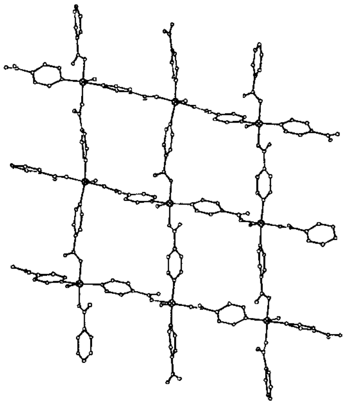

Figure 1. Square pyramidal geometry of Cu(II) ions in **1**.

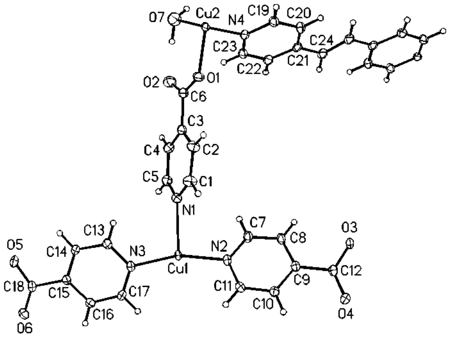

Figure 2. View of the asymmetric unit (with bpen filled out) showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter.

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(6) See, for example: (a) Yaghi, O. M.; Li, G. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 207. (b) Dong, Y.-B.; Layland, R. C.; Pschirer, N. G.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H-C. *Chem. Mater*. **1999**, *11*, 1415.

(7) (a) Evans, O. R.; Xiong, R.-G.; Wang, Z.; Wong, G. K.; Lin, W. *Angew. Chem., Int. Ed*. **1999**, *38*, 536. (b) Lu, J. Y.; Babb, A. M. *Chem. Commun*. **2001**, 821−822.

(8) Crystal data for **2**: FW, 1141.48; monoclinic, space group, $I2/a$; cell dimensions $a = 11.839(1)$, $b = 13.377(1)$, $c = 28.522\ (2)$ Å, $\beta = 98.209(1)°$, $U = 4470.6(6)$ Å^3, $Z = 4$, $D_c = 1.696$ g cm^{-3}, $\mu = 1.497$ mm^{-1}, $T = 223(2)$ K. Reflections collected, 11656; independent reflections, 4119 [$R(\text{int}) = 0.0224$]. Final R indices [$I > 4\sigma(I)$]: $R_1 = 0.0264$, w$R_2 = 0.0785$.

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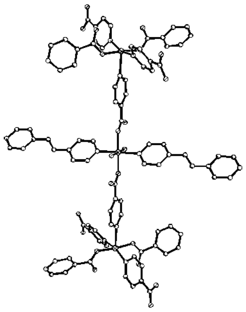

Figure 3. View of the complete coordination spheres about the two independent Cu atoms and the connection between them. Cu atom 1 is square pyramidal and Cu atom 2 is octahedral geometry.

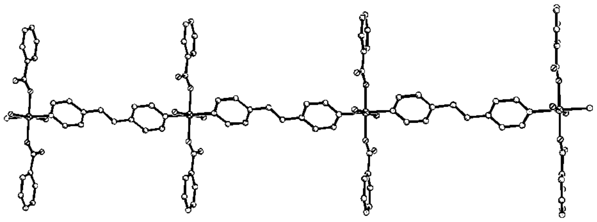

Figure 4. Portion of the middle layer of a triple-layer network along the *b* axis. The middle layer, containing bridging bpen, is sandwiched by layers containing bridging IN.

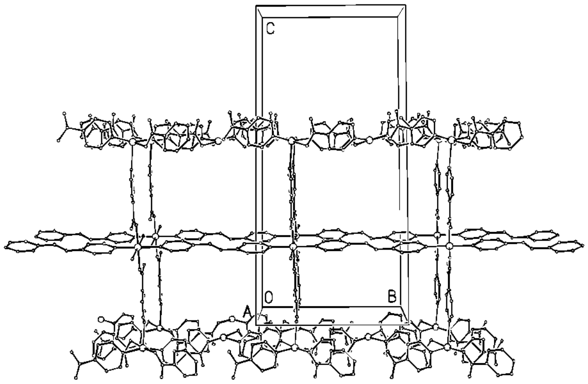

Figure 5. View of a portion of the triple-layer structure.

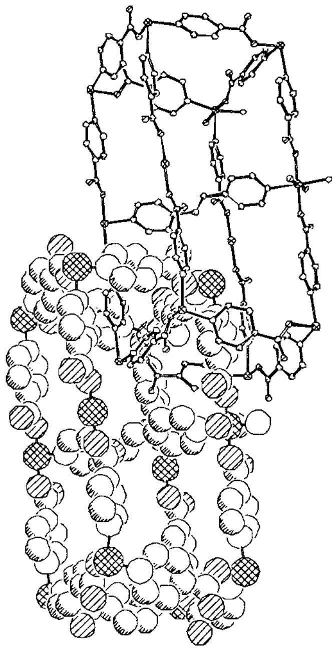

Figure 6. View of two interlocked square columns.

the *b* and *a* axes and terminate along the *c* axis. This novel triple-layer 2-D open framework is then stack-interlocked into a 3-D structure. While single-layer interpenetrating networks are common,[4,5] the multiple-layer stack-interlocked structure in **2** has never been observed, though this may not be surprising. The actual stack-interlocked units are shown in Figure 6. The two square columns are corner-interlocked. The bpen linear unit diagonally bridges octahedral copper centers in the middle of the square column. This framework in **2** is thermally stable up to 280 °C.

The noninterlocking multiple-layer 2-D open framework may have potential applications in many aspects, such as molecular sorption and separation, since it has attractive features from both 3-D and 2-D open-framework structures: open channels in 2-D networks. We are now actively searching for synthetic conditions to prepare multiple-layer 2-D open-framework metal−organic polymers under hydrothermal conditions.

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Supporting Information Available: Crystallographic tables from 1 to 5 and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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