Synthesis and Structure of a New 3D Porous Cu(II)–Benzene-1,3,5-tricarboxylate Coordination Polymer, $[Cu_2(OH)(BTC)(H_2O)]_n \cdot 2nH_2O$

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(Received April 4, 2003; CL-030294)

The reaction of $Cu(NO_3)_2 \cdot 3H_2O$ with benzene-1,3,5-tricarboxylic acid (H_3BTC) and H_2O under hydrothermal conditions affords a new three-dimensional porous coordination polymer, $[Cu_2(OH)(BTC)(H_2O)]_n \cdot 2nH_2O$, which contains 5 × 7 Å dimension lozenge shaped 1D open channels along the crystallographic *a* axis.

The demand for new materials with practical applications has promoted research in the design and synthesis of functional porous coordination polymers that possess attractive properties such as zeolite-like characteristics,[1,2] gas storage,[3–5] nonlinear optical behavior,[6] and magnetism.[7–9] This class of compounds can be easily obtained through self-assembly of metal ions and multifunctional ligands. The versatility of organic functional groups and the diversity of metal coordination geometries have far produced several novel porous coordination polymers. Control of their molecular architecture is facilitated by suitable choices of metal and ligand sets based on their coordination habits and geometric preferences; however, a wide range of possible product phases can be found for most metal-ligand systems. Synthetic conditions such as reaction temperatures, solvents play major roles in determining the outcome.

Benzene-1,3,5-tricarboxylic acid (H_3BTC) is a useful three-connecting ligand for preparing carboxylate polymers from a range of *s*-block and *d*-block divalent transition metal cations by hydrothermal and solution synthesis.[10–13] In this paper, we report a new three-dimensional porous coordination polymer, $[Cu_2(OH)(BTC)(H_2O)]_n \cdot 2nH_2O$ (**1**) built upon copper(II) and BTC. The synthetic procedure of **1** was similar to that of $[Cu_3(BTC)_2(H_2O)_3]_n$ (HKUST-1),[11] merely replacing water/methanol by water as solvent.

The compound **1** was prepared under hydrothermal conditions: an exact amount of H_3BTC (1.5 mmol, 0.315 g) and copper(II) nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$ (0.5 mmol, 0.120 g) were dissolved in 10 mL of water. The mixture was then heated to 120 °C in a 23 mL Teflon-coated stainless-steel autoclave and held at that temperature for 24 h and then cooled to room temperature. The plate-like blue crystals of **1** suitable for X-ray diffraction analysis were collected after washing by water, which was stable in air and insoluble in water and common organic solvents such as methanol, DMF, ether, acetonitrile, $CHCl_3$, benzene and toluene. Elemental analysis (%). Calcd for $C_9H_{10}O_{10}Cu_2$: C, 26.67; H, 2.47; Found: C, 26.93; H, 2.73. By replacing water served as solvent in the former procedure by water/ethanol, $[Cu_3(BTC)_2(H_2O)_3]_n$ can be obtained under the similar conditions.

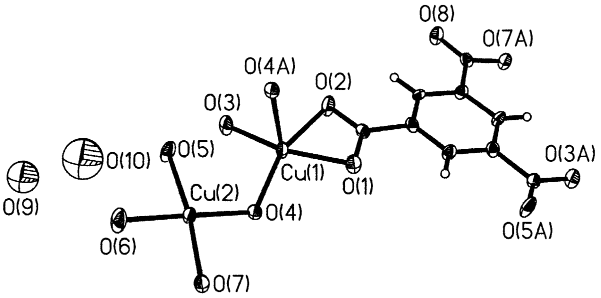

Figure 1. ORTEP drawing of **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Cu(1)–O(1), 1.996(5); Cu(1)–O(2), 2.045(6); Cu(1)–O(3), 1.927(6); Cu(1)–O(4), 1.904(5); Cu(1)–O(4A), 2.351(6); Cu(2)–O(4), 1.910(5); Cu(2)–O(5), 1.982(5); Cu(2)–O(6), 1.927(6); Cu(2)–O(7), 1.949(5); O(1)–Cu(1)–O(2), 65.4(2); O(3)–Cu(1)–O(2), 93.6(2); O(4)–Cu(1)–O(3), 97.8(2); O(4)–Cu(1)–O(1), 99.1(2); O(1)–Cu(1)–O(4A), 96.5(2); O(2)–Cu(1)–O(4A), 91.7(2); O(3)–Cu(1)–O(4A), 91.6(2); O(4)–Cu(1)–O(4A), 109.9(2); O(4)–Cu(2)–O(5), 93.5(2); O(6)–Cu(2)–O(5), 85.1(3); O(6)–Cu(2)–O(7), 87.5(2); O(4)–Cu(2)–O(7), 93.6(2); Cu(1)–O(4)–Cu(2), 119.5(3).

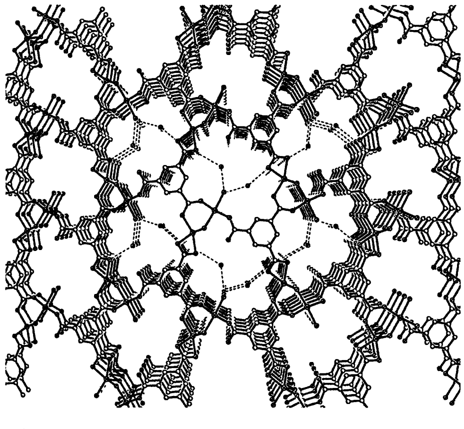

Figure 2. The crystal structure of **1** shown down the crystallographic *a* axis, where lozenge shaped 1D open channels (with edge lengths of 5 and 7 Å) are occupied by water guests.

A single crystal X-ray diffraction study[14] reveals that **1** is a 3D porous coordination polymer consisting of four-coordinate and five-coordinate copper (II) atoms. As is shown in Figure 1, the asymmetric unit consists of two independent copper atoms, one μ_3-hydroxyl group, one BTC ligand, one coordinated H_2O molecule, and two uncoordinated H_2O molecules. The coordination sphere of Cu(1) can be described as a square pyramidal, with three oxygen atoms from two carboxylate

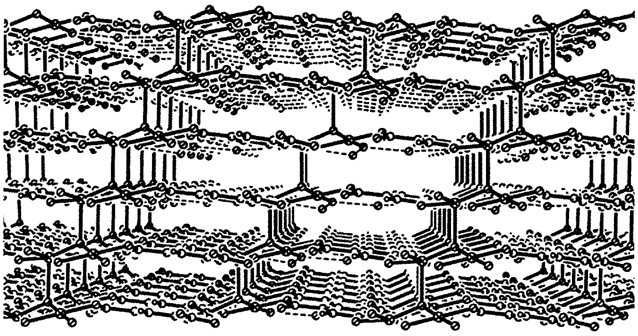

Figure 3. View of **1** along the crystallographic *b* axis showed the distance between the adjacent layers is 2.351 Å.

groups of two different BTC^{3-} ligands and one oxygen atom from a μ_3-hydroxyl group occupy the equatorial position, while one oxygen atom from other μ_3-hydroxyl group occupies the apical position. The square planar copper metal atom (Cu(2)) is coordinated by two oxygen atoms from two carboxylate groups of two different BTC^{3-} ligands, one oxygen atom from μ_3-hydroxyl group, and one oxygen atom from water molecule.

Each Cu(1)···Cu(2) pair is connected through one carboxylate group by μ_2 bonding mode and one μ_3-hydroxy group. The Cu_2 unit, which acts as a node, is connected to six adjacent nodes through three BTC ligands to form a 2D layer parallel to the *bc* (*yz*) plane. The remaining coordination site of the Cu(1) center in each Cu_2 unit is occupied by oxygen atom of μ_3-hydroxy group, which bind the adjacent 2D layers to generate a 3D framework and yield an open 1D channels (approximately 5×7 Å, based on the van der Waals radius), as illustrated in Figure 2. The distance between two adjacent layers is 2.351 Å (Figure 3). The free space accommodates two H_2O molecules per formula unit, and the H_2O molecules coordinated to Cu(2) atoms point toward the center of the channels.

It is worth noting that three carboxylate groups of each BTC ligand in **1** adopt different coordination fashion, that is, monodentate, bridging bidentate, and chelating bidentate, respectively.

In contrast to **1**, the structure of $[Cu_3(BTC)_2(H_2O)_3]_n$ contains the paddle-wheel $Cu_2O_8C_4$ units.[11] Six Cu_2 units and four BTC ions formed an octahedral secondary building units (SBU). The framework was then achieved by connecting the SBU with other units through corner sharing of the octahedra.

In the case of Cu(II) and H_3BTC, we have found that H_3BTC was less dissolved in water than in water/ethanol. It might be stated that the solubility of H_3BTC in different solvents leads to the different outcome.

Under air environment, thermogravimetric analysis (TGA) performed on **1** showed one-step weight loss of H_2O in the range of 120–200 °C. The compound is compositionally stable to 280 °C based on TGA data. However, PXRD analysis after heating indicated that **1** lost the structure at about 230 °C. Analysis of PXRD patterns indicated CuO as the only residue after the sample was heated to 600 °C.

In summary, we have synthesized a new porous coordination polymer, $[Cu_2(OH)(BTC)(H_2O)]_n \cdot 2nH_2O$ just by changing the reaction solvent of the recipe to the HKUST-1. This result indicates that a wide range of possible product phases can be found for the same metal-ligand system.

We are grateful for the financial support from National Nature Science Foundation of China (Nos. 20241004 and 29925309), State Key Basic Research Program of PRC (G200048001), Shanghai Education Committee (02SG01), and Postdoc. Foundation of Shanghai.

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14 Single crystal X-ray data was collected on a Bruker Smart APEX diffractometer at room temperature. Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXTL Version 5.10), and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were treated as idealized contributions. Crystal data for **1**. $C_9H_3O_{10}Cu_2$ (293 K). $M_r = 398.19$, monoclinic, space group *Pn*, $a = 3.4926(10)$ Å, $b = 9.828(3)$ Å, $c = 17.185(5)$ Å, $\beta = 93.753(3)^\circ$, $V = 588.6(3)$ Å^3, $Z = 2$, $D_{calcd} = 2.247$ g/cm^3, absorption coefficient = 3.666 mm^{-1}, total reflections collected 2908, unique 2085 ($R_{int} = 0.0169$), GoF = 1.048, $R1 = 0.0448$, $R_w = 0.1234$ ($I > 2\sigma(I)$), $R1 = 0.0454$, $R_w = 0.1240$ for all data. Crystallographic data (excluding structure factors) for 1 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 207414. Copies of the data can be obtained free of charge in application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).