A Three-dimensional MOF Assembled by Metal-organic Tapes Comprising of Copper(II) Tetranuclear Clusters and 5-Sulfoisophthalates

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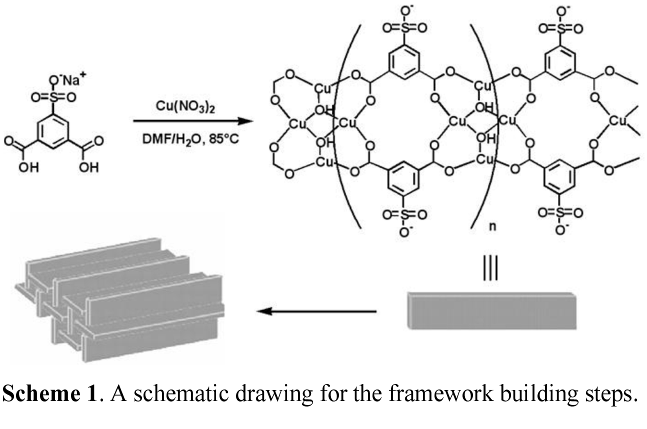
Growing efforts to construct new MOFs (metal-organic frameworks) have been focused at developing functional materials exhibiting applicable catalytic, gas storage and separation, magnetic, and sensing properties.[1] Currently, one of the most challenging goals in the field of MOF chemistry is to build the frameworks by design in order to endow them those properties or improved functions. Several research groups have developed and demonstrated rational design sterategies toward desired framework structures and in turn better functional materials.[2] However, as there are many framework structures that do not follow nature's default network types, many examples for the unprecedented structures need to be explored and classfied to figure out their assembling patterns or rules as demonstrated by the cases of 1D infinite chains.[3] Here we present a rare example that 1D metal-organic frameworks containing an unusual copper tetranuclear inorganic building block are assemlbed to form a 3D framework. Before our work, two MOFs sharing similar structural features as our case were reported.[4] However, our preparation method is simpler and milder than the reported ones,[5] and in addition, the crystal strcuture is slightly different from those due to the changes in the additional coordinating ligands.

Reaction of 5-sulfoisophthalic acid sodium salt with $\mathrm{Cu(NO_3)_2{\cdot}2.5H_2O}$ in a mixed solvent of DMF and water at 85 °C for 2 days produced large rectangular blue crystals of **1** formulated as $\{[\mathrm{Cu_4}\mathbf{L}_2(\mathrm{OH})_2(\mathrm{DMF})_2]\cdot 3(\mathrm{DMF})\}_n$ (**1**) (**L** = 5-sulfoisophthalate, DMF = *N,N*-dimethylformamide). The X-ray crystal structure of **1** revealed the formation of infinite 1D chains or "tapes" composed of tetracopper clusters held by two μ_3-hydroxo groups as inorganic building blocks, and 5-sulfoisophthalates as organic linkers (Scheme 1).[5]



Scheme 1. A schematic drawing for the framework building steps.

The crystallographic asymmetric unit of **1** contains two independent half-occupied copper ions and also a half-occupied **L** (Figure 1). Cu(1) sits on a crystallographic mirror plane (*m*) and Cu(2) does on a 2-fold rotation axis, which requires two symmetry-related copper atoms. These four copper atoms are held by two μ_3-bridging hydroxo groups to form a tetranuclear cluster. These hydroxo oxygen atoms also sit on a mirror plane, and are placed opositely by 0.375(4) Å above and below the mean plane defined by the four copper atoms.

Cu(1) and Cu(2) show a sqare-pyramidal and a distorted octahedral coordiantion geometry, respectively. Cu(1) is coordinated by two oxygen atoms (O(2) and its symmetry-related O(2)) of carboxylate of **L**, one oxygen atom O(1C) of μ_3-bridging hydroxo group, one oxygen atom (O(1S)) of DMF in the equatorial positions. The axial oxygen atom (O(4)) is provided by the sulfonate group of the neighboring

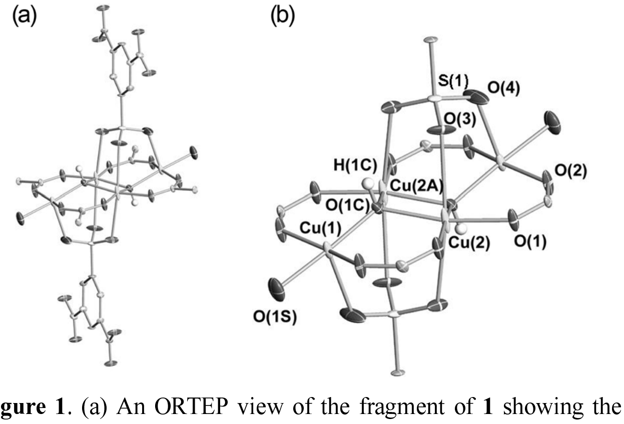


Figure 1. (a) An ORTEP view of the fragment of **1** showing the coordination sphere around tetranuclear copper centers. (b) A closer view around the copper ions with atomic labels. A crystallographic inversion center is present in the middle of the fragment. Selected inter-atomic distances: Cu(1)-O(1C) = 1.936(5), Cu(1)-O(2)$^{\#1}$ = Cu(1)-O(2)$^{\#2}$ = 1.928(4), Cu(1)-O(1S) = 1.955(6), Cu(1)-O(4)$^{\#3}$ = 2.284(7), Cu(2)-O(1C) = Cu(2)-O(1C)$^{\#2}$ = 1.985(3), Cu(2)-O(1) = Cu(2)-O(1)$^{\#1}$ = 1.954(4), Cu(2)-O(3) = Cu(2)-O(3))$^{\#4}$ = 2.610(4), Cu(1)···Cu(1)$^{\#2}$ = 6.137(2), Cu(2)···Cu(2)$^{\#2}$ = 3.006(2), Cu(1)···Cu(2) = 3.417(1) Å. Symmetry transformations used to generate equivalent atoms: #1, −x, −y, z; #2, −x, −y, −z+2; #3, −x−1/2, y+1/2, −z+3/2; #4, −x−1/2, y−1/2, −z+3/2.

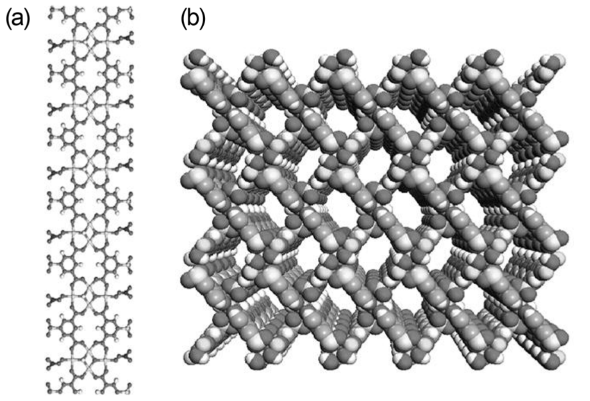


Figure 2. (a) Ball-and-stick drawing of the 1D metal-organic tape. (b) space-filling model of the 3D network produced by the stacking of the 1D tapes adopting a herring-bone-like fashion. Occluded DMF molecules were omitted for simplicity.

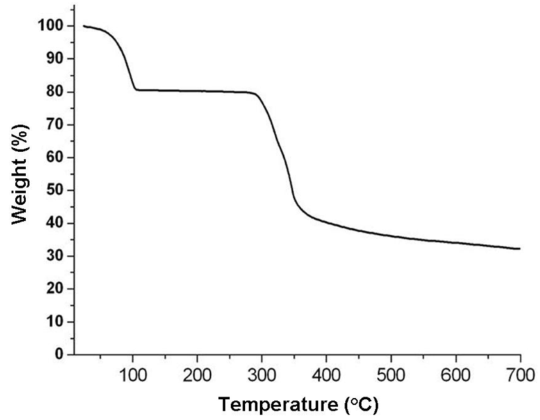


Figure 3. Weight change of **1** measured by a TGA apparatus. Temperature was increased at a rate of 5 °C/min and under a nitrogen atmosphere.

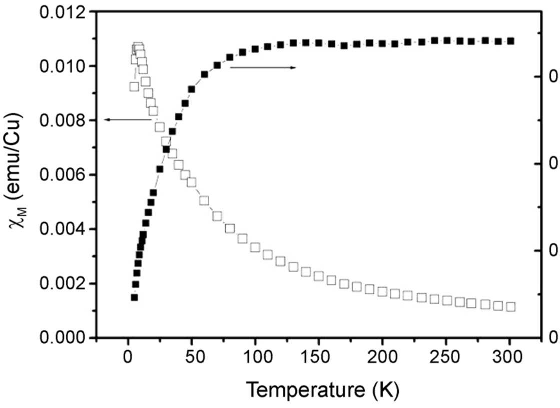


Figure 4. Magnetic property of **1** measured by SQUID.

L. In the equatorial positions, Cu(2) has two oxygen atoms (O(1) and its symmetry-related O(1)) from the sulfonate group of the in-plane **L**, and two hydroxo oxygen atoms as donor atoms. Two axial oxygen atoms are donated by the sulfonate group of the neighboring **L**, and are weakly bound to the copper atom at a distance of 2.610(4) Å. This elongation of the bond distances in the axial directions is attributed to a typical Jahn-Teller effect. These overall coordination feature is similar to that of the tetracopper cluster in a discrete coordination molecule.[6] However, in the complex only two oxygen atoms of the sulfate anions are coordinated to two central copper ions with a bi-mono-dentate fashion, and in addition, two hydroxo groups are placed on the same side of the tetranuclear copper plane.

The infinite 1D metal-organic tape has a width of 14.3 Å and expands along the *c*-axis with anionic sulfonate groups at the peripheral (Figure 2). It is interesting that the directions of the three sulfonyl oxygen atoms were matched exactly to the copper centers of the neighboring metal-organic tapes to give a 3D network. This herring-bone-like stacking of 1D metal-organic tapes produced 1D channels (7 × 8 Å) filled with free DMF molecules.

Thermogravimetric (TG) analysis of the as-synthesized **1** indicated that the framework was stable under nitrogen atmosphere up to 300 °C after full evaporation of the free DMFs at about 100 °C (Figure 3). On the othr hand, the coordinated DMF molecules were too tightly bound to the framework to be removed thermally before the framework collapses. The empty framework seems to be weak in maintaining the void space because it does not uptake nitrogen and hydrogen gases at all. However, it was possible to replace partially the coordinated DMFs with pyridines in the solution; the FT-IR absorption bands of the coordinated DMF at 1660 cm^{-1} and 1195 cm^{-1} decreased significantly, and a new strong peak of pyridine at 756 cm^{-1} was observed. Without the included guest DMF molecules the calcuated solvent accessible volume was 39.4% of the unit cell volume.

The magnetic susceptibility measurements performed over 2-300 K resulted in the curve characteristic of antiferromagnetic interactions among the copper(II) ions (Figure 4). The value of μ_{eff}, 3.32 μ_{B} at 300 K is slightly less than that of four non-interacting Cu(II) ions (≈ 3.80 μ_{B}, assuming g = 2.2), suggesting that the magnetic interaction is weak. The Weiss temperature of –3.41 K calculated in between 100 to 300 K, also implies that **1** is dominated by antiferromagnetic exchange.[7]

In conclusion, we have presented a facile synthesis of a three-dimensional MOF assembled by 1D metal-organic tapes. The unique copper(II) tetranuclear cluster is anticipated to play a role as a versatile building block in forming other MOFs with different network types from that shown in this work.

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5. Synthesis of **1**: 5-Sulfoisophthalic sodium salt (100 mg, 0.37 mmol) and $Cu(NO_3)_2{\cdot}2.5H_2O$ (173 mg, 0.74 mmol) were dissolved in a mixed solution of DMF (6.0 mL) and water (3.0 mL), which was placed in a 20 mL vial with a cap. This solution was kept at 85 °C for 2 days, and then blue rectangular crystals were collected and washed with DMF (160 mg, 78%). Anal. Calcd for $C_{31}H_{43}N_5O_{21}S_2Cu_4$: C, 32.66; H, 3.80; N, 6.14; S, 5.62%. Found: C, 32.35; H, 3.89; N, 6.06; S, 5.78%. Crystal data for **1**: $C_{31}H_{43}N_5O_{21}S_2Cu_4$, Mw = 1139.98, orthorhombic, *Pnnm*, $Z = 2$, $T = 173(2)$ K. $\lambda(\text{Mo-K}_\alpha) = 0.71073$ Å, $a = 11.5537(5)$, $b = 16.7793(8)$, $c = 10.8908(5)$ Å, $V = 2111.3(2)$ Å^3, $d_x = 1.793$ g/cm^3, $\mu(\text{Mo-K}_\alpha) = 2.174$ mm^{-1}, F(000) = 1160, Bruker APEX CCD diffractometer, total 12020 measured reflections, 2528 independent reflections, $R_{int} = 0.0501$. Absorption corrections using SADABS. Refinement on F^2 using SHELXL-97 converged to R1 = 0.0629, wR2 = 0.1754 for 1945 reflections with $I > 2\sigma(I)$, respectively. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-709712). That data can be obtained free of charge via http://www.ccdc.cam.ac.uk/perl/catreq.cgi (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
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