Crystal Engineering of 3D Porous Coordination Polymers through Hydrogen Bonding to Coordination from 1D Helical Chains

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The combination of salicylic acid and 4-aminopyridine leads to a 3D hydrogen bonding network while the replacement of 4-aminopyridine with 4,4′-bipyridine yields the same topological net with big channels via coordination.

The construction of porous framework through crystal engineering[1] is currently attracting a considerable interest because of their potential applications in catalysts,[2] gas sorbents,[3] ion-exchange,[4] and so on. Strategies for assemblies of these novel materials includes hydrogen-bonded architecture, pillared clay mimics, zeolite analogues, and coordination polymer chemistry.[5] A key challenge in the porous coordination polymers is to design and synthesize predictable topological structures or control the dimensionality of coordination polymers.[6]

Salicylic acid, H_2sal, has received a great deal of interest as a bifunctional ligand capable of forming coordination polymers in this laboratory.[7] The structures associated with this ligand are controlled by the extent of deprotonation of the H_2sal, such as sal^- and sal^{2-}, and the nature of the second ligand coordinated to the metal center.[8] The bidentate property of 4-aminopyridine ligand (4AP) reported by Rosseinsky[5] raised our interest to construct high dimensional coordination polymers. Thus the combination of salicylic acid and 4-aminopyridine leads to a helical chain and extended 3D network via hydrogen bonding.

Slow diffusion of 4AP into a water/methanol solution of copper acetate and H_2sal yields pure compound **1**, $[Cu(sal)(4AP)(H_2O)]_n$.[9] The molecular structure of **1**, established by single-crystal X-ray diffraction analysis,[11] is shown in Figure 1(a). Each sal is fully deprotonated, namely sal^{2-}. The sal ligand acts as a bridging ligand to two Cu^{II} via the oxygen atoms. The copper center in **1** is a square pyramidal with three oxygen atoms of the sal and a pyridine-N atom of 4-aminopyridine occupying the basal positions and the oxygen atom of water occupying the apical position. As a consequence of the sal bridge, compound **1** has an extended 1D helical structure as shown in Figure 1(b). Each motif of $[Cu^{II}(sal)]_n$ in the 1D chain is linked through hydrogen bond to three neighbouring chains having opposite helicity with a Cu···Cu separation of 4.692(3) Å. The atoms of water molecules with pyridine-N atoms of 4AP from the neighboring 1D chains form hydrogen bonds [O···N, 2.951(7) Å]. Moreover one-dimensional helical network has three orientational hydrogen-bonded sites, directing a 3D network with small channels (Figure 2). The bifunctional 4-aminopyridine ligand therefore allows the construction of molecular frameworks in which the infinite one-dimensional helical building blocks characteristic of sal are linked to form a hydrogen-bonded three-dimensional pore network. The combination of 4-aminopyridine and water consists of a hydrogen-bond spacer ligand, namely APW, leading to a 3D network with little porosity and the separation of Cu···Cu by APW linker is 9.902(3) Å.

The small porosity in compound **1** is caused by short linker of APW. If we keep the robust of framework supported by sal

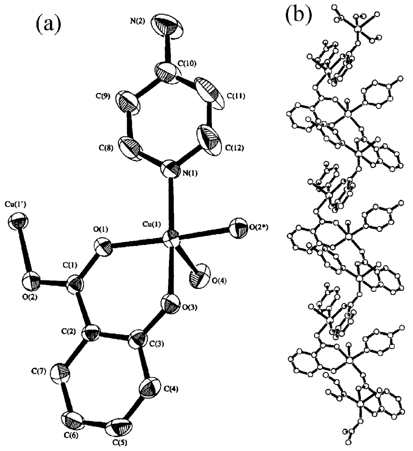

Figure 1. (a) An ORTEP view of **1** with 50% ellipsoids and labelling scheme. Important bond distances (Å):Cu(1)-O(1) 1.942(4), Cu(1)-O(2*) 1.991(3), Cu(1)-O(3) 1.917(3), Cu(1)-O(4) 2.364(4), Cu(1)-N(1) 2.018(3). (b) View of 1D helical chain of **1**.

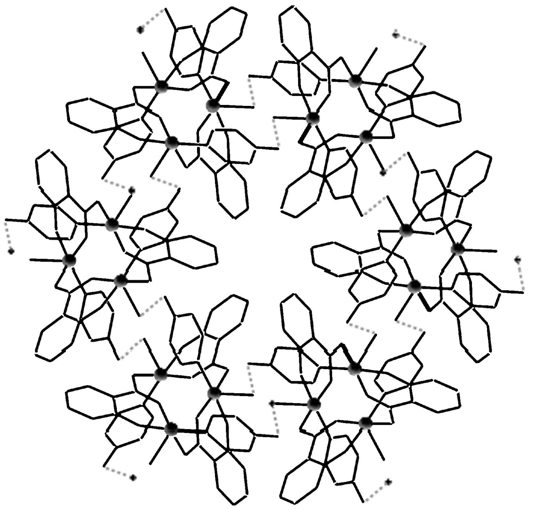

Figure 2. View of 3D hydrogen bonding network of **1** along c axis.

while replace the combination of hydrogen-bond ligand (APW) into a rigid and long spacer ligand, the same topological 3D net and bigger channel will be expected. This idea was achieved by the combination of H_2sal and 4,4′-bipyridine (4,4′-bipy) leading to the formation of compound **2**, $[Cu(sal)(4,4'\text{-bipy})]_n$.[10] The compound **2** was obtained from the reaction of $Cu(CH_3COO)_2$, salicylic acid and 4,4′-bipy in mixed solvents of DMF and methanol.

In compound **2** the copper center has a square pyramidal geometry, and with shorter bond lengths comparing with that of in **1** (Figure 3). And in 1D motif, $[Cu^{II}(sal)]$, of compound **2** is the same as that of compound **1** and the separation distance between two neighboring Cu^{II} ions in the 1D chain of **2** is 4.58(1) Å, much shorter than that of in **1**. Obviously compound **2** has a compact structure comparing with that of compound **1**.

3D coordination polymer of compound **2** is constructed by 1D helical chains of $[Cu^{II}(sal)]_n$ with threefold symmetry and linkers of 4,4′-bipyridine. Six 1D helical chains hold together by 4,4′-bipyridine linkers into a channel with 8.6 × 8.6 Å (Figure 4). The ring of each channel is made up of six sal units joining six Cu^{II} cations. For this compound data collections at room temperature, low temperature or capillary conditions were done while we found it is difficult to locate all solvents, so we dried crystals at vacuum condition 10 h at room temperature before data collection. Compound **2** is stable when heated up to 270 °C and fully desolvated after vacuum degassing 10 h as evidenced by X-ray single-crystal analysis, and nice data collection was obtained, which is few examples of 3D coordination polymers when solvents are removed and still shows structural stability.

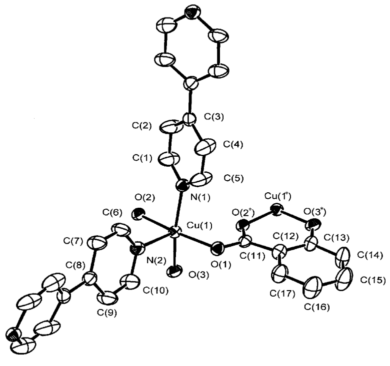

Figure 3. An ORTEP view of **2** with 50% ellipsoids and labelling scheme. Important bond distances (Å): Cu(1)-O(1) 1.977(3), Cu(1)-O(2) 1.933(3), Cu(1)-O(3) 1.901(5), Cu(1)-N(1) 2.055(6), Cu(1)-N(2) 2.301(6).

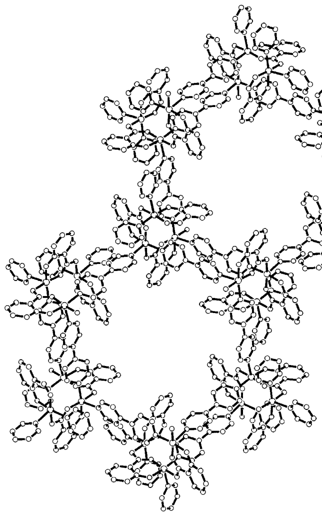

Figure 4. View of 3D network with big channel of **2** along c axis.

We succeeded in synthesizing two compounds based on building blocks, Cu^{II}, H_2sal and N-donor ligands, using layered-solution approach and two 3D coordination polymers assembled by hydrogen bonding and coordination. Our synthetic successful examples are of benefit to design process of crystal engineering of porous coordination polymers.

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9 Prepartion of compound **1**. Crystals were obtained using a three-layer solution in a slender tube. The upper layer (ca. 5 cm) was a methanol solution that contained $Cu(CH_3COO)_2 \cdot H_2O$ (0.05 mol/L) and H_2sal (0.2 mol/L). The middle layer (ca. 2 cm) was mixed solvents of methanol and water with volume ration of 1:1. The lower layer (ca. 5 cm) was an aqueous solution of 4AP (0.2 mol/L). Product crystals were obtained on standing several days at ambient conditions. Elemental analysis for $[Cu(sal)(4AP)(H_2O)]$, Calcd. (%): C: 41.95, H: 3.13, N: 5.43; Found: C: 42.35, H: 2.93, N: 5.61. Yield is 76% based on copper salt.

10 Preparation of compound **2**: The compound was synthesized by similar method in **1**. Products were desolvated under vacuum condition 10 hours. Calcd. for $[Cu(sal)(4,4'\text{-bipy})]$: C: 57.38, H: 3.40, N: 7.87%. Found: C: 57.43, H: 3.35, N: 7.91%. Yield is 84% based on copper salt.

11 Crystal data for **1**: trigonal, R-3(h) (No. 148), $a = 24.247(1)$, $c = 11.3891(6)$ Å, $V = 5798.6(5)$ Å^3, $D_c = 1.607$ g·cm^{-3}, $Z = 18$, $R = 0.036$ and $R_w = 0.044$. Crystal data for **2**: trigonal, R-3 (No. 148), $a = 32.602(2)$, $c = 10.6162(4)$ Å, $V = 9772.0(9)$ Å^3, $Z = 18$, $D_c = 1.088$ g·cm^{-3}, $R = 0.0534$ and $R_w = 0.0683$. CCDC-194731 and CCDC-194732 for compounds **1** and **2**, respectively.

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