

A Unique Three-dimensional MOF with 8-connected bcu Topology out of Customary Building Blocks

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A secondary building unit (SBU)-based approach is an effective strategy for introducing design concepts in the synthesis of new metal-organic frameworks (MOFs).¹ When multinuclear SBUs are linked by linear building blocks, for example, the topology of resulting networks are likely to be predictable based on our experience and the library of basic nets for given connectivities.²

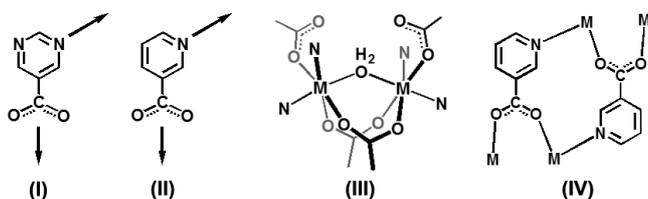
A case that is less certain and less predictable includes when organic building blocks are pluripotent in terms of their connectivities in network structures. We refer one such example to a ligand little known in MOFs, 5-pyrimidinecarboxylate (pmc). With two aromatic nitrogen atoms and one carboxylate group, pmc is a potential tritopic linker, although only one of the two nitrogen atoms may possess sufficient basicity to bind transition metal ions. Under this situation, a question arises whether pmc (I in Scheme 1) would behave in the same way as 3-pyridinecarboxylate (pyc; II in Scheme 1) does in forming extended networks.

This report is a case study for this matter, and a part of our recent efforts to use angular organic building blocks for the synthesis of new porous MOFs.³

Solvothermal reactions of H(pmc) and Co(NO₃)₂·6H₂O in DMF produce small rhomboidal crystals whose composition is [Co₂(OH₂)(pmc)₄](DMF) (**1**) according to X-ray crystallography. The elemental analysis and X-ray powder diffraction (XRPD) studies independently confirm the homogeneity and purity of the bulk product (Figure 1).

A thermal analysis shows a clear plateau to about 250 °C in air before a multi-step weight loss due to the removal of guest DMF and decomposition of the framework occurs (Figure 1). The thermal stability of **1** is further evidenced by XRPD measured after heating the as-synthesized material at 120 °C for 12 h and then at 180 °C for additional 12 h under vacuum (Figure 1).

The structure of **1** is based on a dinuclear SBU in which two



Scheme 1. The binding modes of pmc (I) and pyc (II) ligands and the SBU (III). The double-bridging mode of pyc ligand (IV).

Co²⁺ ions are bridged by a μ -OH₂ ligand and two carboxylate groups (Figure 2a).⁴

Each Co²⁺ ion is further bonded by one carboxylate oxygen and two nitrogen atoms, closing out the octahedral coordination sphere. The oxygen atoms of the terminal carboxylate groups are hydrogen-bonded to the bridging aqua ligand. Overall, the Co₂ unit is supported by 8 pmc ligands which act as simple angular linkers as I in Scheme 1.

The Cambridge Structural Database (CSD)⁵ lists 68 crystal structures having the dimetal unit shown as III in Scheme 1, and four of them are polymeric materials. Of these, two MOFs, [M₂(μ -OH₂)(pyc)₄] (M = Co²⁺, Ni²⁺),⁶ are based on the combination of II and III, and thus are pertinent to **1** that is built from I and III. Unlike **1**, however, those two MOFs are 4- and 5-connected nets despite the SBUs are supported by 8 ligands in almost the same conformation as that of the title MOF. We find that the reduced connectivities are due to the angular ligands doubly bridging between adjacent metal ions (IV in Scheme 1). Such redundant linkages are avoided in **1** because the additional nitrogen donor on pmc compared to pyc ligands provides an alternate way of extending the network with, probably, less strain on the linkers, and therefore all of the 8 ligands in the SBU acts as independent linkers. This analysis simplifies the network structure of **1** to a uninodal

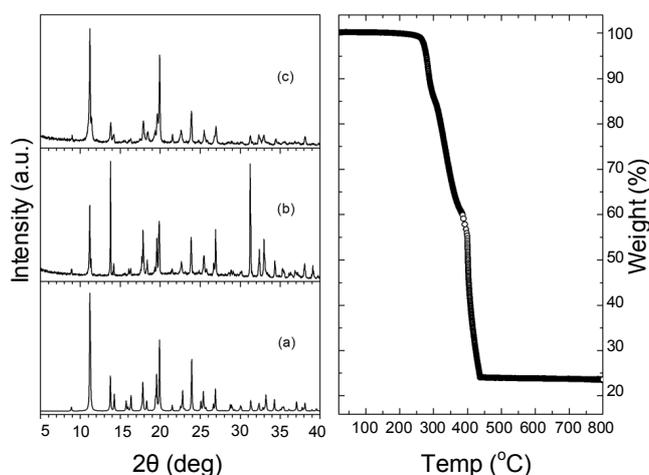


Figure 1. (Left) Simulated (a) and experimental (b) X-ray powder diffraction patterns of **1**. Shown in (c) was measured after heating **1** at 120 °C for 12 h and then at 180 °C for 12 h under vacuum. (Right) TGA profile of as-synthesized **1** measured in the air with the heating rate of 5 °C/min.

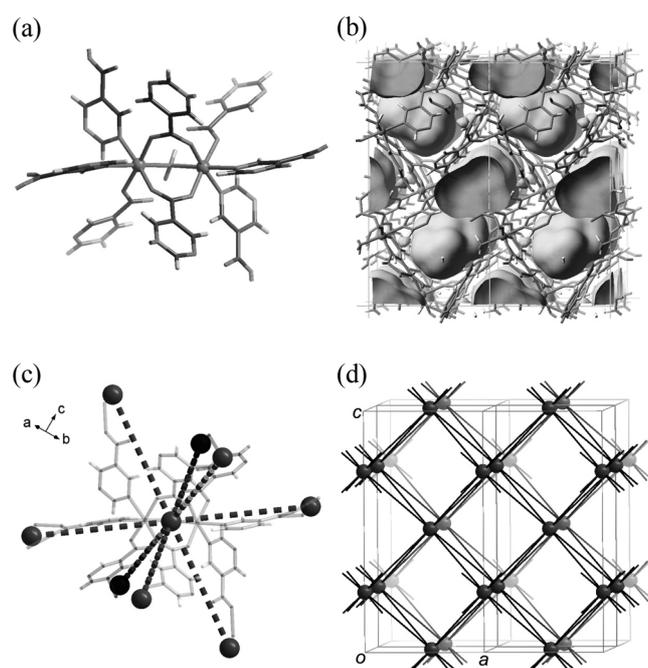


Figure 2. The dinuclear SBU (a) and expanded view of **1** showing the isolated cages (b). (c) The topological model of the SBU as a cubic node. (d) The network structure of **1** stylized according to (c).

8-connected net and the vertex figure to a cube (Figure 2b). The combination of cubic nodes in a uninodal 8-connected net can only be seen in the body-centered cubic lattice (bcu),^{2c} and that is indeed the topology underlying the net of **1** (Figure 2c, 2d). Note that uninodal 8-connected nets are not common in MOFs,⁷ and the bcu net is especially so.⁸

In view of **1** as a porous MOF, straight open channels are expected from the simplified presentation shown in Figure 2d. In fact, the channels are formed by a successive array of edge-sharing octahedral cages. In the actual structure of **1**, however, each cage surrounded by 6 SBUs is isolated from its neighbors by the angular ditopic linkers. A guest DMF which is disordered over two positions is found inside the cage, and therefore the solvent molecule is occluded.⁹ Consequently, removing this guest molecule requires a comprehensive disruption of the links and leads to a decomposition of the framework as shown by the thermal gravimetric analysis. The presence of occluded solvents, on the other hand, suggests that templated synthesis may be a good strategy for obtaining a new MOF from Co²⁺ and pmc ligand.

In brief, pmc is a building block that provides a simple angular linkage similar to pyc ligand. The presence of extra donor atom, however, allows additional degree of freedom in the way SBUs are connected. The unique role of pmc ligand in the phase determination of MOFs necessitates more thorough and systematic investigations towards new porous MOFs.

Experimental Section

H(pmc) (0.240 g, 1.9 mmol) and Co(NO₃)₂·6H₂O (0.282 g,

0.97 mmol) were dissolved in DMF (31.0 mL) and stirred for 2 hours. The pink solution was divided into 2 portions and heated in a sealed vial to 110 °C for 48 hours. The product was collected, washed with DMF and CHCl₃, and dried under vacuum (0.235 g, 69%). Anal. Calcd for C₂₃H₂₁N₉O₁₀Co₂: C, 39.37; H, 3.02; N, 17.98%. Found: C, 39.07, H, 3.04, N, 17.81%. Crystal data for **1**: C₂₃H₂₁N₉O₁₀Co₂, *fw* = 701.35, tetragonal *P*4₃2₁2, *Z* = 4, *T* = 173 K, λ(Mo K_α) = 0.71073 Å, *a* = 11.084(1), *c* = 22.482(3) Å, *V* = 2762.1(5) Å³, ρ_{calcd} = 1.687 g/cm³, μ(Mo K_α) = 1.274 mm⁻¹, F(000) = 1424, Siemens SMART CCD diffractometer, 16911 reflections measured, 3378 independent (*R*_{int} = 0.0266). Final *R*_I = 0.0332, *wR*₂ = 0.0715 for all data, *GOF* on *F*² = 1.094, Flack *x* = 0.010(15). The crystallographic data (CIF) for **1** has been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 729188. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), or electronically via www.ccdc.cam.ac.uk/data_request/cif.

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- The presence of a positionally disordered DMF molecule implies that the solvent cage can accommodate slightly larger molecules, such as DMA or DEF. Indeed, **1** can also be synthesized using DMA or DEF instead of DMF.