Cu₂(OCO)₄ cluster (Cu, blue; C, green; O, red) of square geometry (green) and (b) adamantane cluster (C, green) of tetrahedral geometry (red). These building blocks assemble to adopt the PtS net with its vertices occupied by the clusters to form (c) a decorated PtS framework, where (d) open metal sites point into the pores (same color scheme as in a and b).

![Image](318x558 to 558x734)

**Figure 1.** Design of a decorated framework from (a) paddle-wheel Cu₂(OCO)₄ cluster (Cu, blue; C, green; O, red) of square geometry (green) and (b) adamantane cluster (C, green) of tetrahedral geometry (red). These building blocks assemble to adopt the PtS net with its vertices occupied by the clusters to form (c) a decorated PtS framework, where (d) open metal sites point into the pores (same color scheme as in a and b).

ideal secondary building unit (SBU) toward our objective: Its metal centers adopt a square pyramidal geometry in which the metal ions are held rigidly in the square, and in which the axial position is occupied by labile ligand. It is well-known that in every instance when the axial ligands have been dissociated, the metal sites thus produced bind to a Lewis base atom on a neighboring unit to give cluster dimers or extended chain structures having no OM sites.

Our strategy to prevent coupling of these units and to achieve an MOF with accessible OM sites relies on consideration of the M₂O₄C₄ moiety as an SBU in which the C atoms define a square topology. Since a tetrahedral linker is especially efficient at spacing apart four neighbors, the organic adamantane cluster was chosen as the second SBU (Figure 1b).

To predict the topology of the structure resulting from assembly of squares and tetrahedra, we relied on our thesis that, in general, only a small number of simple, high-symmetry structures will be of overriding importance. Thus, we expected that the product would adopt the PtS topology (Figure 1c) (the simplest, and most symmetrical linkage of tetrahedra and squares), in which each square Pt atom and tetrahedral S atom in PtS would be replaced by a square and a tetrahedral cluster, respectively, to give a decorated form of PtS (Figure 1d). Indeed, this structure yields the desired geometry in which self-aggregation of SBUs is prevented since the labile ligands point toward the centers of voids. This molecular architecture is expected to be stable as it is constructed entirely of C–C, C–O, and Cu–O bonds (compare the stability of MOF-5 constructed of C–C, C–O, and Zn–O bonds). Thermal liberation of the ligands should provide for periodic arrays of accessible OM sites in a porous framework (Figure 1d).

Success of this approach has been demonstrated by performing reactions that give the copper–carboxylate square motif. Here, the addition of Cu(NO₃)₂·2.5H₂O to 1,3,5,7-adamantane tetracarboxylic acid (H₄ATC) in basic aqueous solution at 190 °C yields green crystals of Cu₂(OCO)₄·6H₂O (hereafter termed MOF-11) in 54% yield.

An X-ray diffraction study (Table 1) performed on a single-crystal isolated from the reaction product confirmed the formula.
Figure 2. The single-crystal structures of (a) as-synthesized Cu₂(ATC)·6H₂O (MOF-11) with four water molecules acting as guests and two acting as ligands, and (b) dehydrated MOF-11 shown in line representations with hydrogen atoms of adamantane omitted. (Cu, orange; O, red; C, gray; H of water, white).

Table 1. Crystallographic Data and Important Interatomic Distances for MOF-11

<table>
<thead>
<tr>
<th>crystals, chemical formula</th>
<th>crystal system and space group</th>
<th>unit cell</th>
<th>V (Å³)</th>
<th>Z</th>
<th>R1 [I &gt; 2σ(I)]</th>
<th>Cu–OCO distance (Å)</th>
<th>Cu–Cu distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-synthesized Cu₂(ATC)·6H₂O</td>
<td>monoclinic C2/c</td>
<td>a = 8.5732 Å, b = 8.9732 Å, c = 14.3359 Å, α = 93.92°, β = 87.08°, γ = 98.27°</td>
<td>1040.4 (1)</td>
<td>4</td>
<td>0.0433</td>
<td>1.976 (2)</td>
<td>1.989 (2)</td>
</tr>
<tr>
<td>dehydrated, Cu₂(ATC)</td>
<td>tetragonal P4_2/mmc</td>
<td>a = 8.4671 (2) Å, b = 8.4661 (1) Å, c = 14.444 (1) Å</td>
<td>1035.5 (1)</td>
<td>2</td>
<td>0.0353</td>
<td>1.935 (2)</td>
<td>2.490 (3)</td>
</tr>
</tbody>
</table>

a. Primitive cell. The C-conventional centered cell has a = 12.98658(2) Å, b = 11.2200(1) Å, c = 11.3359 (2) Å, and β = 93.8571(1)°.

16 H₂ATC was prepared according to reported methods: Newkome, G. R.; Nayak, A. R.; Moorefield, C.; Baker, G. J. Org. Chem. 1992, 57, 358–362. Synthesis of H₂ATC: A mixture of H₂ATC (0.069 g, 0.22 mmol) and Cu(NO₃)₂·2H₂O (0.110 g, 0.47 mmol) in aqueous NaOH (6.0 × 10⁻³ M) was heated to 190 °C for 24 h to give green crystals of MOF-11 in 54% yield) along with tiny amounts of Cu₂O. Elemental microanalysis for: (a) as-synthesized Cu₂(ATC)·6H₂O, MOF-11: Calcd: C, 30.94; H, 4.42; N, 0.00; Cu, 23.30%. Found: C, 31.18; H, 4.25; N, 0.08; Cu, 23.39%. (b) Evacuated framework Cu₂(ATC). Calcd: C, 38.63; H, 2.76%. Found: C, 38.75; H, 3.14%.

other molecules as evidenced by their first-order rate constants (k × 10⁸ s⁻¹), 11.1, 5.3, and 1.4, respectively.

The porosity and thermal stability of the anhydrous framework motivated us to carefully examine and compare its crystals with those of the as-synthesized hydrated crystals by optical microscopy. No differences in their morphology and transparency were observed, and we were able to perform a single crystal X-ray diffraction study on the porous material. Its crystal structure showed (Figure 2b) that the anhydrous framework adopts a slightly more relaxed and higher symmetry structure with negligible difference in its crystal volume from that observed for the hydrated form (Table 1). The pores were found to be essentially vacuum with only a negligible 0.16 water per formula unit (2.7% of all water) present in disordered form. The absence of water ligands on Cu is evident from the shorter distance observed for Cu–OCO and a significant shortening of the Cu–Cu distance (Table 1) upon liberation of water—the latter (2.490 Å) being the shortest distance known for Cu(II)–carboxylate compounds.

Magnetic susceptibility data obtained for the as-synthesized MOF-11 follows the expected behavior typically observed for antiferromagnetic coupling in the copper(II) acetate dimer (2J = −280 cm⁻¹); however, the anhydrous material showed increased coupling (2J = −444 cm⁻¹) as expected for the observed shortening of the Cu–O distance found in the X-ray crystal diffraction analysis (Table 1).

At the outset of this study, structural investigations of OM sites in porous materials have been limited to partially ion-exchanged molecular sieves, where metal ions are held into the pores by ionic interactions and a dehydrated Prussian blue-type compound. More recently, open cobalt(II) sites have been characterized in a framework composed of Co(CN)₅³⁻ linked by Li⁺ ions into an extended 3-D structure. Although the latter material showed an exceptionally high affinity for O₂ uptake from air by the cobalt ion sites, the lack of framework rigidity renders the material nonporous. The structure of MOF-11 combines two designed-in important structural properties previously unknown in porous crystals, namely, a rigid architecture that supports permanent porosity and well-defined periodic arrays of covalently held OM sites in extended pores.

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Supporting Information Available: Crystallographic data and sorption isotherms for MOF-11 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.