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$Cu_2(ATC)\cdot 6H_2O$: Design of Open Metal Sites in Porous Metal−Organic Crystals (ATC: 1,3,5,7-Adamantane Tetracarboxylate)

Banglin Chen,[†] M. Eddaoudi,[†] T. M. Reineke,[†] J. W. Kampf,[†]
M. O'Keeffe,[‡] and O. M. Yaghi*[,†]

Materials Design and Discovery Group
Department of Chemistry, University of Michigan
930 North University, Ann Arbor, Michigan 48109-1055
Department of Chemistry and Biochemistry
Arizona State University, Tempe, Arizona 85287-1604

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Metal sites play a central role in the vast majority of molecular recognition processes involving biological and synthetic extended systems due to their ability to impart highly selective and specific molecular transformations, transport, and storage.[1−4] Although extensive research efforts worldwide have been devoted to studying the result of chemical reactions at metal centers, definitive structural characterization of *open* metal (OM) sites, that are coordinatively unsaturated, by single crystal X-ray diffraction have been largely absent. The inherent difficulty in stabilizing such entities in molecular scaffolds arises from their reactive nature and from the lack of structural rigidity around the sites they occupy, which often leads to their aggregation and severe distortion of their local structure features that preclude their characterization as OM sites. In this report, we present a design strategy based on knowledge gained from modular chemistry,[5−14] for producing high concentrations of covalently bound and accessible OM sites into *crystalline* porous materials: An organic adamantane tetrahedral cluster is copolymerized with an inorganic square cluster to yield a porous metal−organic framework (MOF) having a 3-D channel system filled with water guests. The rigid nature of the MOF architecture allows for complete thermal removal of guests including terminal water ligands, originally bound to copper sites, of the square pyramidal clusters to yield a stable framework with periodic arrays of open copper sites. These observations are supported by single-crystal X-ray structures, gas sorption isotherms, elemental microanalyses, exceptional bond lengths, and magnetic coupling constants of the crystals before and after removal of water.

The paddle-wheel cluster motif adopted by hundreds of *discrete* binuclear metal−carboxylates (Figure 1a) forms the basis of an 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.[15] Our strategy to prevent coupling of these units and to achieve an MOF with accessible OM sites relies on consideration of the $M_2O_8C_4$ 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.[6] Thus, we expected that the product will adopt the PtS structure 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[7]), and thermal liberation of the ligands should provide for periodic arrays of accessible OM sites in a porous framework (Figure 1d).

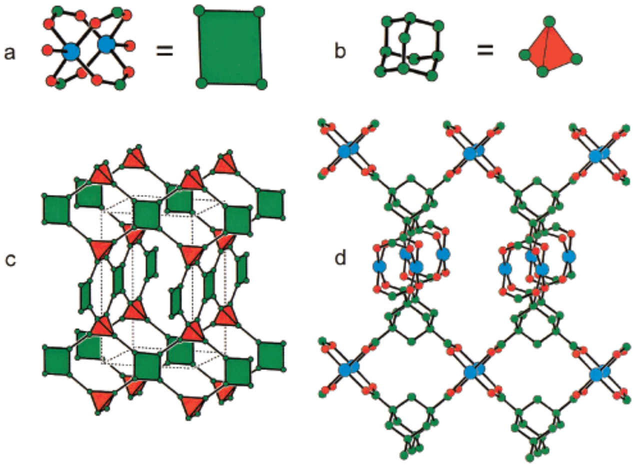

Figure 1. Design of a decorated framework from (a) paddle-wheel $Cu_2(OCO)_4$ cluster (Cu, blue; C, green; O, red) of square geometry (green) and (b) adamantane cluster (C, green) of tetrahedral geometry (red). These building blocks assemble to adopt the PtS net with its vertices occupied by the clusters to form (c) a decorated PtS framework, where (d) open metal sites point into the pores (same color scheme as in a and b).

Success of this approach has been demonstrated by performing reactions that give the copper−carboxylate square motif. Here, the addition of $Cu(NO_3)_2\cdot 2.5H_2O$ to 1,3,5,7-adamantane tetracarboxylic acid (H_4ATC) in basic aqueous solution at 190 °C yields green crystals of $Cu_2(ATC)\cdot 6H_2O$ (hereafter termed MOF-11) in 54% yield.[16]

An X-ray diffraction study (Table 1) performed on a single-crystal isolated from the reaction product confirmed the formula-

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[†] University of Michigan.

[‡] Arizona State University.

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

crystals, chemical formula	crystal system and space group	unit cell	*V* (Å^3)	Z	R1 [$I > 2\sigma(I)$]	Cu−OCO distance (Å)	Cu−Cu distance (Å)
as-synthesized $Cu_2(ATC) \cdot 6H_2O$	monoclinic $C2/c$	$a = 8.5732^a$ Å $b = 8.5732$ Å $c = 14.3359$ Å $\alpha = 93.92°$ $\beta = 87.08°$ $\gamma = 98.27°$	1040.4 (1)	4	0.0433	1.976 (2) 1.989 (2) 1.964 (2)	2.622 (3)
dehydrated, $Cu_2(ATC)$	tetragonal $P4_2/mmc$	$a = 8.4671$ (2) Å $b = 8.4671$ (1) Å $c = 14.444$ (1) Å	1035.5 (1)	2	0.0353	1.935 (2)	2.490 (3)

[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 $\beta = 93.857(1)°$.

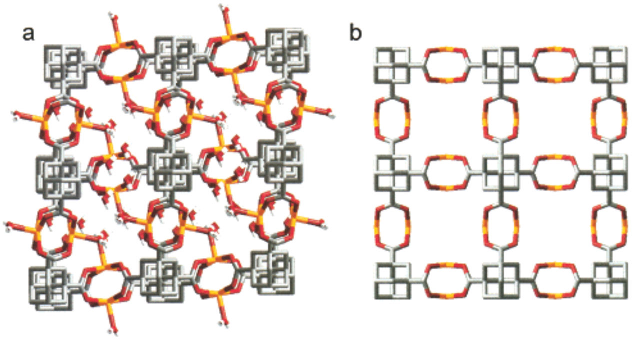

Figure 2. The single-crystal structures of (a) as-synthesized $Cu_2(ATC) \cdot 6H_2O$ (MOF-11) with four water molecules acting as guests and two acting as ligands, and (b) dehydrated MOF-11 shown in line representations with hydrogen atoms of adamantane omitted. (Cu, orange; O, red; C, gray; H of water, white).

tion of MOF-11 and revealed an extended framework having the predicted decorated PtS topology, where each admantane is bound to four $Cu_2O_4C_8$ squares (Figure 2a). Each square has two water ligands ($Cu{-}OH_2 = 2.148$ (3) Å), one bound to each of its copper (II) centers. These point away from the Cu−O−C framework into a 3-D channel system of 6.0−6.5 Å diameter, where four additional water guests per square unit reside. Estimates based on van der Waals radii showed that water ligands and guests occupy approximately 50% of the crystal volume. Liberation of water from the framework was examined by thermal gravimetric analysis, which was performed on as-synthesized MOF-11 sample (65.50 mg) under vacuum (0.050 mTorr). It showed a 14.8% weight loss at 22.0 °C corresponding to the loss of 4.51 H_2O per formula unit, followed at 120 °C by another weight loss to give a total of 19.1%, corresponding to the removal of 5.82 H_2O per formula unit, with no further weight loss observed up to 260 °C. In other words, essentially all water guests and ligands have been liberated to give an anhydrous framework with a thermal stability range 120−260 °C. Furthermore, the rigid and porous nature of the anhydrous framework was evident upon measurement of its gas sorption isotherms, where fully reversible Type I behavior was observed for $N_{2(g)}$ and $Ar_{(g)}$—unequivocally confirming the existence of permanent porosity in anhydrous MOF-11. By assuming a monolayer coverage of N_2 the apparent Langmuir surface area was found to be 560 m^2/g (pore volume = 0.20 cm^3/g). Sorption of organic molecules with progressively larger cross-section such as, CH_2Cl_2 (4.0 Å), C_6H_6 (5.8 Å), CCl_4 (6.0 Å), and C_6H_{12} (6.2 Å), showed a clear molecular-sieving affect with an immeasurably fast uptake of CH_2Cl_2 and a slower uptake by the other molecules as evidenced by their first-order rate constants ($k \times 10^4$ 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.[17]

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});[18] 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).[17]

At the outset of this study, structural investigations of OM sites in porous materials have been limited to partially ion-exchanged molecular sieves,[19] where metal ions are held into the pores by ionic interactions and a dehydrated Prussian blue-type compound.[20] More recently,[4] open cobalt(II) sites have been characterized in a framework composed of $Co(CN)_5^{3-}$ linked by Li^+ ions into an extended 3-D structure. Although the latter material showed an exceptionally high affinity for O_2 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.

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