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Porous Cu–Cd Mixed-Metal–Organic Frameworks Constructed from $Cu(Pyac)_2$ {Bis[3-(4-pyridyl)pentane-2,4-dionato]copper(II)}

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Porous Cu–Cd mixed-metal–organic frameworks $[\{Cd(NO_3)_2\}_2\{(Cu(Pyac)_2\}_3]$ (M′MOF **1**) and $[\{CdCl_2\}\{Cu(Pyac)_2\}_2]$ (M′MOF **2**) $\{Cu(Pyac)_2$ = bis[3-(4-pyridyl)pentane-2,4-dionato]copper(II)} have been synthesized by the reaction of $Cu(Pyac)_2$ with $Cd(NO_3)_2$ and $CdCl_2$. They are noninterpenetrating 1D ladder and 2D square-grid frameworks, constructed from $Cu(Pyac)_2$ building blocks with T-shaped $Cd(NO_3)_2$ nodes and square-planar $CdCl_2$ nodes, respectively. The 1D ladders and 2D square grids are stacked in ABCABC... and ABCDEF... packings, leading to 2D interconnected channels of ca. 5.7 × 10.2 and 4.1 × 9.8 Å in **1** and 1D channels of ca. 8.0 × 8.2 Å in **2**, respectively. The copper sites in these two M′MOFs are coordinated by solvent molecules and exposed to the pores.

There has been extensive interest in porous metal−organic framework (MOF) materials because of their possible applications in gas storage, separation, molecular recognition, magnetism, and catalysis.[1−15] One of the current challenges for synthesis of such porous MOFs is to functionalize their pores, so that they can be well-suited for specific host−guest interactions and practical applications. We believe the recently developed "preconstructed building block" approach can be useful in accomplishing this goal. In this method, metal-containing molecular complexes preconstructed from simple organic linkers combine with other metal ions to construct mixed-metal−organic frameworks (M′MOFs). This approach provides rational design principles for incorporating unsaturated metal centers into porous mixed-metal−organic frameworks. However, this approach has not been extensively explored. Although a number of porous M′MOFs have been reported,[16−25] only a few of these materials show coordinative unsaturation at the transition-metal center.[16−19]

We have been interested in porous supramolecular metal β-diketonates for their host−guest chemistry.[26] For the successful preparation of porous M′MOFs based on metal β-diketonate moieties to be ensured, these moieties must contain donor groups capable of binding to the M′ metal atoms. We chose $Cu(Pyac)_2$ {i.e., bis[3-(4-pyridyl)pentane-2,4-dionato]copper(II); see Scheme 1} as the preconstructed building block for this purpose.[27] As an expanded 4,4′-bipyridine analogue, $Cu(Pyac)_2$ contains both Lewis-base N atoms and Lewis-acid Cu sites. We expected that $Cu(Pyac)_2$ would yield porous M′MOFs upon reaction with metal nodes

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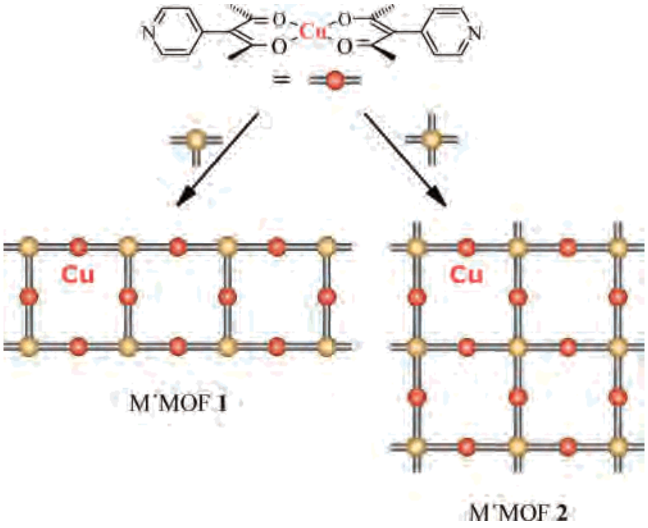
Scheme 1. $Cu(Pyac)_2$ Reacts with $Cd(NO_3)_2$ to Make the 1D Ladder-Type M′MOF **1** and with $CdCl_2$ to Make the 2D Square-grid M′MOF **2**.



of various geometries. We now report that the reactions of $Cu(Pyac)_2$ with $Cd(NO_3)_2$ and $CdCl_2$, acting as T-shaped and square-planar nodes, respectively, produce 1D and 2D porous M′MOFs; see Scheme 1. M′MOF **1** is a 1D ladder framework with the repeating unit $[\{Cd(NO_3)_2\}_2\{Cu(Pyac)_2\}_3]$, and M′MOF **2** is a 2D square-grid framework containing $[\{CdCl_2\}\{Cu(Pyac)_2\}_2]$.

Crystalline **1** was obtained in 60% yield over a period of 2 days by layering a MeOH solution (8 mL) of $Cd(NO_3)_2 \cdot 4H_2O$ (70.0 mg, 0.227 mmol) onto a THF solution (8 mL) of $Cu(Pyac)_2$ (14.0 mg, 0.028 mmol[27]). Similarly, **2** was prepared in 63% yield by layering a THF solution (8 mL) of $Cu(Pyac)_2$ (17.6 mg, 0.036 mmol) onto an aqueous solution (8 mL) of $CdCl_2 \cdot 2.5H_2O$ (224 mg, 0.98 mmol).[28]

The crystal structure of **1** contains 1D ladders in which T-shaped Cd^{2+} nodes (capped by two chelating NO_3^- anions) are bridged by $Cu(Pyac)_2$ building blocks (Figure 1a).[29] The Cd···Cd distances are 19.77 and 19.65 Å for the rung and edge, respectively.

Other examples of 1D ladder frameworks are often interpenetrated, leading to reduced porosity.[30] In contrast, the new Cd−Cu M′MOF **1** is an unusual example of a 1D noninterpenetrating ladder structure, in which these 1D ladders are stacked together in ABCABC packing (Figure 1b). Two other types of packing for noninterpenetrating 1D ladders have been reported: a porous ABAB packing[31] and a nonporous herringbone packing.[32] Our new M′MOF **1** is the first example of a 1D ladder structure with ABCABC packing.

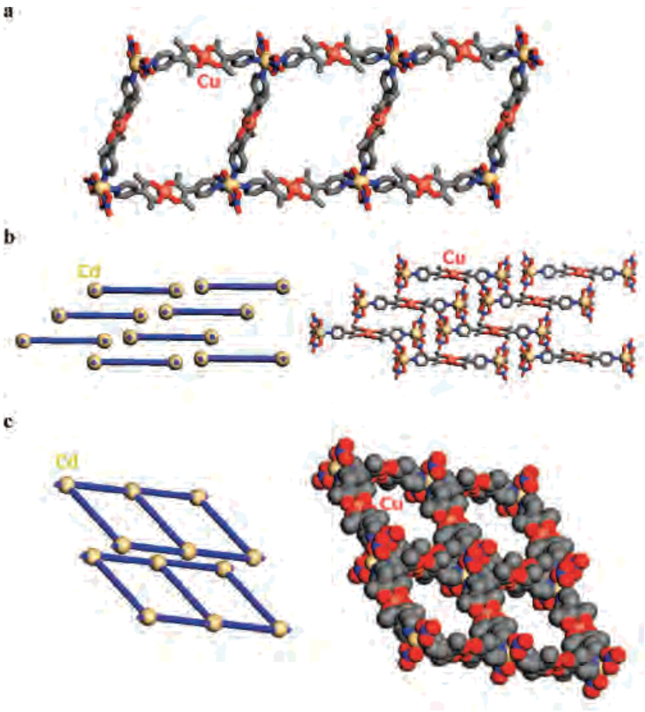


Figure 1. Views of the crystal structure of the $Cd(NO_3)_2-Cu(Pyac)_2$ M′MOF **1** (Cu atoms orange, Cd beige). (a) A portion of one 1D "ladder" unit. (b) View along the "ladder" units, showing the ABCABC... packing. (c) View approximately along the *a* crystallographic axis. On the left is a schematic drawing showing only the Cd atoms, to illustrate the repeating units along two adjacent ladders. The space-filling model on the right shows the channels that pass through successive layers of ladder units.

The pores in one 1D ladder in **1** are close to those in adjacent layers in both the *a* (see Figure 1c) and *b* crystallographic directions. This results in a 2D network of interconnected channels. The channels along *a* have dimensions of ca. 5.7 × 10.2 Å, and those along *b* are ca. 4.1 × 9.8 Å. The pores occupy about 60% of the crystal volume.

The $CdCl_2-Cu(Pyac)_2$ M′MOF **2** has a 2D square-grid structure (Figure 2a) in which $CdCl_2$ units are bridged by $Cu(Pyac)_2$ building blocks.[33] The Cd···Cd and Cu···Cu distances are 19.718 Å, comparable to those in 2D MOFs with large cavities.[34,35] The 2D square-grid layers are stacked

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(28) Anal. M′MOF **1**: Calcd for $[\{Cd(NO_3)_2\}_2\{Cu(Pyac)_2\}_3](MeOH)_3(THF)_{1.5}$ (**1**$\cdot$3MeOH$\cdot$1.5THF, $C_{69}H_{84}Cd_2Cu_3N_{10}O_{28.5}$): C, 43.05; H, 4.40; N, 7.27. Found: C, 43.02; H, 4.00; N, 7.20. M′MOF **2**: Calcd for $[\{CdCl_2\}\{Cu(Pyac)_2\}_2](H_2O)_9(THF)$ (**2**$\cdot 9H_2O \cdot$THF, $C_{44}H_{66}Cl_2CdCu_2N_4O_{18}$): C, 42.30; H, 5.32; N, 4.48. Found: C, 42.40; H, 5.06; N, 4.48.

(29) Crystal data for **1**$\cdot$3MeOH$\cdot 2H_2O$: triclinic, space group $P\bar{1}$, a = 13.817(2) Å, b = 15.205(2) Å, c = 17.044(2) Å, α = 111.732(6)°, β = 111.661(5)°, γ = 94.099(6)°, V = 2987.2(7) Å^3, Z = 2, D_{calc} = 1.023 g cm^{-3}, μ = 0.931 mm^{-1}, R_1 [$I > 2\sigma(I)$] = 0.048, wR_2 (all data) = 0.160 at 230 K.

(30) See, for example, interpenetrated 1D ladders: Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287. Carlucci, L.; Ciani, G.; Proserpio, D. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1799. Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Schröder, M. *J. Am. Chem. Soc.* **2000**, *122*, 4044.

(31) See, for example, AB ladders: Losier, P.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2779. Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **1997**, *36*, 972. Cussen, E. J.; Claridge, J. B.; Rosseinsky, M. J.; Kepert, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 9574.

(32) 1D ladder herringbone packing: Ciurtin, D. M.; Dong, Y.-B.; Smith, M. D.; Barclay, T.; zur Loye, H. C. *Inorg. Chem.* **2001**, *40*, 2825.

(33) Crystal data for **2**$\cdot$6THF$\cdot 0.5H_2O$: monoclinic, space group $C2/m$, a = 21.768(7) Å, b = 21.903(8) Å, c = 7.817(3) Å, β = 106.04(2)°, V = 3582(2) Å^3, Z = 2, D_{calc} = 1.351 g cm^{-3}, μ = 1.018 mm^{-1}, R_1 [$I > 2\sigma(I)$] = 0.065, wR_2 (all data) = 0.195 at 100 K.

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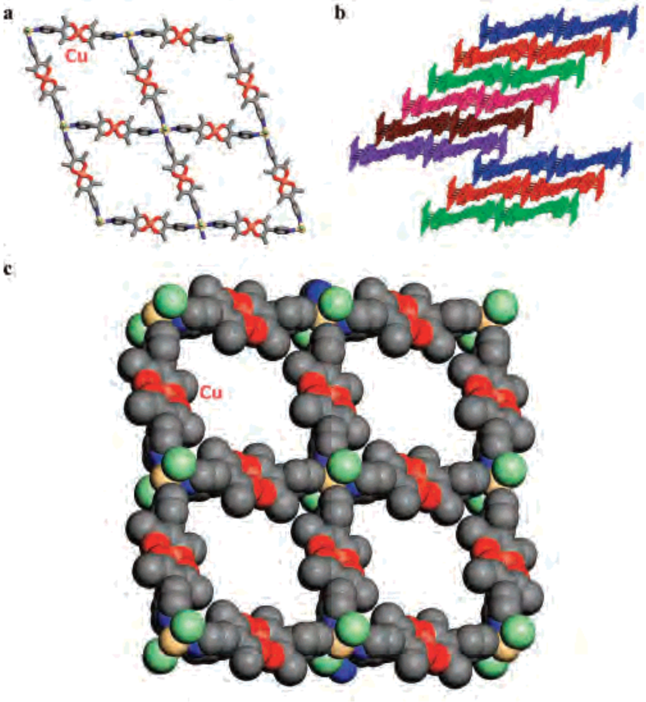

Figure 2. Views of the crystal structure of the $CdCl_2$−$Cu(Pyac)_2$ M′MOF **2**. (a) One square-grid layer. (b) Several square-grid layers, edge-on, showing the ABCDEF... packing. (c) Space-filling model to show the approximate size of the channels.

so as to repeat every six layers (ABCDEF... packing, Figure 2b). This packing leads to a channel with dimensions of ca. 8.0 × 8.2 Å (Figure 2c). The porosity of M′MOF **2** is about 63%.

It is of interest to note that the copper sites in these two porous M′MOFs are accessible for host−guest interactions. Coordination of solvent molecules to the Cu sites is evident in the crystal structures of both **1** and **2**; see Figure 3.

Crystals of M′MOF **1** turn opaque within seconds in air, whereas those of M′MOF **2** gradually turn opaque over a period of ca. 30 min. Thermogravimetric analyses (TGA) of M′MOF **1** and **2** indicate that the solvent/guest molecules are lost over the temperature ranges of 22−67 and 22−100 °C, respectively. The desolvated frameworks are stable up to about 220 and 210 °C, respectively, and then decompose.

Guest-binding sites in porous metal−organic frameworks are important for the development of functional properties.[36−38] We have now shown that our preconstructed building block approach makes it possible to incorporate these kinds of sites into porous materials by rational crystal design principles.

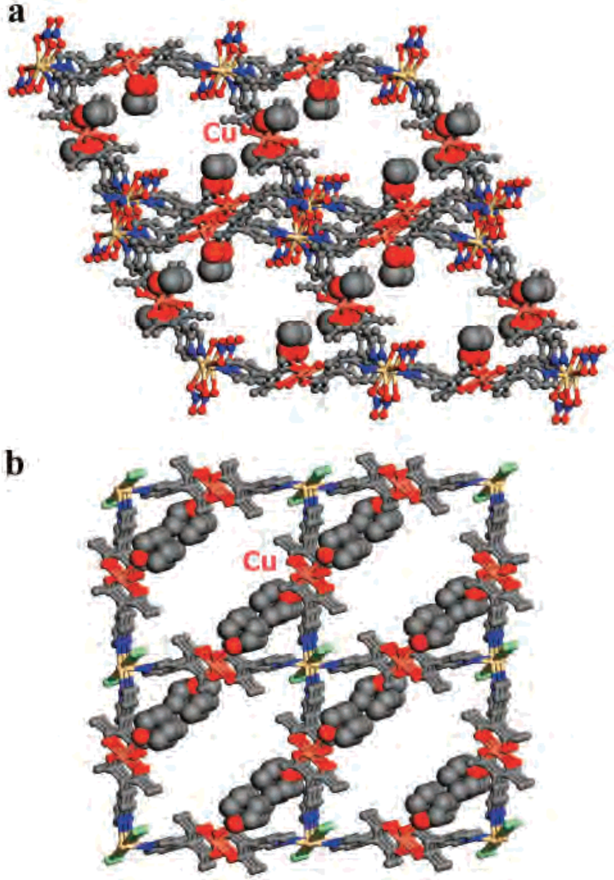

Figure 3. Coordinated solvent molecules in the crystal structures of (a) $Cd(NO_3)_2$−$Cu(Pyac)_2$ M′MOF **1** (coordinated CH_3OH) and (b) $CdCl_2$−$Cu(Pyac)_2$ M′MOF **2** (coordinated THF). Free (uncoordinated) solvent molecules are omitted for clarity.

We are currently endeavoring to synthesize more robust porous mixed-metal−organic frameworks with guest-binding sites that will be appropriate for catalytic and sensor applications.

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Supporting Information Available: X-ray structure data for M′MOFs **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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