Microporous Materials

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Porous Cobalt(II)–Organic Frameworks with Corrugated Walls: Structurally Robust Gas-Sorption Materials[**]

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In memory of Alexander D. Hopkins

There is currently a great deal of interest in the use of porous coordination compounds for storing[1,2] or separating[3] gas molecules. The major driving force for this interest is the search for hydrogen-storage materials.[1] The low activation energy for metal–ligand bond formation makes such materials easier to synthesize than their purely organic counterparts. Various suggestions have been made for the types of components that can encourage the formation of channeled materials.[4] Now that these metal–organic frameworks have been shown to be very promising materials, efforts are underway to determine what structural and chemical features are desirable for the highest gas storage capacity.[5] In addition, the lattice should have a high degree of stability in the absence of guest molecules; that is, it should be truly porous[6] and should be stable to repeated cycles of guest addition and removal.

We have previously shown how a rod-and-spacer approach may be used to obtain porous materials[4e] by solvothermal synthesis.[7] Attempts to use this method to increase the size of the pores by switching from squarate ($C_4O_4^{2-}$) to benzene-1,2,4,5-tetracarboxylate anions led to a decrease in the robustness of the guest-free lattice.[4f] We now report that aromatic ligands with a 1,2,4-substitution pattern may also act as spacers in porous frameworks. The hydrothermal reaction of Co^{II} cations with 2,4-pyridinedicarboxylate (2,4-pdc)[8] and 6-mercapto-3-pyridinecarboxylate (6-mercaptonicotinate, 6-mna) anions[9] resulted in the synthesis of two new channeled solids, $[Co_3(2,4\text{-pdc})_2(\mu_3\text{-OH})_2]\cdot 9H_2O$ (CUK-1; CUK = Cambridge University–KRICT) and $[Co_2(6\text{-mna})_2]\cdot 3H_2O$ (CUK-2). To our knowledge, CUK-2 is the first example of such a material containing organothiolate ligands.

X-ray crystallography revealed that CUK-1 is a complex coordination polymer that crystallizes in the space group

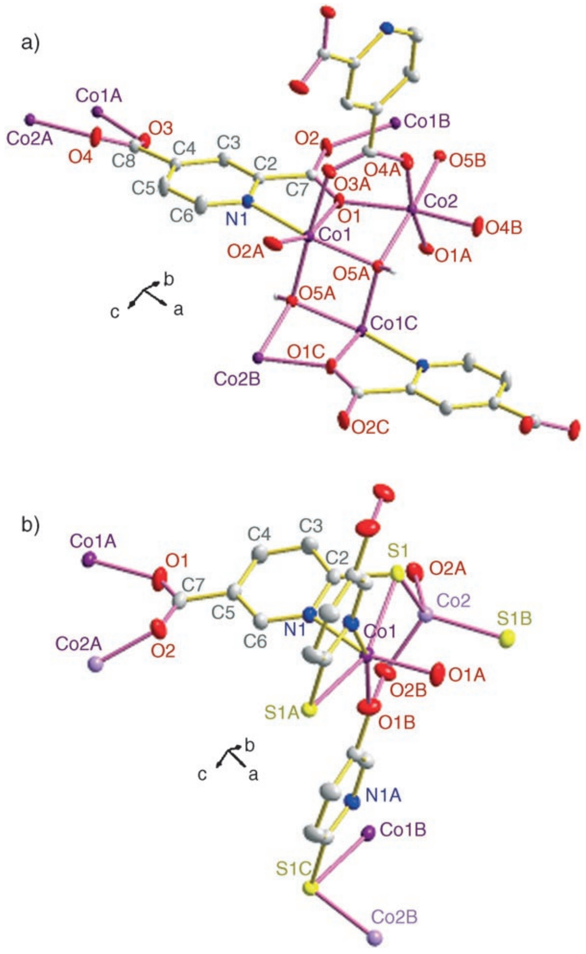

Figure 1. Extended asymmetric units of a) CUK-1 and b) CUK-2. H atoms are omitted for clarity.

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$C2/c$.[10] Two independent metal ions (Co1 and Co2) with distorted octahedral environments are coordinated to one independent 2,4-pdc ligand and one independent hydroxide ligand (Figure 1 a). The 2,4-pdc ligands are each coordinated to five different metal ions through three bridging interactions: two carboxylate bridges and a single-atom oxygen bridge. Triple bridging of the metal ions by the hydroxide ligands produces chains of Co_3 triangles parallel to the c axis, in which the triangles share alternating edges and vertices (Figure 2 a). This topology has been observed a number of times in compounds with the stoichiometry $M_3(L)_2(OH)_2$ (where L is a dianionic ligand).[4e,8] The cobalt–hydroxide chains act as undulating pillars around which the ligands are arranged. In the resulting square grid, the ligands provide the walls of the channels. The positions of nine water molecules within the void space were identified directly from the electron-density map at 180 K. The wall-to-wall separation in CUK-1 is 11.148(4) Å, while the corner-to-corner distance across the channels (Co2–Co2′) is 14.334(4) Å. Hence, the cavities within the material are of considerable capacity.

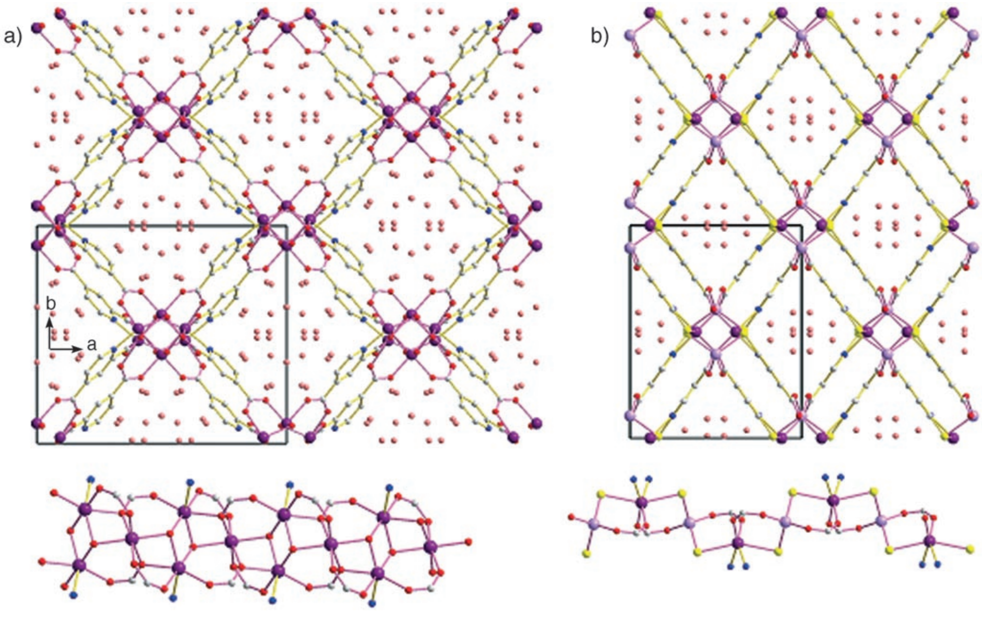

Figure 2. Crystal structures of a) CUK-1 and b) CUK-2, which contain channels surrounded by corrugated walls. For each structure, a single metal–ligand pillar is also shown. Color scheme as in Figure 1; O atoms of solvent H_2O molecules are pink. H atoms are omitted for clarity.

CUK-2 forms deep blue single crystals, which adopt the chiral space group $C222_1$.[10] The asymmetric unit contains a highly distorted octahedral (Co1, purple) and a more regular tetrahedral (Co2, violet) Co^{II} environment (Figure 1 b). Co1 is *N*,*S*-chelated by two 6-mna ligands, each in a four-membered-ring mode (bite angle = 66.60(5)°). Co1 and Co2 are linked by single-atom thiolate bridges, thus, forming cobalt–thiolate helical chains parallel to the c axis, which contain two repeat units (–Co1–S1–Co2–S1A–) per complete rotation (Figure 2 b). Adjacent 6-mna ligands also provide carboxylate bridges between Co1 and Co2, thus, producing an extended structure in CUK-2 that is similar to that in CUK-1. Undulating channels parallel to the cobalt–thiolate chains contain water molecules. However, the pores in CUK-2 (wall-to-wall separation 8.75(4) Å) are significantly smaller than those in CUK-1, resulting in a lower degree of hydration in CUK-2.

Thermogravimetric analysis (TGA) revealed that complete dehydration of both solids is achieved by 120 °C (Figure 3), after which thermal stability is observed to temperatures above 400 °C. X-ray diffraction studies of desolvated materials are the most convincing indicators of true porosity.[11] Hence, freshly synthesized crystals of CUK-1 and CUK-2 were studied by X-ray diffraction at 375(2) K, after initial mounting at 293 K and slow warming ($50\,K\,h^{-1}$) in a stream of dry N_2. The crystals were allowed to equilibrate at 375(2) K for 5 h before full datasets were collected.[12] In both cases, the dehydrated crystals showed no perceptible change in appearance. The high-temperature structures confirm that total removal of guest molecules was achieved without loss of crystallinity. The very low residual electron density indicates that no water remains in the channels. No change in connectivity occurs in either framework upon dehydration; only minimal changes in metal–ligand bond distances are observed. The lattice of CUK-1 undergoes a small distortion, which results in the square channels becoming diamondoid. X-ray analysis of these crystals after re-immersion in water for 1 h showed them to be identical to the as-synthesized material.

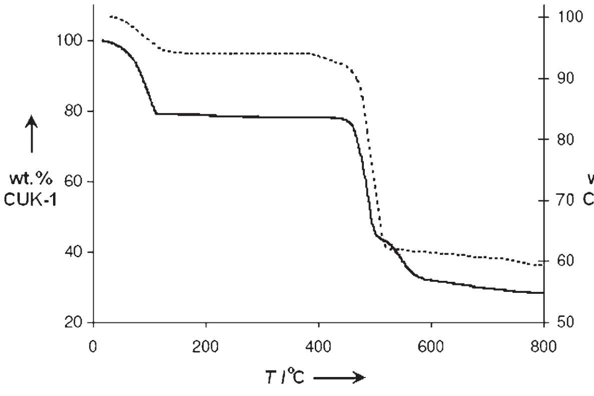

Figure 3. TGA curves for CUK-1 (——) and CUK-2 (-----).

The unsymmetrical nature of the 2,4-pdc and 6-mna ligands encourages head-to-tail packing, as the ligands may slot together in a complementary way. This arrangement leads to the channels having undulating (corrugated) walls in a box-girder motif (Figure 2). This type of construction gives strength to structures such as bridges; therefore, it is logical to suggest that it plays a major role in the stability of guest-free CUK-1 and CUK-2. In comparison, symmetrical ligands such as 1,2,4,5-benzenetetracarboxylate,[4f] terephthalate,[2b] and 4,4′-bipyridyl-*N*,*N*-dioxide[4d] give coordination frameworks that are much less robust when guest-free, as their walls consist of a single layer of ligand molecules and are correspondingly straight.

To confirm the permanent porosity of CUK-1, we obtained the adsorption isotherms of light gases using a volumetric gas-sorption apparatus (Figure 4). The H_2 adsorption isotherm at 77 K shows an uptake of 183 $cm^3 g^{-1}$ (1.6 wt %) at 760 Torr, which is relatively high compared to those of microporous zeolites and aluminophosphates,[13] but lower than those of the metal–organic frameworks with the greatest capacities.[14] In addition, large quantities of O_2 (139 $cm^3 g^{-1}$) and CO_2 (157 $cm^3 g^{-1}$) are adsorbed at 87 and 196 K, respectively, under atmospheric pressure. The adsorption isotherms of these gases reveal type-I behavior, as expected for microporous materials, indicating that these gases are truly adsorbed in the pores. Fitting the Brunauer–Emmett–Teller (BET) equation to the adsorption isotherm of CO_2 gives an estimated specific surface area of 630 $m^2 g^{-1}$, which is close to a typical value for microporous zeolites with high surface areas. Using the Dubinin–Radushkevich equation, the micropore volume of CUK-1 is estimated to be 0.26 $cm^3 g^{-1}$ from the CO_2 adsorption isotherm at 196 K.[15]

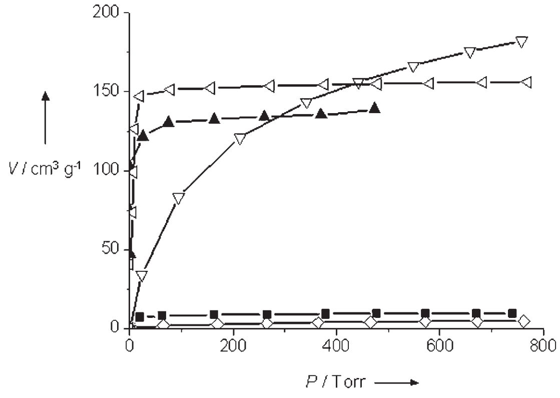

Figure 4. Adsorption of selected gases by CUK-1 dehydrated at 573 K under vacuum: N_2 at 77 K (■), O_2 at 87 K (▲), H_2 at 77 K (▽), CH_4 at 186 K (◇), CO_2 at 196 K (◁).

In contrast, despite the stability of the framework, the N_2 and CH_4 adsorption isotherms measured for CUK-1 at 77 and 186 K, respectively, reveal very low uptakes (Figure 4). CUK-1 shows selective adsorption of O_2 and H_2 over N_2 at low temperatures. To our knowledge, a similar molecular-sieving effect has only been observed in $Mg_3(NDC)_3$ (NDC = 2,6-naphthalenedicarboxylate) at 77 K,[3a] manganese formate at 77 K,[3b] and zeolite 4A at 123 K.[16] Owing to the unusual nature of this result, we have been very careful in verifying it: independent measurements were performed on separate samples at KRICT and at Berkeley. Note that CUK-1 is sufficiently stable for all adsorption measurements to be performed on a single sample.

The study of CO_2 adsorption by CUK-2 also revealed a reversible type-I isotherm characteristic of a microporous material (see Supporting Information, Figure S3). The surface area and micropore volume, estimated by applying the BET and Dubinin–Raduskhvich equations, are 420 $m^2 g^{-1}$ and 0.17 $cm^3 g^{-1}$, respectively. The H_2 adsorption isotherm at 77 K for CUK-2 shows an uptake of 75 $mL g^{-1}$ at 760 Torr, which is relatively low compared to that of CUK-1. Unlike some previous observations,[5f–h] the differing uptakes do not, however, seem to be related to the relative surface areas of the two materials. Interestingly, the BET surface area determined from the CO_2 adsorption isotherm is over three times larger than that determined from the N_2 adsorption isotherm, indicating a significant selectivity of CUK-2 for guest species.

It is not yet clear why CUK-1 and CUK-2 show such large differences in their adsorption behaviors. Our crystal structures of the dehydrated compounds indicate that all small gas molecules should be capable of entering the pores of both materials. It is possible that structural changes may accompany the cooling of dehydrated CUK-1 or the adsorption of certain guest species by CUK-1, preventing molecules from entering the pores the material.

In conclusion, we have demonstrated that the solvent of crystallization may be completely removed from the porous metal–organic materials CUK-1 and CUK-2 with complete retention of the host structures. The use of unsymmetrical organic templates in hydrothermal syntheses imparts these coordination materials with robust frameworks that show promising adsorption characteristics for selected light gases, particularly in the case of CUK-1.

Experimental Section

$[Co_3(2,4\text{-pdc})_2(\mu_3\text{-OH})_2]\cdot 9H_2O$ (CUK-1): A solution of 2,4-pyridinedicarboxylic acid (185 mg, 1.0 mmol) and KOH (1.0 M, 3.0 cm^3) in H_2O (3.0 cm^3) was added to a stirred aqueous solution (4.0 cm^3) of $CoCl_2\cdot 6H_2O$ (357 mg, 1.5 mmol) to give a 3:2:6 ratio of Co/2,4-pdc/OH. The resulting viscous, opaque mixture was heated to 473 K in a 23-cm^3 teflon-lined steel autoclave over 15 h, and then cooled to room temperature over 6 h. The crystalline solid was purified by short cycles (3 × 20 s) of ultrasonic treatment in H_2O (20 cm^3), followed by decanting of the cloudy supernatant. Pure samples of CUK-1 were also obtained in good yield from a 1:1:3 ratio of reactants. Large cherry-red prisms were isolated (yield 149 mg, 33 %). Elemental analysis (%) calcd for $C_{14}H_{24}Co_3N_2O_{19}$: C 24.0, H 3.4, N 4.0; found: C 24.2, H 2.9, N 3.9.

$[Co_2(6\text{-mna})_2]\cdot 3H_2O$ (CUK-2): A solution of 90 % 6-mercapto-3-pyridinecarboxylic acid (155 mg, 0.90 mmol) and KOH (1.0 M, 2.0 cm^3) in H_2O (4.0 cm^3) was stirred during the addition of $CoCl_2\cdot 6H_2O$ (238 mg, 1.0 mmol) dissolved in H_2O (4.0 cm^3). The mixture was heated for 18 h at 200 °C in a 23-cm^3 teflon-lined steel autoclave. Slow cooling over 4 h afforded a few very large blue-black blocks of CUK-2 that were manually isolated from other amorphous products and washed with H_2O (yield 188 mg, 79 %). Elemental analysis (%) calcd for $C_{12}H_{10}Co_2N_2O_6S_2$: C 31.3, H 2.2, N 6.1; found: C 31.4, H 1.8, N 6.1, indicating that the microanalysis sample at room temperature is not as well hydrated as the sample used for X-ray crystallography (see Figure 3).

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[10] Crystal data for CUK-1: $C_{14}H_{26}Co_3N_2O_{19}$, $M_r = 685.01\ \mathrm{g\,mol^{-1}}$, monoclinic, $C2/c$, $a = 17.0783(5)$, $b = 14.3338(4)$, $c = 10.7738(4)$ Å, $\beta = 106.3970(11)°$, $V = 2530.13(14)$ Å^3, $2\theta_{max} = 27.48°$, $\lambda = 0.71073$, $T = 180(2)$ K. 8890 reflections were collected, of which 2889 were unique ($R_{int} = 0.0424$). The structure was solved by direct methods and refined by full-matrix least squares on F^2. $R1 = 0.0495$ ($I > 2\sigma(I)$), $wR2 = 0.0877$ (all data), max/min residual electron density = 0.735/−0.502 e Å^{-3}. Crystal data for CUK-2: $C_{12}H_{12}Co_2N_2O_7S_2$, $M_r = 472.17\ \mathrm{g\,mol^{-1}}$, orthorhombic, $C222_1$, $a = 11.0477(3)$, $b = 13.5918(4)$, $c = 11.9580(4)$ Å, $V = 1795.59(9)$ Å^3, $2\theta_{max} = 27.49°$, $\lambda = 0.71073$ Å, $T = 180(2)$ K. 5446 reflections were collected, of which 2053 were unique ($R_{int} = 0.0288$). The structure was solved by direct methods and refined by full-matrix least squares on F^2. $R1 = 0.0225$ ($I > 2\sigma(I)$), $wR2 = 0.0508$ (all data), max/min residual electron density = 0.248/−0.320 e Å^{-3}.

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[12] Crystal data for dehydrated CUK-1: $C_{14}H_8Co_3N_3O_{10}$, $M_r = 541.01\ \mathrm{g\,mol^{-1}}$, monoclinic, $C2/c$, $a = 18.1020(7)$, $b = 12.7694(5)$, $c = 10.9701(5)$ Å, $\beta = 103.4004(16)°$, $V = 2466.72(18)$ Å^3, $2\theta_{max} = 27.54°$, $\lambda = 0.71073$ Å, $T = 375(2)$ K. 7431 reflections were collected, of which 2818 were unique ($R_{int} = 0.0357$). The structure was solved by direct methods and refined by full-matrix least squares on F^2. $R1 = 0.0471$ ($I > 2\sigma(I)$), $wR2 = 0.0695$ (all data), max/min residual electron density = 0.402/−0.335 e Å^{-3}. Crystal data for dehydrated CUK-2: $C_{12}H_6Co_2N_2O_4S_2$, $M_r = 424.17\ \mathrm{g\,mol^{-1}}$,orthorhombic, $C222_1$, $a = 11.1223(3)$, $b = 13.5606(4)$, $c = 12.1518(3)$ Å, $V = 1832.80(9)$ Å^3, $2\theta_{max} = 25.00°$, $\lambda = 0.71073$ Å, $T = 375(2)$ K. 6040 reflections were collected, of which 1613 were unique ($R_{int} = 0.0367$). The structure was solved by direct methods and refined by full-matrix least squares on F^2. $R1 = 0.0210$ ($I > 2\sigma(I)$), $wR2 = 0.0454$ (all data), max/min residual electron density = 0.178/−0.253 e Å^{-3}. CCDC-605434 (CUK-1), CCDC-605435 (CUK-2), CCDC-60436 (dehydrated CUK-1), and CCDC-605437 (dehydrated CUK-2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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