

## Transformation of a Metal–Organic Framework from the NbO to PtS Net

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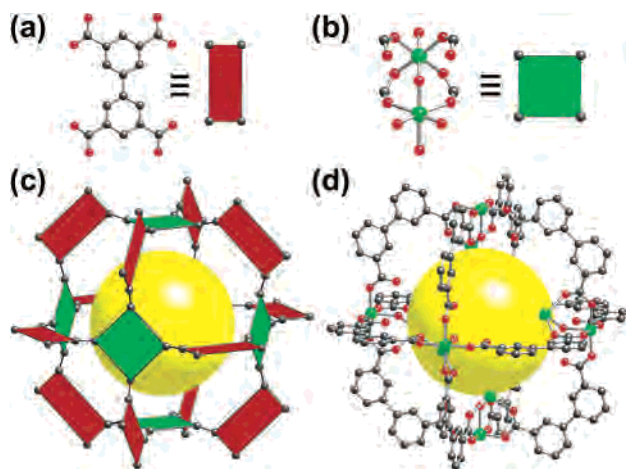
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Two metal–organic frameworks (MOFs), MOF-501 and MOF-502, respectively, formulated as  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})_5 \cdot \text{G}_x$  and  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})(\text{DMF})_2 \cdot \text{G}_x$  (BPTC = 3,3',5,5'-biphenyltetracarboxylate; G = guest molecules), have been synthesized and structurally characterized, and their topologies were found to be based on the NbO (MOF-501) and PtS (MOF-502) nets. Heating MOF-501 in solution results in the more thermodynamically favored MOF-502.

We have identified the most common nets that should result from the assembly of simple molecular shapes. These are referred to as default nets since, among an infinite number of possibilities, they form most frequently in MOF chemistry.<sup>1</sup> In particular, the NbO net was identified as the default for linking square building units that are oriented at 90° to each other, and the PtS net for linking square and tetrahedral building units.<sup>1a</sup> In this report, we exploit the ligand exchange lability of  $\text{Co}(\text{II})^2$  to show that a metal–organic framework (MOF) based on the NbO net (MOF-501) can be converted into one that is based on the PtS net (MOF-502). Structural transformations of MOFs have been reported in several cases<sup>3</sup> and used to tailor porosity in one notable example.<sup>4</sup>

MOF-501 was prepared from reaction of  $\text{H}_4\text{BPTC}$  (0.030 g, 0.09 mmol)<sup>5</sup> (Figure 1a) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.050 g, 0.17 mmol) in a solution containing DMF (3 mL),  $\text{C}_2\text{H}_5\text{OH}$  (3 mL), and  $\text{H}_2\text{O}$  (2 mL). This solution was sealed in a Teflon-lined stainless steel digestion bomb (23 mL) and



**Figure 1.** The crystal structure of  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})_5 \cdot \text{G}_x$  (MOF-501) showing (a) square BPTC (red) and (b) square  $\text{Co}_2(\text{CO}_2)_4$  (green) building units to form an NbO net (c) in the 3-periodic crystal structure (d) (Co, green; C, gray; O, red). Hydrogen atoms, guest molecules, and terminal solvent molecules have been omitted for clarity. Note: The  $\text{Co}_2(\text{CO}_2)_4$  cluster is disordered such that one cobalt center is located in four possible symmetry related positions; however, only one has been selected in making the illustration.

heated to 75 °C at a rate of 2 °C/min for 48 h. It was then cooled to room temperature at 1 °C/min to give orange cubic crystals of MOF-501, which was formulated as  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})_5 \cdot (\text{DMF})_3(\text{EtOH})(\text{H}_2\text{O})_4$  (37% yield, based on  $\text{H}_4\text{BPTC}$ ).<sup>6</sup>

During the synthesis of MOF-501, a small amount of a second phase was observed as purple plates whose proportion

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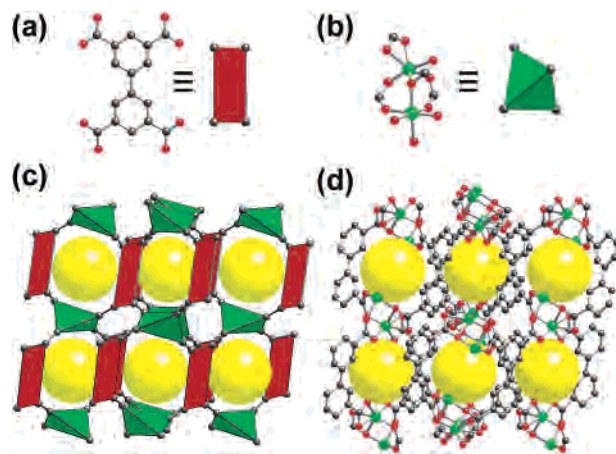
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- (5)  $\text{H}_4\text{BPTC}$  was prepared according to published methods: Coles, S. J.; Holmes, R.; Hursthouse, M. B.; Price, D. J. *Acta Crystallogr., Sect. E* **2002**, *E58*, o626. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ 13.51 (s, 1 H; COOH), 8.51 (t, <sup>3</sup>J(H,H) = 1.47 Hz, 4 H; ArH), 8.42 (d, <sup>3</sup>J(H,H) = 1.47 Hz, 2 H; ArH). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO): δ 166.35, 139.27, 132.36, 131.46, 129.55.

increased when reaction times were extended. Subsequently, a pure sample of the second phase, named MOF-502, was obtained by heating the reaction mixture for 144 h at 75 °C. This was obtained in 56% yield (based on  $\text{H}_4\text{BPTC}$ ) and formulated as  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})(\text{DMF})_2 \cdot (\text{DMF})(\text{H}_2\text{O})_{1.5}$ .<sup>7</sup> The direct transformation of MOF-501 into MOF-502 was also achieved by submerging isolated MOF-501 crystals in the original mother liquor and heating for 96 h at 75 °C.

As-synthesized MOF-501 gradually turns opaque after several days in air. It is insoluble in common organic solvents at room temperature. The guest molecules in freshly synthesized MOF-501 can be partially exchanged by organic solvents such as acetone, dichloromethane, benzene, acetonitrile, and tetrahydrofuran, and crystallinity was maintained for several days.<sup>8</sup> Although MOF-501 exhibits favorable solvent exchange properties, sorption studies of exchanged and evacuated samples indicate that it is nonporous to gases. We attribute the lack of permanent porosity to framework instability caused by loss of coordinated solvent and destabilization of the  $\text{Co}_2(\text{CO}_2)_4$  building units.

Both MOFs were characterized by single crystal X-ray diffraction studies.<sup>9</sup> MOF-501 is constructed from  $\text{Co}_2(\text{CO}_2)_4 \cdot (\text{H}_2\text{O})_5$  units (Figure 1b), in which two Co(II) centers, each having distorted octahedral coordination geometries, are bridged by two bis-monodentate carboxylates and one water molecule. Three terminal water ligands are bound to one of



**Figure 2.** The crystal structure of  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})(\text{DMF})_2 \cdot \text{G}_x$  (MOF-502) showing (a) square BPTC (red) and (b) distorted tetrahedral  $\text{Co}_2(\text{CO}_2)_4$  (green) building units to form an PtS net (c) in the 3-periodic crystal structure (d) (Co, green; C, gray; O, red). Hydrogen atoms, guest molecules, and the terminal solvent molecules have been omitted for clarity.

the Co(II) centers, while the other Co(II) center is coordinated by another water molecule and an oxygen from each of two monodentate carboxylates. The bridging  $\mu_2\text{-OH}_2$  was confirmed as such by comparison of the  $\text{Co}-\mu_2\text{-OH}_2$  bond lengths (1.986(6) and 2.184(9) Å), which clearly supports such assignment. Typical  $\text{Co}-\mu_2\text{-OH}_2$  distances are 2.151(21) Å, whereas  $\text{Co}-\mu_2\text{-OH}$  or  $\text{Co}-\mu_2\text{-O}$  bond lengths are 1.905(19) and 1.794(65) Å, respectively.<sup>10</sup> By considering the points-of-extension of the carboxylate C atoms of the  $\text{Co}_2(\text{CO}_2)(\text{H}_2\text{O})_5$  units, and the 3, 3', 5, and 5' carbon atoms of the organic unit, we observe that two squares are formed (Figure 1a,b). In the overall crystal structure, these square units are linked to produce a 3D-periodic structure that is based on the NbO net (Figure 1c). The crystal structure of MOF-501 (Figure 1d) supports a network of ca. 2700 Å<sup>3</sup> pores in which eight solvent molecules per formula unit reside.<sup>11</sup>

The structure of MOF-502 is also 3-periodic, and is constructed from  $\text{Co}_2(\text{CO}_2)_4(\text{H}_2\text{O})(\text{DMF})_2$  units and BPTC. Here again both Co(II) centers have distorted octahedral geometries and are bridged by three carboxylates: two bis-monodentate and one chelating  $\mu_2\text{-O}$  bridging tridentate (Figure 2b). One Co(II) center has a single water and two terminal DMF molecules while the other has two chelating bidentate carboxylates. When the points-of-extension (carboxylate C atoms) are considered, this unit approximates a tetrahedron, albeit distorted (Figure 2b), which when connected with squares (BPTC) gives the MOF-502 structure that is based on the PtS net (Figure 2c). In the overall crystal structure of MOF-502 (Figure 2d), there are pores of ca. 900 Å<sup>3</sup> which contain three solvent molecules per formula unit.<sup>9</sup>

Noting the distinct connectivity differences between these two structures,<sup>12</sup> the structural transformation must involve cleavage and formation of metal carboxylate bonds in

(6) Elemental microanalysis for **MOF-501**. Calcd for  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})_5 \cdot (\text{DMF})_3(\text{EtOH})(\text{H}_2\text{O})_4 = \text{Co}_2\text{C}_{27}\text{O}_{21}\text{N}_3\text{H}_{51}$ : C, 37.22; H, 5.85; N, 4.82. Found: C, 37.13; H, 5.58; N, 4.86%. FT-IR (KBr 4000–400  $\text{cm}^{-1}$ ): 3400 (br), 2936 (w), 1663 (s), 1622 (s), 1556 (s), 1439 (m), 1424 (s), 1388 (s), 1388 (s), 1368 (s), 1317 (w), 1255 (w), 1113 (w), 909 (w), 777 (m), 726 (m), 660 (m), 456 (w).

(7) Elemental microanalysis for **MOF-502**. Calcd for  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})(\text{DMF})_2 \cdot (\text{DMF})(\text{H}_2\text{O})_{1.5} = \text{Co}_2\text{C}_{25}\text{O}_{13.5}\text{N}_3\text{H}_{32}$ : C, 42.39; H, 4.55; N, 5.93. Found: C, 42.78; H, 4.69; N, 6.04%. FT-IR (KBr 4000–400  $\text{cm}^{-1}$ ): 3400 (br), 2936 (w), 1658 (s), 1627 (s), 1586 (s), 1450 (m), 1444 (s), 1418 (s), 1373 (s), 1317 (m), 1261 (m), 1108 (m), 1062 (w), 940 (w), 914 (w), 833 (w), 777 (s), 726 (s), 685 (s), 665 (s), 456 (w).

(8) **CH<sub>3</sub>COCH<sub>3</sub>**,  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})_5 \cdot (\text{DMF})_{0.2}(\text{CH}_3\text{COCH}_3)_2(\text{H}_2\text{O})_2$ : C, 38.73; H, 4.76; N, 0.40. Found: C, 38.75; H, 4.25; N, 0.48%.  $\text{CH}_2\text{Cl}_2$ ,  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})_5 \cdot (\text{DMF})(\text{CH}_2\text{Cl}_2)_2(\text{H}_2\text{O})_4$ : C, 29.70; H, 4.15; N, 1.65. Found: C, 29.98; H, 4.28; N, 1.94%.  $\text{C}_6\text{H}_6$ ,  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})_5 \cdot (\text{DMF})_{1.25}(\text{C}_6\text{H}_6)_{0.25}(\text{H}_2\text{O})_4$ : C, 35.59; H, 4.81; N, 2.44. Found: C, 35.17; H, 4.82; N, 2.87%.  $\text{CH}_3\text{CN}$ ,  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})_5 \cdot (\text{DMF})(\text{CH}_3\text{CN})_2 \cdot (\text{H}_2\text{O})_5$ : C, 35.45; H, 5.00; N, 5.39. Found: C, 35.63; H, 4.61; N, 5.30%.  $\text{C}_4\text{H}_8\text{O}$ ,  $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})_5 \cdot (\text{DMF})(\text{C}_4\text{H}_8\text{O})(\text{H}_2\text{O})_2$ : C, 38.61; H, 4.89; N, 1.96. Found: C, 38.85; H, 4.87; N, 2.06%.

(9) All crystallographic measurements were made on a Bruker SMART APEX CCD area detector with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) operated at 2000 W power (50 kV, 40 mA). The distance between crystal and detector was 5.056 cm. Both structures were solved by direct methods and subsequent difference Fourier syntheses using the SHELX-TL software suite. All non-hydrogen atoms were refined anisotropically. Contributions from disorder from guest molecules were accounted for using the SQUEEZE subroutine of the PLATON software suite. Crystallographic data for an orange block ( $0.09 \times 0.09 \times 0.09$  mm<sup>3</sup>) of MOF-501 cubic  $Fm\bar{3}m$  (No. 225), with  $a = 28.7135(6)$  Å,  $V = 23673.3(9)$  Å<sup>3</sup>,  $Z = 24$ ,  $\mu(\text{Mo K}\alpha) = 1.586$  mm<sup>-1</sup>,  $d_{\text{calc}} = 0.882$  g cm<sup>-3</sup>,  $T = 153(2)$  K,  $R1$  ( $I > 2\sigma(I)$ ) = 0.1398 and  $wR2$  (all data) = 0.3602, GOF = 1.248. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.326 and  $-0.682$  e<sup>-</sup>/Å<sup>3</sup>, respectively. Crystallographic data for a purple plate ( $0.10 \times 0.09 \times 0.05$  mm<sup>3</sup>) of MOF-502 monoclinic  $P2_1/n$  (No. 14), with  $a = 14.279(3)$  Å,  $b = 13.006(2)$  Å,  $c = 17.515(3)$  Å,  $\beta = 96.872(4)^\circ$ ,  $V = 3229.5(10)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Mo K}\alpha) = 1.434$  mm<sup>-1</sup>,  $d_{\text{calc}} = 1.091$  g cm<sup>-3</sup>,  $T = 153(2)$  K,  $R1$  ( $I > 2\sigma(I)$ ) = 0.0581 and  $wR2$  (all data) = 0.1408, GOF = 1.033. The maximum and minimum peaks in the final difference Fourier map corresponded to 1.013 and  $-0.590$  e<sup>-</sup>/Å<sup>3</sup>, respectively.

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addition to loss of water ligands (dehydration) from MOF-501 to yield MOF-502. Although we do not know the mechanism of this transformation, we believe studies of this kind will contribute to our understanding of how to control geometric and electronic factors within the inorganic units of MOFs. Making use of, or ideally controlling, such transformations will become an essential strategy in the design and synthesis of the next generation of functional MOF materials. This strategy will undoubtedly yield important milestones in highly selective chemical transformations and separations.

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**Supporting Information Available:** Topology illustrations, indexed XRPD patterns, crystallographic details, and CIF data. This material is available free of charge via the Internet at <http://pubs.acs.org>. Additionally, CCDC 257467 and 257468 contain the supporting crystallographic data (CIF) for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.. Fax: +44 1223 336033.

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