

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

Banglin Chen,^{*,†} Nathan W. Ockwig,[‡] Frank R. Fronczek,[§] Damacio S. Contreras,[†] and Omar M. Yaghi^{*,‡}

Department of Chemistry, University of Texas—Pan American, Edinburg, Texas 78541-2999, and Materials Design and Discovery Group, Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055, and Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804

Received October 5, 2004

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.¹ 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.^{1a} 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 cases³ and used to tailor porosity in one notable example.⁴

MOF-501 was prepared from reaction of H_4BPTC (0.030 g, 0.09 mmol)⁵ (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 H_2O (2 mL). This solution was sealed in a Teflon-lined stainless steel digestion bomb (23 mL) and

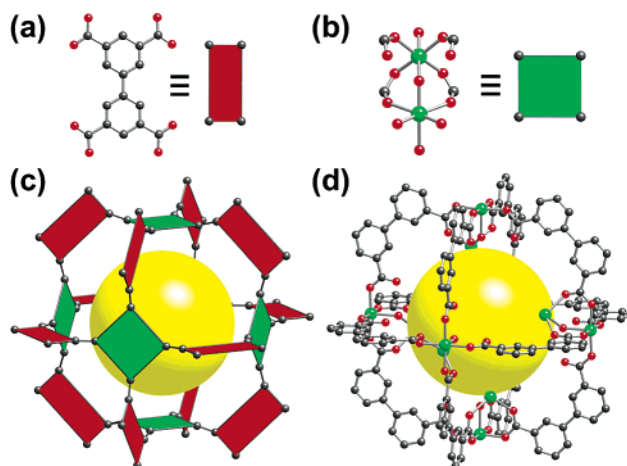


Figure 1. The crystal structure of $\text{Co}_2(\text{BPTC})(\text{H}_2\text{O})_5 \cdot \text{G}_x$ (MOF-501) showing (a) square BPTC (red) and (b) square $\text{Co}_2(\text{CO}_2)_4$ (green) building units to form an NbO net (c) in the 3-periodic crystal structure (d) (Co, green; C, gray; O, red). 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 H_4BPTC).⁶

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

* To whom correspondence should be addressed. E-mail: banglin@utpa.edu (B.C.); oyaghi@umich.edu (O.M.Y.).

[†] University of Texas—Pan American.

[‡] University of Michigan.

[§] Louisiana State University.

- (1) (a) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T. M.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3. (b) Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 8239. (c) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (d) Batten, S. R. *CrystEngComm* **2001**, *3*, 67. (e) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.
- (2) (a) Goshe, A. J.; Crowley, J. D.; Bosnich, B. *Helv. Chim. Acta* **2001**, *84*, 2971. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: Chicago, 1996.

- (3) (a) Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robson, R.; Williams, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 10641. (b) Min, K. S.; Suh, M. P. *J. Am. Chem. Soc.* **2000**, *122*, 6834. (c) Noro, S.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. *J. Am. Chem. Soc.* **2002**, *124*, 2568. (d) Pan, L.; Liu, H.; Lei, X.; Huang, X.; Olson, D. H.; Turro, N. J.; Li, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 542.

- (4) (a) Cussen, E. J.; Claridge, J. B.; Rosseinsky, M. J.; Kepert, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 9574. (b) Bradshaw, D.; Prior, T. J.; Cussen, E. J.; Claridge, J. B.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 6106.

- (5) H_4BPTC was prepared according to published methods: Coles, S. J.; Holmes, R.; Hursthouse, M. B.; Price, D. J. *Acta Crystallogr., Sect. E* **2002**, *E58*, o626. ¹H NMR (400 MHz, *d*₆-DMSO): δ 13.51 (s, 1 H; COOH), 8.51 (t, ³J(H,H) = 1.47 Hz, 4 H; ArH), 8.42 (d, ³J(H,H) = 1.47 Hz, 2 H; ArH). ¹³C NMR (100 MHz, *d*₆-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 H₄BPTC) and formulated as Co₂(BPTC)(H₂O)(DMF)₂·(DMF)(H₂O)_{1.5}.⁷ 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.⁸ 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 Co₂(CO₂)₄ building units.

Both MOFs were characterized by single crystal X-ray diffraction studies.⁹ MOF-501 is constructed from Co₂(CO₂)₄-(H₂O)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

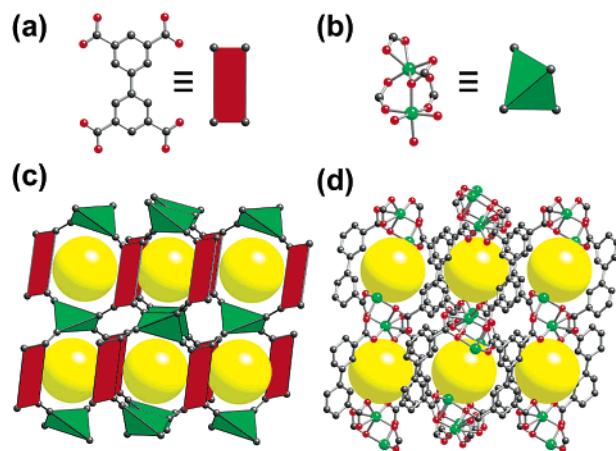


Figure 2. The crystal structure of Co₂(BPTC)(H₂O)(DMF)₂·G_x (MOF-502) showing (a) square BPTC (red) and (b) distorted tetrahedral Co₂(CO₂)₄ (green) building units to form an PtS net (c) in the 3-periodic crystal structure (d) (Co, green; C, gray; O, red). Hydrogen atoms, guest molecules, and the terminal 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 μ_2 -OH₂ was confirmed as such by comparison of the Co– μ_2 -OH₂ bond lengths (1.986(6) and 2.184(9) Å), which clearly supports such assignment. Typical Co– μ_2 -OH₂ distances are 2.151(21) Å, whereas Co– μ_2 -OH or Co– μ_2 -O bond lengths are 1.905(19) and 1.794(65) Å, respectively.¹⁰ By considering the points-of-extension of the carboxylate C atoms of the Co₂(CO₂)₄(H₂O)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 Å³ pores in which eight solvent molecules per formula unit reside.¹¹

The structure of MOF-502 is also 3-periodic, and is constructed from Co₂(CO₂)₄(H₂O)(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 μ_2 -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 Å³ which contain three solvent molecules per formula unit.⁹

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

(6) Elemental microanalysis for **MOF-501**. Calcd for Co₂(BPTC)(H₂O)₅·(DMF)₃(EtOH)(H₂O)₄ = Co₂C₂₇O₂₁N₃H₅₁: C, 37.22; H, 5.85; N, 4.82. Found: C, 37.13; H, 5.58; N, 4.86%. FT-IR (KBr 4000–400 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 Co₂(BPTC)(H₂O)(DMF)₂·(DMF)(H₂O)_{1.5} = Co₂C₂₅O_{13.5}N₃H₃₂: C, 42.39; H, 4.55; N, 5.93. Found: C, 42.78; H, 4.69; N, 6.04%. FT-IR (KBr 4000–400 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) **CH₃COCH₃**, Co₂(BPTC)(H₂O)₅·(DMF)_{0.2}(CH₃COCH₃)₂(H₂O)₂: C, 38.73; H, 4.76; N, 0.40. Found: C, 38.75; H, 4.25; N, 0.48%. CH₂Cl₂, Co₂(BPTC)(H₂O)₅·(DMF)(CH₂Cl₂)₂(H₂O)₄: C, 29.70; H, 4.15; N, 1.65. Found: C, 29.98; H, 4.28; N, 1.94%. C₆H₆, Co₂(BPTC)(H₂O)₅·(DMF)_{1.25}(C₆H₆)_{0.25}(H₂O)₄: C, 35.59; H, 4.81; N, 2.44. Found: C, 35.17; H, 4.82; N, 2.87%. CH₃CN, Co₂(BPTC)(H₂O)₅·(DMF)(CH₃CN)₂·(H₂O)₅: C, 35.45; H, 5.00; N, 5.39. Found: C, 35.63; H, 4.61; N, 5.30%. C₄H₈O, Co₂(BPTC)(H₂O)₅·(DMF)(C₄H₈O)(H₂O)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 α 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 × 0.09 × 0.09 mm³) of MOF-501 cubic *Fm* $\bar{3}m$ (No. 225), with $a = 28.7135(6)$ Å, $V = 23673.3(9)$ Å³, $Z = 24$, $\mu(\text{Mo K}\alpha) = 1.586$ mm⁻¹, $d_{\text{calc}} = 0.882$ g cm⁻³, $T = 153(2)$ 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⁻/Å³, respectively. Crystallographic data for a purple plate (0.10 × 0.09 × 0.05 mm³) 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, $\beta = 96.872(4)^\circ$, $V = 3229.5(10)$ Å³, $Z = 4$, $\mu(\text{Mo K}\alpha) = 1.434$ mm⁻¹, $d_{\text{calc}} = 1.091$ g cm⁻³, $T = 153(2)$ 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⁻/Å³, respectively.

(10) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton. Trans.* **1989**, 12, S1–S83.

(11) The van der Waals radius of C (1.70 Å) and H (1.20 Å) were employed in the determination of the distance parameters. Bondi, A. *J. Phys. Chem.* **1964**, 68, 441–451.

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.

- (12) O'Keeffe, M.; Hyde, B. G. *Crystal Structures: I. Patterns and Symmetry*; Mineralogical Society of America: Washington, DC, 1996. Coordination sequences and Schläfli symbols for NbO and PtS. CS-NbO: 4, 12, 28, 50, 76, 110, 148, 194, 244, 302 in 16 *3c*, *3d*. CS-PtS: 4, 10, 24, 42, 64, 92, 124, 162, 204, 252 in 8 *2c*. CS-PtS: 4, 10, 24, 42, 64, 90, 124, 162, 204, 250 in 8 *2e*. Schläfli-NbO: $6_2 \cdot 6_2 \cdot 6_2 \cdot 8_2 \cdot 8_2$ in 16 *3c*, *3d*. Schläfli-PtS: $4 \cdot 4 \cdot 8_2 \cdot 8_2 \cdot 8_8 \cdot 8_8$ in 8 *2c*. Schläfli-PtS: $4 \cdot 4 \cdot 8_7 \cdot 8_7 \cdot 8_7 \cdot 8_7$ in 8 *2e*.

Acknowledgment. This work was supported by the University of Texas—Pan American through start-up funds and a Faculty Research Council award to B. C., in part by the Welch Foundation grant (BG-0017) to the Department of Chemistry at UTPA, and by the National Science Foundation, for O.M.Y. (DMR-0242630).

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, by emailing 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.

IC048612Y