doi:10.1246/cl.2011.656

Preparation of Porous Cobalt(II) 1,3,5-Benzenetricarboxylates: Product Dependence on the Reaction Solvent and Additive

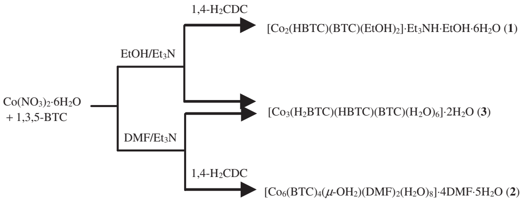
Jinxi Chen*[1,2] and Susumu Kitagawa[2]
[1]*School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, P. R. China*
[2]*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510*

(Received March 31, 2011; CL-110266; E-mail: chenjinxi@seu.edu.cn)

A novel three-dimensional porous coordination polymer, $[Co_2(HBTC)(BTC)(EtOH)_2]{\cdot}Et_3NH{\cdot}EtOH{\cdot}6H_2O$ (**1**) has been synthesized in ethanol at room temperature with 1,4-cyclohexanedicarboxylic acid (1,4-H_2CDC) as an additive. The final product of the reaction is found to be dependent upon the solvent and additive employed. When the solvent is changed from ethanol to dimethylformamide, another complex, $[Co_6(BTC)_4(\mu\text{-}OH_2)(DMF)_2(H_2O)_8]{\cdot}4DMF{\cdot}5H_2O$ (**2**) is instead obtained. Without H_2CDC, a two-dimensional framework, $[Co_3(H_2BTC)(HBTC)(BTC)(H_2O)_6]{\cdot}2H_2O$ (**3**), is produced in either solvents.

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have attracted extensive interest in the past decade because of their intriguing structural diversity and potential applications as functional materials in gas storage,[1] separation processes,[2] drug delivery,[3] catalysis,[4] and chemical sensing.[5] Despite numerous PCPs with unusual structures and often interesting properties being reported, significant challenges still remain in predicting structures based on the ligands and metals used. In particular, the finally obtained structures can be influenced by many factors, including the coordination geometries of metal ions, spatial arrangements of ligands, synthetic approaches, solvent effects, molar ratio of the reagents, temptation by guests or additives, and weaker interactions. It has been shown that among the aforementioned factors, solvents often play crucial roles: they can serve as coligands or guest molecules, and they often participate in weak interactions either among themselves or with the frameworks. The existence of additives is also very important, since most additives participate in weak interactions with the ligands and frameworks and also influence the crystal size and morphology of PCPs particles.[6] During our search for new PCPs, we have been focusing our attention on the reaction of Co salts with 1,3,5-benzenetricarboxylic acid (1,3,5-H_3BTC). H_3BTC is a useful three connecting ligand, and its threefold symmetry makes it very attractive for the preparation of MOFs.[7] It can be partially or fully deprotonated to generate H_2BTC^-, $HBTC^{2-}$, and BTC^{3-} at different pH values, effecting quite a few interesting supramolecular architectures through coordinative interactions and hydrogen bonds. In the current paper, we report the synthesis of three cobalt 1,3,5-benzenetricarboxylates and the influence of solvents and an organic additive, 1,4-cyclohexanedicarboxylic acid (1,4-H_2CDC) on the final products and their structures.

The synthetic routes to the three final products, $[Co_2(HBTC)(BTC)(EtOH)_2]{\cdot}Et_3NH{\cdot}EtOH{\cdot}6H_2O$ (**1**), $[Co_6(BTC)_4(\mu\text{-}OH_2)(DMF)_2(H_2O)_8]{\cdot}4DMF{\cdot}5H_2O$ (**2**), and $[Co_3(H_2BTC)(HBTC)(BTC)(H_2O)_6]{\cdot}2H_2O$ (**3**) are summarized in Scheme 1. All three compounds were synthesized and isolated as single-crystals through a room-temperature diffusion method with yields of 30–45%.[8] Their structures were determined with X-ray single-crystal diffraction, confirming that the coordination networks of two- or three-dimensions are dependent on the solvent and additive used in the synthesis.



Scheme 1. Different final products formed in different solvents with and without an additive.

Crystallization of $Co(NO_3)_2{\cdot}6H_2O$ with 1,3,5-H_3BTC in 1,4-H_2CDC–EtOH–Et_3N medium afforded **1** as a three-dimensional porous PCP. After the ethanol solvent was changed to dimethylformamide, another three-dimensional porous PCP, **2** was isolated. When the additive, 1,4-H_2CDC, was removed from the reaction systems, rather than compound **1** or **2**, a two-dimensional framework, **3** was obtained. Compound **2** was previously synthesized by Zhang and co-workers under solvothermal conditions,[9] while compound **3** was prepared by Ferey and co-workers under hydrothermal conditions,[10] with both their structures reported. We provide herein a brief discussion of the room-temperature liquid–liquid diffusion synthesis and characterization of **2** and **3** to illustrate the importance of reaction conditions with respect to the final products and their structures.

X-ray single-crystal analysis reveals that **1** crystallizes in rhombohedral space group $R\bar{3}$ and features a three-dimensional porous structure.[11] The asymmetric unit of compound **1** consists of two crystallographically independent Co atoms, one BTC, one HBTC, and two ethanol molecules coordinated to the Co(II) cations, one ethanol, six water molecules, and one protonated triethylammonium cation as guests. As shown in Figure 1, both Co cations adopt six-coordinate geometry with average Co–O distances of 2.115 and 2.103 Å for Co(1) and Co(2), respectively. The coordination sphere of Co(1) can be described as octahedral coordinated with two oxygen atoms from two carboxylate groups of two different HBTC ligands, three oxygen atoms from two carboxylate groups of two different BTC ligands, and one oxygen atom from an ethanol molecule. On the other hand, the Co(2) atom is coordinated with four oxygen atoms from three different BTC^{3-} ligands, one oxygen atom from HBTC ligand, and one oxygen atom from an ethanol molecule. Each Co(1)···Co(2) pair is interlinked through two carboxylate groups leading to a Co_2 dimer. Each of the two Co_2

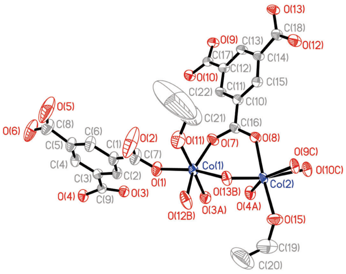


Figure 1. Coordination environments of Co(II) cations in **1**. Guest molecules and hydrogen atoms are omitted for clarity.

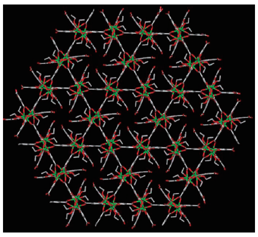


Figure 2. Three-dimensional frameworks shown in **1** along the *c* axis.

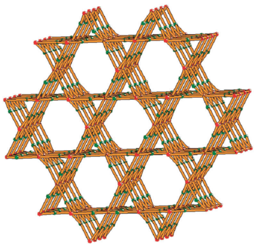


Figure 3. Schematic of topological net simplification for **1**.

dimers is linked through two HBTC ligands to form a Co_4 cluster. Each Co_4 secondary building unit (SBU) is connected to three BTC ligands, and each BTC ligand is further linked to three Co_4 SBUs. Through such connectivity, the three-dimensional framework is thus constructed, as shown in Figure 2. If we consider the Co_4 cluster as a connected node and the BTC anion as a three-connected node, the structure of **1** can be simplified to a (6,3)-connected net with $(4{\cdot}6^2)(4^2{\cdot}6^{10}{\cdot}8^3)$ topology (Figure 3).

After the solvent was changed from ethanol to dimethylformamide, another three-dimensional porous PCP, **2** was instead isolated. The weak basicity of DMF presumably leads to complete deprotonation of H_3BTC. Compound **2** adopts a three-dimensional framework structure that contains a new pseudo-paddle-wheel SBU of $Co_2(CO_2)_4$. When 1,4-H_2CDC was absent from the reaction system, yet another compound, **3** was obtained. Compound **3** is two-dimensional and formed with "dense" stacking of $[Co_3(H_2BTC)(HBTC)(BTC)(H_2O)_6]$ layers. The role of the additive in the synthesis of compounds **1** and **2** is unclear. One possibility is that it may participate in weak interactions with BTC ligands, thus weakening the π–π interactions between benzene rings of BTC ligands. Such π–π interactions are found in compound **3**.

This project was sponsored by the Natural Science Foundation of Jiangsu Province (No. BK2009262).

References and Notes

1 a) D. Tanaka, M. Higuchi, S. Horike, R. Matsuda, Y. Kinoshita, N. Yanai, S. Kitagawa, *Chem.—Asian J.* **2008**, *3*, 1343. b) L. J. Murray, M. Dincă, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294.

2 a) J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477. b) B. Chen, S. Xiang, G. Qian, *Acc. Chem. Res.* **2010**, *43*, 1115.

3 a) P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y. K. Hwang, V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur, R. Gref, *Nat. Mater.* **2010**, *9*, 172. b) K. M. L. Taylor-Pashow, J. D. Rocca, Z. Xie, S. Tran, W. Lin, *J. Am. Chem. Soc.* **2009**, *131*, 14261.

4 a) L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248. b) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450.

5 a) B. Chen, L. Wang, Y. Xiao, F. R. Fronczek, M. Xue, Y. Cui, G. Qian, *Angew. Chem., Int. Ed.* **2009**, *48*, 500. b) A. Lan, K. Li, H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. Hong, J. Li, *Angew. Chem., Int. Ed.* **2009**, *48*, 2334. c) Z. Xie, L. Ma, K. E. deKrafft, A. Jin, W. Lin, *J. Am. Chem. Soc.* **2010**, *132*, 922.

6 a) S. Diring, S. Furukawa, Y. Takashima, T. Tsuruoka, S. Kitagawa, *Chem. Mater.* **2010**, *22*, 4531. b) T. Tsuruoka, S. Furukawa, Y. Takashima, K. Yoshida, S. Isoda, S. Kitagawa, *Angew. Chem., Int. Ed.* **2009**, *48*, 4739.

7 J. Chen, S. Kitagawa, *Chem. Lett.* **2010**, *39*, 1186.

8 All three compounds were prepared through liquid–liquid diffusion at room temperature. H_3BTC (0.108 g, 0.500 mmol), 1,4-H_2CDC (0.086 g, 0.500 mmol), and $Co(NO_3)_2{\cdot}6H_2O$ (0.147 g, 0.500 mmol) were dissolved in EtOH (15 mL), into which a solution of a mixture of triethylamine (0.2 mL) and EtOH (2 mL) was allowed to diffuse slowly. After 4 weeks, compound **1** as red needle-like crystals with yield of 40.9% (based on $Co(NO_3)_2{\cdot}6H_2O$) was isolated from the resulting crystalline solids. Through a similar method but without 1,4-H_2CDC, compound **3** with 2D layer network was obtained. Using DMF as the solvent instead of EtOH, compound **2** was prepared under otherwise the same procedure as **1**. H_3BTC (0.108 g, 0.500 mmol), 1,4-H_2CDC (0.086 g, 0.500 mmol), and $Co(NO_3)_2{\cdot}6H_2O$ (0.147 g, 0.500 mmol) were dissolved in DMF (15 mL). Into the above mixture was allowed to diffuse a mixed solution of triethylamine (0.2 mL) and DMF (2 mL). After 4 weeks, compound **2** was separated from the resulting crystalline solids as dark red crystals with yield of 35.5% (based on $Co(NO_3)_2{\cdot}6H_2O$). Small amount of triethylamine used in the above procedures was to help deprotonate the ligand, H_3BTC. The original pH values of the reaction mixtures for complexes **1**, **2**, and **3** were 4.2, 6.3, and 5.1, respectively.

9 F. Luo, Y.-X. Che, J.-M. Zheng, *Cryst. Growth Des.* **2008**, *8*, 176.

10 C. Livage, N. Guillou, J. Marrot, G. Férey, *Chem. Mater.* **2001**, *13*, 4387.

11 Single-crystal X-ray data were collected at 293 K on a Rigaku Mercury diffractometer with Mo Kα radiation ($\lambda = 0.7101$ Å). The structures were solved by direct methods (SIR97), and refined by full-matrix least-squares on F^2. Crystal data for **1**. $C_{30}H_{36}NO_{19.50}Co_2$ (293 K). $M_r = 840.46$, rhombohedral, space group $R\bar{3}$, $a = 32.8195(15)$ Å, $c = 19.0793(11)$ Å, $V = 17797.4(15)$ Å^3, $Z = 18$, $D_{calcd} = 1.412$ g cm^{-3}, absorption coefficient 0.914 mm^{-1}, total reflections collected 45315, unique 9052 ($R_{int} = 0.0448$), GOF = 1.133, $R1 = 0.0838$, $Rw = 0.2199$ ($I > 2\sigma(I)$). Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-821998. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).