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Guest-induced Single-crystal-to-single-crystal Transformation in Copper Complexes of 1,3,5-Benzenetricarboxylic Acid and 4,4′-Bipyridine

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A 2-dimensional (2D) noninterpenetrated flexible porous coordination polymer, [Cu(HBTC)(4,4′-bpy)]$\cdot$$C_6H_{11}OH$$\cdot$$H_2O$ (**1**), has been synthesized and characterized using single-crystal X-ray diffraction. The cyclohexanol guest molecules in **1** can be removed upon soaking **1** in ethanol. Complex **1** undergoes a single-crystal transformation to form an ethanol solvate, [Cu(HBTC)(4,4′-bpy)(H_2O)]$\cdot$$C_2H_5OH$$\cdot$$2H_2O$ (**2**), and during the process, the octahedral coordination of the copper cation in **1** converts to square-pyramidal coordination in **2**.

In recent years, considerable efforts have been devoted to the design and construction of new porous coordination polymers (PCPs) or metal organic frameworks (MOFs). Besides the efforts in rigid and robust PCPs, there is also growing interest in flexible and dynamic PCPs, in particular, those reversibly change their structures and properties in response to guest exchange.[1] This so-called "structural dynamism" would be a key principle for high selectivity, accommodation, and separation of specific molecules and, at present, is regarded as the basis of the next generation of porous materials.[2] Hence the creation of a host framework that can interact with certain guest molecules in a switchable fashion has implications to the engineering of advanced materials with potential applications in molecular sensing.[3] Guest-induced structural transformation can be expressed in several dynamic behaviors, e.g., sliding motion of layers and breathing of 3-dimensional (3D) networks, rotation or distortion of organic linkers, or change in geometry around metal ions.[4] During our search for new PCPs, we focused our attention on the construction of PCP using mixed ligand systems that facilitate the incorporation of functionality based on the chemical modification in the ligands. It is well-known that copper cations can be simultaneously coordinated by both oxygen- and nitrogen-containing ligands in solution. With an aim of studying the flexiblility of PCPs, we herein choose 1,3,5-benzenetricarboxylic acid (1,3,5-H_3BTC) and 4,4′-bipyridine (4,4′-bpy) as ligands. 1,3,5-H_3BTC has a rich coordination chemistry, and it can be either partially or fully deprotonated to generate H_2BTC^-, $HBTC^{2-}$, and BTC^{3-} at different pH's, effecting quite a few interesting supramolecular architectures through the coordinative interactions and hydrogen bonding. In the current paper, we present the synthesis, structure, and guest-induced structural transformation of a copper complex, [Cu(HBTC)(4,4′-bpy)]$\cdot$$C_6H_{11}OH$$\cdot$$H_2O$ (**1**). To the best of our knowledge, only one coordination polymer with an empirical formula of $Cu(H_2BTC)_2$(4,4′-bpy) has been reported to date.[5] The reported structure was 1-dimensional (1D) chain-based, in which the coordination sphere of copper can be described as a square planar, whereas ours herein is a 2-dimensional (2D) porous coordination polymer with copper adopting an octahedral geometry.

After a solution of 1,3,5-H_3BTC and 4,4′-bpy in cyclohexanol was carefully layered onto an aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$ and allowed to stand for several days at room temperature, blue crystals of **1** were grown on the interface of the two solutions.[6] X-ray single-crystal analysis reveals that **1** crystallizes in an orthorhombic space group *Cmca* and has 2D non-interpenetrated layered frameworks.[7] The asymmetric unit of **1** consists of 1/2 unit of Cu(II), 1/2 HBTC, 1/2 4,4′-bpy, 1/2 cyclohexanol, and 1/2 water molecule. The Cu(1) site has an octahedral geometry and is coordinated by four oxygen atoms from two carboxylate groups and two nitrogen atoms (Figure 1). Each copper atom is linked by two BTC ligands to two neighboring copper atoms to effect a 1D chain, and the adjacent chains are further connected by bpy ligands to form a 2D layered framework. The 2D layered structure can be regarded as the fusion of rectangular (4, 4) topological layers. Within a layer, there are large rectangular cavities and each is enclosed by two BTC and two bpy ligands. The dimension of a rectangular cavity is 11.0 × 9.3 $Å^2$. The effective cavity size in **1** after the removal of van der Waals radii is ca. 8.2 × 5.5 $Å^2$. Owing mostly to such large dimension and the fact that one carboxyl group in the BTC ligand is free, two layered sheets are embedded in each other in a face-to-face manner. As B is the 180° rotation of A, these embedding segments adopt an ABAB sequence along the *c* axis to form 1D rectangular channels with an effective size of 5.0 × 3.3 $Å^2$ (Figure 2). The rectangular channels are filled with cyclohexanol and water molecules.

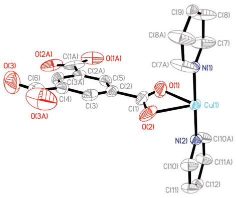

Figure 1. Coordination environment of Cu(II) in **1**. Guest molecules and hydrogen atoms are omitted for clearity.

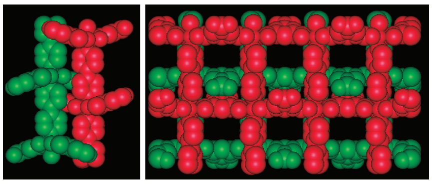

Figure 2. ABAB sequence along the *c* axis (left) and rectangular channels with effective size of 5.0 × 3.3 $Å^2$ along the *b* axis (right) of **1**.

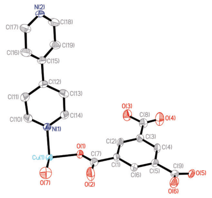

Figure 3. Coordination environment of Cu(II) in **2**. Guest molecules and hydrogen atoms are omitted for clearity.

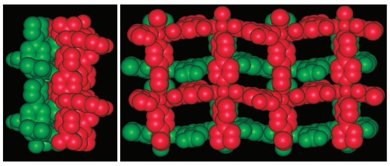

Figure 4. AA sequence along the *c* axis (left) and rectangular channels with effective size of 5.7 × 4.3 Å^2 along the *b* axis (right) of **2**.

The flexibility of **1** was examined by a guest-exchange experiment. Upon soaking complex **1** in ethanol for 3 days, the color of the crystal changes to light blue. The transformation yield is about 40%. Single-crystal analysis suggests that **1** undergoes single-crystal transformation to form an ethanol solvate, [Cu(HBTC)(4,4′-bpy)(H_2O)]•C_2H_5OH•$2H_2O$ (**2**). Complex **2** crystallizes in a monoclinic space group $P2_1/n$ and has 2D noninterpenetrated layered frameworks that encapsulate ethanol and water molecules. The asymmetric unit of **2** consists of one Cu(II) cation, one water molecule, one HBTC, and one 4,4′-bpy coordinated to the Cu(II) cation, and one ethanol and two water molecules as guests. Compared to the octahedral geometry around the Cu cation in complex **1**, the Cu(1) site in **2** has a square-pyramidal geometry and is coordinated by two oxygen atoms from two carboxylate groups, one oxygen atom from water, and two nitrogen atoms (Figure 3). Each copper atom is linked by two BTC ligands to two additional copper atoms to effect a 1D chain, and the adjacent chains are further connected by bpy ligands to form a 2D layered framework. The 2D layered structure can also be regarded as the fusion of rectangular (4, 4) topological layers. Within each layer, there are large rectangular cavities and every one of them is enclosed by two BTC and two bpy ligands. The dimension of a rectangular cavity is 11.1 × 10.4 Å^2. The effective cavity size in **2** after the removal of van der Waals radii is ca. 8.3 × 7.6 Å^2. The 2D (4, 4) network extends along the *ab* plane, and adjacent 2D wave-like layers are packed adopting an AA sequence parallel along the *c* direction with a distance of $1/2b$ and show a relative off-set of $1/2c$ in the *c* direction. This stack fashion forms noninterpenetrated 3D arrays with 1D rectangular channels with an effective size of 5.7 × 4.3 Å^2 (Figure 4). The rectangular channels are filled with ethanol and water molecules.

Although what is attributed to the structural transformation from **1** to **2** is still unclear, the coordinative covalent bonding and Jahn–Teller effect of the copper cation likely play a role. It is noteworthy that after varying the solvent from cyclohexanol to ethanol, complex **2** can also be obtained with a very low yield in one step.

In conclusion, a flexible porous coordination polymer, [Cu(HBTC)(4,4′-bpy)]•$C_6H_{11}OH$•H_2O (**1**), has been synthesized and characterized using single-crystal X-ray diffraction. Complex **1** converts to an ethanol solvate, [Cu(HBTC)(4,4′-bpy)(H_2O)]•C_2H_5OH•$2H_2O$, upon soaking **1** in ethanol.

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References and Notes

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6 A typical procedure for complex **1** is as follows: 1,3,5-H_3BTC (0.105 g, 0.50 mmol) and 4,4′-bpy (0.078 g, 0.50 mmol) were dissolved in cyclohexanol (10 mL) with stirring. The solution was carefully layered onto an aqueous solution of $Cu(NO_3)_2$•$3H_2O$ (0.050 M) and stood undisturbed for several days at room temperature. Blue crystals of **1** were grown on the interface of the two solutions (yield: 20%). Elemental analysis. Calcd for **1** ($C_{25}H_{26}N_2O_8Cu$): C, 54.99; H, 4.80; N, 5.13%. Found: C, 54.68; H, 4.97; N, 5.01%. Elemental analysis. Calcd for **2** ($C_{21}H_{24}N_2O_{10}Cu$): C, 47.77; H, 4.58; N, 5.30%. Found: C, 47.56; H, 4.74; N, 5.19%.

7 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**. $C_{12.5}H_{13}NO_4Cu$ (293 K). $M_r = 273$, orthorhombic, space group *Cmca*, $a = 18.613(3)$ Å, $b = 22.084(4)$ Å, $c = 11.703(2)$ Å, $V = 4810.6(14)$ Å^3, $Z = 16$, $D_{calcd} = 1.502$ g cm^{-3}, absorption coefficient 0.961 mm^{-1}, total reflections collected 9727, unique 2197 ($R_{int} = 0.0490$), GOF = 1.168, $R1 = 0.0634$, $Rw = 0.1678$ ($I > 2\sigma(I)$). Crystal data for **2**. $C_{21}H_{24}CuN_2O_{10}$ (293 K). $M_r = 528$, monoclinic, space group $P2_1/n$, $a = 10.6914(17)$ Å, $b = 20.019(3)$ Å, $c = 11.1071(18)$ Å, $\beta = 91.498(2)°$, $V = 2376.5(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.501$ g cm^{-3}, absorption coefficient 0.975 mm^{-1}, total reflections collected 11786, unique 5214 ($R_{int} = 0.0369$), GOF = 1.041, $R1 = 0.0614$, $Rw = 0.2100$ ($I > 2\sigma(I)$). Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-793562 (**1**) and -793563 (**2**). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).