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A Novel Bilayer Cobalt(II)–Organic Framework with Nanoscale Channels Accommodating Large Organic Molecules

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A unique noninterpenetrated 2D bilayer cobalt(II)–organic framework, $[\{Co(dpe)(NO_2\text{–}BDC)\}\cdot 0.5(dpe)]_n\cdot nH_2O$ (**1**), possessing nanoscale rectangular channels that clathrate large organic molecules, has been hydrothermally synthesized by reaction of cobalt(II) salt with 5-nitro-1,3-benzenedicarboxylic acid ($NO_2\text{–}H_2\text{-}BDC$) and 1,2-bis(4-pyridyl)ethylene (dpe).

The construction of polymeric metal−organic frameworks (MOFs) represents a fast growing area in coordination and supramolecular chemistry. Applications are therefore anticipated as functional solid materials, such as nonlinear optics, molecular selection, ion exchange, and catalysis.[1,2] Various structures with interesting compositions and topologies have been produced through judicious choice of ligand and metal precursor geometry,[3] and especially, those that can act as hosts to capture guest molecules have attracted much attention from chemists.[4] One of the outstanding challenges of designing coordination polymers with porous structures has been the formation of interpenetrated networks, which generally resulted in more condensed structures having either very small pores or no pores at all.[5] The noninterpenetrating square-grid (or rectangular-grid) polymers are an important class of network with predictable openings and can accommodate guest molecules that meet size-exclusion criteria.[6] In an effort to establish strategies aimed at preventing interpenetration and the design of rectangular-grid polymers with large pores, we utilized the pyridyl-type ligand dpe (dpe = 1,2-bis(4-pyridyl)ethylene) with $NO_2\text{−}H_2BDC$ ($NO_2\text{−}H_2\text{-}BDC$ = 5-nitro-1,3-benzenedicarboxylic acid) to generate a metal−organic framework $[\{Co(dpe)(NO_2\text{−}BDC)\}\cdot 0.5(dpe)]_n\cdot nH_2O$ (**1**), which is the first example of a noninterpenetrated 2D bilayer with nanoscale rectangular channels that clathrate large organic molecules. This Communication reports its preparation and crystal structure along with its thermogravimetric analysis result.

The hydrothermal reactions of cobalt(II) salt with dpe and $NO_2\text{−}BDC$ in the molar ratio of 2:2:3:2220 at 200 °C for 3 days led to the formation of deep-red crystalline compound **1**.[7] Compound **1** is insoluble in water and common organic solvents. The IR spectrum of the compound showed the typical antisymmetric (1581 cm^{-1}) and symmetric (1527 and

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(7) Synthesis of **1**: The pH value of an aqueous mixture (10 mL) containing $NO_2\text{−}H_2BDC$ (0.5 mmol), $Co(NO_3)_2\cdot 6H_2O$ (0.5 mmol), and dpe (0.75 mmol) was preadjusted to about 6 with 0.1 M NaOH aqueous solution, and the mixture was transferred into a autoclave Teflon-lined stainless vessel (18 mL). The vessel was sealed and heated to 200 °C for 72 h and then cooled to room temperature at a rate 10 °C/h. Deep-red crystals of **1** were obtained (0.23 g, 84%). Anal. for **1**, Calcd: C, 55.78; H, 3.56; N, 10.01. Found: C, 55.39; H, 3.62; N, 9.96%.

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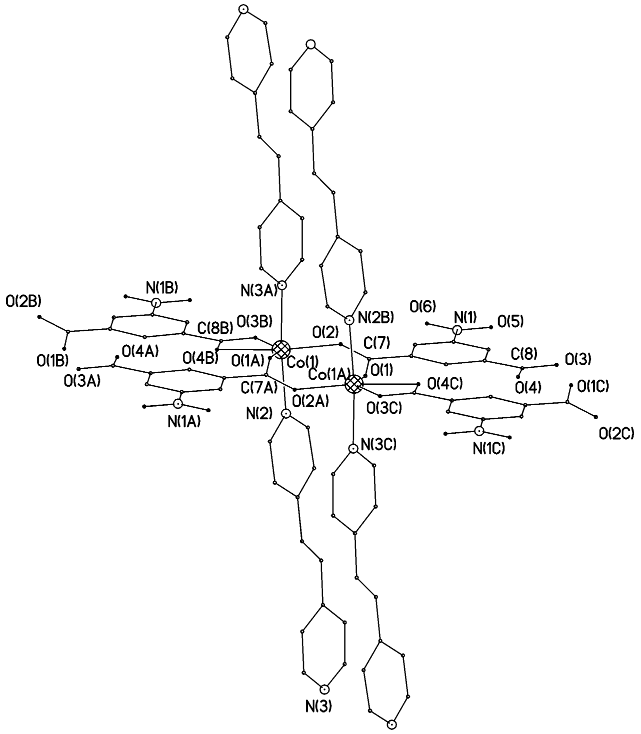

Figure 1. Perspective view of the coordination environment of the cobalt atom and view of the dicobalt moiety in **1**.

1402 cm^{-1}) stretching bands of carboxylate groups. The respective values of [$\nu_{asym}(CO_2) - \nu_{sym}(CO_2)$] clearly indicate the presence of chelating (54 cm^{-1}) and bridging coordination modes (179 cm^{-1}) in **1**.[9] The absence of the expected 1730−1690 cm^{-1} for the protonated carboxylate groups illustrates the complete deprotonation of NO_2−BDC in the reaction with cobalt ion.[10] The emission spectra of the compound in the solid state showed a broad band at $\lambda_{max} = 444$ nm when irradiated at 280 nm, which is nearly the same as that of free dpe ligand. The formula of the crystalline compound was confirmed as $[\{Co(dpe)(NO_2{-}BDC)\}{\cdot}0.5(dpe)]_n{\cdot}nH_2O$ (**1**) by elemental analysis and structural characterization of X-ray single-crystal diffraction.[7,8]

The structure of **1** is a unique two-dimensional bilayer framework in which the asymmetric unit contains 1 cobalt(II) atom, 1 NO_2−BDC molecule, 1 coordinated dpe molecule, 0.5 free dpe molecule, and 1 free water molecule. The cobalt(II) atoms are bridged by both NO_2−BDC and dpe ligands, and all cobalt atoms are equivalent and octahedrally coordinated by a chelating carboxylate group of a NO_2−BDC with Co−O distances of 2.132(2) and 2.249(2) Å, 2 μ_2-bridging carboxylate groups of 2 NO_2−BDC with Co−O distances of 2.040(2) and 2.045(2) Å, and 2 pyridyl N atoms of 2 dpe ligands at trans-positions with Co−N

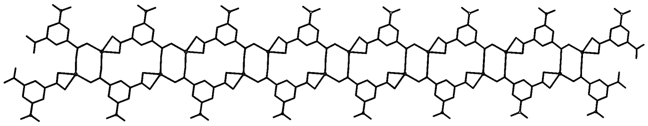

Figure 2. View of the 1D ladder of $[Co_2(NO_2{-}BDC)_2]_n$ in **1**.

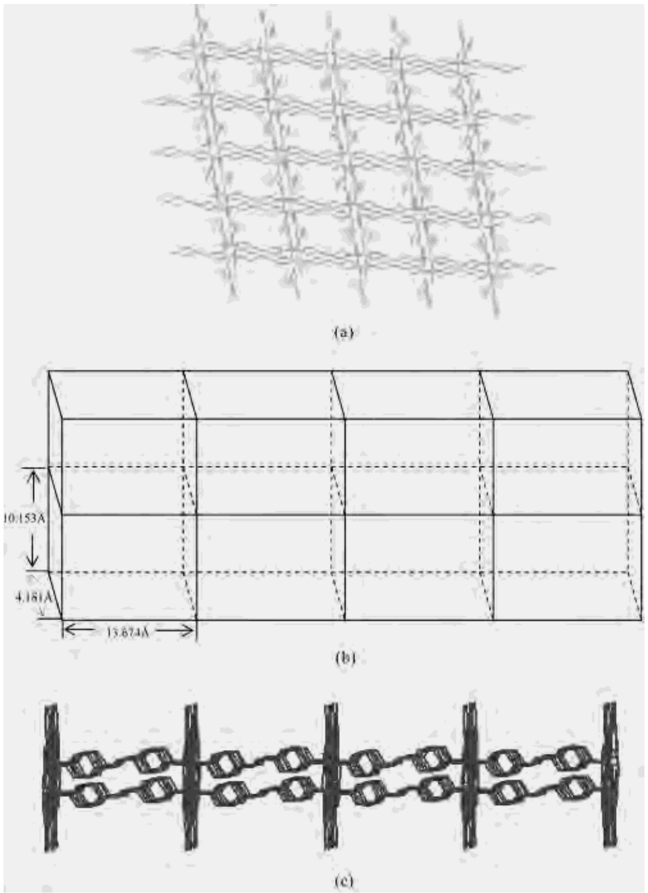

Figure 3. (a) View of the 2D bilayer of **1**, (b) scheme representation of the 2D bilayer of **1**, and (c) side view of the 2D bilayer along the *b*-axis.

distances of 2.146(2) and 2.142(2) Å, as shown in Figure 1. The nitrogen atoms are located in the axial positions with N−Co−N angles of 174.67(7)°, whereas the O−Co−O angles around the Co center range from 59.86(7)° to 155.70(7)°.

The NO_2−BDC acts as a μ_3-bridge in **1** through 1 μ_2-bridging carboxylate and 1 chelating carboxylate to link 3 cobalt(II) ions. The second building unit (SBU) for **1** is a dicobalt carboxylate moiety, where the 2 Co atoms are bridged by 2 μ_2-bridging carboxylate groups of 2 different NO_2−BDC ligands, with Co···Co distance of 4.181 Å. The dicobalt cores are linked by 4 *exo*-tridentate NO_2−BDC ligands to 2 adjacent dicobalt cores to result in a 1D ladder of $[Co_2(NO_2{-}BDC)_2]_n$, and the adjacent ladders are connected by dpe ligands to form a unique 2D bilayer as in Figure 3a. Figure 3b shows that the long dpe ligands act as pillars between adjacent ladders, in which the planar ladder was separated to generate the rectangular cavity. The length of the cavity is established by the distance between cobalt atoms of adjacent ladders ($d_{Co\cdots Co} = 13.674$ Å), and the height of the cavity is established by the adjacent Co···Co distance (10.153 Å) in the side of the $[Co_2(NO_2{-}BDC)_2]_n$

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(8) For X-ray crystallography, see Supporting Information. Crystal data for compound **1**: $C_{26}H_{20}CoN_4O_7$, $M = 559.39$, triclinic, space group $P\bar{1}$, $a = 9.648(2)$ Å, $b = 10.153$ (2) Å, $c = 13.674$ (3) Å, $V = 1213.9(4)$ Å^3, $Z = 2$, R1 = 0.0386 [$I > 2\sigma(I)$], wR2 = 0.1042, and GOF = 0.968.

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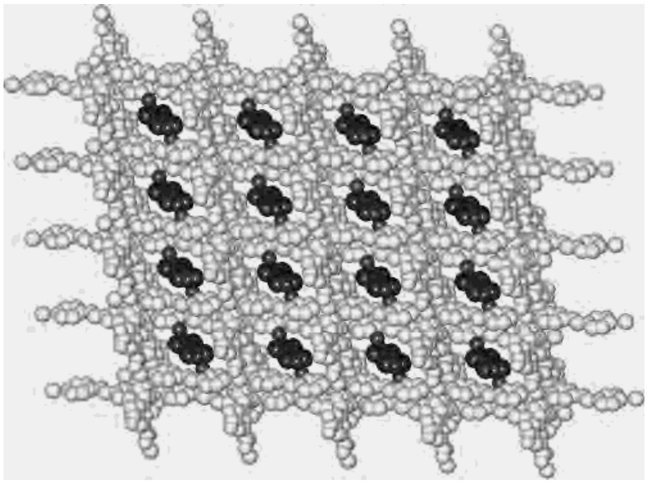

Figure 4. View of the guest molecules clathrated in the channels of **1**.

ladder, while the depth of the cavity is the Co···Co distance (4.181 Å) within the dicobalt core $[Co_2(CO_2)_2]$. The structure can also be regarded as two grid sheets with (4,4) net topology which are constructed through Co centers bridged by NO_2−BDC in the *a*-axis and dpe in the *b*-axis, which are linked by μ_2-bridging carboxylate groups of NO_2−BDC to result in the unprecedented 2D bilayer framework (Figure 3c).[11] The most striking feature of **1** is that the adjacent 2D bilayers are parallel and stacked without interpenetrating to generate nanoscale rectangular channels, which accommodate large dpe organic molecules and free water molecules (Figure 4). Moreover, the guest dpe molecules between adjacent layers are packed next to one another through $\pi\cdots\pi$ interaction with the distance of 3.57 Å between the pyridyl rings, resulting in an additional zigzag chain in each channel. To our knowledge, compound **1** constitutes the first example of a noninterpenetrated 2D bilayer coordination polymer with nanoscale channels that clathrate a large organic guest molecule.[11−14]

Thermogravimetric analysis (TGA) was performed in air at a heating rate of 10 °C/min on a polycrystalline sample of **1**. The result showed the well-separated weight loss steps: a total weight loss of 3.28% occurred over the temperature range 45−110 °C, corresponding to the loss of 1 water molecule per formula (calcd 3.22%), followed by a loss of 16.31% during 160−260 °C, corresponding to the loss of the 0.5 free dpe molecule per formula unit (calcd 16.27%). From 320 to 580 °C, there was the total loss of 50.95% consistent with the removal of coordinated dpe and NO_2−BDC ligands. The remaining weight of 29.36% corresponds to the percentage (29.65%) of the Co and O components, indicating that the final product is Co_2O_3.

Elemental analysis result (C 53.32%; H 2.92%; N 9.38%) of the calcinations product (defined as **1′**) of **1** in air at 270 °C for 8 h shows that the guest molecules are removed in the course of calcinations (calcd for framework formula of $[Co(dpe)(NO_2{-}BDC)]_n$: C, 53.29%; H, 2.89%; N, 9.33%). The X-ray powder diffraction studies reveal that the pattern of **1** is nearly the same as that of **1′**. Both results indicate that the porous network of **1** is retained after the calcinations and removal of guests.

In conclusion, through the hydrothermal reaction of cobalt(II) salt with mixed dicarboxylate and 4,4′-dipyridine-like ligands, we have synthesized a unique 2D bilayer cobalt(II)−organic framework with nanoscale channels accommodating large organic molecules, providing a valuable approach for the construction of new and interesting porous coordination polymers.

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Supporting Information Available: Crystallographic tables and X-ray crystallographic file in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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