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# Syntheses and crystal structures of two structurally diverse cobalt complexes constructed from 5-hydroxyl-1,3-benzenedicarboxylates

Hong-Yin He[a], Yi-Li Zhou[a], Yan Hong[a], Long-Guan Zhu[b,*]

[a]*Department of Chemical Engineering, Jiaxing College, Jiaxing 314001, People's Republic of China*
[b]*Department of Chemistry, Zhejiang University, 38 Zheda Road, Hangzhou 310027, People's Republic of China*

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## Abstract

Two structurally diverse compounds, $\{[Co(4,4'\text{-bipy})(H_2O)_4](hmbdc)(H_2O)\}_n$ (**1**) and $\{[Co(4,4'\text{-bipy})(hmbdc)(H_2O)_2](4,4'\text{-bipy})(DMF)\}_n$ (**2**) ($H_2$hmbdc = 5-hydroxyl-1,3-benzenedicarboxylic acid, 4,4′-bipy = 4,4′-bipyridine), were synthesized using different starting materials and solvents. Compound **1** possesses hydrogen-bonded 3D networks encapsulating 1D covalently bonded infinite $[Co(4,4'\text{-bipy})(H_2O)_4]^{2+}$ chain. Compound **2** shows a 2D architecture and free 4,4′-bipy and DMF molecules fill in the channels of the extended 3D hydrogen bonding network as guest molecules.

*Keywords:* Hydrogen bonding; Crystal structure; Cobalt complex; Diversity; Polymer

## 1. Introduction

The crystal engineering in the field of supramolecular architectures based on metal and organic ligands has been extensively studied in recent years owing to their novel and diverse topologies and potential applications as functional materials [1–3]. In general, two different types of interactions (covalent bonds and noncovalent intermolecular forces) could be used to construct variable supramolecular architectures [4]. On this background, numerous compounds with the $[M(4,4'\text{-bipy})(H_2O)_4]^{2+}$ building blocks have been prepared [5–8], such as $[Zn(H_2O)_4(4,4'\text{-bipy})](NO_3)_2\cdot 2(4,4'\text{-bipy})$, $[Co(H_2O)_4(4,4'\text{-bipy})](PF_6)\cdot 3(\text{-}3(bipy)$, and $[Co(H_2O)_4(4,4'\text{-bipy})](4\text{-abs})_2\cdot H_2O$, which fabricate extended 2D or 3D architectures from 1D covalently bonded chains through hydrogen bonds. Here, we employed 4,4′-bipyridine and 5-hydroxyl-1,3-benzenedicarboxylic acid ($H_2$hmbdc) as mixed organic building blocks to construct two supramolecular structures with uncoordinated $hmbdc^{2-}$ anion and coordinated $hmbdc^{2-}$ ligand, namely $\{[Co(4,4'\text{-bipy})(H_2O)_4](\text{-}hmbdc)(H_2O)\}_n$ (**1**) and $\{[Co(4,4'\text{-bipy})(hmbdc)(H_2O)_2](\text{-}DMF)(4,4'\text{-bipy})\}_n$ (**2**).

## 2. Experimental

### 2.1. Synthesis and IR spectra

$\{[Co(4,4'\text{-bipy})(H_2O)_4](hmbdc)(H_2O)\}_n$ (**1**). Crystals of **1** were grown by layer-method using three-layer solutions in a slender tube with a 0.8 cm diameter. The upper layer solution was 5 mL of $C_2H_5OH$/THF (v/v 2:1) containing 0.03 mol/L $H_2$hmbdc and 0.06 mol/L 4,4′-bipyridine. The bottom layer solution was 5 mL of aqueous solution containing 0.03 mol/L $Co(CH_3COO)_2\cdot 4H_2O$ and the middle layer was 5 mL of $C_2H_5OH/H_2O$ (v/v 1:1) mixed solvent system. After standing for 2 months, purple rod crystals were obtained. They were collected by suction filtration. Anal. Calc. for $C_{18}H_{22}CoN_2O_{10}$: C, 44.55; H, 4.57; N, 5.77%. Found: C, 44.48; H, 4.62; N, 5.71%. IR (KBr pellet, $cm^{-1}$): 3458(s), 3255(s), 1609(s), 1546(s), 1489(m), 1411(s), 1366(s), 1280(m), 1217(w), 1105(w), 1071(w), 983(w), 789(s), 729(m), 680(m), 634(m), 482(w).

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* Corresponding author. Tel.: +86 571 8796 3867; fax: +86 571 8795 1895.

*E-mail address:* chezlg@zju.edu.cn (L.-G. Zhu).

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$\{[Co(4,4'\text{-bipy})(hmbdc)(H_2O)_2](DMF)(4,4'\text{-bipy})\}_n$ (**2**). Eight milliliters of DMF solution containing 4,4′-bipyridine (0.0468 g, 0.3 mmol) and $H_2hmbdc$ (0.0274 g, 0.15 mmol) was slowly added to a previously prepared aqueous solution (8 mL) of $Co(NO_3)_2\cdot 6H_2O$ (0.0438 g, 0.15 mmol). Then the mixed solution was slowly evaporated. After 5 months, red plate crystals were obtained. Anal. Calc. for $C_{31}H_{31}CoN_5O_8$: C, 56.37; H, 4.73; N, 10.60%. Found: C, 56.21; H, 4.75; N, 10.49%. IR (KBr pellet, $cm^{-1}$): 3421(s), 1683(s), 1607(s), 1584(s), 1548(s), 1485(w), 1439(m), 1412(s), 1388(s), 1066(w), 815(w), 804(w), 782(m), 633(m), 606(w), 484(w).

The IR spectra for compounds **1** and **2** show the characteristic vibration peaks of 4,4′-bipyridine and $hmbdc^{2-}$. Compounds **1** and **2** exhibit OH stretching bands at 3458 and 3421 $cm^{-1}$, respectively, indicating the presence of water molecules in both compounds. The well resolved peaks of aromatic rings in **1** and **2** could be clearly observed. The characteristic peaks of the carboxylate groups appear at 1584 and 1548 $cm^{-1}$ for asymmetric vibrations and at 1412 and 1388 $cm^{-1}$ for symmetric vibrations in **2**. In general, the free $hmbdc^{2-}$ could not be distinguished from IR [9]. Therefore, corresponding peaks for asymmetric (1546 $cm^{-1}$) and symmetric (1411 and 1366 $cm^{-1}$) vibrations in **1** were observed due to strong hydrogen bonds between water molecules and $hmbdc^{2-}$.

### 2.2. Single crystal structure determination

X-ray diffraction data were collected for **1** and **2** using Bruker SMART CCD area detector diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program [10]. The structures were solved by direct methods using SHELXS-97 [11] and refined by full matrix least-squares procedures on $F^2_o$ using SHELXL-97 [12] in the WinGX environment [13]. H atoms for OH and $H_2O$ in **1** and **2** were found in Fourier difference syntheses and aromatic hydrogen atoms were placed geometrically in calculated positions and thereafter refined using a riding model. DMF in **2** shows some disorder and atoms of DMF were refined with isotropic displacement parameters. Crystal data and structure refinements are given in Table 1.

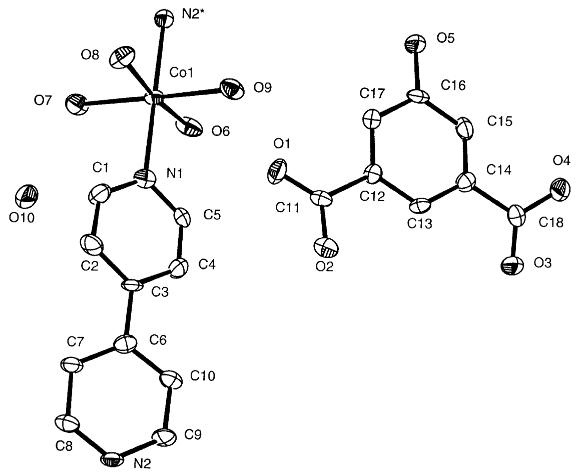

Fig. 1. ORTEP view of compound $\{[Co(4,4'\text{-bipy})(H_2O)_4](hmbdc)(H_2O)\}_n$ (**1**).

Table 1
Crystal data and details of structural determination of compounds **1** and **2**

| Formula | $C_{18}H_{22}CoN_2O_{10}$ | $C_{31}H_{31}CoN_5O_8$ |
|---|---|---|
| Fw | 485.31 | 660.54 |
| Crystal color, shape | purple, rod | red, plate |
| Crystal size (mm) | 0.44×0.26×0.26 | 0.50×0.18×0.14 |
| Space group | Orthorhombic/$Pna2_1$ | Orthorhombic/$Pccn$ |
| $a$ (Å) | 13.4756(17) | 14.078(8) |
| $b$ (Å) | 12.7195(16) | 19.575(12) |
| $c$ (Å) | 11.3990(14) | 22.714(13) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 90 | 90 |
| $\gamma$ (°) | 90 | 90 |
| $V$ (Å$^3$) | 1953.8(4) | 6259(6) |
| $Z$ | 4 | 8 |
| $D$ (Mg/cm$^{-3}$) | 1.650 | 1.402 |
| $T$ (K) | 293±2 | 293±2 |
| $\mu$ (mm$^{-1}$) | 0.941 | 0.606 |
| Measured reflections | 10,991 | 31,726 |
| Observed reflections | 3955 | 5883 |
| $R1$ and $wR2$ ($I>2\sigma(I)$) | 0.046, 0.065 | 0.057, 0.171 |
| $R1$ and $wR2$ (all data) | 0.073, 0.070 | 0.093, 0.188 |
| Number of variables | 313 | 402 |
| Goodness of fit (GOF) | 0.888 | 0.962 |
| Largest difference peak and hole (e Å$^{-3}$) | 0.969, −0.556 | 0.876, −0.631 |

## 3. Results and discussion

Compound **1** consists of 1D covalently bonded chains formed by 4,4′-bipyridine ligands connecting Co atoms,

Table 2
Selected bond lengths (Å) and angles (°) for compound **1**

| | | | |
|---|---|---|---|
| Co1–O6 | 2.075(3) | Co1–O7 | 2.114(3) |
| Co1–O8 | 2.117(3) | Co1–O9 | 2.129(3) |
| Co1–N1 | 2.140(6) | Co1–N2* | 2.146(6) |
| O1–C11 | 1.240(5) | O2–C11 | 1.277(5) |
| C11–C12 | 1.499(6) | O3–C18 | 1.228(5) |
| O4–C18 | 1.276(5) | C14–C18 | 1.510(6) |
| O5–C16 | 1.356(6) | | |
| O6–Co1–O7 | 92.3(1) | O6–Co1–O8 | 173.0(2) |
| O6–Co1–O9 | 91.1(1) | O6–Co1–N1 | 91.3(2) |
| O6–Co1–N2* | 89.3(2) | O7–Co1–O8 | 90.8(1) |
| O7–Co1–O9 | 176.6(1) | O7–Co1–N1 | 88.4(2) |
| O7–Co1–N2* | 92.1(2) | O8–Co1–O9 | 85.9(1) |
| O8–Co1–N1 | 95.1(2) | O8–Co1–N2* | 84.3(2) |
| O9–Co1–N1 | 91.8 (2) | O9–Co1–N2* | 87.7(2) |
| N1–Co1–N2* | 179.2(1) | O1–C11–O2 | 123.5(4) |
| O3–C18–O4 | 123.9(5) | | |

Symmetry code: (*) $x, y, 1-z$.