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Two new Co(II)-MOFs based on polymeric chain building units: Crystal structures, and magnetic properties

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ABSTRACT

Two new Co(II) metal-organic frameworks, namely $[Co_2(bpm)(H_2O)_3(L)]_n$ (**1**) and $\{[Co(bpe)(H_2O)(H_2L)]\cdot(bpe)_{0.5}\cdot(H_2O)\}_n$ (**2**), (H_4L=1,1′:2′,1″-terphenyl-3,3″,4′,5′-tetracarboxylic acid, bpm=bis(4-pyridyl)amine, bpe=1,2-bis(4-pyridyl)ethene), have been obtained under hydrothermal conditions. Both complexes **1** and **2** have been characterized by elemental analysis, IR spectra, single-crystal X-ray diffraction, powder X-ray diffraction (PXRD), and thermogravimetric analysis (TGA). Complexes **1** and **2** consist of 1D Co(II) chains bridging by carboxylate groups in *syn-anti* fashion. **1** shows a novel 3D tri-nodal (4,6,10)-connected net with a $(3.4^3.5^2)_2(3^2.4^{14}.5^{12}.6^{12}.7^4.8)(3^2.4^2.5^5.6^4.7^2)$ topology. While **2** exhibits a 2D **sql** layer. Magnetic susceptibility measurements indicate that both **1** and **2** show weak antiferromagnetic interactions between the adjacent Co(II) ions in 300–8 K for **1** and 300–16 K for **2**, respectively, and then **2** also displays ferromagnetic coupling at lower temperatures.

1. Introduction

Magnetic materials based on transition metal ions with polynuclear units, such as Co(II) and Mn(II), have been extensively studied because a high spin ground state can be obtained from strong exchange interactions between 3d electrons [1–10]. The huge diversity and versatility of coordination and supramolecular chemistry have provided great opportunities to obtain new magnetic materials and to better understand fundamental magnetic phenomena [11–23]. Coordination polymers (CPs) with polynuclear units based on Co(II) and Mn(II), occupy an important position as they represent a perfect combination of magnetic properties and structures [24–30]. Generally, the construction of polynuclear-based MOFs is a rather complex process because these polynuclear units are often *in situ* generated in different reactions. Thus, the variable factors in the assembled processes, such as coordination modes of metal centers and multicarboxylate ligands, will make significant structural changes of the resulting clusters. Multicarboxylate ligands, which are widely employed to construct such extended architectures, not only bind several metal centers of specific coordination geometry to form polynuclear units but also can transmit the magnetic interaction [31–33]. As a derivative of 1,2,4,5-benzenetetracarboxylic acid, 1,1′:2′,1″-terphenyl-4,4′,4″,5-tetracarboxylic acid, a more flexible and bigger ligand, can adopt various coordination modes and allowing higher dimensionality structures. So it has been employed to construct CPs [34–38]. However, polymetallic clusters of 1,1′:2′,1″-terphenyl-3,3″,4′,5′-tetracarboxylic acid (H_4L), an isomeric tetracarboxylic acid, with transition metal is rare until now [39].

In the construction of Co-CPs, mixed-ligand assembly, such as multicarboxylates and N-donor ligands, has been widely utilized for tunability of structural frameworks [40–43]. In our previous work, we have reported several new Co(II)-cluster based mixed-ligand MOFs [44–49], As part of our ongoing interest in understanding the ability of the multicarboxylate to direct the assembly of Co(II)-organic systems, herein, we chose H_4L to induce Co(II)-core aggregation, and different auxiliary N-donor spacers, bis(4-pyridyl)amine (bpm) with –NH– linker or 1,2-bis(4-pyridyl)ethene (bpe) with –CHCH– linker, are introduced to tune the structures of polymetallic Co(II)-clusters and thus the properties of the final network, resulting in two coordination polymers containing similar 1D Co(II) chains bridging by carboxylate groups in *syn-anti* fashion, $[Co_2(bpm)(H_2O)_3(L)]_n$ (**1**), and $\{[Co(bpe)(H_2O)(H_2L)]\cdot(bpe)_{0.5}\cdot(H_2O)\}_n$ (**2**) (Scheme 1). Moreover, their magnetic properties were also investigated and discussed in detail.

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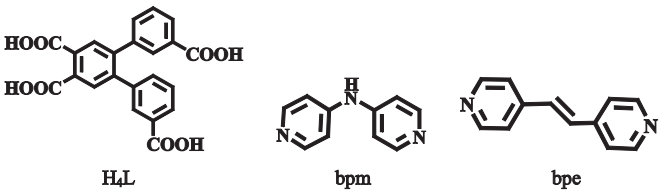

Scheme 1. Structures of the H_4L and N-donor ligands used in this work.

2. Experimental

2.1. Materials and physical measurements

All solvents and reagents were available and were used as received. Elemental analysis for C, H and N was performed on a Flash 2000 organic elemental analyzer. Thermogravimetric analysis was performed on a NETZSCH STA 449C microanalyzer heated from 25 to 900 °C in nitrogen atmosphere. Infrared spectra (4000–600 cm^{-1}) were recorded on a FTIR Nexus spectrophotometer spectrometer. Powder X-ray diffraction (PXRD) patterns were taken on a Rigaku Ultima IV diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5406$ Å), with a scan speed of 5°/min and a step size of 0.02° in 2θ. Variable-temperature magnetic measurements were carried out on a Quantum Design SQUID MPMS XL-7 instrument (2–300 K) in the magnetic field of 1 kOe, and the diamagnetic corrections were evaluated by using Pascal's constants.

2.2. Preparation of complexes 1 and 2.

$[Co_2(bpm)(H_2O)_3(L)]_n$ (1) A mixture of H_4L (0.1 mmol, 40.6 mg), bpm (0.10 mmol, 17.1 mg), $Co(ClO_4)_2{\cdot}6H_2O$ (0.20 mmol, 73.2 mg), NaOH (0.2 mmol, 8 mg) was placed in a Teflon-lined stainless steel vessel (25 mL), heated to 140 °C for 3 days, and then cooled to room temperature over 24 h. Red prism crystals were obtained. Yield: 41.0 mg, 55% (based on H_4L). Elemental analysis (%): calcd for ($C_{32}H_{25}Co_2N_3O_{11}$): C, 51.56; H, 3.38; N, 5.64; Found: C, 51.46; H, 3.44; N, 5.57. IR (KBr, cm^{-1}): 3442 w, 1602 s, 1523 s, 1418 s, 1394 s, 1215 m, 1024 m, 809 s, 754 s.

$\{[Co(bpe)(H_2O)(H_2L)]\cdot(bpe)_{0.5}\cdot(H_2O)\}_n$ (2). 2 was synthesized in the similar way as that described for **1**, except that bpm was replaced by bpe (0.20 mmol, 36.4 mg). Purple block crystals were obtained. Yield: 40.2 mg, 52% (based on H_4L). Elemental analysis (%): calcd for ($C_{40}H_{31}CoN_3O_{10}$): C, 62.18; H, 4.04; N, 5.44; Found: C, 62.09; H, 4.09; N, 5.50. IR (KBr, cm^{-1}): 3510 w, 3430 w, 1676 m, 1602 s, 1535 s, 1406 m, 1264 m, 827 s, 766 s, 698 s.

2.3. X-ray crystallography

Single crystal X-ray diffraction data for complexes **1** and **2** were collected on a Rigaku XtaLAB mini diffractometer equipped with a graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) by using φ/ω scan technique. The structures were solved by direct methods and successive Fourier difference synthesis (SHELXS-97) [50], and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-H atoms (SHELXL-97) [50]. H atoms were assigned with isotropic displacement factors and included in the final refinement with geometrical restrains. Further crystallographic data are shown in Table 1. Selected bond parameters for **1–2** are shown in Table S1, Supplementary information. CCDC Reference no: 958449 for **1** and 958451 for **2**.

Table 1
Crystallographic data and details of diffraction experiments for complexes **1–3**.

	1	**2**
Formula	$C_{32}H_{25}Co_2N_3O_{11}$	$C_{40}H_{31}CoN_3O_{10}$
M_r	745.41	772.61
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	15.9219 (11)	11.020 (2)
b (Å)	7.8232 (6)	9.7200 (19)
c (Å)	16.064 (7)	21.600 (4)
β (°)	112.156 (8)	117.275 (18)
V (Å^3)	2904.8 (4)	2301.0 (8)
Z	4	2
ρ (g cm^{-3})	1.704	1.462
T (K)	273 (2)	296 (2)
R_{int}	0.0209	0.0938
F (000)	1520	1048
GOOF	1.018	1.070
R [$I > 2\sigma(I)$]	$R_1 = 0.0245$[a]	$R_1 = 0.0645$[a]
	$wR_2 = 0.0710$[b]	$wR_2 = 0.1677$[b]
R (all data)	$R_1 = 0.0274$[a]	$R_1 = 0.0885$[a]
	$wR_2 = 0.0741$[b]	$wR_2 = 0.1862$[b]

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$.

3. Results and discussion

3.1. Synthetic chemistry

In this work, NaOH was used to neutralize the H_4L. At first, a molar ratio of 2:1 between NaOH and H_4L was used for preparation of the two complexes, and it is interesting to find out that the 3,3″-carboxylic group in **2** is protonated and free of coordination, while those in **1** were completely deprotonated. When the amount of NaOH used for preparation of **2** was increased to 3 or 4 fold of H_4L, and we only find that the homogeneous product with protonated 3,3″-carboxylate can be obtained by the same hydrothermal process.

3.2. Descriptions of crystal structures

$[Co_2(bpm)(H_2O)_3(L)]_n$ (1). There are three crystallographic independent Co(II) atoms, each taking a distorted octahedral coordination sphere (Fig. 1a). Co1 is six-coordinated by two O atoms of two carboxylate groups from one L^{4-} ligand (O1 and O3), two O atoms of one carboxylate group in chalating fashion from another L^{4-} ligand (O7#1 and O8#1), one coordinated water molecule (O9) and one N atom from bpm (N1). Co2 is coordinated by two aqua ligands (O10 and O10#2) and four O atoms from four L^{4-} ligands (O5, O5#1, O2#3, and O2#4). Co3 center is coordinated by two O atoms from two L^{4-} ligands (O4#5 and O4#6), two coordinated water molecules (O11 and O11#7) and two N atoms from two bpm (N3 and N3#1). L^{4-} ligand adopts the $(\kappa^1\text{–}\kappa^1)\text{–}(\kappa^1\text{–}\kappa^1)\text{–}(\kappa^2)\text{–}(\kappa^1)\text{–}\mu_5$ coordination fashion to bridge two Co1, two Co2 and one Co3 (Scheme 2a). The Co(II) atoms are bridged by carboxylate groups in *syn-anti* modes to form a 1D chain with the Co···Co distances of 5.28 and 5.34 Å, respectively (Fig. 1b). In such 1D chains, there are two kinds of Co(II)-based subunits: one is the trinuclear units $[Co_3N_4(COO)_4]^{2+}$ that consists of two $[Co_1O_5N]$ and one $[Co_3O_4N_2]$ with the Co···Co distances of 5.28. Another is $[Co_2O_6]$ units. Such 1D chains are further interlinked by L^{4-} and bpm ligands to form a 3D network (see Fig. 1c).

Analysis of the network topology of **1** reveals that trinuclear unit acts as a 10-connected node to connect six Co2 atoms and four L^{4-} ligands. Co2 atoms act as 4-connected nodes to connect three trinuclear units and one L^{4-} ligand. And the L^{4-} ligand serves as the 6-connected nodes to join two Co2 atoms and four