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Temperature-controlled two new Co(II) compounds with distinct topological networks: Syntheses, crystal structures and catalytic properties

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ABSTRACT

Two new Co(II) coordination compounds, namely $[Co_2(bptc)(bpp)_2]_n$ (**1**) and $[Co(bptc)_{0.5}(bpp)]_n$ (**2**) (H_4bptc = biphenyl-3,3′,5,5′-tetracarboxylic acid, bpp = 1,3-di(4-pyridyl)propane), have been hydrothermally synthesized from the same reactants *via* tuning the reaction temperature. Single crystal X-ray diffraction analyses revealed that both **1** and **2** feature 2D sheet motifs. Topological analyses revealed that compounds **1** and **2** show distinct topological networks. Under the weak Van der Waals interactions, the 2D sheet motifs of compounds **1** and **2** are further packed into 2D→3D interdigitated supramolecular frameworks. Moreover, the two Co(II) compounds show high catalytic activities for degradation of methyl orange (MO) in a Fenten-like process.

1. Introduction

Coordination polymers (CPs) self-assembled from metal ions and organic ligands have emerged as promising crystalline materials for luminescence sensing, gas adsorption and separation, heterogeneous catalysis, non-linear optics and so on [1–4]. Under this background, a number of CPs with intriguing spatial frameworks and promising properties have been reported in the past few decades, and a series of successful synthetic strategies, such as pillar-layered strategy, mixed-ligand method, postsynthetic modification strategy, second building subunit strategy and so on, have also been established [5–8]. Among the strategies, mixed-ligand strategy was the widely used strategy for the construction of CPs in that two functionally different complementary organic linkers not only can provide an additional level of control in the frameworks and charge density distribution but also can help us obtain the CPs with structural diversities [9–12]. In addition, to create the desired frameworks with promising functionalities, it is also important for us to control the external factors (such as temperature, pH and solvent) and understand the relationship between the structures and external stimuli [13]. Recently, a series of studies for the construction of crystalline materials via tuning reaction parameters have been reported. For example, Yao and his co-workers systematically investigated the pH influence on the structural variations of a series of Zn(II)-based coordination polymers [14]. Bu and his co-workers successfully demonstrated a new temperature-dependent system based on the camphorate anion [15]. Zhang and her co-workers successfully synthesized two new luminescent Zn(II) coordination compounds by controlling the solvent molecules [16]. Based on the aforementioned contents, herein, we exploited H_4bptc and bpp as the mixed ligands to assemble with $Co(NO_3)_2 \cdot 6H_2O$ under hydrothermal conditions. *Via* tuning the reaction temperature, we successfully obtained two new Co(II) coordination polymers, namely $[Co_2(bptc)(bpp)_2]_n$ (**1**) and $[Co(bptc)_{0.5}(bpp)]_n$ (**2**) (H_4bptc = biphenyl-3,3′,5,5′-tetracarboxylic acid, bpp = 1,3-di(4-pyridyl)propane). Compound **1** displays a 2D layered structure with 4-connected topology, and compound **2** also displays a 2D layered structure but with (4,4)-connected topology. Under the weak Van der Waals interactions, the 2D sheets of compounds **1** and **2** are further packed into a 2D→3D interdigitated supramolecular framework. The catalytic properties of compounds **1** and **2** have also been studied in a Fenton-like process for the degradation of MO.

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2. Experimental

2.1. Materials and instrumentation

All reagents and solvents used in this work were commercially purchased from Tianjin Bodi Chemical Co. Ltd. and used without further purification. Elemental analyses for C, H and N were performed on German Elementary Vario EL III instrument. Infrared spectra of the obtained compounds were collected on a Nicolet Magna 750 FT-IR spectrometer in the range of 400–4000 $\mathrm{cm^{-1}}$. Powder X-ray diffraction (PXRD) analyses were conducted on a Miniflex II diffractometer using Cu-$K\alpha$ radiation with a step size of 0.05°. Thermogravimetric analyses (TGA) were carried out on a NETZSCH STA449C thermogravimetric analyser under N_2 atmosphere. Single crystal X-ray diffraction data was collected on Oxford Xcalibur E diffractometer with graphite-monochromated Mo-$K\alpha$ (0.71073 Å).

2.2. Synthesis of $[Co_2(bptc)(bpp)_2]_n$ (**1**)

$Co(NO_3)_2\cdot 6H_2O$ (0.1 mmol, 0.03 g), H_4bptc (0.05 mmol, 0.015 g), bpp (0.1 mmol, 0.0198 g), $NaHCO_3$ (0.4 mmol, 0.034 g) and 8 mL H_2O were sealed into a 23 mL Teflon-lined stainless steel container, and the container was further heated to 120 °C and kept at that temperature for 3 days. After cooling slowly to the temperature, purple prism crystals of **1** were obtained in 32% yield based on $Co(NO_3)_2\cdot 6H_2O$. Anal. Calcd. (%) for **1** $C_{42}H_{34}Co_2N_4O_8$: C, 59.96; N, 6.66; H, 4.04. Found: C, 59.89; N, 6.71; H, 4.02. IR (KBr, $\mathrm{cm^{-1}}$): 2760 m, 1627s, 1560s, 1491s, 1424s, 1312s, 1141w, 1013w, 942w, 834vw, 820w, 766 m, 643vw, 587w, 510w.

2.3. Synthesis of $[Co(bptc)_{0.5}(bpp)]_n$ (**2**)

The synthetic procedure of compound **2** was similar to that of compound **1** except that the reaction temperature was tuned into 140 °C. Purple prism crystals of **2** was obtained in 42% yield based on $Co(NO_3)_2\cdot 6H_2O$. Anal. Calcd. (%) for **2** $C_{21}H_{17}CoN_2O_4$: C, 59.96; N, 6.66; H, 4.04. Found: C, 59.92; N, 6.61.05; H, 3.98. IR (KBr, $\mathrm{cm^{-1}}$): 2780 m, 1624s, 1555s, 1467s, 1357s, 1309s, 1124w, 1014w, 946w, 823w, 758 m, 719vw, 651vw, 591w, 511w.

Table 1
Crystal data and structure refinements for **1**–**2**.

	1	2
Formula	$C_{42}H_{34}Co_2N_4O_8$	$C_{21}H_{17}CoN_2O_4$
Fw	840.59	420.30
Crystal system	monoclinic	monoclinic
Space group	*Cc*	*C*2/*c*
a (Å)	20.2368(8)	16.7429(10)
b (Å)	13.1300(3)	16.4393(5)
c (Å)	17.5451(4)	18.8680(10)
α(°)	90.00	90.00
β(°)	101.322(3)	114.328(6)
γ(°)	90.00	90.00
V ($Å^3$)	4571.2(2)	4732.1(4)
Z	4	8
Density (calculated)	1.221	1.180
Abs. coeff. ($\mathrm{mm^{-1}}$)	0.776	0.749
Total reflections	10512	10433
Unique reflections	5862	3972
Goodness of fit on F^2	1.037	1.045
Final *R* indices [$I > 2\mathrm{sigma}(I^2)$]	$R = 0.0427$, $wR_2 = 0.1279$	$R = 0.0556$, $wR_2 = 0.1613$
R (all data)	$R = 0.0540$, $wR_2 = 0.1357$	$R = 0.0754$, $wR_2 = 0.1726$

2.4. X-ray crystallography

Suitable single crystals of **1**–**2** were carefully selected under an optical microscope and glued to thin glass fibers. The structures were solved by direct methods and refined by full–matrix least–square methods on F^2 by using the SHELXL–97 program package [17], and the absorption corrections were treated using the SADABS program [18]. Non–hydrogen atoms were refined anisotropically, and the H atoms attached to their parent atoms were generated geometrically with fixed isotropic thermal parameters. Detailed crystallographical data for compounds **1** and **2** were summarized in Table 1, and selected bond lengths and angles are given in Table S1.

2.5. Catalytic experimental procedure

The catalytic degradation experiments with compounds **1** and **2** as the heterogeneous catalysts were carried out in a 250 mL round-bottom flask. The reaction solutions were obtained by adding the solid catalysts **1** (or **2**) into MO solution and the initial pH of the reaction solution was adjusted to 3 by 0.1 mol/L H_2SO_4 solution, and then 0.03 g sodium persulfate was added into the prepared reaction solution as the oxidant. All experiments were carried out at a temperature of 30 °C. At the given intervals, 5 mL solution was taken from the reaction mixture, and further filtered through a 0.45 μm membrane filter before measurement. The concentration of the sample solution was determined by measuring absorbance at 506 nm using a double beam UV/vis spectrophotometer. The degradation efficiency of MO is defined as follows:

$$\text{Degradation efficiency} = \frac{(C_0 - C_t)}{C_0} \times 100\% \qquad (1)$$

where C_0 (mg/L) is the initial concentration of MO, and C_t (mg/L) is the concentration of MO at reaction time, t (min).

3. Results and discussion

3.1. Crystal structure of compound **1**

Single crystal X-ray structural analysis revealed that compound **1** crystallizes in the monoclinic *Cc* space group and features a 2D layered motif that further packed into a 2D→3D interdigitated supramolecular framework. The asymmetric unit of **1** contains two crystallographically independent Co(II) ions, one $bptc^{4-}$ ligand and two bpp ligands. As shown in Fig. 1a, both Co1 and Co2 are octahedrally coordinated by four carboxylate oxygen atoms from three $bptc^{4-}$ ligands occupying the equatorial plane and two nitrogen atoms from two bpp ligands occupying two axial sites. The Co–O and Co–N distances are in the range of 1.986(6)-2.203(6) Å, 2.11(4)-2.18(3) Å, respectively, which are comparable with that of previously reported Co(II)-based coordination polymers [19]. Each $bptc^{4-}$ ligand bridges six independent Co(II) centers with its two carboxylate groups both in chelating mode and the other two carboxylate groups both in bis-monodentate mode (Scheme S1a). Two adjacent Co(II) ions are bridged by two bis-monodentate carboxylate groups into a dinuclear $[Co_2(COO)_2]$ subunit with the Co(II)···Co(II) separation of 4.26 Å. These dinuclear $[Co_2(COO)_2]$ subunits are further connected by the $bptc^{4-}$ ligands into a 2D layer (Fig. S1). All bpp ligands linking two adjacent Co(II) ions in *cis-cis* conformation decorate the upper and lower sides of the layer, affording the final 2D layered structure of compound **1** (Fig. 1b). Topologically speaking, both the dinuclear $[Co_2(COO)_2]$ subunits and the $bptc^{4-}$ ligands can be viewed as 4-connected nodes, thus the 2D sheet of compound **1** can be simplified into a 4-connected