

由三羧基配体桥联的含有线性四核钴簇单元的 二维层状配位聚合物的组装和性质

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摘要: 以金属钴盐、2-羟基-1,3,5-苯基三羧酸 (OH-H₃BTC) 为原料, 在碱性条件下, 通过水热方法合成了一个钴配位聚合物 [Co₂(O-BTC)(H₂O)₅]_n (**1**), 并利用 X 射线粉末和单晶衍射、红外光谱、元素分析以及热重等方法对该化合物进行了表征。化合物 **1** 含有线性四核单元 [Co₄O₇], 四核单元内的金属离子是通过羧酸氧原子和羟基氧原子桥联的。该四核单元进一步通过 O-BTC⁴⁻ 配体在 *ab* 平面上形成一个二维层状结构, 相邻的层与层通过氢键作用形成一个三维超分子结构。热重分析结果显示化合物 **1** 在 100 °C 开始失重。磁性研究表明, 化合物 **1** 中相邻的钴离子之间存在反铁磁性相互作用。

关键词: 配位聚合物; 磁性; 四核钴簇

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Assembly and Properties of a 2D Layer Coordination Polymer Containing Linear Tetranuclear Cobalt-Cluster Unit Bridged by Tricarboxylic Acid Ligand

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Abstract: The hydrothermal reaction of cobalt(II) salts with 2-hydroxyl-1,3,5-benzenetricarboxylic acid (OH-H₃BTC) in the presence of sodium hydroxide afforded a cobalt(II) coordination polymer, namely [Co₂(O-BTC)(H₂O)₅]_n (**1**), which has been characterized by powder and single-crystal X-ray diffraction, infrared spectroscopy, elemental analysis, and thermogravimetric analysis. Compound **1** contains a linear tetranuclear unit [Co₄O₇] through the carboxylate oxygen and hydroxyl atoms, which are further linked to form a two-dimensional (2D) layered structure in the *ab* plane by the O-BTC⁴⁻ organic ligands. Adjacent layers are packed along the *c*-axis with the hydrogen bond interactions dominating between the layers to form a three-dimensional (3D) supramolecular structure. Thermal analysis reveals that **1** begins to lose weight at *ca.* 100 °C. Magnetic studies reveal that dominant antiferromagnetic interactions are dominated between the magnetic centers in **1**. CCDC: 1841028.

Keywords: coordination polymer; magnetic properties; tetranuclear cobalt(II)-cluster

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0 Introduction

Coordination polymers (CPs) are an established class of crystalline solids materials that formed by the assembly metal ions or metal cluster units and functional organic ligands, and have attracted significant attention owing to their intriguing architectures and potential applications in many fields, such as gas storage, separation, catalysis, chemical sensors, luminescence^[1-6]. Another field where the CPs have attracted great interest is in the area of molecular magnetic materials^[7-11]. The magnetic properties containing the paramagnetic metal ions or metal cluster units of CPs can be well-tuned by suitable modification of the functional organic ligands, which affect the magnetic exchange pathways of the metal centers^[12-14]. As a class of important functional organic ligands, aromatic multicarboxylate ligands are extensively employed in the synthesis of many CPs for their abundant coordinating modes to metal ions^[15-18]. However, the reported metal carboxylates CPs of a rigid aromatic multicarboxylate combination hydroxyl group are still rare^[19]. On the other hand, in order to construct interesting magnetic materials, it is seen as a general strategy to use paramagnetic transition metal ions with a large spin state, strongly anisotropic spin and suitable bridging ligands through the self-assembly way^[20]. The nature of the paramagnetic metal ions plays an important role in regulating the magnetic properties of CPs. In this work, we report a new Co(II)-based CP that has been synthesized using 2-hydroxyl-1,3,5-benzenetricarboxylic acid (HO-H₃BTC). The HO-H₃BTC ligand with three carboxylic groups and one hydroxyl group, which possess seven coordinated sites and prefer to favor the generation of the high dimensional structure with high rigidity for encapsulating many metal ions, has been used earlier as a useful building unit to obtain a three-dimensional framework^[21]. The CP reported in this paper is formulated as [Co₂(O-BTC)(H₂O)₅]_n (**1**), and it displays two-dimensional (2D) layered structure, which is packed and stabilized by extensive hydrogen bonds among the carboxylate oxygen atoms and coordinated water

molecules to form a three-dimensional supramolecular structure. In addition, the thermal stability and magnetic properties of **1** also were studied.

1 Experimental

1.1 Materials and methods

The ligand HO-H₃BTC was prepared according to the literature procedure^[22]. The other reagents and solvents were commercially available and used without any purification. The infrared spectra (IR) were recorded with a Nicolet iS10 spectrometer by KBr pellets in the range of 4 000~500 cm⁻¹. Elemental analyses (C and H) were performed on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449C instrument under flowing N₂ atmosphere with a heating rate of 10 °C·min⁻¹ from 30 to 800 °C. Powder X-ray diffraction (PXRD) sample was carried out on a Rigaku Ultima IV X-ray diffractometer using Cu Kα (λ=0.154 056 nm) radiation. The measurement was performed over the 2θ range of 5°~50° at room temperature. The operating power was set at 30 mA, 40 kV. The dc magnetic susceptibility data were obtained on polycrystalline samples using a Quantum Design MPMS-XL7 SQUID magnetometer.

1.2 Synthesis of [Co₂(O-BTC)(H₂O)₅]_n (**1**)

A mixture of Co(NO₃)₂·6H₂O (58.2 mg, 0.2 mmol), HO-H₃BTC (22.6 mg, 0.1 mmol), and NaOH (8.0 mg, 0.2 mmol) in H₂O (10 mL) was stirred under ambient condition for 30 min. The mixture was then placed into a Teflon-lined stainless steel container (30 mL) and heated at 160 °C for 72 h. After the mixture was slowly cooled to room temperature, red block-like crystals of **1** were obtained by filtering, washed with distilled water and ethanol, and dried in air. Yield: 8.6 mg (20% based on Co). Elemental analysis Calcd. for C₉H₁₂Co₂O₁₂(%): C 25.12, H 2.79. Found(%): C 25.01, H 2.83. IR (KBr, cm⁻¹): 3 496 (br), 1 612 (s), 1 525 (m), 1 422 (s), 1 383 (s), 1 274 (m), 1 122 (m), 947 (w), 826 (m), 782 (m), 738 (m), 696 (m), 573 (w).

1.3 X-ray crystallography

The single-crystal diffraction data of **1** were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatic

Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at room temperature. Intensity data were collected with a combination of ω and φ scan, which were integrated using the Siemens SAINT program^[23]. The structure was solved by the direct method using SHELXS-97^[24] and refined on F^2 by full-matrix least-squares using SHELXL-2018 program^[25]. All non-hydrogen atoms were refined anis-

otropically. The hydrogen atoms attached to the phenyl group carbon atoms were put in calculated positions, and the coordinated water hydrogen atoms were located from the Fourier maps. The crystallographic data for **1** are listed in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC: 1841028.

Table 1 Crystal data and structure refinement for **1**

	1		
Formula	C ₉ H ₁₂ Co ₂ O ₁₂	V / nm^3	1.304 7(9)
Molecular weight	430.05	Z	4
Crystal system	Monoclinic	$D_c / (\text{g} \cdot \text{cm}^{-3})$	2.189
Space group	$P2_1/c$	μ / mm^{-1}	2.612
a / nm	1.165 7(5)	$F(000)$	864
b / nm	1.527 7(6)	GOF on F^2	1.057
c / nm	0.735 1(3)	$R_1, wR_2^a [I > 2\sigma(I)]$	0.079 2, 0.188 4
$\beta / (^\circ)$	94.721(6)	$R_1, wR_2^a (\text{all data})$	0.084 1, 0.190 7
		$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	4 020, -1 630

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

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for **1**

Co(1)-O(2)A	0.200 1(6)	Co(2)-O(3W)	0.202 0(7)	Co(1)-O(7)	0.201 7(6)
Co(2)-O(4W)	0.206 2(6)	Co(1)-O(1W)	0.213 9(6)	Co(2)-O(5W)	0.204 4(7)
Co(1)-O(2W)	0.206 0(8)	Co(2)-O(3)	0.211 4(6)	Co(1)-O(3)	0.202 4(6)
Co(2)-O(4)	0.227 3(6)	Co(1)-O(7)A	0.201 5(6)	Co(2)-O(5)B	0.196 2(7)
C(7)-O(1)	0.124 0(10)	C(2)-O(7)	0.130 1(10)	C(7)-O(2)	0.125 0(10)
C(9)-O(5)	0.124 3(12)	C(8)-O(3)	0.127 1(9)	C(9)-O(6)	0.124 9(10)
C(8)-O(4)	0.125 6(10)				
O(2)-Co(1)-O(7)A	172.2(2)	O(5)B-Co(2)-O(3W)	91.5(3)	O(2)-Co(1)-O(7)	88.0(2)
O(5)B-Co(2)-O(5W)	88.8(3)	O(7)A-Co(1)-O(7)	84.2(2)	O(3W)-Co(2)-O(5W)	176.7(2)
O(2)-Co(1)-O(3)A	101.3(2)	O(5)B-Co(2)-O(4W)	100.5(3)	O(7)A-Co(1)-O(3)A	86.5(2)
O(3W)-Co(2)-O(4W)	87.54(18)	O(7)-Co(1)-O(3)A	170.7(2)	O(5W)-Co(2)-O(4W)	89.2(2)
O(2)-Co(1)-O(2W)	88.2(3)	O(5)B-Co(2)-O(3)	163.3(3)	O(7)A-Co(1)-O(2W)	91.8(3)
O(3W)-Co(2)-O(3)	95.1(2)	O(7)-Co(1)-O(2W)	98.0(3)	O(5W)-Co(2)-O(3)	85.5(2)
O(3)A-Co(1)-O(2W)	82.5(3)	O(4W)-Co(2)-O(3)	95.2(2)	O(2)-Co(1)-O(1W)	88.5(3)
O(5)B-Co(2)-O(4)	106.2(3)	O(7)A-Co(1)-O(1W)	93.3(3)	O(3W)-Co(2)-O(4)	89.7(2)
O(7)-Co(1)-O(1W)	95.9(3)	O(5W)-Co(2)-O(4)	93.3(3)	O(3)A-Co(1)-O(1W)	84.4(3)
O(4W)-Co(2)-O(4)	153.2(2)	O(2W)-Co(1)-O(1W)	165.6(3)	O(3)-Co(2)-O(4)	58.5(2)
Co(1)A-O(3)-Co(2)	130.6(3)	Co(1)A-O(7)-Co(1)	95.8(2)		

Symmetry codes: A: $-x+2, -y+1, -z+2$; B: $-x+1, y-1/2, -z+3/2$; C: $-x+1, y+1/2, -z+3/2$.

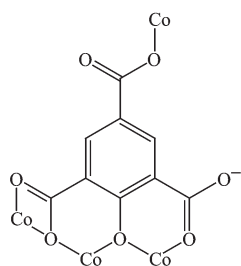
2 Results and discussion

2.1 Description of crystal structure **1**

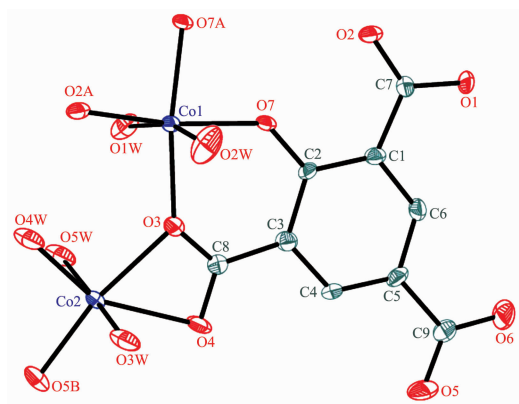
The single-crystal analysis revealed that comp-

ound **1** crystallizes in the monoclinic space group $P2_1/c$. As shown in Fig.1, the asymmetric unit contains two independent Co(II) ions, one O-BTC⁴⁻ anion, and five coordinated water molecules. Both Co1 and Co2 atoms

are six-coordinated with distorted octahedral geometry. For Co1, the four positions are occupied by two carboxylate oxygen atoms (O2A, O3) and hydroxyl group oxygen atoms (O7, O7A) from two equivalent O-BTC⁴⁻ anions. The remaining two positions are occupied by the coordinated water molecules (O1W, O2W). The six coordinated sites around the Co2 atom is provided by three carboxylate oxygen atoms (O3, O4, O5B) from two O-BTC⁴⁻ anions as well as three coordinated water molecules (O3W, O4W, O5W). The Co-O bond lengths fall in the range of 0.196 2~0.227 3 nm. The O-Co-O bond angles are between 84.2°~170.7°. The O-BTC⁴⁻ ligand serves as a hepta-dentate chelator, using its carboxylate and hydroxyl group oxygens to bridge/chelate four Co(II) ions (Scheme 1). This coordinated mode is clearly different from that observed in {[Zn₂(O-BTC)(4,4'-BPY)_{0.5}(H₂O)₃]·1.5H₂O·0.5DMA}_n^[21]. The two equivalent O-BTC⁴⁻ ligands chelate and bridge the Co1 and Co2 atoms through both μ_2 -O7 and μ_3 -O3 units, thus forming a linear tetranuclear unit of [Co₄O₇]. The Co···Co distance 0.299 2 nm over μ_2 -O7 with the



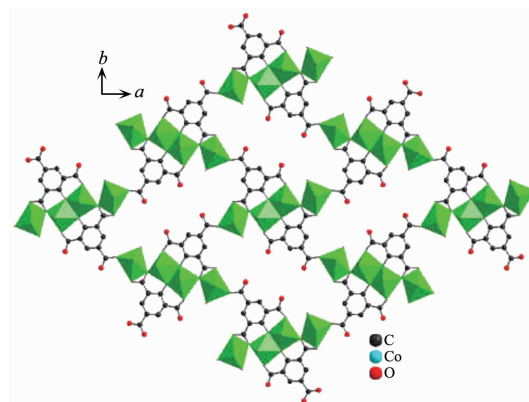
Scheme 1 Coordination mode of O-BTC⁴⁻ anion in **1**



Thermal ellipsoids: 50%; All H atoms are omitted for clarity;
Symmetry codes: A: $-x+2, -y+1, -z+2$; B: $-x+1, y-1/2, -z+3/2$;
C: $-x+1, y+1/2, -z+3/2$

Fig.1 ORTEP view of asymmetric unit of **1**

tetranuclear unit, and 0.375 9 nm over μ_3 -O3 in the tetranuclear units. Neighboring tetranuclear units are linked by the O-BTC⁴⁻ organic ligands, thus leading to an infinite layer structure parallel to the *ab*-plane (Fig.2). The layers are packed along the *c*-axis with the hydrogen bonds and van der Waals interactions dominating between the layers (Fig.3). The distance between the layers is *ca.* 0.38 nm.



All H atoms are omitted for clarity

Fig.2 One layer of **1** in the *ab*-plane

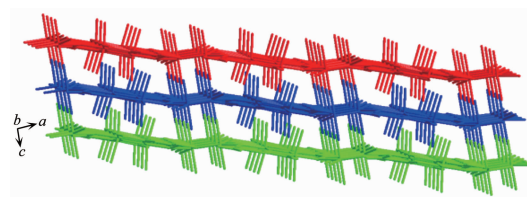


Fig.3 Packing diagram of **1** viewed along the *b*-axis

2.2 PXRD pattern, IR and thermal stability analysis of **1**

To confirm the phase purity of **1**, the powder XRD patterns was recorded for **1** at room temperature. The polycrystalline samples experimental and single-crystal simulated XRD patterns of **1** are shown in Fig. S1, indicating a pure phase of the bulk sample. The different diffraction intensities can be related to the preferred orientation of **1** structure. The broad peak of the IR spectrum centered at 3 450 cm⁻¹ is mainly attributed to the $\nu(\text{OH})$ of the coordinated water molecules stretching vibrations. The absence of strong absorption bands in the area of 1 720 cm⁻¹ confirms the full deprotonation of the carboxylate groups of HO-H₃BTC^[26], which is consistent with the analysis of single-crystal X-ray diffraction (Fig.S2). The thermal

stability of **1** was studied by thermogravimetric analysis (TGA) on the crystalline samples under the N_2 atmosphere from 30 to 800 $^{\circ}C$. As shown in Fig.4, **1** is stable to about 100 $^{\circ}C$, the weight loss of 17.00% in the temperature range of 100~200 $^{\circ}C$ corresponds the section release of five coordinated water molecules (Calcd. 20.8%), and the weight loss between 200 and 450 $^{\circ}C$ is rather small (5.0%). Above the temperature up to 800 $^{\circ}C$, continuous weight loss is found, and the final residue might be CoO (Found: 35.03%; Calcd. 34.85%).

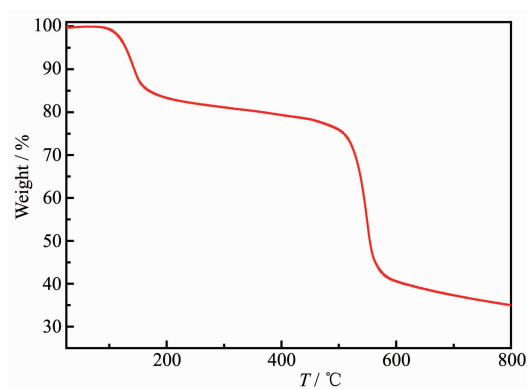


Fig.4 TG curve of **1** in nitrogen atmosphere

2.3 Magnetic properties of **1**

Magnetic measurement was performed on polycrystalline sample of **1** at 1 000 kOe in the temperature range of 2.0~300 K. As shown in Fig.5, the room-temperature value of the $\chi_M T$ is $5.62 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ expected for two Co(II) ions ($S=3/2$, $g=2.0$), attributed to the significant orbital contributions of the purely octahedral geometry Co(II) ion^[27]. On lowering the temperature $\chi_M T$ decreases gradually until 100 K and then more markedly, to reach $0.254 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2.0 K, indicating a dominant antiferromagnetic interaction between the adjacent Co(II) centers. While the high-temperature decrease could be attributed to the combined effect of low-symmetry distortions and spin-orbit coupling on the $^4T_{1g}$ state of octahedral Co(II), the low-temperature decreases strongly hints at the presence of antiferromagnetic exchange coupling interactions mediated by hydroxyl group oxygens and carboxylate oxygen bridges^[28]. This is confirmed by a negative Weiss constant of -28.5 K , which is determined by the Curie-Weiss fit of the susceptibility data

in the temperature range of 50~300 K. The Curie constant is $6.17 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ per Co₂ unit (Fig.S3). The main magnetic exchange pathway is the exchange between adjacent Co(II) ions within the $[\text{Co}_4\text{O}_7]$ cluster to the $\mu_2\text{-O}7_{\text{hydroxyl}}$ and $\mu_3\text{-O}3_{\text{carboxylate}}$ bridges with the exchange angle Co-O_{hydroxyl}-Co of 95.83° and Co-O_{carboxylate}-Co of 130.59° , respectively. Unfortunately, it is difficult to find an exact magnetic interaction to fit the magnetic data for the complicated linear tetranuclear unit $[\text{Co}_4\text{O}_7]$ system. The field dependent magnetization of **1** was also measured at 2.0 K. With the increasing of the external field, the magnetization increases slowly to a value of $2.18N\beta$ at 70 kOe (Fig.6). The value is smaller than the saturated value expected for two Co(II) ions with two effective spins of $S'=1/2$ and a large g value of $4.6\sim 5.0$ ^[29-30].

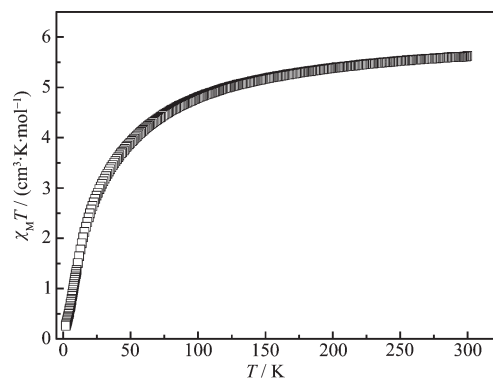


Fig.5 $\chi_M T$ vs T plot for **1**

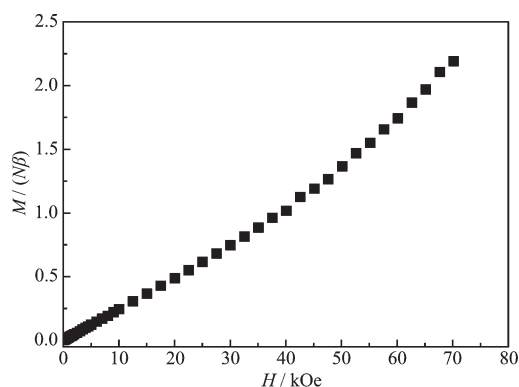


Fig.6 Field-dependent magnetization for **1** at 2.0 K

3 Conclusions

A new 2D cobalt(II)-based coordination polymer with formula $[\text{Co}_2(\text{O-BTC})(\text{H}_2\text{O})_5]_n$ (**1**) based on the rigid tricarboxylic acid ligand 2-hydroxyl-1,3,5-benzenetricarboxylic acid (HO-H₃BTC) has been prepared.

The compound features a two-dimensional layer structure in which the tetranuclear $[\text{Co}_4\text{O}_7]$ units are linked by the organic ligands. The layer structures are further formed into a three-dimensional supramolecular structure through the hydrogen bond interactions. Antiferromagnetic coupling behavior between the metal ions is observed in **1**.

Supporting information is available at <http://www.wjhxxb.cn>

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