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以 2,4,4′-联苯三羧酸及 2,2′-联吡啶构筑的三维钴(Ⅱ)配位聚合物的合成、晶体结构及磁性质

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摘要: 通过水热方法,以 2, 4, 4′-联苯三羧酸(H_3btc)和 2, 2′-联吡啶(2,2′-bpy)与 $CoCl_2·6H_2O$ 反应,合成了 1 个具有三核钴单元的三维配位聚合物$[Co_{1.5}(btc)(2, 2′\text{-}bpy)_{0.5}(2H_2O)]_n$,并对其结构和磁性质进行了研究。结构分析结果表明该聚合物的晶体属于单斜晶系,*I*2/*a* 空间群,*a*=1.774 4(4) nm,*b*=1.142 3(2) nm,*c*=1.890 8(4) nm,*β*=105.18(3)°,*V*=3.698 5(13) nm^3,D_c=1.745 g·cm^{-3},*Z*=8,*R*=0.048 4,*wR*=0.085 2(*I*>2*σ*(*I*))。来自 4 个不同 btc^{3-}配体的 4 个羧基连接相邻的 3 个钴(Ⅱ)离子形成了 1 个三核钴(Ⅱ)的结构单元。这些三核钴(Ⅱ)的结构单元又通过 btc^{3-}配体与钴(Ⅱ)离子的配位作用形成了 1 个三维的框架。研究表明,该聚合物中相邻钴(Ⅱ)离子之间存在铁磁相互作用。

关键词: 配位聚合物; 钴(Ⅱ)配合物; 磁性
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Synthesis, Crystal Structure and Magnetic Properties of a 3D Cobalt(Ⅱ) Coordination Polymer Constructed from Biphenyl-2, 4, 4′-tricarboxylate and 2, 2′-Bipyridine

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Abstract: A coordination polymer, namely $[Co_{1.5}(btc)(2,2′\text{-}bpy)_{0.5}(2H_2O)]_n$(**1**) has been constructed hydrothermally using H_3btc (H_3btc=biphenyl-2,4,4-tricarboxylic acid), 2, 2′-bpy (2, 2′-bpy=2, 2′-bipyridine), and $CoCl_2·6H_2O$. The compound crystallizes in the monoclinic system, space group *I*2/*a* with *a*=1.774 4(4) nm, *b*=1.142 3(2) nm, *c*=1.890 8(4) nm, *β*=105.18(3)°, *V*=3.698 5(13) nm^3, D_c=1.745 g·cm^{-3}, *Z*=8, *R*=0.048 4 and *wR*=0.085 2(*I*>2*σ*(*I*)). The three neighboring Co(Ⅱ) ions are bridged by means of four carboxylate groups from the four different btc^{3-} ligands, giving rise to a centrosymmetric trinuclear Co(Ⅱ) subunit. The adjacent Co_3 subunits are further linked by the btc^{3-} blocks into a 3D framework. Magnetic susceptibility measurement indicates that compound **1** shows a ferromagnetic coupling between the Co(Ⅱ) ions. CCDC: 962833.

Key words: coordination polymer; cobalt(Ⅱ) compound; magnetic properties

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0 Introduction

The design and synthesis of transition coordination polymers have attracted an upsurging research interest not only their versatile architectures[1-3] but also their desirable properties such as luminescent, magnetic, catalytic, and gas absorption and separation properties[4-6]. A basic design route for this kind of polymers is directed by self-assembly of designed organic ligands and inorganic metal cations. Carboxylate groups usually show versatile coordination character and/or bridging modes and thus provide some interesting structures.

Many multi-carboxylate or heterocylic carboxylic acids are used for this purpose [1,4-8]. In order to extend our research in this field, we have selected biphenyl-2, 4, 4-tricarboxylic acid (H_3btc) as a functional building block on account of the following considerations: (a) H_3btc possesses three carboxyl groups that may be completely or partially deprotonated, depending on the pH; (b) it is a flexible ligand allowing the rotation of two phenyl rings around the C-C single bond; (c) to our knowledge, H_3btc has not been adequately explored in the construction of coordination polymers.

Taking into account these factors, we herein report the synthesis, crystal structure, magnetic properties of a Co(Ⅱ) coordination polymer constructed from btc^{3-} and 2, 2′-bpy ligand.

1 Experimental

1.1 Reagents and physical measurements

All chemicals and solvents were of AR grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer.

Thermogravimetric analysis (TG) data were collected on a LINSEIS STA PT1600 thermal analyzer with a heating rate of 10 ℃·min^{-1}. Powder X-ray diffraction patterns (PXRD) were determined with a Rigaku-Dmax 2400 diffractometer using Cu-$K\alpha$ radiation. Magnetic susceptibility data were collected in the 2~300 K temperature range with a Quantum Design SQUID Magnetometer MPMS XL-7 with a field of 0.1 T. A correction was made for the diamagnetic contribution prior to data analysis.

1.2 Synthesis of $[Co_{1.5}(btc)(2,2\text{-bpy})_{0.5}(2H_2O)]_n$(1)

A mixture of $Co(NO_3)_26H_2O$ (0.087 g, 0.3 mmol), H_3btc (0.057 g, 0.2 mmol), 2,2-bpy (0.016 g, 0.1 mmol), NaOH (0.024 g, 0.6 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 ℃ for 3 days, followed by cooling to room temperature at a rate of 10 ℃·h^{-1}. Pink block-shaped crystals of **1** were isolated manually, and washed with distilled water. Yield: 70 % (based on Co). Anal. Calcd. for $C_{20}H_{15}Co_{1.5}NO_8$ (%): C 49.45, H 3.11, N 2.88; Found (%): C 49.82, H 2.93, N 3.17. IR (KBr, cm^{-1}): 3 439m, 1 608s, 1 576s, 1 532m, 1 420m, 1 353s, 1 248w, 1 166w, 925w, 773m, 689m, 664w. The compound is insoluble in water and common organic solvents, such as methanol, ethanol, acetone, and DMF.

1.3 Structure determinations

Single-crystal data of **1** were collected at 293(2) K on a Bruker Smart Apex 1000 CCD diffractometer with Mo $K\alpha$ radiation (λ=0.071 073 nm). A summary of the crystallography data and structure refinement is given in Table 1, and selected bond lengths and angles of the compound **1** are listed in Table 2. The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms (except the those bound to water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogen atoms of water molecules were located by different maps and constrained to ride on their parent O atoms. All calculations were performed using the SHELXTL-97 system[9].

CCDC: 962833.

Table 1 Crystal data for compound 1

Chemical formula	$C_{20}H_{15}Co_{1.5}NO_8$	Crystal size / mm	0.22×0.20×0.18
Molecular weight	485.73	θ range for data collection	3.31~25.04
Crystal system	Monoclinic	Limiting indices	$-20\leqslant h\leqslant 21$, $-13\leqslant k\leqslant 13$, $-14\leqslant l\leqslant 22$
Space group	$I2/a$	Reflections collected / unique (R_{int})	7 586 / 3 272 (0.060 2)
a / nm	1.774 4(4)	D_c / (g·cm^{-3})	1.745
b / nm	1.142 3(2)	μ / mm^{-1}	1.413
c / nm	1.890 8(4)	Data / restraints / parameters	3 272 / 0 / 276
β / (°)	105.18(3)	Goodness-of-fit on F^2	1.047
V / nm^3	3.698 5(13)	Final R indices ($(I\geqslant 2\sigma(I))$) R_1, wR_2	0.048 4, 0.085 2
Z	8	R indices (all data) R_1, wR_2	0.078 2, 0.102 2
F(000)	1 972	Largest diff. peak and hole / (e·nm^{-3})	400 and −502

Table 2 Selected bond length (nm) and bond angles (°) for compound 1

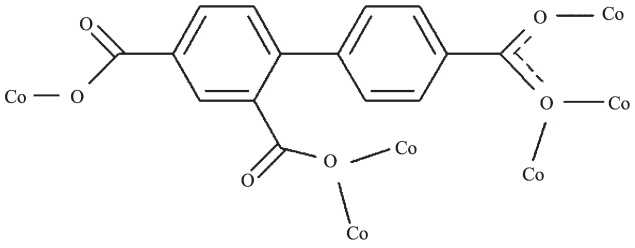
Co(1)-O(1)	0.216 0(3)	Co(1)-O(1)C	0.216 0(3)	Co(1)-O(6)^A	0.209 3(3)
Co(1)-O(6)^B	0.209 3(3)	Co(1)-N(1)	0.209 9(4)	Co(1)-N(1)^C	0.209 9(4)
Co(2)-O(1)	0.210 5(3)	Co(2)-O(4)D	0.204 8(3)	Co(2)-O(5)^B	0.207 6(3)
Co(2)-O(6)^A	0.220 5(3)	Co(2)-O(7)	0.212 4(3)	Co(2)-O(8)	0.210 2(3)
O(6)A-Co(1)-O(6)^B	88.96(15)	O(6)A-Co(1)-N(1)^C	97.20(13)	O(6)B-Co(1)-N(1)^C	171.15(12)
O(6)A-Co(1)-N(1)	171.15(12)	O(6)B-Co(1)-N(1)	97.20(13)	N(1)C-Co(1)-N(1)	77.4(2)
O(6)A-Co(1)-O(1)	81.35(11)	O(6)B-Co(1)-O(1)	87.80(11)	N(1)C-Co(1)-O(1)	86.86(12)
N(1)-Co(1)-O(1)	105.14(12)	O(6)A-Co(1)-O(1)^C	87.80(11)	O(6)B-Co(1)-O(1)^C	81.35(11)
N(1)C-Co(1)-O(1)^C	105.14(12)	N(1)-Co(1)-O(1)^C	86.86(12)	O(1)-Co(1)-O(1)^C	164.80(14)
O(4)D-Co(2)-O(5)^B	175.50(12)	O(4)D-Co(2)-O(8)	95.31(12)	O(5)B-Co(2)-O(8)	88.84(12)
O(4)D-Co(2)-O(1)	91.24(11)	O(5)B-Co(2)-O(1)	84.84(11)	O(8)-Co(2)-O(1)	170.74(12)
O(4)D-Co(2)-O(7)	91.28(12)	O(5)B-Co(2)-O(7)	87.13(12)	O(8)-Co(2)-O(7)	87.89(11)
O(1)-Co(2)-O(7)	98.52(12)	O(4)D-Co(2)-O(6)^A	89.72(11)	O(5)B-Co(2)-O(6)^A	91.76(11)
O(8)-Co(2)-O(6)^A	93.44(11)	O(1)-Co(2)-O(6)^A	80.02(11)	O(7)-Co(2)-O(6)^A	178.25(11)
Co(2)-O(1)-Co(1)	97.26(12)	Co(1)B-O(6)-Co(2)^E	96.27(11)		

Symmetry transformations used to generate equivalent atoms: A: x, $-y+3$, $z+1/2$; B: $-x+1/2$, $-y+3/2$, $-z+3/2$; C: $-x+1/2$, y, $-z+2$; D: $-x$, $y+1$, $-z+2$; E: x, $-y+3$, $z-1/2$

2 Results and discussion

2.1 Description of the structure

The asymmetric unit of compound **1** contains two crystallographically unique Co(Ⅱ) atoms, one btc^{3-} ligand, a half of one chelating 2, 2′-bpy moiety, and two coordinated water molecules. As shown in Fig.1, the Co1 atom is located at the inversion site and is coordinated by four O atoms from the four different btc^{3-} ligands and two N atoms from one 2, 2′-bpy moiety, thus forming an octahedral geometry. The six-coordinate Co2 atom adopts a distorted octahedral geometry, filled by four O atoms from the four distinct btc^{3-} ligands and two O atoms of the two coordinated water molecules. The Co-O bond lengths range from 0.204 8(3) to 0.220 5(3) nm, while the Co-N distance is 0.209 9(4) nm, which are in good agreement with those distances observed in some other Co(Ⅱ) compounds[10-11]. The btc^{3-} ligand adopts the μ_6-coordination mode (Scheme 1), in which the carboxylate groups show the μ_3-η^2:η^1 tridentate, μ_2-η^2:η^0 bidentate, and μ_1-η^1:η^0 monodentate modes. The dihedral angle of two benzene rings in btc^{3-} is 34.30°. The three neighboring Co(Ⅱ) ions are bridged by means of four



Scheme 1 Coordination mode of the btc^{3-} ligand in compound **1**

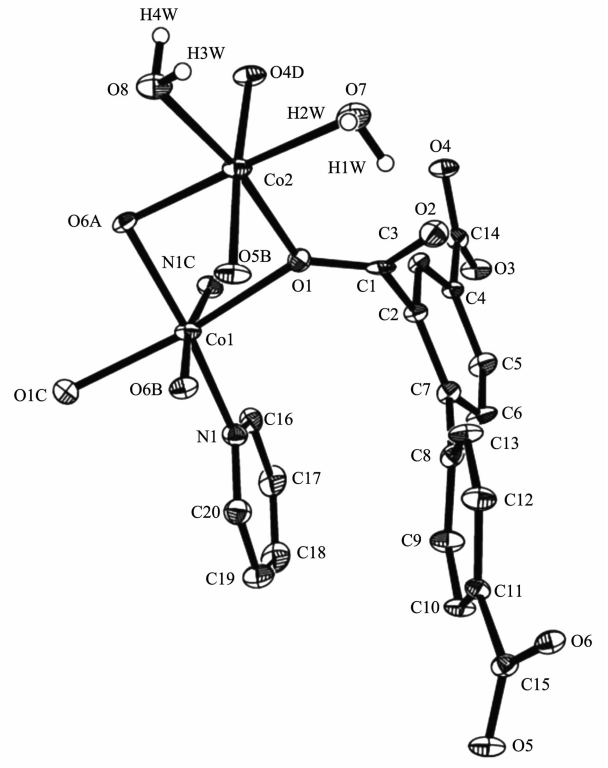
carboxylate groups from the four different btc^{3-} ligands, giving rise to a centrosymmetric trinuclear Co(Ⅱ) subunit (Fig.2). In this bent tricobalt(Ⅱ) unit, the distances of Co1…Co2 and Co2…Co2^{i} are 0.320 1(3) and 0.472 7 (3) nm, respectively. The Co_3 units are multiply linked by the btc^{3-} blocks to form a 3D framework (Fig.3), having the shortest distance of 0.830 9(3) nm between the neighboring Co_3 units.

2.2 TG analysis and PXRD results

To study the stability of compound **1**, its thermal behavior was investigated under nitrogen atmosphere by TGA. As shown in Fig.4, compound **1** loses its two coordinated water molecules (Expt. 7.35%; Calcd. 7.41%) in the 136~187 ℃ range, followed by the decomposition at 345 ℃. Powder X-ray diffraction experiment was carried out for compound **1**. The pattern for the as-synthesized bulk material closely matches the simulated one from the single-crystal structure analysis, thus confirming the purity of bulk sample (Fig.5).

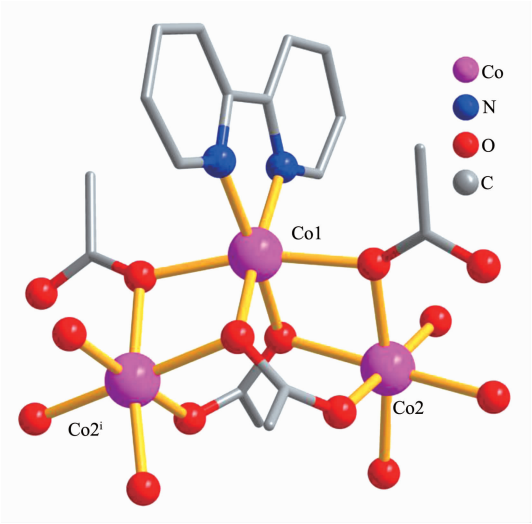
2.3 Magnetic properties

Variable-temperature magnetic susceptibility measurement was performed on powder samples of compound **1** in the 2~300 K temperature range (Fig.6). As shown in Fig.6, the $\chi_M T$ value at room temperature is 4.83 $cm^3 \cdot mol^{-1} \cdot K$, which is much larger than that



H atoms were omitted for clarity except those bonding to oxygen atoms; Symmetry code: A: x, $-y+3$, $z+1/2$; B: $-x+1/2$, $-y+3/2$, $-z+3/2$; C: $-x+1/2$, y, $-z+2$; D: $-x$, $y+1$, $-z+2$

Fig.1 Drawing of the asymmetric unit of compound **1** with thermal ellipsoids at 30% probability level



Symmetry code: ⁱ $-x+1/2, y, -z+2$.

Fig.2　Trinuclear Co(Ⅱ) unit

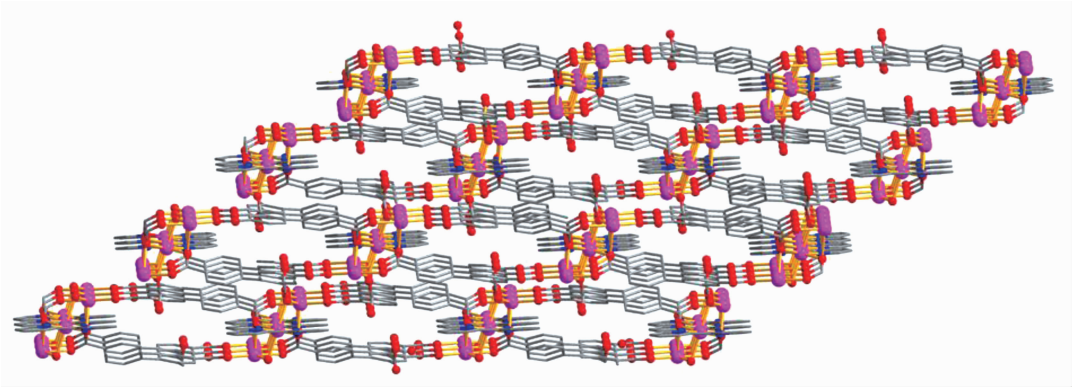


Fig.3　A perspective of 3D framework along the *ac* plane

the value (2.81 $cm^3 \cdot mol^{-1} \cdot K$) expected for one and a half magnetically isolated high-spin Co(Ⅱ) ions with the $S=3/2$, revealing a significant orbital contribution as also found in other high spin Co compounds [12]. Upon cooling, the value decreases gradually, and

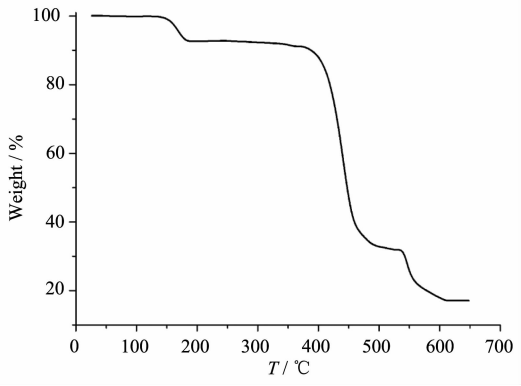


Fig.4　TG plot of compound **1**

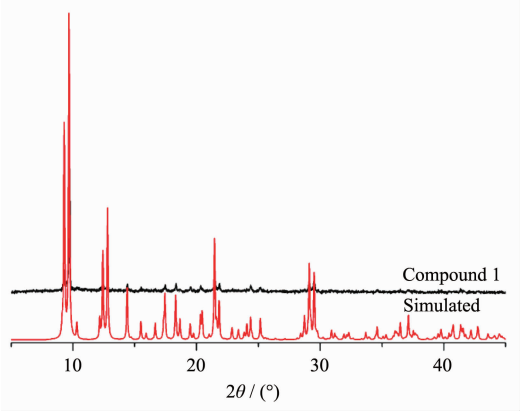
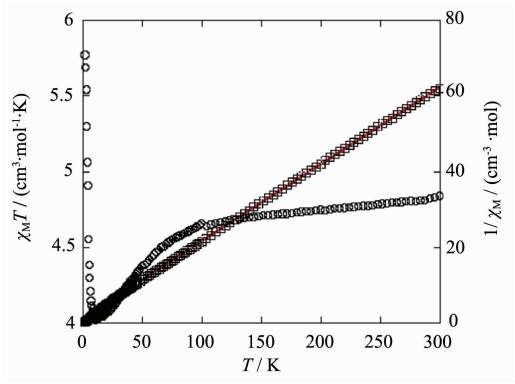


Fig.5　PXRD pattern of compound **1** at room temperature

reaches a minimum of 4.02 $cm^3 \cdot mol^{-1} \cdot K$ at 11.4 K. In the region of 300 to 11.4 K, the magnetic properties of compound **1** are typical for the single-ion behavior of the Co(Ⅱ) ion. Below 11.4 K, the ferromagnetic coupling between the Co(Ⅱ) atoms overcomes the effect



Solid line show the Curie-Weiss fitting.

Fig.6 Temperature dependence of $\chi_M T$ and $1/\chi_M$ vs. T for compound **1**

of the spin-orbital coupling and compensates the decrease of $\chi_M T$, leading to a sharp increase of $\chi_M T$ up to a maximum of 5.77 cm^3·mol^{-1}·K at 2.0 K. Between 50 and 300 K, the magnetic susceptibilities can be fitted to the Curie-Weiss law with C_M=4.71 cm^3·mol^{-1}·K and θ=−0.29 K. This contribution of a spin-orbital interaction diminishes the ferromagnetic exchange, resulting in a small negative Weiss constant[13]. Since the trinuclear subunits in **1** are well separated by the long btc^{3-} blocks, the ferromagnetic behavior is likely to arise from the two adjacent metal ions bridged by carboxylate groups within the trinuclear subunit. According to the structure of compound **1**, there are two sets of magnetic exchange pathways within the trinuclear cluster via different types of carboxylate bridges (Fig.2), which should be attributed to the overall ferromagnetic coupling between the Co (Ⅱ) centers within the Co_3 unit.

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