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研究简报

含有双螺旋链的配位聚合物$[Co(dpa)prz_{0.5}]_n$的合成、晶体结构及磁性质

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Synthesis, Crystal Structure and Magnetic Properties of A Coordination Polymer $[Co(dpa)prz_{0.5}]_n$ with Double-Helix Chains

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Abstract: A coordination polymer $[Co(dpa)prz_{0.5}]_n$ (**1**) with double-helix chains has been constructed hydrothermally using H_2dpa (H_2dpa=diphenic acid), prz (prz=piperazine) and $Co(NO_3)_2\cdot 6H_2O$. The structure and magnetic properties of the complex were investigated. The complex crystallizes in triclinic system and $P\bar{1}$ space group. Each Co atom is five-coordinated and takes a distorted tetragonal pyramid geometry. Two carboxylates of the H_2dpa ligands bridge four Co(Ⅱ) ions to form infinite right-handed or left-handed helical -C-O-Co- chains. The two types of helical chains are interconnected to each other through the Co(Ⅱ) centers to produce double-helix chains. The chains form a 2D sheet through the coordination interaction of prz molecules between adjacent chains. The sheets are further interlinked by hydrogen bond interactions to generate 3D coordination frameworks. Magnetic studies for complex **1** show stronger antiferromagnetic coupling between the Co(Ⅱ) ions. CCDC: 709275.

Key words: helical chain; coordination polymer; cobalt(Ⅱ) complex; magnetic properties

0 Introduction

Recently, much interest has been focused on the controlled syntheses of magnetic metal-organic frameworks (MOFs) from multi-carboxylate ligands[1]. In the designed synthesis of coordination polymers, diphenic acid (H_2dpa) is an excellent aromatic dicarboxylate ligand, especially on the formation of helical chain structure[2]. In order to investigate the magnetic properties of such helical polymers, we designed and synthesized a coordination polymer $[Co(dpa)prz_{0.5}]_n$ (**1**) with double-helix chains.

Herein, we report the synthesis, crystal structure, and magnetic properties of the compound.

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1 Experimental

1.1 Reagents and physical measurements

All chemicals and solvents were of A.R. 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. 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(dpa)prz$_{0.5}$]$_n$ (1)

A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.146 g, 0.5 mmol), H_2dpa (0.120 g, 0.5 mmol), NaOH (0.040 g, 1.0 mmol), prz (0.044 g, 0.5 mmol) and water/methanol (10 mL, 2∶1) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 180 ℃ for 3 days, followed by cooling to room temperature at a rate of 10 ℃·h^{-1}. Pink needle-shaped crystals of **1** were isolated in 80% yield, and washed with distilled water. Anal. Calcd for $C_{16}H_{13}NO_4Co$ (%): C 56.16, H 3.83, N 4.09; Found (%): C 55.84, H 3.59, N 4.08. IR (KBr, cm^{-1}): 2 362m, 1 626s, 1 588m, 1 562w, 1 470w, 1 396s, 1 287w, 1 094m, 1 001 m, 877s, 838m, 762s,709m, 678s, 471s.

1.3 Structure determinations

Single-crystal diffraction data of **1** was collected at 273(2) K on a Bruker Smart Apex 1000 CCD diffractometer with Mo $K\alpha$ radiation (λ=0.071 073 nm). A total of 3 581 reflections were collected in the range of 1.87°<θ<25.05° with 2 499 independent ones (R_{int}=0.013 4). The structure was solved using direct method, which yielded the positions of all non-hydrogen atoms. These were refined first with isotropically and then with anisotropically. All the hydrogen atoms 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. All calculations were performed using the SHELXTL system of computer program[3]. The crystallographic data are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

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Table 1　Crystal data for complex 1

Chemical formula	$C_{16}H_{13}CoNO_4$	Crystal size / mm	0.30×0.28×0.26
Molecular weight	342.2	θ range for data collection / (°)	1.87~25.05
Crystal system	Triclinic	Limiting indices	$-8 \leqslant h \leqslant 8, -11 \leqslant k \leqslant 10, -13 \leqslant l \leqslant 13$
Space group	$P\bar{1}$	Reflections collected / unique (R_{int})	3 581 / 2 499 (0.013 4)
a / nm	0.727 8(4)	Observed reflections ($I>2\sigma(I)$)	2 266
b / nm	0.960 6(6)	D_c / (Mg·m^{-3})	1.594
c / nm	1.137 3(7)	μ / mm^{-1}	1.221
α / (°)	82.717(9)	Data / restraints / parameters	2 499 / 0 / 203
β / (°)	73.446(8)	Goodness-of-fit on F^2	1.009
γ / (°)	69.349(8)	Final R indices ($I\geqslant 2\sigma(I)$) R_1, wR_2	0.030 7, 0.068 6
V / nm^3	0.712 8(7)	R indices (all data) R_1, wR_2	0.035 2, 0.070 5
Z	2	Largest diff. peak and hole / (e·nm^{-3})	421 and −445
F(000)	350		

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

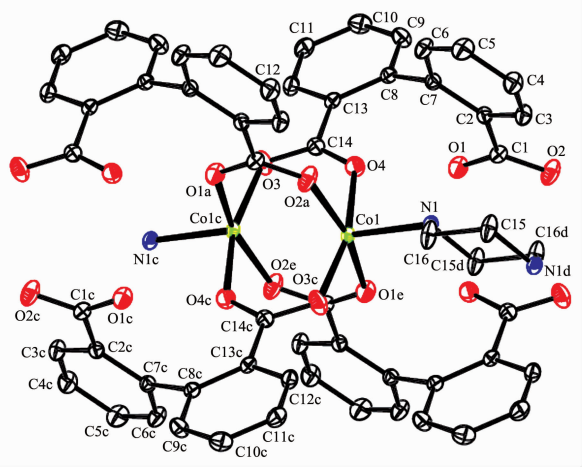
Co(1)-N(1)	0.211 9(2)	Co(1)-O(1)#2	0.203 36(18)	Co(1)-O(2)#3	0.207 1(2)
Co(1)-O(3)#1	0.202 9(2)	Co(1)-O(4)	0.203 84(19)		
O(3)#1-Co(1)-O(1)#2	90.44(9)	O(3)#1-Co(1)-O(4)	164.62(7)	O(1)#2-Co(1)-O(4)	89.52(9)
O(3)#1-Co(1)-O(2)#3	87.71(9)	O(1)#2-Co(1)-O(2)#3	164.72(7)	O(4)-Co(1)-O(2)#3	88.28(9)
O(3)#1-Co(1)-N(1)	98.02(9)	O(1)#2-Co(1)-N(1)	102.96(8)	O(4)-Co(1)-N(1)	96.97(8)
O(2)#3-Co(1)-N(1)	92.32(8)				

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y+2, -z+1$; #2: $-x+2, -y+2, -z+1$; #3: $x-1, y, z$.

2 Results and discussion

2.1 Structure description

The crystal structure of the complex **1** is shown in Fig.1. The Co(Ⅱ) exhibits distorted square pyramidal geometry, which four carboxylate oxygen atoms locate in the basal plane and one nitrogen atom from the prz ligand occupys the vertical position. The Co-O bond lengths are among 0.202 9(2)~0.207 1(2) nm and Co-N bond distance is 0.211 9(2) nm, respectively, which are in good agreement with those observed in other Co(Ⅱ) complexes[1d,4]. Two carboxylates of the H_2dpa ligands bridge four Co(Ⅱ) ions to form infinite right-handed or left-handed helical -C-O-Co- chains (Fig.2). The Co⋯Co separation in the chain is 0.727 8(4) nm. The two types of helical chains are interconnected to each other through the Co(Ⅱ) centers to produce double-helix chains. A dinuclear Co(Ⅱ) secondary building unit exists in the chains. The chains form a 2D sheet through the coordination interaction of prz molecules between adjacent chains (Fig.3). The sheets are further interlinked by hydrogen bond interactions to generate 3D coordination frameworks (Table 3).



Symmetry code: a: $-x+1, -y+2, -z+1$; c: $x-1, y, z$; d: $-x+2, -y+1, -z+1$; e: $x+1, y, z$

H atoms were omitted for clarity

Fig.1 Coordination structure of complex **1**

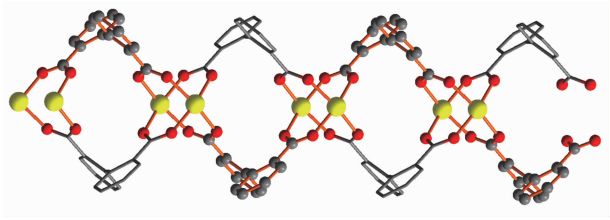


Fig.2 Double helix chains of the compound **1**

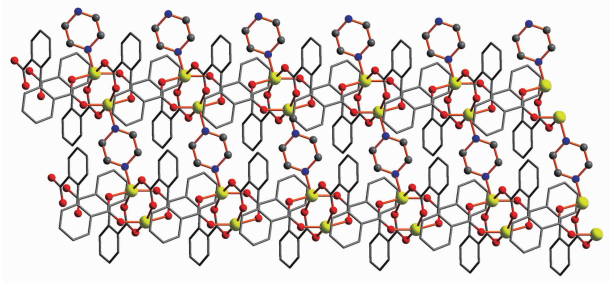


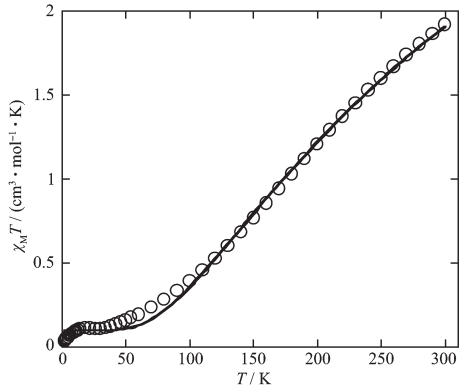
Fig.3 2D sheet formed through the coordination interaction of prz molecules between adjacent chains

Table 3 Hhydrogen bonds and angles for compound 1

D–H⋯A	*d*(D-H) / nm	*d*(H⋯A) / nm	*d*(D⋯A) / nm	∠(DHA) / (°)
C(3)–H(3)⋯O(2)	0.093	0.241	0.274 2(4)	101
C(12)–H(12)⋯O(3)	0.093	0.240	0.273 7(4)	101

2.2 Magnetic properties

The magnetic behaviors of **1** are shown in Fig.4. The $\chi_M T$ value of 1.86 $cm^3 \cdot K \cdot mol^{-1}$ (3.85μ_B) at room temperature is close to the expected value of 1.87 $cm^3 \cdot K \cdot mol^{-1}$ (3.87μ_B) for one magnetic isolated high-spin Co(Ⅱ) ion. Upon lowering the temperature, the $\chi_M T$ value decreases rapidly from temperature to 0.126 $cm^3 \cdot K \cdot mol^{-1}$ at 40 K. In the temperature range 2~40 K, it decreases slowly. Based on the structure for **1**, we attempt to interpret the magnetic behavior of **1** by fitting its magnetic data with Bleaney-Bowers equation to characterize the intradimer interaction defined as *J*



Solid line corresponds to the best-fit curve

Fig.4 Temperature dependence of $\chi_M T$ vs *T* for **1**

together with the application of a molecular field model defined as zJ' to account for interdimer magnetic interactions. The best parameters obtained by a standard leastsquares fitting were g=2.62(2), J=−81.704 5(3) cm^{-1}, and zJ' =−1.283 4(5) cm^{-1}. The agreement factor R = 8.14×10^{-4} ($R=\sum[(\chi_MT)_{obs}-(\chi_MT)_{calc}]^2/\sum[(\chi_MT)^2_{obs}$). The large antiferromagnetic coupling observed in this compound can be attributed to the small Co ⋯ Co separation (0.273 1(11) nm) in the intradimer.

References:

[1] (a)Li W, Li M X, Shao M, et al. *Inorg. Chem. Commun.*, **2008**, **11**:954~957

(b)Qi Y, Che Y X , Zheng J M. *Cryst. Growth Des.*, **2008**,**8**: 3602~3608

(c)Li W, Ju Z F, Yao Q X, et al. *Crystengcomm*, **2008**,**10**:1325 ~1327

(d)Lu W G, Gu J Z, Jiang L, et al. *Cryst. Growth Des.*, **2008**,**8**: 192~199

[2] (a)Yin P X, Zhang J, Li Z J, et al. *Inorg. Chim. Acta*, **2007**,**360**: 3525~3532

(b)Wang R H, Gong Y Q, Han L, et al. *J. Mol. Struct.*, **2006**, 784:1~6

(c)Yin P X, Zhang J, Li Z J, et al. *Inorg. Chem. Commun.*, **2008**,**11**:134~137

(d)Wang R H, Hong M C, Luo J H, et al. *Chem. Commun.*, **2003**:1018~1019

(e)Xu X X, Lu Y, Wang E B, et al. *Cryst. Growth Des.*, **2006**, **6**:2029~2035

[3] Sheldrick G M. *SHELXL NT Version* 5.1, *Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[4] (a)Zhao X J, Du M, Wang Y, et al. *J. Mol. Struct.*, **2004**,**692**: 155~161

(b)Nowlin T, Subramanian S, Cohn K. *Inorg. Chem.*, **1992**,**11**: 2907~2912