

二咪唑基苯及硫酸根构筑的钴配位聚合物的合成、晶体结构和磁性质

陈满生^{1,2} 曾巨澜^{*2} 张春华^{*1} 邝代治¹ 邓奕芳¹ 聂 雪¹

(¹ 功能金属有机材料湖南省普通高等学校重点实验室, 衡阳师范学院化学与材料科学系, 衡阳 421008)

(² 长沙理工大学化学与生物工程学院电力与交通材料保护湖南省重点实验室, 长沙 410004)

摘要: 由溶剂热法合成了钴化合物 $[\text{Co}(\text{dib})(\text{SO}_4)]$ (**1**) (dib=1,4-二咪唑基苯), 并对其进行了元素分析、IR 及 X-射线衍射法表征。晶体结构表明: 配合物 **1** 属于单斜晶系, $C2/c$ 空间群。配合物 **1** 是由桥联配体 1,4-二咪唑基苯连接成二维层状结构, 该二维层被硫酸根离子拓展成三维层柱状结构。配合物 **1** 的磁性测试研究表明它具有弱反铁磁性。

关键词: 钴配合物; 晶体结构; 柱层状; 磁性质

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Synthesis, Crystal Structure and Magnetic Properties of Cobalt Coordination Compound Constructed from 1,4-Di(1-imidazolyl)benzene and Sulfate

CHEN Man-Sheng^{1,2} ZENG Ju-Lan^{*2} ZHANG Chun-Hua^{*1}

KUANG Dai-Zhi¹ DENG Yi-Fang¹ NIE Xue¹

(¹Key Laboratory of Functional Organometallic Materials of Hengyang Normal University,

College of Hunan Province, Department of chemistry and Materials Science, Hengyang, Hunan 421008, China)

(²Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation,

School of Chemistry and Biological Engineering, Changsha University of Science and Technology, Changsha 410004, China)

Abstract: A cobalt coordination polymers $[\text{Co}(\text{dib})(\text{SO}_4)]$ (**1**) was obtained by solvothermal assembly of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ with sodium formate in the presence of N-donor ligands, namely 1,4-di(1-imidazolyl)benzene (dib). Compound **1** crystallizes in monoclinic system, space group $C2/c$ with $a=1.972\ 26(7)$ nm, $b=0.977\ 0(3)$ nm, $c=1.1839\ 6(4)$ nm, $\beta=96.479(2)^\circ$, $V=2.266\ 8(13)$ nm³, $Z=4$, $\text{C}_{24}\text{H}_{20}\text{N}_8\text{CoO}_4\text{S}$, $M_r=575.47$, $D_c=1.686\ \text{g} \cdot \text{cm}^{-3}$, $\mu=0.903\ \text{mm}^{-1}$, $F(000)=1\ 180$, $R_{\text{int}}=0.018\ 3$, $R=0.024\ 6$, $wR=0.072\ 6$. Single-crystal X-ray diffraction analysis revealed that each dib ligand in turn uses its two imidazole groups to connect two metal centers, then the two-dimensional (2D) layer is formed. On the other hand, the 2D layers are further connected by sulfate to give a three-dimensional (3D) pcu topologic structure. In addition, the magnetic property of complex **1** has been investigated in the temperature range of 1.8~300 K, and the results show the weak antiferromagnetic interactions between Co(II) ions bridged by sulfate. CCDC: 878879.

Key words: Co(II) complex; crystal structure; layer-pillared; magnetic property

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*通讯联系人。E-mail: zhangchunhua668@163.com, julan_zeng@163.com; 会员登记号: S06N7223M1009。

0 Introduction

In recent years, many interest has been devoted to the development of rational synthetic routes to novel one-, two- and three-dimensional crystal frameworks, due to their potential applications in many areas such as ion-exchange, nonlinear optics, molecular sieves, gas storage, catalysis, magnetism, and so on^[1-9]. However, the control of synthesis of supramolecular compounds is still a fascinating challenge. Our strategy in this approach is using the organic functional ligand 1,4-di(1-imidazolyl)benzene (dib), which is very similar to the 4,4'-bipyridine, a few structures is known to date^[10-14]. In order to further investigate the dib ligand with organic carboxylate ligands on the coordination architectures and related properties, herein we report the synthesis, crystal structure and magnetic property of a new 3D coordination compound, namely [Co(dib)(SO₄)] (**1**).

1 Experimental

1.1 Materials and instruments

The reagents were used as commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The ligand dib was prepared as reported previously^[15]. The IR spectra were recorded on Bruker Vector22 FT-IR spectrophotometer using KBr discs. Thermogravimetric analyses were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10 °C·min⁻¹. Magnetic measurements for complex **1** in range of 1.8~300 K were performed on a MPMS-SQUID magnetometer at a field of 2 kOe on crystalline samples in the temperature

settle mode. The diamagnetic contributions of the samples were corrected by using Pascal's constants.

1.2 Synthesis of the compound 1

Complex **1** was synthesized by solvothermal method in a 16 mL Teflon-lined autoclave by heating a mixture containing CoSO₄·7H₂O (29.9 mg, 0.1 mmol), HCOONa (13.7 mg, 0.2 mmol), and dib (20.1 mg, 0.1 mmol) dissolved in 8 mL DMF and heated at 120 °C for 4 d. Block red single crystals of **1** were collected by filtration and washed by water and ethanol for several times with a yield of 45% (based on dib). Anal. Calcd. for C₂₄H₂₀CoN₈O₄S (%): C 50.05; H 3.48; N 19.46; found (%): C 50.11; H 3.39; N 19.40. IR (KBr pellet, cm⁻¹): 3 319(s), 1 531(s), 1 500(w), 1 448(w), 1 313(w), 1 267(m), 1 109(s), 1 070(s), 962(w), 938(m), 824(m), 738(m), 650(m), 618(m).

1.3 X-ray crystallography

The X-ray diffraction measurement for **1** was performed on the Bruker Apex-II CCD diffractometer with graphite-monochromated Mo K α radiation (λ = 0.071 075 nm) at room temperature. The data were integrated by using the SAINT program^[16], which also did the intensity corrections for Lorentz and polarization effect. An empirical absorption correction was applied using the SADABS program^[17]. The structures were solved by direct methods using the program SHELXS-97 and all the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package^[18-19]. Crystal data and structure refinement parameters are listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

CCDC: 878879.

Table 1 Crystal data and structure parameters for complex 1

Empirical formula	C ₂₄ H ₂₀ CoN ₈ O ₄ S	Z	4
Formula weight	575.47	Absorption coefficient / mm ⁻¹	0.903
Temperature / K	296(2)	$F(000)$	1 180
Crystal system	monoclinic	Crystal size / mm	0.22×0.16×0.10
Space group	$C2/c$	θ / (°)	2.08 to 26.00
a / nm	1.972 26(7)	Reflections collected / unique	8 796/2 227 (R_{int} =0.018 3)
b / nm	0.977 0(3)	Data / restraints / parameters	2 227 / 0 / 175
c / nm	1.183 96(4)	Goodness of fit on F^2	1.012

Continued Table 1

$\beta / (^{\circ})$	96.479(2)	Final R indices ($I > 2\sigma(I)$)	$R_1=0.024\ 6$, $wR_2=0.072\ 6$
V / nm^3	2.266\ 8(13)	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	269 and -306
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.686		

Table 2 Selected bond lengths (nm) and bond angle ($^{\circ}$)

Co(1)-O(1)	0.206\ 83(12)	Co(1)-N(1)	0.214\ 67(13)	Co(1)-N(1) ^A	0.214\ 67(13)
Co(1)-O(1) ^A	0.206\ 83(12)	Co(1)-N(4) ^B	0.215\ 78(13)	Co(1)-N(4) ^C	0.215\ 78(13)
O(1)-Co(1)-N(1) ^A	89.48(6)	O(1)A-Co(1)-N(1) ^A	90.52(6)	N(1) ^A -Co(1)-N(4) ^B	96.62(5)
N(1)-Co(1)-N(4) ^B	83.38(5)	O(1)A-Co(1)-N(1)	89.48(6)	O(1) ^A -Co(1)-N(4) ^C	87.05(5)
O(1)-Co(1)-O(1) ^A	180.00(11)	N(1)-Co(1)-N(1) ^A	180.00(8)	O(1)-Co(1)-N(4) ^C	92.95(5)
O(1) ^A -Co(1)-N(4) ^B	92.95(5)	O(1)-Co(1)-N(1)	90.52(6)	O(1)-Co(1)-N(4) ^B	87.05(5)
N(4) ^B -Co(1)-N(4) ^C	180.00(11)	N(1) ^A -Co(1)-N(4) ^C	83.38(5)	N(1)-Co(1)-N(4) ^C	96.62(5)

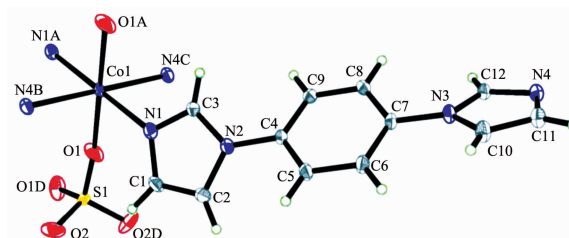
Symmetry code: ^A 2-x, -y, -z, ^B 1/2+x, 1/2-y, -1/2+z, ^C 3/2-x, -1/2+y, 1/2-z.

2 Results and discussion

2.1 Structure description

The dib reacted with $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ under solvothermal conditions to give complex **1**. Single-crystal X-ray diffraction study reveals 3D of **1** that crystallizes in space group $C2/c$. The coordination environment around the Co(II) in complex **1** is shown in Fig.1. The central Co(II) atom is located in a slightly distorted octahedron coordination environment: four N atoms (N1, N1A, N1B, N1C) from four dib ligands in the equatorial plane and the other two O atoms (O1 and O1A) from water molecules in axes sites. The Co-O bond-distances are the same distance of 0.206 83 (12) nm, and Co-N bond-distances are 0.214 67 (13) and 0.21578 (13) nm. Then the cobalt ions are bridged by dib ligands to form a 2D infinite layer structure $[\text{Co}(\text{dib})]_n$ (Fig.2). It is noteworthy that these layers are further connected by SO_4^{2-} anions extend it into the three-dimensional (3D) layer-pillared architecture (Fig.2), which is entirely different

from the reported complexes^[10-11]. To further understand this 3D structure of **1**, the Co(II) center is considered as the nodes, the topology of **2**, calculated by TOPOS^[20], is a uniform 3D 6-connected pcu as shown in Fig.3.

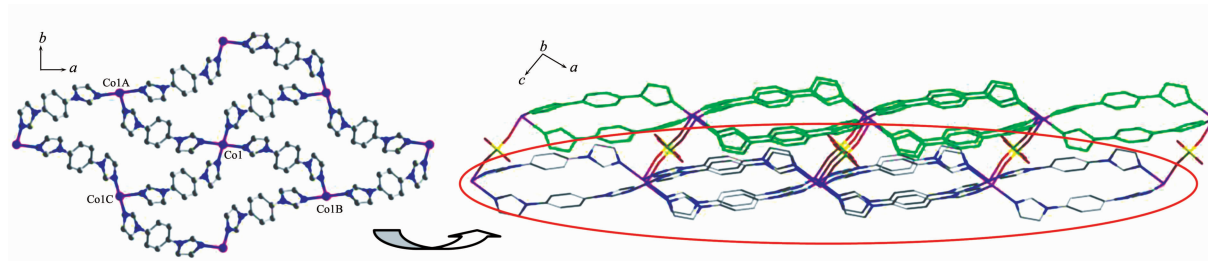


Symmetry code: A: $-1+x, 1+y, z$, B: $1-x, -y, 1-z$, C: $-1+x, y, z$, D: $-x, -y, 2-z$

Fig.1 Coordination enviroment of Co(II) in complex **1** with 30% thermal ellipsoids

2.2 IR, TG and Magnetic Property

The infrared spectra of the title complexes have been recorded and some important assignments are shown above. No strong IR band from $-\text{COOH}$ appeared at nearly $1\ 660\ \text{cm}^{-1}$, indicating that the formate ligands are not existed in it, and peaks at $1\ 109$, $1\ 070$ and



Symmetry code: A : $-1+x, 1+y, z$, B: $1-x, -y, 1-z$, C: $-1+x, y, z$

Fig.2 2D layer structure linked by dib ligands and Co(II) centers and 3D layer-pillared structure

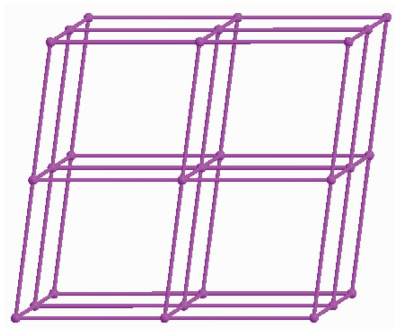
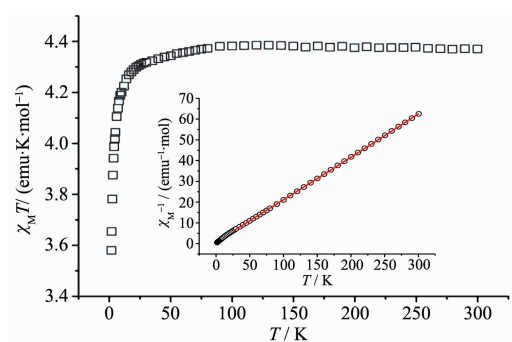


Fig.3 Topologically representation of the pcu 3D structure of **1**

962 cm^{-1} could be assigned to characteristic peaks of SO_4^{2-} . These IR results are coincident with the crystallographic structural analyses. The results of thermogravimetric analyses (TGA) indicate that no weight loss is found before 380 $^{\circ}\text{C}$ in compound **1**, and above this temperature, the structure collapsed due to the liberation of the organic ligands dib.

The magnetic susceptibilities were measured on a crystalline sample of **1** in the temperature range from 1.8 to 300 K under 2 kOe using a SQUID magnetometer. At room temperature, the observed $\chi_{\text{M}}T$ value is 4.37 $\text{emu} \cdot \text{K} \cdot \text{mol}^{-1}$, which is slightly larger than the expected value of 3.75 $\text{emu} \cdot \text{K} \cdot \text{mol}^{-1}$ corresponding to two Co(II) ($S=3/2$) ions bridged by SO_4^{2-} anion with the $\text{Co} \cdots \text{Co}$ distances of ca. 0.59 nm (Fig.4). Upon cooling from 300 to 100 K the values of $\chi_{\text{M}}T$ decrease slowly, and then rapidly reach a value of 3.57 $\text{emu} \cdot \text{K} \cdot \text{mol}^{-1}$ at 1.8 K. The χ_{M}^{-1} versus T plot follows the Curie-Weiss law with $C=2.77 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$, $\theta=-2.89$ K. The negative θ value suggests that there is a weak



The red solid line shows the Curie-Weiss fitting

Fig.4 Temperature dependence of $\chi_{\text{M}}T$ and χ_{M}^{-1} for **1**

antiferromagnetic interaction among cobalt (II) atoms transferred through SO_4^{2-} anion.

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