

## 研究简报

## 具有梯形结构钴(II)配位聚合物的合成及晶体结构

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分类号: O614.7+11Synthesis and Crystal Structure of a Novel Cobalt (II)  
Coordination Polymer with Molecular Ladder StructureWU Jie-Ying<sup>\*1</sup> PAN Yue-Li<sup>1</sup> ZHANG Xuan-Jun<sup>2</sup> ZHANG Ming-Liang<sup>1</sup> TIAN Yu-Peng<sup>1,3</sup> FUN Hoong-Kun<sup>4</sup><sup>(1)</sup> Department of Chemistry, Anhui University, Hefei 230039)<sup>(2)</sup> Department of Chemistry, University of Science and Technology of China, Hefei 230026)<sup>(3)</sup> State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093)<sup>(4)</sup> X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia 11800 USM, Penang, Malaysia)

Co(NO<sub>3</sub>)<sub>2</sub>, N-carbazolyacetic acid and 4,4'-bipyridyl can give rise to a novel coordination polymer [Co<sub>2</sub>(Cabo)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(4,4'-bipy)<sub>2</sub>]<sub>n</sub> using a fritted U-tube. Single crystal X-ray diffraction displays in the complex, each Co(II) is six-coordinated by two N atoms from different 4,4'-bipyridyl ligands, two O atoms of the bridge from two N-carbazolyacetic acid and two O atoms of one nitrate anion to form a distorted octahedral. Two O atoms of the carboxyl group act as bridge to link two Co(II) atoms. The resulting structure is a ladder polymer. CCDC: 211713.

Keywords: cobalt complex molecular ladder N-carbazolyacetic acid 4,4'-bipyridyl

## 0 Introduction

In recent years, there has been increasing interest in the areas of the crystal engineering and the design of solid-state architecture<sup>[1]</sup>. Inorganic-organic supramolecular architectures derived from building blocks that are linked by coordinate covalent bond<sup>[2]</sup>, hydrogen bon-

ds<sup>[3]</sup> aromatic  $\pi \cdots \pi$  stacking constitute an active field in the synthesis of interesting topological structures and potential functional materials. Self-assembly is currently the most efficient approach toward the design of one-, two-, and three- dimensional organic-inorganic hybrid frameworks. However, the factors influencing

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the information of coordination polymers are still not well understood in spite of the fact the self-assembly of these architectures has been documented to be highly influenced by various factors such as the nature of metal ions<sup>[4]</sup>, templates<sup>[5]</sup>, counterions<sup>[6]</sup>, and experimental conditions<sup>[7,8]</sup>, much work is required to extend the knowledge of the relevant structural types and establish proper synthetic strategies leading to the desired species.

There are particular interests in the carbazole compounds due to their variety applications such as photoconductivity<sup>[9, 10]</sup>, second<sup>[10, 11]</sup> and third order<sup>[12]</sup> nonlinear optical responses and rich luminescence<sup>[11, 13-15]</sup>. At present work we introduce the carbazole group into metal complexes using N-carbazolyacetic acid and have obtained a cobalt coordination polymer with a novel ladder structure in ethanol solution.

## 1 Experimental

### 1.1 Materials

All chemicals and solvents were dried and purified by usual methods. The N-carbazolyacetic acid was synthesized according to the literature method<sup>[16]</sup>. Elemental analyses were performed with a Perkin-Elmer 240 instrument. IR spectra were recorded with a Nicolet FT-IR 170SX instrument in the 4000 ~ 400  $\text{cm}^{-1}$  region.

### 1.2 Synthesis of the



The complex was prepared by self-assembly of cobalt nitrate with 4, 4'-bipyridyl and N-carbazolyacetic acid in ethanol. Crystals were obtained by using a U-tube. 4, 4'-bipyridyl solution was placed on one side of the U-tube, and on the other side cobalt nitrate and N-carbazolyacetic acid were added (approximately a stoichiometric amount), followed by enough ethanol to equalized the same pressure on both sides. After 5-6 days, well-formed red crystals were obtained within the solutions of both sides. Anal. Calc. for  $\text{C}_{24}\text{CoH}_{19}\text{N}_4\text{O}_5$ : C, 57.38; H, 3.81; N, 11.15%. Found: C, 57.26; H, 3.92; N, 11.08%. IR (KBr pettet,  $\text{cm}^{-1}$ ): 1600 (vs), 1488 (vs), 1456 (s), 1388(s), 1355

(m), 1355(m), 1318(s), 1265(m), 1211(m), 1114(vs), 1008(vs), 811(s), 757(s), 723(m), 629 (m).

### 1.3 X-ray Crystallography

A single crystal with dimensions 0.26 mm  $\times$  0.20 mm  $\times$  0.14 mm of the title compound was selected and sealed in a capillary containing the mother liquor. Intensity data collections were performed using a Siemens SMART CCD area detector diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.071073$  nm). The structure was solved with direct methods using the program SHELXTL (Sheldrick, 1997)<sup>[17]</sup> and refined anisotropically with SHELXTL using full-matrix least-squares procedure giving for the complex a final  $R_1$  value of 0.0495 for 308 parameters and 5212 unique reflections with  $I \geq 2\sigma(I)$  and  $wR_2$  of 0.1041 for all 12911 reflections. All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedure. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms and fixed displacement parameters. The crystal data and refinement details are listed in Table 1, selected bond distances and angles in Table 2.

CCDC: 211713.

## 2 Results and Discussion

The IR data of free nitrate anion is about 1400 ~ 1300  $\text{cm}^{-1}$ , 820  $\text{cm}^{-1}$ , 690  $\text{cm}^{-1}$ <sup>[18]</sup>, the IR spectral data of nitrate anion after coordination is 1488  $\text{cm}^{-1}$ , 1318  $\text{cm}^{-1}$ , 1211  $\text{cm}^{-1}$ , 1114  $\text{cm}^{-1}$ , which are higher than that of its free state. Obviously, Co (II) atom is bonded by two O atoms from nitrate anion and gives rise to great influence toward the free nitrate anion. The stretching vibration of the carboxyl group in N-carbazolyacetic ligand IR spectral was observed at 1600  $\text{cm}^{-1}$  and 1456  $\text{cm}^{-1}$ , respectively, where  $\Delta\nu(\nu_{\text{asym}} - \nu_{\text{sym}})$  is 144  $\text{cm}^{-1}$ . The band of  $\nu_{\text{C=O}}$  at 1720  $\text{cm}^{-1}$  is absent in the IR spectrum of the complex. The facts show that the carboxyl group of the N-carbazolyacetic ligand exhibits the typical bridging coordination mode<sup>[19]</sup>.

The molecular structure of the complex consists of

Table 1 Crystallographic Data for 1

empirical formula	C <sub>24</sub> H <sub>19</sub> CoN <sub>4</sub> O <sub>5</sub>
formal weight	502.36
temperature / K	293 (2)
wavelength / nm	0.071073
crystal system	monoclinic
space group	P2 <sub>1</sub> /n
a / nm	1.13818(2)
b / nm	1.62570(1)
c / nm	1.24825(2)
V / nm <sup>3</sup>	2.14853(5)
Z	4
D <sub>c</sub> / (Mg · m <sup>-3</sup> )	1.553
absorption coefficient / mm <sup>-1</sup>	0.845
F(000)	1032
crystal size / mm <sup>3</sup>	0.26 × 0.20 × 0.14
reflections collected	12911
unique reflections	5212
observed reflections [I > 2σ(I)]	3139
number of parameters	308
goodness-of-fit on F <sup>2</sup> (S)	0.847
final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0495, wR <sub>2</sub> = 0.1041
R indices (all data)	R <sub>1</sub> = 0.0899, wR <sub>2</sub> = 0.1139
largest diff. peak and hole / (e · nm <sup>-3</sup> )	513 and -941

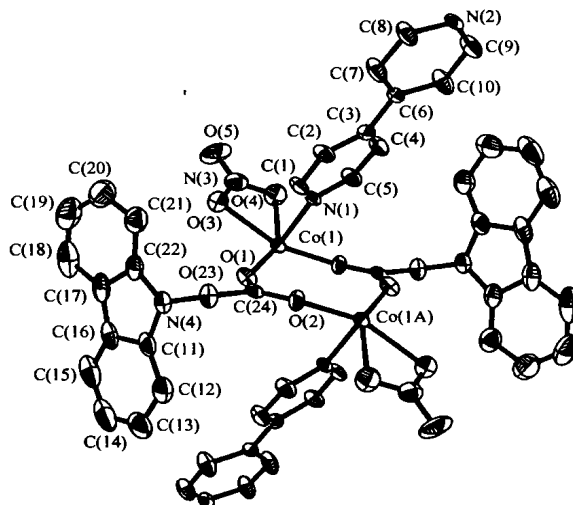
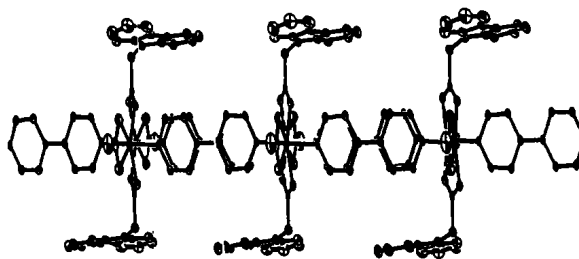
$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|;$$

$$wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table 2 Selected Bond Lengths (nm) and Angles (°) for 1

Co(1)-O(1)	0.20185(19)
Co(1)-O(2)	0.20265(19)
Co(1)-N(1)	0.2138(2)
Co(1)-N(2)	0.2153(2)
Co(1)-O(3)	0.2186(2)
Co(1)-O(4)	0.2222(2)
O(1)-Co(1)-O(2)	123.13(8)
O(1)-Co(1)-N(1)	92.82(8)
O(2)-Co(1)-N(1)	92.01(8)
O(2)-Co(1)-N(2)	89.53(8)
N(1)-Co(1)-N(2)	178.39(8)
O(1)-Co(1)-O(3)	91.00(9)
O(2)-Co(1)-O(3)	145.56(9)
N(1)-Co(1)-O(3)	90.59(8)
N(2)-Co(1)-O(3)	87.87(8)
O(1)-Co(1)-O(4)	149.07(9)
O(2)-Co(1)-O(4)	87.73(8)
N(1)-Co(1)-O(4)	87.51(9)
N(2)-Co(1)-O(4)	92.08(9)
O(3)-Co(1)-O(4)	58.07(9)
C(24)-O(1)-Co(1)	141.41(19)
C(24)-O(2)-Co(1)	132.56(18)
N(3)-O(3)-Co(1)	93.96(18)
N(3)-O(4)-Co(1)	92.39(18)

infinite  $[\text{Co}_2(\text{Cabo})_2(\text{NO}_3)_2(4,4'\text{-bipy})_2]$  molecular ladders as shown in Fig. 2. In the  $[\text{Co}_2(\text{Cabo})_2]$  fragments, the O atoms of two carboxylate bridges and the

Fig. 1 Molecular structure of  $[\text{Co}_2(\text{Cabo})_2(\text{NO}_3)_2(4,4'\text{-bipy})_2]$ .Fig. 2 Crystal ladder structure of  $[\text{Co}_2(\text{Cabo})_2(\text{NO}_3)_2(4,4'\text{-bipy})_2]$ .

two cobalt atoms are almost coplanar (the mean deviation: 0.0200 nm). Two N atoms from different 4,4'-bipyridyl ligands, two O atoms of the bridge from two N-carbazolylacetic acid and two O atoms of one nitrate anion form a distorted octahedral  $\text{CoN}_2\text{O}_4$ . Two nearest Co(II) atoms with a distance of 0.3934 nm are connected by two N-carbazolylacetic acid resulting in a dinuclear framework (Fig. 1). The carbazole rings are almost parallel to each other and the pyridyl rings of each 4,4'-bipyridyl in the complex are virtually coplanar with each other, only with a smaller average twisted angle of 15.8°.

In nitrate anion of the complex, the N(3)-O(3), N(3)-O(4) and N(3)-O(5) bond lengths are 0.1266(3) nm, 0.1263(3) nm and 0.1224(3) nm, respectively. The bond lengths of N(3)-O(3), N(3)-O(4) is same and  $\Delta\nu(\nu_{\text{asym}} - \nu_{\text{sym}})$  is 170  $\text{cm}^{-1}$  of the nitrate anion IR spectral above. The facts show that nitrate

anion behaves as a bidentate ligand in the prepared complex. The atoms of O(3), O(4), O(5), N(3) and Co(1) is nearly planar. Fig. 2 displays a ladder structure of the polymer.

As state above, the report gives an example that organic functional group can be introduced into inorganic framework by the formation of coordination polymer.

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