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# 研究简报

# 一维链钴配位聚合物{[Co(H<sub>2</sub>O)<sub>4</sub>(3,3'-azpy)](3,3'-azpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>}<sub>n</sub> 的结构和性质的研究

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# Structure and Properties of a One-Dimensional Chain Cobalt Coordination Polymer, $\{[Co(H_2O)_4(3, 3'-azpy)](3, 3'-azpy)_3(PF_6)_2\}_n$

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The complex {[Co(H<sub>2</sub>O) 4(3, 3'-azpy)] (3, 3'-azpy) 3(PF<sub>6</sub>) 2] (3, 3'-azpy = 3, 3'-azobispyridine) has been synthesized and characterized. The crystal (C<sub>40</sub>H<sub>40</sub>F<sub>12</sub>CoN<sub>16</sub>O<sub>4</sub>P<sub>2</sub>,  $M_r = 1157.75$ ) belongs to the triclinic system, space group  $P\overline{1}$  with the following crystallographic parameters: a = 10.759(2), b = 11.012(2), c = 23.207(4)Å:  $\alpha = 85.330(10)$ ,  $\beta = 83.470(10)$ ,  $\gamma = 69.770(10)^{\circ}$ ; V = 2560.6(8)Å<sup>3</sup>,  $D_c = 1.502g \cdot cm^{-3}$ ,  $\mu$ (Mo  $K\alpha$ ) = 0.498mm<sup>-1</sup>, F(000) = 1178, Z = 2, and final  $R_1 = 0.0469$ , w $R_2 = 0.1053$  for observed reflections 5549 ( $I > 2.00 \sigma(I)$ ). The X-ray analysis reveals that cobalt (II) cation coordination environment is a distorted octahedral geometry, the Co<sup>2+</sup> ion is coordinated by four oxygen atoms of water in the equatorial plane, while the two nitrogen atoms of 3, 3'-azpy occupy the axial positions. The complex forms a one-dimensional chain structure via 3, 3'-azpy bridging ligand. The one-dimensional chain forms three-dimensional network by hydrogen bonds and  $\pi$ - $\pi$  interactions.

Keywords: crystal structure one-dimensional chain cobalt complex azobispyridine

### 0 Introduction

The development of inorganic supramolecular ar-

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chitectures is a rapidly developing area of research that has implications for the rational design of functional materials<sup>[1, 2]</sup>. A convenient path to obtain a polymeric

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structure is to use a bifunctional ligand such as pyrazine, 4, 4'-bipyridine or 4, 4'-azobispyridine, to link metal ions to form an infinite structure<sup>[3, 4]</sup>. The unique directionality, strength, and complementary of non-covalent hydrogen and coordinated bonding play an important role in the construction of a variety of motifs for molecular self-assembly and recognition<sup>[5, 6]</sup>. However networks constructed by incorporation of metal ions within ordered hydrogen-bonded systems by the concurrent action of both extended coordination and hydrogen bonds have not yet attracted great attention. In an attempt to prepare supramolecular architectures by using ligand 3, 3'-azobispyridine (3, 3'-azpy), we obtained a one-dimensional chain cobalt complex and for which the three-dimensional network is constructed by hydrogen bonds and  $\pi$ - $\pi$  interactions. Here we report the structure and properties of 3, 3'-azpy complex {[ $C_0(H_2O)_4(3, 3'-azpy)$ ] (3, 3'-azpy) <sub>3</sub>( $PF_6$ ) <sub>2</sub>} <sub>n</sub> (1).

#### **1** Experimental

#### 1.1 Material and Instruments

All reagents were of AR grade and were used without further purification. 3, 3'-azobispyridine (3, 3' -azpy) was prepared following the literature method<sup>[7]</sup>. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyser. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000 ~ 400cm<sup>-1</sup> region. Magnetic susceptibilities were measured in the solid state using a CAHN-2000 Faraday balance with  $[Ni(en)_2]S_2O_3$  as a standard at 6000G magnetic field.

Synthesis of {[Co(H<sub>2</sub>O)<sub>4</sub>(3, 3'-azpy)](3, 3'-azpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>}, (1)

 $Co(ClO_4)_2 \cdot 6H_2O$  (0.366g, 1mmol) and KPF<sub>6</sub> (0.368g, 2mmol) were dissolved in 20mL water, then an ethanol solution (20mL) of 3, 3'-azpy (0.184g, 1mmol) was added. The result solution was continuously stirred for 30 min and then filtered, the filtrate was placed on the bench top for about one month at room temperature. The red single crystals suitable for X-ray diffraction were obtained. Yield: 0.183g 第18卷

(63. 3% based on 3, 3'-azpy). Found: C, 41. 37; H. 3. 42; N, 19. 14 for  $C_{40}H_{40}F_{12}CoN_{16}O_4P_2$  calcd.: C, 41. 50; H. 3. 48; N, 19. 36%.

#### 1.3 X-ray Single Crystal Structure Determination

A single crystal with approximate dimensions of 0.54mm × 0.36mm × 0.16mm was selected for X-ray diffraction analysis. All intensity data were collected on SIEMENS P4 four-circle diffractometer with a graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$ Å) using  $\omega/2\theta$  scan type at 290(2) K. A total of 9852 reflections were collected in the range  $1.77^{\circ} < \theta <$ 25.01°, of which 9014 were independent. 5549 observable reflections with  $I > 2 \sigma(I)$  were used in structure solution and refinements. The corrections for Lp factors and empirical absorption were applied to the intensity data. The structure was solved by direct methods. The position of hydrogen atoms were calculated using idealized geometry except the hydrogen atoms of coordination water which were obtained from successive Fourier syntheses. The structure was refined on  $F^2$  by full-matrix least-squares method using the SHELXTL-97 program package on a 586 computer. All non-hydrogen atoms were refined anisotropically. The final refinements converged at R = 0.0469, wR =0. 1053 with  $w = 1 / [\sigma^2 (F_0^2) + (0.0590 P)^2]$ , where  $P = (F_0^2 + 2F_c^2)/3$ . The maximum shift  $(\Delta / \sigma)_{max}$  is 0.001 and the goodness of fit S = 0.909. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.586 e  $\cdot$  Å<sup>-3</sup> and -0.356 e  $\cdot$  Å<sup>-3</sup>, respectively.

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#### 2 Results and Discussion

#### 2.1 Crystal Structure

Selected bond lengths and bond angles are shown in Table 1. The molecular structure of the complex (1) is shown in Fig. 1. The X-ray structure analysis shows that complex (1) consists of coordination  $[Co(H_2O)_4$ (3, 3'-azpy)]<sup>2+</sup> cation, disorder PF<sub>6</sub><sup>-</sup> anions and uncoordinated 3, 3'-azpy ligand. The cobalt (II) cation coordination environment is a distorted octahedral geometry. Co<sup>2+</sup> ion is coordinated by four oxygen atoms of

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Table 1 Selected Bond lengths (Å) and Angles (°)										
Co-O(1)	2.036(3)	Co-O(2)	2.113(3)	Co-O(3)	2.117(3)	Co-O(4)	2.042(3)			
Co-N(1)	2.163(2)	Co-N(3)	2.161(2)							
O(1)-Cu-O(2)	89. 26(13)	O(1)-Cu-O(3)	92.18(13)	O(1)-Co-O(4)	176.75(10)	O(2)-Co-O(3)	178.41(12)			
$O(2)-C_{0}-O(4)$	89.18(12)	O(3)-Co-O(4)	89.42(12)	N(1)-Co-N(3)	179.36(10)	O(1)-Co-N(1)	92.13(10)			
O(1)-Co-N(3)	87.49(10)	O(2)-Co-N(1)	88.87(10)	O(2)-Co-N(3)	91.64(10)	O(3)-Co-N(1)	90.40(10)			
O(3)-Co-N(3)	89.10(10)	O(4)-Co-N(1)	90.69(10)	O(4)-Co-N(3)	89.71(10)					



Fig. 1 Molecular structure of the complex 1 Displacement ellipsoids are shown at 30% probability.

coordination water (Co-O(1) 2.036(3); Co-O(2) 2.113(3); Co-O(3) 2.117(3); Co-O(4) 2.042(3) Å) in the equatorial plane and mean deviation from plane is 0.0284Å, while the two nitrogen atoms of 3, 3'-azpy (Co-N(1) 2.163(2); Co-N(3) 2.161(2) Å) occupy the axial positions. 3, 3'-azpy ligand exhibits a trans-form isomer. The complex forms a one-dimensional chain structure via 3, 3'-azpy bridging ligand. The distances of two cobalt atoms separated by bridging ligand 3, 3'-azpy for the Co···CoA and the Co···CoB are 11.931 and 11.863Å, respectively (Fig. 2).



Fig. 2 One-dimensional chain structure of complex 1

Hydrogen bonds O-H···N  $(O(4) \cdots N(5) = 2.809$ (4) Å,  $O(1) \cdots N(8) (-x + 1, -y, -z) = 2.824(4)$  Å,  $O(3) \cdots N(9) = 2.749(4)$ Å,  $O(4) \cdots N(12)(-x +$  $1, -\gamma, -z - 1$  = 2.756(4) Å) of intra-chain, involving the water molecules coordinated to cobalt atoms and the uncoordinated 3, 3'-azpy bases (acting as spaces) form Co-H<sub>2</sub>O····3, 3'-azpy····H<sub>2</sub>O-Co-3, 3'-azpy rings [Co-O(4) ...3, 3'-azpy...O(1) (-x+1, -y, -y)(-z) -Co-3, 3'-azpy and Co-O(3) ...3, 3'-azpy...O(4)  $(-x+1, -\gamma, -z-1)$  -Co-3, 3'-azpy]. Hydrogen bonds  $O-H\cdots N (O(1)\cdots N(15) = 2.726(4) \text{ Å}, O(2)\cdots$ N(13) = 2.726(4)Å) of adjacent chains, involving the water molecules coordinated to cobalt atoms and the uncoordinated 3, 3'-azpy bases (acting as spaces) form long Co-H<sub>2</sub>O····3, 3'-azpy····H<sub>2</sub>O-Co bridges. The hydrogen bonds are also formed between hydrogen atoms of coordination H2O and F atoms of disorder PF6 anions  $(O(3) \cdots F(9), 2.846\text{\AA}; O(4) \cdots F(9'), 3.016$ (19)Å). The hydrogen bonds are presented in Table 2.

N(9) and N(15) pyridyl rings of 3, 3'-azpy stack with a face-to-face separation of ca. 3.5 ~ 3.7Å, indicating a significant  $\pi$ - $\pi$  interaction<sup>18,91</sup>. N(5) and N (13) (x - 1, y, z) (separation ca. 3.4 ~ 3.7Å), N(8) and N(13) (1 - x, -y, -z) pyridyl rings (separation ca. 3.4 ~ 3.7Å), N(9) and N(15) pyridyl rings (separation ca. 3.5 ~ 3.7Å), N(9) and N(12) (1 - x, -1 - y, -1 - z) pyridyl rings (separation ca. 3.5 ~ 3.8Å) and N(12) and N(15) (2 - x, -1 - y, -1 - z) pyridyl rings (separation ca. 3.5 ~ 3.9Å) also involve  $\pi$ - $\pi$  interactions. The one-dimensional chain complex forms three-dimensional network structure via hydrogen bonds and  $\pi$ - $\pi$  interactions in the crystal packing as illustrated in Fig. 3.

## 2.2 Infrared Spectrum and Magnetic Measurement

IR spectra shown the bands are as follows: 3607v. 2900 ~ 3300v, 1667m, 1601v, 1431vs, 1323w.

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Table 2 Distance (Å) and Angles (°) in Hydrogen Bonds

atom involue		angle		
atom involve	Donor-H	H-Acceptor	Donor-Acceptor	Donor-II-Acceptor
$O(1) - H \cdots N(15)$	0.813(10)	1.921(13)	2.726(4)	170(4)
$O(1) - H \cdots N(8)$	0.816(10)	2.029(17)	2.824(4)	165(4)
$O(2) = H \cdots N(13)$	0.817(10)	1.911(12)	2.726(4)	174(4)
$O(2) = H \cdots F(3)$	0.815(10)	2.20(2)	2.955(4)	153(4)
$O(3) = H \cdots N(9)$	0.821(10)	1.943(14)	2.749(4)	167(4)
$O(3) = H \cdots F(9)$	0.816(10)	2.14(3)	2.884(11)	151(4)
$O(3) = H \cdots F(9')$	0.816(10)	2.20(2)	3.016(19)	176(4)
$O(4) = H \cdots N(5)$	0.818(10)	2.002(13)	2.809(4)	168(4)
$O(4) = H \cdots N(12)^{b}$	0.819(10)	1.937(11)	2.756(4)	178(4)

Symmetry transformations used generate equivalent atoms: a: -x + 1, -y, -z; b: -x + 1, -y, -z - 1



Fig. 3 Molecular packing in the crystal structure of the complex 1

1192vs, 1115v, 1026s, 857vs, 698vs, 633m, 559vs and 521wcm<sup>-1</sup>. The strong peaks at  $1431cm^{-1}$  belong to the N = N stretch vibration of azo group<sup>[10]</sup>. The strong peaks at 857 and 559cm<sup>-1</sup> belong to PF<sub>6</sub><sup>-</sup> stretch vibration.

The magnetic moment of the complex 1 is 4.82 B. M. at 300K. The value is greater than the spin-only value 3.87B. M. for one local S = 3/2, suggesting an orbital contribution of the high spin Co (II) to the magnetic moment. The magnetic moment exhibits continuous decrease upon cooling to 4.79B. M. at 75K.



Fig. 4 Plot of  $1/\chi_m$  versus T for the complex 1

Variable-temperature magnetic susceptibility studies in the temperature range 75 ~ 300K, showed that the compound 1 obey the Curie-Weiss law,  $\chi_{\rm m} = C/(T - \theta)$ , with values of  $\theta = 5.586$ K, C = 2.877emu · K · mol<sup>-1</sup>(Fig. 4). There is a weak anti-ferromagnetic interaction between the cobalt (II) ions via 3. 3'-azpy bridging in the complex 1.

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