研究简报

一维链状配位聚合物$[Co(imbz)_2(H_2O)_2]_n$ [imbz = 4′-(1-咪唑基亚甲基)苯甲酸根]的合成及晶体结构

邹志红*,[1] 李东风[2] 樊 键[2] 孙为银[2]
([1] 东南大学化学化工系, 南京 210096)
([2] 南京大学配位化学研究所, 配位化学国家重点实验室, 南京 210093)

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Synthesis and Crystal Structure of a New One-Dimensional Chain Coordination Polymer, $[Co(imbz)_2(H_2O)_2]_n$[imbz = 4′-(Imidazol-1-ylmethyl)benzoate Anion]

ZOU Zhi-Hong*,[1] LI Dong-Feng[2] FAN Jian[2] SUN Wei-Yin[2]
([1] *Department of Chemistry and Chemical Engineering, Southeast University, Nanjing* 210096)
([2] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing* 210093)

A new coordination polymer $[Co(imbz)_2(H_2O)_2]_n$ [imbz = 4′-(imidazol-1-ylmethyl) benzoate anion] was synthesized and characterized by x-ray crystallography. The title complex crystallizes in monoclinic, space group $P2_1/c$, $a = 10.910(2)$, $b = 8.8720(18)$, $c = 11.252(2)$ Å, $\beta = 92.20(3)°$, $V = 1088.3(4)$ Å^3, $Z = 2$, $D_c = 1.518$ g·cm^{-3}, $\mu = 0.836$ cm^{-1}, $F(000) = 514$, $R = 0.0679$, w$R = 0.1710$. Each Co(Ⅱ) atom has a distorted octahedral coordination geometry and is six-coordinated by two water molecules and four imbz ligands. Each imbz ligand connects two Co(Ⅱ) to generate an infinite 1D twisted chain structure.

Keywords: 4′-(imidazol-1-ylmethyl)benzoate crystal structure cobalt complex coordination polymer

0 Introduction

Numerous unique frameworks have been reported by assembly of rational designed organic ligands with metal ions over the past decade[1~3]. It is known that both imidazole and carboxylate are

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*通讯联系人。
第一作者:邹志红,女,38 岁,硕士,研究方向:配位化学。

functional groups for coordination to transition metal ions to form complexes[4~6]. However, ligands containing both imidazole and carboxylate groups are not well known except the histidine residue and its derivatives[7]. Neutral coordination networks with large cavities, which are available for guest molecules, can be obtained by reaction of ligands with carboxylate groups and metal ions[8, 9]. We have recently synthesized a novel ligand with both imidazole and carboxylate groups, namely 4′-(imidazol-1-ylmethyl)benzoic acid (imbzH), and we report herein the synthesis and crystal structure of its cobalt (Ⅱ) complex, [Co(imbz)$_2$(H$_2$O)$_2$]$_n$.

1 Experimental

The imbzH ligand was prepared readily by hydrolysis of cyanobenzyl-1-imidazole in hydrochloric acid[10]. Pink crystals of good quality were obtained in about 80% yield by slow diffusion between two layers of aqueous solution (10mL) of Co(OAc)$_2$ · 4H$_2$O and piperidinium salt of imbzH in methanol (10mL) in molar ratio 1∶2 at room temperature.

A single crystal of dimensions 0.34 × 0.30 × 0.28mm was mounted and data collection were performed on a Noius CAD4 four-circle diffractometer by using graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073Å). A total of 1875 independent reflections were collected in the variable ω-scan mode. 1394 reflections with $I > 2\sigma(I)$ were used in the structure determination and refinement. The structure was solved by direct methods and refined on F^2 using full-matrix least-square calculations. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms generated geometrically.

2 Results and Discussion

A perspective view of the complex with the atom numbering scheme is shown in Fig. 1. Crystallographic data: [Co(imbz)$_2$(H$_2$O)$_2$], formula $C_{22}H_{22}CoN_4O_6$, Mr = 497.37, monoclinic, space group $P2_1/c$, a = 10.910(2), b = 8.8720(18), c = 11.252(2) Å, β = 92.20(3)°, V = 1088.3(4)

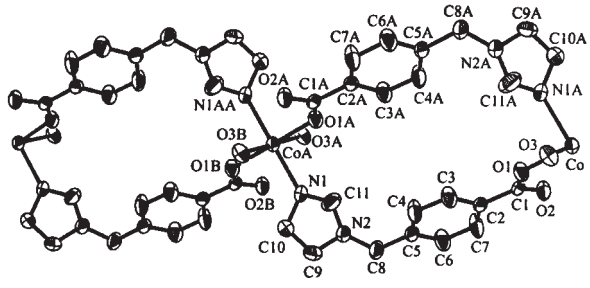

Fig. 1 Molecule structure with atom numbering scheme of [Co(imbz)$_2$(H$_2$O)$_2$]$_n$

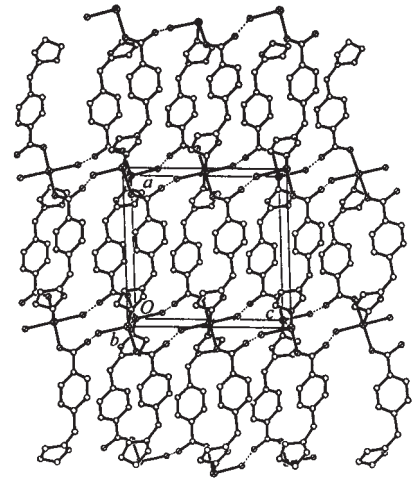

Fig. 2 Crystal packing diagram of [Co(imbz)$_2$(H$_2$O)$_2$]$_n$

Å^3, $Z = 2$, $D_c = 1.518 g \cdot cm^{-3}$, $\mu = 0.836 cm^{-1}$, $F(000) = 514$, $R = 0.0679$, $wR = 0.1710$. The Co (Ⅱ) atom is six-coordinated by four imbz ligands and two water molecules, and has a distorted octahedral coordination geometry with the N_2O_4 binding set. Two N atoms of imidazole are from two imbz ligands, two O atoms of benzoate from the other two imbz ligands and two O atoms of two H_2O. Each imbz ligand connects two Co (Ⅱ) to generate an infinite 1D chain structure. The Co-O1, Co-N1A and Co-O3 bond lengths are 2.094(4), 2.117(6) and 2.128(5) Å, respectively. Two nearest Co (Ⅱ) atoms with a distance of 10.91Å are connected by two imbz-ligands resulting in a dinulear macrocyclic framework (Fig. 1).

The water oxygen atoms form O – H···O[O3A···O2($-x$, $-y$, $-z$) = 2.730(7) Å, O3A – H3A···O2($-x$, $-y$, $-z$) = 147°; O3B···O2(x, 0.5 – y, 0.5 + z) = 2.775(7)Å, O3B – H3C···O2(x, 0.5 – y, 0.5 + z) = 146°] hydrogen bonds with carbonyl oxygen atom of adjacent chain to give three-dimensional network structure in the crystal packing as illustrated in Fig. 2.

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