第 24 卷第 10 期
2008 年 10 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.24 No.10
1718~1720

研究简报

一维链状配位聚合物[Cd{5-(NO$_2$)sal}$_2$(2,2′-bipy)]$_n$ 的合成与晶体结构

温德才* 谢 静 钟春龙 拓宏桂
(龙岩学院化学系,龙岩 364000)

关键词:配位聚合物;5-硝基水杨酸;镉(Ⅱ);晶体结构
中图分类号:O614.24+2 **文献标识码**:A **文章编号**:1001-4861(2008)10-1718-03

Synthesis and Crystal Structure of 1D Coordination Polymer [Cd{5-(NO$_2$)sal}$_2$(2,2′-bipy)]$_n$ with 5-nitrosalicylate Ligand

WEN De-Cai* XIE Jing ZHONG Chun-Long TA Hong-Gui
(*Department of Chemistry, Longyan University, Longyan, Fujian* 364000)

Abstract: A coordination polymer of [Cd{5-(NO$_2$)sal}$_2$(2,2′-bipy)]$_n$ (5-(NO$_2$)sal=5-nitrosalicylate, 2,2′-bipy=2,2′-bipyridine) was synthesized by hydrothermal reaction and characterized by elemental analysis, IR and X-ray diffraction single crystal structure analysis. The title complex crystallizes in monoclinic with space group *C*2/*c*, *a*=2.730 8(16) nm, *b*=1.272 3(5) nm, *c*=0.674 5(3) nm, β=96.73(2)°, *V*=2.327(2) nm^3, *Z*=4, *R*=0.022 2, *wR*=0.057. The 5-nitrosalicylate anions doubly bridge the Cd(Ⅱ) atoms to form one-dimensional polymeric chain with the repeated eight-membered ring units (Cd-O-C-O)$_2$. The crystal structure is stabilized by intra- and interchain hydrogen bonds interactions. CCDC: 694568.

Key words: coordination polymer; 5-nitrosalicylic acid; cadmium(Ⅱ); crystal structure

Salicylic acid and its substituted derivatives continue to attract attention because of its versatile coordination modes and biological applications[1~3]. Many complexes with salicylic acid and N-donor ligands, such as 2,2′-bipyridine, 1,10-phenanthroline and 4,4′-bipyridine, were found to display diverse structure types[4~8]. In addition, the coordination geometry of metal ion and the shape and bonding mode of the ligand are generally the primary considerations in metal-mediated self-assembly reactions. Relatively small changes in the bridging ligand can give rise to large changes in the overall structure of the assembly[9]. For example, Liu et al. reported a 1D left- and right-handed helical chain complex [Co{3,5-(NO$_2$)$_2$sal}(phen)]$_n$[10], and a 1D polymeric chain complex [Cd{3,5-(NO$_2$)$_2$sal}(2,2′-bipy)]$_n$[11] consisting of the repeated basic four-membered ring units and eight-membered ring units. In compared with many 3,5-dinitrosalicylate complexes, only a few 5-nitrosalicylate complexes have been found. Recently, we reported a novel molecular square structure complex Co$_4$(phen)$_4$(5-(NO$_2$)sal}$_4$[12]. As part of our ongoing investigation, a new Cd^{Ⅱ} complex with 5-(NO$_2$)sal ligand, has been prepared and its structure determined.

1 Experimental

1.1 Reagent and apparatus

All of the chemicals were obtained from commercial sources and were used without further

收稿日期:2008-04-21。收修改稿日期:2008-07-08。
福建省教育厅资助项目(No.JA02261);龙岩市科技局资助(No.2003LY03)。
*通讯联系人。E-mail:wendecai1227@yahoo.com.cn
第一作者:温德才,男,42 岁,博士,副教授;研究方向:配位化学。

purification. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN elemental analyzer. The IR spectra were recorded on a BRUKER EQUINOX 55 FTIR spectrometer using KBr pellet.

1.2 Synthesis of [Cd{5-(NO$_2$)sal}(2,2-bipy)]$_n$

A mixture of $Cd(NO_3)_2\cdot 6H_2O$ (0.035 g, 0.1 mmol), 2,2′-bipy (0.016 g, 0.1 mmol), 5-nitrosalicylic acid (0.037 g, 0.2 mmol) and distilled water (10 mL) was put into a Teflon-lined autoclave (20 mL) and then heated at 413 K for 48 h. Yellow block-like crystals of **1** in 85% yield based on Cd. Anal. Found (%): C 45.76; H 2.67; N 8.75. Calc. for $C_{24}H_{16}N_4O_{10}Cd$ (M_r=632.81) (%): C 45.55; H 2.55; N 8.85.

1.3 Crystal structure determination

A yellow block-like single crystal with dimensions of 0.33 mm × 0.30 mm × 0.28 mm for the title complex was used for X-ray diffraction structure analysis. Data collection was carried out at 293 K on a Rigaku RAXIS-RAPID Weissengberg IP diffractometer with graphite monochrocmatized Mo $K\alpha$ radiation (λ=0.071 073 nm) using ω scan mode. A total of 10 992 reflections and 2 674 unique ones (R_{int}=0.028 7) were collected in the range of 3.00°≤θ≤27.48°, of which 2 490 reflections with $I>2\sigma(I)$ were considered as observed and used in the succeeding structural calculations. The structure was solved by direct method and difference Fourier syntheses. All non-hydrogen atoms with the anisotropical thermal parameters were refined by full-matrix least-squares method on F^2. The aromatic H atoms were positioned geometrically and were included in the refinement in the riding-model approximation [C-H=0.093 nm and U_{iso}(H)=1.2U_{eq}(C)]. The hydroxyl H atom was found in a difference Fourier map and were refined with distance restraints of O-H=0.082(1) nm and U_{iso}(H)=1.2U_{eq} (O). All calculations were carried out with SHELX-97 program[13].

The Crystal belongs to monoclinic system, the space group is $C2/c$, with the crystal cell parameters a=2.730 8(16) nm, b=1.272 3(5) nm, c=0.674 5(3) nm, β=96.73(2)°, and V=2.327(2) nm^3, M_r=632.81, D_c=1.806 g·cm^{-3}, μ=1.009 mm^{-1}, F(000)=1 264, Z=4, R=0.022 2, wR=0.057 0, S=1.066, Δ/σ=0.000, $(\Delta\rho)_{max}$=374 e·nm^{-3} and $(\Delta\rho)_{min}$=−734 e·nm^{-3}.

CCDC: 694568.

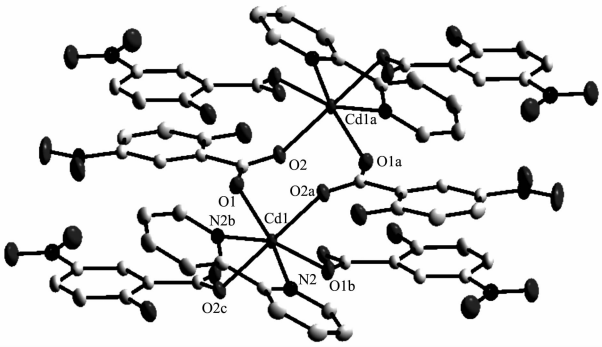
2 Results and discussions

2.1 IR spectra

The IR spectrum of the title complex reveals two strong bonds of the carboxylic groups at 1 604 and 1 445 cm^{-1} for the asymmetric vibrations and symmetric vibrations, respectively. The difference between the asymmetric and symmetric stretching vibrations ($\Delta\nu$=$\nu_{as}(COO^-)-\nu_s(COO^-)$) indicates that the 5-nitrosalicylate anions coordinated as a bridging carboxylic group[14]. A band at 1 513 cm^{-1} is assigned to ν_{as}(aromatic NO_2) and a band at 1 337 cm^{-1} is assigned to ν_s(aromatic NO_2)

2.2 Crystal structure

The crystal structure of the title complex was constructed from one-dimensional polymeric chain with the repeated eight-membered ring units. A segment of the molecular structure of the title complex is illustrated in Fig.1. The selected bond distances and angles of the title complex are given in Table 1.



Symmetry codes: a: 1−x, 1−y, 1−z; b: 1−x, y, 1.5−z; c: x, 1−y, 0.5+z

Fig.1 A segment of the molecular structure of the title complex with 30% probability ellipsoid; H atoms have been omitted for clarity

The Cd(Ⅱ) atom in the title complex is coordinated by four O atoms from four 5-nitrosalicylate ligands and two N atoms from a 2,2′-bipy ligand in a distorted octahedral coordination geometry. The 2,2′-bipy ligand lies on a twofold axis and chelates to the Cd(Ⅱ) atom with normal bond distances and angles. The two rings in the 2,2′-bipy ligand are a little twisted relative to each other with a dihedral angle of 13.26(7)°.

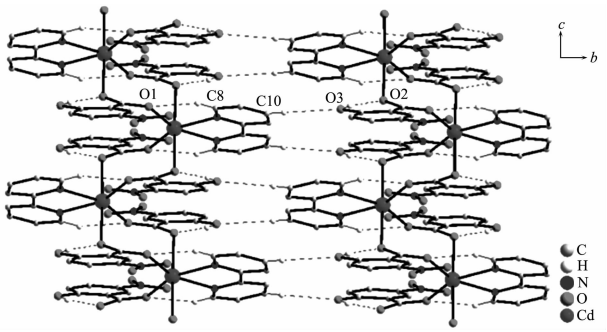
The 5-nitrosalicylate ligands act as bridging ligands in the title complex. Each 5-nitrosalicylate

Table 1 Selected bond lengths (nm) and angles (°) for the title complex

Cd(1)-O(1)	0.221 3(2)	Cd(1)-O(1)^{a}	0.221 3(2)	Cd(1)-N(2)	0.235 0(2)
Cd(1)-N(2)^{a}	0.235 0(2)	Cd(1)-O(2)^{b}	0.236 2(2)	Cd(1)-O(2)^{c}	0.236 2(2)
O(1)-Cd(1)-O(1)^{a}	115.47(8)	O(1)-Cd(1)-N(2)	156.63(5)	O(1)a -Cd(1)-N(2)	87.49(6)
O(1)-Cd(1)-N(2)^{a}	87.49(6)	O(1)a-Cd(1)-N(2)^{a}	156.63(5)	N(2)-Cd(1)-N(2)^{a}	70.08(8)
O(1)-Cd(1)-O(2)^{b}	87.96(6)	O(1)a-Cd(1)-O(2)^{b}	92.94(6)	N(2)-Cd(1)-O(2)^{b}	95.50(5)
N(2)a-Cd(1)-O(2)^{b}	83.11(5)	O(1)-Cd(1)-O(2)^{c}	92.94(6)	O(1)a-Cd(1)-O(2)^{c}	87.96(6)
N(2)-Cd(1)-O(2)^{c}	83.11(5)	N(2)a-Cd(1)-O(2)^{c}	95.50(5)	O(2)b-Cd(1)-O(2)^{c}	178.32(6)

Symmetry codes: [a] $-x+1, y, -z+3/2$; [b] $x, -y+1, z+1/2$; [c] $-x+1, -y+1, -z+1$.

ligand is coordinated to two Cd(Ⅱ) via two oxygen atoms from a carboxylate group. The dihedral angle of the carboxylate group and the aromatic ring in 5-nitrosalicylate ligand is 8.9(2)°. Two 5-(NO_2)sal ligands bridge two Cd(Ⅱ) atoms to form zigzag chain along the c axis (Fig.2). The polymeric chain has a repeat unit formed by two 5-(NO_2)sal ligand and two Cd(Ⅱ) atoms related by an inversion centre. The repeat unit of the eight-membered ring (Cd-O-C-O)$_2$ assumes a chair-like structure. The Cd ⋯ Cd separation in the eight-membered ring is 0.466 9(1) nm.



Symmetry codes: a: $x+1, y+1, -z+1.5$; b: $-x+1, y, -z+1.5$

Fig.2 Extended 2D structure in the title complex; Hydrogen bonds are shown as dashed lines

In the title complex, the hydroxyl group is involved in an intramolecular hydrogen bond with the carboxyl O atom. The phenyl hydrogens of 2,2′-bipy form weak intra- and interchain C–H⋯O hydrogen bonds with the carboxyl and hydroxyl O atoms, resulting in extended 2D supramolecular network structure (Table 2, Fig.2).

Table 2 Hydrogen bond lengths and angles for the complex

D–H⋯A	*d*(D-H) / nm	*d*(H⋯A) / nm	*d*(D⋯A) / nm	∠(DHA) / (°)
O(3)–H(3)⋯O(2)	0.081(1)	0.180(1)	0.254 6(2)	154(2)
C(10)–H(10A)⋯O(3)^{a}	0.093	0.269	0.336 3(3)	129.8
C(8)–H(8A)⋯O(1)^{b}	0.093	0.256	0.317 9(3)	124.3

Symmetry code: [a] $x+1, y+1, -z+1.5$; [b] $-x+1, y, -z+1.5$.

References:

[1] Lemoine P, Viossat B, Dung N H, et al. *J. Inorg. Biochem.*, **2004**,**98**:1734~1749

[2] Thurston J H, Kumar A, Hofmann C, et al. *Inorg. Chem.*, **2004**,**43**:8427~8437

[3] Wang Y, Odoko M, Okabe N. *Acta Cryst.*, **2004**,**C60**:m479~m481

[4] Zhu L G, Kitagawa S, Miyasaka H, et al. *Inorg. Chim. Acta*, **2003**,**355**:121~126

[5] Yin M C, Yuan L J, Ai C C, et al. *Polyhedron*, **2004**,**23**:529~536

[6] He X, Bi M H, Ye K Q, et al. *Inorg. Chem. Commun.*, **2006**,**9**:1165~1168

[7] Wen D C, Liu S X, Ribas J. *Inorg. Chem. Commun.*, **2007**,**10**:661~665

[8] Wen D C, Liu S X, Ribas J. *Polyhedron*, **2007**,**26**:3849~3856

[9] Lehaire M L, Scopelliti R, Herdeis L, et al. *Inorg. Chem.*, **2004**,**43**:1609~1617

[10] Wen D C, Liu S X, Lin M. *J. Mol. Struct.*, **2007**,**876**:154~161

[11] Wen D C, Liu S X. *Chinese J. Struct. Chem.*, **2007**,**11**:1360~1366

[12] Wen D C, Xie T Y. *Inorg. Chem. Commun.*, **2007**,**10**:1531~1533

[13] Sheldrick G M. *SHELX*-97, *Program for Delermination of Crystal Structure*, University of Göttingen, Germany, **1997**.

[14] Zheng Y, Xu D M, Liu S X. *Inorg. Chim. Acta*, **1999**,**294**:163~169