



## 3-乙氧基水杨醛缩 *N,N*-双(3-氨基丙烷)-甲基氨 Zn(II) 配合物的合成、晶体结构及荧光性质

台夕市<sup>\*1</sup> 冯一民<sup>1</sup> 孔凡元<sup>1</sup> 王大奇<sup>2</sup> 谭民裕<sup>3</sup>

(<sup>1</sup> 潍坊学院化学化工系, 潍坊 261061)

(<sup>2</sup> 聊城大学化学化工学院, 聊城 252059)

(<sup>3</sup> 兰州大学化学化工学院, 兰州 730000)

关键词: 3-乙氧基水杨醛缩 *N,N*-双(3-氨基丙烷)-甲基氨; Zn(II)配合物; 合成; 晶体结构; 荧光性质

中图分类号: O614.24<sup>1</sup>

文献标识码: A

文章编号: 1001-4861(2008)02-0319-05

## Synthesis, Crystal Structure and Fluorescence Property of 3-ethoxysalicylaldehyde-*N,N*-bis(3-aminopropyl)-methylamine Zn(II) Complex

TAI Xi-Shi<sup>\*1</sup> FENG Yi-Min<sup>1</sup> KONG Fan-Yuan<sup>1</sup> WANG Da-Qi<sup>2</sup> TAN Min-Yu<sup>3</sup>

(<sup>1</sup>College of Chemistry and Chemical Engineering, Weifang University, Weifang, Shandong 261061)

(<sup>2</sup>College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059)

(<sup>3</sup>College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000)

**Abstract:** The reaction of 3-ethoxysalicylaldehyde-*N,N*-bis(3-aminopropyl)methylamine with Zn(II) acetate in CH<sub>3</sub>CH<sub>2</sub>OH followed by recrystallization in CH<sub>3</sub>CH<sub>2</sub>OH gave rise to colourless block crystals of 3-ethoxysalicylaldehyde-*N,N*-bis(3-aminopropyl)methylamine Zn(II). The compound has been characterized by elemental analysis, IR spectrum, molar conductivity and X-ray diffraction structure determination single crystal. It crystallizes in monoclinic, space group *P2<sub>1</sub>/c* with *a*=1.028 91(13) nm, *b*=1.400 35(12) nm, *c*=1.733 69(19) nm, *V*=2.476 6(5) nm<sup>3</sup>, *Z*=4, *M<sub>r</sub>*=504.91, *D<sub>c</sub>*=1.354 g·cm<sup>-3</sup>, *T*=298(2) K, *F*(000)=1 064, *μ*(Mo *Kα*)=0.102 7 cm<sup>-1</sup>, *R*=0.068 4 and *wR*=0.185 3 for 2 940 observed reflections with *I*>2σ(*I*). The fluorescence properties of ligand and the complex also have been investigated. The results show that the fluorescence intensity of the Zn(II) complex is very stronger than the ligand. In the crystal, the molecules form 1D chain structure by π-π stacking. CCDC: 675010.

**Key words:** 3-ethoxysalicylaldehyde-*N,N*-bis(3-aminopropyl)methylamine; Zn(II) complex; synthesis; crystal structure; fluorescence property

Schiff-base ligands are able to coordinate metals through imine nitrogen and another group, usually linked to the aldehyde. Modern chemists still prepare Schiff-bases, and nowadays active and well-designed

Schiff-base ligands are considered to be “privileged ligands”<sup>[1-3]</sup>. In fact, Schiff bases are able to stabilize many different metals in various oxidation states. Schiff bases and their metal complexes play a key role

收稿日期: 2007-09-24。收修改稿日期: 2007-12-12。

国家自然科学基金项目(No.20671073)和潍坊市科技发展计划项目资助。

\*通讯联系人。E-mail: taixishi@lzu.edu.cn

第一作者: 台夕市, 男, 36 岁, 教授, 研究方向: 功能配合物化学。

in understanding the coordination chemistry of transition metal ions<sup>[4]</sup>. In particular, the bidentate ligands containing imine groups have been used as modulators of structural, electronic, antitumor activity and fluorescence properties of transition metal centres<sup>[5-8]</sup>. In order to investigate further the coordination and the properties of zinc complexes with Schiff bases ligands, as parts of our studies on the synthesis, characterization and properties of Schiff bases ligands and their metal complexes, we herein report the synthesis and structural characterization of a new zinc complex, Zn (3-ethoxysalicylaldehyde-*N,N*-bis (3-aminopropyl)methylamine).

## 1 Experimental

### 1.1 General

3-ethoxysalicylaldehyde, *N,N*-bis (3-aminopropyl)methylamine, Zn(II) acetate and all the other reagents were of analytical grade and used without further purification. The experiments were carried out in open air. The elemental analyses were performed on a model Elementar Vario III EL elemental analyzer. IR spectrum was recorded on a Nicolet AVATAR 360 spectrophotometer as KBr pellet (4 000~400 cm<sup>-1</sup>). TG-DTA analysis was recorded on a NETZSCH-Geratebau GmbH thermal analyzer. The molar conductance value was determined on a DDS-11A conductivity meter with methanol as solvent (10<sup>-3</sup> mol·L<sup>-1</sup> solution) at 25 °C. The fluorescence measurements were made on a PE LS-55 spectrometer equipped with quartz cuvettes of 1 cm path length.

### 1.2 Synthesis of the ligand

The ligand was prepared by reaction of 3-ethoxysalicylaldehyde with *N,N*-bis (3-aminopropyl)methylamine by a method similar to literature<sup>[9]</sup>. Yield 80%. Elemental analysis calcd for C<sub>25</sub>H<sub>33</sub>N<sub>3</sub>O<sub>4</sub> (%): C, 68.03, H, 7.94, N, 9.52; Found (%): C, 68.36, H, 7.86, N, 9.36. IR (KBr pellet, cm<sup>-1</sup>)  $\nu$ : 3 450(w) (N-H), 3 268 (m) (O-H), 1 638(m) (C=N).

### 1.3 Synthesis of the title complex

The complex was prepared by the following procedure: 1 mmol of Zn(II) acetate was added to the solution of 3-ethoxysalicylaldehyde-*N,N*-bis (3-aminopropyl)methylamine (1 mmol) in a 10 mL of CH<sub>3</sub>CH<sub>2</sub>OH. The mixture was continuously stirred for 3 h at refluxing temperature, evaporating some ethanol, then the product was collected by filtration, yield 68%. Elemental analysis calcd for C<sub>25</sub>H<sub>33</sub>N<sub>3</sub>O<sub>4</sub>Zn (%): C, 59.52, H, 6.55, N, 8.33; Found (%): C, 59.26, H, 6.32, N, 8.56. IR (KBr disk)  $\nu$ : 3 401(w) (N-H), 1 612 (m) (C=N). The single crystal suitable for X-ray determination was obtained by evaporation from ethanol solution after two weeks.

### 1.4 Crystal structure determination

The single crystal suitable for structure determination was obtained by evaporation from ethanol solution after two weeks. A colourless single crystal with dimensions of 0.46 mm × 0.42 mm × 0.39 mm was selected for X-ray structure analysis. The data were collected on a Bruker Smart-1000 CCD diffractometer with a graphite-monochromatized Mo *K*α radiation ( $\lambda$ =0.071 073 nm) at 298 K. A total of 12 242 reflections were collected in the range 1.88°~25.01° by using an  $\omega$  scan mode, of which 4 373 were unique ( $R_{int}$ =0.068 4) and 2 940 with  $I>2\sigma(I)$  were considered as observed. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques with SHELX-97 program<sup>[10]</sup>. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The refinement was converged at  $R$ =0.068 4, and  $wR$ =0.185 3 ( $w=1/[\delta^2(F_o^2)+(0.113\ 2P)^2+5.038\ 3P]$ ,  $P=(F_o^2+2F_c^2)/3$ ,  $S=1.069$ ,  $(\Delta/\sigma)_{max}=0.000$ ). The largest peak in the final difference Fourier map is 1 144 e<sup>-</sup>·nm<sup>-3</sup> and the minimum peak is -701 e<sup>-</sup>·nm<sup>-3</sup>. The crystal data and experimental parameters relevant to the structure determination are listed in Table 1.

CCDC: 675010.

Table 1 Crystal structure parameters of the title complex

Formula	C <sub>25</sub> H <sub>33</sub> N <sub>3</sub> O <sub>4</sub> Zn	$\mu(\text{Mo } K\alpha) / \text{cm}^{-1}$	0.1027
Formula weight	504.91	Calculated density / (g·cm <sup>-3</sup> )	1.354
Crystal system	Monoclinic	$F(000)$	1064

Continued Table 1

Space group	$P2_1/c$	Crystal size / mm	$0.46 \times 0.42 \times 0.39$
$a$ / nm	1.028 91(13)	$\theta$ range for data collection / ( $^\circ$ )	1.88 to 25.01
$b$ / nm	1.400 35(12)	Limiting indices	$-12 \leq h \leq 12, -16 \leq k \leq 16, -20 \leq l \leq 12$
$c$ / nm	1.733 69(19)	Reflections collectioned / unique	12 242 / 4 373
$\beta$ / ( $^\circ$ )	97.503(2)	Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.068\ 4, wR_2=0.185\ 3$
$V$ / nm <sup>3</sup>	2.476 6(5)	$R$ indices (all data)	$R_1=0.103\ 0, wR_2=0.220\ 4$
$Z$	4	Largest diff. peak and hole / ( $e \cdot \text{nm}^{-3}$ )	1 144 and -701

## 2 Results and discussion

### 2.1 Properties of the complex

The result of elemental analysis indicated that the composition of the complex conforms to Zn(3-ethoxysalicylaldehyde-*N,N*-bis (3-aminopropyl)methylamine), and that the complex conform to 1:1 metal-to-ligand stoichiometry.

The complex is soluble in DMF, DMSO, methanol, ethanol, insoluble in benzene, diethyl ether and tetrahydrofuran. The molar conductance values of the complex measured in methanol solution is  $9.2\ \text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ , indicating that it is nonelectrolyte<sup>[11]</sup>.

### 2.2 IR spectra

In the IR spectrum, the band at  $1\ 638\ \text{cm}^{-1}$  in the free ligand can be assigned to  $\nu(\text{C}=\text{N})$ . In the complex, the band of  $\nu(\text{C}=\text{N})$  is shifted by  $26\ \text{cm}^{-1}$  (from  $1\ 638$  to  $1\ 612$ ), indicating that the nitrogen atoms of  $\text{C}=\text{N}$  take part in coordinated with Zn(II) ion<sup>[5]</sup>. The strong band at  $1\ 225\ \text{cm}^{-1}$  in the free ligand assigned to  $\nu(\text{C}-\text{O})$  vibration of phenolic group, however, it shifts to  $1\ 205\ \text{cm}^{-1}$  in the complex. This shows that the oxygen atom of phenolic hydroxyl coordinates to the met-

al ions. The weak bands at  $448\ \text{cm}^{-1}$  may be assigned to Zn-O (phenolic oxygen) vibrations<sup>[5]</sup>. In addition, there do not appear new bands at  $1\ 610 \sim 1\ 550\ \text{cm}^{-1}$  and  $1\ 420 \sim 1\ 300\ \text{cm}^{-1}$ , indicating that the complex does not contain  $\text{CH}_3\text{COO}^-$  anions, which is in agreement with the result of the conductivity experiment and elemental analysis.

### 2.3 Crystal structure

The selected bond distances and bond angles are listed in Table 2. The molecule structure of the title complex is shown in Fig.1. Fig.2 shows the packing of the molecules in the unit cell.

The title compound crystallizes in monoclinic system, space group  $P2_1/c$ , with one cell contains four unique unit ( $Z=4$ ) and per unit contains one complex molecule. The crystal structure of the title compound consists of neutral complex, Zn(3-ethoxysalicylaldehyde-*N,N*-bis(3-aminopropyl)methylamine). The penta-coordinate ligand is chelated to the Zn(II), forming a distorted trigonal bipyramid structure. The distances of the two exactly the same in Zn-O bonds are  $0.195\ 9(4)\ \text{nm}$  and Zn-N bonds are in the range of and  $0.205\ 8(6) \sim$

Table 2 Select bond lengths (nm) and bond angles ( $^\circ$ )

Zn(1)-O(1)	0.195 9(4)	C(2)-C(3)	0.140 4(9)	C(3)-O(1)	0.128 9(7)
Zn(1)-O(3)	0.195 9(4)	C(2)-C(7)	0.140 9(9)	C(4)-O(2)	0.136 2(8)
Zn(1)-N(1)	0.205 8(6)	C(11)-C(12)	0.141 0(10)	O(3)-C(12)	0.130 7(8)
Zn(1)-N(2)	0.207 1(6)	C(12)-C(13)	0.141 1(10)	O(4)-C(13)	0.142 4(9)
Zn(1)-N(3)	0.217 9(5)	C(8)-O(2)	0.141 8(8)		
O(1)-Zn(1)-O(3)	120.14(19)	N(2)-Zn(1)-N(3)	87.9(2)	C(3)-O(1)-Zn(1)	130.2(4)
O(3)-Zn(1)-N(1)	96.0(2)	C(1)-N(1)-C(19)	120.4(6)	C(12)-O(3)-Zn(1)	124.3(4)
O(1)-Zn(1)-N(1)	89.4(2)	C(1)-N(1)-Zn(1)	125.1(5)	C(22)-N(2)-Zn(1)	115.6(5)
N(1)-Zn(1)-N(2)	174.4(2)	C19(1)-N(1)-Zn(1)	114.4(5)	C(10)-N(2)-Zn(1)	123.2(5)
O(1)-Zn(1)-N(2)	89.07(19)	O(1)-Zn(1)-N(3)	125.9(2)	N(1)-Zn(1)-N(3)	88.6(2)
O(3)-Zn(1)-N(3)	113.79(19)	O(3)-Zn(1)-N(2)	89.4(2)		

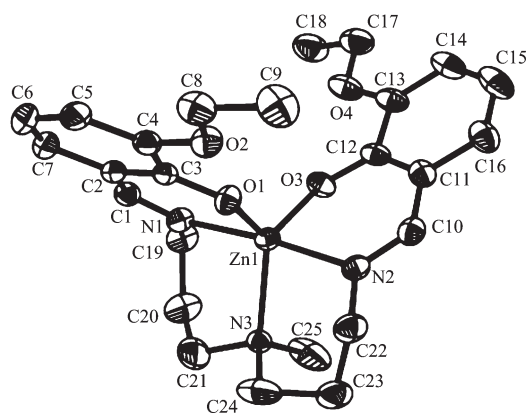


Fig.1 Structure of the complex

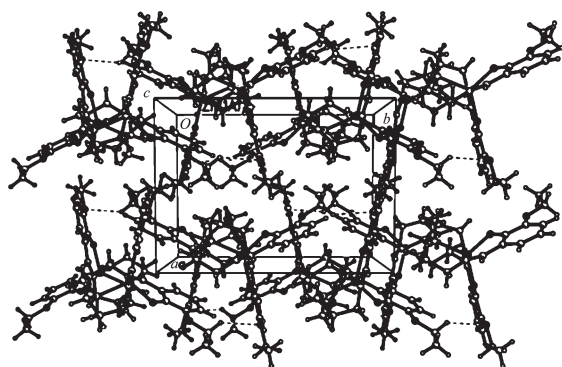


Fig.2 Packing of the complex in the unit cell

0.217 9(5) nm, respectively. They are similar to the Zn-O and Zn-N bond lengths reported previously<sup>[6]</sup>. The bond lengths of Zn-O are much shorter than that of Zn-N, which shows that the strength of Zn-O bonds is stronger than Zn-N bonds. The benzyl rings in the molecule do not show any unusual features, and the bond lengths and bond angles are within the range of normal values. Each molecule contains four six-member rings [1 C(1)-C(2)-C(3)-O(1)-Zn(1)-N(1), 2 C(10)-C(11)-C(12)-O(3)-Zn(1)-N(2), 3 N(2)-C(22)-C(23)-C(24)-N(3)-Zn(1), 4 N(3)-C(21)-C(20)-C(19)-N(1)-Zn(1)] by the Zn(II) center. The dihedral angles of plane 1, plane 2, plane 3 and plane 4 are 110.0°, 37.8° and 15.5°, respectively. Which indicate that the four planes in the molecule is not coplanar.

The C-O bond lengths in the title complex are significantly different. The O(1)-C(3) and O(3)-C(12) bond distances are obviously shorter than O(2)-C(4) and O(4)-C(13) due to the coordination of O(1) and O(3) atoms to metal ions (Table 2). Fig.2 displays the molecular forms 1D chain structure by  $\pi$ - $\pi$  stacking.

## 2.4 Fluorescence studies

The fluorescence properties of ligand and the Zn(II) complex in CH<sub>3</sub>CH<sub>2</sub>OH were investigated. The Zn(II) complex displays a fluorescence emission maximum at 515 nm ( $\lambda_{\text{ex}}$ =394 nm), however, the emission maximum of the ligand is 545 nm ( $\lambda_{\text{ex}}$ =390 nm) (Fig.3). From Fig.3, we can see that the fluorescence intensities of the Zn(II) complex is stronger than that of the ligand in the same concentration. This may the energy gap between the triplet levels of ligand and the emitting level of Zn(II) favor to the energy transfer process for Zn(II).

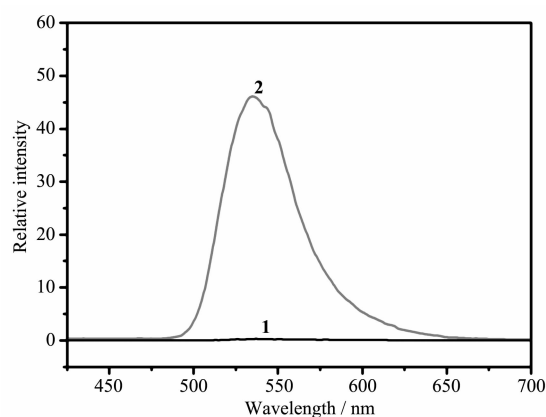


Fig.3 Emission spectrum of the Zn(II) complex and the ligand

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## 纪念张青莲教授诞辰100周年学术论文专集 征稿启事

2008年7月31日是我国著名化学家、教育家、中国科学院院士、我国稳定同位素化学的奠基人张青莲教授诞辰100周年纪念日。张青莲教授1930年毕业于光华大学,1936年获德国柏林大学博士学位,此后在瑞典皇家科学院工作了1年,于1937年回国,先后在中央研究院、光华大学、西南联合大学、清华大学和北京大学从事教学和科研工作将近70年。张青莲教授一生为我国无机化学的发展和人才的培养做出了不可磨灭的贡献,不论是早期的还是后来的许多论文都成为了重水研究的经典文献。他主持的科研组历时12年完成了10项原子量新值的测定工作,为国际原子量委员会所采纳。他主编了18卷共700万言的巨著《无机化学丛书》。1951年起,他先后担任过中国化学会常务理事,《化学学报》主编,《中国科学》、《科学通报》、《无机化学学报》等期刊的编委或顾问;他曾任法国《无机化学评论》的编辑,美国《质谱评论》的顾问编辑,中国质谱学会理事长,国际纯粹化学与应用化学联合会(IUPAC)原子量与同位素丰度委员会銜称委员等职。1955年被聘为中国科学院数理化学部委员(院士)。

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