

## 一个基于双(2-苯并咪唑基)刚性配体 Zn(II)配合物: 合成、晶体结构及光致发光性质

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**摘要:** 合成了一个配合物  $[\text{Zn}(\text{OBimB})\text{Cl}_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (OBimB 为 1,2-双(2-苯并咪唑基)苯), 并用 X 射线单晶衍射仪测定了其晶体结构。晶体属单斜晶系,  $P2_1/c$  空间群, 晶胞参数为:  $a=1.251\ 22(9)\ \text{nm}$ ,  $b=1.039\ 80(7)\ \text{nm}$ ,  $c=1.827\ 94(11)\ \text{nm}$ ,  $\beta=95.508(2)^\circ$ ,  $V=2.367\ 2(3)\ \text{nm}^3$ ,  $Z=4$ ,  $D_c=1.509\ \text{g} \cdot \text{cm}^{-3}$ 。最后精修结果为:  $R_1=0.043\ 0$ ,  $wR_2=0.093\ 9$ 。在配合物结构中每个 Zn(II) 原子分别与 2 个来自 V 构型 OBimB 配体的 N 原子、2 个氯离子进行配位, 形成了 1 个扭曲的四面体结构。配体和配合物的光致发光测试显示光发射属于配体的分子内荧光。

**关键词:** 锌(II)配合物; 双苯并咪唑; 晶体结构; 光致发光

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## A Zinc(II) Complex Based on a Rigid Ligand Containing Bis(2-benzimidazolyl) Groups: Synthesis, Crystal Structure, and Photoluminescent Property

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**Abstract:** A complex  $[\text{Zn}(\text{OBimB})\text{Cl}_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$  based on a rigid bis(benzimidazoles) ligand OBimB (OBimB = 1,2-bis(2-benzimidazolyl)benzene) has been synthesized and structurally characterized by X-ray single crystal diffractometry. The complex crystallizes in monoclinic system,  $P2_1/c$  space group with the cell parameters of  $a=1.251\ 22(9)\ \text{nm}$ ,  $b=1.039\ 80(7)\ \text{nm}$ ,  $c=1.827\ 94(11)\ \text{nm}$ ,  $\beta=95.508(2)^\circ$ ,  $V=2.367\ 2(3)\ \text{nm}^3$ ,  $Z=4$ , and  $D_c=1.509\ \text{g} \cdot \text{cm}^{-3}$ , the final  $R_1=0.043\ 0$ ,  $wR_2=0.093\ 9$ . In the structure of the complex the Zn atom is coordinated by two N atoms from a twisted V-shape conformational OBimB ligand and two  $\text{Cl}^-$  anions in a distorted tetrahedral geometry. The photoluminescence measurements of the ligand and the complex show that the emissions are assigned to the intraligand fluorescence. CCDC: 861572.

**Key words:** zinc(II) complex; bis(benzimidazoles); crystal structure; photoluminescence

## 0 Introduction

The coordination chemistry of bis(2-benzimidazole) compounds have attracted much attention in

recent years, such as the usefulness as geometrically constraining ligands<sup>[1]</sup>, supramolecular aggregates formed with transition metal ions<sup>[2-3]</sup>. The metal complexes of bis(2-benzimidazole) compounds also reveal potential

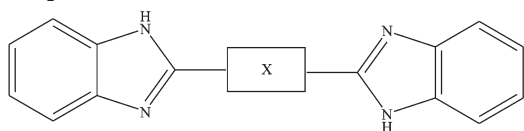
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applications as new functional materials, such as optics<sup>[4-6]</sup>, polymerization catalysis<sup>[7-8]</sup>, magnetism<sup>[1,9]</sup>, and models for biological systems<sup>[10-11]</sup>.

The spacer X of bis (2-benzimidazole) can be flexible or rigid. In recent literature, a large number of coordination compounds with flexible bis (2-benzimidazolyl)alkanes ligands have been synthesized. Owing to the length of the bridging alkane chain, the anion and the solution, mononuclear<sup>[12-14]</sup>, binuclear<sup>[2,15-17]</sup> and multinuclear<sup>[3-4]</sup> complexes are formed. In contrast to flexible ligands, the studies about such complexes with bis (2-benzimidazolyl) ligands of rigid spacer are as yet very limited<sup>[1,18-19]</sup>. In this paper, we reported the synthesis, crystal structure, and photoluminescent property of a new Zinc(II) complexes with 1,2-bis(2-benzimidazolyl)benzene (OBimB),  $[\text{Zn}(\text{OBimB})\text{Cl}_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$ .



## 1 Experimental

### 1.1 Materials and measurement

All the chemical reagents for synthesizing the ligand OBimB and the title complex were purchased commercially and used without further purification. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 1400C analyzer. IR spectra were recorded in the range of 400~4 000  $\text{cm}^{-1}$  on a Nicolet 170SX spectrometer with pressed KBr pellets. UV-Vis spectra were taken on a Perkin-Elmer UV-Vis spectrometer. Luminescence spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer.

### 1.2 Preparation of the complexes

The bidentate ligand 1,2-bis (2-benzimidazolyl) benzene (OBimB) was synthesized by condensing *o*-diaminobenzene with *o*-phthalic acid according to the method of the literature<sup>[19]</sup> with minor revisions. *o*-diaminobenzene (4.7 g, 44 mmol) and *o*-phthalic acid (3.3 g, 20 mmol) were finely ground together and heated to 230  $^{\circ}\text{C}$  in 40 mL polyphosphoric acid and stirred for 4 h. The reaction mixture was poured into ice water with vigorous stirring after the mixture had

cooled down to 100  $^{\circ}\text{C}$ . The precipitate was then filtered off and stirred in a saturated sodium bicarbonate solution for 12 h. The raw solid was recrystallized from hot methanol to give light yellow product (Yield, 38%). IR(KBr): 3 049(w), 2 878(w), 1 620(w), 1 534(w), 1 441(s), 1 317(m), 1 280(m), 1 007(m), 764(s).

$[\text{Zn}(\text{OBimB})\text{Cl}_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$ :  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  (0.027 g, 0.2 mmol) and OBimB (0.06 g, 0.2 mmol) were added to ethanol (10 mL) and acetonitrile (10 mL), and the mixture was stirred and refluxed for half an hour. Then DMF (2 mL) was added. The resulting colorless solution was filtered and the filtrate was allowed to stay at ambient temperature for a period of about 2 d, to give colorless block crystals (yield: 38%) suitable for structural determinations. Anal. Calcd.(%) for  $\text{C}_{23}\text{H}_{23}\text{Cl}_2\text{N}_5\text{O}_2\text{Zn}$ : C 51.37, H 4.31, N 13.02; found (%): C 51.40, H 4.33, N 13.05.

### 2.3 X-ray crystallography

Block shaped crystals of the title complex was mounted on a Bruker SMART 1000 CCD area detector X-ray single crystal diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ) and a  $\varphi$ - $\omega$  scanning mode at 293(2) K. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods via SHELXS 97 program<sup>[20]</sup> and refined by full-matrix least squares on  $F^2$  via SHELXL 97 program<sup>[21]</sup>. The correct positions for the metal atoms were deduced from E-map. Subsequent least-squares refinement and difference fourier calculations revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. H atoms were positioned geometrically ( $\text{C-H}=0.093\ \text{nm}$ ) and allowed to ride on their parent atoms with  $U_{\text{iso}}(\text{H})=1.2$  times  $U_{\text{eq}}(\text{C})$ . Crystallographic data for the complexes are listed in Table 1.

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## 2 Results and discussion

### 2.1 Description of the crystal structure

The ORTEP diagram of  $[\text{Zn}(\text{OBimB})\text{Cl}_2]$  of the title complex with the atomic numbering scheme is

**Table 1 Crystals and structures refinement data for the title complex**

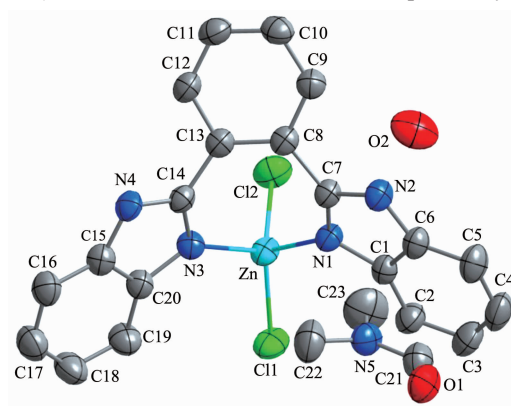
Empirical formula	C <sub>23</sub> H <sub>23</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>2</sub> Zn	<i>F</i> (000)	1 104
Formula weight	537.73	Crystal size / mm	0.20×0.10×0.10
Temperature / K	293(2)	$\theta$ range for data collection / (°)	3.27~27.48
Crystal system	Monoclinic	Limiting indices	$-16 \leq h \leq 16, -13 \leq k \leq 13, -23 \leq l \leq 23$
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	Reflections collected	21 929
<i>a</i> / nm	1.251 22(9)	Independent reflections	5 396 ( <i>R</i> <sub>int</sub> =0.052 8)
<i>b</i> / nm	1.039 80(7)	Reflection observed	3 788
<i>c</i> / nm	1.827 94(11)	Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
$\beta$ / (°)	95.508(2)	Data/restraints/parameters	5 396 / 2 / 307
<i>V</i> / nm <sup>3</sup>	2.367 2(3)	Goodness-of-fit on <i>F</i> <sup>2</sup>	1.003
<i>Z</i>	4	Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>R</i> <sub>1</sub> =0.043 0, <i>wR</i> <sub>2</sub> =0.093 9
<i>D</i> <sub>c</sub> / (g·cm <sup>-3</sup> )	1.509	<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.068 6, <i>wR</i> <sub>2</sub> =0.108 9
$\mu$ / mm <sup>-1</sup>	1.294	Largest diff. peak and hole / (e <sup>-</sup> ·nm <sup>-3</sup> )	516 and -661

**Table 2 Selected bond lengths (nm) and bond angles (°) for the complex**

Zn-N(1)	0.202 0(2)	N(1)-C(7)	0.132 2(3)	N(3)-C(14)	0.133 1(3)
Zn-N(3)	0.200 3(2)	N(1)-C(1)	0.139 7(3)	N(3)-C(20)	0.139 6(4)
Zn-Cl(1)	0.224 02(8)	N(2)-C(7)	0.135 4(3)	N(4)-C(14)	0.134 6(3)
Zn-Cl(2)	0.222 55(9)	N(2)-C(6)	0.137 9(4)	N(4)-C(15)	0.137 3(4)
N(3)-Zn-N(1)	96.86(9)	N(1)-Zn-Cl(1)	114.59(7)	C(1)-N(1)-Zn	127.73(18)
N(3)-Zn-Cl(2)	112.43(7)	Cl(2)-Zn-Cl(1)	112.93(3)	C(7)-N(2)-C(6)	108.1(2)
N(1)-Zn-Cl(2)	106.63(7)	C(7)-N(1)-C(1)	106.3(2)	C(14)-N(3)-Zn	123.24(19)
N(3)-Zn-Cl(1)	112.28(7)	C(7)-N(1)-Zn	125.90(17)	C(20)-N(3)-Zn	130.67(18)

shown in Fig.1, respectively, showing 50% probability displacement ellipsoids. The selected bond lengths and bond angles are listed in Table 2. The center Zn atom in the title complex is coordinated by two N atoms from a OBimB molecule and two Cl<sup>-</sup> anions in a distorted tetrahedral geometry. The bond angles around Zn atom are in the range of 96.86(9)°~114.59(7)°. The Zn-N distances are almost similar (Zn-N(1) 0.202 0(2) nm and Zn-N(3) 0.200 3(2) nm. The Zn-Cl bond lengths are 0.224 02(8) and 0.222 55(9) nm, respectively. The OBimB ligand affords two coordination sites and chelates a Zn atom to form a seven-member ring, resulting in the construction of a mononuclear complex. The overall structure of the ligand can be described as twisted V-shaped conformation, so that the two coordinated N-atoms of the benzimidazoles are more exposed for metal binding. The dihedral angles of the benzimidazolyl ring planes (comprising imidazole ring atoms N1, C1, C6, N2, N7 is designed

as plane 1 and N3, C14,C15, N4,C20, as plane 2) with the central phenyl ring plane (comprising atoms C8-C13) are 47.34° and 38.09°, respectively. The



Hydrogen atoms were omitted for clarity

**Fig.1** Structure of the title complex at 50% probability displacement ellipsoids with atomic numbering scheme

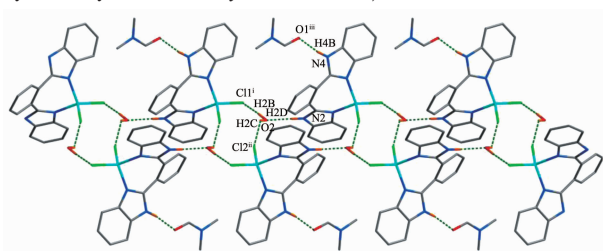
dihedral angle between the planes (plane 1 and 2) of the benzimidazolyl group in the ligand is 57.41°

Table 3 Hydrogen bonds of the complex

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
O(2)-H(2B)...Cl(1) <sup>i</sup>	0.085	0.241	0.322 9(3)	162.3
O(2)-H(2C)...Cl(2) <sup>ii</sup>	0.085	0.262	0.326 6(3)	134.0
N(4)-H(4B)...O(1) <sup>iii</sup>	0.086	0.189	0.274 8(3)	171.4
N(2)-H(2D)...O(2)	0.086	0.186	0.270 5(3)	169.3

Symmetry codes: <sup>i</sup>  $x, y-1, z$ ; <sup>ii</sup>  $-x, -y+1, -z$ ; <sup>iii</sup>  $x, -y+1/2, z-1/2$ .

In the complex, an amine NH group of the OBimB ligand is involved in hydrogen-bonding with H<sub>2</sub>O molecule (N2-O2 0.270 5(3) nm), and there also exist weak hydrogen bonds between the H<sub>2</sub>O molecule and Cl<sup>-</sup> anion (O2-Cl1<sup>i</sup> 0.322 9(3) nm; O2-Cl2<sup>ii</sup> 0.326 63 nm; symmetry codes: <sup>i</sup>  $x, y-1, z$ ; <sup>ii</sup>  $-x, -y+1, -z$ ). These hydrogen bonds link the complex units into a one-dimensional (1D) chain (Fig.2). The other amine NH group of the OBimB ligand is involved in hydrogen-bonding with DMF molecule (N4-O1<sup>iii</sup> 0.274 8(3) nm, symmetry code:  $x, -y+1/2, z-1/2$ ).



Symmetry code: <sup>i</sup>  $x, y-1, z$ ; <sup>ii</sup>  $-x, -y+1, -z$ ; <sup>iii</sup>  $x, -y+1/2, z-1/2$

Fig.2 1D chain structure formed by N-H...O and O-H...Cl hydrogen bonds interactions

## 2.2 UV-Vis Spectra

UV-Vis spectra of the ligand OBimB and the complexes in ethanol solution exhibit similar transitions (Fig.3), which suggests that these absorptions are owned

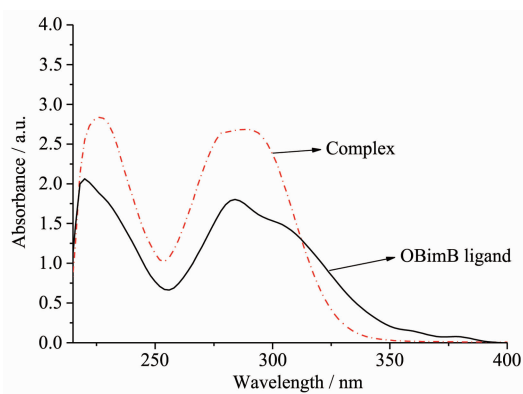


Fig.3 UV-Vis spectra of the complex and the OBimB ligand

to the ligand. The two transitions can be assigned to intramolecular charge transfer transitions of the ligand and ascribed to  $\pi \rightarrow \pi^*$  transitions in the ligand. The absorption peaks of the complexes (226 and 292 nm) are slightly red-shifted comparing to the ligand (222 and 284 nm), which shows that the transitions of the ligand are slightly disturbed by the coordination field of metal ion. The weak absorption band at 350~390 nm for the ligand is as a result of  $n \rightarrow \pi^*$  transitions in the ligands. The absorption of the complex at this band is almost disappear, which can be ascribed to the coordination of N atoms with Zn atom.

## 2.3 Photoluminescence

The emission spectra of the ligand and the complex were investigated in the solid state at room temperature. As shown in Fig.4, the ligand displays a broad emission band around 407.2 nm upon excitation at 270 nm. The complex exhibits an emission peak at 400.8 nm. The complex shows weak emission and the emission peak has a small blue-shift of 6.4 nm compared to that of the ligand, which can be as a result of the coordination of N atoms with Zn atom. Due to quite similar band profiles of the ligand and the complex, the emissions are tentatively assigned to the intraligand fluorescence<sup>[22]</sup>.

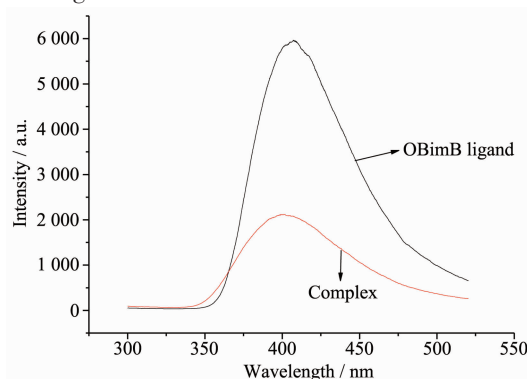


Fig.4 Emission spectra of the OBimB ligand and the complex in the solid state at room temperature

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