

## 一个双核锌(II)配合物 $[\text{Zn}_2(\text{L})_2(\text{Mf})_2]$ 的合成、结构、热稳定性及荧光性质

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### Synthesis, Structure, Thermal Stability and Fluorescence of One Binuclear Zn(II) Complex $[\text{Zn}_2(\text{L})_2(\text{Mf})_2]$

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**Abstract:** The binuclear Zn(II) complex  $[\text{Zn}_2(\text{L})_2(\text{Mf})_2]$  with 2-hydroxyacetophenone benzoylhydrazone ( $\text{H}_2\text{L}$ ) and monodentate *N*-heterocycle, morphine (*Mf*) has been synthesized and characterized by elemental analysis, IR, UV, molar conductivity, TG and X-ray diffraction structural analysis. Crystal data: monoclinic, space group  $P2_1/n$  with  $a=1.263\ 9(6)$  nm,  $b=1.085\ 2(4)$  nm,  $c=1.313\ 4(5)$  nm,  $\beta=92.16(2)^\circ$ ,  $V=1.800(1)$  nm<sup>3</sup>,  $Z=2$ ,  $D_c=1.493$  g·cm<sup>-3</sup>,  $\mu=1.388$  mm<sup>-1</sup>,  $F(000)=840$ , and final  $R=0.038\ 4$ ,  $wR=0.087\ 9$ . The two Zn(II) centers in the centrosymmetric binuclear complex are bridged by phenolic oxygen atoms with Zn···Zn separation of  $0.315\ 0(1)$  nm. The coordination geometry of each Zn(II) atom is trigonal bipyramidal. The fluorescence activities of ligand and the complex were also studied. CCDC: 712643.

**Key words:** Zn(II) complex; Schiff base; crystal structure; thermal stability analysis; fluorescence

## 0 Introduction

Dinuclear metal compounds have been of interest for many years. These complexes play an important role in the developing of coordination chemistry related to catalysis and enzymatic reactions, magnetism, optical materials and molecular architectures<sup>[1-5]</sup>. Tridentate Schiff-bases are regarded as a good type of chelating ligands for transition metal. For example, aroylhydrazo-

nes of salicylaldehyde and its derivatives can bind to a given metal ion through phenolate oxygen, imine nitrogen and amide oxygen atoms<sup>[6,7]</sup>. In addition, the phenolate-O site can function as a bridging site to furnish dinuclear complexes, which simultaneously having other ancillary ligands in their coordination positions<sup>[4,8,9]</sup>. Neutral *N*-donor pyridine or  $\alpha$ -methyl pyridine has been used as the ancillary ligand in those reported complexes<sup>[4,8]</sup>. In the following account, we

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have described the synthesis, characterization and the crystal structure of binuclear zinc compound [Zn<sub>2</sub>(L)<sub>2</sub>(Mf)<sub>2</sub>] with 2-hydroxyacetophenone benzoylhydrazone (H<sub>2</sub>L) and monodentate *N*-heterocycle, morphine (Mf). As far as we know, compound [Zn<sub>2</sub>(L)<sub>2</sub>(Mf)<sub>2</sub>] is the first example of binuclear hydrazone compound with morphine as an ancillary ligand.

## 1 Experimental

### 1.1 Reagents and physical measurements

The ligand (H<sub>2</sub>L) was synthesized according to the reported method<sup>[10]</sup>. All other chemicals were analytical reagent grade and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried with an Elementar Vario EL III microanalyser. IR spectra were recorded on a Perkin-Elmer spectrum 2000 spectrophotometer with KBr pellets in the range of 4 000 ~400 cm<sup>-1</sup>. Electronic spectra in solid state were recorded on a Perkin Elmer lamda 900 spectrometer. Fluorescent studies were conducted on an Edinburgh FL-FS920 TCSPC system in solid state at room temperature. The molar conductance value was measured on a DDS-11A conductivity meter with DMF as solvent (10<sup>-5</sup> mol·L<sup>-1</sup> solution) at 25 °C. Thermal analyses were performed on a TGA-SDTA 851° thermogravimetric analyzer, with a heating rate of 10 °C·min<sup>-1</sup> under a nitrogen atmosphere.

### 1.2 Synthesis of the title complex [Zn<sub>2</sub>(L)<sub>2</sub>(Mf)<sub>2</sub>]

To H<sub>2</sub>L (1 mmol) in DMF (5 mL) was added an

equimolar amount of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in methanol (5 mL). After stirring for 15 min, 0.2 mL morphine was added to the solution. The resulting yellow solution was stirred at room temperature for an additional period of 1 h, filtered, and allowed to stand at room temperature for 2 weeks. Yellow crystals of the title complex suitable for X-ray diffraction were formed. Yield: 52%. Anal. Calc. For C<sub>38</sub>H<sub>42</sub>N<sub>6</sub>O<sub>6</sub>Zn<sub>2</sub> (found, %): C56.38 (56.49), H5.23(5.14), N10.38(10.51).

### 1.3 Crystal structure determination

A yellow single crystal with dimensions of 0.18 mm×0.24 mm×0.46 mm was selected for structural analysis. Diffraction data were collected at a Rigaku RAPID Weissengberg IP diffractometer with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm) and the  $\omega$  scan mode. A total of 17 699 reflections were collected in the range of  $3.01^\circ \leq \theta \leq 27.48^\circ$ , of which 4 107 were unique and 3 027 reflections with  $I > 2\sigma(I)$  were considered as observed and used for structure solution and refinement. The structure was solved by direct method with SHELXS-97<sup>[11]</sup> and refined by full-matrix least squares calculations with SHELXL-97<sup>[12]</sup>. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located from the geometrical calculation and refined isotropically. Crystallographic data and structure refinement data for the title complex are listed in Table 1.

CCDC: 712643.

Table 1 Crystallographic and structure refinement data for the title complex

Formula	C <sub>38</sub> H <sub>42</sub> N <sub>6</sub> O <sub>6</sub> Zn <sub>2</sub>	<i>T</i> / K	293
Formula Weight	809.52	$\mu$ / mm <sup>-1</sup>	1.388
Crystal size / mm	0.18×0.24×0.46	<i>F</i> (000)	840
Crystal system	<i>P</i> 2 <sub>1</sub> / <i>n</i>	$\theta$ range / (°)	3.10~27.48
Space group	Monoclinic	Index ranges	-16 ≤ <i>h</i> ≤ 16, -14 ≤ <i>k</i> ≤ 14, -17 ≤ <i>l</i> ≤ 17
<i>a</i> / nm	1.263 9(6)	Reflections collected / unique ( <i>R</i> <sub>int</sub> )	17 699 / 4 107 (0.048 3)
<i>b</i> / nm	1.085 2(4)	Observed reflections [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	3 027
<i>c</i> / nm	1.313 4(5)	Number of parameters	236
$\beta$ / (°)	92.16(2)	<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.038 4, 0.087 9
<i>V</i> / nm <sup>3</sup>	1.800(1)	Goodness-of-fit on <i>F</i> <sup>2</sup>	1.066
<i>Z</i>	2	$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ / (e·nm <sup>-3</sup> )	467, -430
<i>D</i> <sub>c</sub> / (g·cm <sup>-3</sup> )	1.493	( $\Delta/\sigma$ ) <sub>max</sub>	0.000

<sup>a</sup>  $R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$ ;  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2 \}^{1/2}$ .

## 2 Results and discussion

### 2.1 IR Spectra and molar conductivity

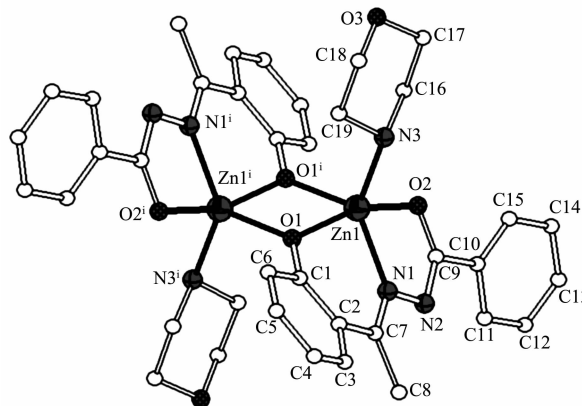
IR spectra of the complex do not display the C=O stretch of the amide functionality observed for the free ligand at  $1\,651\text{ cm}^{-1}$ . The observation is consistent with the deprotonation and enolization of the amide functionality<sup>[6,13]</sup>. A new band appearing in  $1\,241\text{ cm}^{-1}$  in the complex was assigned to the  $\nu(\text{C-O})$  (enolate) mode<sup>[14]</sup>. The strong band at  $1\,607\text{ cm}^{-1}$  associated with  $\nu(\text{C=N})$  of the free ligand shifts to a lower wave number (observed at  $1\,592\text{ cm}^{-1}$ ) indicating the coordination of azomethine nitrogen to the metal. Furthermore, the bands in the regions  $434\sim 524$  and  $584\sim 697\text{ cm}^{-1}$  may be assigned to the stretching modes of the metal to ligand bonds,  $\nu(\text{Zn-N})$  and  $\nu(\text{Zn-O})$ <sup>[15]</sup>.

The molar conductance value of the complex measured in DMF solution is  $8.6\text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ , indicating that it is nonelectrolyte<sup>[16]</sup>.

### 2.2 Description of the structure of the title complex

The molecular structure is shown in Fig.1. The selected bond lengths and angles of the title complex are given in Table 2. The structure consists of a centrosymmetric binuclear entity with a coplanar  $\text{Zn}_2(\mu\text{-O})_2$  fragment. Phenolic oxygen atoms bridge the Zn(II) ions with the  $\text{Zn1-O1}^i$  and  $\text{Zn1}^i\text{-O1}$  bonds of  $0.200\,3(2)\text{ nm}$  [symmetry code:  $i-x, 1-y, 1-z$ ]. The torsion angle  $\text{Zn1-O1-Zn1}^i\text{-O1}^i$  is  $0.00^\circ$ . Each Zn(II) center exists in a distorted trigonal bipyramidal geometry, as evidenced by the structural index parameter  $\tau$ <sup>[17]</sup> which is 0.52. The value is consistent with that of 0.57 in the binuclear complex  $[\text{Zn}_2(\text{SHSH})_2]$

$(2\text{-Me-py})_2$ <sup>[18]</sup> with the same coordination geometry. The basal plane is defined by N1, N3 and  $\text{O1}^i$ . And two other oxygen atoms (O1, O2) occupy the two axial sites, with the bond angle of  $\text{O2-Zn1-O1}$  being  $160.08(7)^\circ$ . There is almost no deviation of the zinc center from the basal plane, with a mean deviation of  $0.003\,92\text{ nm}$  from the least-square plane constituted by Zn1, N1, N3 and  $\text{O1}^i$ . And the torsion angle  $\text{N1-O1}^i\text{-N3-Zn1}$  is  $4.10(5)^\circ$ .



All hydrogen atoms are omitted for clarity;

Symmetry code:  $i-x, 1-y, 1-z$

Fig.1 Molecular structure of the title complex

The bond distances, Zn-N (ave  $0.206\,4\text{ nm}$ ) and Zn-O (ave  $0.203\,0\text{ nm}$ ), are comparable to those found in the similar compound  $[\text{Zn}_2(\text{SHSH})_2(2\text{-Me-py})_2]$ <sup>[18]</sup>. The  $\text{Zn1}\cdots\text{Zn1}^i$  separation is  $0.315\,0(1)\text{ nm}$ . The  $\text{Zn-O(Ph)-Zn}$  bridging angle is  $101.52(8)^\circ$ , very close to  $100.57^\circ$  in  $[\text{Zn}_2(\text{SHSH})_2(2\text{-Me-py})_2]$ <sup>[18]</sup>. Double-bond character is present in C7-N1 and C9-N2, as judged from their bond lengths ( $0.128\,7(3)$ ,  $0.131\,9(3)\text{ nm}$ ), which is in agreement with an enolic form of  $\text{H}_2\text{L}$ <sup>[10,18]</sup>. The C9-O2 bond length of  $0.127\,2(3)\text{ nm}$  approaches the value of  $0.127\,3\text{ nm}$  expected for an enolic form of the hydrazone ligand<sup>[18]</sup>.

Table 2 Select bond lengths (nm) and bond angles ( $^\circ$ ) for the title complex

Zn1-O1 <sup>i</sup>	0.200 3(2)	Zn1-O2	0.202 5(2)	Zn1-N1	0.206 2(2)
Zn1-O1	0.206 3(2)	Zn1-N3	0.206 5(2)	O1-C1	0.133 8(3)
O2-C9	0.127 2(3)	N1-C7	0.128 7(3)	N1-N2	0.139 5(3)
N2-C9	0.131 9(3)				
O1 <sup>i</sup> -Zn1-O2	102.89(8)	O1 <sup>i</sup> -Zn1-N1	127.55(7)	O2-Zn1-N1	78.89(7)
O1 <sup>i</sup> -Zn1-O1	78.48(8)	O2-Zn1-O1	160.08(7)	N1-Zn1-O1	84.60(7)
O1 <sup>i</sup> -Zn1-N3	102.81(7)	O2-Zn1-N3	99.06(8)	N1-Zn1-N3	129.03(8)
O1-Zn1-N3	99.99(7)				

Symmetry code:  $i-x, 1-y, 1-z$ .

Each tridentate hydrazone ligand combines with one Zn(II) atom resulting in one five-membered and one six-membered chelating rings. The five-membered chelating ring consisting of atoms Zn1, O2, C9, N1, N2 is planar, with mean deviation of 0.005 3 nm. However, the six-membered chelating ring involving atoms C1, C2, C7, N1, O1, Zn1 is non-planar, confirmed by the mean deviation of 0.017 0 nm. The two phenyl rings in each ligand, C1-C6 and C9-C15, make a dihedral angle of 49.9 (1)°, indicating each ligand in the title complex is non-planar.

### 2.3 Electronic spectra

The electronic spectra were recorded in solid state for the free ligand and the title complex (Fig.2). They both have absorptions locating in the range of 250~275 and 300~350 nm corresponding to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions<sup>[19]</sup>. The compound displays an electronic spectral band at *ca.* 390 nm, which may be assigned to the ligand-to-metal charge transfer (LMCT) transition<sup>[7]</sup>.

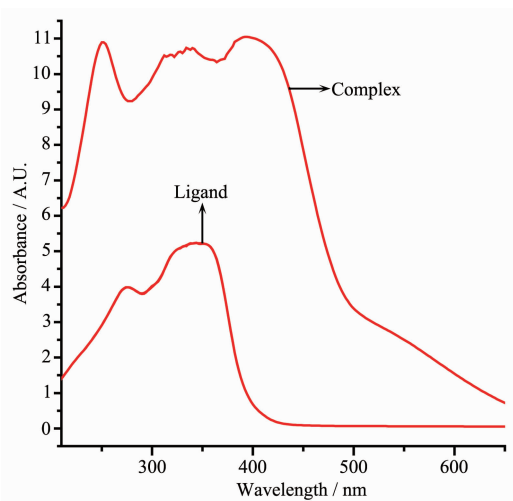


Fig.2 UV spectra of ligand and complex

### 2.4 Fluorescent properties

The fluorescent properties of the title complex and the free ligand were investigated in the solid state at room temperature (Fig.3). The free ligand shows an emission band at 523 nm ( $\lambda_{ex}=369$  nm), and the title complex exhibits a stronger blue emission with a maximum at 478 nm upon excitation at 393 nm. The emission of the free ligand may be a  $\pi^* \rightarrow \pi$  transition, while the emission of the title complex exhibits an obvious blue shift compared to that of the free ligand,

which could be assigned to the ligand-to-metal charge transfer (LMCT)<sup>[20,21]</sup>.

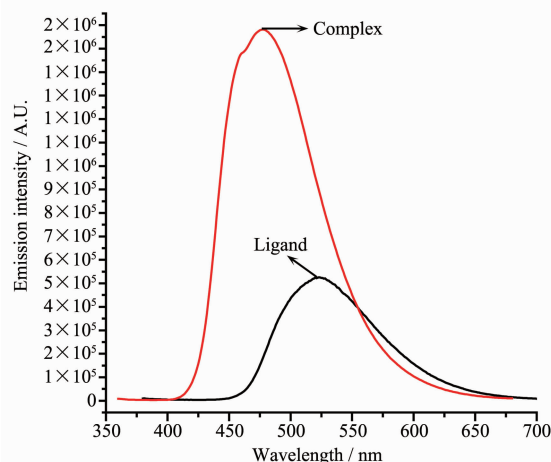


Fig.3 Solid-state fluorescent emission spectrum of  $H_2L$  and the title complex  $[Zn_2(L)_2(Mf)_2]$

### 2.5 Thermal analysis

The TG-DTG curves of the title complex exhibit three weight loss stages (Fig.4). The first weight loss of 21.60% occurred over the temperature range 240~300 °C with the DTG peaks at 288.9 °C, corresponding to the removal of two coordinated morphine molecules (calcd. 21.52%). Then, the weight loss of 24.30% between 300 and 525 °C with the DTG peaks at 524.9 °C may be attributed to the loss of two phenolic radical ( $C_6H_5O$ ) fragments (calcd. 23.00%). A further burning decomposition occurred over 525 °C, with a mass remnant of 20.89% at ~920 °C corresponding roughly to the deposition of ZnO (calcd. 20.10%). The results show that the compound has higher thermal stability.

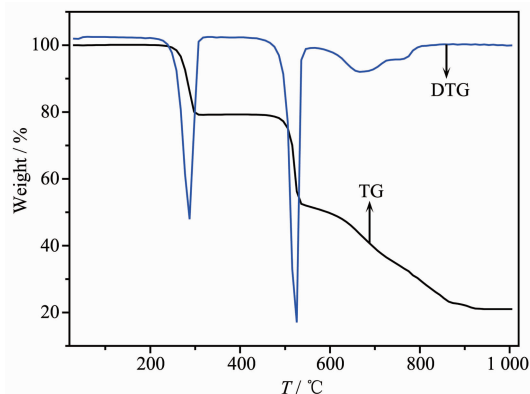


Fig.4 TG-DTG curve of the title complex

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