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Solvolthermal Synthesis, Structure, and Properties of a Novel Dinuclear Zinc(II) Complex[1]

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Abstract—A novel centrosymmetric dinuclear zinc(II) complex, $[Zn_2L_2]$, was prepared from 2-bromo-6-[(3-cyclohexylaminopropylimino)methyl]phenol (H_2L), 3,5-dichlorosalicylaldehyde, and zinc acetate under solvolthermal conditions. There occurs a rarely-seen 1,3-hydride shift reaction during the process. Structure of $[Zn_2L_2]$ has been characterized by elemental analysis, IR spectra, and single crystal X-ray diffraction (CIF file CCDC no. 956057). The Zn···Zn separation is 3.163(1)°. Each Zn atom in the complex is in a trigonal-bipyramidal coordination. Thermal stability and fluorescence property of $[Zn_2L_2]$ were studied. The complex displays intraligand π–π^* fluorescence and can potentially serve as photoactive material.

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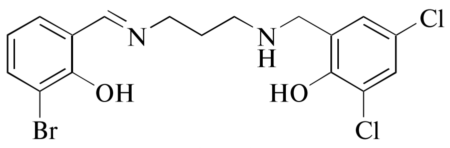
INTRODUCTION

Schiff bases are a kind of versatile ligands in coordination chemistry which are readily synthesized from the reaction of primary amines with carbonyl-containing compounds. In recent years, much work has been carried out on the syntheses and properties of Schiff bases and their complexes [1–5]. You and coworkers have prepared some Schiff base complexes with solvolthermal method [6–8]. It was found that the mono-Schiff base ligand 4-chloro-2-[(3-cyclohexylaminopropylimino)methyl]phenol can be transformed to bis-Schiff base ligand *N*,*N*'-bis(5-chlorosalicylidene)-1,3-propanediamine under solvolthermal condition [8]. Then, they reported three interesting dinuclear zinc(II) complexes derived from mono-Schiff bases bearing 2-[3-cyclohexylaminopropylimino]methyl]phenol backbone under solvolthermal conditions [9, 10]. It is interesting that the mono-Schiff bases underwent structural transformation during the reactions. As further investigation on this interesting reaction under solvolthermal conditions, in the present work, a new centrosymmetric dinuclear zinc(II) complex $[Zn_2L_2]$, where L is the dianionic form of 2-[(3-{[1-(3-bromo-2-hydroxyphenyl)methylidene]amino}propylamino)methyl]-4,6-dichlorophenol (H_2L), has been prepared and structurally characterized.



(H_2L)

EXPERIMENTAL

Materials and physical measurements. 3,5-Dichlorosalicylaldehyde, 3-bromosalicylaldehyde, and *N*-cyclohexylpropane-1,3-diamine with AR grade were purchased from Lancaster. Other reagents and solvents were purchased from Shanghai Chemical Reagent Company and used as received. The mono-Schiff base 2-bromo-6-[(3-cyclohexylaminopropylimino)methyl]phenol was prepared according to the literature method [11]. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were measured with a Nicolet FT-IR 170-SX spectrophotometer. Thermal stability analysis was performed on a PerkinElmer Pyris Diamond TG–DTA thermal analyses system. Luminescence spectra were reported on a JASCO FP-6500 spectrofluorimeter (solid) in the range of 200–850 nm.

Synthesis of $[Zn_2L_2]$. 2-Bromo-6-[(3-cyclohexylaminopropylimino)methyl]phenol (0.1 mmol, 33.9 mg), 3,5-dichlorosalicylaldehyde (0.1 mmol, 19.0 mg), and zinc acetate (0.1 mmol, 22.0 mg) were mixed in methanol. The mixture was stirred at room temperature for 10 min and transferred to a stainless steel bomb, which was sealed, heated at 150°C for 12 h, and cooled grad-

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ually to room temperature. Colorless thin needle-like single crystals of the complex, suitable for X-ray diffraction, were collected by filtration. The yield was 63%.

For $C_{34}H_{30}N_4O_4Cl_4Br_2Zn_2$			
anal. calcd., %:	C, 41.2;	H, 3.1;	N, 5.7.
Found, %:	C, 41.0;	H, 3.0;	N, 5.5.

IR data (KBr; ν, cm^{-1}): 3225 w ν(N–H), 1629 s ν(C=N).

X-ray crystallography. Diffraction intensities for complex **I** were collected at 298(2) K using Bruker SMART CCD detector with MoK_α radiation (λ = 0.71073 Å). The collected data were reduced using SAINT [12], and multiscan absorption corrections were performed using SADABS [13]. The structure was solved by direct method and refined against F^2 by full-matrix least-squares method using SHELXTL [14]. All non-hydrogen atoms were refined anisotropically. The amino H was located from a difference Fourier map and refined isotropically, with N–H distance restrained to 0.90(1) Å. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. A summary of the crystallographic data are given in Table 1. Coordinate bond lengths and angles are listed in Table 2.

Supplementary material for the structure has deposited with the Cambridge Crystallographic Data Centre (no. 956057; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystalloraphic data and structure refinement for [Zn_2L_2]

Parameter	Value
Fw	990.98
Crystal shape/colour	Block/colorless
Crystal size, mm	0.25 × 0.23 × 0.23
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	7.3839(6)
b, Å	23.096(2)
c, Å	10.4023(8)
β, deg	98.099(2)
V, Å^3	1756.3(2)
Z	2
μ(MoK_α), mm^{-1}	3.991
T_{min}/T_{max}	0.4353/0.4604
ρ_{calcd}, g cm^{-3}	1.874
Reflections collected	16343
Independent reflections (R_{int})	3226 (0.0652)
Observed reflections ($I \geq 2\sigma(I)$)	2011
Parameters refined	229
Restraints	1
Goodness of fit on F^2	1.088
R_1, wR_2 ($I \geq 2\sigma(I)$)	0.0756, 0.1857
R_1, wR_2 (all data)	0.1302, 0.2110
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.582/–0.905

Table 2. Coordinate bond lengths (Å) and angles (deg) for [Zn_2L_2]*

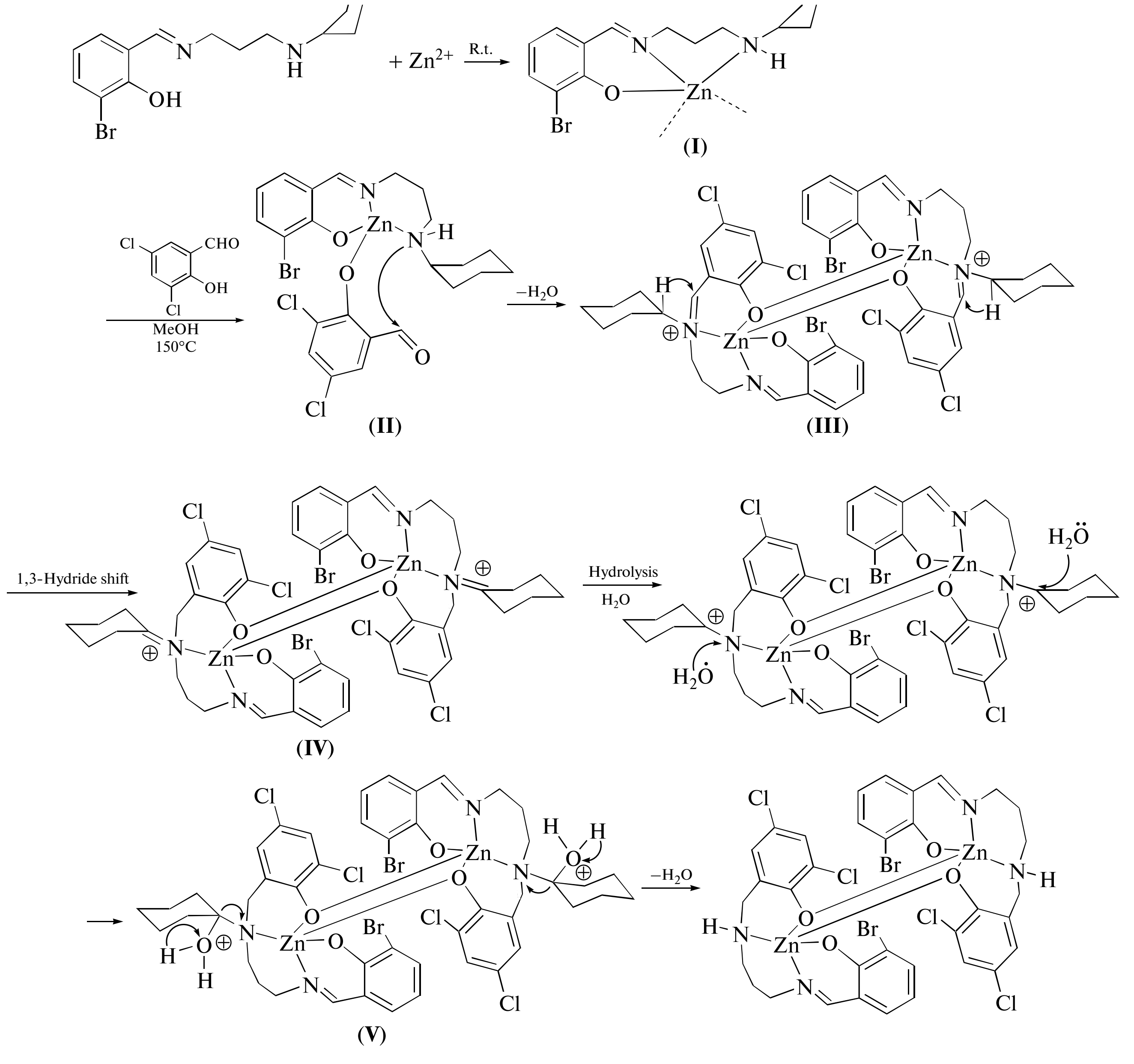
Bond	*d*, Å	Bond	*d*, Å
Zn(1)–O(1)	1.981(6)	Zn(1)–O(2)	2.089(6)
Zn(1)–O(2*A*)	2.016(5)	Zn(1)–N(1)	2.110(8)
Zn(1)–N(2)	2.099(8)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Zn(1)O(2*A*)	114.3(3)	O(1)Zn(1)O(2)	90.5(2)
O(2)Zn(1)O(2*A*)	79.2(2)	O(1)Zn(1)N(2)	130.3(3)
O(2*A*)Zn(1)N(2)	114.7(3)	O(2)Zn(1)N(2)	90.5(3)
O(1)Zn(1)N(1)	86.9(3)	O(2*A*)Zn(1)N(1)	98.5(2)
O(2)Zn(1)N(1)	175.5(3)	N(2)Zn(1)N(1)	94.0(3)

* Symmetry code for *A*: $-x$, $1 - y$, $-z$.

RESULTS AND DISCUSSION

The zinc complex was prepared by reaction of the mono-Schiff base with 3,5-dichlorosalicylaldehyde and zinc acetate in methanol under solvolthermal conditions.

The possible mechanism for the reaction preporation of the complex is shown below:



In the presence of Zn^{2+} ions, the reaction underwent a 1,3-hydride shift process [9, 15–17]. Under solvolthermal conditions, 3,5-dichlorosalicylaldehyde reacted with **I**, generating intermediate zinc complex (**II**). In II, there is a condensation reaction between the coordinated 3,5-dichlorosalicylaldehyde and the mono-Schiff base ligand, which forms an imine cationic intermediate (**III**). Further, **III** changed to the following imine cationic intermediate (**IV**) undergoing a 1,3-hydride shift process to give the intermediate (**V**), which maybe the main step of the reaction mechanism. After a serials of hydrolysis reactions, the final dinuclear zinc(II) complex, $[Zn_2L_2]$, was formed.

When compared with those complexes prepared under common condition with Schiff bases derived from *N*-cyclohexylpropane-1,3-diamine [11, 18], we

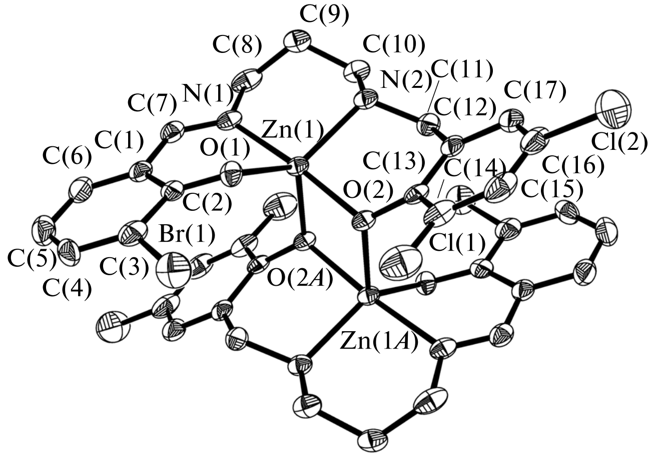


Fig. 1. The molecular structure of $[Zn_2L_2]$. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms except for the amino H are omitted for clarity. Atoms labeled with the suffix *A* or unlabeled atoms are at the symmetry position $-x$, $1 - y$, $-z$.

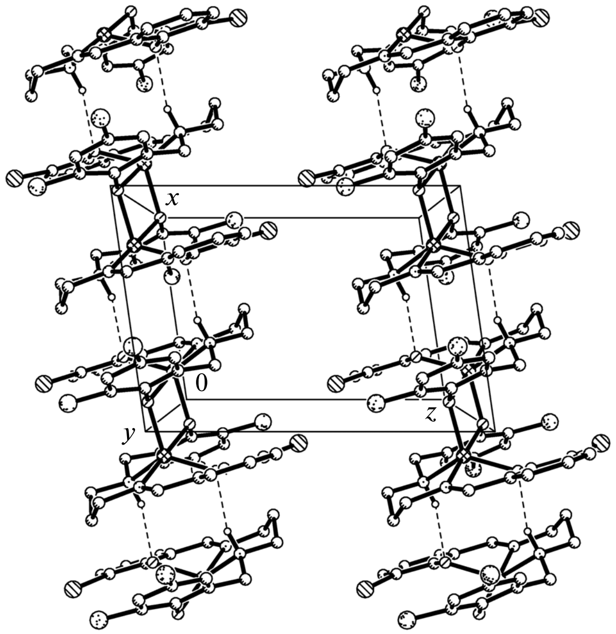


Fig. 2. Molecular packing of $[Zn_2L_2]$, viewed along the *y* axis. Hydrogen bonds are drawn as dashed lines.

can observe that the cyclohexyl groups of the Schiff bases can remove away only under solvolthermal conditions.

The molecular structure of $[Zn_2L_2]$ is shown in Fig. 1. X-ray crystallography reveals that the complex is a centrosymmetric phenolate O-bridged dinuclear zinc(II) species, with the inversion center located at the midpoint of the two metal atoms. The Zn···Zn separation is 3.163(1) Å.

The C(10)–N(2) bond length of 1.460(12) Å confirms it as a single C–N bond. Furthermore, the difference Fourier map of the complex reveals that there is one H atom attached to N(2). Each Zn atom in the complex is in a trigonal-bipyramidal coordination, with one amino N and two phenolate O atoms from two Schiff base ligands defining the equatorial plane, and with one imino N and one phenolate O atoms of one Schiff base ligand occupying the two axial positions. The Zn atom deviates from the least-squares plane defined by the equatorial donor atoms by 0.100(2) Å. The coordinate bond lengths in the complex are comparable to those reported in similar zinc(II) complexes [9, 10]. The ZnL unit in $[Zn_2L_2]$ is butterfly-shaped, with the dihedral angle formed by the two benzene rings of 17.0(5)°. The chelate ring formed by the atoms Zn(1), N(1), C(8)–C(10), and N(2) in the complex has chair conformation. The diagonally positioned atoms, Zn(1) and C(9), are shifted from the least-squares plane defined by the atoms N(1), N(2), C(8), and C(10) by –0.613(2) and 0.706(6) Å, respectively. The chelate ring formed by the atoms Zn(1), N(2), C(11)–C(13), and O(2) in the complex has boat conformation. The diagonally positioned atoms, O(2) and C(11), are shifted from the least-squares plane defined by the atoms Zn(1), N(2), C(12), and C(13) by 0.385(2) and 0.665(6) Å, respectively.

In the crystal structure of $[Zn_2L_2]$, dinuclear zinc complex molecules are linked via intermolecular N(2)–H(2)···O(1) hydrogen bonds (N(2)–H(2) 0.90(1), H(2)···O(1)^i 2.16(2), N(2)···O(1)^i 3.045(9) Å, N(2)–H(2)···O(1)^i 168(9)°; symmetry code: ^{i} $1 - x$, $1 - y$, $- z$), forming 1D chains running along *x* axis (Fig. 2).

In the IR spectrum of $[Zn_2L_2]$, there exists a characteristic N–H vibration at 3225 cm^{-1}. The strong absorption band at 1629 cm^{-1} can be attributed to the vibration of the azomethine groups, ν(C=N). The medium band at 1263 cm^{-1} may be attributed to the strecting vibration of the C–N bonds.

Differential thermal and thermal gravimetric analyses were conducted to examine the stability of the complex (Fig. 3). There is one step of losing weight from 320 to 620°C. The final residue is ZnO.

The fluorescence property of the complex was studied at room temperature (298 K) in the solid state. Fig. 4 is the emission spectrum of $[Zn_2L_2]$. The emission band of the complex is from 400 to 600 nm, with $\lambda_{max} = 447$ nm ($\lambda_{ex} = 350$ nm). For zinc(II) complexes, no emission originating from metal-centered MLCT/LMCT excited states are expected, since the Zn^{2+} ion is difficult to oxidize or reduce due to its stable d^{10} configuration. Thus, the emission observed in

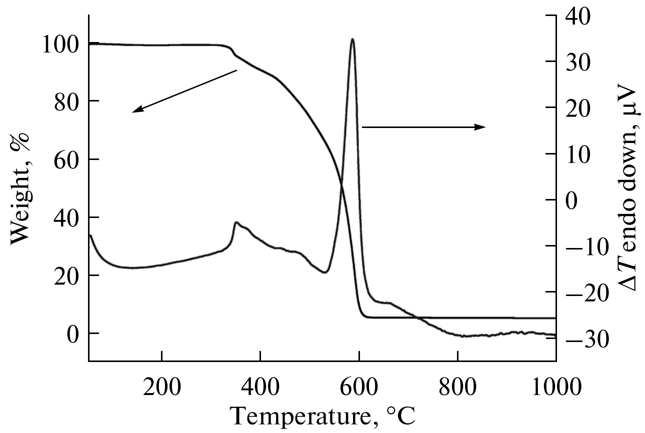


Fig. 3. DT–TGA curves of $[Zn_2L_2]$.

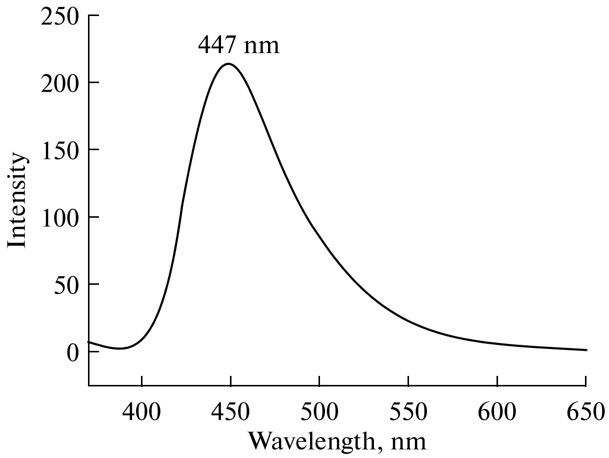


Fig. 4. Emission spectrum of $[Zn_2L_2]$.

the complex is tentatively assigned to the π–π* intraligand fluorescence [19].

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