

## КРАТКИЕ СООБЩЕНИЯ

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CHARACTERIZATION AND CRYSTAL STRUCTURE OF A NOVEL TETRANUCLEAR ZINC(II) COMPLEX DERIVED FROM *N,N'*-BIS(2-HYDROXY-5-METHOXYBENZYLIDENE)PROPANE-1,3-DIAMINEG.-H. Sheng<sup>1</sup>, X.-S. Cheng<sup>2</sup>, Z.-L. You<sup>2</sup>, H.-L. Zhu<sup>1</sup><sup>1</sup>*School of Life Sciences, Shandong University of Technology, P. R. China*

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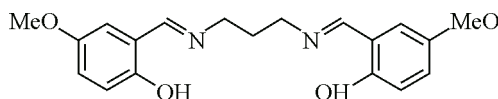
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A novel tetranuclear zinc(II) complex  $[Zn_4Br_4L_2(H_2L)]$ , where L and  $H_2L$  are the dianionic and zwitterionic forms of *N,N'*-bis(2-hydroxy-5-methoxybenzylidene)propane-1,3-diamine, is prepared and structurally characterized by elemental analysis, IR spectrum, and single crystal X-ray crystallography. The complex crystallizes in the monoclinic space group  $C2/c$ , with unit cell dimensions  $a = 38.338(2) \text{ \AA}$ ,  $b = 10.5662(5) \text{ \AA}$ ,  $c = 17.4607(8) \text{ \AA}$ ,  $\beta = 113.767(2)^\circ$ ,  $V = 6473.3(6) \text{ \AA}^3$ ,  $Z = 4$ ,  $R_1 = 0.0686$ , and  $wR_2 = 0.1752$ . The inner Zn atoms are five-coordinated in a square pyramidal geometry, and the outer Zn atoms are four-coordinated in a tetrahedral geometry. The intramolecular Zn...Zn distance is  $3.103(1) \text{ \AA}$ .

**Keywords:** Schiff base, zinc complex, tetranuclear complex, crystal structure.

Polynuclear structures of complexes with bridging groups are currently attracting much attention for their interesting structures and wide applications [1–3]. Schiff bases derived from salicylaldehyde and its derivatives are a kind of versatile ligands in coordination chemistry. The rational design and construction of polynuclear structures of complexes with Schiff bases are of particular interest in coordination and structural chemistry. A preferred way to construct polynuclear complexes is the use of suitable bridging groups, such as  $N_3^-$ ,  $NCS^-$ ,  $N(CN)_2^-$ , dicarboxylate, 4,4'-bipy, and so on [4–7]. A number of polynuclear complexes derived from bis-Schiff bases have been reported [8–10]. As a continuation of our work on preparing polynuclear complexes with novel structures, in this paper, a new bis-Schiff base ligand across-bridged tetranuclear zinc(II) complex  $[Zn_4Br_4L_2(H_2L)]$ , where L and  $H_2L$  are the dianionic and zwitterionic forms of *N,N'*-bis(2-hydroxy-5-methoxybenzylidene)propane-1,3-diamine (Scheme 1), was obtained. To our knowledge, only one copper complex derived from  $H_2L$  has been reported so far [11].

Scheme 1. Schiff base  $H_2L$ 

**Experimental. General methods and materials.** Starting materials, reagents, and solvents with analytical grade were purchased from commercial suppliers and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets in the range  $4000\text{--}400 \text{ cm}^{-1}$ . Molecular

Table 1

*Crystallographic data and refinement parameters for the complex*

|  |  |
|--|--|
| Formula  | C <sub>57</sub> H <sub>62</sub> Br <sub>4</sub> N <sub>6</sub> O <sub>12</sub> Zn <sub>4</sub> |
| <i>M<sub>r</sub></i>   | 1604.2   |
| <i>T</i> , K   | 298(2)   |
| Crystal shape / color  | Block / colorless  |
| Crystal size, mm <sup>3</sup>  | 0.22×0.21×0.18   |
| Crystal system   | Monoclinic   |
| Space group  | <i>C2/c</i>  |
| <i>a</i> , <i>b</i> , <i>c</i> , Å   | 38.338(2), 10.5662(5), 17.4607(8)  |
| β, deg.  | 113.767(2)   |
| <i>V</i> , Å <sup>3</sup>  | 6473.3(6)  |
| <i>Z</i>   | 4  |
| <i>D<sub>c</sub></i> , g/cm <sup>-3</sup>  | 1.646  |
| μ(MoK <sub>α</sub> ), mm <sup>-1</sup>   | 3.994  |
| <i>F</i> (000)   | 3208   |
| Independent / Observed reflections ( <i>I</i> ≥ 2σ( <i>I</i> ))                          | 6026 / 3723  |
| Min. and max. transmission   | 0.4736 and 0.5333  |
| Parameters   | 381  |
| Restraints   | 1  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>   | 1.015  |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )] <sup>a</sup> | 0.0686, 0.1752   |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data) <sup>a</sup>                   | 0.1232, 0.2091   |

$$^a R_1 = F_0 - F_c / F_0, wR_2 = [\sum w(F_0^2 - F_c^2) / \sum w(F_0^2)]^{1/2}.$$

conductance was measured with a DDS-11A conductometer. Single crystal structural X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer.

**Synthesis of Schiff base H<sub>2</sub>L.** The yellow crystalline product of the Schiff base was prepared by a reaction of 5-methoxysalicylaldehyde (0.02 mol, 3.04 g) with propane-1,3-diamine (0.01 mol, 0.74 g) in methanol and subsequent evaporation of the solvent. *Anal.* Calc. for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>: C 66.6, H 6.5, N 8.2 %. Found: C 66.8, H 6.5, N 8.1 %. Characteristic IR data (KBr, cm<sup>-1</sup>): 1633 (C=N).

**Synthesis of the [Zn<sub>4</sub>Br<sub>4</sub>L<sub>2</sub>(H<sub>2</sub>L)] complex.** To a methanolic solution (20 ml) of H<sub>2</sub>L (0.17 g, 0.5 mmol) a methanolic solution (10 ml) of ZnBr<sub>2</sub> (0.11 g, 0.5 mmol) was added with stirring. The mixture was stirred for 30 min at room temperature to give a colorless solution. After keeping the solution in air for a few days, colorless block-shaped crystals of the complex, suitable for X-ray crystal structural determination, were formed on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol, and dried in air. Yield 38 %. Characteristic IR data (KBr, cm<sup>-1</sup>): 3217 (w), 1640 (C=N). *Anal.* Calc. for C<sub>57</sub>H<sub>62</sub>Br<sub>4</sub>N<sub>6</sub>O<sub>12</sub>Zn<sub>4</sub>: C 42.7, H 3.9, N 5.2 %. Found: C 42.5, H 3.8, N 5.3 %.

**X-ray crystallography.** Diffraction intensities for the complex were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector diffractometer with MoK<sub>α</sub> radiation (λ = 0.71073 Å). The collected data were reduced with SAINT [12], and multi-scan absorption correction was performed using SADABS [13]. The structure was solved by a direct method and refined against *F*<sup>2</sup> by the full-matrix least-squares method using SHELXTL [14]. All non-hydrogen atoms were refined anisotropically. The amino hydrogen atom was located from a difference Fourier map and refined isotropically, with the N—H distance restrained to 0.90(1) Å. The remaining hydrogen atoms were placed in the calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Selected bond distances (Å) and angles (deg.) for the complex

| Bond distances |            | Bond angles |            |             |            |
|----------------|------------|-------------|------------|-------------|------------|
| Zn1—O1         | 2.050(5)   | O5—Zn1—N2   | 104.2(3)   | O5—Zn1—O1   | 105.2(2)   |
| Zn1—N1         | 2.063(7)   | O5—Zn1—N1   | 112.6(3)   | O5—Zn1—O2   | 89.6(2)    |
| Zn1—O5         | 1.970(5)   | N2—Zn1—O1   | 146.4(3)   | N2—Zn1—N1   | 95.1(3)    |
| Zn2—O2         | 1.963(5)   | O1—Zn1—N1   | 88.4(2)    | N2—Zn1—O2   | 87.5(2)    |
| Zn2—Br2        | 2.3611(16) | O1—Zn1—O2   | 76.8(2)    | N1—Zn1—O2   | 156.1(3)   |
| Zn1—O2         | 2.068(5)   | O2—Zn2—O1   | 80.5(2)    | O2—Zn2—Br1  | 116.05(17) |
| Zn1—N2         | 2.043(7)   | O1—Zn2—Br1  | 112.85(17) | O2—Zn2—Br2  | 109.97(16) |
| Zn2—O1         | 1.997(5)   | O1—Zn2—Br2  | 115.99(17) | Br1—Zn2—Br2 | 116.43(6)  |
| Zn2—Br1        | 2.3280(14) |             |            |             |            |

**Results and discussion. Chemistry.** The Schiff base  $H_2L$  was readily prepared by the reaction of 5-methoxysalicylaldehyde with propane-1,3-diamine in methanol. The zinc complex was prepared by the reaction of equimolar quantities of  $H_2L$  with  $ZnBr_2$  in methanol, which is soluble in DMF, DMSO, methanol, ethanol, and acetonitrile. The molar conductivity of the complex measured in acetonitrile at a concentration of approximately  $10^{-3}$  M is  $23 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ , indicating the non-electrolytic nature of the complex in solution [ 15 ]. Single crystals of the complex are stable up to 273 °C.

**Structural description of the complex.** The molecular structure of the complex is shown in Fig. 1. X-ray crystallography reveals that the complex is a zwitterionic bis-Schiff base bridged tetranuclear zinc(II) species. The complex possesses a crystallographic two-fold rotation axis symmetry. The  $Zn1 \cdots Zn1A$  distance is 9.742(2) Å (symmetry code for A:  $-x, y, 1/2-z$ ). There are two intramolecular  $N-H \cdots O$  hydrogen bonds in the zwitterionic Schiff base ligand. The dihedral angle between the two benzene rings in the zwitterionic ligand is 86.3(3)°.

In each  $[Zn_2Br_2L]$  moiety, the  $Zn \cdots Zn$  distance is 3.103(1) Å. The Zn1 atom is five-coordinated in a square pyramidal geometry, with two phenolate O and two imine N atoms of the dianionic Schiff

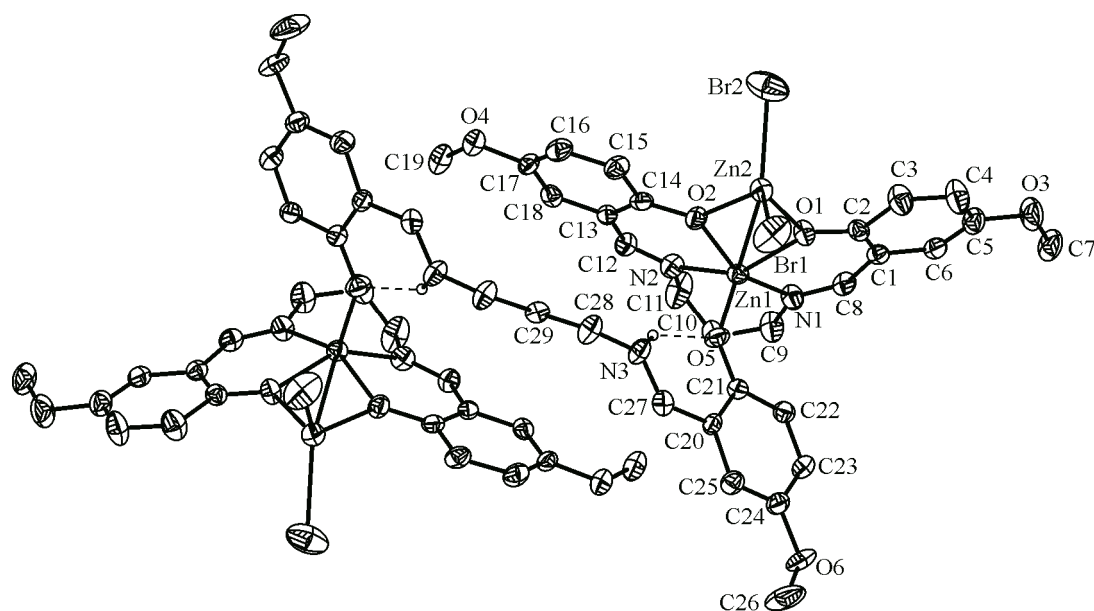
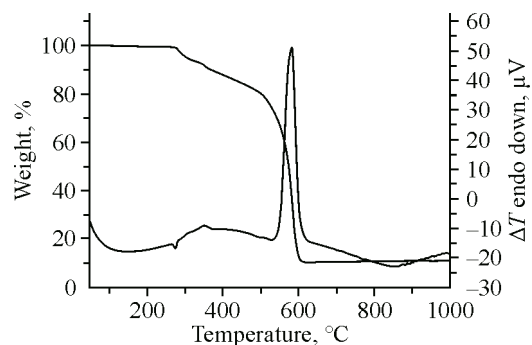


Fig. 1. A perspective view of the molecular structure of the complex with the atom labeling scheme. Thermal ellipsoids are drawn at the 30 % probability level. Unlabelled atoms are at the symmetry position  $-x, y, 1/2-z$

Fig. 2. DT-TGA curve of the complex



base ligand defining the basal plane, and with one phenolate O atom of the zwitterionic ligand occupying the apical position. The Zn atom deviates from the plane defined by the four basal donor atoms by 0.480(2) Å. The substantial distortion of the square pyramid is revealed by the bond angles among apical and basal donor atoms, ranging from 89.6(2)° to 112.6(3)°. Coordination number 5 for zinc(II) complexes is very common and usually presents either a square-pyramidal or a trigonal-bipyramidal geometry, or any of the distorted intermediate geometries. For a pentacoordinated metal center, the distortion of the coordination environment from square-pyramidal to trigonal-bipyramidal can be calculated from the Addison distortion index  $\tau$  defined as  $\tau = (\beta - \alpha)/60$ , where  $\alpha$  and  $\beta$  are the two largest coordinate angles, and  $\tau = 0$  represents a perfect square pyramid;  $\tau = 1$  represents a perfect trigonal bipyramid [ 16 ]. In the present complex, the calculated  $\tau$  value is 0.162, suggesting that it is best described as a distorted square-pyramidal geometry.

The Zn2 atom is coordinated by two phenolate O atoms of the dianionic Schiff base ligand and two bromide atoms, forming a tetrahedral geometry. The coordinate bond angles range from 80.5(2)° to 116.4(1)°, indicating the difference from the ideal values of 109°28' for the perfect tetrahedral geometry. The distortion of the tetrahedral coordination is mainly caused by the tensile force of the four-membered chelate ring Zn1—O1—Zn2—O2. The four-membered bridging ring Zn1—O1—Zn2—O2 in the complex is not planar, but presents a slightly distorted roof-shape.

The dihedral angle between the two substituted benzene rings in the dianionic Schiff base ligand is 25.1(3)°. The Zn—O and Zn—N bond lengths in the complex are comparable to the corresponding values observed in other Schiff base zinc(II) complexes [ 10, 17, 18 ].

**IR spectra.** The IR spectra of the Schiff base and the complex provide information about the metal-ligand bonding. The weak and broad absorption centered at 3317  $\text{cm}^{-1}$  is assigned to the O—H groups of the free Schiff base. In the spectrum of the complex, the weak and sharp band at 3217  $\text{cm}^{-1}$  is assigned to the vibration of the N—H groups. The strong absorption band at 1627  $\text{cm}^{-1}$  for the free Schiff base ligand is assigned to the azomethine groups,  $\nu(\text{C}=\text{N})$  [ 19 ]. The band is shifted to a higher wavenumber of 1640  $\text{cm}^{-1}$  in the spectrum of the complex, which is attributed to the coordination of the azomethine nitrogen atoms to the metal atoms. The strong absorption band of the Ar—O bonds for the free Schiff base is located at 1227  $\text{cm}^{-1}$ , which is observed at a lower wavenumber for the complex (1215  $\text{cm}^{-1}$ ). The weak bands in the region 400—600  $\text{cm}^{-1}$  for the complex may be assigned to the Zn—O, Zn—N, and Zn—Br vibrations.

**Thermal stability of the complex.** Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the complex (Fig. 2). The first step started at 273 °C and completed at 512 °C, corresponding to the loss of the cross Schiff base ligand. The observed weight loss of 21.9 % is very close to the calculated value (22.1 %). The second step from 512 °C to 615 °C corresponds to the loss of the remaining contents of the Schiff base ligands, and the formation of the final product (ZnO). The observed weight loss of 67.3 % is close to the calculated value (67.7 %). The total weight loss of 89.3 % is close to the calculated value (89.9 %).

CCDC-942643 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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