

## Syntheses, Structures and Coordination Behavior of Central Hydroxyl Group Containing Polydentate Ligands

Jun JIA<sup>1</sup>, Xing Wang WANG<sup>1</sup>, Yi Li ZHAO<sup>2</sup>, Yu ZHU<sup>1</sup>, Jing Chao TAO<sup>1\*</sup>

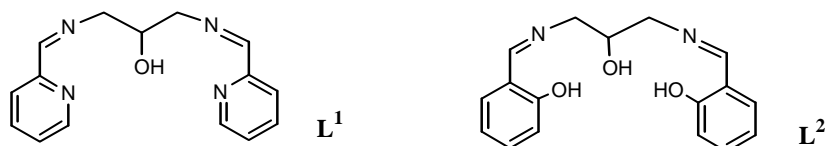
<sup>1</sup> Department of Chemistry, Zhengzhou University, Zhengzhou 450052

<sup>2</sup> Chemical Engineering Institute of Henan Province, Zhengzhou 450052

**Abstract:** Two central hydroxyl group containing Schiff base type ligands L<sup>1</sup> and L<sup>2</sup> as well as their metal complexes L<sup>1</sup>·2CuCl<sub>2</sub>·3H<sub>2</sub>O and L<sup>2</sup>·Zn<sub>2</sub>Cl<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>OH were synthesized and characterized. The crystal and molecular structures of L<sup>2</sup> and its zinc complex indicated well the means of coordination behavior. Both the two ligands showed good ion transport ability for alkali, alkaline earth and transition metal ions.

**Keywords:** Polydentate ligand, coordination, synthesis, crystal structure.

Proteins containing dinuclear Cu (II), Zn (II) centers play paramount roles in biology<sup>1</sup>. As mimetic of metal-dependent esterase, dinuclear Cu (II) and Zn (II) complexes have received a great deal of attentions<sup>2-6</sup>. They are of interest in the field of biomimetic chemistry to provide an improved understanding of the function of the biological sites and as potential catalysts for substrate oxidations. Schiff base type polydentate ligands which contain central hydroxyl group have been widely used in the field of chemistry and biomimetic chemistry owing to their abilities to form stable complexes<sup>7-9</sup>. In this paper, the synthesis and characterization of two central hydroxyl group containing Schiff base type ligands L<sup>1</sup> and L<sup>2</sup> as well as their metal complexes L<sup>1</sup>·2CuCl<sub>2</sub>·3H<sub>2</sub>O and L<sup>2</sup>·Zn<sub>2</sub>Cl<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>OH were reported. The crystal and molecular structures of L<sup>2</sup> and L<sup>2</sup>·Zn<sub>2</sub>Cl<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>OH were also studied.



### Ligand Synthesis

Elemental analysis was carried out with a Carlo Erba 1106 elemental analyzer. Infrared spectra were recorded on a Shimadzu IR435 spectrometer on KBr disks. UV spectra

\*E-mail: jctao@zzu.edu.cn

were measured in acetonitrile on a Shimadzu UV 2100 spectrophotometer.  $^1\text{H}$  NMR was recorded on a Bruker-400 spectrometer using TMS as internal standard.

*1, 3-Bis(2-pyridylideneamino)propan-2-ol L<sup>1</sup>*

1,3-Diaminopropan-2-ol (0.62 g, 6.9 mmol) in methanol (10 mL) was added to a solution of freshly distilled 2-pyridinecarboxaldehyde (1.47 g, 13.8 mmol) in methanol (10 mL) under  $\text{N}_2$  atmosphere. After stirring for 12 h at room temperature, the reaction mixture was evaporated to dryness on a rotary evaporator. The residue obtained was extracted with dry diethyl ether (50 mL) in a Soxhlet extractor over a period of 3 h. The extract was concentrated to about 25 mL and the resulting solution was allowed to stand overnight at  $-20^\circ\text{C}$ . The white solids precipitated were collected by filtration and dried, yield 72%. mp  $68-70^\circ\text{C}$ . Anal. Calcd. for  $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}$ : C 67.16, H 5.97, N 20.89; found: C 67.26, H 6.03, N 21.09. IR (KBr,  $\text{cm}^{-1}$ ): 3350, 1640, 1590, 1560, 1440, 1100.  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ): 4.18-4.24 (m, 1H, CHOH), 3.74-3.79 (m, 2H,  $-\text{CH}_2-$ ), 3.93-3.97 (m, 2H,  $-\text{CH}_2-$ ), 7.82-8.63 (m, 8H, H-Py), 8.39 (s, 2H, CH=N). UV ( $\text{CH}_3\text{CN}$ ,  $\lambda_{\text{max}}$ ): 268.5 nm.

*1,3-Bis(salicylideneamino)propan-2-ol L<sup>2</sup>*

The solution of freshly distilled salicylaldehyde (0.903 g, 7.4 mmol) and 1, 3-diaminopropan-2-ol (0.33 g, 3.7 mmol) in methanol (20 mL) was stirred under  $\text{N}_2$  for 10 h at room temperature. The resulting yellow solid precipitated after standing overnight was filtered, washed with ethanol and dried in vacuum over  $\text{P}_2\text{O}_5$  (yield 87.1%). After recrystallization from diethyl ether, yellow microcrystalline solid was obtained. mp  $96-98^\circ\text{C}$ . Anal. Calcd. for  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3$ : C 68.46, H 6.04, N 9.39; found: C 68.46, H 6.15, N 9.71. IR (KBr,  $\text{cm}^{-1}$ ): 3300, 1630, 1580, 1500, 1460, 1210, 1050, 750.  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ): 4.26-4.29 (m, 1H,  $>\text{CHO}$ ), 3.71-3.76 (d, 2H,  $-\text{CH}_2-$ ), 3.85-3.90 (d, 2H,  $-\text{CH}_2-$ ), 6.87-6.91 (t, 2H, H-Ph), 6.95-6.97 (d, 2H, H-Ph), 7.26-7.28 (d, 2H, H-Ph), 7.31-7.35 (t, 2H, H-Ph), 8.41 (s, 2H, CH=N). UV ( $\text{CH}_3\text{CN}$ ,  $\lambda_{\text{max}}$ ): 316.0, 255.5, 227.5 nm.

### Preparation of Complexes

*L<sup>1</sup>·2CuCl<sub>2</sub>·3H<sub>2</sub>O*

0.5 g of  $\text{L}^1$  (1.87 mmol) dissolved in methanol (10 mL) was slowly added to a stirred solution of cupric chloride (0.635 g, 3.73 mmol) in methanol (15 mL). The green precipitates obtained were collected by filtration and then recrystallized from ethanol (30 mL), producing 0.81 g of green crystalline solid  $\text{L}^1\cdot 2\text{CuCl}_2\cdot 3\text{H}_2\text{O}$  (yield 70%), mp  $158-160^\circ\text{C}$ . Anal. Calcd. for  $\text{C}_{15}\text{H}_{16}\text{N}_4\text{OCu}_2\text{Cl}_4\cdot 3\text{H}_2\text{O}$ : C 30.45, H 3.72, N 9.48; found: C 30.26, H 3.52, N 9.45. IR (KBr,  $\text{cm}^{-1}$ ): 3350, 1630, 1600, 1480, 1450, 1300, 1090, 780. UV ( $\text{CH}_3\text{CN}$ ,  $\lambda_{\text{max}}$ ): 282.4 nm.

*L<sup>2</sup>·Zn<sub>2</sub>Cl<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>OH*

The ligand  $\text{L}^2$  (0.30 g, 1.01 mmol) in methanol (8 mL) was added dropwise to a stirred

solution of zinc chloride (0.30 g, 2.2 mmol) in methanol (15 mL). The mixture was stirred overnight at room temperature and then evaporated to dryness on a rotary evaporator. The residue obtained was dissolved in hot ethanol (15 mL) and the solution was allowed to stand at room temperature for several days. The yellow crystals precipitated were collected to give the complex of  $L^2 \cdot Zn_2Cl_2 \cdot C_2H_5OH$ . Yield 85%, mp 200°C(dec.). Anal. Calcd. for  $C_{19}H_{23}Cl_2N_2O_4Zn_2$ : C 41.91, H 4.04, N 5.15; Found: C 41.84, H 4.14, N 5.10. IR (KBr,  $cm^{-1}$ ): 3359, 1623, 1557, 1476, 1435, 1291, 1118, 769. UV( $CH_3CN$ ,  $\lambda_{max}$ ): 357.5, 267.0, 231.5 nm.

### X-Ray Diffraction Analysis on $L^2$ and $L^2 \cdot Zn_2Cl_2 \cdot C_2H_5OH$

The single crystals of  $L^2$  and  $L^2 \cdot Zn_2Cl_2 \cdot C_2H_5OH$  were grown from dry diethyl ether and ethanol, respectively, at room temperature. All measurement were made on a RAXIS-IV imaging plate area detector with graphite monochromated  $M_oK$  radiation. Determination of the crystal class, orientation matrix and accurate uni-cell parameters were performed according to the established procedures.

The crystal structures of  $L^2$  and  $L^2 \cdot Zn_2Cl_2 \cdot C_2H_5OH$  are illustrated in **Figure 1** and **Figure 2**, respectively. The molecular structure of  $L^2$  showed that the imino N atoms in the bridging chain form intramolecular H-bonds with the phenolic protons, to form two six-member rings with different orientation. From the pentadentate ligand, a novelty dinuclear Zn complex ( $L^2 \cdot Zn_2Cl_2 \cdot C_2H_5OH$ ) was obtained as described above. The molecule possesses a two fold axis of symmetry through two zinc atoms which symmetrically located between the two coordination centers. One of the zinc atoms was five coordinated by two N atoms, two phenolic O atoms and an ethanol molecule as a pyramid, the other was four coordinated by two phenolic O atoms and two Cl atoms as a tetrahedron. The intramolecular distance between Zn(1) and Zn(2) is 3.1244(9) Å, indicating that there is a strong electrostatic force between the two Zn atoms. The dihedral angle of the two coordination planes is 174.6(2)°. The bond angle of O(1)-Zn(1)-O(2)[77.02(13)°] is slightly smaller than that of O(1)-Zn(2)-O(2)[79.60(13)°], which is probably due to the different coordination surroundings. One of the Cl atoms coordinated to Zn(1) forms two H-bonds with both the central OH in one molecule and the ethanol OH in another, which makes individual complexes cross-linked regularly.

### Cation Transport Properties of the Ligands

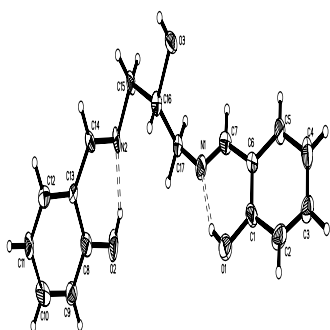
In order to evaluate the potential of the Schiff base type compounds as ion carriers, liquid membrane transport of alkali, alkaline earth and transition-metal cations were carried out. Take picrate as the companion anion, the transport experiments were performed in a chloroform membrane system. The concentration of picrate in the receiving phase was measured at time intervals (**Table 1**).

**Table 1** The rates of cation transport by prepared ionophores ( $L^1$  and  $L^2$ ) ( $10^{-6}$  mol  $h^{-1}$ )

Ionophore	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Mg <sup>2+</sup>	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>
$L^1$	40.97	4.47	0.64	0.29	0.33	0.59	0.50
$L^2$	53.06	19.95	0.84	0.10	0.10	0.36	0.23

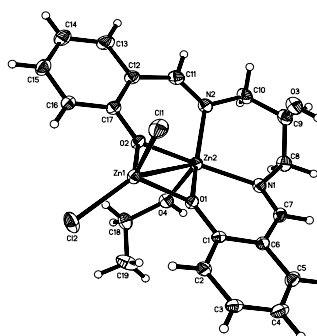
It has been shown that the transport abilities of both the two ionophors are much stronger for transition metal cations, such as  $\text{Cu}^{2+}$ , than alkali and alkaline earth metal cations. The transport abilities of  $\text{L}^1$  and  $\text{L}^2$  for all the cations studied decreased in the order:  $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} \gg \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{Li}^+$ . The transport selectivity of the two ionophors for  $\text{Cu}^{2+}/\text{Co}^{2+}$  were as high as 64.32 and 63.17, respectively.

**Figure 1** Molecular structures of compound  $\text{L}^2$



$\text{L}^2$ : Formula:  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3$ , F.W. 298.33, Space group: CC,  $a=35.771(7)\text{\AA}$ ,  $b=11.290(2)\text{\AA}$ ,  $c=16.354(3)\text{\AA}$ ,  $\beta=109.07(3)^\circ$ ,  $Z=16$ ,  $F(000)=2528$ ,  $2\theta$  range:  $2.40-45.10$ , Total no. of variables Reflections: 7649, No. of unique reflections with  $I>3\sigma(I)$ : 5068, Final no. of variable: 794,  $R=0.0639$ ,  $R_w=0.172$

**Figure 2** Molecular structures of  $\text{L}^2\cdot\text{Zn}_2\text{Cl}_2\cdot\text{C}_2\text{H}_5\text{OH}$



$\text{L}^2\cdot\text{Zn}_2\text{Cl}_2\cdot\text{C}_2\text{H}_5\text{OH}$ :  $\text{C}_{19}\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_4\text{Zn}_2$ , F.W. 544.03, Space group:  $\text{P}2_1/\text{n}$ ,  $a=10.035(2)\text{\AA}$ ,  $b=8.6841(17)\text{\AA}$ ,  $c=25.666(5)\text{\AA}$ ,  $\beta=101.23(3)^\circ$ ,  $Z=4$ ,  $F(000)=1104$ ,  $2\theta$  range  $3.24-45.02^\circ$ , No. of variables Reflections: 6716, No. of unique reflections with  $I>3\sigma(I)$ : 4054, Final no. of variables: 267,  $R=0.0603$ ,  $R_w=0.1282$

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