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Synthesis and Crystal Structures of Two Zinc(II) Complexes Derived from 4-bromo–2-(cyclopentyliminomethyl)phenol with Different Solvents[1]

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Abstract—Two new mononuclear zinc(II) complexes, $[ZnL_2]$ (**I**) and $[ZnL_2] \cdot 2MeOH$ (**II**) (HL = 4-bromo–2-(cyclopentyliminomethyl)phenol), were synthesized by the reaction of the Schiff base HL with zinc acetate in ethanol and methanol solutions, respectively. Both complexes were characterized by elemental analyses and single-crystal X-ray diffraction. The crystal of **I** is orthorhombic: space group *Pbca*, a = 14.711(3), b = 13.223(3), c = 24.870(5) Å, V = 4837.8(18) Å^3, Z = 8. The crystal of II is monoclinic: space group $C2/c$, a = 20.581(5), b = 10.660(3), c = 15.428(4) Å, β = 119.919(3)°, V = 2933.7(13) Å^3, Z = 4. The Zn atom in each complex is four-coordinated by two imine N and two phenolic O atoms, forming a tetrahedral geometry. Complex **II** possesses crystallographic two-fold rotation axis symmetry.

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INTRODUCTION

Schiff bases prepared by the condensation of salicylaldehydes with primary amines are an important class of versatile ligands. Transition metal complexes derived from Schiff bases have been wide investigated due to their versatile structures and wide applications [1–3]. The study of the variety of products in self-assembly processes between labile metal atoms and Schiff bases is an interesting topic in supramolecular and coordination chemistry. Factors that affect the coordination topologies include not only the highly influential factors of metal and ligand coordination preferences, but also solvent-based influences, which have extensively been investigated for silver(I) complexes [4, 5]. However, for zinc complexes with Schiff bases, solvent-based influences on the structures have seldom been reported [6]. In the present paper, two new mononuclear zinc(II) complexes $[ZnL_2]$ (**I**) and $[ZnL_2] \cdot MeOH$ (**II**) (HL = 4-bromo–2-(cyclopentyliminomethyl)phenol) have been synthesized from different solvents.

EXPERIMENTAL

Materials and Measurements

5-Bromosalicylaldehyde and cyclopentylamine of AR grade were purchased from Aldrich. CHN elemental analyses were performed with a PerkinElmer 240C elemental analyzer. IR spectra (KBr disks) were recorded on a PerkinElmer 257 spectrophotometer.

[1] The article is published in the original.

Synthesis of HL

The Schiff base HL was prepared by the condensation reaction of equimolar 5-bromosalicylaldehyde with cyclopentylamine in a methanol solution at room temperature. The yield was 97%.

For $C_{12}H_{14}BrNO$			
anal. calcd, %:	C, 53.8;	H, 5.3;	N, 5.2.
Found, %:	C, 54.1;	H, 5.4;	N, 5.0.

*Synthesis of $[ZnL_2]$ (**I**)*

An ethanol solution (50 ml) of $Zn(CH_3COO)_2 \cdot 2H_2O$ (110.0 mg, 0.5 mmol) was added to an ethanol solution (50 ml) of HL (268.2 mg, 1.0 mmol), and the mixture was stirred at room temperature for 30 min. Colorless, X-ray quality crystals of I were obtained after a week by allowing the solution to evaporate in air. The yield was 201.0 mg (67%).

For $C_{24}H_{26}Br_2N_2O_2Zn$ (M = 599.66)			
anal. calcd, %:	C, 48.1;	H, 4.4;	N, 4.7.
Found, %:	C, 48.6;	H, 4.7;	N, 4.5.

*Synthesis of $[ZnL_2] \cdot 2MeOH$ (**II**)*

Complex **II** was synthesized by a similar procedure as that for **I**, with the solvent ethanol replaced by methanol,

yielding colorless X-ray quality crystals of **II** after a week. The yield was 172.8 mg (52%).

For $C_{26}H_{34}Br_2N_2O_4Zn$ (M = 663.74)

anal. calcd, %:	C, 47.0;	H, 5.2;	N, 4.2.
Found, %:	C, 46.6;	H, 5.4;	N, 4.2.

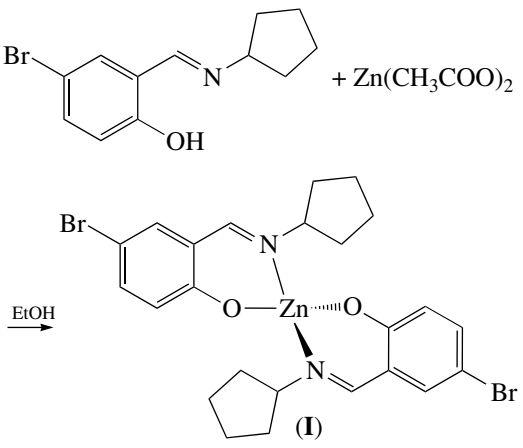
X-ray Structure Determination

The single crystals of the two complexes were chosen and glued to thin glass fibers by epoxy glue in air for data collection. The diffraction data were collected on a Bruker Apex2 CCD with MoK_α radiation (λ = 0.71073 Å) at 298(2) K using the ω scan method. The structures were solved by direct methods and difference Fourier synthesis. Crystal data collection, parameters, and refinement statistics for the two complexes are listed in Table 1. All of the non-H atoms were refined anisotropically. The H atoms of the two complexes were included in calculated positions and assigned to isotropic thermal parameters, which were set to ride on the parent atoms. All calculations were performed using the SHELXTL-97 package [7].

The atomic coordinates and other parameters of structures **I** and **II** have been deposited with the Cambridge Crystallographic Data Center (no. 718319 (**I**) and 718320 (**II**); deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The condensation reactions of aldehydes with primary amines readily produce Schiff bases with quantitative yields and high purity. The Schiff base HL is yellow crystallite, which can be dissolved by methanol and ethanol. Both complexes were synthesized according to the procedure as shown by Eqs. (1) and (2):



(**I**) (1)

Table 1. Crystallographic and experimental data for the complexes **I** and **II**

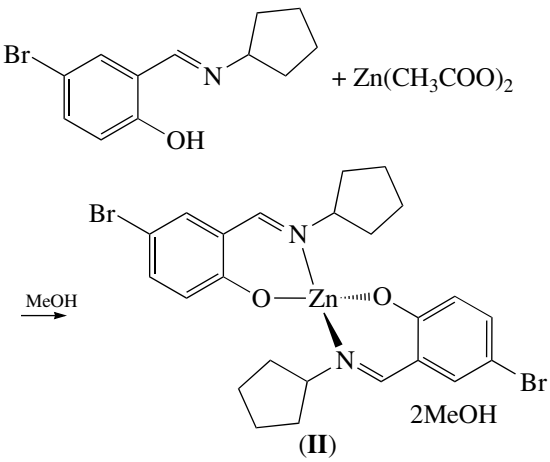
Parameter	Value	
	I	**II**
Crystal shape/color	Block/colorless	Block/colorless
Crystal size, mm	0.20 × 0.18 × 0.17	0.37 × 0.35 × 0.32
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*C*2/*c*
a, Å	14.711(3)	20.581(5)
b, Å	13.223(3)	10.660(3)
c, Å	24.870(5)	15.428(4)
β, deg	90	119.919(3)
V, Å^3	4837.8(18)	2933.7(13)
Z	8	4
μ_{Mo}, mm^{-1}	1.224	3.593
T_{min}	0.477	0.350
T_{max}	0.526	0.393
Reflections/parameters	5544/280	3316/161
Independent reflections	2165	2231
F(000)	2400	1344
Goodness of fit on F^2	1.003	1.041
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0792, 0.1198	0.0461, 0.1136
R_1, wR_2 (all data)*	0.2228, 0.1624	0.0787, 0.1306

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (deg) for the complexes

Bond	*d*, Å	Bond	*d*, Å
I		**II**	
Zn(1)–O(1)	1.905(5)	Zn(1)–O(1)	1.925(2)
Zn(1)–N(1)	2.001(6)	Zn(1)–N(1)	1.991(3)
Zn(1)–O(2)	1.913(5)		
Zn(1)–N(2)	2.007(6)		
Angle	ω, deg	Angle	ω, deg
I		**II**	
O(1)Zn(1)O(2)	118.8(2)	O(1)Zn(1)O(1)^i	114.23(17)
O(2)Zn(1)N(1)	114.4(2)	O(1)Zn(1)N(1)^i	113.42(11)
O(2)Zn(1)N(2)	95.8(2)	O(1)Zn(1)N(1)	97.04(11)
O(1)Zn(1)N(1)	95.1(2)	N(1)Zn(1)N(1)^i	122.79(16)
O(1)Zn(1)N(2)	111.9(2)		
N(1)Zn(1)N(2)	122.7(2)		

Note: Symmetry code: $^i 1 - x, y, 1/2 - z$.



(2)

(**II**)

The only difference is the solvent used in the synthesis and crystallization of the complexes: EtOH for **I** and MeOH for **II**.

The IR spectrum of HL shows the characteristic ν(O–H) absorption band at 3437 cm^{-1}, which absents after complexation. The absorption attributed to the ν(C=N) vibrations is at 1635 cm^{-1} for HL. However, the corresponding vibrations in the two complexes are shifted 16 cm^{-1} to lower wave numbers as that described in similar Schiff base complexes [8, 9]. The strong absorption band observed for HL at 1281 cm^{-1} can be attributed to the phenolic stretch. The bands are observed at higher wave numbers at 1302 cm^{-1} for both complexes, suggesting involvement of the oxygen atom of the C–O group in coordination. The close resemblance of the shape and the positions of the absorption bands in the IR spectra suggests similar structures of the complexes. The absorption band of the methanol

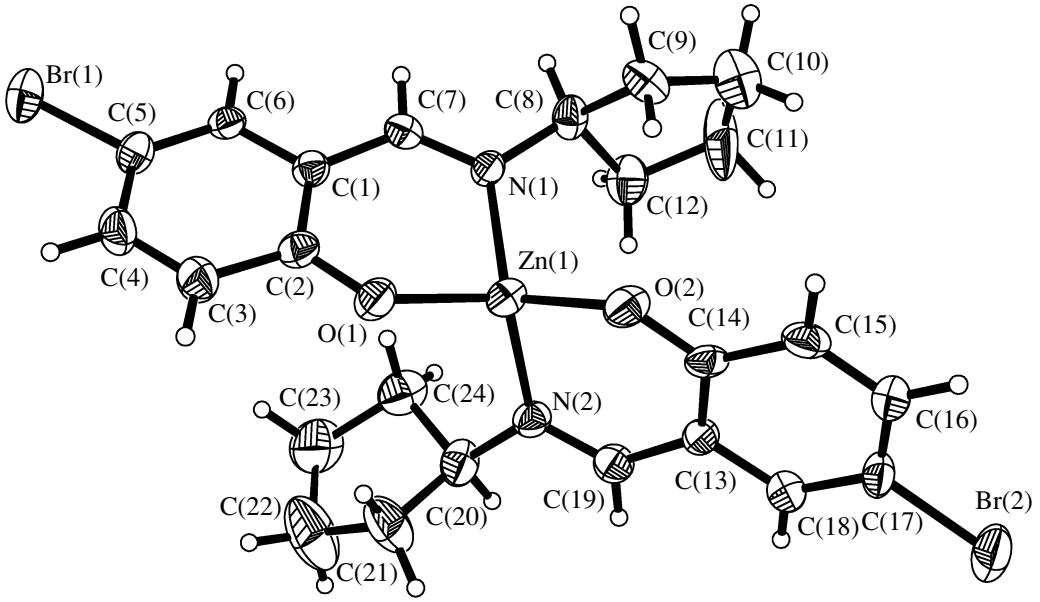


Fig. 1. Molecular structure of **I** at 30% ellipsoid.

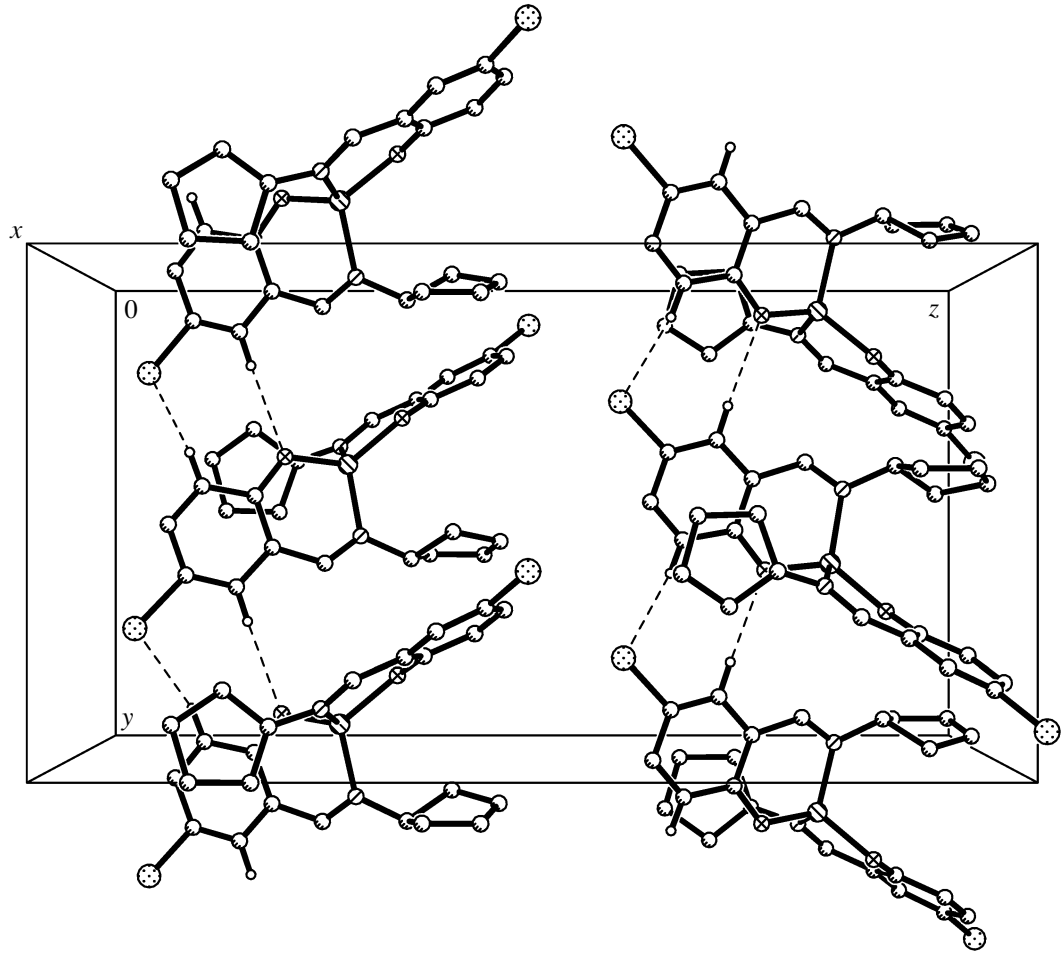


Fig. 2. Molecular packing diagram of **I** viewed along the *x* axis. Intermolecular hydrogen bonds are shown as dashed lines.

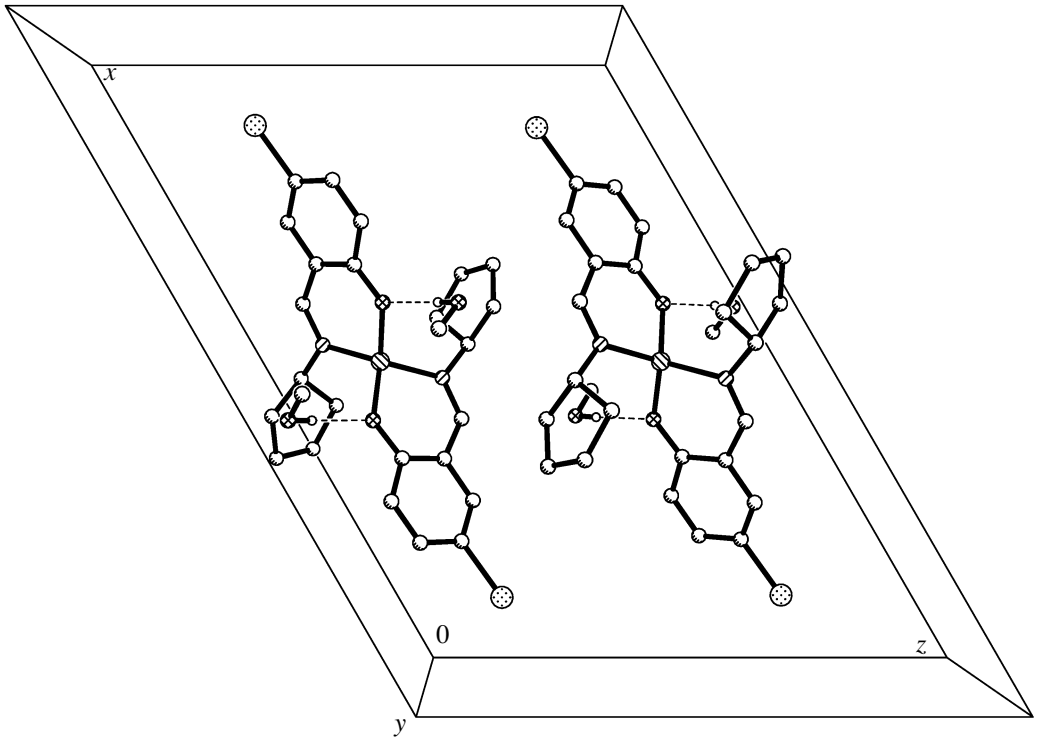


Fig. 3. Molecular packing diagram of **II** viewed along the *y* axis. Intermolecular hydrogen bonds are shown as dashed lines.

Table 3. Hydrogen bond distances (Å) and bond angles (deg) for the complexes I and II*

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
I				
C(3)–H(3)···Br(1)^{ii}	0.93	2.92	3.739(4)	148
C(6)–H(6)···O(1)^{iii}	0.93	2.53	3.456(4)	177
II				
O(2)–H(2)···O(1)^{iv}	0.82	1.95	2.758(4)	171

* Symmetry codes: $^{ii}1/2 - x, -1/2 + y, z$; $^{iii}1/2 - x, 1/2 + y, z$; $^{iv}1/2 - x, -1/2 + y, 1/2 - z$.

O–H vibration is not observed in **II**, what might be caused by the escape of the methanol molecules during grind under the infrared lamp.

Selected bond lengths and angles are listed in Table 2. The molecular structure of **I** is shown in Fig. 1. Both complexes are mononuclear zinc compounds. The major difference between the complexes is in the components of the molecules: complex **I** synthesized and crystallized in ethanol solution has no ethanol molecules in the crystal structure, while complex **II** synthesized and crystallized in methanol solution has methanol molecules in the crystal structure.

In both complexes, the Zn atom is four-coordinated in a tetrahedral geometry by two phenolic O and two imine N atoms from two Schiff base ligands. The structure of the zinc complex molecule of **II** is similar to that of **I** but possesses crystallographic two-fold rotation axis symmetry. The ZnO_2N_2 tetrahedral coordination in each complex is slightly distorted with angles subtended at the Zn atom in the range 95.1(2)°–122.7(2)° for **I** and 97.0(2)°–122.8(2)° for **II**. The coordinate bond lengths in both complexes are comparable to each other and also comparable to those in the similar Schiff base zinc complexes [10–12]. The dihedral angle between the two benzene rings in **I** and **II** are 79.7(6)° and 87.2(3)°, respectively.

In the crystal structure of **I**, molecules are linked through intermolecular C–H···Br and C–H···O hydrogen bonds (Table 3), forming chains running along the *y*axis (Fig. 2). In the crystal structure of **II**, the methanol molecules are linked to the zinc complex molecules through intermolecular O–H···O hydrogen bonds (Table 3, Fig. 3).

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