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Synthesis and Crystal Structures of Two Zinc(II) Complexes Derived from N-Isopropyl-N'-[1-(2-Methoxyphenyl)methylidene]ethane-1,2-Diamine[1]

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Abstract—Two isostructural mononuclear zinc(II) complexes, $[ZnLBr_2]$ (**I**) and $[ZnLI_2]$ (**II**), derived from the Schiff base N-isopropyl-N'-[1-(2-methoxyphenyl)methylidene]ethane-1,2-diamine (L), have been synthesized and characterized by elemental analysis, IR spectra, and X-ray single-crystal diffraction. The crystal of **I** is monoclinic: space group $P2_1/n$, a = 14.476(1) Å, b = 7.327(1) Å, c = 17.528(1) Å, β = 101.153(1)°, V = 1824.0(3) Å^3, Z = 4. The crystal of **II** is monoclinic: space group $P2_1/n$, a = 14.482(1), b = 7.329(1), c = 17.528(1) Å, β = 101.195(2)°, V = 1825.0(3) Å^3, Z = 4. The Zn atom in each complex is four-coordinated in a tetrahedral coordination, with one imine N and one amine N atoms of L, and two halide atoms. Both complexes and the Schiff base were tested in vitro for their antibacterial activities.

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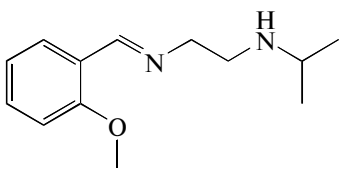
INTRODUCTION

Schiff bases are readily synthesized by the condensation reaction of aldehydes with primary amines, which have been widely investigated for their antibacterial and antitumor activities [1–3]. The metal complexes of Schiff bases have also been received much attention. These complexes not only play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [4–6], but also exhibit interesting biological activities [7–9]. The Schiff base N-isopropyl-N'-[1-(2-methoxyphenyl)methylidene]ethane-1,2-diamine (L)



derived from 2-methoxybenzaldehyde and N'-isopropylethane-1,2-diamine, is a versatile tridentate ligand, the complexes of which have never been reported so far. The halide anions such as Br^- and I^- are preferred ligands which easily coordinate to the metal atoms through either terminal or bridging modes [10–13]. In this paper, two isostructural mononuclear zinc(II) complexes, $[ZnLBr_2]$ (**I**) and $[ZnLI_2]$ (**II**), have been synthesized and structurally characterized. The antibacterial activities against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescens*, were evaluated for the complexes.

EXPERIMENTAL

Materials and measurements. 2-Methoxybenzaldehyde and N'-isopropylethane-1,2-diamine with AR grade were obtained from Aldrich and were used as received. Elemental analyses were performed using a PerkinElmer 240C analytical instrument. Infrared spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer with KBr pellets.

Synthesis of L. The Schiff base L was prepared by refluxing of 2-methoxybenzaldehyde (136.2 mg, 1.0 mmol) and N'-isopropylethane-1,2-diamine (102.2 mg, 1.0 mmol) in 30 mL of methanol for half an hour according to the scheme:

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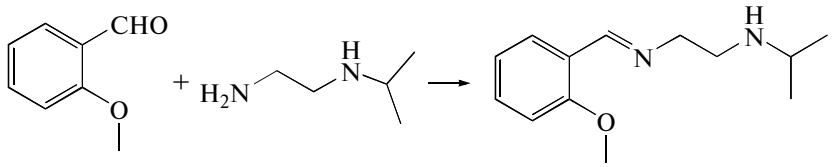


The clear yellow solution was evaporated to give yellow oil. The yield was 98%.

For $C_{13}H_{20}N_2O$			
anal. calcd., %:	C, 70.9;	H, 9.2;	N, 12.7.
Found, %:	C, 70.6;	H, 9.2;	N, 12.8.

Synthesis of [$ZnLBr_2$] (I). To a zinc(II) bromide (22.5 mg, 0.1 mmol) solution in methanol (10 mL), a solution of L (22.0 mg, 0.1 mmol) in methanol (5 mL) was added with stirring. The mixture was stirred for half an hour and filtered. The filtrate was kept undisturbed at room temperature for a week. Colorless block-shaped crystals of **I** suitable for X-ray diffraction were obtained on slow evaporation of the solvent. Crystals were isolated by filtration and dried in air. The yield was 72% with respect to L.

For $C_{13}H_{20}Br_2N_2OZn$			
anal. calcd., %:	C, 35.0;	H, 4.5;	N, 6.3.
Found, %:	C, 35.4;	H, 4.7;	N, 6.5.

Synthesis of [$ZnLI_2$] (II). To a zinc(II) iodide (31.9 mg, 0.1 mmol) solution in methanol (10 mL), a solution of L (22.0 mg, 0.1 mmol) in methanol (5 mL) was added with stirring. The mixture was stirred for half an hour and filtered. The filtrate was kept undisturbed at room temperature for three days. Colorless block-shaped crystals of **II** suitable for X-ray diffraction were obtained on slow evaporation of the solvent. Crystals were isolated by filtration and dried in air. The yield was 63% with respect to L.

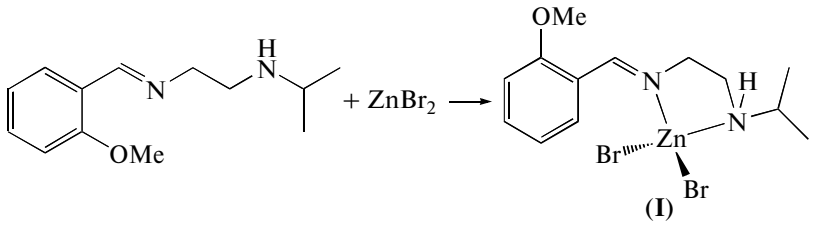
For $C_{13}H_{20}I_2N_2OZn$			
anal. calcd., %:	C, 28.9;	H, 3.7;	N, 5.2.
Found, %:	C, 28.6;	H, 3.8;	N, 5.1.

X-ray structure determination. Suitable single crystals with high quality of complexes **I** and **II** were selected and mounted on a Bruker Smart 1000 CCD area-detector diffractometer with graphite monochromatized MoK_α radiation (λ = 0.71073 Å). Diffraction data for both complexes were collected by ω scan mode at 298(2) K. Data reduction and cell refinement were performed by the SMART and SAINT programs [14]. Empirical absorption correction was applied by using SADABS [15]. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXL97 package [16]. The non-H atoms in the structures were subjected to refined anisotropic refinement. Hydrogen atoms were located in geometrically and treated with the riding mode. Crystallographic data and experimental details for the complexes are summarized in Table 1. Selected bond lengths and angles for the complexes are listed in Table 2. The atomic coordinates and other parameters of structures **I** and **II** have been deposited with the Cambridge Crystallographic Data Centre (nos. 743331 for **I** and 743332 for **II**; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

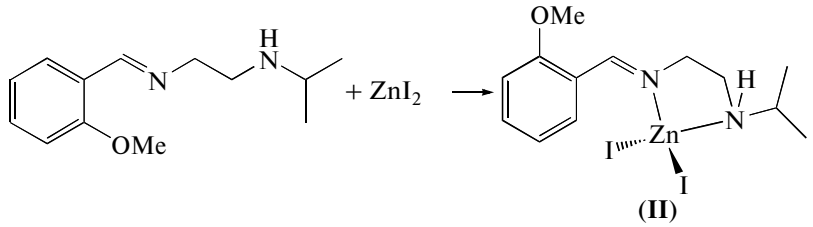
Antibacterial activity. The antibacterial activities of the Schiff base L and both complexes were tested in vitro against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescens* using Mueller-Hinton (MH) medium (casein hydrolysate 17.5 g, soluble starch 1.5 g, beef extract 1000 mL). The minimum inhibitory concentrations (MIC) of the test compounds were determined by a colorimetric method using the dye MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) [17]. A solution of the compound (50 μg mL^{-1}) in DMSO was prepared and graded quantities of the test compounds were incorporated in specified quantity of sterilized liquid MH medium. A specified quantity of the medium containing the compound was poured into microtitration plates. Suspension of the microorganism was prepared to contain about 10^5 colony forming units cfu mL^{-1} and applied to microtitration plates with serially diluted compounds in DMSO to be tested and incubated at 37°C for 24 h. After the MICs were visually determined on each of the microtitration plates, 50 μL of PBS (Phosphate Buffered Saline 0.01 mol L^{-1}, pH 7.4: $Na_2HPO_4 \cdot 12H_2O$ 2.9 g, KH_2PO_4 0.2 g, NaCl 8.0 g, KCl 0.2 g, distilled water 1000 mL) containing 2 mg of MTT was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed, and 100 μL of isopropyl alcohol containing 5% 1 mol L^{-1} HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density was measured with a microplate reader at 550 nm. The observed MICs are presented in Table 3.

RESULTS AND DISCUSSION

The two isostructural zinc(II) complexes were synthesized according to the similar procedure:



(I)



(II)

Both complexes were soluble in methanol, ethanol, and acetonitrile, insoluble in water.

Fig. 1 gives the perspective views of **I**. Complexes **I** and **II** are isostructural mononuclear zinc(II) compounds. The Zn atom in each complex is four-coordinate in a tetrahedral geometry, with one imine N and one amine N atoms of L, and with two halide atoms (Br for **I** and I for **II**). The distortion of the tetrahedral coordination is revealed by the coordinate bond angles, ranging from 85.3(2)° to 121.0(1)° for **I** and from 85.8(2)° to 120.9(1)° for **II**. The bond angles of N(1)Zn(1)N(2) in both complexes are much smaller than the ideal value for an ideal tetrahedral geometry, which is caused by the strain created by the five-membered chelated ring Zn(1)N(1)C(9)C(10)N(2). The Zn–N bond lengths in both complexes are comparable to each other, and within normal values when compared to other Schiff base zinc(II) complexes [18, 19]. The bond lengths of Zn–Br and Zn–I are also typical [20, 21]. As expected, the Zn(1)–N(1) (iminic) bonds are shorter than the Zn(1)–N(2) (aminic) bonds. It is notable that the methoxy groups in both complexes are at the opposite sites of the ZnX_2 (X = Br for **I** and X = I for **II**) groups, which is caused by the hindrance effects.

In the crystal structures of **I** and **II**, molecules are linked through intermolecular hydrogen bonds (N–H···Br for **I** and N–H···I for **II**, forming chains running along the *y* axis (Fig. 2 for **I** and Fig. 3 for **II**).

The infrared spectra of L and the two complexes provide information about the metal–ligand bonding, which consistent with the crystal structures that revealed from the X-ray diffraction. The sharp absorption band at 3213 cm^{-1} in the spectrum of L is assigned to the vibration of the NH group. The strong absorption band at 1637 cm^{-1} in the spectrum of L is assigned to the azomethine group, which confirms to the formation of the Schiff base. The band shifted towards lower frequencies (1623 cm^{-1} for **I** and **II**), indicating the coordination of azomethine nitrogen atoms to the zinc atoms. The Zn–Br and Zn–I vibrations in both complexes were observed at 327 and 332 cm^{-1}, respectively, as weak bands.

The Schiff base L and the two complexes were screened in vitro for antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescens* by the MTT method. The MICs of the compounds against the bacteria are presented in Table 3. The Penicillin was used as a reference.

The Schiff base L shows antibacterial activity against *Staphylococcus aureus*, and shows weak or no activity against *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas fluorescens*. Complexes **I** and **II** show stronger activities against the four bacteria than those of L. Even though the activities against *Bacillus subtilis* and *Staphylococcus aureus* of the compounds are less than those of the Penicillin, it is interesting that the activities against *Escherichia coli* and *Pseudomonas fluorescens* of the complexes are superior to the Penicillin, and deserve further investigation.

Table 1. Crystallographic data and structural refinements for **I** and **II**

Parameter	Value	
	I	**II**
Mr	445.5	539.5
T, K	298(2)	298(2)
Colour; habit	Colorless; block	Colorless; block
Crystal size, mm	0.23 × 0.20 × 0.20	0.23 × 0.20 × 0.20
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	14.476(1)	14.482(1)
b, Å	7.327(1)	7.329(1)
c, Å	17.528(1)	17.528(1)
β, deg	101.153(1)	101.195(2)
V, Å^3	1824.0(3)	1825.0(3)
Z	4	4
ρ_{calcd}, g/cm^3	1.622	1.964
μ, mm^{-1}	5.723	4.724
θ Range, deg	1.67–27.00	1.67–26.89
F(000)	880	1024
T_{min} and T_{max}	0.353 and 0.394	0.410 and 0.452
Measured reflections	10423	10678
Unique reflections (R_{int})	3865 (0.0279)	3930 (0.0476)
Observed reflections ($I \geq 2\sigma(I)$)	3103	2713
Parameters	175	175
Goodness-of-fit on F^2	1.053	0.983
R ($I \geq 2\sigma(I)$)	$R_1 = 0.0744$, $wR_2 = 0.2133$	$R_1 = 0.0336$, $wR_2 = 0.0634$
R (all data)	$R_1 = 0.0853$, $wR_2 = 0.2330$	$R_1 = 0.0599$, $wR_2 = 0.0736$
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	0.79, −0.61	0.65, −0.47

Table 2. Selected bond lengths (Å) and bond angles (deg) for complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Zn(1)–N(1)	2.068(6)	Zn(1)–N(2)	2.091(6)
Zn(1)–Br(1)	2.5575(9)	Zn(1)–Br(2)	2.5367(9)
	II		
Zn(1)–N(1)	2.049(3)	Zn(1)–N(2)	2.097(3)
Zn(1)–I(1)	2.5390(5)	Zn(1)–I(2)	2.5551(5)
Angle	ω, deg	Angle	ω, deg
	I		
N(1)Zn(1)N(2)	85.3(2)	N(1)Zn(1)Br(2)	109.34(17)
N(2)Zn(1)Br(2)	110.56(16)	N(1)Zn(1)Br(1)	115.41(17)
N(2)Zn(1)Br(1)	109.56(16)	Br(2)Zn(1)Br(1)	121.00(4)
	II		
N(1)Zn(1)N(2)	85.78(12)	N(1)Zn(1)I(1)	109.36(9)
N(2)Zn(1)I(1)	110.46(8)	N(1)Zn(1)I(2)	115.26(9)
N(2)Zn(1)I(2)	109.61(8)	I(1)Zn(1)I(2)	120.86(2)

Table 3. Antibacterial activity

Compound	MIC, μg mL^{-1}			
	Bacillus subtilis	*Escherichia coli*	*Pseudomonas fluorescens*	*Staphylococcus aureus*
L	61.3	45.6	>100	27.2
I	8.3	15.3	40.9	6.2
II	7.7	21.0	34.2	10.8
Penicillin	1.3	>100	>100	2.1

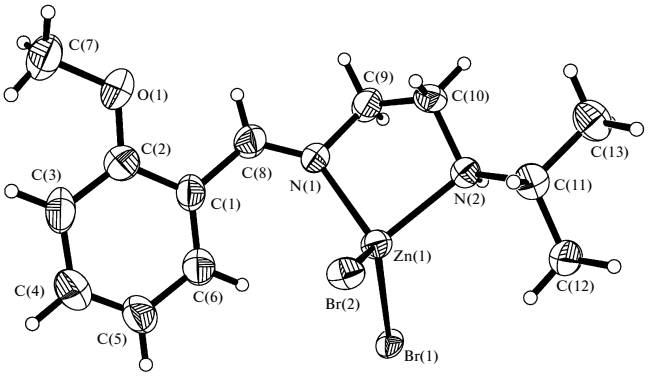


Fig. 1. Molecular structure of **I**. Displacement is drawn at the 30% probability level.

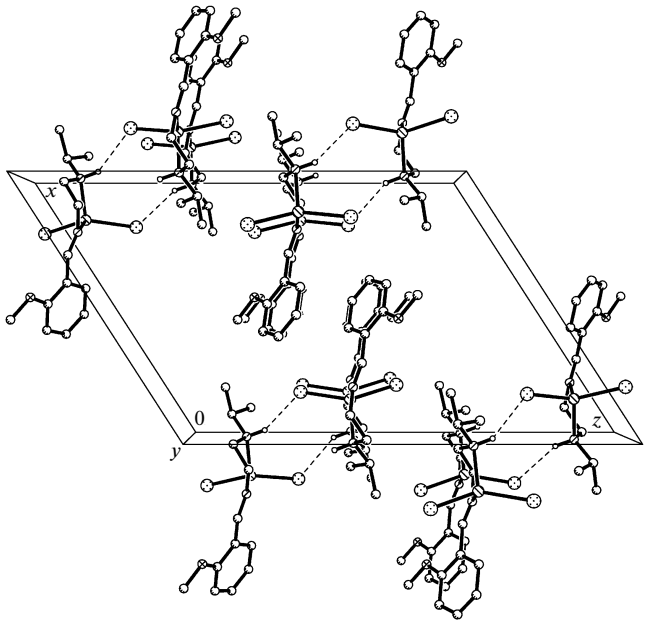


Fig. 2. Molecular packing of **I**, viewed along the *y* axis. Hydrogen bonds are shown as dashed lines.

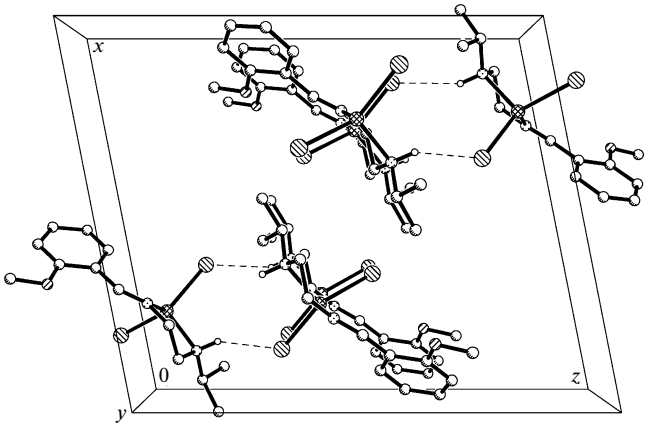


Fig. 3. Molecular packing of **II**, viewed along the *y* axis. Hydrogen bonds are shown as dashed lines.

ACKNOWLEDGMENTS

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REFERENCES

1. Chohan, Z.H., ul-Hassan, M., Khan, K.M., et al., *J. Enzyme Inhib. Med. Chem.*, 2005, vol. 20, no. 2, p. 183.
2. Zhang, J., Pan, F., Cheng, H., et al., *Russ. J. Coord. Chem.*, 2010, vol. 36, no. 7, p. 514.
3. Iqbal, A., Siddiqui, H.L., Ashraf, C.M., et al., *Chem. Pharm. Bull.*, 2007, vol. 55, no. 7, p. 1070.
4. Lalehzari, A., Desper, J., and Levy, C.J., *Inorg. Chem.*, 2008, vol. 47, no. 3, p. 1120.
5. Shit, S., Sen, S., Mitra, S., et al., *Transition Met. Chem.*, 2009, vol. 34, no. 3, p. 269.
6. Xu, B., Jiang, W., Zhang, J., et al., *Transition Met. Chem.*, 2009, vol. 34, no. 3, p. 293.
7. Bagihalli, G.B., Avaji, P.G., Patil, S.A., et al., *Eur. J. Med. Chem.*, 2008, vol. 43, no. 12, p. 2639.
8. Chohan, Z.H., Arif, M., and Rashid, A., *J. Enzyme Inhib. Med. Chem.*, 2008, vol. 23, no. 6, p. 785.
9. Chohan, Z.H., Arif, M., Shafiq, Z., et al., *J. Enzyme Inhib. Med. Chem.*, 2006, vol. 21, no. 1, p. 95.
10. Svoboda, I., Arici, C., Nazir, H., et al., *Acta Crystallogr., E*, 2001, vol. 57, no. 12, p. m584.
11. Taylor, M.K., Stevenson, D.E., Berlouis, L.E.A., et al., *J. Inorg. Biochem.*, 2006, vol. 100, no. 2, p. 250.
12. Pettinari, C., Cingolani, A., and Bovio, B., *Polyhedron*, 1996, vol. 15, no. 1, p. 115.
13. Tandon, S.S., Thompson, L.K., Bridson, J.N., et al., *Inorg. Chem.*, 1992, vol. 31, no. 22, p. 4635.
14. *SMART and SAINT, Area Detector Control and Integration Software*, Madison (WI, USA): Siemens Analytical X-Ray Systems, Inc., 1996.
15. Sheldrick G.M., *SADABS, Program for Empirical Absorption Correction of Area Detector Data*. Göttingen (Germany): Univ. of Göttingen, 1996.
16. Sheldrick G.M., *SHELXTL, Version 5.1, Software Reference Manual*, Madison (WI, USA): Bruker AXS, Inc., 1997.
17. Meletiadis, J., Meis, J.F., Mouton, J.W., et al., *J. Clin. Microbiol.*, 2000, vol. 38, no. 8, p. 2949.
18. Zakrzewski, G. and Lingafelter, E.C., *Inorg. Chim. Acta*, 1970, vol. 4, p. 251.
19. Trosch, A. and Vahrenkamp, H., *Z. Anorg. Allg. Chem.*, 2004, vol. 630, no. 12, p. 2031.
20. Bartnik, R., Lesniak, S., Laurent, A., et al., *Acta Crystallogr., C*, 1983, vol. 39, no. 8, p. 1034.
21. Fustero, S., Piera, J., Sanz-Cervera, J.F., et al., *Tetrahedron*, 2006, vol. 62, no. 7, p. 1444.