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Syntheses, Crystal Structures, and Fluorescence Properties of Zinc(II) Complexes with Multi-Dentate Schiff Bases[1]

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Abstract—Two new structurally similar mononuclear Schiff base zinc(II) complexes, [ZnBr(ClMP)] (**I**) and [ZnCl(NMP)] (**II**) (ClMP = 4-chloro-2-[(3-morpholin-4-ylpropylimino)methyl]phenolate; NMP = 4-nitro-2-[(3-morpholin-4-ylpropylimino)methyl]phenolate), and two new dinuclear Schiff base zinc(II) complexes, $[Zn_2(EMP)_2I_2]$ (**III**), and $[Zn_2(MPA)(CH_3OH)_2(N_3)_2]$ (IV) (EMP = 5-diethylamino-2-[(2-dimethylaminoethylimino)methyl]phenolate; MPA = N,N'-bis(3-methoxysalicylidene)propane-1,3-diamine), have been prepared and characterized mainly by single-cyrstal X-ray diffraction. Complex **I** crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions: a = 15.116(3), b = 9.465(1), c = 23.714(4) Å, β = 104.358(2)°, V = 3286.9(8) Å^3, Z = 8, R_1 = 0.0439, and wR_2 = 0.0736. Complex **II** crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions: a = 7.253(2), b = 16.652(4), c = 13.568(3) Å, β = 96.600(2)°, V = 1627.8(6) Å^3, Z = 4, R_1 = 0.0417, and wR_2 = 0.0809. Complex **III** crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions: a = 27.962(2), b = 8.246(2), c = 31.605(3) Å, β = 90.343(2)°, V = 7287.4(15) Å^3, Z = 8, R_1 = 0.0721, and wR_2 = 0.1709. Complex **IV** crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions: a = 20.483(3), b = 11.344(2), c = 14.909(3) Å, β = 131.650(1)°, V = 2588.6(7) Å^3, Z = 4, R_1 = 0.0343, and wR_2 = 0.0792. Each Zn atom in **I** and **II** are four-coordinated in a tetrahedral geometry by the NNO donor set of the Schiff base ligand and one halide atom. The Zn atoms in **III** are in square pyramidal coordination, and those in **IV** are in octahedral and tetrahedral coordination. Thermal stability and fluorescence properties of the complexes **I** and **II** have also been determined.

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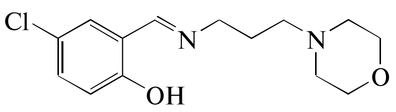
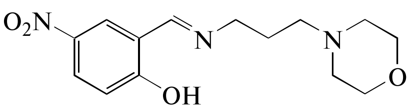
INTRODUCTION

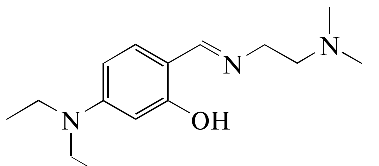
Schiff base complexes have been received considerable attention for their importance in the fields of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [1–5]. Zinc is an important element in biological systems, functions as the active site of hydrolytic enzymes, such as carboxypeptidase and carbonic anhydrase where it is in a hard-donor coordination environment of nitrogen and oxygen atoms [6]. Schiff base zinc complexes have been proved to possess interesting fluorescence properties [7–10]. As a continuation of our work on the Schiff base complexes [11–13], we report in this paper the syntheses, crystal structures, thermal stability, and fluorescene properties of four new Schiff base zinc(II) complexes, [ZnBr(ClMP)] (**I**), [ZnCl(NMP)] (**II**), $[Zn_2(EMP)_2I_2]$ (**III**), and $[Zn_2(MPA)(CH_3OH)_2(N_3)_2]$ (**IV**) (ClMP = 4-chloro-2-[(3-morpholin-4-ylpropylimino)methyl]phenolate, NMP = 4-nitro-2-[(3-morpholin-4-ylpropylimino)methyl]phenolate, EMP = 5-diethylamino-2-[(2-dimethylaminoethylimino)methyl]phenolate, MPA = N,N'-bis(3-methoxysalicylidene)propane-1,3-diamine).



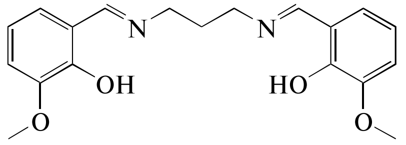
HClMP



HNMP



HEMP



H_2MPA

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EXPERIMENTAL

Materials and measurements. Commercially available 5-chlorosalicylaldehyde, 5-nitrosalicylaldehyde, 4-diethylaminosalicylaldehyde, 3-methoxysalicylaldehyde, N,N-dimethylethane-1,2-diamine, propane-1,3-diamine, and 3-morpholin-4-ylpropylamine were purchased from Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. The Schiff base H_2MPA was prepared according to the literature procedure [14]. C, H and N elemental analyses were performed with a PerkinElmer elemental analyser. Thermal stability analysis was performed on a PerkinElmer Pyris Diamond TG-DTA thermal analyses system. Fluorescence spectra were recorded with an F-2500 FL Spectrophotometer analyzer.

Synthesis of the Schiff base HClMP. 5-Chlorosalicylaldehyde (1.0 mmol, 0.156 g) and 3-morpholin-4-ylpropylamine (1.0 mmol, 0.144 g) were dissolved in EtOH (20 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a yellow solution. The solvent was evaporated to give yellow gummy product of HClMP.

For $C_{14}H_{19}N_2O_2Cl$

anal. calcd., %:	C, 59.5;	H, 6.8;	N, 9.9.
Found, %:	C, 59.4;	H, 6.7;	N, 10.0.

Synthesis of the Schiff base HMP. 5-Nitrosalicylaldehyde (1.0 mmol, 0.167 g) and 3-morpholin-4-ylpropylamine (1.0 mmol, 0.144 g) were dissolved in EtOH (20 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a yellow solution. The solvent was evaporated to give yellow gummy product of HNMP.

For $C_{14}H_{19}N_3O_4$

anal. calcd., %:	C, 57.3;	H, 6.5;	N, 14.3.
Found, %:	C, 57.1;	H, 6.6;	N, 14.5.

Synthesis of the Schiff base HEMP. 4-Diethylaminosalicylaldehyde (1.0 mmol, 0.193 g) and N,N-dimethylethane-1,2-diamine (1.0 mmol, 0.088 g) were dissolved in EtOH (20 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give an orange solution. The solvent was evaporated to give orange gummy product of HEMP.

For $C_{15}H_{25}N_3O$

anal. calcd., %:	C, 68.4;	H, 9.6;	N, 16.0.
Found, %:	C, 68.3;	H, 9.6;	N, 15.8.

Synthesis of I. A MeOH solution (5 mL) of $ZnBr_2$ (0.1 mmol, 22.5 mg) was added to a MeOH solution (10 mL) of HClMP (0.1 mmol, 28.2 mg) with stirring. The mixture was stirred for 30 min to give a clear colourless solution. The resulting solution was allowed to stand in air for a few days. Colourless block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold EtOH, and dried in a vacuum over anhydrous $CaCl_2$. The yield was 15.5 mg (36% on the basis of HClMP).

For $C_{14}H_{18}N_2O_2ClBrZn$

anal. calcd., %:	C, 39.4;	H, 4.2;	N, 6.6.
Found, %:	C, 39.2;	H, 4.3;	N, 6.5.

Synthesis of II. A MeOH solution (5 mL) of $ZnCl_2$ (0.1 mmol, 13.6 mg) was added to a MeOH solution (10 mL) of HNMP (0.1 mmol, 29.3 mg) with stirring. The mixture was stirred for 30 min to give a clear colourless solution. The resulting solution was allowed to stand in air for a few days. Colourless block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold EtOH, and dried in a vacuum over anhydrous $CaCl_2$. The yield was 17.0 mg (43% on the basis of HNMP).

For $C_{14}H_{18}N_3O_4ClZn$

anal. calcd., %:	C, 42.8;	H, 4.6;	N, 10.7.
Found, %:	C, 42.6;	H, 4.6;	N, 10.5.

Synthesis of III. A MeOH solution (5 mL) of ZnI_2 (0.2 mmol, 62.0 mg) was added to a MeOH solution (10 mL) of HEMP (0.1 mmol, 26.3 mg) with stirring. The mixture was stirred for 30 min to give a clear light yellow solution. The resulting solution was allowed to stand in air for a few days. Light yellow block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold EtOH, and dried in a vacuum over anhydrous $CaCl_2$. The yield was 41.0 mg (45% on the basis of HEMP).

For $C_{30}H_{47}N_6O_2I_2Zn_2$

anal. calcd., %:	C, 39.7;	H, 5.2;	N, 9.3.
Found, %:	C, 39.5;	H, 5.3;	N, 9.2.

Synthesis of IV. A MeOH solution (5 mL) of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2 mmol, 54.3 mg) was added to the mixture of a MeOH solution (10 mL) of H_2MPA (0.1 mmol, 34.2 mg) and sodium azide (0.2 mmol, 13.0 mg) with stirring. The mixture was stirred for 30 min to give a clear colourless solution. The resulting solution was allowed to stand in air for a few days. Colourless block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with

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

Parameter	Value			
	I	**II**	**III**	**IV**
Fw	427.0	393.1	908.3	619.2
Crystal shape/color	Block/colourless	Block/colourless	Block/colourless	Block/colourless
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$C2/c$	$C2/c$
a, Å	15.116(3)	7.253(2)	27.962(2)	20.483(3)
b, Å	9.465(1)	16.652(4)	8.246(2)	11.344(2)
c, Å	23.714(4)	13.568(3)	31.605(3)	14.909(3)
β, deg	104.358(2)	96.600(2)	90.343(2)	131.650(1)
V, Å^3	3286.9(8)	1627.8(6)	7287.4(15)	2588.6(7)
Z	8	4	8	4
T, K	298(2)	298(2)	298(2)	298(2)
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	4.092	1.695	3.045	1.905
ρ_{calcd}, g cm^{-3}	1.726	1.604	1.656	1.589
F(000)	1712	808	3608	1272
Crystal size, mm	0.17 × 0.15 × 0.15	0.27 × 0.23 × 0.23	0.27 × 0.23 × 0.23	0.28 × 0.27 × 0.23
T_{min}	0.5430	0.6575	0.4936	0.6175
T_{max}	0.5788	0.6965	0.5410	0.6684
Reflections collected	7005	3556	7919	2958
Observed reflections ($I \geq 2\sigma(I)$)	3627	2479	5377	2039
Parameters	379	208	387	188
Restraints	0	0	0	8
Goodness of fit on F^2	0.952	1.007	1.095	1.022
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0439, 0.0736	0.0417, 0.0809	0.0721, 0.1709	0.0343, 0.0792
R_1, wR_2 (all data)*	0.1207, 0.0923	0.0747, 0.0911	0.1077, 0.1916	0.0599, 0.0899

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

cold EtOH and dried in a vacuum over anhydrous $CaCl_2$. The yield was 33.5 mg (54% on the basis of HMPA).

For $C_{21}H_{28}N_8O_6Zn_2$			
anal. calcd., %:	C, 40.7;	H, 4.6;	N, 18.1.
Found, %:	C, 40.8;	H, 4.5;	N, 18.0.

X-ray structure determination. Diffraction intensities for the complexes **I–IV** were collected at 298(2) K using a Bruker SMART 1K area-detector with $\mathrm{Mo}K_\alpha$ radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program [15], and multi-scan absorption corrections were performed using the SADABS program [16]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL version 5.1 [17]. All of the non-hydrogen atoms were refined anisotropically. The methanol H atom in **IV** was located from a difference Fourier map and refined isotropically with O–H distance restrained to 0.85(1) Å. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 866689 (**I**), 866690 (**II**), 866855 (**III**), and 638069 (**IV**)); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The molecular structures of complexes **I** and **II** are shown in Fig. 1a and 1b, respectively. The structures of the complexes are very similar to each other. There two independent molecules in the asymmetric unit of **I**. The Zn atom in each of the complexes is coordinated by the phenolate O, imine N, and morpholine N atoms of the Schiff base ligand and one halide atom (Br for **I** and Cl for **II**). The stereochemistry around the Zn atoms in the complexes can be described as distorted tetrahedral configuration. The coordinate bond angles range from 95.1(2)° to 118.9(1)° for **I** and from 95.4(1)° to 122.5(1)° for **II**, indicating the difference from the ideal values of 109°28′ for the perfect tetrahedral geometry. The distorsion of the tetrahedral coordination is mainly caused by the tensile force of the Schiff base ligands. The Zn–O and Zn–N bond lengths in the complexes are similar to each other, and all of which are comparable to the corresponding values observed in other Schiff base zinc(II) complexes [18, 19]. As expected, the coordinate bonds involving amine atoms are longer than those involving imine atoms [20].

Figure 1c gives a perspective view of the complex **III** together with the atomic labeling system. The complex is a phenolate-O bridged dinuclear zinc(II) compound. Each Zn atom in the complex is five-coordinated in a square-pyramidal coordination, with two phenolate O, one imine N, and one amine N atoms from two Schiff base ligands EMP defining the basal plane, and with one **I** atom occupying the apical position. The substantial distortion of the square pyramids is revealed by the bond angles among apical and basal donor atoms, ranging from 100.1(2)° to 115.0(2)° for Zn(1), and from 107.3(2)° to 113.4(2)° for Zn(2). The Zn atoms deviate from the least-squares planes defined by the corresponding basal donor atoms in the direction of the apical positions by 0.674(2) Å for Zn(1), and 0.721(2) Å for Zn(2).

The 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, τ, which defined as $\tau = (\beta - \alpha)/60$, where α and β are the largest coordinate angles, and $\tau = 0$ represents perfect square-pyramidal, $\tau = 1$ represents perfect trigonal-bipyramidal [21]. In the present complex, the calculated

Table 2. Selected bond lengths (Å) and angles (deg) in complexes **I–IV***

Bond	*d*, Å	Bond	*d*, Å
		I	
Zn(1)–O(1)	1.915(3)	Zn(1)–N(1)	1.985(4)
Zn(1)–N(2)	2.089(3)	Zn(1)–Br(1)	2.3386(8)
Zn(2)–O(3)	1.911(3)	Zn(2)–N(3)	2.000(3)
Zn(2)–N(4)	2.107(4)	Zn(2)–Br(2)	2.3454(9)
		II	
Zn(1)–O(1)	1.925(2)	Zn(1)–N(1)	1.991(2)
Zn(1)–N(2)	2.075(2)	Zn(1)–Cl(1)	2.2128(10)
		III	
Zn(1)–O(1)	1.985(5)	Zn(1)–N(1)	2.069(8)
Zn(1)–O(2)	2.086(6)	Zn(1)–N(2)	2.240(8)
Zn(1)–I(1)	2.584(1)	Zn(2)–O(1)	2.081(5)
Zn(2)–O(2)	2.028(5)	Zn(2)–N(4)	2.103(8)
Zn(2)–N(5)	2.200(8)	Zn(2)–I(2)	2.582(1)
		IV	
Zn(1)–O(1)	2.026(2)	Zn(1)–N(1)	2.041(2)
Zn(1)–O(3)	2.279(2)	Zn(2)–N(2)	1.958(2)
Zn(2)–O(1)	2.036(2)		
Angle	ω, deg	Angle	ω, deg
		I	
O(1)Zn(1)N(1)	95.12(15)	O(1)Zn(1)N(2)	117.62(13)
N(1)Zn(1)N(2)	97.88(14)	O(1)Zn(1)Br(1)	116.07(10)
N(1)Zn(1)Br(1)	117.55(11)	N(2)Zn(1)Br(1)	110.57(10)
O(3)Zn(2)N(3)	95.81(14)	O(3)Zn(2)N(4)	121.14(14)
N(3)Zn(2)N(4)	95.50(14)	O(3)Zn(2)Br(2)	117.01(11)
N(3)Zn(2)Br(2)	118.94(11)	N(4)Zn(2)Br(2)	106.73(10)
		II	
O(1)Zn(1)N(1)	95.41(9)	O(1)Zn(1)N(2)	122.48(10)
N(1)Zn(1)N(2)	96.94(10)	O(1)Zn(1)Cl(1)	115.39(8)
N(1)Zn(1)Cl(1)	119.18(8)	N(2)Zn(1)Cl(1)	106.40(7)
		III	
O(1)Zn(1)N(1)	144.1(3)	O(1)Zn(1)O(2)	76.4(2)
N(1)Zn(1)O(2)	83.6(3)	O(1)Zn(1)N(2)	96.9(3)
N(1)Zn(1)N(2)	79.3(3)	O(2)Zn(1)N(2)	139.5(3)
O(1)Zn(1)I(1)	115.0(2)	N(1)Zn(1)I(1)	100.1(2)
O(2)Zn(1)I(1)	113.0(2)	N(2)Zn(1)I(1)	106.0(2)
O(2)Zn(2)O(1)	75.6(2)	O(2)Zn(2)N(4)	135.7(3)
O(1)Zn(2)N(4)	81.7(3)	O(2)Zn(2)N(5)	96.2(3)
O(1)Zn(2)N(5)	142.4(3)	N(4)Zn(2)N(5)	79.3(3)
O(2)Zn(2)I(2)	113.4(2)	O(1)Zn(2)I(2)	109.7(2)
N(4)Zn(2)I(2)	109.9(2)	N(5)Zn(2)I(2)	107.3(2)
		IV	
O(1)Zn(1)O(1*A*)	77.3(1)	O(1)Zn(1)N(1)	91.7(1)
O(1)Zn(1)N(1*A*)	168.7(1)	N(1)Zn(1)N(1*A*)	99.5(1)
O(1)Zn(1)O(3)	92.0(1)	O(1)Zn(1)O(3*A*)	89.3(1)
N(1)Zn(1)O(3)	88.8(1)	N(1)Zn(1)O(3*A*)	90.1(1)
O(3)Zn(1)O(3*A*)	178.3(1)	N(2)Zn(2)N(2*A*)	116.1(2)
N(2)Zn(2)O(1*A*)	114.6(1)	N(2)Zn(2)O(1)	114.4(1)
O(1)Zn(2)O(1*A*)	76.8(1)		

* Symmetry code for *A*: $-x, y, 1/2 - z$.

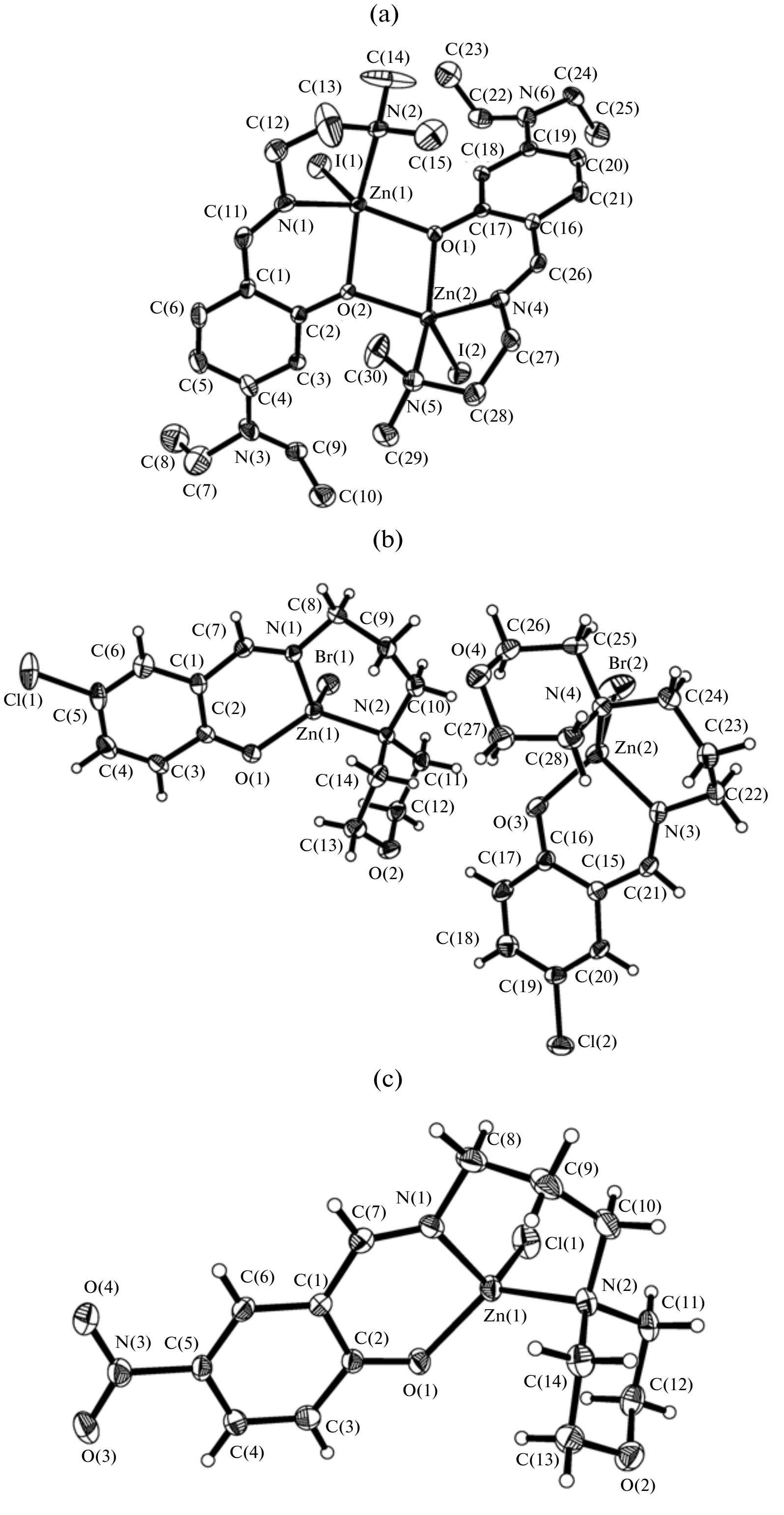

Fig. 1. Molecular structure of **I** (a), **II** (b), and **III** (c) at 30% probability displacement.

τ values are 0.077 for Zn(1) and 0.112 for Zn(2), suggesting they are best described as distorted square-pyramidal geometry.

The four-membered bridging ring Zn(1)–O(1)–Zn(2)–O(2) in complex **III** is not planar, but presents a slightly distorted roof-shape. The Zn···Zn distance in

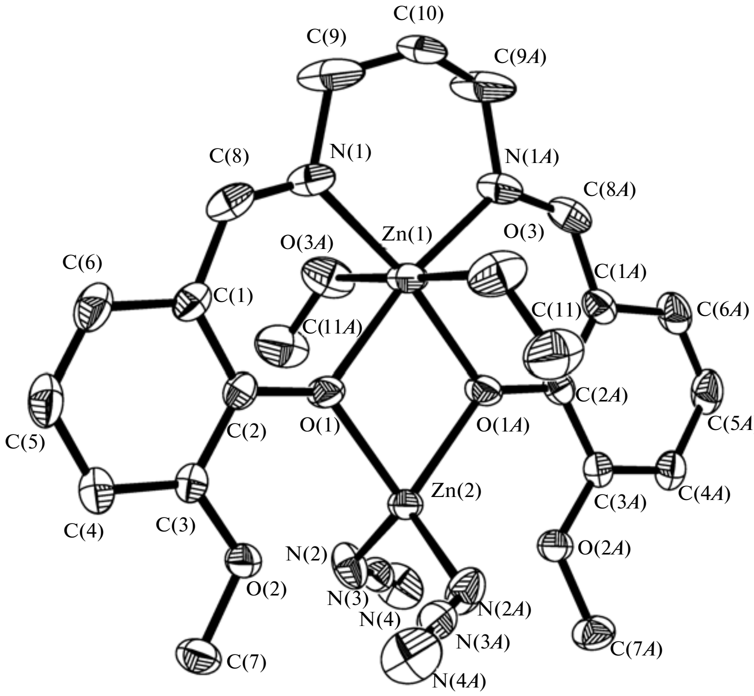

Fig. 2. Molecular structure of **IV** at 30% probability displacement. Atoms labled with A are at the symmetry position –*x*, *y*, 1/2 – *z*.

the complex is 3.194(2) Å. The Zn···Zn distance, as well as the coordinate bond lengths in the complex, are comparable to those in similar dinuclear Schiff base zinc(II) complexes [22, 23].

Fig. 2 gives a perspective view of the complex **IV** together with the atomic labeling system. The complex is a phenolate-O bridged dinuclear zinc(II) compound, which possesses crystallographic two-fold rotation axis symmetry. The inner Zn atom is six-coordinate in an octahedral geometry with two phenolate O and two imine N atoms of the Schiff base ligand MPA defining the equatorial plane and with two O atoms from two methanol molecules occupying the axial positions. The octahedron is elongated as evidenced by the longer distances of the axial bonds than those of the equatorial bonds. The outer Zn atom is four-coordinated in a tetrahedral geometry by two O atoms of MPA and two N atoms from two azide ligands. The substantial distortion of the tetrahedral coordination is revealed by the coordinate bond angles, ranging from 76.8(1)° to 116.1(2)°. The Zn···Zn distance in the complex is 3.177(2) Å. The dihedral angle between two benzene rings of MPA is 3.1(2)°. The azide ligands are nearly linear and show bent coordination mode with the Zn(2) atom [N(2)–N(3)–N(4)/Zn(2)–N(2)–N(3) = 176.0(3)°/130.9(2)°]. The Zn···Zn distance, as well as the coordinate bond lengths in the complex are comparable to those in **III** and in other similar dinuclear Schiff base zinc(II) complexes [22, 23].

In the crystal structure of **IV**, molecules are linked through intermolecular O–H···N hydrogen bonds to forming 1D chains, as shown in Fig. 3.

Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of complexes **I** and **II**. For the DT–TGA of **I** (Fig. 4a), the first step started at about 220°C and was completed at about 378°C, corresponding to the loss of the Br ligand. The observed weight loss of 18.5% is very close to the calculated value (18.7%). The second step, from 380 to 610°C, corresponds to the loss of the Schiff base ligand and the formation of the final product (ZnO). The observed weight loss of 63.5% in this step is close to the calculated value (62.3%). The total weight loss of 82.0% is close to the calculated value (81.0%). For the DT–TGA of **II** (Fig. 4b), the first step started at about 230°C and was completed at about 290°C, corresponding to the loss of the Cl ligand. The observed weight loss of 9.4% is close to the calculated value (9.0%). The second step, from 300 to 637°C, corresponds to the loss of the Schiff base ligand and the formation of the final product (ZnO). The observed weight loss of 71.5% in this step is close to the calculated value (70.2%). The total weight loss of 80.9% is close to the calculated value (79.3%).

Owing to the excellent luminescent properties of d^{10} metal ions, the solid state photoluminescence of the complexes were investigated at room temperature. For **I**, upon excitation at 367 nm, the emission spectrum of the complex shows one emission band at 449 nm

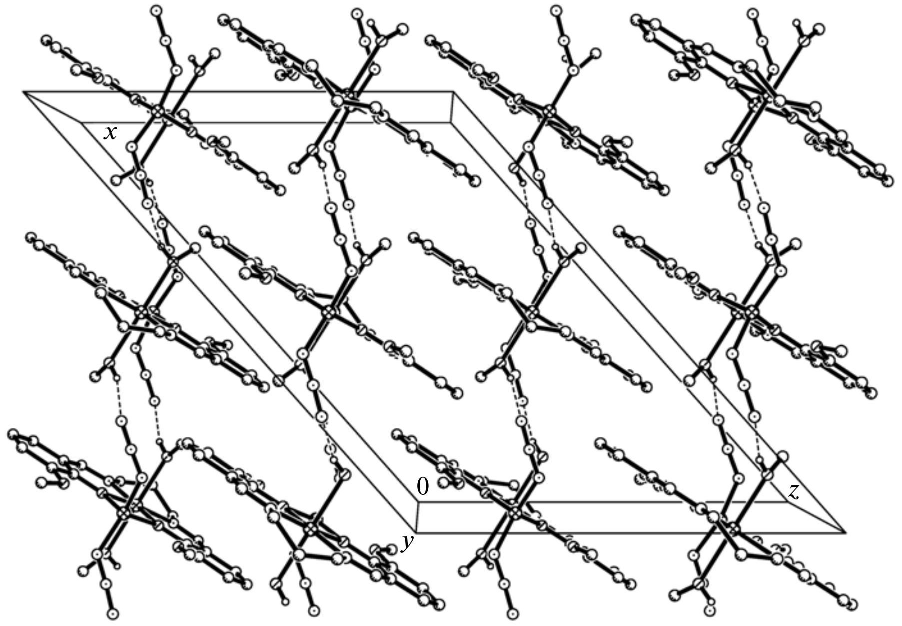

Fig. 3. The 1D chain structure of **IV**, viewed along the *y* axis. Hydrogen bonds are drawn as dashed lines.

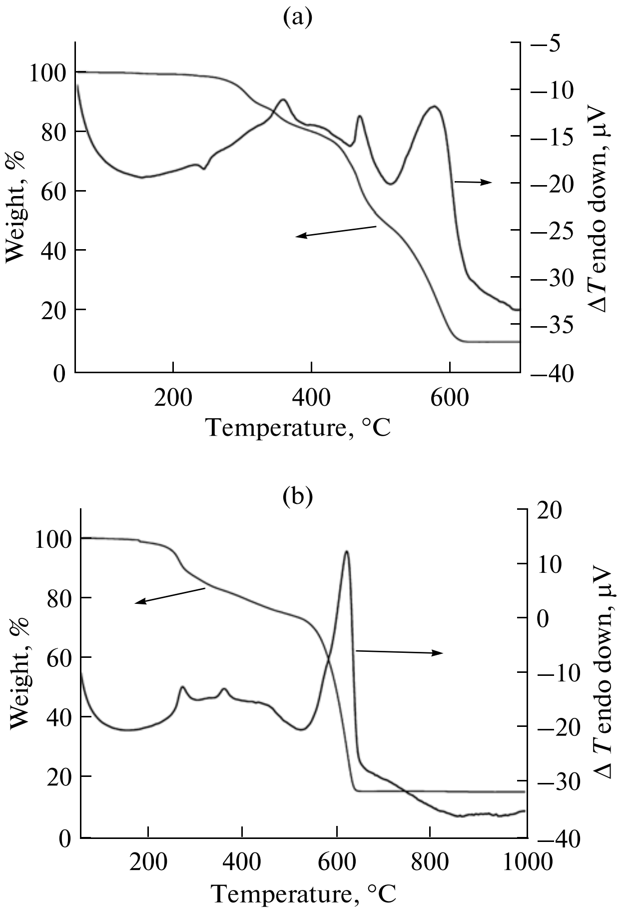

Fig. 4. DT–TGA curve of **I** (a) and **II** (b).

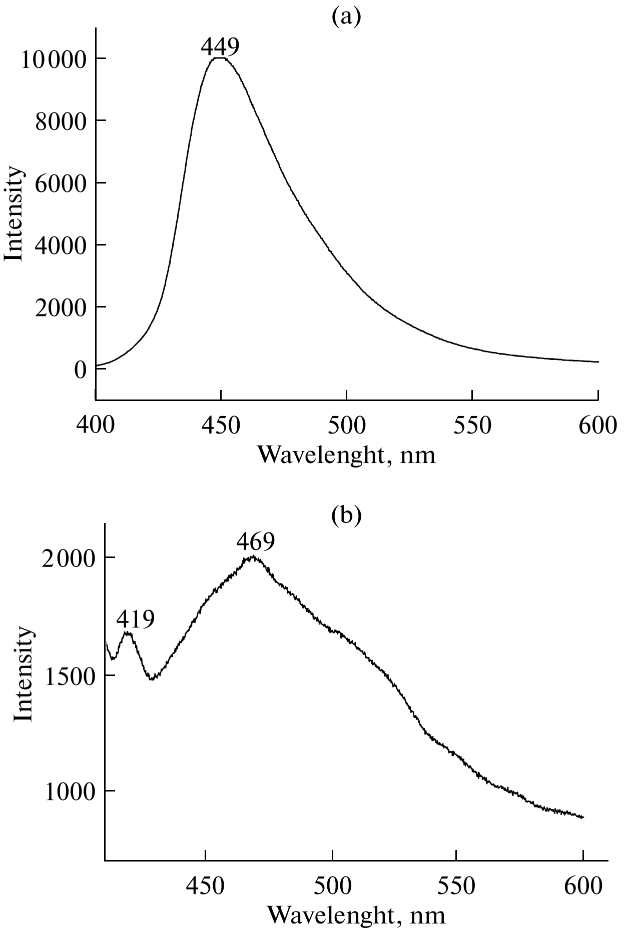

Fig. 5. Solid state fluorescent emission spectrum of **I** (a) and **II** (b).

(Fig. 5a). For **II**, upon excitation at 367 nm, the emission spectrum of the complex shows two emission bands at 419 and 469 nm (Fig. 5b).

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