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Syntheses, Characterization, Crystal Structures and Fluorescence Property of Zinc(II) Complexes with Schiff Bases[1]

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Abstract—Two new mononuclear Schiff base zinc(II) complexes, $[ZnCl_2(L^1)] \cdot MeOH$ (**I**) and $[Zn(L^2)_2]$ (**II**) (L^1 = 2-bromo-4-chloro-6-[(2-ethylammonioethylimino)methyl]phenolate; L^2 = 2-bromo-4-chloro-6-(isopropyliminomethyl)phenolate), have been prepared and characterized by elemental analyses, infrared and UV-Vis spectroscopy, and single-cyrstal X-ray diffraction (CIF files CCDC nos. 1408962 (**I**), 1408961 (**II**)). Complex **I** crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 9.859(1)$, $b = 13.015(2)$, $c = 19.817(3)$ Å, $\alpha = 73.591(2)°$, $\beta = 76.032(2)°$, $\gamma = 82.966(2)°$, $V = 2363.0(5)$ Å^3, $Z = 4$, $R_1 = 0.0925$, and $wR_2 = 0.2257$. Complex **II** crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 7.6387(7)$, $b = 22.307(2)$, $c = 21.443(2)$ Å, $\beta = 96.216(3)°$, $V = 3632.4(6)$ Å^3, $Z = 8$, $R_1 = 0.0651$, and $wR_2 = 0.1100$. The both Zn atoms in **I** is four-coordinated in a tetrahedral geometry by the NO donor set of the Schiff base ligand, and two Cl ligands. The Zn atom in **II** is in a tetrahedral geometry by two N and two O atoms from two Schiff base ligands. Crystals of the complexes are stabilized by hydrogen bonds and weak $\pi\cdots\pi$ interactions. Fluorescence property of the complexes have been determined.

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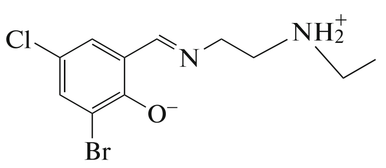
INTRODUCTION

Schiff base complexes have received considerable attention for their importance in the field 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 [6]. Schiff base zinc complexes have 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 two new Schiff base zinc(II) complexes, $[ZnCl_2(L^1)] \cdot MeOH$ (**I**) and $[Zn(L^2)_2]$ (**II**) (L^1 = 2-bromo-4-chloro-6-[(2-ethylammonioethylimino)methyl]phenolate; L^2 = 2-bromo-4-chloro-6-(isopropyliminomethyl)phenolate).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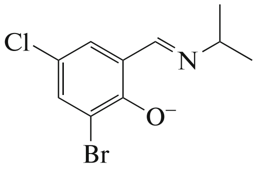
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EXPERIMENTAL

Materials and measurements. Commercially available 3-bromo-5-chlorosalicylaldehyde, *N*-ethylethane-1,2-diamine, and isopropylamine were purchased from Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. The Schiff bases were prepared according to the literature procedure [14]. C, H, and N elemental analyses wre performed with a Per-

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kin-Elmer elemental analyser. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region. Fluorescence spectra were recorded with an F-2500 FL Spectrophotometer analyzer.

Synthesis of I. A MeOH solution (5 mL) of $ZnCl_2$ (0.1 mmol, 13.6 mg) was added to a MeOH solution (10 mL) of L^1 (0.1 mmol, 30.5 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 MeOH and dried in a vacuum over anhydrous $CaCl_2$. The yield was 21.0 mg (44%).

IR data (KBr; ν, cm^{-1}): 3453 m, 3126 m, 1629 s, 1509 w, 1446 s, 1308 w, 1207 m, 1157 s, 1075 s, 993 m, 861 m, 745 m, 541 m, 465 m. UV-Vis data in acetonitrile (λ_{max}, nm (ε, L mol^{-1} cm^{-1})): 270 (10255), 387 (7860).

For $C_{12}H_{18}N_2O_2Cl_3BrZn$

anal. calcd., %:	C, 30.41;	H, 3.83;	N, 5.91.
Found, %:	C, 30.23;	H, 3.92;	N, 6.03.

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 L^2 (0.1 mmol, 27.6 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 MeOH and dried in a vacuum over anhydrous $CaCl_2$. The yield was 33.5 mg (54%).

IR data (KBr; ν, cm^{-1}): 1620 s, 1433 s, 1150 s, 1080 s, 955 m, 851 m, 743 w, 532 m. UV-Vis data in acetonitrile (λ_{max}, nm (ε, L mol^{-1} cm^{-1})]: 275 (11730), 381 (8570).

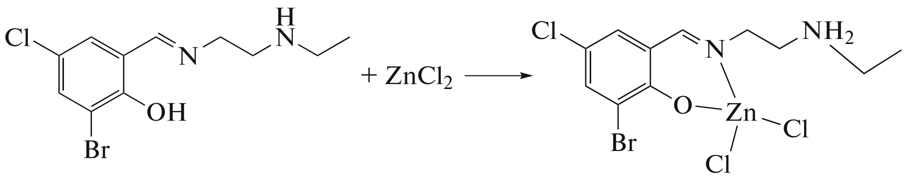
For $C_{20}H_{20}N_2O_2Cl_2Br_2Zn$

anal. calcd., %:	C, 38.96;	H, 3.27;	N, 4.54.
Found, %:	C, 39.10;	H, 3.38;	N, 4.43.

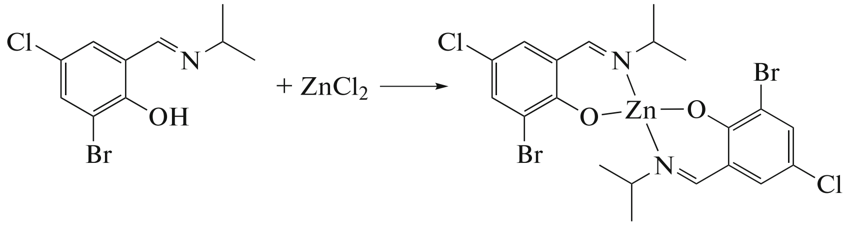
X-ray structure determination. Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector with MoK_α radiation (λ = 0.71073 Å). The collected data were reduced using SAINT [15], and multi-scan absorption corrections were performed using SADABS [16]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using SHELXTL [17]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. 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. 1408962 (**I**), 1408961 (**II**)); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The complexes were prepared by the reaction of the Schiff bases with zinc chloride:



(I)



(II)

Table 1. Crystallographic data and refinement parameters for structures **I** and **II**

Parameter	Value	
	I	**II**
Fw	473.9	616.5
Crystal shape/color	Block/colourless	Block/colourless
Crystal size, mm	0.23 × 0.23 × 0.20	0.17 × 0.15 × 0.15
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a, Å	7.6387(7)	9.859(1)
b, Å	22.307(2)	13.015(2)
c, Å	21.443(2)	19.817(3)
α, deg		73.591(2)
β, deg	96.216(3)	76.032(2)
γ, deg		82.966(2)
V, Å^3	3632.4(6)	2363.0(5)
Z	8	4
μ(MoK_α), mm^{-1}	3.997	4.666
ρ_{calcd}, g cm^{-3}	1.733	1.733
Reflections/parameters	6447/385	8509/531
Restraints	0	0
Observed reflections ($I \geqslant 2\sigma(I)$)	4192	4947
F(000)	1888	1216
T_{min}	0.4600	0.5043
T_{max}	0.5020	0.5412
Goodness of fit on F^2	1.094	1.024
R_1, wR_2 ($I \geqslant 2\sigma(I)$)*	0.0651, 0.1100	0.0925, 0.2257
R_1, wR_2 (all data)*	0.1185, 0.1279	0.1534, 0.2730

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

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

Bond	*d*, Å	Bond	*d*, Å
I			
Zn(1)–O(1)	1.938(5)	Zn(1)–N(1)	2.036(6)
Zn(1)–Cl(2)	2.223(2)	Zn(1)–Cl(3)	2.231(2)
Zn(2)–O(2)	1.943(5)	Zn(2)–N(3)	2.030(5)
Zn(2)–Cl(5)	2.216(2)	Zn(2)–Cl(6)	2.241(2)
II			
Zn(1)–O(1)	1.923(7)	Zn(1)–O(2)	1.909(7)
Zn(1)–N(1)	1.981(9)	Zn(1)–N(2)	1.986(9)
Zn(2)–O(3)	1.950(7)	Zn(2)–O(4)	1.910(7)
Zn(2)–N(3)	1.990(9)	Zn(2)–N(4)	1.987(9)
Angle	ω, deg	Angle	ω, deg
I			
O(1)Zn(1)N(1)	95.0(2)	O(1)Zn(1)Cl(2)	111.59(16)
N(1)Zn(1)Cl(2)	113.01(18)	O(1)Zn(1)Cl(3)	115.60(17)
N(1)Zn(1)Cl(3)	107.46(18)	Cl(2)Zn(1)Cl(3)	112.84(9)
O(2)Zn(2)N(3)	95.0(2)	O(2)Zn(2)Cl(5)	112.04(16)
N(3)Zn(2)Cl(5)	112.46(17)	O(2)Zn(2)Cl(6)	114.12(17)
N(3)Zn(2)Cl(6)	107.58(17)	Cl(5)Zn(2)Cl(6)	114.01(10)
II			
O(2)Zn(1)O(1)	115.5(3)	O(2)Zn(1)N(1)	109.4(4)
O(1)Zn(1)N(1)	94.8(3)	O(2)Zn(1)N(2)	96.1(3)
O(1)Zn(1)N(2)	109.8(3)	N(1)Zn(1)N(2)	132.5(4)
O(4)Zn(2)O(3)	110.9(3)	O(4)Zn(2)N(4)	97.0(3)
O(3)Zn(2)N(4)	107.9(3)	O(4)Zn(2)N(3)	114.9(4)
O(3)Zn(2)N(3)	95.6(3)	N(4)Zn(2)N(3)	130.3(4)

For complex **I**, the Cl atoms are coordinated to the Zn center. While for complex **II**, Cl atoms are not parcipatate in coordination. Both complexes are crystallized as colourless single crystals, which are stable in air at room temperature, soluble in common polar organic solvents, such as DMSO, DMF, MeOH, EtOH, MeCN, and Me_2CO, and insoluble in water and Et_2O.

The medium and sharp absorption at 3126 cm^{-1} and the medium and broad absorption centered at 3453 cm^{-1} for complex **I** can be assigned to ν(N–H) and ν(O–H), respectively. Strong absorptions centered at 1629 cm^{-1} for complex **I** and 1620 cm^{-1} for complex **II** are assigned to azomethine, ν(C=N) [18]. In both complexes, the Schiff base ligand coordina-

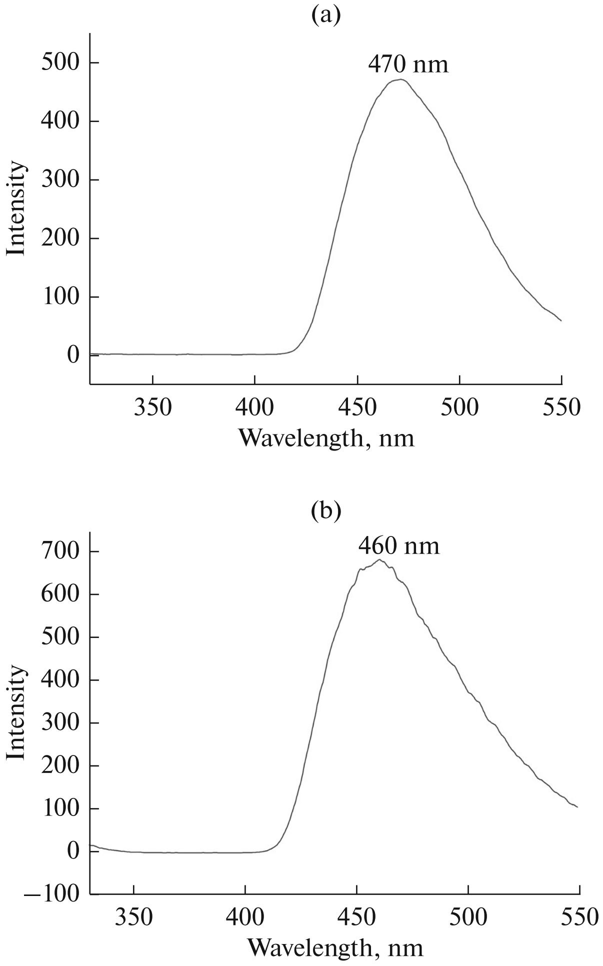


Fig. 1. Solid state fluorescent emission spectra of **I** (a) and **II** (b).

tion to the metal atoms is also substantiated by weak bands at low wavenumbers.

In the UV-Vis spectra of the complexes, the absorption centered at about 380 nm is assigned to ligand-to-metal charge transfer. The absorption frequencies ascribed to the benzene π-π^* transition are centered at 270 nm for complex **I** and 275 nm for complex **II**.

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 289 nm, the emission spectrum of the complex shows one emission band at 470 nm (Fig. 1a). For **II**, upon excitation at 291 nm, the emission spectrum of the complex shows one emission band at 460 nm (Fig. 1b).

The molecular structure of complex **I** is shown in Fig. 2a. The asymmetric unit of the compound contains two independent zinc complex molecules and two methanol molecules. The Zn atom is coordinated by the phenolate O and imine N atoms of the Schiff base ligand, and two chloride atoms, forming a tetrahedral coordination. The coordinate bond angles range from 95.0(2)° to 115.6(2)° for Zn(1) molecule, and from 95.0(2)° to 114.1(2)° for Zn(2) molecule, indicating the difference from the ideal value of 109.5° 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 two complex molecules are similar to each other, and all of which are comparable to the corresponding values observed in similar Schiff base zinc(II) complexes [19, 20]. The amine atoms are protonated, which are not involved in coordination. In

Table 3. Geometric parameters of hydrogen bonds for complexes **I**, **II***

D–H···A	Distance, Å			D–H···A, deg
	D–H	H···A	D···A	
		I		
O(4)–H(4)···Br(2)^{i}	0.82	2.88	3.492(6)	133
O(4)–H(4)···O(2)^{i}	0.82	2.09	2.856(7)	154
O(3)–H(3)···Br(1)	0.82	2.99	3.516(6)	125
O(3)–H(3)···O(1)	0.82	2.09	2.875(7)	160
N(4)–H(4*B*)···Cl(6)	0.90	2.47	3.253(7)	145
N(4)–H(4*A*)···Cl(5)^{i}	0.90	2.97	3.553(7)	124
N(4)–H(4*A*)···O(4)	0.90	2.02	2.772(8)	141
N(2)–H(2*B*)···Cl(2)^{i}	0.90	2.68	3.322(6)	130
N(2)–H(2*B*)···O(3)^{i}	0.90	2.12	2.818(8)	134
N(2)–H(2*A*)···Cl(3)	0.90	2.37	3.153(6)	146
		II		
C(16)–H(16)···O(3)^{ii}	0.93	2.55	3.424(3)	157
C(17)–H(17)···O(3)^{ii}	0.93	2.58	3.460(3)	158
C(37)–H(37)···O(1)^{iii}	0.93	2.48	3.395(3)	167

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

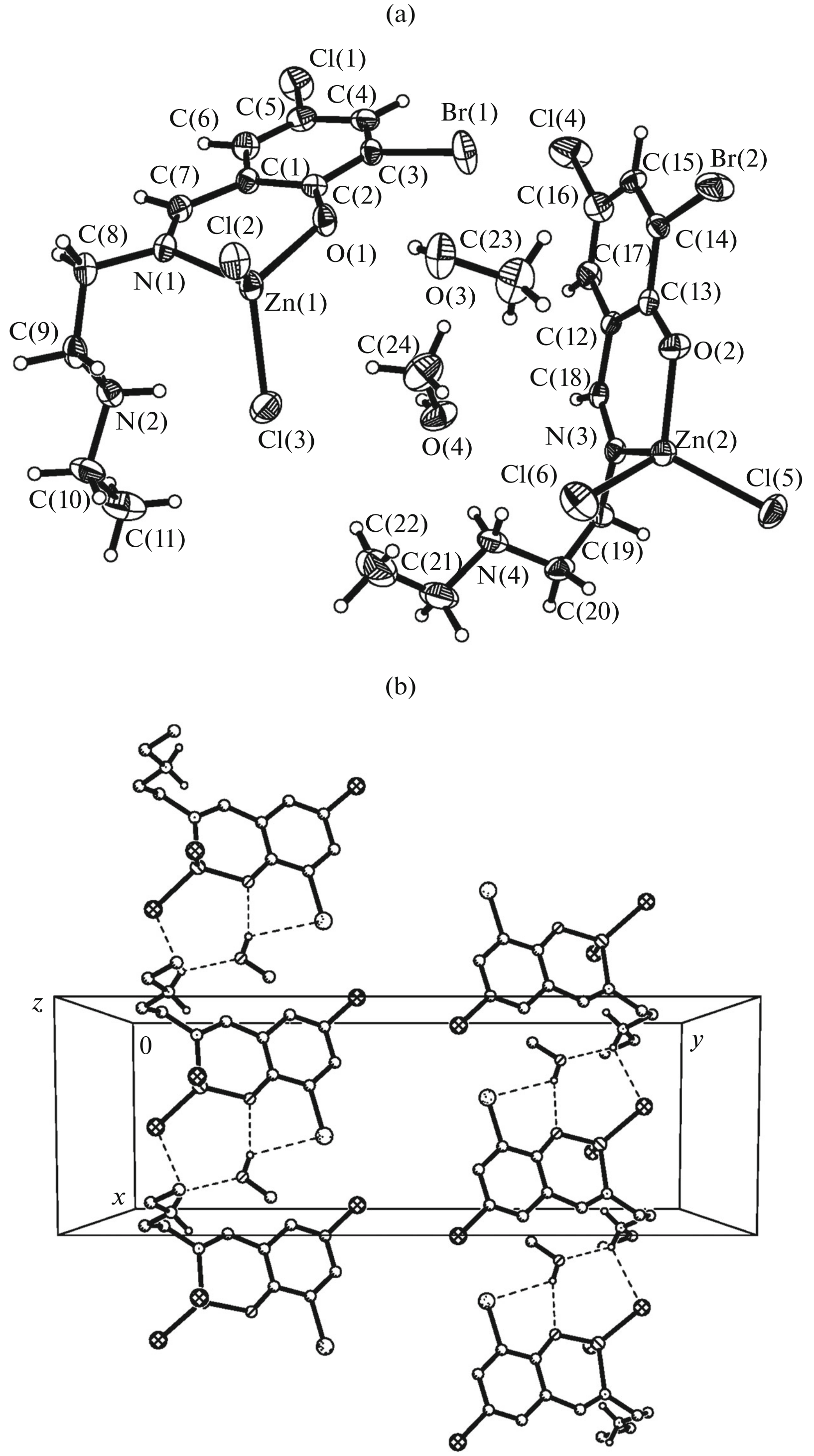


Fig. 2. Molecular structure of **I** at 30% probability displacement (a); the 1D chain structure of **I**, viewed along the *z* axis (hydrogen bonds are drawn as dashed lines) (b).

the crystal structure, the complex molecules are linked by methanol molecules through intermolecular O–H···Br, O–H···O, N–H···Cl, and N–H···O hydrogen bonds (Table 3), to form 1D chains along the *x* axis direction (Fig. 2b).

The molecular structure of complex **II** is shown in Fig. 3a. The asymmetric unit of the compound contains two independent zinc complex molecules. The both Zn atoms is coordinated by two phenolate O and two imine N atoms from two Schiff base ligands,

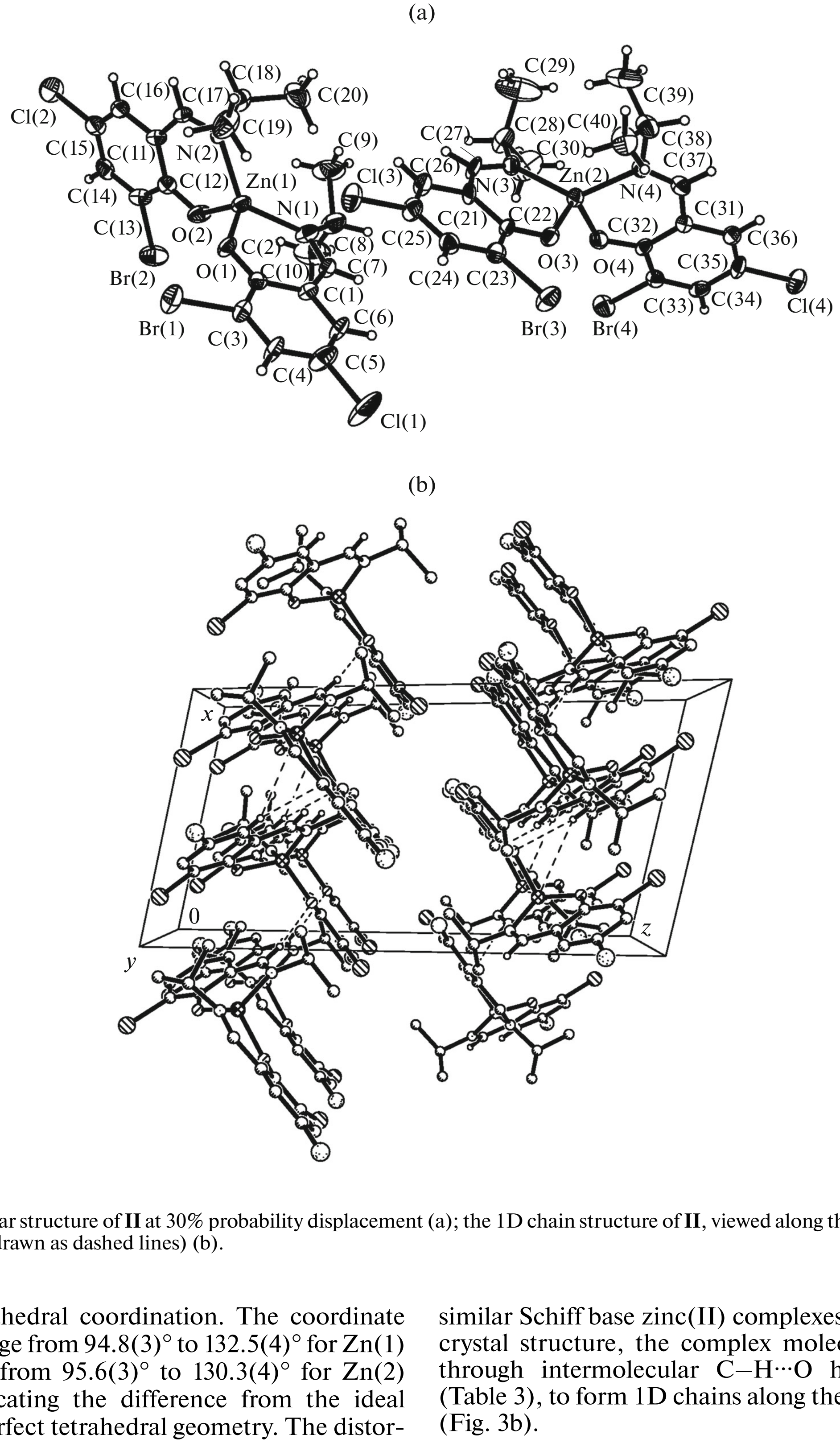


Fig. 3. Molecular structure of **II** at 30% probability displacement (a); the 1D chain structure of **II**, viewed along the *y* axis (hydrogen bonds are drawn as dashed lines) (b).

forming a tetrahedral coordination. The coordinate bond angles range from 94.8(3)° to 132.5(4)° for Zn(1) molecule, and from 95.6(3)° to 130.3(4)° for Zn(2) molecule, indicating the difference from the ideal value for the perfect tetrahedral geometry. The distortion 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 two complex molecules are similar to each other, and all of which are comparable to the corresponding values observed in similar Schiff base zinc(II) complexes [21, 22]. In the crystal structure, the complex molecules are linked through intermolecular C–H···O hydrogen bonds (Table 3), to form 1D chains along the *x* axis direction (Fig. 3b).

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