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Synthesis, Spectral and Thermal Studies of Zinc(II) and Mercury(II) Complexes with Bidentate Schiff-Base Ligand (234-MeO-Ba)$_2$En: the Crystal Structure of Zn(234-MeO-Ba)$_2$En)I$_2$[1]

A. D. Khalaji[a, *], S. Jalali Akerdi[b], G. Grivani[b], H. Stoeckli-Evans[c], and D. Das[d]
[a] *Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran*
[b] *School of Chemistry, Damghan University, Damghan, Iran*
[c] *Institute of Physics, Laboratory of Physical Chemistry, University of Neuchâtel, Neuchâtel, Switzerland*
[d] *Department of Chemistry, the University of Burdwan, Burdwan, West Bengal, India*
**E-mail: ad.khalaji@gu.ac.ir*

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Abstract—New Symmetric bidentate Schiff-base ligands N,N′-*bis*(2,3,4-trimethoxybenzylidene)-1,2-diaminoethane, (234-MeO-Ba)$_2$En, and its corresponding zinc(II) and mercury(II) complexes, Zn((234-MeO-Ba)$_2$En)I$_2$ (**I**), Hg((234-MeO-Ba)$_2$En)Cl$_2$ (II) have been synthesized and characterized by elemental analyses (CHN), FT-IR and ^{1}H NMR spectroscopy. The thermal behaviors of complexes were study using thermogravimetry in order to evaluate their thermal stability and thermal decomposition pathways. The crystal structure of **I** was determined from single-crystal X-ray diffraction. The coordination polyhedron about the zinc(II) center in complex **I** is best described as a distorted tetrahedron.

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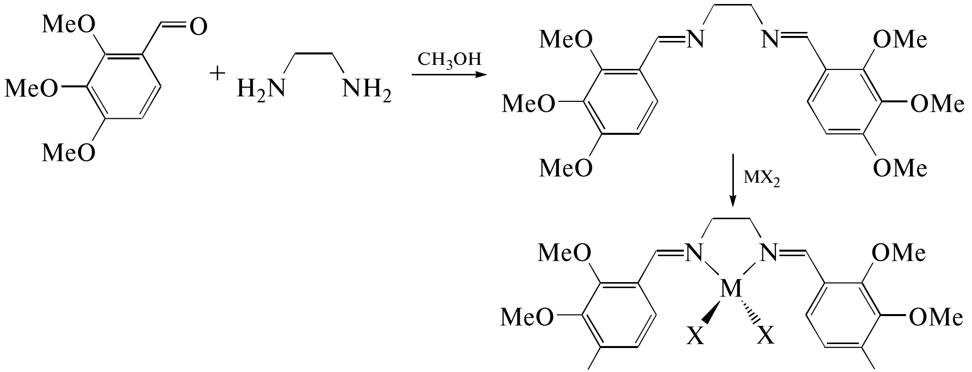
INTRODUCTION

The design and preparation of new Schiff-base ligands is an interesting step in the development of transition metal complexes, which exhibit unique properties and geometry [1, 2]. These ligands have played a special role as chelating ligands in transition metal complexes due to stability of complexes under a variety of oxidative and reductive conditions [3, 4]. Transition metal complexes with bidentate Schiff-base ligands, find applications as catalysts in the synthesis of organic compounds [5], these complexes are an important class of coordination chemistry not only because they have found important applications in catalysis, but also they have interesting properties and geometries [6, 7].

Although the coordination chemistry of symmetric bidentate Schiff-base ligands with copper(I) has been extensively studied [6, 7], there are few data on zinc(II) [8, 9] and mercury(II) [10] complexes with these ligands. In a continuation of our work on the preparation of transition metal complexes with bidentate Schiff-base ligands [6, 7, 9], here we report the synthesis and characterization of two new zinc(II) and mercury(II) complexes with Schiff-base ligand **(234-MeO-Ba)$_2$En**)–Zn((234-MeO-Ba)$_2$En)I$_2$ (**I**) and Hg((234-MeO-Ba)$_2$En)Cl$_2$ (**II**). The scheme of the synthesis of the ligand and its complexes **I** and **II** is given below:



(I, II)

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where X = I for Zn(II) and Cl for Hg(II) complexes.

EXPERIMENTAL

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Infrared spectra were recorded using KBr disks on a FT-IR PerkinElmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. ^{1}H NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz for the Schiff-base ligands and their complexes. All chemical shifts are reported in δ units downfield from TMS. Thermogravimetric analyses were done on a PerkinElmer TGA/DTA lab system **I** (Technology by SII) in nitrogen atmosphere with a heating rate of 20°C/min from 35–700°C.

Synthesis of (234-MeO-Ba)$_2$En. A solution of 2,3,4-trimethoxybenzaldehyde (3.92 g, 0.02 mol) in 25 ml methanol was heated for 15 min at 50°C and then stirred for about 15 min . To this stirring solution, a solution of ethylenediamine (0.6 g, 0.01 mol) in 15 ml methanol was added dropwise with constant stirring. The mixture was heated at about 50°C for 1.5 h and then allowed to cool overnight at 273 K. The resulting crude solid was collected by filtration and dried at room temperature. Crystals were grown by the slow evaporation technique at room temperature in 25 ml of methanol as a solvent for 5 days. At the period of supersaturation, tiny crystals were nucleated. They were allowed to grow to a maximum possible dimension and then filtered. The yield of colorless crystals was 88%.

For $C_{22}H_{28}N_2O_6$

anal. calcd., %:	C, 63.44;	H, 6.78;	N, 6.73.
Found, %:	C, 63.49;	H, 6.79;	N, 6.76.

IR (KBr; ν, cm^{-1}): 2834 s (CH=N), 2847–3047 m (CH aromatic and aliphatic), 1637 s (C=N); ^{1}H NMR ($CDCl_3$; δ, ppm): 3.81 (s., 6H), 3.83 (s., 6H), 3.87 (s., 6H), 4.02 (s., 4H), 6.67 (d., 2H), 7.64 (d., 2H), 8.51 (s., 2H).

Synthesis of I. To a stirring solution of the (234-MeO-Ba)$_2$En ligand (0.2 mmol, in 5 ml of chloroform) was added ZnI_2 (0.2 mmol) in 10 ml of methanol, and the mixture was stirred for 10 min in air at room temperature and then was left at 273 K for several days without disturbance of yielding suitable crystals of **I** that subsequently were filtered off and washed with Et_2O. The yield of colorless crystals was 83%.

For $C_{22}H_{28}N_2O_6I_2Zn$

anal. calcd., %:	C, 35.91;	H, 3.83;	N, 3.80.
Found, %:	C, 35.96;	H, 3.60;	N, 3.81.

IR (KBr; ν, cm^{-1}): 2833 s (CH=N), 2855–3057 m (CH aromatic and aliphatic), 1628 s (C=N); ^{1}H NMR ($CDCl_3$; δ, ppm): 3.70 (s., 6H), 3.71 (s., 6H), 3.79 (s., 6H), 3.81 (s., 4H), 6.83 (d., 2H), 7.53 (d., 2H), 8.37 (s., 2H).

Synthesis of II. To a stirring solution of the (234-MeO-Ba)$_2$En ligand (0.2 mmol, in 5 ml of acetonitrile) was added $HgCl_2$ (0.2 mmol) in 20 ml methanol, and the mixture was refluxed for 30 min in air. The solvent was evaporator on a rotary evaporated at 40°C under reduced pressure. The white solid residue was dissolved in 15 ml of chloroform and filtered off. The filtrate was left at 273 K for several days without disturbance of yielding microcrystals of **II** that subsequently were filtered off and washed with Et_2O. The yield of colorless crystals was 75%.

For $C_{22}H_{28}N_2O_6Cl_2Hg$

anal. calcd., %:	C, 38.40;	H, 4.10;	N, 4.07.
Found, %:	C, 37.66;	H, 3.82;	N, 4.08.

IR (KBr; ν, cm^{-1}): 2835 s (CH=N), 2861–3035 m (CH aromatic and aliphatic), 1625 s (C=N); ^{1}H NMR ($CDCl_3$; δ, ppm): 3.73 (s., 6H), 3.77 (s., 6H), 3.82 (s., 6H), 3.87 (s., 4H), 6.87 (d., 2H), 7.63 (d., 2H), 8.49 (s., 2H).

X-ray crystallography determination. Single crystals suitable for the X-ray crystallographic abalysis of **I** were obtained as colorless plates by slow evaporation of the solvent methanol at 273 K (crystal size of **I**: 0.10 × 0.18 × 0.24 mm). The intensity data for **I** were collected at 173 K on a Stoe Mark II-Image Plate Diffraction System [11] equipped with a two-circle goniometer and using MoK_α graphite monochromated radiation ($\lambda = 0.71073$ Å). Image plate distance was 130 mm, ω rotation scans 0°–180° at $\phi = 0°$, and 0°–62.0° at $\phi = 90°$, step $\Delta\omega = 1.3°$, exposures of 7 min per image, 2θ range 1.76°–52.59°, $d_{\min}$–$d_{\max}$ = 23.107–0.802 Å. The structure was solved by direct methods using the SHELXS-97 programm [12]. The refinement and all further calculations were carried out using SHELXL-97 [12]. The H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. An empirical absorption correction was applied using the MULscanABS routine in PLATON [13]. The molecule has crystallographic C_2 symmetry with the zinc(II) atom sitting on the 2-fold rotation axis. Crystallographic data and details of data collection and structure refinement are given in Table 1.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 784976; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystallographic data and structure refinement for **I**

Parameters	Value
Formula weight	735.63
Crystal system; space group	Monoclinic; *C*2/c
a, Å	10.6239(6)
b, Å	12.0163(6)
c, Å	20.4757(13)
β, deg	96.290(5)
V, Å^3	2598.2(3)
Z	4
ρ_{calcd}, mg m^{-3}	1.881
F(000)	1432
μ, mm^{-1}	3.36
Index ranges	$-14 \le h \le 14$, $-16 \le k \le 16$, $-28 \le l \le 27$
T_{min}	0.693
T_{max}	1.315
Measured reflections	20027
Independent reflections	3507
Reflection with $I > 2\sigma(I)$	2617
R_{int}	0.088
S	1.04
R ($F^2 > 2\sigma(F^2)$)	0.050
wR (F^2)*	0.106
Parameters	153
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.25/–0.96

$^*w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 7.8636P]$, where $P = (F_o^2 + 2F_c^2)/3$.

RESULTS AND DISCUSSION

The Schiff-base ligand N,N′-*bis*(2,3,4-trimethoxybenzylidene)-1,2-diaminoethane, (234-MeO-Ba)$_2$En, was synthesized by mixing of ethylenediamine and 2,3,4-trimethoxybenzaldehyde. The reaction of MX$_2$ and 234-MeO-Ba)$_2$En in methnol–chloroform or methanol–acetonitrile solvent mixture at room temperature (**I**) and at 313 K (**II**) results in monomeric complexes. The Schiff-base ligand is soluble in a range of common organic solvents, such as methanol, ethanol, chloroform, dichloromethane, acetone, acetonitrile, dimethylformamide and dimethylsulfoxide, but insoluble in water. The complexes are only soluble in coordination solvents, such as dimethylformamide, and dimethylsulfoxide but insoluble in a range of common organic solvent, such as methanol, ethanol, chloroform, dichloromethane, acetone, acetonitrile, and water.

^{1}H NMR spectra of the ligand was recorded using CDCl$_3$ and its zinc(II) and mercury(II) complexes were recorded using DMSO-*d*^{6} are summarized in Experimental and are shown in Fig. 1. The ^{1}H NMR spectra of the ligand and its complexes suggest that the ligand has symmetrical structure in the complexes. The Zn(II) and Hg(II) complexes exhibit similar signals to the free ligands, indicating the coordination of the ligands to the metal ions [8–10]. All methylene and methoxy protons appear as a singlet in the region 3.6–4.0 ppm. In a region of 6.60–7.65 ppm chemical schifts were assigned to hydrogen of symmetrical aromatic ring of ligands. The ^{1}NMR spectra of the Schiff-base ligands and their complexes showed a singlet in the region 8.37–8.65 ppm, which has been assigned to the azomethine (HC=N) proton. The most characteristic absorptions of the bidentate Schiff-base ligand (234-MeO-Ba)$_2$En and its zinc(II) and mercury(II) complexes are presented in Experimental. The complexes exhibit ligand absorption at different frequencies indicating the coordination of the ligands [8–10]. The ν(C=N) band, which appear at 1637 cm^{-1} in the free ligand (234-MeO-Ba)$_2$En shift to lower frequency (1628 cm^{-1} (**I**) and 1625 cm^{-1} (**II**)) upon complexation.

Thermogravimetric analyses of the complexes under N$_2$ were examined, and the TG curves are shown in Fig. 2. Complex **I** is stable up to 470 K, and during further heating undergoes decomposition in three stages. Complex **I** shows a weight loss of 20.68% (~152.12 g) in the temperature range 470–487 K, 28.52% (~209.80 g) in the temperature range 487–824 K and 29.56% (~217.45 g) in the temperature range 824–1015 K.

Mercury(II) complex (**II**) is stable up to 449 K, and during further heating undergoes decomposition in two stages. In the first stage, complex **II** shows a weight loss of 50.55% (~347.77 g) in the temperature range 449–571 K and in the second decomposition stag, shows a weight loss of 45.51% (~313.09 g) in the temperature range 571–1015 K.

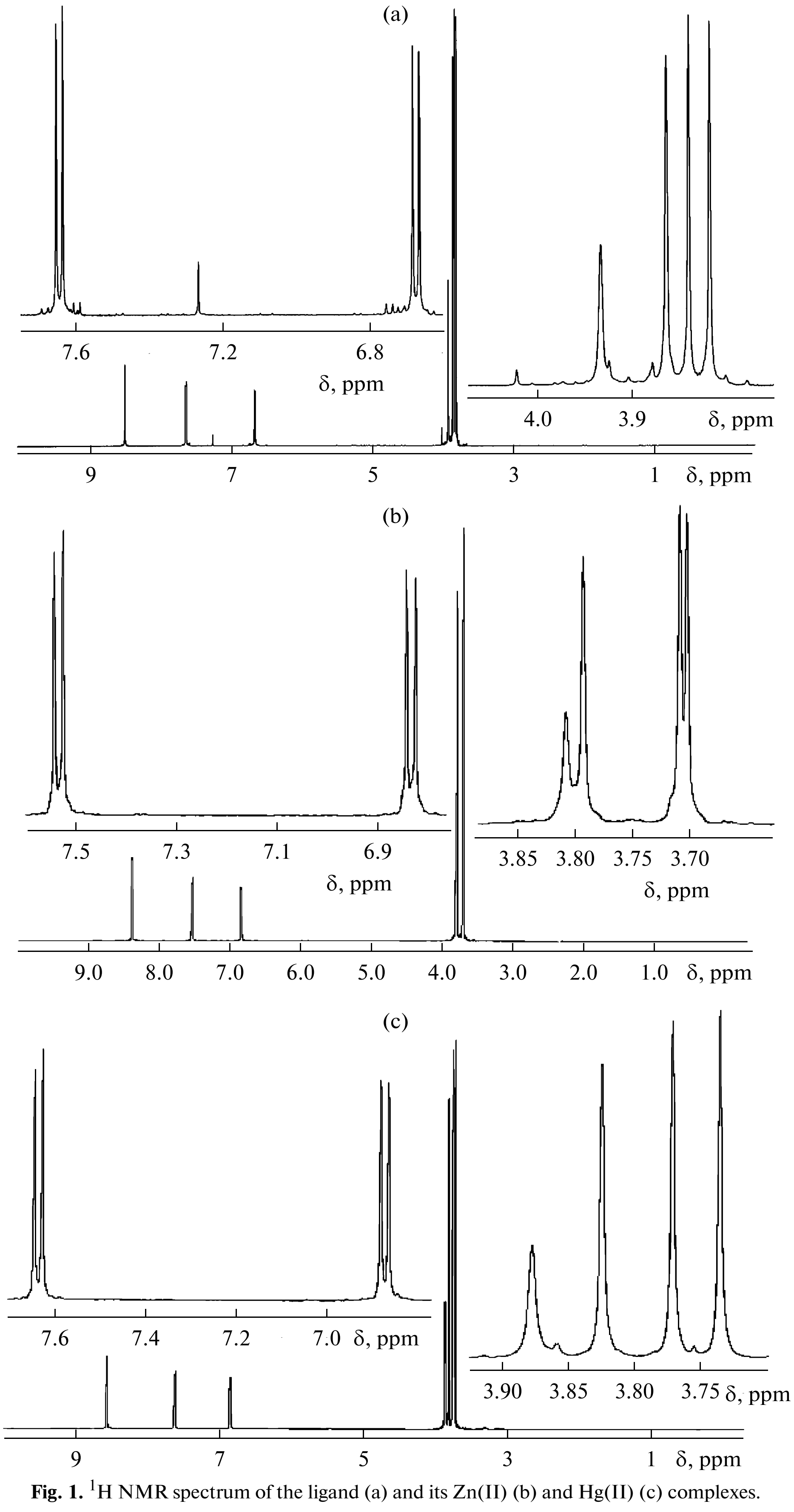

Fig. 1. ^{1}H NMR spectrum of the ligand (a) and its Zn(II) (b) and Hg(II) (c) complexes.

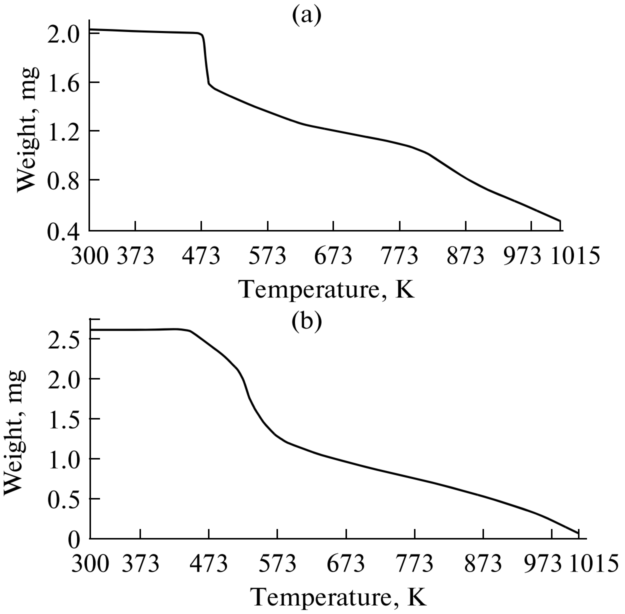

Fig. 2. The TG curves of the Zn(II) (a) and Hg(II) (b) complexes.

The molecular structure of **I** with the atom-numbering schemes is presented in Fig. 3. Selected bond distances and angles are given in Table 2. The molecular structure of **I** shows that zinc(II) is coordinated by the bidentate Schiff-base ligand (234-MeO-Ba)En_2 and two iodine ions. A tetrahedral geometry might be expected for a four coordinated zinc(II) center, the geometry around the zinc(II) ion in **I** is distorted by the restricting bite of chelate angle $N(1)Zn(1)N(1)^i$ (83.33(15)° of the Schiff-base ligands. This angle is in the range of 82°–89° found for ethylenediamine chelate compounds [6–10] and much less than 109.5°. On the contrary the $I(1)Zn(1)I(1)^i$ angle has opened up to 126.56(3)°. The NZnI angles are also distorted from the tetrahedral valueses (Table 2).

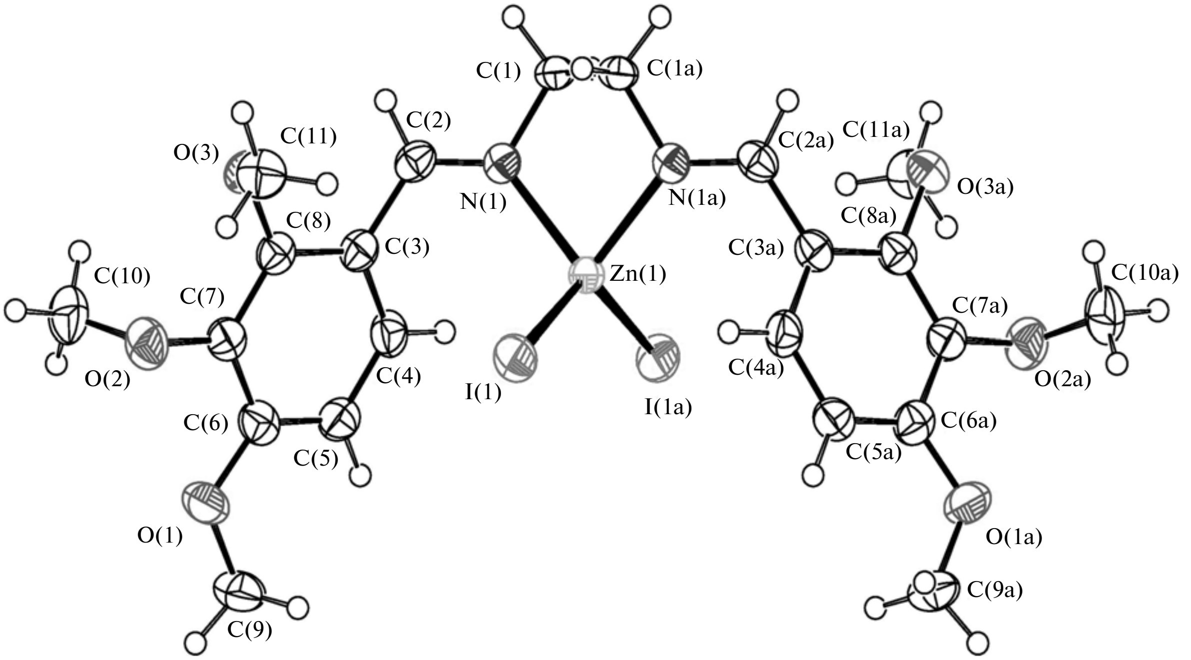

Fig. 3. Molecular structure of **I** with the atom-numbering scheme. Atomic displacement parameters are shown at 50% probability level.

Table 2. Selected bond distances, bond angles (ω), and torsion angles (φ) of **I***

Bond	d, Å	Bond	d, Å
Zn(1)–I(1)	2.5486(5)	N(1)–C(1)	1.469(6)
Zn(1)–N(1)	2.067(4)	N(1)–C(2)	1.271(6)
Angle	ω, deg	Angle	ω, deg
I(1)Zn(1)N(1)	108.63(9)	Zn(1)N(1)C(2)	129.2(3)
I(1)Zn(1)I(1)^{i}	126.56(3)	N(1)Zn(1)N(1)^{i}	83.33(15)
I(1)Zn(1)N(1)^{i}	110.64(10)	Zn(1)N(1)C(1)	108.7(3)
N(1)C(2)C(3)	122.5(4)	N(1)C(1)C(1)^{i}	108.4(4)
Angle	φ, deg	Angle	φ, deg
C(2)N(1)C(1)C(1)^{i}	127.7(5)	N(1)C(2)C(3)C(8)	140.5(5)
C(1)N(1)C(2)C(3)	178.8(4)	N(1)C(2)C(3)C(4)	−36.7(7)

* Symmetry codes: ^{i} $-x + 2, y, -z + 1/2$.

The Zn–N bond lengths of 2.067(14) Å and Zn–I bond lengths of 2.548(1) Å in **I** agree well with the same distances in other tetrahedral zinc(II) complexes [9]. The geometry about the zinc(II) center in these complexes is also approximately tetrahedral with distortion indicated by the unequal metal–ligand bond distances and angles. In order to obtain a low structure preference energy for other complexes with d^{10} ions, then a distorted tetrahedral structure can be inferred for other zinc(II) and mercury(II) complexes [8–10]. The Schiff-base ligand (234-MeO-Ba)$_2$En adopts a Z,Z configuration in these complexes [8–10]. The value for the dihedral angles C(1)N(1)C(2)C(3) is 178.8(4)° and C(2)C(3)C(8)C(7) is −174.6(4)° in **I**, indicating an almost planar configuration of this moiety for complex **I** studied here [9]. Selected torsion angles are given in Table 2. The geometry of hydrogen bonds in **I** is given in Table 3. Complex **I** exhibits different hydrogen bonding patterns built up from non-classical C–H···O hydrogen bonds in the crystal structure.

Table 3. Geometric parameters of hydrogen bond for **I***

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
C(1)–H(1A)···I(1)^{ii}	0.99	3.06	3.848(4)	138
C(10)–H(10B)···O(3)^{iii}	0.98	2.57	3.282(8)	130
C(11)–H(11B)···O(2)	0.98	2.58	3.136(7)	116

* Symmetry codes: ^{ii} $-x + 3/2, y + 1/2, -z + 1/2$; ^{iii} $-x + 1, -y + 1, -z$.

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