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**CHARACTERIZATION AND COMPUTATIONAL STUDIES
OF ZINC(II)-HALIDE COMPLEXES WITH A BIDENTATE SCHIFF BASE
LIGAND (2,5-MeO-ba)₂En: THE CRYSTAL STRUCTURE OF (2,5-MeO-ba)₂En**

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In this study four coordinated complexes of zinc(II) halides with a new symmetrical bidentate Schiff base ligand (2,5-MeO-ba)₂En are synthesized and characterized. The metal to ligand ratio of the complexes is found to be 1:1 with the formula of Zn((2,5-MeO-ba)₂En)X₂ (X = Cl (**1**), Br (**2**), I (**3**)). The crystal structure of the Schiff base ligand (2,5-MeO-ba)₂En is determined by X-ray crystallography from single crystal data. Also, the optimized geometries of the Schiff base ligand (2,5-MeO-ba)₂En and its zinc(II) complexes are calculated using the density functional theory method (B3LYP/6-31G). The obtained structural parameters of (2,5-MeO-ba)₂En are in agreement with the experimental data.

Keywords: zinc(II) halides, Schiff base, crystal structure, density functional theory.

Azomethines (known as Schiff bases) formed by the condensation of a primary amine and an aldehyde [1, 2] developed as a new class of organic compound in 1864 by Hugo Schiff [3] have been widely used as ligands in the preparation of transition metal complexes [4, 5] The coordination behavior of Schiff base ligands depends on the metal ion, the reaction conditions, and the nature of the anion used [4—12]. Schiff base compounds have played an important role in the development of coordination chemistry [4—12]; they exhibit photochromism and thermochromism [13], anti-microbial activity [16—18] and are used in non-linear optics [14, 15], anion sensors [19] and other applications. Zinc(II) complexes with Schiff base ligands have been investigated particularly for their catalytic activities [20] and as potential luminescent materials [21]. As an additional contribution to the synthesis, characterization and crystal structures of transition metal Schiff base complexes and in the course of our ongoing studies of these kinds of materials [22—24], we describe here the preparation, characterization and computational studies of a new symmetrical bidentate Schiff base ligand (2,5-MeO-ba)₂En and its Zn(II) complexes (Fig. 1).

EXPERIMENTAL

All reagents and solvents for the synthesis and analysis were commercially available and used as received without further purifications. Infrared spectra were recorded using KBr disks on a FT—IR Perkin—Elmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. ¹H-NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz for the Schiff base ligand and at 400 MHz for the zinc(II) complexes. All chemical shifts are reported in δ units downfield from TMS.

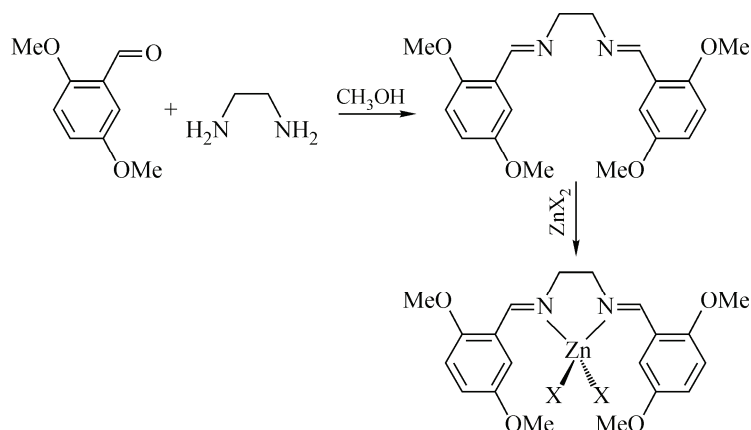


Fig. 1. Chemical structure of the Schiff base ligand (2,5-MeO-ba)₂En and its Zn(II) complexes.
X = Cl (1), Br (2), and I (3)

Preparation of (2,5-MeO-ba)₂En. A solution of 2,5-dimethoxybenzaldehyde (0.02 mol) in 25 ml of methanol was heated for 25 min at 50 °C and then stirred for about 25 min. To this stirring solution, a solution of ethylenediamine (0.01 mol) in 20 ml of methanol was added

dropwise under constant stirring. The mixture was heated at about 50 °C for 1.5 h and then allowed to cool overnight to room temperature. After evaporation of the solvent the resulting crude solid was collected by filtration and dried at room temperature. Colorless crystals were grown by the slow evaporation technique at room temperature in 25 ml of a methanol-chloroform (1:4 v/v) solution for 5 days. At the period of super saturation, tiny crystals were nucleated. They were allowed to grow to a maximum possible size, then filtered off from the mother liquor and were finally dried at room temperature. The yield was 91 %. Anal. Calc., %: C, 67.39; H, 6.79; N, 7.86 %. Found, %: C, 67.24; H, 6.73; N, 7.32 %. FT—IR (KBr pellet, cm⁻¹): 2834 (—HC=N), 2880—2970 (C—H aliphatic), 3012 (C—H, aromatic), 1635 (s, C=N). ¹H NMR (CDCl₃, δ(ppm)): 3.75 (s, 6H), 3.78 (s, 6H), 3.86 (s, 4H), 6.80 (d, 2H), 6.91 (dd, 2H), 7.46 (d, 2H), 8.67 (s, 2H).

General procedure for the zinc(II) complexes. The Zn(II) complexes were synthesized by the addition of the (2,5-MeO-ba)₂En ligand (0.2 mmol, in 5 ml of chloroform) to a solution of anhydrous metal salts (ZnX₂, 0.2 mmol, 10 ml methanol). The resulted solution was stirred in air at room temperature for about 2 h and then left at 273 K for several days without disturbance, yielding single crystals of the complexes which subsequently were filtered off and washed with Et₂O.

Zn((2,5-MeO-ba)₂En)Cl₂ (1): Bright yellow crystals. The yield was 86 %. Anal. Calc., %: C, 48.75; H, 4.91; N, 5.66 %. Found, %: C, 46.14; H, 4.99; N, 5.45 %. FT—IR (KBr pellet, cm⁻¹): 2837 (—HC=N), 2900–2980 (C—H aliphatic), 3001 (C—H, aromatic), 1628 (s, C=N). ¹H NMR (CDCl₃, δ(ppm)): 3.66 (s, 6H), 3.70 (s, 6H), 3.81 (s, 4H), 6.96 (s, 4H), 7.29 (s, 2H), 8.54 (s, 2H).

Zn((2,5-MeO-ba)₂En)Br₂ (2): Bright yellow crystals. The yield was 83 %. Anal. Calc., %: C, 41.30; H, 4.16; N, 4.82 %. Found, %: C, 41.12; H, 4.04; N, 4.88 %. FT—IR (KBr pellet, cm⁻¹): 2834 (—HC=N), 2900—2970 (C—H aliphatic), 3001 (C—H, aromatic), 1618 (s, C=N). ¹H NMR (CDCl₃, δ(ppm)): 3.67 (s, 6H), 3.70 (s, 6H), 3.83 (s, 4H), 6.97 (s, 4H), 7.30 (s, 2H), 8.55 (s, 2H).

Zn((2,5-MeO-ba)₂En)I₂ (3): Bright yellow crystals. The yield was 85 %. Anal. Calc., %: C, 35.55; H, 3.58; N, 4.15 %. Found, %: C, 35.75; H, 3.44; N, 4.17 %. FT—IR (KBr pellet, cm⁻¹): 2832 (—HC=N), 2900—2965 (C—H aliphatic), 2994 (C—H, aromatic), 1617 (s, C=N). ¹H NMR (CDCl₃, δ(ppm)): 3.67 (s, 6H), 3.70 (s, 6H), 3.81 (s, 4H), 6.98 (s, 4H), 7.29 (s, 2H), 8.54 (s, 2H).

Single crystal X-ray analysis. A single crystal of the Schiff base ligand (2,5-MeO-ba)₂En with the dimensions 0.24×0.11×0.09 mm³ was chosen for the X-ray diffraction study. Crystallographic measurements were conducted at room temperature with a four circle Gemini CCD diffractometer of Oxford Diffraction, Ltd., using CuK_α radiation (λ = 1.54184 Å). The crystal structures were solved by direct methods with the SIR2002 program [25] and refined with the Jana2006 program package [26] by the full-matrix least-squares technique on F². The molecular structure plots were prepared by ORTEP III [27] for Windows. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice they were nevertheless kept in ideal positions during the refinement. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as 1.2U_{eq} of the parent atom. Crystallographic data and details of the data collection and structure refinements are listed in Table 1.

Table 1

Crystal data and summary of experimental details for the (2,5-MeO-ba)₂En ligand

Empirical formula	C ₂₀ H ₂₄ N ₂ O ₄
Formula weight	356.4
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>T</i> , K	120
<i>a</i> , <i>b</i> , <i>c</i> , Å	4.51540(10), 14.3707(3), 14.3946(3)
β, deg.	92.6738(18)
<i>V</i> , Å ³	933.04(3)
<i>Z</i>	2
μ, mm ⁻¹	0.72
<i>T</i> _{min} , <i>T</i> _{max}	0.860, 0.934
Measured / Independent reflections	4263 / 1465
Reflection with <i>I</i> > 3σ(<i>I</i>)	1277
<i>R</i> _{int}	0.013
<i>S</i>	1.76
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.031
<i>wR</i> (<i>F</i> ²)	0.090
Parameters	119
Δρ _{max} / Δρ _{min} , e/Å ⁻³	0.13 / -0.13
Crystal size, mm	0.24×0.11×0.09

Computational details. The geometry of the Schiff base ligand (2,5-MeO-ba)₂En and its zinc(II) complexes **1**–**3** have been optimized using the HF model with the B3LYP/6-31g basis set. All HF calculations were performed using the Gaussian 98 R-A.9 package [28].

RESULTS AND DISCUSSION

The analytical and physical data of the Schiff base ligand (2,5-MeO-ba)₂En and its Zn(II) complexes are given in the EXPERIMENTAL section. The analytical data show that the metal to ligand ratio is 1:1 in all the complexes. The Schiff base ligand (2,5-MeO-ba)₂En was synthesized in a one-step process and characterized by elemental analyses, infrared and ¹H NMR spectroscopy, and single crystal X-ray crystallography. Zinc(II) complexes Zn(2,5-MeO-ba)₂EnX₂ (X = Cl (**1**), Br (**2**), I (**3**)) were characterized by elemental analyses, infrared and ¹H NMR spectroscopy.

The Schiff base ligand (3,4-MeO-ba)₂En is soluble in common solvents such as CHCl₃ and CH₂Cl₂, while the respective Zn complexes are soluble in DMF and DMSO, but insoluble in EtOH, MeOH, CHCl₃, and CH₂Cl₂. All complexes synthesized in this work are stable at room temperature in the solid state. The stability of dissolved complexes depends on the nature of the solvent. They are stable in coordinating solvents such as DMF and DMSO at room temperature for about 10 days and at 273 K for about 20 days. The Schiff base ligand (2,5-MeO-ba)₂En was obtained as colorless prism crystals with 93 % yield, and this yield was higher than the yield of the complexes. The Schiff base ligand (2,5-MeO-ba)₂En coordinated to metal ions as a chelating ligand to form mononuclear four coordinated zinc(II) complexes with suggested structures is shown in Fig. 1.

The IR spectra of the free (2,5-MeO-ba)₂En ligand exhibit the characteristic band of the imine group (—C=N—), which appears at 1635 cm⁻¹ [22]. This band is shifted in the complexes toward lower frequencies because of the coordination of the nitrogen atom to the metal ion [22], and appears at 1628 cm⁻¹ (**1**), at 1618 cm⁻¹ (**2**), and at 1617 cm⁻¹ (**3**). The observed red shift of the —C=N— vibration with an additional coordination to the Zn atom can be attributed to the metal-to-ligand π-back

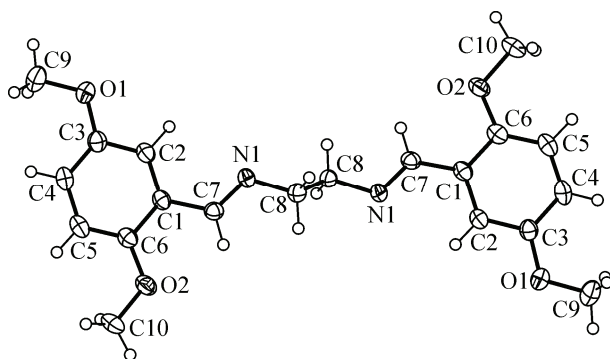


Fig. 2. Molecular structure of the Schiff base ligand (2,5-MeO-ba)₂En, showing 50 % probability displacement ellipsoids and atom numbering

bonding. The ligand stretching vibrations at about 2850–3010 cm⁻¹ assigned to C—H iminic, aromatic, and aliphatic groups are shifted to lower energy after coordination to metal ions. In the infrared spectra of the complexes, the bands in the range 440–500 cm⁻¹ that are absent in the spectrum of the pure ligand may be due to the

vibrational modes of Zn—N bonds, supporting the coordination of two iminic nitrogen atoms [29].

The ¹H NMR spectra of the (2,5-MeO-ba)₂En ligand and its complexes were recorded using CDCl₃ and DMSO-*d*⁶ as the solvent respectively, and their data were summarized in the EXPERIMENTAL section. The Schiff base ligand has a symmetric nature, therefore the hydrogen atoms in the two halves of the —CH₂—CH₂— are equivalent [30, 31]. For example, two hydrogen atoms of the azomethine groups (—CH=N—) have one signal in the ¹H NMR spectrum. The azomethine groups (—CH=N—) were shown at δ = 8.67 ppm as a singlet. In the metal complexes, these groups shifted to the lower regions due to the coordination of the nitrogen atom of the —CH=N— group to metal ions [30—33]. Aromatic ring protons of (2,5-MeO-ba)₂en are shown in the range of δ = 6.80 to δ = 6.91 ppm. In the ¹H NMR spectrum of the complexes, the aromatic ring protons are shifted to lower regions. In the ligand, hydrogen atoms of the methoxy groups are observed at δ = 3.75 and δ = 3.78, and the signals of these protons are shifted to weak fields after coordination [30—33].

Crystal structure of the Schiff base ligand (2,5-MeO-ba)₂En. The Schiff-base ligand (2,5-MeO-ba)₂En crystallizes in the centrosymmetric space group *P*2₁/*c*. The C₂₀H₂₄N₂O₄ molecule has a centre of symmetry with one half-molecule in the asymmetric unit. The molecular structure of (2,5-MeO-ba)₂En with the atom numbering scheme is given in Fig. 2 and the crystal packing in the unit cell is shown in Fig. 3. Selected bond distances and angles are listed in Table 2. All bond distances and angles are normal and are in good agreement with those reported for similar Schiff-base compounds [23]. The C(7)=N(1) bond length of 1.2660(14) Å conforms to the value for a double bond, while the C(8)—N(1) bond length of 1.4544(15) Å conforms to the value for a single bond, as in similar Schiff base compounds [23]. The C(1)—C(7)—N(1) and C(7)—N(1)—C(8) bond angles are 121.90(10)° and 117.30(9)° respectively, which is consistent with the *sp*² hybrid character of C(7) and N(1) atoms. The two 2,5-dimethoxybenzylidene groups in (2,5-MeO-ba)₂en (Fig. 3) are bridged by the —CH₂—CH₂— fragment *via* two C=N double bonds, with the C(1)...C(1*i*) distance between aromatic rings of *ca* 8.283 Å. A weak C(5)—H(5)⋯N(1) hydrogen bond with the H—N distance of 2.6039(9) Å

Table 2

Selected bond distances (Å) and angles (deg.) for (2,5-MeO-ba)₂En

Distances	Exp.	B3LYP (6-31G)	Angles	Exp.	B3LYP (6-31G)
O(1)—C(3)	1.3727(14)	1.3781	C(3)—O(1)—C(9)	117.99(9)	117.58
O(1)—C(9)	1.4183(16)	1.4567	C(7)—N(1)—C(8)	117.30(9)	117.49
N(1)—C(7)	1.2660(14)	1.2792	C(2)—C(1)—C(6)	119.06(10)	118.85
N(1)—C(8)	1.5444(15)	1.5785	C(2)—C(1)—C(7)	120.21(9)	120.41
O(2)—C(6)	1.3705(13)	1.3781	C(6)—O(2)—C(10)	117.44(9)	118.33
O(2)—C(10)	1.4230(14)	1.4585	N(1)—C(7)—C(1)	121.90(10)	121.69
C(1)—C(7)	1.4753(15)	1.4712	N(1)—C(8)—C(8 ⁱ)	110.21(9)	108.63
C(8)—C(8 ⁱ)	1.5135(16)	1.5451	C(6)—C(1)—C(7)	120.72(9)	119.87

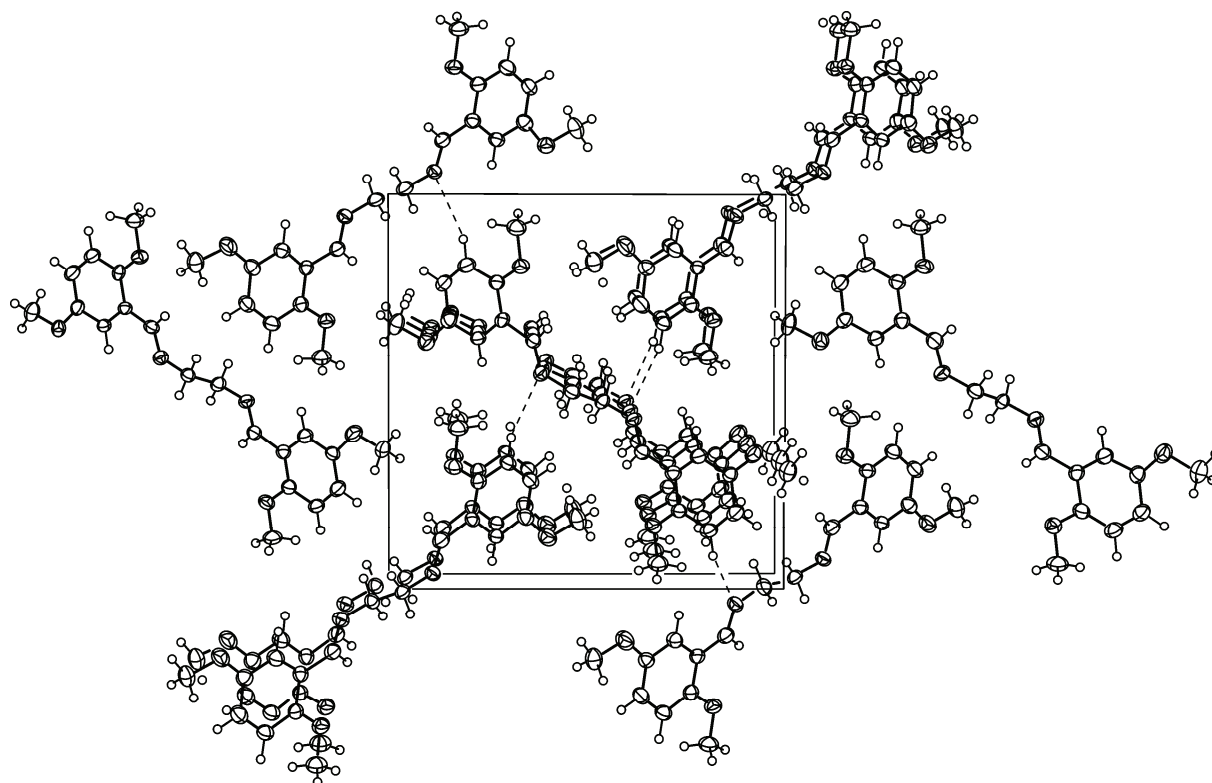


Fig. 3. Crystal packing of the Schiff base ligand $(2,5\text{-MeO-ba})_2\text{En}$, viewed along the a axis and showing a weak $\text{C5-H5}\cdots\text{N1}$ hydrogen bond

and the C-H-N angle $163.485(71)^\circ$ exists in the structure. This bond connects the molecules into a slab extended along the bc plane, without connection in a direction.

Structural description of zinc(II) complexes from theoretical studies. As shown in Figs. 4, 5, and 6, our theoretical results demonstrate that the zinc(II) ion is coordinated with two nitrogen imines of the Schiff base ligand and two halide ions, forming a four-coordination tetrahedral geometry. Selected theoretical bond distances and angles of the described coordination environment of zinc(II) complexes are given in Table 3.

Depending on the halide effects, the coordination geometry of the zinc(II) complexes containing bidentate Schiff base ligands does not differ from tetrahedral. In the presence of the bidentate N_2 Schiff base ligand, the coordination geometry around the zinc(II) ion adopts a distorted tetrahedral geometry.

Table 3

Selected theoretical bond distances (\AA) and angles (deg.) for **1**, **2**, and **3**

Distances				Angles				Angles			
	1	2	3		1	2	3		1	2	3
N10—C11	1.488	1.474	1.474	N10Zn13N14	88.80	84.78	84.77	Zn13N10C1	128.62	126.42	126.40
N10—C1	1.289	1.292	1.292	X28Zn13X29	118.01	132.86	139.53	Zn13N10C11	107.13	107.47	107.71
N14—C12	1.497	1.476	1.477	X28Zn13N10	108.62	110.0	108.54	Zn13N14C12	108.23	107.01	106.26
N14—C15	1.293	1.293	1.295	X29Zn13N10	108.49	102.70	106.70	Zn13N14C15	133.90	132.61	133.69
N14—Zn13	1.928	2.069	2.070	X28Zn13N14	111.09	110.19	109.73	C11N10C1	124.22	125.88	125.74
N10—Zn13	1.929	2.060	2.066	X29Zn13N14	117.49	105.61	106.70	N10C1C2	129.58	129.33	129.32
X29—Zn13	2.293	2.386	2.571					C12N14C15	117.39	119.76	119.42
X28—Zn13	2.295	2.377	2.561					N14C15C16	125.00	124.68	124.84

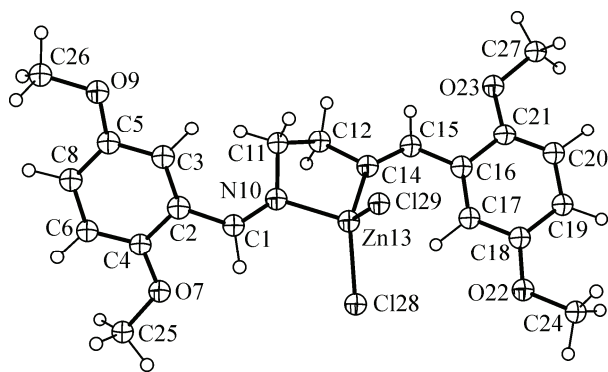


Fig. 4. Molecular structure of **1** from the calculation

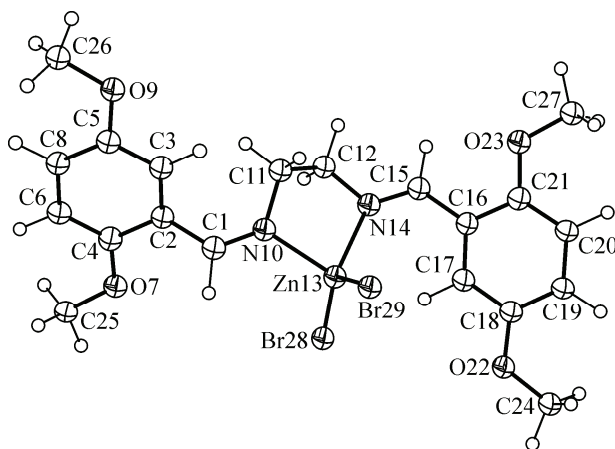


Fig. 5. Molecular structure of **2** from the calculation

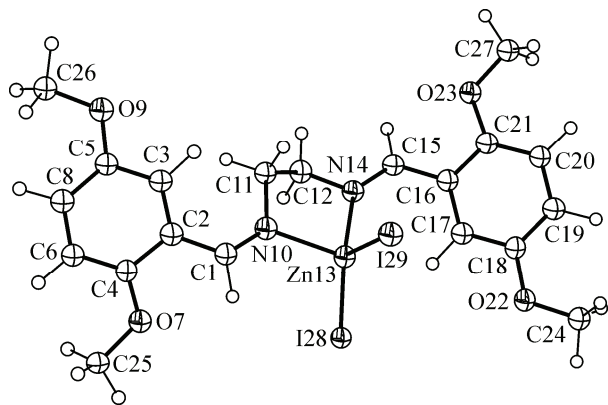


Fig. 6. Molecular structure of **3** from the calculation

Theoretical results (Table 3) show that the Zn—X distances are longer than those of Zn—N bonds. The Zn—N bond distances are 1.92 Å, 2.06 Å, and 2.07 Å in **1–3** respectively, while the Zn—I distances are 2.29 Å, 2.38 Å, and 2.57 Å in **1–3** respectively [31, 32]. The C=N double bond distances are of about 1.29 Å in all complexes, while the N—C single bond distances are of about 1.48 Å in all complexes [31, 32].

It is worth noting the angular deviations of the coordination environment from the ideal tetrahedral geometry: NZnN (88.88° in **1**, 84.78° in **2** and 84.77° in **3**) and XZnX (118.01° in **1**, 132.86° in **2** and 139.53° in **3**). However, the XZnX angles have opened up due to the steric effect from the bulky X groups [31, 32]. These deviations reflect the chelating ring strain in the place of imine nitrogen atoms. The four NZnX bond angles are found to be in the range 108–111° in **1**, 102–105° in **2**, and 106–109° in **3**, which are different from those in a regular tetrahedron (109.5°).

CONCLUSIONS

In summary, a new Schiff base ligand (2,5-MeO-ba)₂En and its zinc(II) complexes were synthesized and characterized by elemental analyses, FT—IR and ¹H NMR spectroscopy. The crystal and molecular structure of the Schiff base ligand (2,5-MeO-ba)₂En was successfully characterized. Elemental analyses confirm the chemical composition of the synthesized compounds, while FT—IR and ¹H NMR spectroscopy confirm the functional groups, particularly —HC=N imine groups, of the compounds. The Schiff base ligand (2,5-MeO-ba)₂En has a centre of symmetry with one half-molecule in the asymmetric unit.

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