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Ni(II), Cu(II), and Zn(II) Complexes of Tetradentate Schiff Base Containing Two Thiadiazoles Units: Structural, Spectroscopic, Magnetic Properties, and Molecular Modeling Studies

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ABSTRACT: *Four new mononuclear metal complexes with a mononucleating Schiff base ligand containing two thiadiazoles units have been synthesized. The ligand and metal complexes were characterized by elemental analyses, IR, ^1H, and ^{13}C NMR, UV–vis, ESR, electrospray ionization mass spectra, and magnetic susceptibility measurements. Electronic spectra, magnetic susceptibility measurement, and molecular modeling studies support octahedral geometry around the Ni(II), Cu(II), and Zn(II) ions. The magnetic properties were investigated, and ferromagnetic coupling is observed in Cu(II) and Ni(II) complexes. In addition, total energy and heat of formation calculated for conformers of the Schiff base ligand by the semiempirical AM1 calculations have shown that E,Z-isomer of the ligand is more stable (about 5.3 kcal/mol) than E,E- and Z,Z-isomers.* Heteroatom Chem 19:700–712, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20496

INTRODUCTION

Tetradentate Schiff bases derived from 2 equiv of salicylaldehyde and 1 equiv of a variety of alkyl or aryl diamines have been known for decades. Schiff base complexes containing different central metals such as Co, Ni, Cu, and Zn play a central role as chelating ligands in main group and transition metal coordination chemistry [1–4]. Transition metal complexes of tetradentate Schiff base ligands have been used as model analogues of certain metal enzymes [5–7], in catalysis and material chemistry [8–11], in various other fields such as illness treatment, biochemical reaction, and biological regulator [12], and have specific activities in pharmacology and physiology. Furthermore, the 1,3,4-thiadiazole ring system is known to possess several biological activities

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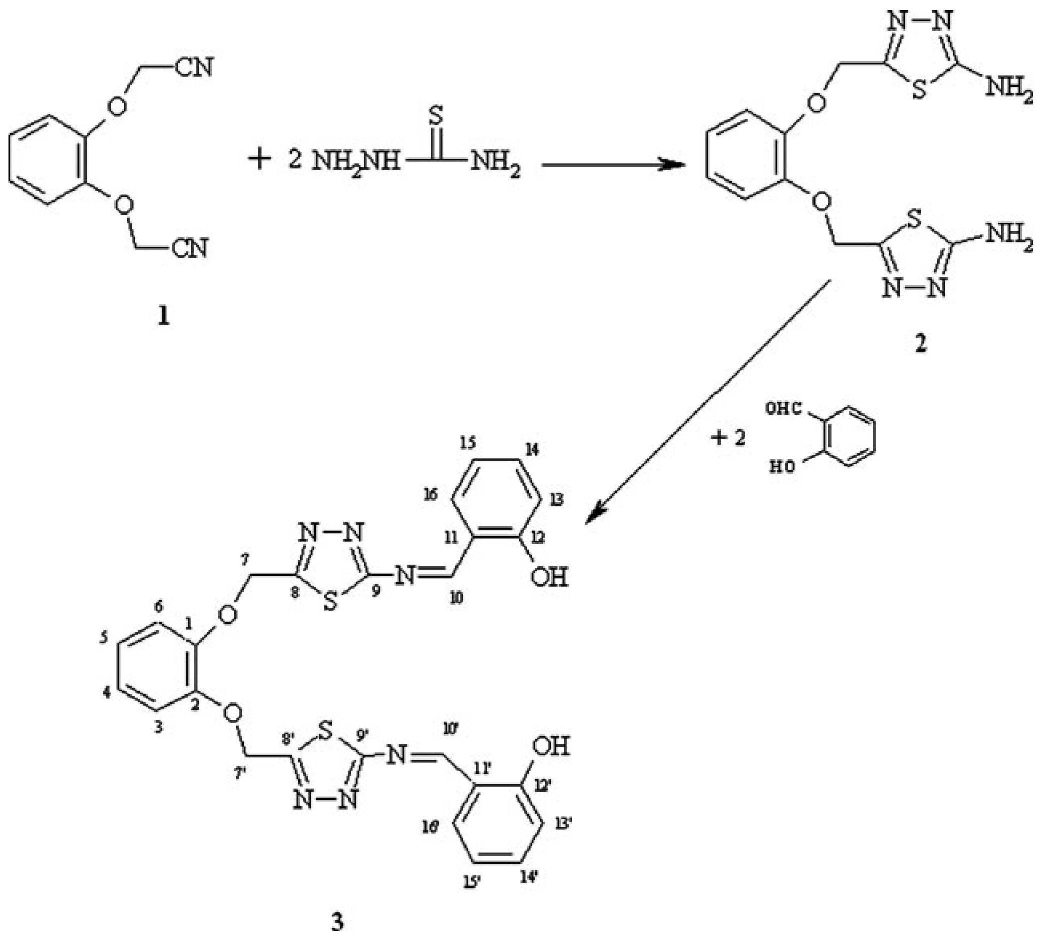

SCHEME 1 Synthetic route to Schiff base ligand (**3**).

and its antibacterial properties have been widely described [13–15]. Therefore, people have a great interest in Schiff bases synthesis, structure, and application of this kind of complexes.

Although a large number of complexes of structural types such as $M(N_2O_2)$ have been synthesized and characterized, complexes of the mononucleating Schiff base ligand derived from salicylaldehyde containing a thiadiazole unit are rather scarce. Through the loss of the two hydroxyl protons, these ligands have been used to form neutral complexes with a number of divalent metal ions [16–18].

Here we focus on the preparation, characterization, and molecular modeling calculations of a tetradentate Schiff base ligand, 1,2-bis[2-[(5-methoxy-[1,3,4]thiadiazol-2-ylimino)-methyl]-phenol]-benzene (H_2L) containing two thiadiazoles units (Scheme 1), and its mononuclear Cu(II), Ni(II), and Zn(II) complexes. The characterization of the ligands and complexes by elemental analyses, mass, NMR, UV–vis, ESR, IR spectra, and magnetic susceptibilities was also investigated in detail.

EXPERIMENTAL

Materials

Salicylaldehyde was purchased from Merck (Frankfurten, Germany) and was used without further purification. 2-[2-(Cyanomethoxy)phenoxy]-acetonitrile (**1**) was synthesized according to the procedure described in [19].

Physical Measurements

Melting points (mp) were determined on a Büchi 530 apparatus in open capillary tubes and are uncorrected. IR spectra were recorded on a Matson 1000 model FTIR spectrophotometer as KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer using DMSO-d_6 as a solvent. Chemical shifts (δ) are reported in parts per million (ppm) relative to an internal standard of Me_4Si. Electronic spectra were obtained on an ATI Unicam UV2 model UV–vis spectrophotometer. Room temperature (20°C) magnetic susceptibilities

(Sherwood Scientific MXI model Gouy magnetic balance) were recorded at Department of Chemistry, 19 Mayis University, Samsun, Turkey. Elemental analyses were determined on a LECO CHNSO-932 autoelemental analyses apparatus. Copper and nickel were determined by atomic absorption spectral techniques using standard flames [20]. Zinc was estimated in complexometric titration against EDTA [21]. The ESR spectra were recorded on a Varian model E 109C spectrometer in X-band with 100 kHz modulation frequencies. The g value was determined in comparison with a diphenylpicrylhydrazyl sample of $g = 2.0036$. Errors for g and A parameters of the complexes are ±0.001 and ±0.05 G, respectively. Electrospray ionization mass spectrometry (ESI-MS) was performed on a VG 7070 spectrometer at Department of Chemistry, Karadeniz Technical University, Trabzon, Turkey.

Synthesis of the Ligand

5-({2-[(2-Amino-1,3,4-thiadiazole-5-yl)methoxy]-phenoxy}methyl)2-amino-1,3,4- thiadiazoles ($C_{12}H_{12}N_6O_2S_2$; **2***).* A mixture of compound **1** (0.01 mol) and thiosemicarbazide (2.73 g, 0.03 mol) in trifluoroacetic acid (5 cm^3) at 60–70°C was stirred for 4 h. The reaction mixture was poured into 200-cm^3 ice-cold water and neutralized with aq. ammonia. The precipitate was filtered and washed with hot water and then dried. The resulting white product recrystallized in DMSO–water (1:4) and isolated with 89% yield. mp 247–248°C.

1,2-Bis[2-[(5-myethoxy-[1,3,4]thiadiazol-2-ylimino)-methyl]-phenol]benzene ($C_{26}H_{20}N_6O_4S_2$; **3***).* Salicylaldehyde (35 mmol; 3.7 cm^3) was added to **2** (3.36 g, 10 mmol) under nitrogen atmosphere. After stirring for 5 h at 160°C, the mixture was kept in the refrigerator for 30 min. Cold diethyl ether was then added to a reddish brown reaction mixture and then a canary yellow microcrystalline solid product precipitated. It was filtered off, washed with water, EtOH, and Et_2O to remove excess of salicylaldehyde and dried over P_2O_5 in vacuo. mp 196–198°C.

*Preparation of Metal Complexes (**4–7**)*

The complexes $[CuL(H_2O)_2]$, $[NiL(H_2O)_2]$, and $[ZnL]{\cdot}2H_2O$ were obtained according to the following procedure:

A solution of NaOH (4 mmol) in 4 cm^3 water was added to a suspension of H_2L (2 mmol) in 5 cm^3 hot EtOH. After stirring for 30 min at 50°C, a solution of metal nitrates $[Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O]$ was added to the solution of sodium salt of the ligand. The mixture was then refluxed for 6 h, the precipitate was filtered off, washed with water, EtOH, and Et_2O, and dried over P_2O_5 in vacuo. mp of all complexes was >300°C.

RESULTS AND DISCUSSION

The ligand was derived from the condensation of **2** with salicylaldehyde without using any solvent and is abbreviated as H_2L (**3**). Cu(II), Ni(II), and Zn(II) complexes have been synthesized by the reaction of the ligand mixture in EtOH with an aqueous solution of NaOH and metal nitrates. In the proposed structure of the Schiff base (**3**), N_2O_2 units are available for the complexation of a metal ion in a square–planar coordination geometry. The structural formula of the Schiff base ligand, as a canary yellow solid material, and metal complexes was verified by elemental analysis, ^1H NMR, ^{13}C NMR, IR, UV–vis, and mass spectral data presented in Tables 1–3. All the complexes and the ligand are very stable at room temperature in air, insoluble in water and common organic solvent such as EtOH, $CHCl_3$, and CH_3CN. The complexes have low solubility, whereas the ligand has high solubility in DMSO, DMF, and pyridine. The characterization of the complexes

TABLE 1 Observed Frequencies and Proposed Mode of Assignments for the H_2L and Its Metal Complexes

		ν(C=N)	ν(C=N)					
Compound	*ν(OH)*	*Azomethine*	*Thiadiazole*	*$\nu(CH_2)$*	*ν(C—O)*	*$\nu(NH_2)$*	*ν(M—O)*	*ν(M—N)*
2	–	–	1513	2980	1124	3301, 3115	–	–
3	3412	1607	1497	2917	1185	–	–	–
4	3409	1615	1496	2925	1150	–	536	435
5	3400	1622	1496	2923	1185	–	520	422
6	3360	1613	1496	2923	1157	–	532	434

TABLE 2 Elemental Analyses, Magnetic Moments, UV–Vis Spectral Data of H_2L and Its Cu^{II}, Ni^{II}, and Zn^{II} Complexes

Compound	*Color*	*Yield (%)*	μ_{eff} *per Molecule at 297 K (BM)*	*Found (Calcd.) (%)* C	H	N	M	λ_{max}, *(nm)*
3 $C_{26}H_{20}N_6O_4S_2$	Yellow	97	–	57.2 (57.3)	3.9 (3.7)	15.4 (15.4)	–	306, 358, 405
4 $C_{26}H_{22}N_6O_6S_2Cu$-	Green	84	1.98	48.9 (48.6)	3.6 (3.4)	13.2 (13.1)	9.8 (9.9)	584, 730
5 $C_{26}H_{22}N_6O_6S_2Ni$	Brown	88	4.74	49.2 (49.0)	3.2 (3.5)	13.4 (13.2)	9.5 (9.2)	590, 603, 809
6 $C_{26}H_{22}N_6O_6S_2Zn$	Yellow	84	Diamagnetic	48.4 (48.5)	3.1 (3.4)	13.4 (13.0)	10.3 (10.2)	299, 377

includes elemental analysis, ESI mass, IR, UV–vis, ESR, and magnetic susceptibilities. Elemental analysis and ESI mass spectral data show that all the complexes have a 1:1 metal:ligand ratio and contain two water molecules.

Spectral Characterization

The condensation of **2** with salicylaldehyde has been indicated by the elimination of two equally intense, sharp IR bands at 3301 and 3115 cm^{-1} corresponding to ν (NH_2) in free aminothiadiazole. An intense band that appears at 1607 cm^{-1} in the condensed product, H_2L, is assigned to ν(C=N) and a medium intensity band centered around 3412 cm^{-1} for ν (OH). The IR bands that are most useful for determining the mode of thiadiazole uncoordination are shown in Table 1. The ν (C=N) azomethine bands of the Schiff base (1607 cm^{-1}) undergo small shifts to higher frequencies in the spectra of the complexes (1615–1622 cm^{-1}), indicating coordination of the azomethine [22]. All the complexes exhibit medium intense broad bands centered at 3400–3360 cm^{-1} assigned to coordinated water. All the complexes show medium intense bands at 536–520 cm^{-1} and 441–422 cm^{-1}, suggesting the presence of the ν (M—O) and ν(M—N), respectively. That any absorption bands belonging to nitrates are not seen in the spectra of all the complexes, indicating that neutral complexes were formed. In general, the complexes exhibited very similar IR features indirectly, evidencing that complexes of the Schiff base have similar structures.

The electronic absorption spectra of the complexes in pyridine less than 400 nm are dominated by the intense bands due to intraligand transition of the Schiff base (H_2L) or/and a charge-transfer transition. The pyridine solution of Cu(II) complex (**4**) displays a broad absorption at 584 nm and a weak shoulder at 730 nm. The position of the band and their weak intensity ($\varepsilon = 80$–220 M^{-1} cm^{-1}) has been assigned to d–d transition $^2E_g \rightarrow {}^2B_{1g}$ and $^2E_g \rightarrow {}^2A_{1g}$. This supports the distorted octahedral Cu(II) complex, which is usual in the d^9 case [23,24]. Nickel(II) complex (**5**) exhibits transitions at 809, 603, and 590 nm. Three bands in the Ni(II) complex may correspond to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}$ (F), and $^3A_{2g}(F) \rightarrow {}^3T_{1g}$ (P) transitions, respectively. This supports the octahedral orientation of donor centers around the metal ion. No d–d transition is expected for d^{10} Zn(II) complex (**6**), and a square-planar structure is very unlikely because Zn(II) ion generally forms tetrahedral complexes because of its d^{10} electronic configuration. The absorption maxima at 299 and

TABLE 3 ^{1}H NMR and ^{13}C NMR Data for **2** and **3**

*^{1}H NMR Data for **2***	*^{13}C NMR Data for **2***	*^{1}H NMR Data for **3***	*^{13}C NMR Data for **3***	
5.25s. (OCH_2, 4H)	65.1(OCH_2), 169.8, 154.1(Het.C)	5.428 and 5.505s. (—OCH_2, 2H)	C-1,2	136.405
6.94–7.16d. (Ph, 4H)	147.3, 122.0, 115.2 (Ph)	6.946–7.248m. (Ar—H, 8H, and —OH, 2H)	C-3,6	115.11
7.30s. (NH_2, 4H)		7.534–7.738m. (Ar—H, 4H)	C-4,5	122.522
		8.407 and 10.319s. (N=CH—, 2H)	C7,7′	64.888
			C8,8′	160.690
			C-9,9′	191.581
			C-10,10′	160.696
			C-11,11′	119.434
			C-12,12′	146.813
			C-13,13′	117.181
			C-14,14′	129.038
			C-15,15′	122.211
			C-16,16′	136.40

s: Singlet, d: doublet, m: multiplet.

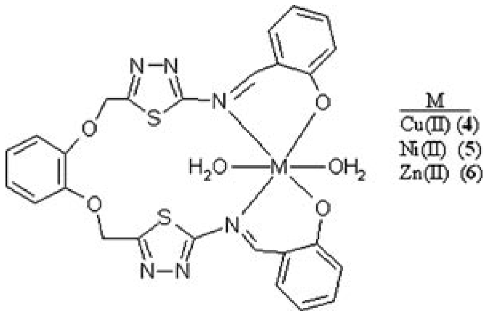

FIGURE 1 Proposed structure for the mononuclear Cu(II), Ni(II), and Zn(II) complexes.

377 nm can be attributed to intraligand transitions only [25].

The ^{1}H NMR spectra of DMSO-d_6 solution of the ligand (**3**) show well-resolved signals as expected (Table 3). The careful analyses of the ^{1}H NMR spectra of the ligand show the presence of two components. These are assigned as (*E,Z*)- and (*E,E*)-diasteromers. In the ^{1}H NMR (DMSO-d_6, δ) spectrum of the ligand, two singlets were observed at δ 5.428 and 5.505 ppm (–OCH_2, 4H), a multiplet at δ 6.946–7.248 ppm (Ar-H, 8H, and —OH, 2H), a multiplet at δ 7.534–7.738 ppm (Ar-H, 4H), two singlets at δ 8.407 and 10.319 ppm (—N=C—H, 2H) (Fig. 3). After D_2O was added, a decrease in the integrated intensity of the multiplet at δ 6.946–7.248 ppm was observed because of the absence of the —OH proton signals. Each of —OCH_2— and —N=C—H protons having two different chemical shifts show that the ligand is the (*E,Z*)- and (*E,E*)-isomeric mixture (Fig. 3). This is consistent with the results of the semiempirical AM1 calculations. The *E,Z*/*E,E* isomer ratio can also be

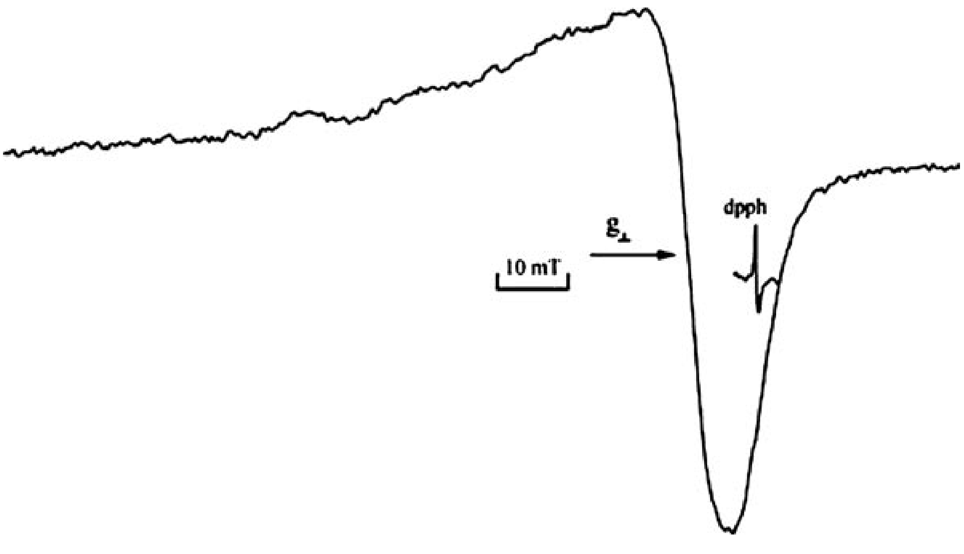

FIGURE 2 ESR spectra of the Cu(II) complex.

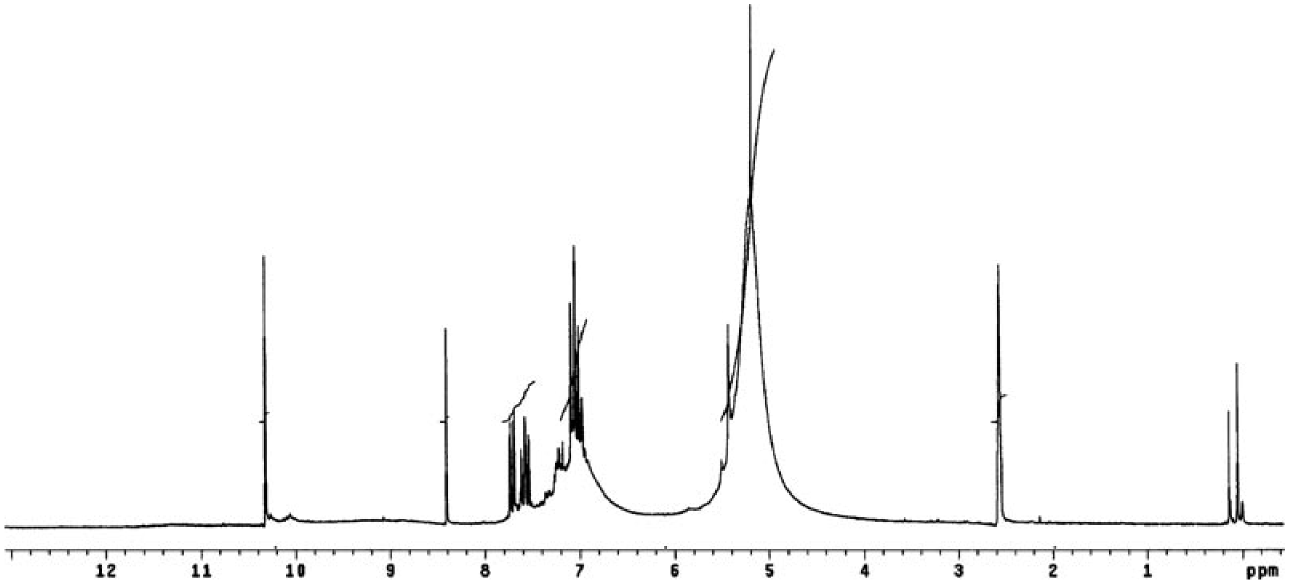

FIGURE 3 ^{1}H NMR spectra of the ligand in DMSO-d_6.

easily quantified by the NMR techniques. The intensities of the ^{1}H signals at δ 8.407 and 10.319 have allowed us to measure the ratio of *E,Z*/*E,E* isomers, and the percentage of the isomers in DMSO-d_6 is 71.26% *E,Z*- and 28.74% *E,E*-isomers. Because of the fact that the distance between OH-based H atom and N=C-based N atom in the *E*-part is shorter than it is in the *Z*-part (2.14 Å in the *Z*-part, 4.82 Å in the *E*-part from the AM1 calculation), stronger hydrogen bond can be formed in the *E*-part of the ligand. So, the proton signal of the azomethine in the *E*-part shifts to the lower field. ^{13}C NMR spectral data are also consistent with the structure of the ligand (Table 3).

An analysis by ESI-mass data of the molecular ion of H_2L and its Cu(II), Ni(II), Zn(II), and Co(II) complexes indicated at *m/z* 545.1 (87%) $[M+1]^+$ (a base peak at *m/z* 223.9), at *m/z* 643.2 (15%) $[M+2]^+$, at *m/z* 636.0 (34%) $[M]^+$, and at *m/z* 644.0 (28%) $[M+2]^+$, respectively. The mass spectra and fragmentation pattern of Cu(II) complex are shown in Figs. 8 and 9. These mass spectral data show that mononuclear metal complexes were formed.

ESR and Magnetic Properties

The magnetic susceptibility measurements exhibit the paramagnetic behavior of the complexes. The Zn(II) complex is expectedly diamagnetic (Table 2). The magnetic moment per metal ion follows **4**, 1.98 and **5**4.74 (Table 2). The results exhibit higher magnetic moment than that of spin-only values. The magnetic moment data of the Cu(II) complex at room temperature correspond to one unpaired electron. Paramagnetic behavior of the Ni(II) complex supports octahedral geometry [23].

The X-band powder ESR spectrum of the Cu(II) complex (**4**) shown in Fig. 3 was recorded at room temperature. The spin Hamiltonian parameters of $[CuL(H_2O)_2]$ (**4**) are listed in Table 4. The ESR spectra for polycrystalline sample of $[CuL(H_2O)_2]$ (**4**) at 300 K is characterized by an axial symmetric g tensor with $g|| > g_\perp > 2.03$ [26–28] (Table 4 and Fig. 2.

Computational Studies

Semiempirical Calculations. To obtain the most probable molecular conformations and stabilization of the ligand and to explain ^{1}H NMR spectra, energy minimization studies of the ligand were carried out, using the molecular mechanics MM+ module and AM1 semiempirical calculations in a HyperChem 7.01 program package on a Pentium 4 computer [29]. The semiempirical AM1 calculations have shown

TABLE 4 X-Band ESR Spectral Data of the Cu(II) Complex

Complex	$g_{\|}$	$g_\perp$	$A_\perp$	$A_{\|}$
$[CuL(H_2O)_2]$ (**4**)	2.277	2.068	25	166

$A_\perp$ and $A_{||}$ values are given of G (Gauss).

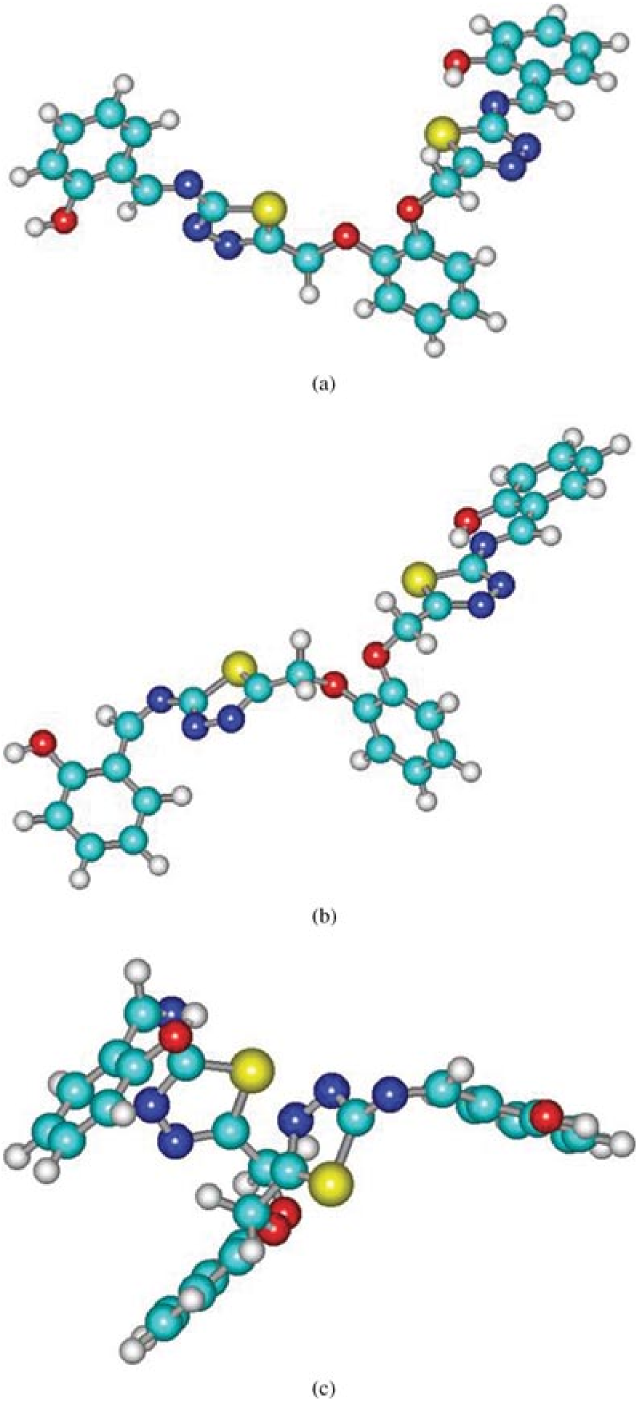

FIGURE 4 The lowest energy conformations by AM1 optimized geometries (a) *E*,*E*-isomer, (b) *E*,*Z*-isomer, (c) *Z*,*Z*-isomer of the Schiff base ligand, and its E_{tot}, ΔH_f energies (kcal/mol) and dipole moments (Debye).

that the *E*,*Z*-isomer of the Schiff base ligand is more stable at 0.5 and 5.3 kcal/mol than *E*,*E*- and *Z*,*Z*-isomers, respectively (Fig. 4).

DFT Calculations. Because single crystals could not be obtained for these complexes, it was thought worthwhile to obtain structural information. Molecular modeling studies were carried out by using hybrid density functional theory. Support of the experimental data and findings is the main concern of the theoretical investigation. All calculations were performed with the Gaussian program [30] using

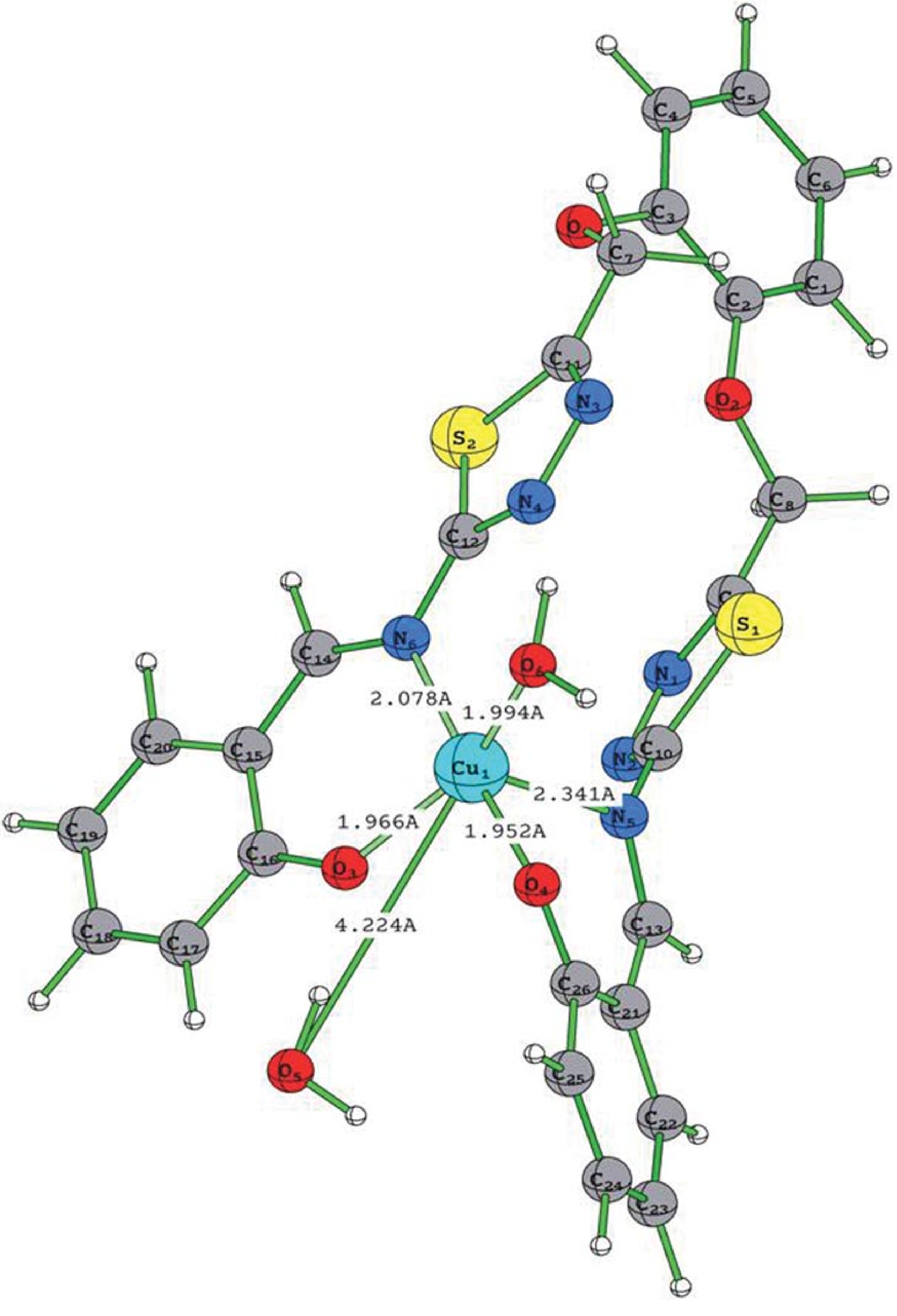

FIGURE 5 Energy minimized, hexacoordinated, octahedral copper complex.

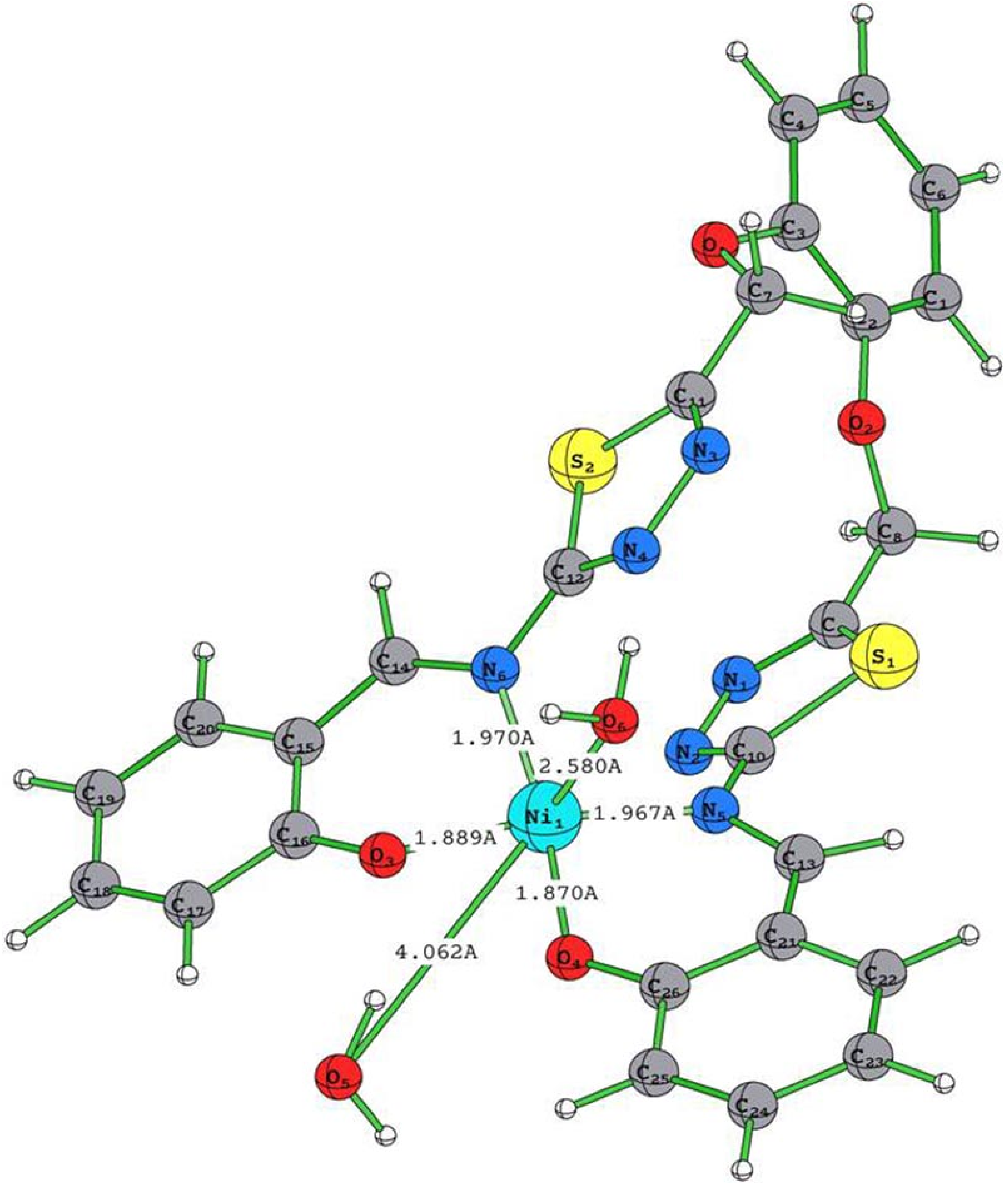

FIGURE 6 Energy minimized, hexacoordinated, octahedral nickel complex.

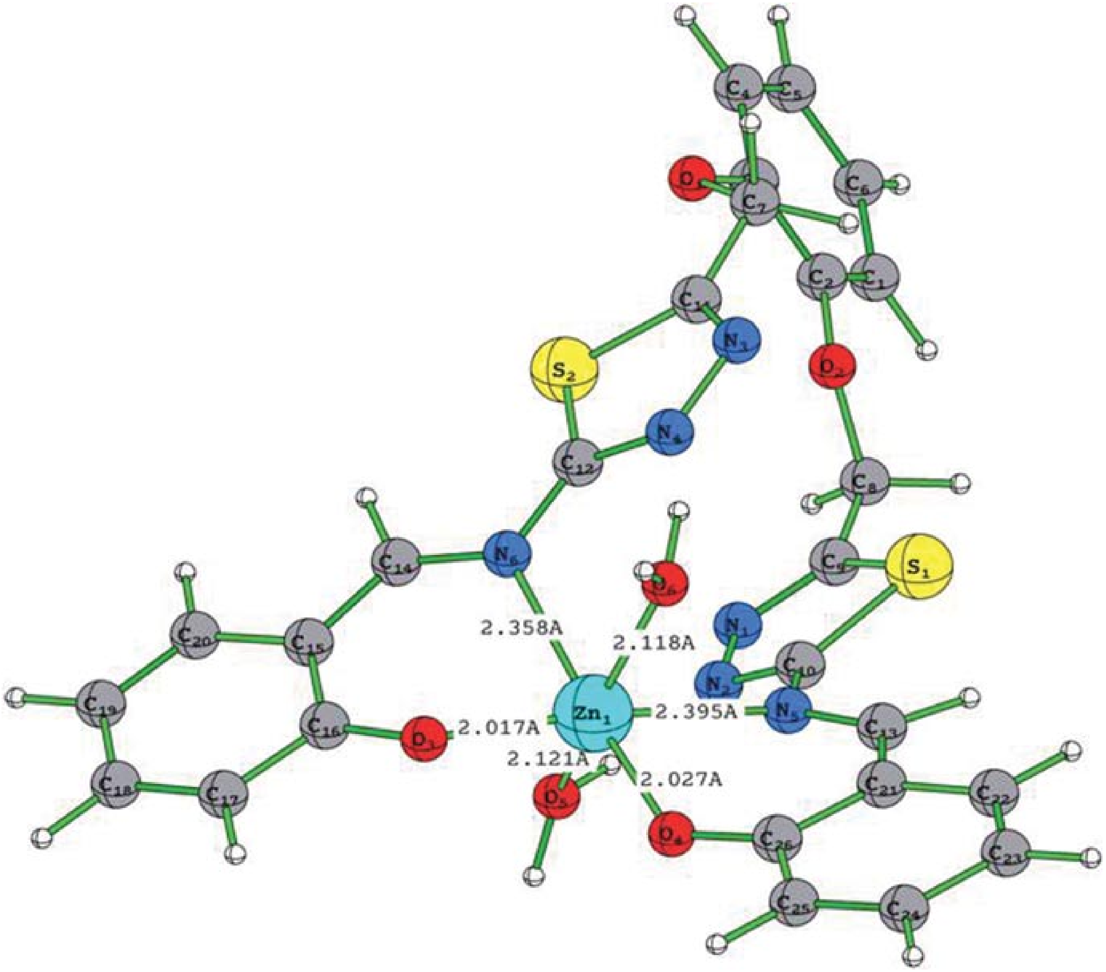

FIGURE 7 Energy minimized, hexacoordinated, octahedral zinc complex.

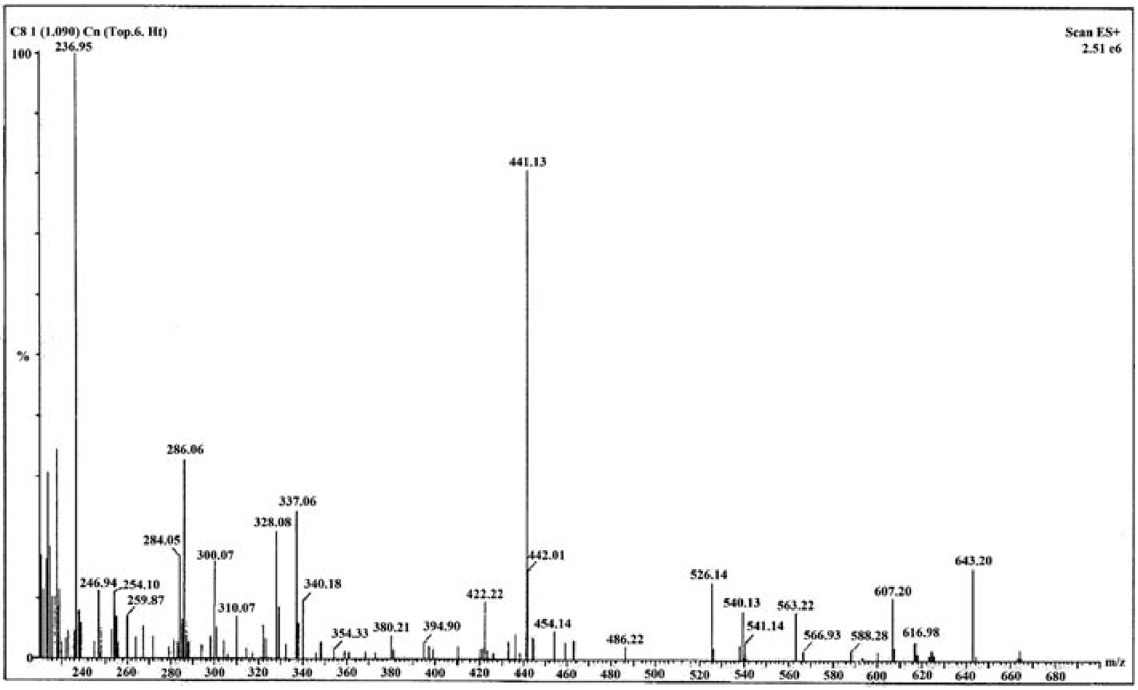

FIGURE 8 The mass spectra of Cu(II) complex.

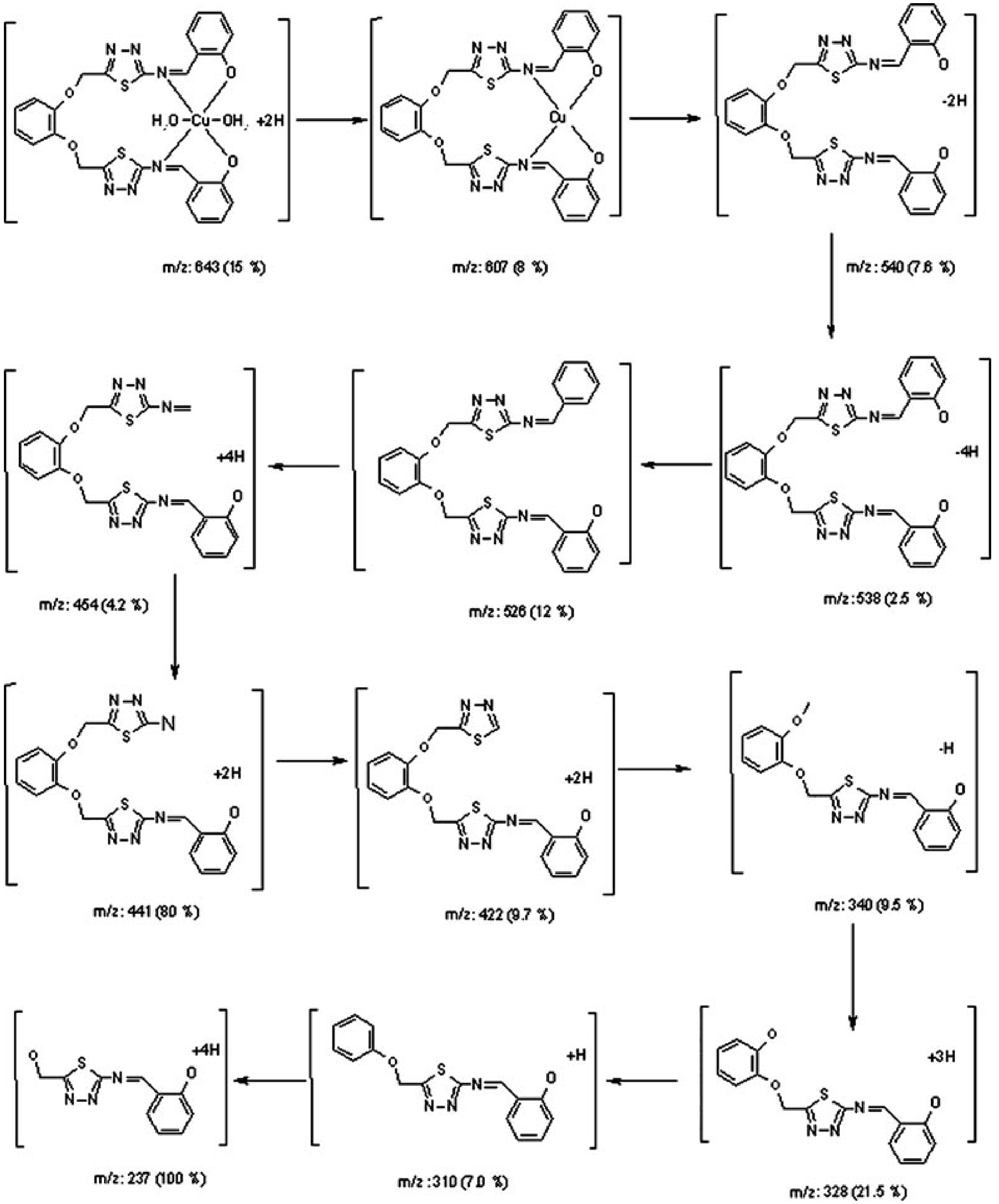

FIGURE 9 Fragments observed in the mass spectrum of the Cu(II) complex.

TABLE 5 Total Energy of Geometry Optimized Tetra-, Penta-, and Hexacoordinated Metal Complexes

Complex	*Total Energy (in Hartrees)*
Ni tetracoordinated	−1820.195
Ni pentacoordinated	−1896.623
Ni hexacoordinated	−1973.064
Cu tetracoordinated	−1847.026
Cu pentacoordinated	−1923.446
Cu hexacoordination	−1999.903
Zn tetracoordinated	−1716.515
Zn pentacoordinated	−1792.954
Zn hexacoordinated	−1869.407

TABLE 6 Geometrical Parameters for Hexacoordinated Metal Complexes[a]

Parameter	*Theoretical (B3LYP/LANL2DZ)*
Ni(1)–O(3)	1.889
Ni(1)–O(4)	1.870
Ni(1)–O(5)	4.062
Ni(1)–O(6)	2.580
Ni(1)–N(5)	1.967
Ni(1)–N(6)	1.970
O(5)–Ni(1)–O(6)	100.7
C(16)–O(3)–Ni(1)–O(6)	133.4
O(5)–Ni(1)–N(5)–C(10)	139.2
Cu(1)–O(3)	1.966
Cu(1)–O(4)	1.952
Cu(1)–O(5)	4.224
Cu(1)–O(6)	1.994
Cu(1)–N(5	2.341
Cu(1)–N(6)	2.078
O(5)–Cu(1)–O(6)	127.3
C(16)–O(3)–Cu(1)–O(6)	105.3
O(5)–Cu(1)–N(5)–C(10)	139.4
Zn(1)–O(3)	2.017
Zn(1)–O(4)	2.027
Zn(1)–O(5)	2.121
Zn(1)–O(6)	2.118
Zn(1)–N(5)	2.395
Zn(1)–N(6)	2.358
O(5)–Zn(1)–O(6)	155.5
C(16)–O(3)–Zn(1)–O(6)	117.9
O(5)–Zn(1)–N(5)–C(10)	53.2

[a] The atomic-numbering scheme is given in Figs. 5–7.

Becke three-parameters hybrid exchange functional combined with Lee–Yang–Parr correlation functional [31,32]. DFT geometry optimizations were performed using LANL2DZ basis set [33].

Elemental analysis and mass spectral data show that all the complexes have two water molecules in the structure. To decide whether water molecules are coordinated to the metal ions in the structures of the complexes, we investigated about the lowest energy conformations, bond lengths, and coordinate covalent bond angles of the complexes. As it has been shown in Table 5, Ni(II), Cu(II), and Zn(II) complexes having hexacoordination are more stable than those having tetra- and pentacoordination, because they have the lowest energy conformation. Theoretically calculated geometrical parameters are presented in Table 6. All the coordinative covalent bond lengths and bond angles are in accordance with the octahedral geometry (Figs. 5–7).

CONCLUSIONS

Tetradentate Schiff base ligand obtained from the condensation of **2** with salicylaldehyde. Mononuclear complexes of Cu(II), Ni(II), and Zn(II) have been synthesized, and structural investigation using spectral, magnetic data, and molecular modeling calculations suggests the octahedral geometry for Cu(II), Ni(II), and Zn(II) complexes. ESR spectra of Cu(II) complex also show the distorted octahedral geometry. The magnetic properties of the complexes were investigated, and ferromagnetic coupling is observed in Cu(II) and Ni(II) complexes.

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