# Synthesis, Characterization and Thermal Behavior of Some Zn(II) Complexes with Ligands Having 1,3,4-Thiadiazole Moieties

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ABSTRACT: Some new zinc(II) complexes of the type  $[Zn(L^{1})_{2}(C_{2}H_{5}OH)_{2}] \cdot C_{2}H_{5}OH, [Zn(L^{2})_{2}Cl_{2}] \cdot H_{2}O, and$  $[Zn_2(L^3)_2(H_2O)_4Cl_4]$ , where  $HL^1 = N-[5'-amino-2]$ , 2'-bis(1,3,4-thiadiazole)-5-yl]-2-hydroxybenzaldehyde *imine*,  $L^2 = N \cdot (5 \cdot ethyl \cdot 1, 3, 4 \cdot thiadiazole \cdot 2 \cdot yl) tereph$ thalaldehyde imine, and  $L^3 = N, N'$ -bis[5-(4-nitro phenyl)-1,3,4-thiadiazole-2-yl]terephthalaldehydediimine have been synthesized and characterized by IR, <sup>1</sup>H NMR spectra, elemental analyses, magnetic susceptibility, UV-vis. and thermogravimetry-differential thermal analysis (TGA-DTA). On the basis of electronic spectral studies, an octahedral environment around the Zn(II) ion has been suggested. <sup>1</sup>H NMR spectra of the metal complexes of ligands were found to be in agreement with the proposed stoichiometry. The presence of water molecules and ethanol in the Zn(II) complexes is also indicated by the thermal studies. © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:14-23, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20572

#### INTRODUCTION

During the past two decades, considerable attention has been paid to the chemistry of the transition metal complexes of Schiff bases containing nitrogen and other donors [1–3]. Since the first preparation of thiadiazole, numerous research investigations have focused on thiadiazoles and their derivatives. It is known that the thiadiazole themselves and their derivatives have been used as antibacterial, antifungal, insecticidal [4,5], herbicidal, pesticidal, and antitumor agents [6,7]. The ligands used in this work (Figs. 1–3) have two different and important functionalities: thiadiazole and azomethine.

The present investigation is concerned with the preparation and characterization of Zn(II) chelates with the bidentate Schiff bases derived from 1,3,4-thiadiazole derivatives with salicylaldehyde and terephthalaldehyde.

#### EXPERIMENTAL

#### Reagents and Instrumentation

All solvents were analytical-grade reagents, used as purchased. The metal salt  $ZnCl_2$  and starting materials for the ligand were obtained from Merck, Aldrich, Fluka, and Alfa Aesar (Ankara, Turkey). Compounds (HL<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup>) were synthesized as described in the literature [8–10].

Elemental analyses were carried out on a Leco CHNS-O model 932 elemental analyzer. <sup>1</sup>H NMR spectra were recorded using a model Bruker GmbH DPX-300 MHz FT spectrometer. IR spectra were recorded on Perkin Elmer Precisely Spectrum One spectrometer on KBr disks in the wave number range of 4000–400 cm<sup>-1</sup>. Electronic spectral studies

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FIGURE 1 Synthesis of the ligand: N-[5'-Amino-2,2'-bis(1,3,4-thiadiazole)-5-y1]-2-hydroxybenzaldehyde imine (HL<sup>1</sup>).

were conducted on a Shimadzu model UV-1700 spectrophotometer in the wavelength 1100-200 nm. Magnetic susceptibilities measurements were performed using the standard Gouy tube technique using Hg[Co(SCN)<sub>4</sub>] as a calibrant. Thermal analyzers (TGA and DTA) were carried out in nitrogen atmosphere with a heating rate of  $15^{\circ}$ C/min using Shimadzu DTG-60 AH (Shimadzu DSC 60 A) thermal analyzers.

### *Synthesis of 2-Amino-5-(2-amino-1,3,4-thiadiazoleyl)-1,3,4-thiadiazole* (1)

A mixture of acid (0.04 mol), thiosemicarbazide (0.104 mol), and POCl<sub>3</sub> (0.104 mol) was warmed at 60°C for 1 h, than the temperature was raised to 95°C for an additional 3 h. The mixture was then poured into the least amount of required crushed ice, cooled to 15°C and the pH was adjusted to  $\approx$ 5 with 10 M NaOH. The resulting solid was crystallized from DMF-ethanol to get HL<sup>1</sup> [8].

# *Synthesis of N-[5'-Amino-2,2'-bis(1,3,4-thiadiazole)-5-yl]-2-hydroxybenzaldehyde Imine (HL<sup>1</sup>)*

A solution of 2-amino-5-(2-amino-1,3,4-thiadiazoleyl)-1,3,4-thiadiazole (1) 4 g (0.02 mol) in 15 mL EtOH was added slowly and dropwise into a solution of salicylaldehyde 2.44 g (0.02 mol). The mixture was stirred at 60°C for 30 min Five drops of 3 mL glacial acetic acid (AcOH) were added to the above-mentioned solution to keep pH  $\sim$ 5. The resultant solution was heated in an electro-magnetic stirring apparatus to reflux for 3 h. A poor yellow colored precipitation was filtered and washed with EtOH, then dried in air [8].

## *Synthesis of N-(5-Ethyl-1,3,4-thiadiazole-2-yl)terephthalaldehyde Imine(L<sup>2</sup>)*

2-Amino-5-ethyl-1,3,4-thiadiazole 0.26 g (0.002 mol) in ethanol 20 mL was added to a hot ethanol solution 15 mL of terephthalaldehyde 0.27 g (0.002 mol). The pH was adjusted to  $\approx$ 5 using glacial acetic acid (3 mL). The resultant solution was heated in an electro-magnetic stirring apparatus to reflux for 8 h. After cooling, the solution of the Schiff base was stirred for an additional 10 min and finally poured into a beaker containing 100 mL of water. The new mixture was stirred for 20 min, and the resulting dark yellow solid was collected by filtration, washed several times with water, and dried in air for 48 h. The product was recrystallized from ethanol and washed with cold ethanol [9].

#### *Synthesis of N,N'-bis*[5-(4-Nitrophenyl)-1,3,4thiadiazole-2-yl]terephthalaldehydediimine (L<sup>3</sup>)

Terephthalaldehyde (5.42 g, 0.01 mol) in hot ethanol (20 mL) was added to a hot DMF solution (30 mL) of 5-nitrophenyl-1,3,4-thiadiazole-2-amine (4.44 g, 0.02 mol). Then 2–3 drops of conc.  $H_2SO_4$  were added, and the mixture was refluxed for 3 h. The precipitated ligand was filtered off, recrystallized from ethanol, and dried in air at room temperature [10]. Some properties of the synthesized ligands are given in Table 1.

#### Synthesis of Complexes

Synthesis of the  $[Zn(L^1)_2(C_2H_5OH)_2] \cdot C_2H_5OH$ Complex. The ligand HL<sup>1</sup> 0.61 g (0.002 mol) was dissolved in 20 mL DMF in a 100-mL round-bottomed flask. A solution of 0.41 g (0.001 mol) metal salt ZnCl<sub>2</sub> in 10 mL of absolute ethanol was added dropwise



FIGURE 2 Synthesis of the ligand: N-(5-ethyl-1,3,4-thiadiazole-2-yl)terephthalaldehyde imine (L<sup>2</sup>).



FIGURE 3 Synthesis of the ligand: N,N'-bis[5-(4-nitrophenyl)-1,3,4-thiadiazole-2-yl]terephthal aldehyde diimine (L<sup>3</sup>).

for 15 min with continuous stirring at room temperature. The reaction mixture was then further refluxed for 6 h at 100–120°C. The resulting precipitate was filtered off and washed with DMF and absolute ethanol, respectively, then dried in air.

Synthesis of the  $[Zn(L^2)_2Cl_2] \cdot H_2O$  Complex. 1.49 g (0.006 mol) of ligand L<sup>2</sup> was dissolved in 20 mL absolute ethanol in a 100-mL round bottomed flask. A solution of 0.41 g (0.003 mol) of ZnCl<sub>2</sub> in 10 mL absolute ethanol was added dropwise for 10 min with continuous stirring at room temperature. The mixture was refluxed overnight. Then the volume of the solutions was reduced to about 10 mL and complex was precipitated with chloroform–acetone (1:2) to give a gray product. The precipitate was filtered, washed with methanol, and then dried at room temperature.

Synthesis of the  $[Zn_2(L^3)_2(H_2O)_4Cl_4]$  Complex. The ligand L<sup>3</sup> 0.70 g (0.001 mol) was dissolved in 20 mL DMF in a 100-mL round-bottomed flask. A solution of 0.14 g (0.001 mol) metal salt  $ZnCl_2$  in 10 mL of absolute ethanol was added dropwise for 15 min with continuous stirring at room temperature. The reaction mixture was then further refluxed for 8 h at 100–120°C. The resulting precipitate was filtered off and washed with DMF and absolute ethanol, respectively, then dried at room temperature.

#### RESULTS AND DISCUSSION

This study was completed in four stages. In the first stage, the 2-amino-5-(2-amino-1,3,4thiadiazoleyl)-1,3,4-thiadiazole (1) compound, as stated in the Experimental section, was synthesized according with to the method described in the literature [8]. Then, N-[5'-amino-2,2'-bis(1,3,4thiadiazole)-5-yl]-2-hydroxybenzaldehyde imine (HL<sup>1</sup>) was obtained by the reaction of 2-amino-5-(2amino-1,3,4-thiadiazoleyl)-1,3,4-thiadiazole (1) and

**TABLE 1**Colors, Formula, Formula Weight, Yields, Melting Points, Magnetic Moments, and Elemental Analysis Results of the<br/>Ligands  $HL^1$ ,  $L^2$ , and  $L^3$  and Their Complexes

	FW (g/mol)	Мр ( <sup>°</sup> С)	Yield (%)	μ <sub>eff</sub> ( <b>BM)</b> <sup>a</sup>	Elemental Analyses/(%) Calculated (Found)			
Compounds					С	Н	Ν	S
[HL <sup>1</sup> ] C <sub>11</sub> H <sub>8</sub> N <sub>6</sub> S <sub>2</sub> O (pale yellow)	304.00	330	66	-	43.42 (43.31)	2.63 (2.44)	27.63 (26.49)	21.05 (21.02)
[L <sup>2</sup> ] C <sub>12</sub> H <sub>11</sub> N <sub>3</sub> SO (orange)	245	170	60	_	58.76 (58.72)	4.49 (4.22)	17.14 (17.20)	13.06 (13.32)
[L <sup>3</sup> ] C <sub>24</sub> H <sub>14</sub> N <sub>8</sub> S <sub>2</sub> O <sub>4</sub> (dark red)	542	325	62	_	53.14 (52.98)	2.58 (2.53)	20.66 (20.48)	11.81 (12.09)
[Zn(L <sup>1</sup> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ] ·C <sub>2</sub> H <sub>5</sub> OH (yellow) C <sub>28</sub> H <sub>32</sub> N <sub>12</sub> S <sub>4</sub> O <sub>5</sub> Zn	809.38	340	50	Dia	41.51 (40.97)	3.95 (3.88)	20.76 (20.64)	15.82 (15.66)
[Zn(L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O (gray) C <sub>24</sub> H <sub>24</sub> N <sub>6</sub> S <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub> Zn	644.28	230	52	Dia	44.70 (44.95)	3.73 (3.51)	13.04 (12.88)	9.93 (9.89)
$\begin{array}{l} [Zn_2(L^3)_2(H_2O)_4Cl_4] \\ (brownish yellow) \\ C_{24}H_{22}N_8S_2O_8Cl_4Zn_2 \end{array}$	834.66	358	64	Dia	32.49 (32.15)	2.48 (2.30)	12.63 (12.54)	7.22 (6.98)

salicylaldehyde. In the second stage, the *N*-(5ethyl-1,3,4-thiadiazole-2-yl) terephthalaldehyde imine ( $L^2$ ) compound was synthesized by the reaction of terephthalaldehyde and 2-amino-5ethyl-1,3,4-thiadiazole, which was provided by Merck chemical company. In the third stage, the *N*,*N*'-bis[5-(4-nitrophenyl)-1,3,4-thiadiazole-2-yl] terephthalaldehydediimine ( $L^3$ ) compound was synthesized by the reaction of 5-nitrophenyl-1,3,4thiadiazole-2-amine and terephthalaldehyde. In the last stage, the complexes were synthesized by the reaction of these ligands (HL<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup>) with ZnCI<sub>2</sub> metal salt.

Schiff bases and their metal complexes are stable toward air and moisture. The Schiff bases are soluble in dimethylformamide, whereas the complexes are sparingly soluble in hot dimethylformamide and dimethylsulfoxide.

The ligands (HL<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup>) and their new complexes were characterized by elemental analyses (Table 1) and the spectral data that allowed us to assign the coordination mode of ligands in these complexes. As seen from the data given in Table 1, the elemental analyses data of the new complexes are within  $\pm 0.4\%$  of the theoretical data calculated for the proposed formulas. The complexes have a metal: ligand ratio of 1:1 and 1:2 according to the elemental analyses results. In addition, there are ethanol and water molecules.

#### Infrared Spectra

The IR data of the spectra of Schiff bases and their complexes are listed in Table 2. The IR spectra of the complexes are compared with those of the free ligands to determine the coordination sites that may involve chelation. There are some guide peaks in the spectra of the ligands, which are helpful in achieving this goal. The position and/or the intensities of these peaks are expected to change upon chelation.

The spectra of all complexes exhibited intense broad bands at 3615–3363 cm<sup>-1</sup> due to  $\nu$ (OH) of lattice and coordinated water or ethanol molecules [11]. The presence of hydrate or/and coordinated water molecules or ethanol molecule was also confirmed by elemental analyses and thermogravimetric analyses [12].

In the IR spectrum of 2-amino-5-(2-amino-1,3,4-thiadiazoleyl)-1,3,4-thiadiazole (1) the characteristic peaks are at 3340 and 3280 cm<sup>-1</sup>  $\nu_{as}$ (NH<sub>2</sub>) and  $\nu_s$ (NH<sub>2</sub>), 1628 cm<sup>-1</sup> $\nu$ (C=N) in thiadiazole and 1514 cm<sup>-1</sup> $\delta$  (NH), respectively [8].

Compounds	Spectral Data				
Ligand LH <sup>1</sup>	IR: ν (cm <sup>-1</sup> ): (OH) 3379, (NH <sub>2</sub> ) 3284, (C−H) <sub>arom</sub> 3119, (CH=N) 1679, (C=C) 1610, (>C=N−N=C<) 1492–1430, (C−O) 1302, (N−N) 1060–948, (C−S−C) 758–754 IR: δ (cm <sup>-1</sup> ): (NH) 1570				
	<sup>1</sup> Η NMR (DMSO- <i>d</i> <sub>6</sub> ) δ: 11.20 (s, 1H, Ar-O <u>H</u> ), 9.00 (s, 1H, C <u>H</u> =N), 6.50–8.50 (m, 4H, Ar-C <u>H</u> ), 8.40 ( 2H, N <u>H</u> <sub>2</sub> )				
$[Zn(L^1)_2(C_2H_5OH)_2] \cdot C_2H_5OH$	IR, $\nu$ (cm <sup>-1</sup> ): (OH) 3615–3406, (NH <sub>2</sub> ) 3270, (C–H) <sub>arom</sub> 3127, (CH=N) 1664, (C=C) 1601, (>C=N-N=C<) 1489–1432, (C-O) 1286, (N–N) 1063–949, (C–S–C) 760-758, (M–O) 567, (M–N) 465; IR, $\delta$ (cm <sup>-1</sup> ): (NH) 1572				
	<sup>1</sup> H NMR (DMSO- <i>d</i> <sub>6</sub> ), δ: 9.20 (s, 1H, C <u>H</u> =N), 6.60–8.58 (m, 4H, Ar-C <u>H</u> ), 8.42 ( 2H, N <u>H</u> <sub>2</sub> ), 1.12 (3H, CH <sub>3</sub> ), 3.45 (2H, CH <sub>2</sub> )				
Ligand L <sup>2</sup>	IR: ν (cm <sup>-1</sup> ): (C−H) <sub>arom</sub> 3090–3082, (C−H) <sub>alift</sub> 2865–2806, (C=O) 1692, (CH=N) 1629, (>C=N−N=C<) 1498–1444, (N−N) 1045–980, (C−S−C) 772				
	<sup>1</sup> H NMR (DMSO- <i>d</i> <sub>6</sub> ), δ: 10.10 (s, 1H, –CO <u>H</u> ), 9.10 (s, 1H, C <u>H</u> =N), 8.20–6.80 (m, 4H, Ar-C <u>H</u> ), 3.40 (2H, CH <sub>2</sub> ), 1.20 (3H, CH <sub>3</sub> )				
$[Zn(L^2)_2Cl_2]\cdot H_2O$	IR, $\nu$ (cm <sup>-1</sup> ): (OH) 3505–3363, (C–H) <sub>arom</sub> 3070, (C–H) <sub>alift</sub> 2860–2800, (C=O) 1690, (CH=N) 1610, (>C=N-N=C<) 1496–1430, (N–N) 1013–1004, (C–S–C) 770 $\nu$ (M–N): 522				
	<sup>1</sup> H NMR (DMSO- <i>d</i> <sub>6</sub> ), δ: δ <sub>H</sub> = 10.80 (s, 1H, -COH), 9.15 (s, 1H, C <u>H</u> =N), 8.10–6.90 (m, 4H, Ar-CH), 3.30 (2H, CH <sub>2</sub> ), 1.36 (3H, CH <sub>3</sub> )				
Ligand L <sup>3</sup>	IR: ν (cm <sup>-1</sup> ): (C–H) <sub>arom</sub> 3154–3006, (C–H) <sub>alift</sub> 2945–2791, (CH=N) 1676–1624, (>C=N–N=C<) 1568–1482, (NO <sub>2</sub> ) 1349, (C–S–C) 752–687				
	<sup>1</sup> H NMR (DMSO- $d_6$ ), $\delta$ : 9.20 (s, 2H, C <u>H</u> =N), 8.50–7.70 (m, 12H, Ar-C <u>H</u> )				
[Zn <sub>2</sub> (L <sup>~</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> Cl <sub>4</sub> ]	IR: $\nu$ (cm <sup>-</sup> ): (OH) 3500–3384, (C–H) <sub>arom</sub> 3116–3026, (C–H) <sub>alift</sub> 2923–2750, $\nu$ (CH=N) 1660-1612, (>C=N–N=C<) 1565–1483, (NO <sub>2</sub> ) 1347, (C–S–C) 740–673, (M–N) 460 <sup>1</sup> H NMR (DMSO- <i>ds</i> <sub>6</sub> ), $\delta$ : 9.30 (s, 2H, C <u>H</u> =N), 8.55–7.78 (m, 12H, Ar-C <u>H</u> )				

**TABLE 2** Spectral Data of Ligands LH<sup>1</sup>, L<sup>2</sup>, and L<sup>3</sup> and Their Complexes

In the IR spectra of the ligand HL<sup>1</sup>, the most characteristic bands are at 3379 cm<sup>-1</sup> $\nu$ (OH) and 1679 cm<sup>-1</sup> azomethine  $\nu$ (HC=N) and 3284 cm<sup>-1</sup>  $\nu$ (NH<sub>2</sub>). The absence of  $\nu$ (C=O), and  $\nu$ (NH<sub>2</sub>) peaks in the spectra of ligand indicates that the expected imino compound was formed by condensation from 2-amino-5-(2-amino-1,3,4-thiadiazoleyl)-1,3,4-thiadiazole (1) and salicylaldehyde, and it is also shown that there are no residual starting materials left in the ligand compound as well [12,13].

The IR spectrum of the 2-amino-5-(2-amino-1,3,4-thiadiazoleyl)-1,3,4-thiadiazole (1) exhibits a NH<sub>2</sub> peak at 3280 cm<sup>-1</sup>. The position of this band remains almost unaffected, showing only minor shifts to lower frequency in the spectra of metal complex indicating thereby the noninvolvement of the NH<sub>2</sub> group in the coordination [14].

The IR spectra of the  $[Zn(L^1)_2(C_2H_5OH)_2]$ . C<sub>2</sub>H<sub>5</sub>OH complex indicated the disappearance of the OH band from the spectra of complex displacement of phenolic proton by a metal ion. The IR spectrum for intensity of the OH band indicates partial removal of proton from the OH group [13].

In the Schiff base ligand HL<sup>1</sup>, the strong band observed 1679 cm<sup>-1</sup>can be assigned to the  $\nu$ (C=N) azomethine stretching vibration. On complexation, this band was shifted (1664 cm<sup>-1</sup>) to lower frequency of the azomethine nitrogen atom to the central metal ion [15].

The  $\nu$ (C–O) phenolic band in the [Zn(L<sup>1</sup>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub> OH)<sub>2</sub>]·C<sub>2</sub>H<sub>5</sub>OH complex was shifted to lower frequency in the 1286 cm<sup>-1</sup>range, indicating the coordination of the phenolic oxygen atom with the metal ion [16].

In the complexes, weak bands in the 465<sup>-</sup> and 567 cm<sup>-1</sup> range can be attributed to  $\nu$ (M–N) and  $\nu$ (M–O), respectively. From the IR results, it may be concluded that the Schiff base ligand HL<sup>1</sup> is bidentate and coordinates with the metal ion through the phenolic oxygen and azomethine nitrogen atoms [17].

Other characteristic IR bands observed in the spectra of the Schiff bases at 1492–1430, 1060–948, and 758–754 cm<sup>-1</sup> are assigned to the  $\nu(>C=N-N=C<)$ ,  $\nu(N-N)$ , and  $\nu(C-S-C)$  modes of vibrations, respectively, of the thiadiazole ring. In the spectra of the complex, the  $\nu(>C=N-N=C<)$ ,  $\nu(N-N)$ , and  $\nu(C-S-C)$  vibrations remain almost unchanged, indicating, thereby, noninvolvement of the ring nitrogen and sulfur in the coordination [13].

The IR spectra of the Schiff base (L<sup>2</sup>) reported here showed the absence of bands at  $\approx$ 1700, 3287, and 3108 cm<sup>-1</sup> due to carbonyl  $\nu$ (C=O) and  $\nu$ (NH<sub>2</sub>) stretching vibrations (present in the start-

ing materials) and the appearance of a strong new band at 1629 cm<sup>-1</sup> assigned to azomethine  $\nu$ (C=N) vibration [18].

The spectra of the free ligand L<sup>2</sup> display band at 1692 cm<sup>-1</sup> due to  $\nu$ (C=O). The position of  $\nu$ (C=O) is found to be dependent on the electronic nature of the p-substituents [19]. The  $\nu$ (C=O) stretching vibration that is useful for diagnosis of coordination located at 1692 cm<sup>-1</sup> for ligand remains at the same position as in L<sup>2</sup>, indicating that the  $\nu$ (C=O) group does not coordinate with the metal atoms [20].

The infrared spectra of the ligand show bands 1629 and 1498-1444 cm<sup>-1</sup>, which may be assigned to be  $\nu$ (C=N) (the azomethine group) and  $\nu(>C=N-N=C<)$  (ring), respectively. The first band is shifted toward the lower frequency region (19 cm<sup>-1</sup>) in the  $[Zn(L^2)_2Cl_2]\cdot H_2O$  complex, indicating the coordination of the azomethine nitrogen atom of the Schiff base. However, the second band  $\nu(>C=N-N=C<)$  (ring) is found to split into two: one almost located at the original position, indicating noncoordinated at the  $\nu$ (C=N), and other shifted to lower frequency 1430 cm<sup>-1</sup>, arising due to the coordinated  $\nu$ (C=N) mode. The splitting of the  $\nu(>C=N-N=C<)$  (ring) absorption band suggests that only one of the ring nitrogen is involved in coordination and other is free and noncoordinated. This is further supported by a new band at 522 cm<sup>-1</sup> assignable to  $\nu$ (M–N) in the complex. The  $\nu$ (C–S–C) band in the ligand occurs at 772 cm<sup>-1</sup>, which remains unaltered in the spectra of the complex, indicating the noncoordination of sulfur atom of the thiadiazole ring [21].

In the IR spectrum of the ligand  $L^3$ , most characteristic bands are at 1568 -1482 cm<sup>-1</sup>  $\nu$ (>C=N-N=C<) in thiadiazole, 1676-1624 cm<sup>-1</sup>  $\nu$ (C=N), 1349 cm<sup>-1</sup> $\nu$ (NO<sub>2</sub>), and 752– 687 cm<sup>-1</sup>  $\nu$ (C–S–C). The Absence of  $\nu$ (C=O), and  $\nu(NH_2)$  peaks in the spectra of the ligand indicates that the expected imino compound was formed by condensation from 5-nitrophenyl-1,3,4-thiadiazole-2-amine and terephthalaldehyde. And it is also shown that no residual starting materials were left in the ligand compound as well [22].

The azomethine  $\nu$ (C=N) bands in the spectra of ligand L<sup>3</sup> lying at 1676–1624 cm<sup>-1</sup> displayed a shift to lower wave numbers (1660–1612) in the spectra of [Zn<sub>2</sub>(L<sup>3</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>Cl<sub>4</sub>] complex, indicating that the C=N nitrogen atom coordinates to the metal ion in this complex [18].

The band due to  $\nu(NO_2)$  in the spectra of ligand was observed at the same positions in the spectra of the complexes, showing that the NO<sub>2</sub> group in these complexes did not participate in the complex formation [19].



FIGURE 4 Suggested structure of the octahedral Zn(II) complex of the ligand HL<sup>1</sup>.

In the spectra of the  $[Zn_2(L^3)_2(H_2O)_4Cl_4]$  complex, the  $\nu(>C=N-N=C<)$  vibrations remain almost unchanged indicating, thereby, noninvolvement of the ring nitrogen in-coordination. The  $\nu(C-S-C)$  undergoes a negative shift in the complex, indicating the coordination of ring sulfur to copper [4]. The coordination through the azomethine nitrogen and sulfur is further supported by the occurrence of new bands at 460 and 360 cm<sup>-1</sup> in the spectra of the complex, which may be assigned to  $\nu(M \rightarrow N)$  and  $\nu(S \rightarrow M)$  vibration, respectively [23,24]. However, the IR spectrum of the complex (M-S) bands could not be observed, that we have studied in 4000–400 cm<sup>-1</sup> range.

The IR bands of  $\nu(H_2O)$  of coordinated water appeared at 820–840 cm<sup>-1</sup>, indicating the binding of water molecules to the metal ions [25].

The coordinated halogen in the complexes shows a far IR absorption peak in the range 294– 230 cm<sup>-1</sup>, which may be attributed to  $\nu$ (M–Cl) [15,26]. However, the IR spectrum of the complexes (M-CI) bands could not be observed, which we have studied in 4000–400 cm<sup>-1</sup> range.

In the Zn(II) complexes of the HL<sup>1</sup>, L<sup>2</sup>, and L<sup>3</sup> ligands, the chloride ions are coordinate with the metal ions (see Figs. 5 and 6). In the CI<sup>-</sup> test with AgNO<sub>3</sub>, precipitation of white AgCI salt does not immediately become evident.

#### <sup>1</sup>H NMR Spectrum

The <sup>1</sup>H NMR spectrum of Schiff bases as well as their Zn(II) complexes was recorded in dimethylsulfoxide (DMSO- $d_6$ ) solution using tetramethylsilane (TMS) as an internal standard. The <sup>1</sup>H NMR spectra of the Schiff bases (HL<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup>), their diamagnetic Zn(II) complexes, and the chemical shifts of the different types of protons are listed in Table 2. The Schiff base exhibited signals due to all expected protons in their expected regions. These were compared



FIGURE 5 Suggested structure of the octahedral Zn(II) complex of the ligand L<sup>2</sup>.



FIGURE 6 Suggested structure of the octahedral Zn(II) complex of the ligand L<sup>3</sup>.

with the reported signals of known structurally related compounds and give further support for the composition of Schiff bases as well as their complexes suggested by their IR and elemental analyses data. A comparison of the chemical shifts of the uncomplexed Schiff bases shows that the resonances are shifted upon complexation. Upon examination, it was found that the phenolic-OH signal, appeared in the spectrum of ligand HL<sup>1</sup> at 11.20 ppm, is completely disappeared in the spectra of its Zn(II) complex, indicating that the OH proton was removed by the chelation with the Zn(II) ion. In the spectra of Schiff bases, protons of the azomethine group downfield shifted in the Zn(II) complexes, indicating participation of this group in coordination of the metals ions. The signals observed at 3.45 and 3.70 ppm with an integration corresponding to protons in the case of  $[Zn(L^2)_2Cl_2] \cdot H_2O$  and  $[Zn_2(L^3)_2(H_2O)_4Cl_4]$  complexes, respectively, are assigned to water molecules.

#### Magnetic Susceptibility and Electronic Spectra Measurements

The UV-vis spectra of the ligands and their complexes were recorded in the DMF solution in the wavelength range from 200 to 800 nm. The corresponding electronic transitions are presented in Table 3. The band appearing in the range of 218–318 nm is attributed to  $\pi \rightarrow \pi^*$  transition of the benzene ring of the ligand HL<sup>1</sup>. This band is redshifted to 265– 328 nm. The other bands observed in the region 318– 387 nm in the free ligand are reasonably accounted for  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions for the phenolic-OH and azomethine moieties, respectively [8]. In the [Zn(L<sup>1</sup>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>]·C<sub>2</sub>H<sub>5</sub>OH complex, these bands are shifted to longer wavelength as a result of the coordination to the metal, confirming the formation of the Schiff base metal complex.

The diamagnetic  $[Zn(L^1)_2(C_2H_5OH)_2]\cdot C_2H_5OH$ complex of the HL<sup>1</sup> ligand did not show any d–d bands, and their spectra are only dominated by charge transfer bands. The charge transfer band at 377–460 nm was assigned to  ${}^2E_g \rightarrow {}^2T_{2g}$ transitions, possibly in an octahedral environment.

In the spectrum of the ligand L<sup>2</sup>, the bands 350– 390 nm range are assigned to the  $n \rightarrow \pi^*$  transitions of the azomethine group and thiadiazole ring. During the formation of the complex, these bands are shifted to lower wavelength, suggesting that the nitrogen atoms of the azomethine group and thiadiazole ring are coordinated to the metal ion. The values in the 300–350 nm range are attributed to the  $\pi \rightarrow \pi^*$  transition of the aromatic and thiadiazole ring. In the spectra of the complex, these bands are shifted slightly to lower wavelength [9,27].

TABLE 3 Electronic Spectral Data of the Ligands HL<sup>1</sup>, L<sup>2</sup>, and L<sup>3</sup> and Their Complexes (nm) (in DMF)

Compounds	Wavelength (nm) ( $\varepsilon$ )				
[HL <sup>1</sup> ]	218–318, 387 (1125, 160) $\pi \rightarrow \pi^*, n \rightarrow \pi^*$				
[L <sup>2</sup> ]	304–354 <sup><i>a</i></sup> , 390 (1400 <sup><i>a</i></sup> , 150) $\pi \rightarrow \pi^*$ , $n \rightarrow \pi^*$				
[L <sup>3</sup> ]	304, 370 (30100, 22300) $\pi \rightarrow \pi^*, \ n \rightarrow \pi^*$				
$[Zn(L^1)_2(C_2H_5OH)_2]\cdot C_2H_5OH$	265 (1100) $\pi \to \pi^*$	377, 460 (7300–330) L $\rightarrow$ M $^2E_q \rightarrow {}^2T_{2q}$			
[Zn(L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]⋅H <sub>2</sub> O	301–313 (1600–1200) $\pi \to \pi^*, \ n \to \pi^*$	360 (6900) L → M			
$[Zn_2(L^3)_2(H_2O)_4CI_4]$	265, 330 (31100,16100) $\pi \to \pi^*, n \to \pi^*$	345–350 (12500) L $\rightarrow$ M			

 $\varepsilon = Molar extinction coefficient (L mol<sup>-1</sup> cm<sup>-1</sup>).$ 

<sup>a</sup>maximum wavelength in 340 nm.

The electronic spectrum of the  $[Zn(L^2)_2Cl_2]$ ·H<sub>2</sub>O complex shows an absorption band at 360 nm, attributed to the L  $\rightarrow$  M transition, which is compatible with this complex having an octahedral structure [28].

The spectrum of the ligand L<sup>3</sup> shows an intense band at 304 nm, which is attributed to  $\pi \rightarrow \pi^*$  transition within the benzene ring and a double bond of the azomethine group. The band around 370 nm is due to the  $n \rightarrow \pi^*$  transition of the nonbonding electrons present in the nitrogen of the thiadiazole group in the Schiff base. In the complex, this band undergoes a hypsochromic shift due to coordination of the Schiff base ligand to metal ion [10,29]. The electronic spectra of the [Zn<sub>2</sub>(L<sup>3</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>Cl<sub>4</sub>] complex exhibited only high-intensity band at 345–350 nm, which is assigned to a ligand metal charge transfer. The [Zn<sub>2</sub>(L<sup>3</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>Cl<sub>4</sub>] complex is diamagnetic and has an octahedral geometry.

#### Thermal Studies

The thermal stability of the ligands and their complexes was investigated by a combination of TGA and DTA. The TGA and DTA curves were obtained at a heating rate of 15°C/min in a nitrogen atmosphere over the temperature range of 25–800°C. The thermal data are summarized in Table 4. The results are in good agreement with the theoretical formula suggested by the elemental analyses. The weight losses for ligand and complexes were calculated within the corresponding temperature ranges.

The ligand  $HL^1$  is stable up to 50.37°C, and its decomposition started at this temperature. The ligand shows five-step weight loss. The loss of the OH and NH<sub>2</sub> groups and simultaneously in the first and second steps between 50.37 and 333.56°C with one endothermic DTA peak at 83.35°C and violently one exothermic peak at DTA 219.48°C. The 30 step in the 333.56-470.18°C range corresponds to the exothermic elimination of the second thiadiazole rings. The experimental mass loss of 55.55% agrees well with the calculated mass loss of 55.56%. The 40 step in the 470.18–645.25°C range corresponds to the exothermic elimination of the benzene ring. The experimental mass loss of 25.18% agrees well with the calculated mass loss of 25.33%. The final step in the 645.25°C step shows elimination of one of the CH=N group. The experimental mass loss of 7.41% agrees well with the calculated mass loss of 8.88% [8,30].

The decomposition curve of  $Zn(L^1)_2(C_2H_5OH)_2]$ . C<sub>2</sub>H<sub>5</sub>OH begins by a step at 75.12–175.46°C, displaying (% experimental weight 5.68; calculated weight 5.19) weight loss corresponding to the removal of C<sub>2</sub>H<sub>5</sub>OH. The second stage ending at 175.46– 350.35°C is assigned to the elimination of  $2C_2H_5OH$ groups from the ligand accompanied by weight loss (% experimental weight 11.37; calculated weight 11.11) [31]. The third step (350.35–458.16°C) can be ascribed to the removal of the remaining  $C_4N_4S_2$ group by weight loss of (% experimental weight 24.71; calculated weight 23.70).

The ligand L<sup>2</sup> is stable up to 115.26, but then it decomposes in three steps 115.26–200.46°, 200.46–300.24,° and 300.24–620.88°C. In the decomposition of the ligand, the weight losses correspond to the removal of the  $-CH_2CH_3$ , -CHO, and thiadiazole group at the first, second, and third stages of decomposition, respectively. The DTA curve of the ligand exhibits three endothermic peaks at 104.35, 190.30, and 217.25°C, and one exothermic peak at 313.58°C. The three stages of the ligand decomposition are irreversible [9,10].

The  $[Zn(L^2)_2Cl_2]$ ·H<sub>2</sub>O complex was stable up to 87.0°C, and its decomposition started at this temperature. The first step in the temperature range 87.35–121.42°C was accounted for the loss of water molecules of hydration (% experimental weight 2.79; calculated weight 2.96). The second step of decomposition within the temperature range 121.42– 200.28°C corresponds to the loss of 2Cl, 2CH<sub>2</sub>CH<sub>3</sub>, and C<sub>8</sub>H<sub>5</sub>O groups (% experimental weight 56.63; calculated weight 57.03). In the DTA curve, a sharp endothermic peak observed in the range 120.34°C for the complex of Zn(II), in conjunction with the mass loss in the TGA curve corresponding to water molecule, confirms the stoichiometry [Zn(L<sup>2</sup>)<sub>2</sub>Cl<sub>2</sub>]·H<sub>2</sub>O of the Zn(II) complex [32,33].

The ligand L<sup>3</sup> is stable up to  $150.34^{\circ}$ C but then it decomposes in two steps corresponding to the temperature range  $150.34-495.12^{\circ}$  and  $495.12-800.46^{\circ}$ C. In the decomposition of the ligand, the weight losses correspond to the removal of the  $2C_{6}H_{4}NO_{2}$  and the other parts of the ligand at the first and second stages of decomposition, respectively. The TGA curve of the ligand exhibits three exothermic peaks at 217.43, 495.56, 626.24°C. The two stages of the ligand decomposition are irreversible [10,34].

The  $[Zn_2(L^3)_2(H_2O)_4Cl_4]$  complex was stable up to 110.00°C, and its decomposition started at this temperature. The first step in the temperature range 110.00–285.25°C was accounted for the loss of coordinated water molecules (% experimental weight 8.12; calculated weight 8.15). In the DTA curve, a sharp endothermic peak observed in range 160.8°C for the complex of Zn(II), in conjunction with the mass loss in the TGA curve corresponding to four water molecules, confirms the stoichiometry  $[Zn_2(L^3)_2(H_2O)_4Cl_4]$  of the Zn(II) complex. The second step of decomposition within the temperature

Equation	Temperature (° C)	Percent Loss in Weight Percent Found (Percent Calculated),	Decomposition Products
C <sub>11</sub> H <sub>8</sub> N <sub>6</sub> S <sub>2</sub> O [HL <sup>1</sup> ]	50.37–333.56	10.85 (11.11)	OH vs. NH <sub>2</sub> N-N N-N // \\ // \\
$C_{11}H_5N_5S_2$	333.56–470.18	55.56 (55.55)	s s
$C_7H_5N$ CHN	470.18–645.25 645.25	25.33 (25.18) 8.88 (7.41)	N=CH
$C_{12}H_{11}N_{3}SO$ $C_{12}H_{11}N_{3}SO$ $C_{10}H_{6}N_{3}SO$ $C_{0}H_{5}N_{2}S$	20.46–200.46 200.46–300.24 300.24–620.88	_ 11.84 (11.85) 11.84 (11.85) 34.29 (34.81)	
$C_7H_5N$ $C_{24}H_{14}N_8S_2O_4[L^3]$	620.88 25.00–150.34		Thermal stability
$C_{24}H_{14}N_8S_2O_4$	150.34–495.12	45.01(44.44)	$2 - \sqrt{NO_2}$
$C_{12}H_6N_6S_2$	495.12-810.46	54.98(54.07)	
$ \begin{array}{l} [Zn(L^1)_2(C_2H_5OH)_2] \cdot C_2H_5OH \ C_{28}H_{32}N_{12}S_4O_5Zn \\ C_{26}H_{26}N_{12}S_4O_4Zn \end{array} $	75.12–175.46 175.46–350.35	5.68(5.19) 11.37(11.11)	C <sub>2</sub> H <sub>5</sub> OH 2C <sub>2</sub> H <sub>5</sub> OH N-N
$C_{22}H_{12}N_{12}S_4O_2Zn$ $C_{18}H_8N_6S_2O_2Zn$	350.35–458.16 458.16-	24.71(23.70)	2 H <sub>2</sub> N-(L <sub>S</sub> )
$\begin{array}{l} [Zn(L^2)_2Cl_2]\cdot H_2O\ C_{24}H_{24}Cl_2ZnN_6S_2O_3\\ C_{24}H_{20}Cl_2ZnN_6S_2O\end{array}$	87.35–121.42 121.42–200.28	2.79 (2.96) 56.63 (57.03)	Two hydrated water $2CH_2CH_3$ , $2CI$ and
			2 сн- Сн- Ён
$C_{16}H_4ZnN_6S_2$	200.28		
$[Zn_2(L^3)_2(H_2O)_4Cl_4]C_{24}H_{22}N_8S_2O_8Cl_4Zn_2$	25.00-110.00		Thermal stability
C <sub>24</sub> H <sub>22</sub> N <sub>8</sub> S <sub>2</sub> O <sub>8</sub> Cl <sub>4</sub> Zn <sub>2</sub> C <sub>24</sub> H <sub>14</sub> N <sub>8</sub> S <sub>2</sub> O <sub>4</sub> Cl <sub>4</sub> Zn <sub>2</sub>	110.00–285.25 285.25–420.40	8.15(8.12) 15.99(15.15)	Four coordinated water 4Cl
$C_{24}H_{14}N_8S_2O_4Zn_2 \\ C_{12}H_8N_6S_2Zn_2$	420.40–480.65 480.65	29.62(29.13)	2 — NO2

TABLE 4	Proposed Decomposition	Steps and the	Respective Mass	Losses of Ligands HL	<sup>1</sup> , L <sup>2</sup> , and L	<sup>3</sup> and their Complexes
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range 285.25–420.40°C corresponds to the loss of Cl ligands (% experimental weight 15.15; calculated weight 15.99). In the Zn(II) complex, the endothermic peak at 360.4°C is related to the decomposition of Cl ligands [35,36]. The 30 step in the 420.40–480.65°C range corresponds to the exothermic elimination of the  $2C_{12}H_8N_2O_4$  (% experimental weight 29.13; calculated weight 29.62).

The final products during thermal analysis of the ligand and its complexes were not identified because ligand and its complexes could not completely decomposed until 800°C temperature. The continuation of the decomposition indicates that a higher thermal stability of the complexes. Such stability may refer to the presence of one or/two fivemembered rings [31].

Single crystals of the complexes could not be isolated from any solutions, thus no definite structure could be described. However, the analytical, spectroscopic, and magnetic data enable us to propose the possible structure.

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