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## Spectral Characterization of a New Cyclobutane and Thiazole Substituted Schiff Base Ligand and Its Co(II), Cu(II), Ni(II), and Zn(II) Complexes

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### ABSTRACT

A novel bidentate Schiff base ligand containing cyclobutane and 2,4-disubstituted thiazole rings, 4-(1-methyl-1-mesylcyclobutane-3-yl)-2-(2-hydroxy-5-methoxy benzylidenehydrazino) thiazole (HL), and its mononuclear complexes with a 1 : 2 metal : ligand ratio have been prepared with acetate salts of Co(II), Cu(II), Ni(II), and Zn(II) in ethanol. The authenticity of the ligands and their complexes has been established by microanalyses,  $\Delta m$ , IR,  $^1H$  and  $^{13}C$  NMR spectra, and by magnetic susceptibility measurements. The thermal properties of all complexes have been studied by TG and DSC techniques. All the complexes were found to be mononuclear.

**Key Words:** Cyclobutane; Thiazole; Schiff base; Complexes.

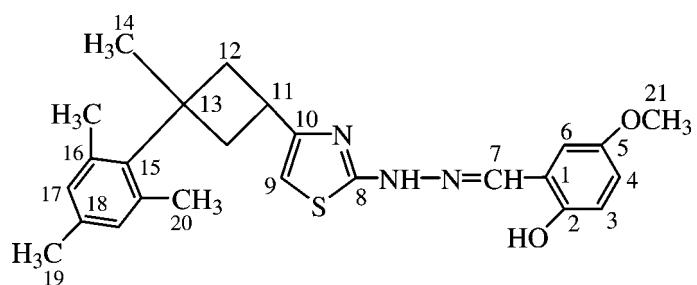
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## INTRODUCTION

Previously, as a part of our research program concerning the chelating behavior of 2,4-disubstituted thiazoles, we have examined the coordination properties of some 2,4-disubstituted thiazoles in several transition metal complexes.<sup>[1-4]</sup> Metal complexes of some 2,4-disubstituted thiazole derivatives have been found, in some instances, to have enhanced or modified activity in comparison to the uncomplexed ligand. Thiosemicarbazones, cyclobutanes, thiazoles, and Schiff bases are of great importance for the preparation of various pharmaceuticals and are used in many other areas of chemistry as starting materials. Schiff bases derived from salicylaldehydes are well known polydentate ligands.<sup>[5]</sup> It has been shown that Schiff base complexes derived from 4-hydroxysalicylaldehyde and amines have strong anticancer activity.<sup>[6]</sup> Some thiazole derivatives containing the tetralin moiety have been synthesized and used in biological activity studies.<sup>[7]</sup> Recently, there has been considerable interest in the chemistry of Schiff base compounds containing thiosemicarbazones and their metal complexes due to their biological activities<sup>[8]</sup> and nonlinear optical properties.<sup>[9]</sup> Research has concentrated on different properties of poly-substituted cyclobutane derivatives for a number of years.<sup>[10]</sup> Our group has been heavily engaged in the synthesis of novel 1,1,3-trisubstituted cyclobutane thiazoles and their Schiff base derivatives.<sup>[11]</sup> These compounds, containing cyclobutane, thiazole, and Schiff base functions in their molecules, seem to be suitable candidates for further chemical modifications and may be pharmacologically active ligands.

Since this ligand (Fig. 1) has not been reported in the literature, this article deals with its preparation and characterization, as well as its complexes with cobalt(II), copper(II), nickel(II), and zinc(II) acetates.



**Figure 1.** Structure of the ligand.



**EXPERIMENTAL**

Thiosemicarbazide, 2-hydroxy-5-methoxybenzaldehyde, and metal acetates were purchased from Merck (pure) and were used without further purification. The 1-methyl-1-mesityl-3-(2-chloro-1-oxoethyl) cyclobutane was prepared according to a known procedure<sup>[12]</sup> and was purified by column chromatography prior to use. Solvents were of analytical grade and purified by standard methods where necessary.

**Physical Measurements**

Elemental analyses were performed on a LECO CHNSO-932 auto elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer using KBr pellets. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian-Gemini 200 MHz at 50.34 MHz or a JEOL FX-90Q spectrometer. The electronic spectra of the ligand and the complexes were recorded in DMF solutions using a CECIL model CE 5502 UV-Vis spectrophotometer. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature (20°C) using Hg[Co(SCN)<sub>2</sub>] as the calibrant. Melting points were determined on a Gallenkamp melting point apparatus and checked by differential scanning calorimetry (DSC) and are uncorrected. Thermogravimetric curves were recorded on a Shimadzu TG-50 thermo balance. Metal contents of the complexes were determined by an ATI Unicam (Model 929) atomic absorption spectrophotometer in solutions prepared by decomposing the compounds in concentrated HCl and subsequent dilution with 0.01 M HCl.

**Synthesis of 1-(2-Hydroxy-5-Methoxybenzylidene) Thiosemicarbazide (1)**

To a solution of thiosemicarbazide (0.9113 g, 10 mmol) in 50 mL absolute EtOH, a solution of 5-methoxysalicylaldehyde (1.5215 g, 10 mmol) in 20 mL absolute EtOH were added dropwise at 60–70°C with continuous stirring. The solid compound started to form 5 min later. The course of the reaction was monitored by IR spectroscopy. After completing the reaction, the mixture was left to stand overnight. The solid product was filtered off, washed with H<sub>2</sub>O several times, dried in air and crystallized from aqueous EtOH (1:3). The product is very soluble in Me<sub>2</sub>CO, DMF, THF, or DMSO, and insoluble in MeOH, EtOH, or CHCl<sub>3</sub>.



### Synthesis of the Ligand (2)

To a suspension of 1-(2-hydroxy-5-methoxybenzylidene) thiosemicarbazide (1.1264 g, 5 mmol) in 30 mL DMSO, a solution of 1-methyl-1-mesityl-3-(2-chloro-1-oxoethyl) cyclobutane (1.3225 g, 5 mmol) in 20 mL absolute ethanol was added dropwise at ca. 30–40°C with continuous stirring while monitoring the reaction with IR. After completing the addition of the  $\alpha$ -haloketone, the temperature of the mixture was raised to 50–55°C. Monitoring the presence of the carbonyl group of 1-methyl-1-mesityl-3-(2-chloro-1-oxoethyl) cyclobutane is easily done by IR and thus it is very easy to determine when the reaction is complete. The solution was then made alkaline (if necessary) with an aqueous solution of NH<sub>3</sub> (5%) and the orange solid of HL was separated. The precipitate was filtered, washed with aqueous NH<sub>3</sub> solution several times, dried in air and crystallized from ethanol, dried and stored in a desiccator over CaCl<sub>2</sub>. The shiny crystals are very soluble in Me<sub>2</sub>CO, DMF, THF, CHCl<sub>3</sub>, and DMSO, and sparingly soluble in MeOH and EtOH.

### Synthesis of the Complexes

The ligand HL (0.2176 g, 0.50 mmol) was suspended in 15–20 mL absolute ethanol. A solution of 0.25 mmol of the metal salt [Co(AcO)<sub>2</sub>·4H<sub>2</sub>O (0.0623 g), Cu(AcO)<sub>2</sub>·H<sub>2</sub>O (0.0499 g), Ni(AcO)<sub>2</sub>·4H<sub>2</sub>O (0.0623 g), Zn(AcO)<sub>2</sub>·2H<sub>2</sub>O (0.0549 g)] in 10 mL EtOH was added dropwise with continuous stirring. In the case of cobalt(II) complex, a slow stream of nitrogen was passed through the solution. Every mixture was refluxed for 1 hr and then left to stand overnight at room temperature. The complexes, precipitated as micro crystals, were filtered, washed with cold ethanol and water several times and dried in vacuum at 60°C (over P<sub>4</sub>O<sub>10</sub>) and stored in a desiccator over CaCl<sub>2</sub>. Yields, melting points, elemental analysis results, and characteristic IR bands (NaCl cell) are given in Tables 1 and 2.

## RESULTS AND DISCUSSION

Synthetic pathways for the preparation of the ligand are shown in Fig. 2. One of the starting substances, 1-(2-hydroxy-5-methoxybenzylidene) thiosemicarbazide **1** was synthesized by condensation of thiosemicarbazide and 5-methoxy salicylaldehyde in absolute ethanol at 60–70°C. The new ligand 4-(1-methyl-1-mesitylcyclobutane-3-yl)-2-(2-hydroxy-5-methoxybenzylidenehydrazino) thiazole **2**, was then prepared by a one-step reaction of 1-methyl-1-mesityl-3-(2-chloro-1-oxoethyl) cyclobutane with **1**. The



**Table 1.** Analytical and physical data of the compounds

Compound	F.W. (g mol <sup>-1</sup> )	Color	M.P. (°C)	Yield (%)	Elemental analyses %calc. (found)		
					C	H	N
(1) C <sub>9</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> S	225.05	Light yellow	231	94	47.99 (48.11)	4.92 (5.02)	18.65 (18.27)
HL (2) C <sub>25</sub> H <sub>29</sub> N <sub>3</sub> O <sub>2</sub> S	435.58	Orange	219	67	68.93 (68.78)	6.71 (6.82)	9.65 (9.64)
(L) <sub>2</sub> Co C <sub>50</sub> H <sub>56</sub> CoN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	928.08	Dark green	314	81	64.71 (65.02)	6.08 (6.11)	9.06 (9.17)
[(L) <sub>2</sub> Cu] <sub>2</sub> C <sub>50</sub> H <sub>56</sub> CuN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	1865.46	Dark green	272	78	64.39 (64.44)	6.05 (6.13)	9.01 (8.95)
(L) <sub>2</sub> Ni C <sub>50</sub> H <sub>56</sub> NiN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	927.84	Green	345	84	64.72 (64.78)	6.08 (6.17)	9.06 (8.93)
(L) <sub>2</sub> Zn C <sub>50</sub> H <sub>56</sub> ZnN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	934.54	Yellow	300	80	64.26 (64.34)	6.04 (5.97)	8.99 (9.14)



**Table 2.** Infrared spectral data (cm<sup>-1</sup>) of the ligand and its complexes.<sup>a</sup>

Compound	$\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{N})$ azomethine	$\nu(\text{C}=\text{N})$ thiazole	$\nu(\text{N}-\text{H})$	$\nu(\text{C}-\text{S}-\text{C})$	$\mu_{\text{eff}}$ (B.M.)
(1)	3310 s	1039 s	1584 vs	—	3125 s	—	—
HL (2)	3270 s	1144 s	1564 vs	1614 s	3110 s	584 s	—
(L) <sub>2</sub> Co	—	1163 s	1584 vs	1609 s	3116 w	583 s	4.05
(L) <sub>2</sub> Cu] <sub>2</sub>	—	1163 m	1574 vs	1610 s	3120 w	583 m	1.02
(L) <sub>2</sub> Ni	—	1163 m	1584 vs	1610 s	3116 w	583 m	3.88
(L) <sub>2</sub> Zn	—	1163 m	1584 vs	1614 s	3118 w	583 m	dia

*Note:* m, medium; s, strong; vs, very strong; w, weak.



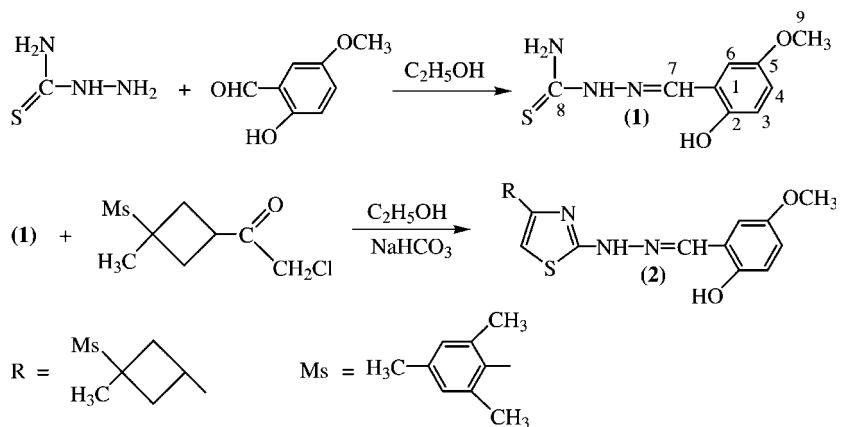


Figure 2. Synthesis of the ligand.

compound is very soluble in  $\text{CHCl}_3$ ,  $\text{Me}_2\text{CO}$ ,  $\text{DMSO}$ , and  $\text{DMF}$ , and partially soluble in organic solvents such as  $\text{EtOH}$  and  $\text{MeOH}$ . Furthermore, the hot solution of the ligand was used for the preparation of the complexes.

It is necessary to say that this ligand is the product of a difficult, tedious, and time consuming an organic synthesis.

### IR Spectra

The most important infrared spectral bands of **1**, the ligand and the complexes are provided in Table 2. In the IR spectrum of **1**, five sharp and intense bands were observed in the range of  $3415\text{--}3125\text{ cm}^{-1}$ . These bands belong to the  $-\text{NH}_2$ ,  $-\text{NH}-$ , and  $-\text{OH}$  stretching vibrations of the molecule. Two of them are from  $-\text{NH}_2$ , one from  $-\text{NH}-$  and one from  $-\text{OH}$ . The other signal could not be identified. In the case of the ligand, this unidentified band was not observed. The  $\text{C}=\text{S}$  stretching of the molecule is observed at  $1114\text{ cm}^{-1}$ . The IR spectra of **1** showed no aliphatic bands. The  $\text{C}=\text{N}$  (azomethine) group vibration is observed at  $1584\text{ cm}^{-1}$  for **1**. In the IR spectrum of **2**, stretching vibrations for  $\text{NH}_2$  and  $\text{C}=\text{S}$  were not observed, but there are new peaks at  $1614$  and  $2978\text{--}2927\text{ cm}^{-1}$  for  $\text{C}=\text{N}$  (thiazole) and aliphatics, respectively. Observation of the absence of  $\text{C}=\text{O}$ ,  $\text{C}-\text{Cl}$ ,  $\text{C}=\text{S}$ , and  $\text{NH}_2$  absorptions in the IR spectra of the ligand  $\text{HL}$ , and existing characteristic peaks indicate the formation of the expected compound.

The strong and sharp band observed at  $3110\text{ cm}^{-1}$  for the ligand, can be attributed to  $-\text{NH}-$  group vibrations. The ligand exhibited a broad, medium-intensity band in the  $2700\text{--}2560\text{ cm}^{-1}$  range which is assigned to the



intramolecular H-bonding vibrations ( $O-H \cdots N$ ). As is known, this situation is common for aromatic azomethine compounds containing *o*-OH groups.<sup>[13]</sup> The azomethine group vibration of the free ligand occurs at  $1564\text{ cm}^{-1}$ . In the free ligand, the band exhibited at  $3270\text{ cm}^{-1}$  can be attributed to the phenolic ( $O-H$ ) group vibration.<sup>[13]</sup> The characteristic band for C–O of the ligand is observed at  $1144\text{ cm}^{-1}$ . The aliphatic group vibrations indicating that the compound contains cyclobutane which is in the  $2978\text{--}2927\text{ cm}^{-1}$  range. The C=N group vibration in the thiazole ring is observed at  $1614\text{ cm}^{-1}$  for HL. Another group, C–S–C, which may be affected by the complexation, exhibits a band at  $584\text{ cm}^{-1}$  for the ligand HL.

### <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the starting substance **1**, the ligand, and the Zn(II) complex were recorded in DMSO-d<sub>6</sub>. The <sup>1</sup>H NMR and <sup>13</sup>C NMR signals are given in detail as following.

Characteristic <sup>1</sup>H NMR spectra, in DMSO-d<sub>6</sub>, of the starting substance **1** showed signals at: 3.73 (s, 3H) –CH<sub>3</sub>; 6.81 (s, 2H) –NH<sub>2</sub>; 7.49 (s, 1H) Ar-H; 8.04 (s, 1H) Ar-H; 8.16 (s, 1H) Ar-H; 8.38 (s, 1H) N=CH–; 9.49 (s, 1H) –NH–; 11.39 (s, 1H) –OH ppm and characteristic <sup>13</sup>C NMR peaks are at (in DMSO-d<sub>6</sub>): 122.41 (C<sub>1</sub>), 152.45 (C<sub>2</sub>), 111.35 (C<sub>3</sub>), 120.02 (C<sub>4</sub>), 154.14 (C<sub>5</sub>), 118.81 (C<sub>6</sub>), 141.12 (C<sub>7</sub>), 178.43 (C<sub>8</sub>), 57.37 (C<sub>9</sub>) ppm.

The ligand HL **2** showed following <sup>1</sup>H NMR signals in DMSO-d<sub>6</sub>, at: 1.53 (s, 3H) –CH<sub>3</sub>; 2.17 (s, 9H) –CH<sub>3</sub> on mesitylene; 2.51–2.62 (m, 4H) –CH<sub>2</sub>–; 3.39 (q, 1H, J: 7) =CH–; 3.71 (s, 3H) –CH<sub>3</sub> methoxy; 6.42 (s, 1H) =CH–S on thiazole ring; 6.72 (s, 2H) aromatics; 6.83 (s, 2H) aromatics; 7.11 (s, 1H) aromatic; 8.17 (s, 1H) N=CH– azomethine; 9.65 (s, 1H) –NH–; 11.12 (s, 1H) –OH ppm.

Characteristic <sup>13</sup>C NMR peaks are at (in DMSO-d<sub>6</sub>): 121.97 (C<sub>1</sub>), 151.64 (C<sub>2</sub>), 112.10 (C<sub>3</sub>), 118.76 (C<sub>4</sub>), 155.74 (C<sub>5</sub>), 118.64 (C<sub>6</sub>), 145.98 (C<sub>7</sub>), 167.54 (C<sub>8</sub>), 109.20 (C<sub>9</sub>), 154.02 (C<sub>10</sub>), 40.06 (C<sub>11</sub>), 41.51 (C<sub>12</sub>), 42.57 (C<sub>13</sub>), 26.36 (C<sub>14</sub>), 138.43 (C<sub>15</sub>), 131.87 (C<sub>16</sub>), 131.45 (C<sub>17</sub>), 135.50 (C<sub>18</sub>), 22.84 (C<sub>19</sub>), 21.85 (C<sub>20</sub>), 57.15 (C<sub>21</sub>) ppm.

The <sup>1</sup>H NMR spectra of the Zn(II) complexes of the ligand showed the same resonances as those of HL except for the absence of the OH proton resonance and a small shift was observed for the azomethine proton resonance.

The <sup>1</sup>H NMR spectra of the Zn(II) complex gave signals at: 1.57 (s, 3H) –CH<sub>3</sub>, 2.21 (s, 9H) –CH<sub>3</sub> on mesitylene; 2.49–2.63 (m, 4H) –CH<sub>2</sub>–, 3.42 (q, 1H, J: 7) =CH–, 3.73 (s, 3H) –CH<sub>3</sub> methoxy, 6.40 (s, 1H) =CH–S on thiazole ring, 6.78 (s, 2H) aromatics, 6.81 (s, 2H) aromatics, 7.13 (s, 1H) aromatics, 8.21 (s, 1H) N=CH–S, 9.63 (s, 1H) –NH– ppm.



<sup>13</sup>C NMR spectra of the Zn(II) complex gave signals at: 121.88 (C<sub>1</sub>), 151.76 (C<sub>2</sub>), 112.11 (C<sub>3</sub>), 118.76 (C<sub>4</sub>), 155.71 (C<sub>5</sub>), 118.65 (C<sub>6</sub>), 146.14 (C<sub>7</sub>), 167.56 (C<sub>8</sub>), 109.20 (C<sub>9</sub>), 154.04 (C<sub>10</sub>), 40.05 (C<sub>11</sub>), 41.51 (C<sub>12</sub>), 42.57 (C<sub>13</sub>), 26.34 (C<sub>14</sub>), 138.40 (C<sub>15</sub>), 131.88 (C<sub>16</sub>), 131.45 (C<sub>17</sub>), 135.54 (C<sub>18</sub>), 22.84 (C<sub>19</sub>), 21.84 (C<sub>20</sub>), 57.16 (C<sub>21</sub>) ppm.

It is important to emphasize that the <sup>1</sup>H NMR resonances of the O–H groups at 11.39 and 11.12 ppm for **1** and for the HL ligand, respectively, are broad singlets and are due to the presence of intramolecular hydrogen bonding.<sup>[14]</sup> This situation is supported by the IR spectra of the molecules. The <sup>1</sup>H NMR signal observed for the protons of C–OH and –NH– disappeared upon addition of D<sub>2</sub>O to the solution. The singlet proton resonances in the <sup>1</sup>H NMR spectra for **1** and the ligand at 8.38 and 8.17 ppm, respectively, have been assigned to the azomethine group protons. The aromatic ring resonances are observed at 7.49–8.16 and 6.72–7.11 ppm as singlet or doublets for **1** and the ligand HL, respectively. A more detailed spectral investigation of a similar cyclobutane compound can be found in the literature.<sup>[4]</sup>

The <sup>13</sup>C NMR spectral data of the ligand confirm the <sup>1</sup>H NMR spectral results. The elemental analysis results of **1**, **2**, and metal derivatives of **2**, given in Table 1 were also found to agree with their proposed constitutions.

### Metal Complexes of HL Ligand

Mononuclear complexes were obtained after reaction of the ligand with Co(II), Cu(II), Ni(II), and Zn(II) acetates. In general, the reactions of the ligand HL with the metal acetates were rapid and gave good yields of the complexes corresponding to the general formula M(L)<sub>2</sub>; they are stable at room temperature and soluble in Me<sub>2</sub>CO, DMF, DMSO, and CHCl<sub>3</sub>. In every complex, one metal ion is coordinated to two azomethine nitrogen atoms and two oxygen atoms of two ligand molecules (Fig. 3).

The IR spectra of all mononuclear complexes, noting that the copper complex is dimeric, were very similar to those of their ligand except for the disappearance of the OH stretching frequency and the shift of the azomethine and C–O stretch of the ligand. The azomethine stretching vibration of the ligand is shifted to higher frequencies of 1584, 1574, 1584, and 1584 cm<sup>−1</sup> for Co(II), Cu(II), Ni(II), and Zn(II) metal complexes of the ligand HL, respectively. At the same time, the C–O stretching vibrations of the ligand are also shifted to the same higher frequency 1163 cm<sup>−1</sup> for the above metal ion complexes. The –NH– band is shifted to higher frequency relative to the free ligand and loses its intensity, to be almost invisible. These shifts and loss of intensity probably result from changes in the electronic state when the ligand coordinates, and the N=CH loses some of its double band

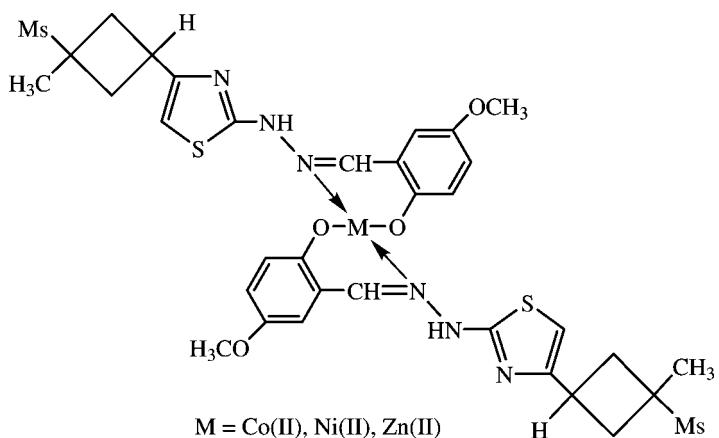


Figure 3. Suggested structure of the complexes.

character. These results indicate the effectiveness of two functional groups of the ligand by complexation with metal salts. Despite their presence in the ligand and the possibility of complexation by the C=N group and sulfur atoms in the thiazole ring, the unchanged band positions for these groups in the IR spectra of the complexes indicate that the thiazole ring does not complex to the metal.

### Thermal Studies

The thermogravimetric (TG) curves for the complexes were obtained at a heating rate of 10°C/min and a 30 mL/min flowing nitrogen atmosphere over a temperature range of 20–800°C. Approximately 10 mg samples of the complexes were used in each case. The TG curves showed that the thermal decomposition of the complexes takes place in three steps, except the Cu(II) complex which decomposes in several steps. It is possible that the different groups in the ligand lead to a decrease in the stability of all the complexes. Furthermore, it is known that the electronegativity and the atomic radius of the central metal atom also effects the thermal stability.<sup>[13,14]</sup> Thermogravimetric studies of all the complexes showed no weight loss up to 145°C, indicating absence of water in the complexes. The first step in the decomposition sequence corresponds to the loss of mesityl groups in the Co, Ni, and Zn complexes. In the second step, cyclobutane and thiazole groups eliminate from the complexes. The inflation of the TG curves of all the complexes at a temperature under 658°C indicates the decomposition of the fully organic part



of the chelate, leaving metallic oxide at the final temperature.<sup>[14,15]</sup> The observed weight losses for all complexes are in good agreement with the calculated values from their chemical formulas given in Table 1. All the complexes completely decompose to the corresponding metal oxides, CoO, CuO, NiO, or ZnO.

### Electronic Spectra

The electronic spectra of the ligand and the complexes were recorded in  $1 \times 10^{-3}$  mol L<sup>-1</sup> DMF solution at room temperature. The spectra of HL show three group bands at about 225–260, 330–365, and 440–485 nm regions as maximum or shoulder bands. The bands at the first region are assigned to intraligand  $\pi \rightarrow \pi^*$  transitions. The bands at the maximum or shoulder in the 44–480 nm region are attributed to dipolar ketoamine tautomer forms of its zwitterionic dipolar structure which is characteristic for salicylaldimines.<sup>[16]</sup> In the complexes, the imino  $\pi \rightarrow \pi^*$  transition is shifted to a longer wavelength as a consequence of coordination when binding with metal, confirming the formation of Schiff base metal complexes.<sup>[17]</sup>

In the electronic spectra of M(L)<sub>2</sub> compounds in DMF solutions, bands at 386–440 and 465–535 nm, attributable to d  $\rightarrow$  d transitions of the metals, were observed.<sup>[18]</sup> In these regions, the appearance of the bands attributable to the metal-to-ligand charge transfer transition probably arise from the metal-t<sub>2g</sub>-to ligand  $\pi^*$ , which are considered to be sensitive to changes in molecular geometry. In the complexes, the low intensity bands in the 500–625 nm range are consistent with d  $\rightarrow$  d transitions of the metal ions and intraligand n  $\rightarrow$   $\pi^*$  transitions.<sup>[19]</sup> The more intense 330–465 nm bands in the complexes may be due to the coincidence of charge transfer, d  $\rightarrow$   $\pi^*$  and L  $\rightarrow$  M transitions.<sup>[19]</sup>

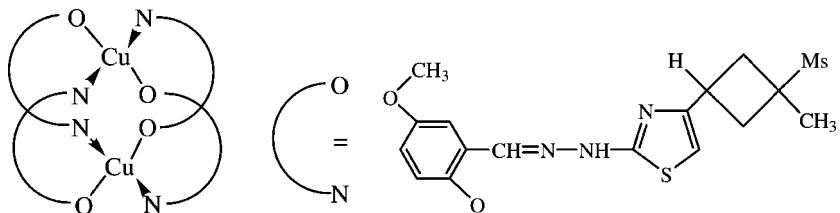
### Conductance Measurements

The Co(II), Cu(II), Ni(II), and Cu(II) complexes of the ligand are nonelectrolytes as shown by their molar conductivity ( $\Lambda_m$ ) measurements in DMF, which are in the range<sup>[20]</sup> 1.02–3.10  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

### Magnetic Susceptibility

As is known, magnetic susceptibility measurements provide information regarding the structure of the complexes. The magnetic moments of the complexes were measured at room temperature. The cobalt(II), copper(II),





**Figure 4.** Suggested structure of the Cu(II) complex.

and nickel(II) complexes of the ligand are paramagnetic, and their magnetic susceptibilities are 4.05, 1.02, and 3.88 BM., respectively, for the HL complexes. The zinc(II) complex of the present ligand is diamagnetic. These data indicate two unpaired electrons for Ni(II) and three for Co(II). The magnetic moment of the Co(II) complex of ligand at room temperature falls in the range 4–5 B.M., which is characteristic for mononuclear, high-spin, tetrahedral Co(II) complexes. The magnetic moment values of the Ni(II) complex of the ligand is also consistent with a tetrahedral geometry.<sup>[21]</sup>

Cu(II) complexes exhibit a wide range of geometries, often with low symmetry and in most geometries the electronic spectra exhibit a very broad band with a maximum, which contains all the expected transitions. On the other hand, the copper complex of the present ligand has an unexpected magnetic moment, 1.02 B.M. This means that the copper complex has a dimeric structure. Clearly the single unpaired electron on the copper atoms interacts, or “couples,” antiferromagnetically, to produce a low-lying singlet (diamagnetic).<sup>[22]</sup> In this case, the copper complex may be a mixture of diamagnetic and ferromagnetic crystals. For all of these complexes, the elemental analysis results are in good agreement with the proposed structure. On the basis of the spectral and magnetic data, the cobalt(II), nickel(II), and zinc(II) complexes have tetrahedral geometry, while the copper complex is in a square-planar structure. The suggested structure for the Cu(II) complex is shown in Fig. 4.

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