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# Cobalt(II), Copper(II), Nickel(II), and Zinc(II) Complexes of Naphthaldehyde Thiazolyl Hydrazones

**by İ. Yilmaz and A. Çukurovali***

*Chemistry Department, Faculty of Arts and Sciences, Firat University, 23119 Elazig, Turkey*

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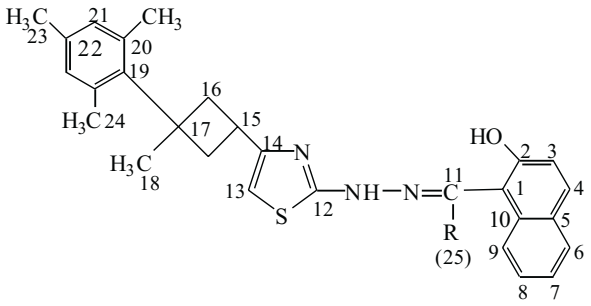
Two new Schiff base ligands containing 2,4-disubstituted thiazoles and cyclobutane rings, 2-hydroxy-1-naphthaldehyde [4-(3-methyl-3-mesitylcyclobutyl)-1,3-thiazol-2-yl] hydrazone (**$L^1H$**) and 1-(2-hydroxy-1-naphthyl)etanone [4-(3-methyl-3-mesityl-cyclobutyl)-1,3-thiazol-2-yl] hydrazone (**$L^2H$**) and their mononuclear complexes with a 1:2 metal:ligand ratio have been prepared from chloride salts of Co(II), Cu(II), Ni(II) and Zn(II) in EtOH. The authenticity of new ligands and their complexes have been established by elemental analyses, infrared, $^1$H and $^{13}$C NMR spectra, and by magnetic susceptibility measurements. Thermal properties of the ligands and complexes have been studied by thermogravimetric analysis (TGA) technique. The novel complexes of transition metal ions contain two monoanionic, bidentate NO ligands. It was found that all the complexes are mononuclear.

**Key words**: 2,4-disubstituted thiazole, Schiff base, cyclobutane, hydrazone, complexes

Schiff base derivatives and their metal complexes, which are known since 19$^{th}$ century, have played a key role in the development of coordination chemistry, resulting in an enormous number of publications [1–7] and found wide range applications. These applications include NMR contrast agents, biological markers, photodynamic therapy and phosphoryl transfer catalysts, *etc*. and they are considered to be suitable models for pyridoxal and, in general, $B_6$ vitamins [8,9]. Thiazoles represent a very interesting class of compounds, because of their wide applications in pharmaceutical, phytosanitary, analytical and industrial aspects, *e.g*. as fungicides, anthelmintics, and herbicides [10]. On the other hand, cyclobutane carboxylic acids in different forms were described as highly potent l-Glutamate, *N*-methyl-d-aspartate (NMDA) agonist, NMDA antagonists and anticonvulsive drugs [11–13]. Combining these facts along with the data, that some Schiff base complexes containing pyridoxal have notable antitumor activity [14], led us to the preparation of these ligands and their metal complexes. These ligands containing cyclobutane, thiazole and Schiff base functions in their molecules seem to be suitable candidates for further chemical modifications and may be pharmacologically active and useful as ligands in coordination chemistry. This paper deals with the preparation and characterization of the complexes formed between the Schiff base ligands (Scheme 1) and cobalt(II), copper(II), nickel(II) and zinc(II) metal salts. As far as we know, this is the first report on these ligands.

*Address for correspondence to Alaaddin Çukurovali: E-mail: acukurovali@firat.edu.tr



**Scheme 1.** Structure of the ligands.

## EXPERIMENTAL

2-Hydroxy-1-napthaldehyde, 2-hydroxy-1-acetylnapthaldehyde and thiosemicarbazide were purchased from Merck (pure) and were used without further purification. 1-Mesityl-l-methyl-3-(2-chloro-1-oxoethyl) cyclobutane was prepared by literature [15] method and purified by column chromatography.

**Physical measurements**: Elemental analyses were determined on a LECO CHNSO-932 auto elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Varian-Gemini 200 MHz at 50.34 MHz spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature (20℃) using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants. Melting points were determined on a Gallenkamp apparatus, checked by DSC technique and are uncorrected. The thermogravimetric, TGA, curves for the ligands and the complexes were obtained at a heating rate of 10℃/min in a nitrogen atmosphere between 20–900°C. Approximately 10 mg of samples of the ligands and complexes were used in each case. All the thermogravimetric curves have been obtained in 30 mL/min flowing nitrogen atmosphere.

**Preparation of 1-(2-hydroxynaphthylidene) thiosemicarbazide (1)**: To a solution of thiosemicarbazide (0.9113 g, 10 mmole) in 50 ml absolute EtOH, a solution of $\beta$-hydroxy-$\alpha$-naphthalaldehyde (1.72 g, 10 mmole) in 20 ml absolute EtOH were added dropwise at 60–70°C with continuous stirring. 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 cold ethanol several times, dried in air and crystallized from aqueous EtOH (1:3). Anal. Calcd. for $C_{12}H_{11}N_3OS$: C, 58.76; H, 4.52; N, 17.13; S, 13.07. Found: C, 58.86; H, 4.62; N, 16.94; S, 12.93. Characteristic $^{1}H$ NMR peaks (DMSO-$d_6$, TMS, $\delta$ ppm): 7.25 (d, $J_o$ = 8.91 Hz, 1H), 7.43 (t, $J_o$ = 7.17 Hz, 1H), 7.61 (t, $J_o$ = 7.02, 1H), 7.91 (m, 3H), 8.27 (s, 1H, azomethine), 8.56 (s, 1H), 9.10 (s, 1H), 10.22 (s, 1H, -OH), 11.44 (s, 1H, -NH-). Characteristic $^{13}C$ NMR peaks (DMSO-$d_6$, TMS, $\delta$ ppm): 110.63 ($C_1$), 157.50 ($C_2$), 119.21 ($C_3$), 133.37 ($C_4$), 129.56 ($C_5$), 128.77 ($C_6$), 124.33 ($C_7$), 123.79 ($C_8$), 128.94 ($C_9$), 132.38 ($C_{10}$), 143.91 ($C_{11}$), 178.10 ($C_{12}$).

**Preparation of 1-(2-hydroxy-1-acetylnaphthylidene) thiosemicarbazide (2)**: This compound was prepared by an analogous procedure, using 2-hydroxy-1-acetylnaphtol and thiosemicarbazide in ethanol solvent. Anal. Calcd. for $C_{13}H_{13}N_3OS$: C, 60.21; H, 5.05; N, 16.20; S, 12.37. Found: C, 59.83; H, 5.11; N, 16.34; S, 12.47. Characteristic $^{13}C$ NMR peaks (DMSO-$d_6$, TMS, $\delta$ ppm): 2.45 (s, 3H), 7.38–7.87 (m, 7H, aromatics plus $-NH_2$), 8.31–8.36 (m, 1H, aromatics), 10.83 (s, 1H, -OH), 11.17 (s, 1H, -NH-). Characteristic $^{13}C$ NMR peaks ($CDCl_3$, TMS, $\delta$ ppm): 114.45 ($C_1$), 156.58 ($C_2$), 119.53 ($C_3$), 134.13 ($C_4$), 129.02 ($C_5$), 127.13 ($C_6$), 126.40 ($C_7$), 124.81 ($C_8$), 126.71 ($C_9$), 129.34 ($C_{10}$), 136.04 ($C_{11}$), 180.21 ($C_{12}$), 16.02 ($C_{13}$).

**Preparation of Schiff base ligands (3, 4)**: The Schiff base ligands used in this work, $L^1H$ and $L^2H$, were prepared by similar methods. To a suspension of (5 mmol) of [for $L^1H$, 1-(2-hydroxynaphthylidene) thiosemicarbazide (1.225 g), for $L^2H$, 1-(2-hydroxy-1-acetylnaphthylidene) thiosemicarbazide (1.2967 g)] in 30 mL EtOH-DMSO (50%), a solution of 1.3225 g (5 mmole) of 1-mesityl-1-methyl-3-(2-chloro-1-oxoethyl) cyclobutane in 20 mL EtOH-DMSO (50%), was added dropwise at *ca* 30–40°C with continu-

ous stirring and monitoring of the course of 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 carbonyl group of 1-mesityl-1-methyl-3-(2-chloro-1-oxoethyl) cyclobutane enables to determine the end of the reaction. The precipitates obtained by addition of an aqueous solution of $NH_3$ (5%) were filtered off, washed with aqueous $NH_3$ solution several times, dried in air and crystallized from EtOH-DMSO (50%) mixture again dried and stored in a desiccator over $CaCl_2$. Anal. Calcd. for $C_{28}H_{29}N_3OS$: C, 73.81; H, 6.42; N, 9.22; S, 7.04. Found: C, 74.12; H, 6.63; N, 9.36; S, 7.17. and Anal. Calcd. for $C_{29}H_{31}N_3OS$: C, 74.17; H, 6.65; N, 8.95; S, 76.83. Found: C, 74.22; H, 6.72; N, 9.11; S, 7.07. Characteristic $^1$H NMR peaks for ($L^1$H) (DMSO-$d_6$, TMS, $\delta$ ppm): 1.53 (s, 3H, -$CH_3$), 2.17 (s, 9H, -$CH_3$ on mesitylene), 2.45–2.66 (m, 4H, -$CH_2$- on cyclobutane), 3.45 (q, 1H, >CH- on cyclobutane), 6.42 (s, 1H, =CH-S on thiazole), 6.72 (s, 2H, aromatics on mesitylene), 7.20–7.87 (m, 5H, aromatics), 8.56 (d, 1H, aromatic), 8.93 (s, 1H, azomethine), 11.35 (br, 1H, -OH), 12.02 (s, 1H, -NH-). Characteristic $^{13}$C NMR peaks for ($L^1$H) (DMSO-$d_6$, TMS, $\delta$ ppm): 111.62 ($C_1$), 158.25 ($C_2$), 120.13 ($C_3$), 133.42 ($C_4$), 130.55 ($C_5$), 129.30 ($C_6$), 125.02 ($C_7$), 123.02 ($C_8$), 129.85 ($C_9$), 132.87 ($C_{10}$), 145.88 ($C_{11}$), 169.64 ($C_{12}$), 101.84 ($C_{13}$), 149.81 ($C_{14}$), 31.98 ($C_{15}$), 41.70 ($C_{16}$), 44.79 ($C_{17}$), 26.31 ($C_{18}$), 138.17 ($C_{19}$), 135.53 ($C_{20}$), 131.71 ($C_{21}$), 136.43 ($C_{22}$), 21.68 ($C_{23}$), 22.85 ($C_{24}$). Characteristic $^1$H NMR peaks for ($L^2$H) (DMSO-$d_6$, TMS, $\delta$ ppm): 1.51 (s, 3H, -$CH_3$ on cyclobutane), 2.15 (s, 9H, -$CH_3$ on mesitylene), 2.40–2.63 (m, 7H, -$CH_2$- on cyclobutane plus –$CH_3$ on azomethine), 3.45 (q, 1H, >CH- on cyclobutane), 6.27 (s, 1H, =CH-S on thiazole), 6.71 (s, 2H, aromatics on mesitylene), 7.37–7.86 (m, 6H, aromatics plus –NH-), 8.31 (m, 1H, aromatics), 11.41 (br, 1H, -OH). Characteristic $^{13}$C NMR peaks for ($L^2$H) ($CDCl_3$, TMS, $\delta$ ppm): 114.62 ($C_1$), 157.68 ($C_2$), 119.68 ($C_3$), 131.72 ($C_4$), 129.01 ($C_5$), 126.53 ($C_6$), 124.55 ($C_7$), 124.44 ($C_8$), 126.42 ($C_9$), 129.14 ($C_{10}$), 145.81 ($C_{11}$), 169.87 ($C_{12}$), 99.36 ($C_{13}$), 150.30 ($C_{14}$), 31.05 ($C_{15}$), 41.73 ($C_{16}$), 44.26 ($C_{17}$), 26.18 ($C_{18}$), 136.39 ($C_{19}$), 135.71 ($C_{20}$), 127.07 ($C_{21}$), 136.25 ($C_{22}$), 21.85 ($C_{23}$), 22.85 ($C_{24}$), 16.03 ($C_{25}$).

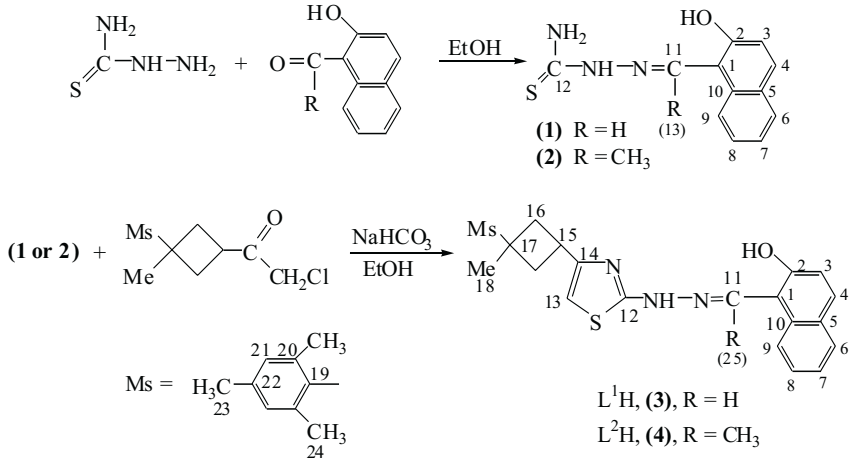
**Preparation of complexes**: In each case, to a suspension of the ligand $L^1$H (0.246 g, 0.50 mmol), or $L^2$H (0.248 g, 0.50 mmol) in absolute ethanol (15–20 mL), a solution of 0.25 mmol of the metal salt [$Co(AcO)_2 \cdot 4H_2O$ (0.0623 g), $Cu(AcO)_2 \cdot H_2O$ (0.0499 g), $Ni(AcO)_2 \cdot 4H_2O$ (0.0623 g) or $Zn(AcO)_2 \cdot 2H_2O$ (0.0549 g)] in ethanol (10 mL) was added dropwise with continuous stirring. In the case of Co(II) complexes, a slow stream of nitrogen was passed through the solution. Every mixture was refluxed for 1 hour and then left to stand overnight at room temperature. The complexes precipitated as microcrystals were filtered, washed with cold ethanol and water several times and dried in vacuum at 60°C (over $P_4O_{10}$) and stored in a desiccator over $CaCl_2$. Yields, melting points, elemental analysis results and characteristic IR bands (NaCl cell) are given in Tables 1 and 2. The $^1$H NMR spectra of the $(L^1)_2$Zn complex showed signals at (DMSO-$d_6$, $\delta$, ppm): 1.52 (s, 6H, -$CH_3$), 2.15 (s, 18H, -$CH_3$), 2.48–2.73 (m, 8H, -$CH_2$-), 3.42 (q, $J$ = 8.9 Hz, 2H, >CH-), 6.44 (s, 2H, =CH-S), 6.78 (s, 4H, aromatics on mesitylene), 6.95–7.55 (m, 10H, aromatics), 8.57 (d, 2H, aromatics), 8.78 (s, 2H, N=CH-), 11.87 (s, 2H, -NH-); and $(L^2)_2$Zn complex gave signals at (DMSO-$d_6$, $\delta$, ppm): 1.55 (s, 6H, -$CH_3$), 2.21 (s, 18H, -$CH_3$), 2.47–2.57 (m, 8H, -$CH_2$-), 3.44 (q, $J$ = 8.9 Hz, 2H, >CH-), 6.32 (s, 2H, =CH-S), 6.82 (s, 4H, aromatics on mesitylene), 7.41–7.77 (m, 12H, aromatics plus -NH-), 8.33 (m, 2H, aromatics).

## RESULTS AND DISCUSSION

The general method employed to prepare some of the starting substances and the ligands is shown in Scheme 2. Overall the reactions proceeded smoothly in good yields. The characterization of all the compounds synthesized here was obtained by a combination of IR, $^1$H and $^{13}$C NMR and microanalysis techniques. The analytical characterization data of **1**, **2**, $L^1$H, $L^2$H, and the complexes are summarized in Tables 1 and 2. One of the starting substances, 1-mesityl-1-methyl-3-(2-chloro-1-oxoethyl) cyclobutane was prepared according to the previously published procedure [15]. The compound is very soluble in polar organic solvents, such as EtOH, $CHCl_3$, MeOH, and in nonpolar organic solvents, such as diethyl ether and benzene. Substituted benz-

aldehyde derivatives of thiosemicarbazide were freshly prepared in excellent yields according to the well-known Schiff base methods. The $L^1H$ ligand is very soluble in $Me_2CO$, $CHCl_3$, THF, DMF or DMSO, soluble in EtOH, and sparingly soluble in MeOH, and $L^2H$ is very soluble in $Me_2CO$, $CHCl_3$, THF, DMF or DMSO, and sparingly soluble in MeOH an EtOH. Furthermore, hot solutions of the ligands were used during complexation. Attempts to crystallize the ligand complexes in different solvents failed. In general, reactions of the ligands, $L^1H$ and $L^2H$, with metal salts were quick and gave mononuclear complexes corresponding to the general formula $(L)_2M$ with good yields. They are stable at room temperature and are soluble in $Me_2CO$, DMF, DMSO and sparingly soluble in $CHCl_3$.

The IR spectra of **1** and **2** showed similar spectra. Five different strong and sharp peaks were observed for both compounds in the 3450–3120 $cm^{-1}$ region of the spectrum. Two of them are from $–NH_2$, one from –NH-, and one from –OH; the other one has not been identified. In the case of the ligands, this peak could not be observed. Their C=S peaks were observed at 1119 and 1114 $cm^{-1}$, respectively for **1** and **2**, while azomethine peaks of compounds are at 1634 and 1629 (>C=N-) $cm^{-1}$, respectively. On the other hand, any C=O peak for the compounds is not observed. Therefore, observed data in their IR spectra imply the existence of compounds.




**Scheme 2.**

The IR spectral data of the ligands and their metal complexes are listed in Table 2. Since there are no C=S, C=O, $-CH_2$-Cl and $-NH_2$ absorptions in the IR spectra of the ligands $L^1H$ and $L^2H$, these peaks indicate the formation of the expected compounds. The strong bands observed at 3151 and 3129 $cm^{-1}$, respectively for the ligands $L^1H$ and $L^2H$, can be attributed to the -NH- group vibration. In the complexes, these bands are not shifted, but lost their intensities, and therefore it may be that the nitrogen atom of this group is not coordinated to the metal ions. The ligands exhibit broad medium intensity bands in the 2978–2871 $cm^{-1}$ range which are assigned the intermolecular

H-bonding vibrations (O-H···N). This situation is common for aromatic azomethine compounds containing *o*-OH groups [16]. In the complexes, these bands disappear completely. The azomethine group vibrations of the free ligands occur at 1624 and 1635 (>C=N-) $cm^{-1}$, respectively. In the IR spectra of complexes, these bands shift to lower frequencies and, at the same time, their intensities are lower. These results indicate that the azomethine groups were highly affected by complexation. For the free ligands, the bands at 1184 and 1277 $cm^{-1}$, respectively for $L^1H$ and $L^2H$, can be attributed to the phenolic (C–O) group vibration [17]. In the metal complexes, these bands are shifted to different frequencies after complexation; lower frequencies (1164–1169 $cm^{-1}$) for $L^1H$ and higher frequencies (1184–1187 $cm^{-1}$) for $L^2H$, indicating coordination of oxygen to the metal atoms.

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

| Compounds | F.W/g·mol$^{-1}$ | Color | M.p. (°C) | Yield (%) | $\mu_{eff}$ (B.M.) |
|---|---|---|---|---|---|
| $C_{12}H_{11}N_3OS$ (**1**) | 245.30 | Light Brown | 271 | 94 | – |
| $C_{12}H_{13}N_3OS$ (**2**) | 259.33 | Canary Yellow | 239 | 96 | – |
| $C_{28}H_{29}N_3OS$ (**3**) | 455.62 | Yellow | 221 | 83 | – |
| $(L^1)_2Co$ | | | | | |
| $C_{56}H_{56}N_6O_2S_2Co$ | 968.15 | Dark Brown | 263 | 65 | 4.17 |
| $(L^1)_2Cu$ | | | | | |
| $C_{56}H_{56}N_6O_2S_2Cu$ | 972.76 | Dark Green | 247 | 57 | 1.78 |
| $(L^1)_2Ni$ | | | | | |
| $C_{56}H_{56}N_6O_2S_2Ni$ | 967.91 | Light Green | 303 | 81 | 3.88 |
| $(L^1)_2Zn$ | | | | | |
| $C_{56}H_{56}N_6O_2S_2Zn$ | 974.61 | Dark Green | 317 | 68 | Dia |
| $C_{29}H_{31}N_3OS$ (**4**) | 469.64 | Brown | 169 | 81 | – |
| $(L^2)_2Co$ | | | | | |
| $C_{58}H_{60}N_6O_2S_2Co$ | 996.20 | Black | >320 | 73 | 4.23 |
| $(L^2)_2Cu$ | | | | | |
| $C_{58}H_{60}N_6O_2S_2Cu$ | 1000.81 | Black | 305 | 64 | 1.69 |
| $(L^2)_2Ni$ | | | | | |
| $C_{58}H_{60}N_6O_2S_2Ni$ | 995.96 | Light Green | 319 | 77 | 3.75 |
| $(L^2)_2Zn$ | | | | | |
| $C_{58}H_{60}N_6O_2S_2Zn$ | 1002.66 | Light Brown | 312[d] | 69 | Dia |

d: decomposition.

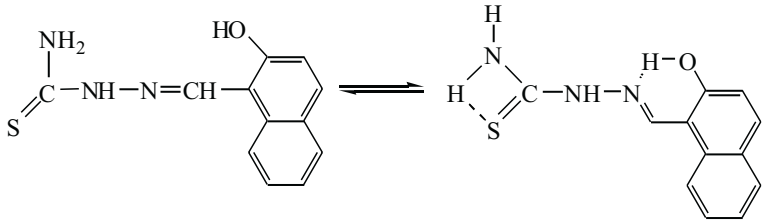
The $^1H$ NMR spectra of the starting substances **1**, **2**, and ligands were recorded in DMSO-$d_6$, and assignments are given in detail in the Experimental section. As expected from the structures of starting substances **1** and **2**, only aromatic, -NH-, $–NH_2$, -N=CH- and –OH peaks were observed. These are all singlets and each one indicates one proton intensity, according to the integral of the spectra at 400 MHz NMR. This

situation implies that the thioamide part of the molecule has a hydrogen bonding (H···S), shown in Scheme 3. Two of them are broad singlets supporting our hydrogen bonding interpretation. All of these protons, except azomethine proton, are $D_2O$ exchangeable protons. –OH group signals for both compounds are broad singlets. This is the result of the presence of intramolecular hydrogen bonding [18]. Phenolic –OH groups of both compounds exhibit the downfield signals, according to –OH of a free phenol. Since the molecules have electron-attracting hetero-atom groups, this is an expected result. $H_7$ and $H_8$ protons on the naphthalene ring of the compounds exhibited doublet signals. These are expected couplings and their coupling constants confirm the character of the signals. The $^{13}C$ NMR assignments of both compounds given in the Experimental section and the obtained signals are in good agreement with the expected data from the formulas given in Scheme 1. The elemental analysis results given in Table 1 and IR spectral bands given in Table 2 support these findings. On the other hand, the detailed $^1H$ NMR spectral data of the compounds are given in Experimental section and a more detailed spectral investigation of a similar cyclobutane compound, synthesized and published by the same authors, can be found in the literature [19].

**Table 2.** Characteristic IR bands data ($cm^{-1}$) of the ligands and complexes as KBr pellets.

| Compound | $\upsilon$(OH) | $\upsilon$(N–H) | $\upsilon(CH_3)/\upsilon(CH_2)$ | $\upsilon$(C=N)] thiazole | $\upsilon$(C=N) azomethine | $\upsilon$(C–O) | $\upsilon$(C=S) |
|---|---|---|---|---|---|---|---|
| (**1**) | 3450 | 3165 | – | – | 1634 | 1189 | 1119 |
| (**2**) | 3431 | 3156 | – | – | 1629 | 1289 | 1114 |
| $L^1H$ (**3**) | 3430 | 3151 | 2978–2930 | 1599 | 1624 | 1184 | – |
| $(L^1)_2Co$ | – | 3146 | 2978–2930 | 1599 | 1614 | 1164 | – |
| $(L^1)_2Cu$ | – | 3146 | 2978–2930 | 1599 | 1612 | 1164 | – |
| $(L^1)_2Ni$ | – | 3146 | 2978–2930 | 1604 | 1612 | 1169 | – |
| $(L^1)_2Zn$ | – | 3146 | 2978–2930 | 1602 | 1612 | 1169 | – |
| $L^2H$ (**4**) | 3429 | 3129 | 2951–2871 | 1565 | 1635 | 1277 | – |
| $(L^2)_2Co$ | – | – | 2951–2871 | 1567 | 1614 | 1284 | – |
| $(L^2)_2Cu$ | – | – | 2951–2871 | 1569 | 1614 | 1287 | – |
| $(L^2)_2Ni$ | – | – | 2951–2871 | 1567 | 1614 | 1264 | – |
| $(L^2)_2Zn$ | – | – | 2951–2871 | 1564 | 1614 | 1284 | – |

As expected from the formulas very similar spectra, except absence of azomethine signal of $L^2H$, were obtained for the ligands. The single proton resonance at 8.93 ppm for $L^1H$ in the $^1H$ NMR spectra has been assigned to the azomethine group proton. The $–CH_2-$ proton resonances, which indicate the compounds with cyclobutane ring, are at 2.45–2.66 and 2.40–2.63 ppm regions, respectively for $L^1H$ and $L^2H$ li-

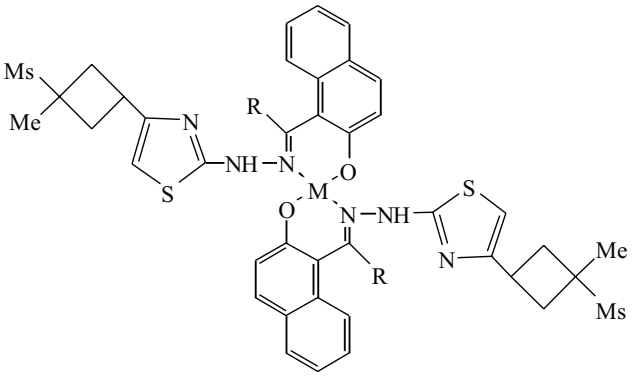


**Scheme 3.** Scheme of the hydrogen bonding of **1**.

gands. The $^1$H resonance of the O-H group at 10.35 and 11.41 ppm as broad singlets for both ligands is due to the presence of hydrogen bonding [18], formed between azomethine and *o*-OH of the molecules. The $^1$H NMR signal observed for the protons of C-OH and -NH- disappeared upon addition of $D_2O$ to the solution. The aromatic ring resonances observed at 6.72–7.87 and 6.71–7.86 ppm as singlets, doublets or triplets are in agreement with the proposed structures, for $L^1$H and $L^2$H, respectively. The detailed $^1$H NMR spectral data of the ligands are given in Experimental section. The Zn(II) complexes of the ligands showed the same resonances as those of $L^1$H and $L^2$H, except for the absence of the OH proton resonance and a small shift was observed for the azomethine proton resonance. The signal of methine proton of the molecules, which should be 3.26–3.38 ppm, is overlapped with DMSO H-D exchange signals. Other signals in the spectrum of the complexes are very broad with high multiplicity. However, in comparison to the $^1$H NMR spectra of the ligands, the signals can be attributed to the specific protons. The detailed $^{13}$C NMR spectral data are also given in the Experimental section. Azomethine carbon atoms are observed at 145.88 ppm and 145.81 ppm respectively for $L^1$H and $L^2$H. The $^{13}$C NMR spectral data of the ligands confirm the $^1$H spectral results. The data obtained from elemental analyses, IR, and $^1$H and $^{13}$C NMR spectra of $L^1$H and $L^2$H are consistent with data expected from the formula given in Schemes 1 and 2.

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 and are listed in Table 1. Co(II), Cu(II) and Ni(II) complexes of both ligands are paramagnetic, while their Zn(II) complexes are diamagnetic, and their magnetic susceptibilities are: 4.17, 1.78 and 3.88 B.M. respectively for $L^1$H ligand complexes; 4.23, 1.69 and 3.75 B.M. respectively for $L^2$H ligand complexes. These data indicate two unpaired electrons for Ni(II) and three for Co(II). The magnetic moments of the Co(II) complexes of both ligands at room temperature fall in the range 4 to 5 B.M., which is characteristic for mononuclear, high-spin, tetrahedral Co(II) complexes. The magnetic moment values of the Ni(II) complexes of the ligands are also consistent with a tetrahedral geometry [20,21]. As easily can be seen from the data, there are fairly shifts on the azomethine carbon and aromatic carbon which bound to the phenolic oxygen. These results also support the coordination of copper and zinc metals *via* azomethine and phenolic oxygen. The elemental analysis

results of the complexes are in good agreement with the proposed formulas. The suggested structure of the complexes is shown as Scheme 4.




**(1)**, R = H; **(2)**, R = $CH_3$; M = Co(II), Cu(II), Ni(II), Zn(II)

**Scheme 4.** Suggested structure of the complexes.

The TGA curves studied in the 20–900°C temperature range showed that the thermal decomposition of the ligands and the complexes takes place in different steps, Table 3. It is possible that the different groups in the ligands 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 affect the thermal stability [22,23].

**Table 3.** TGA data of the ligands and the complexes.

| Compound | First step, °C | Second step, °C | Third step, °C | Fourth step, °C |
|---|---|---|---|---|
| $L^1H$ (**3**) | 256–474 | 558–782 | – | – |
| $(L^1)_2Co$ | 178–329 | 329–362 | 362–428 | 428–529 |
| $(L^1)_2Cu$ | 171–221 | 221–371 | 371–505 | 505–656 |
| $(L^1)_2Ni$ | 282–463 | 463–705 | – | – |
| $(L^1)_2Zn$ | 245–328 | 328–511 | 511–562 | 562–729 |
| $L^2H$ (**4**) | 245–390 | 495–635 | – | – |
| $(L^2)_2Co$ | 195–313 | 313–379 | 379–446 | 446–547 |
| $(L^2)_2Cu$ | 196–280 | 280–347 | 347–530 | – |
| $(L^2)_2Ni$ | 262–312 | 312–345 | 345–361 | 361–479 |
| $(L^2)_2Zn$ | 260–377 | 377–494 | 494–662 | – |

The ligand $L^1H$ is stable up to 256°C, whereas the ligand $L^2H$ is stable up to 245°C. As can be seen in the TGA data, each ligand decomposes in two steps. The first step in the decomposition sequence corresponds to the loss of mesityl groups from the molecules. In the second step, cyclobutane and thiazole groups decompose gradually. The TGA curves showed that the thermal decomposition of the complexes takes place in three or four steps, except the $(L^1)_2Ni$ complex which decomposes in two steps. The most stable complex of the ligands is $(L^1)_2Ni$ complex. The temperature range for the dehydration process shows a strong relationship with the binding mode of water molecules of the respective metal complexes. Since no elimination of water is observed on TGA curves this implies that not any one of the ligands and complexes contains hydration or coordinated water. Since, the ligands and complexes have been dried to the constant weight at 110°C, it is an expected result. The inflection point of the TGA curves of all the complexes at a temperature under [529°C for $(L^1)_2Co$, 656°C for $(L^1)_2Cu$, 705°C for $(L^1)_2Ni$ and 729°C for $(L^1)_2Zn$, 547°C for $(L^2)_2Co$, 530°C for $(L^2)_2Cu$, 479°C for $(L^2)_2Ni$ and 662°C for $(L^2)_2Zn$] indicates the decomposition of the fully organic part of the chelate, leaving metallic oxide at the final temperature. The observed weight losses for all complexes are in good agreement with the calculated values from the formulas given in Table 1. All the complexes completely decompose to the corresponding metal oxides, $Co_3O_4$, CuO, NiO or ZnO.

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