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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Synthesis and Structural Studies of 2,2'-[(2*E*,5*E*)-hexane-2,5-diylidenedi-nitrilo]-dibenzenethiol and 2-Hydroxybenzaldehyde (2*E*,5*E*)-hexane-2,5-diylidenehydrazone ligands and their Mononuclear Cu(II) and Ni(II) Complexes

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**To cite this Article** Karabocek, Nevin , Kucukdumlu, Asligul , Ekmekcioglu, Pinar and Karabocek, Serdar(2009) 'Synthesis and Structural Studies of 2,2'-[(2*E*,5*E*)-hexane-2,5-diylidenedi-nitrilo]-dibenzenethiol and 2-Hydroxybenzaldehyde (2*E*,5*E*)-hexane-2,5-diylidenehydrazone ligands and their Mononuclear Cu(II) and Ni(II) Complexes', Journal of Macromolecular Science, Part A, 46: 10, 1007 – 1014

**To link to this Article:** DOI: 10.1080/10601320903158727

**URL:** <http://dx.doi.org/10.1080/10601320903158727>

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# Synthesis and Structural Studies of 2,2'-[(2*E*,5*E*)-hexane-2,5-diylidenedi-nitrilo]-dibenzenethiol and 2-Hydroxybenzaldehyde (2*E*,5*E*)-hexane-2,5-diylidenehydrazone ligands and their Mononuclear Cu(II) and Ni(II) Complexes

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Received January 2009, Accepted April 2009

Monomeric copper(II) and nickel(II) complexes with tetradentate two new ligands, 2,2'-[(2*E*,5*E*)-hexane-2,5-diylidenedi-nitrilo]dibenzenethiol(H<sub>2</sub>L) and 2-hydroxybenzaldehyde (2*E*,5*E*)-hexane-2,5-diylidenehydrazone(H<sub>2</sub>L<sup>1</sup>) have been synthesized and characterized by elemental analyses, magnetic moments, molar conductance, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR, IR, mass spectral studies, theoretical calculations (MM2 and AM1) molecular methods. The mononuclear metal complexes of H<sub>2</sub>L and (H<sub>2</sub>L<sup>1</sup>) were found to have a 1:1 metal:ligand ratio. Elemental analyses, stoichiometric and spectroscopic data of metal complexes indicated that the metal ions were coordinated to the sulphur (-SH) and/or (-OH) oxygen and imine nitrogen atoms (C=N). All of the data obtained from spectral, and molecular mechanics (MM2) or semi empirical calculations (AM1) studies support the structural properties of ligands and its Cu(II) and Ni(II) metal complexes.

**Keywords:** Hydrazones, Schiff bases, copper(II) and nickel(II) complexes

## 1 Introduction

There is a continuing interest in metal complexes of Schiff bases. Because of the presence of both hard nitrogen or oxygen and soft sulphur donor atoms in the backbones of these ligands, they readily coordinate with a wide range of transition metal ions yielding stable and intensely coloured metal complexes, some of which have been shown to exhibit interesting physical and chemical properties (1–3) and potentially useful biological activities (4–6). Many reports are available for the preparation and properties of model copper complexes which mimic copper-containing metalloproteins such as hemocyanine and tyrosinase. Two noticeable properties of copper proteins are an intense absorption band (7–9) near 600 nm and relatively high copper(II)/copper(I) reduction potentials (2–4). Attention was particularly focused on their correlation with the active site of metalloenzymes and metalloproteins containing dinu-

clear metalcenters in order to elucidate the factors that determine the reversible binding and activation of O<sub>2</sub> in various natural oxygen transport systems and mono- and dioxygenases and to mimic their activity (7–9).

The condensation of alkyl and aromatic primary amines with carbonyl groups yields Schiff bases (10–13) that are still now regarded as one of the most potential group of chelators for facile preparations of metallo-organic hybrid materials. In the past two decades, the properties of Schiff base metal complexes stimulated much interest for their noteworthy contributions to single molecule-based magnetism, material science (14), catalysis of many reactions like carbonylation, hydroformylation, oxidation, reduction and epoxidation (15), etc. Copper(II) Schiff base complexes with pseudohalides are well known for their preparational accessibilities, exhibiting the flexibility of the coordination geometry around the metal center (16). The coordination number usually varies from four to six depending upon the donor site geometry around the metal by the ligand itself.

In the present paper, novel complexes derived from (2, 2'-[(2*E*,5*E*)-hexane-2,5-diylidenedinitrilo]-dibenzenethiol (H<sub>2</sub>L) and 2-hydroxybenzaldehyde (2*E*,5*E*)-hexane-2,5-diylidenehydrazone, (H<sub>2</sub>L<sup>1</sup>) are reported. Copper(II) and

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nickel(II) complexes were prepared and characterized by elemental analyses, magnetic susceptibilities, molar conductance, IR, UV-Vis, mass spectral studies. In this studies, it was observed that 2-hydroxybenzaldehyde (2E,5E)-hexane-2,5-diylidenehydrazone ( $H_2L^1$ ) formed intramolecular hydrogen bonds to produce a chalet containing seven atoms but other ligand, 2,2'-(2E,5E)-hexane-2,5-diylidenedinitrilo]dibenzenethiol ( $H_2L$ ), did not form any hydrogen bond. However, the formation of a chalet containing six atom is an expected situation.

## 2 Experimental

$^1H$ -NMR and  $^{13}C$ -NMR spectra were recorded on a Varian Gemini 200 spectrometer. DMSO- $d_6$  and  $CDCl_3$  was used as solvent. Chemical shifts ( $\delta$ ) were reported in ppm relative to tetramethylsilane, using the solvent signal as internal reference. Elemental analyses (C, H, N and S contents) were performed on a Costech 4010 CHNS Elemental analyzer, and metal contents were estimated. The methylene ( $-CH_2$ ) proton signal was observed at 7.26 ppm an unexpected situation IR spectra were recorded on an ATI Unicam Matson 1000 Model FTIR spectrophotometer and UV/Vis spectra on an ATI Unicam UV2 Model UV/Vis spectrophotometer. Mass spectra [ESI] were recorded on Micromass Quanto LC-MS/MS spectrophotometer. The molar conductance was measured with Metrohm 660 conductivity in DMF solution. Room temperature magnetic susceptibility measurements were done on a PAR model 155 vibrating sample magnetometer. All chemicals were of the highest quality available, obtained from local suppliers, and used as received. Conformational analysis was made by using the Allger's MM2 method. The Smart Minimizer was used for energy minimization, which was a combination of methods, starting with the Steepest Descent Method, followed by the Fletcher-Reeves and Block-diagonal Newton-Raphson methods, and ending with the accurate Polak-Ribiere method. The semi empirical AM1 calculations used MOPAC/AM1 version 6.03, including electronic properties, optimized geometries, total energy, dipole moment and heat of formation known as SCF method (17).

### 2.1 Synthesis of the 2,2'-(2E,5E)-hexane-2,5-diylidenedinitrilo]dibenzenethiol, ( $H_2L$ )

2,5-hexadione (2.28 g, 20 mmol) and *o*-aminothiophenol (5 g 40 mmol) were mixed together in absolute EtOH (15 mL). This solution was stirred for 24 h at room temperature. The precipitated product was filtered off, washed with EtOH. Then the ligand was crystallized in  $(CH_3)_2CO-H_2O$  (4/1). This pale-white crystalline product was isolated by vacuum filtration, then the product was dried *in vacuo*. Yield: 5.9 g (90%), m.p. 123°C. Ms: (ESI)  $m/z = 365.4 [M+2H_2O+1]^+$  (100), 326.25  $[M-2]^+$  (20), 224.17(80),

133.06 (45), 120.04 (48). Elemental analysis: Calc.: C%, 65.80; H%, 6.14; N%, 8.53; S%, 19.52; Found: C%, 65.70; H%, 6.20; N%, 8.60; S%, 19.55.  $^{13}C$ -NMR spectra, [ $CDCl_3$ ,  $\delta$  (ppm),  $J$  (Hz)]:  $\delta = 12.6 (-CH_3)$ ; 106.18( $-CH_2-$ ); 125.94, 127.15, 128.5, 129.35, 136.13, 136.78(-Ar); 165.15(C=N).

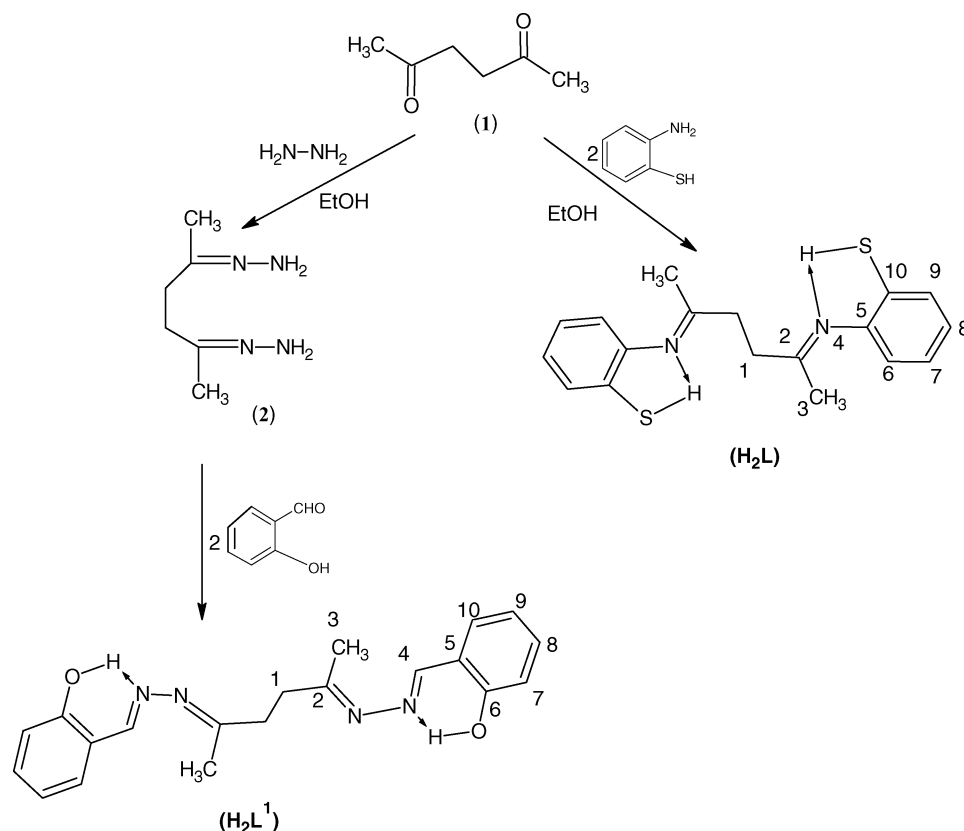
### 2.2 Synthesis of the 2-Hydroxybenzaldehyde (2E,5E)-hexane-2,5-diylidenehydrazone, ( $H_2L^1$ )

2,5-hexadione (4.56 g, 40 mmol) and hydrazinehydrat (4 g 80 mmol) were mixed together in absolute EtOH (30 mL). This solution was stirred for 12 h at room temperature. The white precipitated product was filtered off and then washed with EtOH. Then, the hexane-2,5-dione dihydrazone (2) was crystallized in  $(CH_3)_2CO$ . This white crystalline product was isolated by vacuum filtration, then the product was dried *in vacuo*. Yield: 5 g (87%), Hexane-2,5-dione dihydrazone, (2): % calculated C, 50.68; H, 9.92; N, 39.40; Found: C, 50.70; H, 9.85; N, 39.45. Freshly prepared, the hexane-2,5-dione dihydrazone, (2) (2.84 g, 20 mmol) and salicylaldehyde (4.9 g 40 mmol) were mixed together in absolute EtOH (30 mL). This solution was stirred for 24 h at room temperature. The precipitated product was filtered off, washed with EtOH. Then the ligand was crystallized in EtOH. This yellow crystalline product was isolated by vacuum filtration, then the product was dried *in vacuo*. Yield: 5 g (70%), m.p. 209°C. Elemental analysis: Calc.: C%, 68.57; H%, 6.28; N%, 15.99; Found: C%, 68.60; H%, 6.25; N%, 16.1. Ms: (ESI)  $m/z = 350.57 [M]^+$  (25), 231.25(100).  $^{13}C$ -NMR spectra, [ $CDCl_3$ ,  $\delta$  (ppm),  $J$  (Hz)]:  $\delta = 11.4 (-CH_3)$ ; 102.1( $-CH_2-$ ); 117.38, 119.98, 132.81, 133.70, 136.15, 160.0(-Ar); 164.97 (C=N).

### 2.3 Synthesis of the Cu(II), Ni(II) Complexes

A sample of the ligand  $H_2L$  or  $H_2L^1$  (0.001 mol) was dissolved in  $(CH_3)_2CO$  (20 mL). A solution of  $Cu(ClO_4)_2 \cdot 6H_2O$  and/or  $Ni(ClO_4)_2 \cdot 6H_2O$  (0.001 mol) in  $(CH_3)_2CO$  (20 mL) was added to the ligand solution and this mixture was heated under reflux for 2 h. The resulting solution was filtered while it was hot. As the solution cooled, a product precipitated. This product was filtered off, washed with  $H_2O$ . Then the solid product was dried *in vacuo*.

For ( $CuL$ ): % calculated C, 36.60; H, 3.10; N, 4.74; Cu, 10.75, Found: C, 36.5; H, 3.15; N, 4.60; Cu, 10.60. Ms: (ESI)  $m/z = 590.49[M-1]^+$ . For  $NiL$ : % calculated C, 36.92; H, 3.07; N, 4.79; Ni, 10.08, found C, 36.95; H, 3.15; N, 4.67; Ni, 9.90. Ms: (ESI)  $m/z = 585.55[M-1]^+$ . Elemental analysis: Calc. (for  $(CuL^1)$ ): Calc. C%, 39.28; H%, 3.60; N%, 9.16; Cu%, 10.40; Found: C%, 39.35; H%, 3.55; N%, 9.20; Cu%, 10.50. Ms: (ESI)  $m/z = 614.49[M+1]^+$  (20) Elemental analysis: Calc. (for  $NiL^1$ ) Calc. C%, 39.54; H%, 3.30; N%, 9.23; Ni%, 9.72; Found: C%, 39.45; H%, 3.25; N%, 9.15; Ni%, 9.80. Ms: (ESI)  $m/z = 608.55[M-1]^+$  (30).



Sch. 1. Preparation of ligands,  $(H_2L)$  and  $(H_2L^1)$ .

### 3 Results and Discussion

2,2'-(2E,5E)-hexane-2,5-diylidenedi-nitrilo]-dibenzenehydrazide ( $H_2L$ ) and 2-hydroxybenzaldehyde (2E,5E)-hexane-2,5-diylidenedi-nitrilo]-dibenzenehydrazide ( $H_2L^1$ ) were prepared in EtOH by reacting 2,5-hexadione with *o*-aminothiophenol and hydrazinehydrate, salicylaldehyde (Scheme 1). The ligands ( $H_2L$  and  $H_2L^1$ ) were verified by elemental analysis and

$^1H$ -NMR,  $^{13}C$ -NMR, and IR data (Table 1–3). In addition, its copper(II) and nickel(II) complexes were verified by elemental analyses and magnetic moment, UV-Vis and IR data (Tables 2–3). In the proposed structures of ( $H_2L$ )  $N_2S_2$  and ( $H_2L^1$ )  $N_2O_2$ , units are available for the complexation of metal ions in square-planar coordination geometry. The corresponding copper(II) and nickel(II) complexes (3–6) have been prepared with a reaction of the

Table 1.  $^1H$ -NMR data of ligands ( $H_2L$ ,  $H_2L^1$ ) and Ni(II) complexes

	$CH_2-1$	$CH_3-3$	<i>Ar-H</i>	$-OH$	$N=C-H$	$S-H$
$H_2L$	5.97 (s, 4H)	1.98(s, 6H)	7.18–7.54 (m, 8H)	—	—	7.39 (br. s, 2H)
$H_2L^1$	7.27 (s, 4H)	1.57 (s, 6H)	6.93–7.43 (m, 8H)	8.72 (s, 2H)	11.40(s, 2H)	—

Table 2. Characteristic IR bands of the ligand and its metal complexes (in  $cm^{-1}$ )

Comp.	$\nu(O-H)$	$\nu(S-H)$	$\nu_{sym}(C-S)$	$\nu_{asym}C-S$	$\nu(C=N)$	$\nu(C-O)$	$\delta(O-H)$	$\nu(M-O)$	$\nu(M-N)$	$\nu(ClO_4)$
$H_2L$	—	2736	738	761	1582	—	—	—	—	—
$H_2L^1$	3450	—	—	—	1623	1272	1324	—	—	—
CuL, 3	3435(br)	—	730	759	1583	—	—	—	450	1093-1144-622
NiL, 4	3436(br)	—	725	750	1575	—	—	—	580	1088-1111-1144-626
CuL $^1$ , 5	3435(br)	—	—	—	1614	1260	1314	550	460	1196-1148-625
NiL $^1$ , 6	3425(br)	—	—	—	1623	1250	1310	580	475	1070-1111-1121-627

**Table 3.** Analytical and physical data of the ligand and its metal complexes

Comp.	Formula (F.W. g.mol <sup>-1</sup> )	Color	$\mu_{ef}^a$	$\Lambda^b / \text{Scm}^2 \text{mol}^{-1}$	Yield	d-d	n- $\pi^b$
H <sub>2</sub> L	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> S <sub>2</sub>	Green-white	—	—	90	—	345
H <sub>2</sub> L <sup>1</sup>	C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub>	Yellow	—	—	70	—	340
CuL	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>8</sub> Cl <sub>2</sub> Cu	Green-brown	1.80	235	65	500	350
NiL	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>8</sub> Cl <sub>2</sub> Ni	Red	Diamag.	244	70	486	355
CuL <sup>1</sup>	C <sub>20</sub> H <sub>20</sub> N <sub>4</sub> O <sub>10</sub> Cl <sub>2</sub> Cu	Deep-brown	1.74	230	75	475	360
NiL <sup>1</sup>	C <sub>20</sub> H <sub>20</sub> N <sub>4</sub> O <sub>10</sub> Cl <sub>2</sub> Ni	Red	Diamag.	250	70	505	365

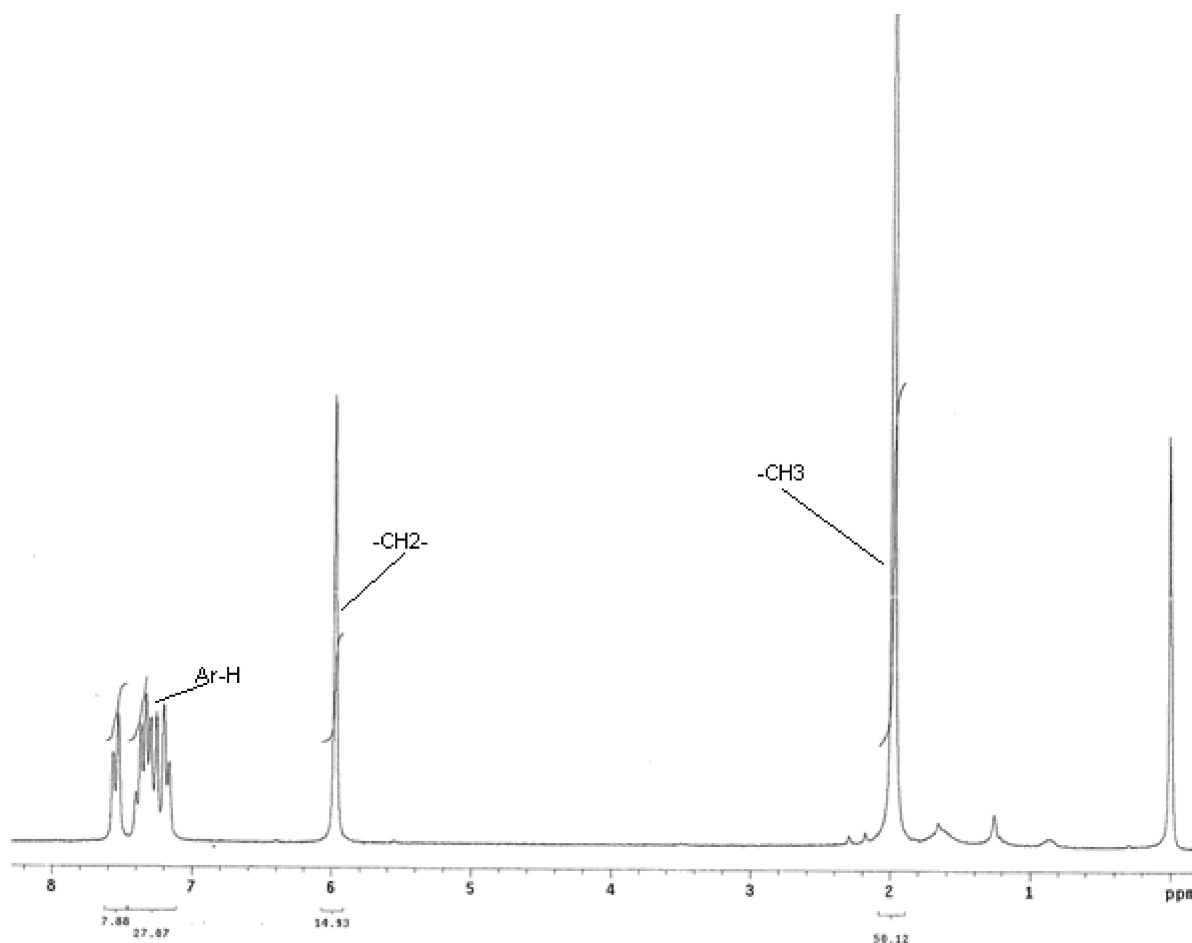
<sup>a</sup>Per metal atom at 297 K(B.M.).

<sup>b</sup>UV/Vis spectra and molar conductance were taken in DMF.

ligand mixture in (CH<sub>3</sub>)<sub>2</sub>CO with copper(II) and nickel(II) salts.

The <sup>1</sup>H-NMR spectra of a CDCl<sub>3</sub> solution of Schiff base ligand (H<sub>2</sub>L) and hydrazone, (H<sub>2</sub>L<sup>1</sup>) were given Table 1. The spectrum of the ligand (H<sub>2</sub>L) shows singlet at 1.98(-CH<sub>3</sub>, 6H), singlet at 5.97 (-CH<sub>2</sub>, 4H) (11), triplet at 7.32 (J<sub>6,7</sub> = J<sub>8,9</sub> 7.4 Hz) (Ar-H, C-7 and C-8, 4H), doublet at 7.18 (J<sub>6,7</sub> = 7.4 Hz) (Ar-H, C-6, 2H), doublet at 7.54 (J<sub>8,9</sub> = 7.4 Hz) (Ar-H, C-9, 2H) (Fig. 1). The Schiff base ligand proton signals at 7.39 p.p.m. belonging to -OH protons disappear

on deuterium exchange. The spectrum of the ligand (H<sub>2</sub>L<sup>1</sup>) shows singlet at 1.57(-CH<sub>3</sub>, 6H), singlet at 7.26 (-CH<sub>2</sub>, 4H) (Fig. 2A and B) (11), singlet at 8.72 (N=CH, 2H), singlet at 11.40 (O-H, 2H) and AA'BB' system *ca.* at 6.93-7.43 (Ar-H, 8H). The ligand (H<sub>2</sub>L<sup>1</sup>) proton signals at 11.40 p.p.m. belonging to -O-H protons disappear on deuterium exchange. In the <sup>1</sup>H-NMR spectra, integrated data are consistent with formula. In the <sup>13</sup>C-NMR spectra of H<sub>2</sub>L and H<sub>2</sub>L<sup>1</sup> nine and ten resonances were observed respectively, which is also consistent with the formula. In the <sup>1</sup>H-NMR spectrum of



**Fig. 1.** <sup>1</sup>H-NMR spectra of Ligand (H<sub>2</sub>L) in CDCl<sub>3</sub>.

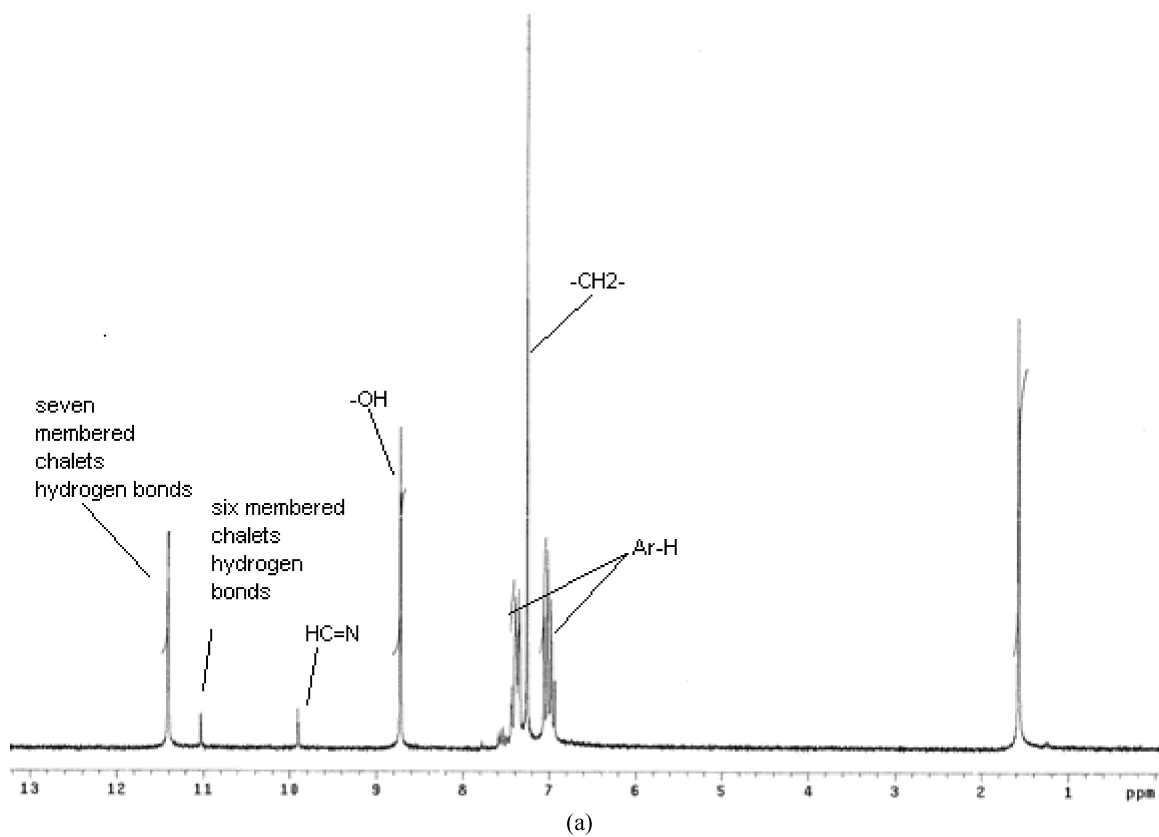


Fig. 2. (A) <sup>1</sup>H-NMR spectra of Ligand (H<sub>2</sub>L<sup>1</sup>) in CDCl<sub>3</sub>.

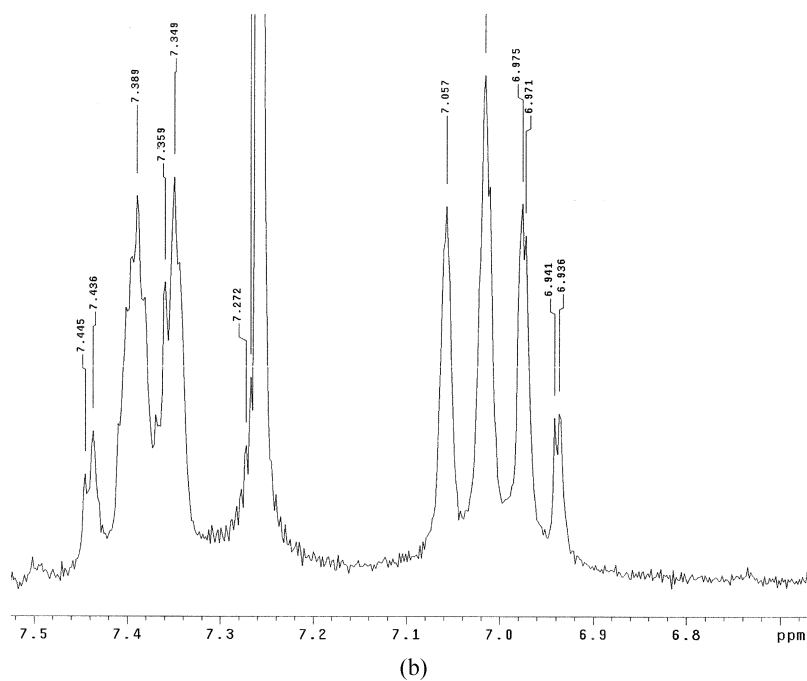
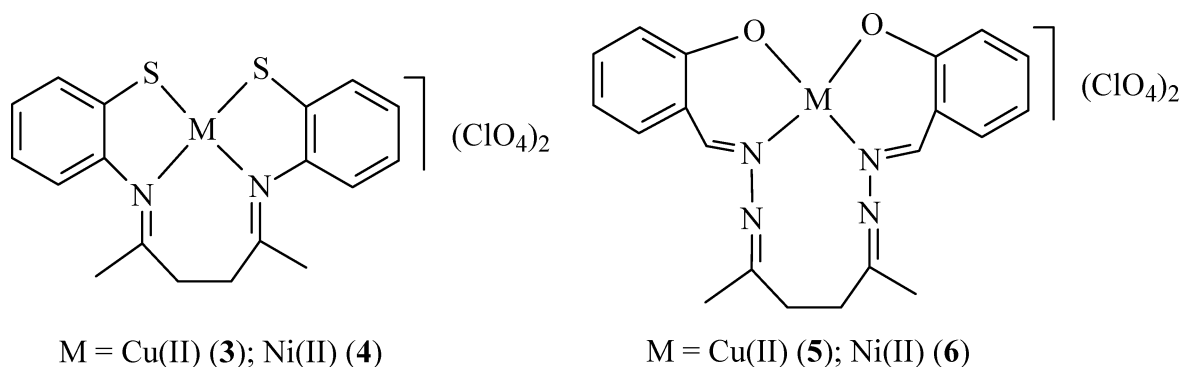


Fig. 2. (B) <sup>1</sup>H-NMR expanded spectra of Ligand (H<sub>2</sub>L<sup>1</sup>) in CDCl<sub>3</sub> (in aromatic region).



**Fig. 3.** Proposed structures for the copper(II) complexes.

the hydrazone, ( $H_2L^1$ ) two short singlets were observed at 9.90 and 11.09 ppm. This was also an unexpected situation. In the  $^1H$ -NMR spectra of the hydrazone ( $H_2L^1$ ), it was observed that the integrated data of proton signals at 11.40, 9.90 and 11.09 p.p.m are consistent with 2H. This was attributed to the formation of intramolecular hydrogen bonding, and a seven-membered and six-membered chalet H bonds were observed at 11.40 and 11.09 ppm respectively. Other signal was attributed to free OH resonance at 9.90 ppm. The methylene ( $-CH_2$ ) proton signals were observed at 5.97 and 7.26 ppm. It was also an unexpected situation. These were attributed to the formation of intramolecular hydrogen bond and tautomerism. Bayer et al. were also reported the same results (11).

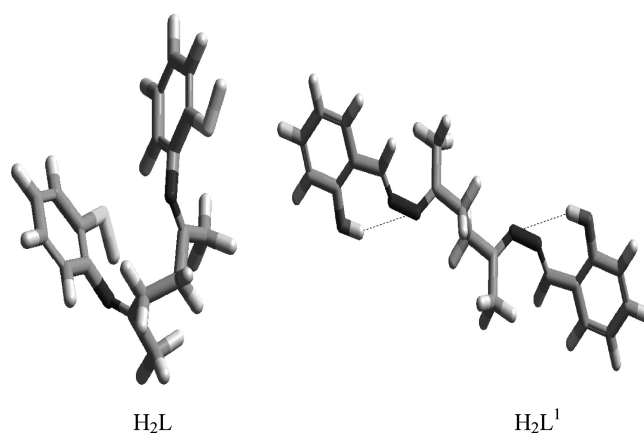
The mass spectra (ESI) exhibited the molecular ion at  $m/z = 365.4 [M+2H_2O+1]^+$  and  $m/z = 350.57 [M]^+$  (25) for  $H_2L$  and  $H_2L^1$ , respectively, which indicates formation of the ligands. The molecular ion peak appeared at ( $m/z$ , ESI) 590.49  $[M-1]^+$  for the  $[CuL](ClO_4)_2$ , at 585.55  $[M-1]^+$  for  $[NiL](ClO_4)_2$ ; at 614.49  $[M+1]^+$  for the  $[CuL^1](ClO_4)_2$ , at ( $m/z$ ) 608.55  $[M-1]^+$  for for  $[NiL^1](ClO_4)_2$ . The mass spectra of the compounds showed the formation of the ligands and its metal complexes.

Relevant IR bands were given in Table 2. In general, the complexes exhibited very comparable IR features suggesting that they were of similar structure. The presence or absence of certain bands in the generally complicated IR spectra has been used to establish the nature of the complexes. In the IR spectrum of ligand ( $H_2L$ ), a weak band was observed for  $\nu$  ( $-S-H$ ) at *ca.* 2736  $cm^{-1}$  and a sharp band for  $\delta$  (C-S) at *ca.* 738  $cm^{-1}$ . In the IR spectrum of ligand ( $H_2L^1$ ), a weak band was observed for  $\nu$  (O-H) *ca.* at 3450  $cm^{-1}$  and a sharp band for  $\nu$  (C=N) *ca.* at 1623  $cm^{-1}$ . The metal complexes were observed to have bands at 1093, 1144 and 622  $cm^{-1}$  for  $CuL$  and 1088, 1111, 1144 and 626 for  $NiL$ , featuring typical characteristics of uncoordinated perchlorates (18–20). In the IR spectrum, the S-H vibration wasn't observed at 2736  $cm^{-1}$  for complexes (**3**, **4**) (11). The complexes were observed to have bands at 1196, 1148 and 625  $cm^{-1}$  for  $CuL^1$  and 1070, 1111, 1121 and 627 for  $NiL^1$  featuring typical characteristics of uncoordinated perchlo-

rates (19–22). IR data confirm the binding of the copper(II) nickel(II) by  $N_2S_2$  and  $N_2O_2$  donor groups of the present ligands ( $H_2L$ ,  $H_2L^1$ ) and support the tentative structure of the complexes (Fig. 3). The significant shifts in  $\nu$  (C=N) and  $\nu$  (S–H) upon complexation are consistent with complex formation and support the concept of coordination of the ligand through the nitrogen and sulphur atoms.

The room temperature magnetic moment of all the copper(II) and nickel(II) complexes showed a normal magnetic moment (Table 3). The magnetic moment data of the copper(II) complexes (**3** and **5**) are *ca.* 1.80 B.M., corresponding to one unpaired electron. All the nickel(II) complexes (**4**, **6**) were diamagnetic. The copper(II) and nickel(II) complexes may be considered to have tetragonal geometry (22, 23).

Although the electronic spectra of copper(II) complexes with polydentate Schiff base ligands were not in general good indicators of geometry, they helped to support it. The electronic spectra of ligand and copper(II) complex were taken in DMF. In the UV-Vis spectra, characteristic bands of the Schiff base ligand were observed. The absorption bands were given in Table 3. The absorption  $\lambda_{max}$  of the free ligands  $H_2L$ ,  $H_2L^1$  and their metal complexes were



**Fig. 4.** Calculated (MM2) conformation for ligands  $H_2L$  and  $H_2L^1$  (Total strain energy  $H_2L = 6.70$ ;  $H_2L^1 = 9.70$  kcal/mol).

**Table 4.** The strain energies of the most stable conformations of the ligands (H<sub>2</sub>L and H<sub>2</sub>L<sup>1</sup>) from the MM2 force field calculations (energies in kcal/mol)

Comp.	Total	Bond	Angle	Dihedral	Vdw	Stretch-bend	Electrostatic
H <sub>2</sub> L	6.70	0.74	3.93	-9.73	10.78	0.19	0.79
H <sub>2</sub> L <sup>1</sup>	9.70	1.10	4.95	-16.66	18.13	0.12	2.06

**Table 5.** The most stable conformations energy of the ligands (H<sub>2</sub>L and H<sub>2</sub>L<sup>1</sup>) from the semiempirical MM1 force field calculations (in kcal/mol)

Comp.	Total	Binding	Isolated Atomic	Electronic	Core-Core Interaction	Heat of Formation	Total Dipole (Debyes)
H <sub>2</sub> L	-77977.14	-4392.07	-73585.07	-594515.10	516537.96	84.79	2.212
H <sub>2</sub> L <sup>1</sup>	-99839.49	-5084.98	-94754.51	-686612.37	586772.88	50.18	0.00

seen in the region 250, 280 nm. These bonds were attributed to benzene  $\pi \rightarrow \pi^*$  transition (24-29). The band around 350 nm was due to the  $n \rightarrow \pi^*$  transition of the non-bonding electron present on the nitrogen or oxygen and/or sulphur atom in the Schiff bases. In the complexes (3-6), d-d transitions were observed at *ca.* 475–505 nm. The energy of the d-d transition suggested a distorted tetragonal geometry (22-30). The molar conductance data were given in Table 3. These values were in the range expected to 1:2 for the perchlorate complexes (31).

A geometric optimization of the synthesized ligands (H<sub>2</sub>L and H<sub>2</sub>L<sup>1</sup>) were made by the methods of molecular mechanics (32) (MM2) in order to establish a stable conformation, and the data were compared with the experimental data. The most stable conformations of these two ligands (H<sub>2</sub>L and H<sub>2</sub>L<sup>1</sup>) were given in Figure 4 and its theoretical calculated data were given in Table 4. The total strain energy of the most stable conformation for H<sub>2</sub>L and H<sub>2</sub>L<sup>1</sup> were calculated to be 6.70 and 9.70 kcal/mol, respectively. The analysis of total strain energies for both of the ligand conformations (H<sub>2</sub>L and H<sub>2</sub>L<sup>1</sup>) showed that the energies were primarily due to especially the angle, bond, electrostatic and van der Waals strain interactions (Table 4). In the molecular mechanics (32) (MM2) calculations, it was observed that 2-hydroxybenzaldehyde (2E,5E)-hexane-2,5-diylidenehydrazone (H<sub>2</sub>L<sup>1</sup>) formed seven-member intramolecular hydrogen bonds but other ligand, 2,2'-[(2E,5E)-hexane-2,5-diylidenedinitrilo]dibenzenethiol (H<sub>2</sub>L), (Fig. 4) did not. In the <sup>1</sup>H-NMR spectrum, the experimental results were confirmed by theoretical calculations. But, unexpected behaviours were observed in the formation of intramolecular hydrogen bonding with chalets containing seven atoms, not the expected six atoms. In addition, total, binding, isolated atomic, electronic, core-core interaction energy, heat of formation and total dipole were calculated for the both ligands (H<sub>2</sub>L and H<sub>2</sub>L<sup>1</sup>) by semi empirical AM1 calculations (17, 33). The theoretical data were given Table 5.

## 4 Conclusions

In the present study, we have demonstrated the preparation of Schiff base and hydrazone ligand providing N<sub>2</sub>S<sub>2</sub> or N<sub>2</sub>O<sub>2</sub> donor array moiety, and their four mononuclear copper(II) and mononuclear nickel(II) complexes. Although, the nickel(II) complexes (4, 6) were diamagnetic, the copper(II) complexes(3, 5) were paramagnetic. The metal ion was complexed with nitrogen and sulphur or oxygen atoms of ligands (H<sub>2</sub>L and H<sub>2</sub>L<sup>1</sup>) in a distorted tetragonal geometry for metal ions. All of the data obtained from spectral data, and molecular mechanics (MM2) or semi empirical calculations (AM1) studies supported the structural properties of ligands and its Cu(II) and Ni(II) metal complexes.

## Acknowledgement

This work was supported by Karadeniz Technical University Research Fund, and its project code is 2005.111.02.2.

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