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Ahmed A. El-Asmy<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt

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## Synthesis and spectroscopic characterization of N-substituted thiosemicarbazone complexes

Ahmed A. El-Asmy\*

Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt

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Complexation between Co(II), Ni(II), and Cu(II) with some 3,4-hexanedione bis[N-substituted thiosemicarbazones] has been investigated. The ligands release the two hydrazine hydrogens during the complex formation and act as binategative tetradentate ( $N_2S_2$ ) except  $[Cu(H_2Hx4M)Cl_2]$  and  $[Cu(H_2Hx4Et)Cl_2] \cdot 2H_2O$  in which the ligands behave as neutral tetradentate. The magnetic moments and electronic spectra provide information about the geometry of the complexes, which is supported by calculating the ligand field parameters for the Co(II) complexes. Most Ni(II) complexes are diamagnetic, indicative of a square-planar structure. The bands observed in Nujol are shifted to higher energies in dimethylformamide (DMF) solution, suggesting a weak interaction with the solvent. The ESR spectra of the complexes in solid and DMF solution exhibit axial symmetric g-tensor parameters with  $g_{\parallel} > g_{\perp} > 2.0023$ . The molecular parameters of  $[Ni(Hx4M)]$  have been calculated theoretically by semiempirical PM3 method. Also, the electronic transitions were calculated theoretically and found approximately similar to those recorded experimentally.

**Keywords:** complexes; thiosemicarbazones; spectral and magnetic studies; molecular parameters

### 1. Introduction

The antimicrobial and antitumor activities of many thiosemicarbazones and their metal complexes have been tested (1); the nature of the substituent on the thiosemicarbazone moiety showed a great dependence. The fungicidal activity of thiosemicarbazones is due to their ability to form stable chelates with the essential metal ions in which the fungus needs in its metabolism (2). In addition, mono- and polynuclear Schiff base Cu(II) complexes based on thiosemicarbazone serve as models for galactose oxidase and are used as an effective oxidant. The redox behavior of the Cu(II) model has a special interest in some biological systems (3, 4). Diacetylmonoxime thiosemicarbazone was found effective against vaccinia infections in mice (5) which probably acted by removing some essential metal ions from the vaccinia virus by chelation (6, 7). Copper is an essential constituent of about 30 enzymes and glycol-proteins, and is required for the synthesis of hemoglobin and for some biological processes (8, 9). Ni(II) and Cu(II) complexes of 2,3-butanedione bis(N(3)substituted thiosemicarbazones) were studied, and some ligands and their complexes were solved by

\*Email: aelasmy@yahoo.com

x-ray crystallography (10). The crystal structure of Cu(II) complexes of 3,4-hexanedione bis(3-piperidylthio-semicarbazone), [Cu(HxPip)] and 3,4-hexanedione bis(3-hexamethyleneiminylthiosemicarbazone), [Cu(HxHexim)] was reported (11).

Herein, the synthesis and spectral information of Co(II), Ni(II), and Cu(II) complexes of 3,4-hexanedione bis[N-substituted thiosemicarbazones] are reported. No work was done on most of these ligands as well as on their Co(II) and Ni(II) complexes. One of the advantages of these ligands is their ability to form stable complexes having three rings (five-membered ring) with the metal(II) ions. Also, the substituent may play an important role in the biological activity of the ligands and their complexes. Trials will be done now to study their antimicrobial and antiinflammation activities.

## 2. Experimental

### 2.1. Synthesis of ligands

The ligands (abbreviated as H<sub>2</sub>Hx4M, H<sub>2</sub>Hx4Et, H<sub>2</sub>Hx4Ph, and H<sub>2</sub>HxPip, H<sub>2</sub>HxHexim) were prepared, similar to those reported earlier (H<sub>2</sub>HxPip and H<sub>2</sub>HxHexim) (11), by the reaction of 0.05 mol of 3,4-hexanedione with 0.1 mol of 4-methyl, 4-ethyl, 4-phenyl, 3-piperidyl, and/or 3-hexamethyleneiminylthiosemicarbazide in 50 ml ethanol with five drops of glacial acetic acid. The reaction mixture was boiled under reflux on a water bath for 2–3 h. After evaporation, the precipitate formed was separated by filtration, recrystallized using ethanol, and dried. The proposed formulae of the ligands are in good agreement with the stoichiometry concluded from analytical data and confirmed from IR and <sup>1</sup>H NMR spectra; the molecular structures are shown as in Figure 1. The names and <sup>1</sup>H NMR spectral data of the ligands are listed in Table 1, while their IR bands are listed in Table 3. The ligands have electronic spectral bands which are similar in both solid and dimethylformamide (DMF) solution and exist in the range 38,000–27,000 cm<sup>-1</sup> corresponding to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  bands (12). In H<sub>2</sub>HxPip and H<sub>2</sub>HxHexim, more bands are observed at 24,000 and 20,000 cm<sup>-1</sup>, which may be due to charge transfer transitions.

### 2.2. Synthesis of complexes

Two types of complexes were evaluated. [Cu(H<sub>2</sub>Hx4M)Cl<sub>2</sub>] and [Cu(H<sub>2</sub>Hx4Et)Cl<sub>2</sub>]2H<sub>2</sub>O were prepared by heating a mixture of H<sub>2</sub>Hx4M or H<sub>2</sub>Hx4Et (3 mmol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (3 mmol) in 30 ml ethanol on a water bath for 1 h. The rest of the complexes were prepared by heating a mixture of H<sub>2</sub>Hx4M, H<sub>2</sub>Hx4Et, H<sub>2</sub>Hx4Ph, H<sub>2</sub>HxPip, or H<sub>2</sub>HxHexim (3 mmol) and Co(II) or Ni(II) acetate salts (3 mmol) in 30 ml aqueous-ethanol solution (v/v) under reflux on a water bath

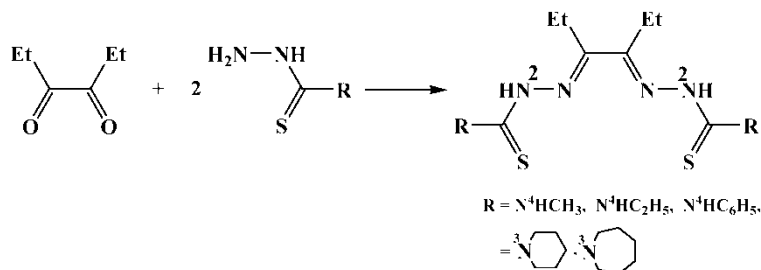


Figure 1. Procedure for preparing the ligands.

Table 1. Name and  $^1\text{H}$  NMR spectral data of 3,4-hexanedione bis[N-substituted thiosemicarbazones].

Ligand	Solvent	N(2)H	N(4)H	CH <sub>3</sub>	N-CH <sub>3</sub>	C-CH <sub>3</sub>
3,4-hexanedione bis(thiosemicarbazone), H <sub>2</sub> Hx4H	—	—	—	—	—	—
3,4-hexanedione bis(4-methylthiosemicarbazone), H <sub>2</sub> Hx4M	D <sub>6</sub> -DMSO	8.27	10.32	2.99	3.04	2.87
3,4-hexanedione bis(4-ethylthiosemicarbazone), H <sub>2</sub> Hx4Et	D <sub>6</sub> -DMSO CDCl <sub>3</sub>	8.25 7.28	10.26 8.75	2.85 2.64	3.57 3.80	— 2.62
3,4-hexanedione bis(4-phenylthiosemicarbazone), H <sub>2</sub> Hx4Ph	—	—	—	—	—	—
3,4-hexanedione bis(3-piperidylthiosemicarbazone), H <sub>2</sub> HxPip	D <sub>6</sub> -DMSO CDCl <sub>3</sub>	9.51 8.49	— —	2.67 2.57	3.79 —	— —
3,4-hexanedione bis(3-hexamethyleneiminylthiosemicarbazone), H <sub>2</sub> HxHexim	D <sub>6</sub> -DMSO	9.31	—	2.68	3.87	—

for 4–6 h. The precipitate was filtered off, washed with diethylether, and finally dried in a vacuum desiccator.

### 2.3. Physical measurements

Partial elemental analyses (C, H, and N) were performed at the Microanalytical Unit of Cairo University. Cobalt, nickel, and copper analyses were carried out according to the standard methods to confirm the formation of complexes. The IR were recorded, as KBr discs, on a Mattson 5000 FTIR spectrophotometer (400–4000  $\text{cm}^{-1}$ ) at Mansoura University, Egypt, and Magna 850 (200–600  $\text{cm}^{-1}$ ) at Illinois State University, Normal, USA. The electronic spectra, as Nujol mulls and DMF solution, were recorded on a UV<sub>2-100</sub> Unicam UV/Vis at Mansoura University, Egypt. The  $^1\text{H}$  NMR spectra of the ligands, in  $d_6$ -DMSO, (300 MHz), were recorded on a Varian Gemini spectrometer at Illinois State University, Normal, USA. The magnetic moment values were evaluated at room temperature ( $25 \pm 1$  °C) using a Johnson Matthey magnetic susceptibility balance at Mansoura University, Egypt. The ESR spectra of the Cu(II) complexes were recorded as solid and solution at 298 K and 77 K in 3 mm pyrex tube on a Bruker EMX spectrometer at Illinois State University, Normal, USA.

### 2.4. Molecular calculations

All calculations were carried out by HyperChem 7.51 software package (13). The molecular geometry of the Ni(II) complex is first optimized at molecular mechanics (MM+) level. Semi empirical method PM3 is then used for optimizing the full geometry of the system using Polak–Ribiere (conjugate gradient) algorithm and Unrestricted Hartree–Fock is employed keeping RMS gradient of 0.01  $\text{kcal}/\text{\AA}^{-1} \text{mol}^{-1}$ . The electronic spectrum was computed using ZINDO/S method.

## 3. Results and discussion

Co(II), Ni(II), and Cu(II) ions formed stable complexes with the investigated thiosemicarbazones. The color, molar conductance, and partial elemental analysis are listed in Table 2. The complexes are soluble in EtOH, DMF, and other solvents. Their molar conductances ( $10^{-3} \text{mol L}^{-1}$ ) in DMF were found in agreement with non-electrolytes (14).

Table 2. Color, molar conductance, and partial elemental analyses of the complexes.

Complex	Color	$\Lambda_m^a$	% Found (Calculated)		
			C	H	N
[Co(Hx4H)]	Brown	10.6	30.3 (30.1)	4.4 (4.4)	26.5 (26.3)
[Co(Hx4M)(H <sub>2</sub> O) <sub>2</sub> ]	Dark brown	6.1	31.4 (31.5)	5.5 (5.8)	22.3 (22.0)
[Co(Hx4Et)(H <sub>2</sub> O) <sub>2</sub> ]	Dark brown	7.7	34.7 (35.2)	6.1 (6.4)	20.8 (20.5)
[Co(Hx4Ph)] <sub>2</sub> H <sub>2</sub> O	Brown	8.6	47.8 (47.5)	4.2 (4.7)	18.1 (17.9)
[Co(Hxhexim)(H <sub>2</sub> O) <sub>2</sub> ]	Dark brown	13.1	46.4 (46.4)	6.9 (7.4)	16.3 (16.2)
[Ni(Hx4H)]	Greenish yellow	12.6	30.3 (30.1)	4.4 (4.4)	26.5 (26.3)
[Ni(Hx4M)]	Greenish brown	6.1	34.7 (34.8)	4.9 (5.3)	24.5 (24.4)
[Ni(Hx4Et)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	Brown	5.4	33.9 (33.7)	6.1 (6.6)	19.5 (19.6)
[Ni(Hx4Ph)]	Greenish yellow	5.6	50.9 (51.2)	4.2 (4.7)	17.6 (17.9)
[Ni(HxPip)]	Olive green	4.0	46.9 (47.7)	6.2 (6.7)	18.6 (18.5)
[Ni(Hxhexim)(H <sub>2</sub> O)]	Olive green	8.6	47.9 (48.1)	6.6 (7.2)	17.2 (16.8)
[Cu(H <sub>2</sub> Hx4M)Cl <sub>2</sub> ]	Red brown	7.1	28.8 (28.4)	4.9 (4.7)	20.4 (19.8)
[Cu(H <sub>2</sub> Hx4Et)Cl <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	Brown	3.9	28.9 (29.7)	6.4 (6.1)	17.1 (17.3)
[Cu(Hx4Ph)]	Brown	4.9	49.7 (50.1)	4.3 (4.7)	17.3 (17.7)

Note: <sup>a</sup>Molar conductance in DMF (ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>).

### 3.1. IR spectra

The IR assignments of the useful bands for elucidating the coordination sites of the ligands are included in Table 3. The introduced ligands may coordinate through two modes:

- (i) Neutral tetradentate through C=N and C=S in [Cu(H<sub>2</sub>Hx4M)Cl<sub>2</sub>] and [Cu(H<sub>2</sub>Hx4Et)Cl<sub>2</sub>]<sub>2</sub>H<sub>2</sub>O. The shifts of  $\nu(\text{C}=\text{N})$  and  $\nu(\text{N}-\text{N})$  bands are due to the participation of the azomethine groups in bonding with the appearance of a new band due to  $\nu(\text{M}-\text{N})$ . The shift of  $\nu(\text{C}=\text{S})$  to lower wavenumbers is followed by the appearance of a new band attributed to  $\nu(\text{M}-\text{S})$  (15).
- (ii) Binegative tetradentate in the rest of the complexes through C=N<sub>oxime</sub> and C-S which confirmed from the shift of  $\nu(\text{C}=\text{N})$  (16) and the thione groups are deprotonated by the presence of a band due to  $\nu(\text{C}-\text{S})$ . Strong evidence for nitrogen and sulfur coordination is the appearance of a new bands due to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{S})$ , as shown in Table 3. The 3347, 841, and 528 cm<sup>-1</sup> bands in the hydrated Co(II) complexes are attributed to  $\nu(\text{OH})$ ,  $\rho_r(\text{H}_2\text{O})$ , and  $\rho_w(\text{H}_2\text{O})$ , respectively, and confirm water of coordination (17).

### 3.2. Spectral and magnetic studies

The magnetic moments and the electronic spectral bands of the Co(II), Ni(II), and Cu(II) complexes are given in Table 4. The Co(II) complexes measured magnetic moments in the range 2.72–5.04 BM. [Co(Hx4M)(H<sub>2</sub>O)<sub>2</sub>] and [Co(Hx4ph)]<sub>2</sub>H<sub>2</sub>O have magnetic moments of 5.04 and 4.43 BM, respectively, in the range reported for octahedral and tetrahedral geometries, respectively. [Co(HxHexim)(H<sub>2</sub>O)<sub>2</sub>] has 1.02 BM which is lower than the values reported for either low-spin octahedral or square-planar complexes; the color and electronic spectral data suggest the first proposal. The lower value may be due to antiferromagnetic behavior. The value measured for [Co(Hx4Et)(H<sub>2</sub>O)<sub>2</sub>] is near the values reported for the presence of three unpaired electrons.

Most Ni(II) complexes are diamagnetic, indicative of a square-planar structure (N<sub>2</sub>S<sub>2</sub> coordination) similar to those reported earlier (10). Figure 2 is a representative example. [Ni(Hx4Et)(H<sub>2</sub>O)<sub>2</sub>] measured 2.17 BM; the value is low compared with those measured for octahedral and tetrahedral structures.

Table 3. Assignments of the IR spectral bands of the ligands and their complexes.

Compound	$\nu(\text{N}^4\text{H})$	$\nu(\text{N}^2\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{N}^*)$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
H <sub>2</sub> Hx4H	3259	3153	1597	–	799	–	–	–
H <sub>2</sub> Hx4M	3351	3186	1575	–	831	–	–	–
H <sub>2</sub> Hx4Et	3341	3159	1586	–	803	–	–	–
H <sub>2</sub> Hx4Ph	3301	3159	1586	–	800	–	–	–
H <sub>2</sub> HxPip	–	3163	1574	–	806	–	–	–
H <sub>2</sub> HxHexim	–	3185	1568	–	802	–	–	–
[Co(Hx4H)]	3312	–	1539	–	–	698	–	–
[Co(Hx4M)(H <sub>2</sub> O) <sub>2</sub> ]	3317	–	1550	1575	–	771	446	344
[Co(Hx4Et)(H <sub>2</sub> O) <sub>2</sub> ]	3176	–	1569	1586	–	745	452	363
[Co(Hx4Ph)] <sub>2</sub> H <sub>2</sub> O	3189	–	1552	1595	–	733	411	330
[Co(Hxhexim)(H <sub>2</sub> O) <sub>2</sub> ]	–	–	1554	1604	–	764	432	339
[Ni(Hx4H)]	3334	–	1569	1600	–	610	440	388
[Ni(Hx4M)]	3350	–	1542	1572	–	750	402	384
[Ni(Hx4Et)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	3328	–	1550	1574	–	740	437	352
[Ni(Hx4Ph)]	3292	–	1589	1602	–	755	431	353
[Ni(HxPip)]	–	–	1552	1569	–	743	437	351
[Ni(Hxhexim)(H <sub>2</sub> O)]	–	–	1558	1599	–	758	432	328
[Cu(Hx4H)]	3337	–	1562	1603	–	697	430	386
[Cu(H <sub>2</sub> Hx4M)Cl <sub>2</sub> ]	3322	3224	1560	–	–	811	436	381
[Cu(H <sub>2</sub> Hx4Et)Cl <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	3338	4230	1576	–	–	785	440	396
[Cu(Hx4Ph)]	3286	–	1549	1582	–	750	415	363

[Cu(H<sub>2</sub>Hx4Et)Cl<sub>2</sub>]<sub>2</sub>H<sub>2</sub>O and [Cu(Hx4H)] measured normal values; the others have lower values indicating interaction between the copper centers; the lower the value the higher the interaction.

The solution and solid spectra of the complexes are approximately the same; changes are recorded with the spectra of their ligands. The band at 22,000–26,000 cm<sup>-1</sup> in the spectra of the complexes may be due to S→M (LMCT) as those reported earlier (18).

The spectra of Co(II) complexes except [Co(Hx4Ph)]<sub>2</sub>H<sub>2</sub>O are characterized by two bands at 20,880–19,145 and 16,930–17,110 cm<sup>-1</sup> attributed to <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub>(ν<sub>2</sub>) and <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>(P)(ν<sub>3</sub>), respectively, similar to those reported for octahedral complexes (19). The ligand field parameters (*B*, β, 10*Dq*) are calculated and their values (Table 4) agree fairly with those reported for octahedral Co(II) complexes. It is worthy to note that the values of 10*Dq* may be taken as a good criteria for investigating the strength of the ligands (H<sub>2</sub>Hx4Et > H<sub>2</sub>HxHexim > H<sub>2</sub>Hx4M) based on the crystal field splitting energy. Considerable reduction in the *B* values from 971 in the free metal ion to 791–947 cm<sup>-1</sup> in the complexes and β from unity to 0.81 indicates to some extent covalent character of L–M bonds (20). [Co(Hx4Ph)]<sub>2</sub>H<sub>2</sub>O showed electronic spectral band at 17,710 cm<sup>-1</sup> due to <sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>1</sub>(F) in a tetrahedral structure (21); its ligand field parameters are *B* = 429 cm<sup>-1</sup>, β = 0.44, and 10*Dq* = 5884 cm<sup>-1</sup>. The value of β indicates a strong covalent bond. The ν<sub>1</sub>(<sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>2</sub>) is not observed in the instrument range and equals 10*Dq* value (5884 cm<sup>-1</sup>). The ν<sub>2</sub> is calculated from the relation:

$$10Dq = \left( \frac{\nu_2 + \nu_3}{3} \right) - 5B.$$

The value 6377 cm<sup>-1</sup> is in the range reported for the ν<sub>1</sub> transition in the proposed structure.

The electronic spectra of Cu(II) complexes gave one band at 18,305–18,845 cm<sup>-1</sup> assigned to <sup>2</sup>E<sub>g</sub> ← <sup>2</sup>T<sub>2g</sub>. The broadness of the band may be due to Jahn-Teller effect, which enhances the distortion in octahedral geometry (22). The spectrum of [Cu(Hx4Ph)] showed two bands at 18,965 and 16,570 cm<sup>-1</sup>, in solid state, corresponding to <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>E<sub>g</sub> and <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub> in a square-planar geometry (23). In DMF solution, one band is observed and is shifted to higher energy, suggesting a weak interaction with the solvent.

Table 4. Magnetic moments and electronic spectral bands of the compounds.

Compound	$\mu_{\text{eff}}$ (BM)	State	Intraligand and charge transfer ( $\text{cm}^{-1}$ )	d-d transition ( $\text{cm}^{-1}$ )	Ligand field parameters $B; \beta; 10Dq$
H <sub>2</sub> Hx4H		Solid DMF	28,660; 23,090 27,800; 28,90		
H <sub>2</sub> Hx4M		Solid DMF	38,060; 26,140; 31,230; 29,740; 28,120 34,520; 31,290; 29,860; 28,900		
H <sub>2</sub> Hx4Et		Solid DMF	36,020; 32,370; 31,110; 29,620; 28,060 34,400; 30,995; 29,740; 28,780		
H <sub>2</sub> Hx4Ph		Solid DMF	37,040; 35,420; 31,590; 27,400 34,760; 29,260; 28,420		
H <sub>2</sub> HxPip		Solid DMF	39,310; 32,340; 28,840; 24,110 33,870; 29,080; 23,570; 20,580		
H <sub>2</sub> HxHexim		Solid DMF	35,180; 28,720; 23,270; 20,820 34,770; 29,720; 23,040; 20,460		
[Co(Hx4H)]	2.99	Solid DMF	37,940; 32,910; 24,230 34,705;	19,320 18,485; 16,630; 15,670	
[Co(Hx4M)(H <sub>2</sub> O) <sub>2</sub> ]	5.04	Solid DMF	26,205 34,525; 27,225	20,880; 16,930 21,655; 11,740	947; 0.97; 8966
[Co(Hx4Et)(H <sub>2</sub> O) <sub>2</sub> ]	3.11	Solid DMF	38,475; 26,745 34,405; 30,575; 26,865	17,650; 11,120 19,145; 17,770	791; 0.81; 9497
[Co(Hx4Ph)] <sub>2</sub> H <sub>2</sub> O	4.43	Solid DMF	36,980; 24,110 34,405; 33,450; 24,890	17,710; 11,060 17,590; 11,530	429; 0.44; 5884

[Co(Hxhexim)(H <sub>2</sub> O) <sub>2</sub> ]	2.72	Solid DMF	36,860; 25,550 34,465; 31,890; 25,910	19,740; 17,110 20,340; 17,290	846; 0.87; 9311 905; 0.93; 9052
[Ni(Hx4H)]	0.00	Solid DMF	33,330; 30,395; 25,010	24,290; 16,690; 14,830	
[Ni(Hx4M)] <sup>a</sup>	0.00	Solid DMF	33,570 34,650; 30,870	20,460; 16,690; 14,120 23,690; 16,570; 14,890	
[Ni(Hx4Et)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	2.17	Solid DMF	29,500; 34,760; 30,100;	24,710; 18,540; 15,190 24,470; 16,510; 14,830	940; 0.90; 7990 086; 0.92; 7395
[Ni(Hx4Ph)]	0.00	Solid DMF	35,780; 31,830; 34,650; 29,680;	21,360; 17,400; 14,060 23,320; 16,990; 14,770	
[Ni(HxPip)]	0.00	Solid DMF	36,650; 29,560; 34,110; 32,610;	22,200; 16,870; 14,740 21,600; 14,240; 13,520	
[Ni(Hxhexim)(H <sub>2</sub> O)]	0.00	Solid DMF	29,670; 23,510 34,770; 28,420	20,040; 14,480 22,260; 14,650	
[Cu(Hx4H)]	1.69	Solid DMF	26,205; 20,580 28,900; 20,580	15,550 18,545	
[Cu(H <sub>2</sub> Hx4M)Cl <sub>2</sub> ]	1.53	Solid DMF	30,815; 27,465; 20,400 34,765; 31,830; 28,130; 20,700	18,845 18,905	
[Cu(H <sub>2</sub> Hx4Et)Cl <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	1.97	Solid DMF	31,235; 27,525; 24,470; 20,040 34,825; 31,710; 28,180; 20,580	18,965 19,845	
[Cu(Hx4Ph)]	1.47	Solid DMF	35,305; 30,695; 24,110 33,570; 31,595; 25,490; 20,460	18,305; 16,570 18,425	

Note: <sup>a</sup>The values calculated theoretically are: 15,129, 16,393, 25,252, 28,818, and 33,898 cm<sup>-1</sup>.



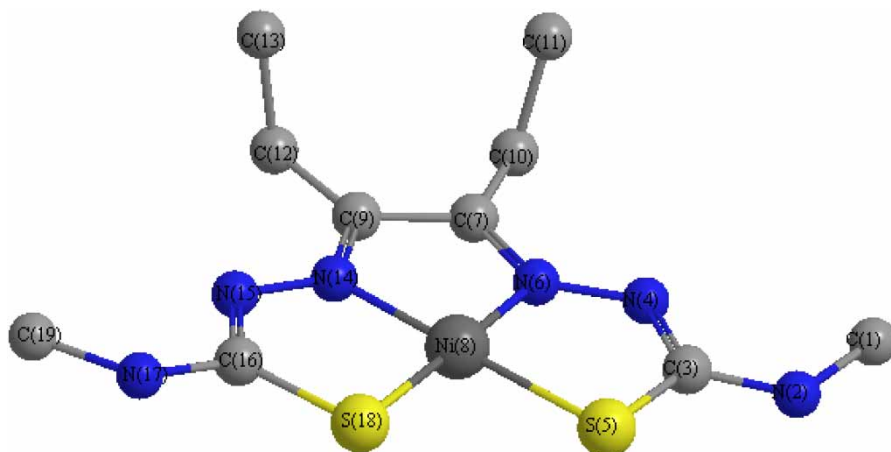


Figure 2. Optimized geometry of [Ni(Hx4M)].

In the spectra of solid Ni(II) complexes, except [Ni(Hx4Et)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O, there are two main bands at 22,200–20,460 and 14,740–14,060 cm<sup>-1</sup> assignable to the d–d transitions. In the DMF solutions, the first band is observed at high energy (23,690–22,260 cm<sup>-1</sup>), indicating strong interaction with DMF. In [Ni(Hx4Et)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O, the spectra are different where three bands observed at 24,710, 18,540, and 15,190 are attributed to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> (P) (ν<sub>3</sub>) and <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> (ν<sub>2</sub>) transitions, in an octahedral structure. The ligand field parameters were found in the ranges reported for the suggested structure. The bands in DMF solution are similar but lower than those observed in solid.

The bond lengths and bond angles of the Ni(II) complex are presented in Table 5. Also, the dipole moment (2.543 D), highest occupied molecular orbital (HOMO) (−7.9295 eV), lowest unoccupied molecular orbital (LUMO) (−1.1191 eV), and the heat of formation (−78.3218 Kcal/mol) are calculated. Figure 2 represents the optimized geometry drawn for the lowest energy form.

Table 5. The bond lengths and the bond angles calculated for the Ni(II) complex.

Bond length	(Å)	Bond angle	(°)
Ni(8)–S(18)	2.20257	S(5)–Ni(8)–N(6)	91.713
Ni(8)–S(5)	2.20216	N(6)–Ni(8)–N(14)	87.509
Ni(8)–N(6)	1.83133	N(14)–Ni(8)–S(18)	91.625
Ni(8)–N(14)	1.83066	S(5)–Ni(8)–S(18)	89.153
S(18)–C(16)	1.76028	S(5)–Ni(8)–N(14)	179.209
C(16)–N(15)	1.37141	S(18)–Ni(8)–N(6)	179.132
N(15)–N(14)	1.34697	S(18)–C(16)–N(15)	123.862
N(14)–C(9)	1.34045	C(16)–N(15)–N(14)	113.740
C(9)–C(7)	1.46783	N(15)–N(14)–Ni(8)	120.079
C(7)–N(6)	1.34073	Ni(8)–S(18)–C(16)	90.676
N(6)–N(4)	1.34645	Ni(8)–S(5)–C(3)	90.6082
N(4)–C(3)	1.37209	S(5)–C(3)–N(4)	123.948
C(3)–S(5)	1.75952	C(3)–N(4)–N(6)	113.751
		N(4)–N(6)–Ni(8)	119.964
		Ni(8)–N(6)–C(7)	112.856
		N(6)–C(7)–C(9)	113.347
		C(7)–C(9)–N(14)	113.446
		Ni(8)–N(14)–C(9)	112.83

Table 6. ESR spectral data of the Cu(II) complexes.

Complex	Phase state	$g_{1or} (g_{//})$	$g_2$	$g_3 (g_{\perp})$	$A_o$ (G)	$A_N$ (G)	$g_o$	$G$
[Cu(Hx4H)]	Solid RT	2.105	2.041	2.029			2.058	3.620
	Solid 77 K	2.102	2.040	2.028			2.057	3.643
	Solid RT	2.126	2.037	–	–		2.066	
[Cu(H <sub>2</sub> Hx4M)Cl <sub>2</sub> ]	Solid 77 K	2.127	2.039	2.031	–		2.066	4.096
	Solution RT				92	16.7	2.062	
	Solid RT	2.112	2.031	–	110		2.058	
[Cu(H <sub>2</sub> Hx4Et)Cl <sub>2</sub> ]2H <sub>2</sub> O	Solid 77 K	2.111	2.030	2.028			2.056	3.964
	Solution RT				92.5	15.2	2.062	
	Solid RT	2.111	2.034	2.029			2.058	3.827
[Cu(Hx4Ph)]	Solid RT						2.058	
	Solid 77 K						2.032	

### 3.3. ESR spectra

To obtain further information about the stereochemistry of the complexes, ESR spectra were recorded and their spin Hamiltonian parameters were calculated (Table 6). The room temperature solid state and 77 K have ESR spectra quite similar to the copper complexes and exhibit an axially symmetric  $g$ -tensor parameters with  $g_{\parallel} > g_{\perp} > 2.0023$ , indicating that the copper site has a  $d_{x^2-y^2}$  ground state (24, 25). In DMF solution, the complexes gave four resolved lines of isotropic spectra with  $g_o = 2.062$  and  $A_o$  ca. 90 G (Table 4). On the two highest field lines there was nitrogen superhyperfine coupling ( $A_N$  ca 16 G) indicating nitrogen coordination.

In axial symmetry,  $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ , where  $G$  is the exchange interaction parameter. The calculated  $G$  values (Table 4) of the Cu(II) complexes are lower than 4, suggesting copper–copper exchange interactions, while in [Cu(Hx4M)(H<sub>2</sub>O)<sub>2</sub>] it is 4.096, suggesting the absence of exchange coupling between copper(II) centers (26). The band corresponding to the forbidden magnetic dipolar transition is not observed at half-field (ca. 1600 G,  $g = 4.0$ ), indicating mononuclear complexes (27).

## References

- (1) Petering, H.B.; Buskirk, H.H.; Underwood, G.E. *Cancer Res.* **1964**, *24*, 367–372; Van Giessen, G.H.; Crim, J.A.; Petering, D.H. *J. Nat. Cancer Inst.* **1973**, *51*, 139–146.
- (2) Sharma, V.; Sharma, V.; Bohra, R.; Drake, J.E.; Hursthouse, M.B.; Light, M.E. *Inorg. Chim. Acta* **2007**, *360*, 2009–2015.
- (3) Sevagapandian, S.; Rajagopal, G.; Nehru, K.; Athappan, P. *Transition Met. Chem.* **2000**, *25*, 388–393.
- (4) Llanguri, R.; Morris, J.J.; Stanley, W.C.; Bell-Loncella, E.T.; Turner, M.; Boyko, W.J.; Bessel, C.A. *Inorg. Chim. Acta* **2001**, *315*, 53–65.
- (5) Thompson, L.R.; Jeanette, D.; Russell, B.P.; Hitchings, H.G. *Proc. Soc. Exp. Biol. Med.* **1953**, *84*, 496.
- (6) Perrin, D.D. *Topics in Current Chemistry*; Springer Verlag: New York, 1976; p. 181–217.
- (7) El-Ayaan, U.; Abu El-Reash, G.; Kenawy, I.M. *Synth. React. Inorg. Met. Org. Chem.* **2003**, *33*, 327–342.
- (8) Sorensen, E.M.B. *Metal Poisoning in Fish*; CRC Press: Boston, MA, USA, 1991; p. 235.
- (9) Khalifa, M.E.; Akl, M.A.; Ghazy, S.E. *Chem. Pharm. Bull.* **2001**, *49*, 664–701.
- (10) West, D.X.; Ives, J.S.; Bain, G.A.; Liberta, A.E.; Martinez, J.V.; Ebert, K.H.; Ortaega, S.H. *Polyhedron* **1997**, *16*, 1895–1899.
- (11) Gasinski, J.P.; Bianchani, J.R.; Cueva, J.C.; El-Saied, F.A.; El-Asmy, A.A.; West, D.X. *Z. Anorg. Allg. Chem.* **2003**, *629*, 202–206.
- (12) Yadav, P.N.; Demertzis, M.A.; Kovala-Demertzi, D.; Skoulika, S.; West, D.X. *Inorg. Chim. Acta* **2003**, *349*, 30–34.
- (13) HyperChem 7. 51 Version, Hypercube Inc., FL, USA, 2003.
- (14) Bindu, P.; Kurup, M.R.P. *Ind. J. Chem.* **1997**, *36A*, 1094–1100.
- (15) Souza, P.; Sanchez-Kaiser, F.; Moguer, J.R.; Arquero, A. *Transition Met. Chem.* **1987**, *12*, 128.
- (16) West, D.X.; Dietrich, S.L.; Thientanavanich, I.; Brown, C.A.; Liberta, A.E. *Transition Met. Chem.* **1994**, *19*, 195–199.
- (17) El-Asmy, A.A.; Hafez, M.A.; Saad, E.M.; Taha, F.T. *Transition Met. Chem.* **1994**, *19*, 603–605.
- (18) El-Asmy, A.A.; Khalifa, M.E.; Hassanian, M.M.; *Synth. React. Inorg. Met. Org. Chem.* **2001**, *31*, 1787–1801.
- (19) Aly, A.A.M.; El-Meligy, M.S.; Zidan, A.S.; El-Shabasy, M. *An. Quim.* **1990**, *86*, 19.
- (20) El-Asmy, A.A.; Shaibi, Y.M.; Shedaiwa, I.M.; Khattab, M.A. *Synth. React. Inorg. Met. Org. Chem.* **1990**, *20*, 461–481.

- (21) El-Asmy, A.A.; El-Sonbati, A.Z.; Ba-Issa, A.A. *Transition Met. Chem.* **1990**, *15*, 222–225.
- (22) Mostafa, S.; Bekheit, M.M.; El-Agez, M.M. *Synth. React. Inorg. Met. Org. Chem.* **2000**, *30*, 2029–2049.
- (23) Tarafder, H.T.M.; Chew, K.; Crouse, A.K.; Ali, M.A.; Yamin, M.B.; Fun, K.H. *Polyhedron* **2002**, *21*, 2683–2690.
- (24) Speie, G.; Csihony, J.; Whalen, A.M.; Pie-pont, C.G. *Inorg. Chem.* **1996**, *35*, 3519–3523.
- (25) Mesa, J.L.; Pizarro, J.L.; Arriortua, M.I. *Cryst. Res. Technol.* **1998**, *33*, 489–495.
- (26) Kasumo, V.T. *Spectrochim. Acta* **2001**, *57A*, 1649–1662.
- (27) Wellman, J.A.; Hulsbergen, F.B. *J. Inorg. Nucl. Chem.* **1978**, *40*, 143–149; Sagakuchi, U.; Addison, A.W. *J. Chem. Soc. Dalton Trans.* **1979**, 660.