

# Synthesis and Characteristics of *N*-(Glyoxyldioxime)-*N'*-(2-hydroxybenzylidene)-1,4-diaminonaphthalene and Its Metal Complexes<sup>1</sup>

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**Abstract**—A new vic-dioxime, *N*-(glyoxyldioxime)-*N'*-(2-hydroxybenzylidene)-1,4-diaminonaphthalene, was synthesized proceeding from naphthalene. Its complexes of nickel, copper and cobalt were prepared. The vic-dioxime and its complexes were characterized by FT-IR, UV, <sup>1</sup>H NMR, mass spectrometry, elemental analysis, DTA/TG analysis techniques and conductometric measurements.

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Vicinal dioximes and their complexes constitute an important class of compounds having versatile reactivities. The exceptional stability and unique electronic properties of the vic-dioximes complexes can be attributed to their planar structure which is stabilized by hydrogen bonds [1]. These compounds were tested as liquid crystal, gas sensors, and inhibitors for chemical warfare agents [2–4]. Numerous oximes and Schiff bases and their metal complexes have been investigated [5, 6]. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure [7]. Acyclic ligands containing nitrogen, oxygen and sulphur donor atoms in their structures can act as effective chelating agents for transition and nontransition metal ions [8]. In this study, amphi-choloroglyoxime, anti-choloroglyoxime, 4-nitro-1-naphthylamine and FeO(OH) were prepared by published procedures [9–14]. A new vic-dioxime, *N*-(glyoxyldioxime)-*N'*-(2-hydroxybenzylidene)-1,4-diaminonaphthalene H<sub>2</sub>L (**III**) was synthesized using

naphthalene as starting material, and its Ni(II), Co(II), and Cu(II) complexes were prepared.

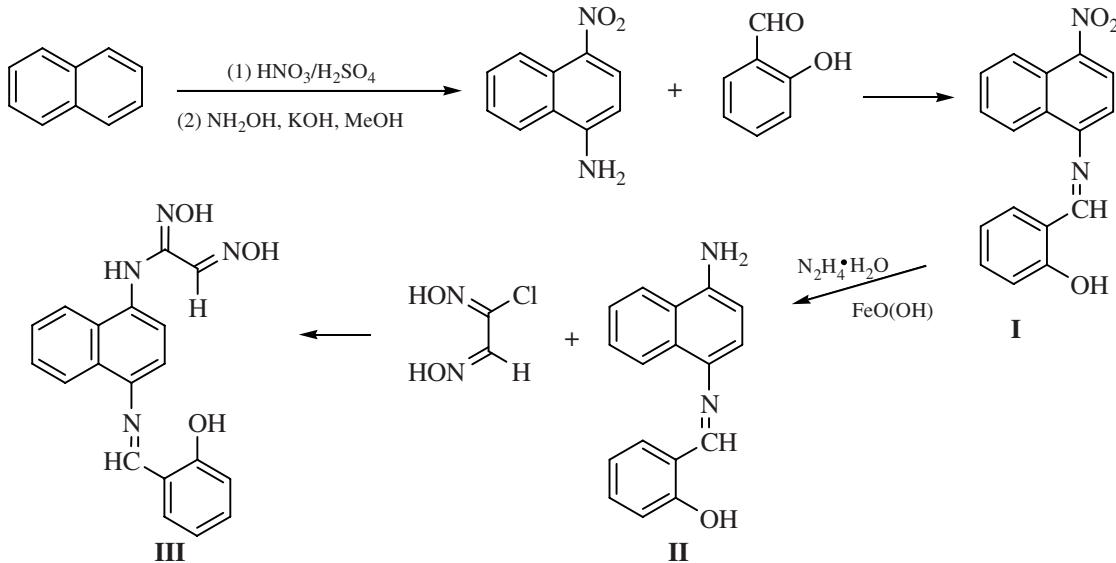
In order to understand the structure of the new oxime and free Schiff base ligands, <sup>1</sup>H NMR spectra were employed. The assignments of the chemical shifts in the <sup>1</sup>H NMR spectra are listed in Table 1.

The singlet (2H) observed at 12 ppm was assigned to the =NOH proton of H<sub>2</sub>L. The singlet (1H) observed at 8.9 ppm was assigned to the protons of CH and to the proton of the aldoxime group. The multiplet (10H) observed at 8.4–6.7 ppm corresponded to the aromatic ring protons of the H<sub>2</sub>L. Furthermore, the singlets at 15.1 and 3.8 ppm were attributed to the protons of phenolic OH and NH groups in the ligand H<sub>2</sub>L, respectively.

The assignment of the most characteristic IR bands is given in Table 2.

The vibrations of the sterically hindered oxime groups of the free Schiff base ligand [H<sub>2</sub>L] are observed at 3400–3500 cm<sup>-1</sup> [15, 16]. When the spectra of the complexes are compared with those of the uncomplexed imine oxime ligand the v(C=N) band

<sup>1</sup>The text was submitted by authors in English.



is shifted to lower frequency [17, 18]. This indicated that the imine nitrogen was coordinated to the metal ion. The absorption bands in the region 525–560 cm<sup>-1</sup> and 400–420 cm<sup>-1</sup> in the spectra of complexes belong to v(M–N) [17] and v(M–O) [18].

The analytical data for the ligands and their metal complexes are listed in Table 3.

The composition of Ni and Co complexes corresponds to a general formula [M<sub>3</sub>(H<sub>2</sub>L)<sub>2</sub>]. The Schiff base ligand is soluble in common organic solvents. All

complexes are soluble in DMF, DMSO and insoluble in the other organic solvents. The electronic absorption spectral data of the free ligand and their complexes are given in Table 4.

In the spectra of the Schiff base ligand bands at 231–267 nm are attributed to the benzene π–π\* transitions [19–21]. The bands at 332–431 nm are assigned to the imine π–π\* transition. Compared to the free ligand, the imine π–π\* transitions of the complexes were shifted to some extent, because the imine

**Table 1.** <sup>1</sup>H NMR spectra of the Schiff base ligands

Comp. no.	δ, ppm	Assignment
I	8.9 s (1H) 8.4 d (1H), 8.2 d (1H), 8.1 d (1H), 8.0 d (1H), 7.7 d (1H), 7.5 d.d (1H), 7.3 d.d (1H), 7.2 d.d (1H), 6.7 d (1H) 15.1 br (1H)	-CH=N- Aromatic ring (H) Phenolic OH
II	8.9 s (1H) 8.4 d (1H), 8.2 d (1H), 8.1 d (1H), 8.0 d (1H), 7.7 d (1H), 7.5 d.d (1H), 7.3 d.d (1H), 7.2 d.d (1H), 6.7 d (1H) 15.1 br (1H) 4.2 s (2H)	-CH=N- Aromatic ring (H) Phenolic OH NH <sub>2</sub>
III	12 s (2H) 8.9 s (1H) 8.4 d (1H), 8.2 d (1H), 8.1 d (1H), 8.0 d (1H), 7.7 d (1H), 7.5 d.d (1H), 7.3 d.d (1H), 7.2 d.d (1H), 6.7 d (1H) 8.1 s (1H) 15.1 br (1H) 3.8 s (1H)	=NOH -CH=N- Aromatic ring (H) -CH=N- Phenolic OH NH

**Table 2.** Infrared spectral data of the free ligands and their complexes

Compound	O–H	C=N	N–H	C–H (Ar)	C=C	C–N	N–O	M–N	M–O
<b>I</b>	3360	1642	—	3070	1585	1155	985	—	—
<b>II</b>	3350	1645	3330	3065	1585	1150	—	—	—
<b>III</b>	3400	1640	3320	3070	1590	1150	970	—	—
Ni <sub>3</sub> [H <sub>2</sub> L] <sub>2</sub> ·4H <sub>2</sub> O	3300–3500 (H <sub>2</sub> O)	1650	—	3060	1590	1165	950	525	400
Co <sub>3</sub> [H <sub>2</sub> L] <sub>2</sub> ·10H <sub>2</sub> O	3300–3500 (H <sub>2</sub> O)	1645	—	3065	1585	1160	960	560	410
Cu[H <sub>2</sub> L] <sub>2</sub>	3350	1645	3290	3060	1585	1150	960	550	420

**Table 3.** Some analytical data and physical properties of the Schiff base ligands and complexes

Compound	Formula	Molecular weight	mp, °C	Yield, %	Found (calculated), %		
					C	H	N
<b>I</b>	C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	292.3	155	61	69.48 (69.86)	4.03 (4.11)	9.93 (9.59)
<b>II</b>	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O	262.3	120	92	77.80 (77.86)	5.44 (5.34)	10.39 (10.69)
<b>III</b>	C <sub>19</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub>	348.3	160	57	65.18 (65.52)	4.25 (4.60)	15.95 (16.09)
Ni <sub>3</sub> [H <sub>2</sub> L] <sub>2</sub> ·4H <sub>2</sub> O	C <sub>42</sub> H <sub>42</sub> N <sub>8</sub> Ni <sub>3</sub> O <sub>14</sub>	1058.9	230 decomp.	77	47.58 (47.64)	3.97 (4.00)	10.54 (10.58)
Co <sub>3</sub> [H <sub>2</sub> L] <sub>2</sub> ·10H <sub>2</sub> O	C <sub>42</sub> H <sub>54</sub> Co <sub>3</sub> N <sub>8</sub> O <sub>20</sub>	1167.7	>300	71	43.14 (43.20)	4.62 (4.66)	9.55 (9.60)
Cu[H <sub>2</sub> L] <sub>2</sub>	C <sub>38</sub> H <sub>30</sub> CuN <sub>8</sub> O <sub>6</sub>	758.2	195	55	60.07 (60.19)	3.96 (3.99)	14.72 (14.78)

nitrogen was involved in coordination with the metal ion. The molar conductance values of the Ni(II), Co(II), and Cu(II) complexes are in the range 5 to 32 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> in 10<sup>-3</sup> M DMF solutions indicating the non-electrolytic nature of these compounds [18].

The thermogravimetric analysis was carried out in the temperature range 0–1100°C. The samples were placed in platinum crucibles and α-Al<sub>2</sub>O<sub>3</sub> was used as the reference material. Heating was performed under N<sub>2</sub> atmosphere at a flow rate of 60 ml min<sup>-1</sup>. The sample size was limited to 2–8 mg, and the heating rate was adjusted to 10°C/min in all cases.

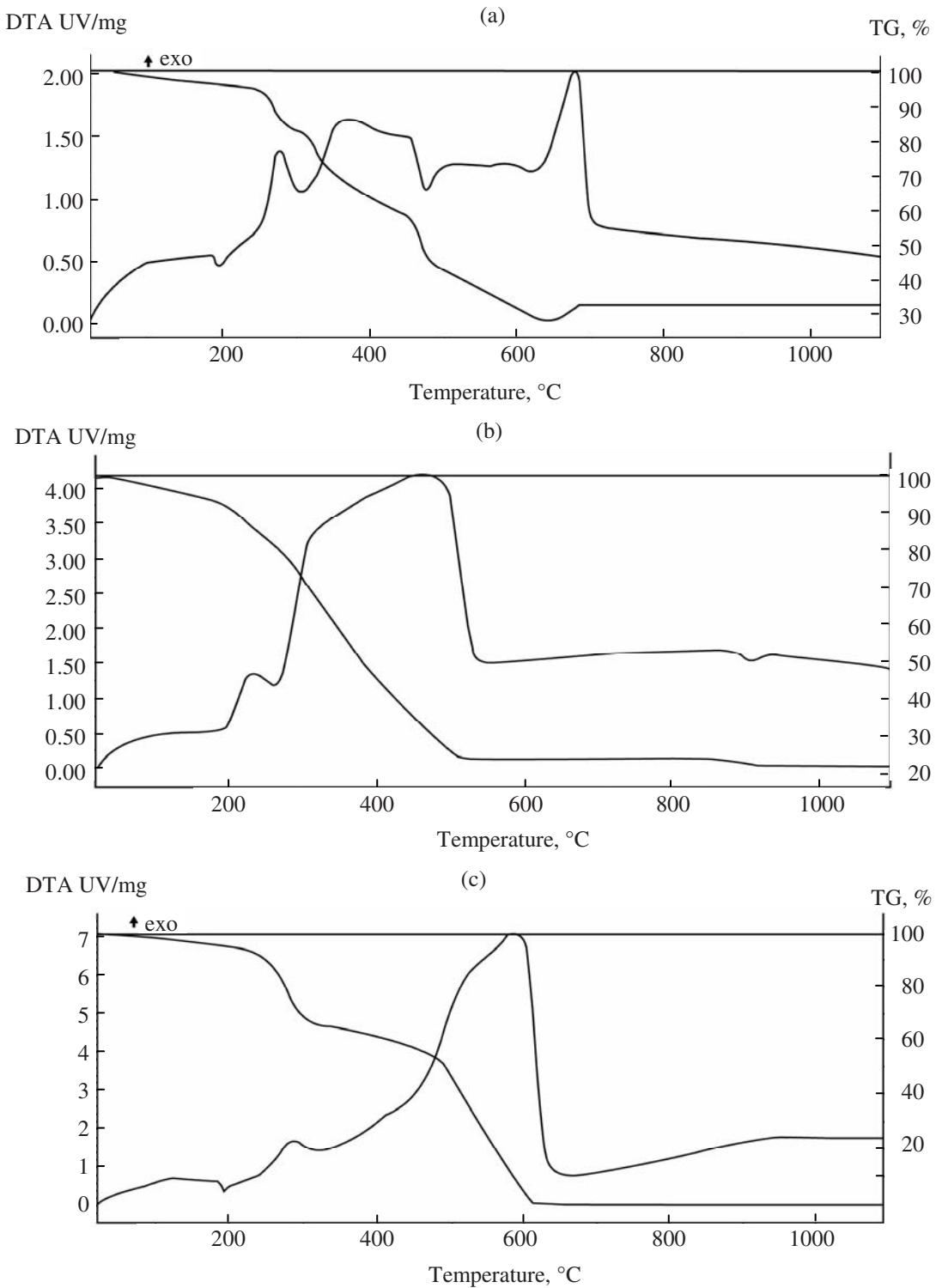
It is noted from the TG analysis that the Ni(II) complex of H<sub>2</sub>L loses 92.13% of its original mass between 198 and 650°C and the 7.87% residue is a greenish-black solid. The DTA/TG data for the Ni complex are shown in Fig. 1a. The sample decomposes in four stages. The first decomposition occurs between 198 and 250°C with 11.21% mass loss, the second decomposition occurs between 250 and 300°C with 24.33% mass loss, the third decomposition occurs between 300 and 450°C with 54.08% mass loss, and the fourth decomposition stage between 425 and 640°C, with 72.44% mass loss.

The theoretical mass of the remaining NiO is 7.12% in agreement with 7.87% from the TG studies. The theoretical mass losses in the second, third, and fourth decomposition stages are 24.19, 54.33, and 72.24% respectively in agreement with the experimental values 24.33, 54.08, and 72.44.

The DTA/TG diagrams of the Co(II) complex are shown in Fig. 1b. It was found from TG analysis that the sample starts losing mass at 200°C and ends at 900°C after losing 93.6% of its mass and becoming a black-brown residue which correspond to 6.40% of the total mass. The examination of TG curve showed that the sample decomposes in three stages. The sample loses 10.40% of mass between 100 and 200°C, 25.15% of the mass between 200 and 270°C, and 94.88%

**Table 4.** Magnetic moments and electronic spectral data of the Schiff base ligand and its metal complexes

Compound	μ <sub>eff</sub>	λ <sub>max</sub> , nm
<b>III</b>	—	430, 399, 359, 335, 322, 267, 211
Ni <sub>3</sub> [H <sub>2</sub> L] <sub>2</sub> ·4H <sub>2</sub> O	2.51	430, 332, 266, 251, 232
Co <sub>3</sub> [H <sub>2</sub> L] <sub>2</sub> ·10H <sub>2</sub> O	3.62	430, 335, 265, 251, 231
Cu[H <sub>2</sub> L] <sub>2</sub>	1.69	651, 502, 431, 401, 321, 247



**Fig. 1.** DTA/TG diagrams of  $\text{H}_2\text{L}$  with (a) Ni(II), (b) Co(II), (c) Cu(II).

between 270 and 900°C. The TG analysis showed that the Co(II) complex yields in pyrolysis a solid product of mass 6.40% corresponding to the theoretical mass of 6.42% for CoO. The Co(II) complex decomposition in three stages predicts theoretical losses of 10.16, 25.60, and 94.91% of its mass during pyrolysis, respectively in good agreement with the mass losses derived from TG curve: 10.40, 25.15, and 94.88%. The TG studies on the Cu(II) complex of H<sub>2</sub>L showed that the initial mass loss occurred at 195°C. Decomposition ends with a total mass loss of 90.80% at 650°C leaving a black solid residue corresponding to a mass of 9.80%. DTA/TG diagrams of the Cu(II) complex are shown in Fig. 1c. It was observed from the TG curve that the sample decomposes in three stages and it loses 4.52%, 29.03 and 67.20% of its mass in each stage, respectively. The temperatures ranges of these decomposition are 195–240, 240–330, and 330–615°C, respectively. The theoretical mass losses of each stage are as follows; 4.48, 28.26, 67.26% where the corresponding experimental percent mass losses are 4.52, 29.08, 67.20%, respectively. It was concluded from TG studies that all the Ni(II), Co(II) and Cu(II) complexes examined were converted on pyrolysis to the corresponding oxides [22].

## EXPERIMENTAL

Elemental analyses for carbon, hydrogen, and nitrogen were obtained on a Carlo Erba 1106 analyser. Jasco FT/IR-300E spectrometer was used for characterization of compounds by IR spectra. The electronic spectra in the 200–800 nm range were recorded in DMF on a spectrophotometer Shimadzu UV-160A. Conductivities were measured in DMF at 24°C using a conductivity meter LF330/SET. Magnetic moments were measured by the Gouy method using Hg[Co(SCN)<sub>4</sub>] as calibrant. <sup>1</sup>H NMR spectrum of the ligand H<sub>2</sub>L was recorded on a Bruker Avance-500 NMR instrument. DTA/TG spectra of the complexes were recorded by A Setaram Setys Evolution TGA-DTA/DSC 1750 thermal analysis system. Chemicals used in the study were purchased from Sigma-Aldrich, and all of them were purified by published procedures [23].

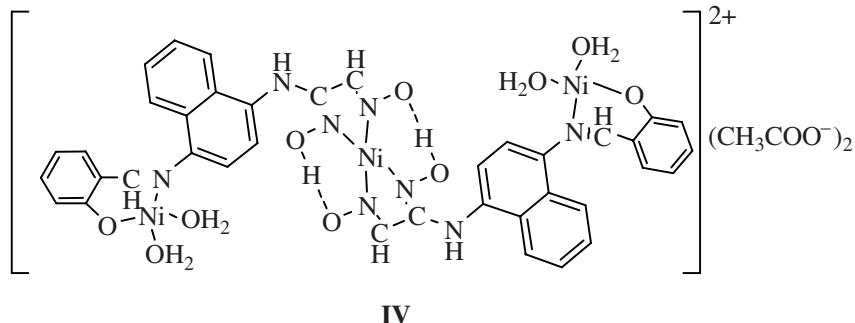
**Synthesis of 2-[(4-nitronaphthalen-1-ylimino)methyl]phenol (**I**).** 4-Nitro-1-naphthylamine (5.64 g, 0.03 mol) dissolved in anhydrous ethanol (50 ml) was added with constant stirring to a solution of salicylaldehyde (3.66 g, 0.03 mol) in anhydrous ethanol. The mixture was stirred with a magnet stirrer

and refluxed for 24 h. After cooling, the resulting precipitate was filtered off, recrystallized from anhydrous ethanol, washed several times with diethyl ether, and dried over calcium chloride under a vacuum. Yield: 61%, mp 155°C, in the FAB-MS *m/z*: 291.8 (*M*<sup>+</sup>).

**Synthesis of 2-[(4-aminonaphthalen-1-ylimino)methyl]phenol (**II**).** For 0.5 h, 0.5 g of FeO(OH) was activated in water as catalyst and then it was added to the solution of **I** (5.35 g, 0.018 mol in 130 ml of anhydrous ethanol). Into the mixture a solution of hydrazinium hydroxide (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 1.37 g in anhydrous ethanol) was added dropwise in 5 min and refluxed for 5 h. Catalyst was filtered off after cooling the reaction mixture to room temperature. Excess ethanol was removed under a vacuum to give yellow solid residue. The product was recrystallized from anhydrous ethanol. Yield: 92%, mp 120°C, in the FAB-MS *m/z*: 262.7 (*M*<sup>+</sup>).

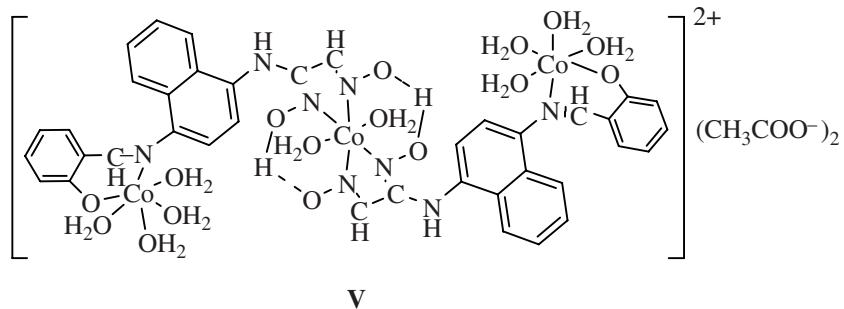
**Synthesis of *N*-(glyoxyldioxime)-*N'*-(2-hydroxybenzylidene)-1,4-diaminonaphthalene (**III**, H<sub>2</sub>L).** A water solution of NaHCO<sub>3</sub> (0.84 g, 10 mmol) was added to a solution of **II** (1.32 g, 5 mmol in 40 ml of anhydrous ethanol), then a solution of anti-chloroglyoxime (0.613 g, 5 mmol in 30 ml of anhydrous ethanol) synthesized by the method described previously was added dropwise to the mixture at room temperature within 2 h. The mixture heated on a water bath at 60–70°C was stirred for 5 h more. The yellow mixture was filtered and excess of ethanol was removed by evaporation on a rotary evaporator. The product was precipitated by the addition of diethyl ether. The product was filtered off, washed with diethyl ether several times, and dried under a vacuum for 24 h. Yield: 57%, mp: 160°C, in the FAB-MS *m/z*: 347.9 (*M*<sup>+</sup>).

**Synthesis of Ni<sub>3</sub>(H<sub>2</sub>L)<sub>2</sub>·4H<sub>2</sub>O complex (**IV**).** A solution of 3 mmol of the metal salt [Ni(CH<sub>3</sub>COO)<sub>2</sub>·6H<sub>2</sub>O, 0.357 g] in 20 ml of distilled water was added to the solution of the ligand **III** (2 mmol, 0.696 g) in 20 ml of ethanol. The pH of the mixture was adjusted to 4.5–5.0 with the addition of 0.100 N NaOH solution. In order to complete the precipitation, the mixture was kept on a water bath at 25°C for 2 h. The complex formed was filtered off, washed with water, diethyl ether, and cold ethanol, then dried in a vacuum at 70°C. Yield: 77%, mp 230°C (decomposition point), in the FAB-MS *m/z*: 1058.1 (*M*<sup>+</sup>).



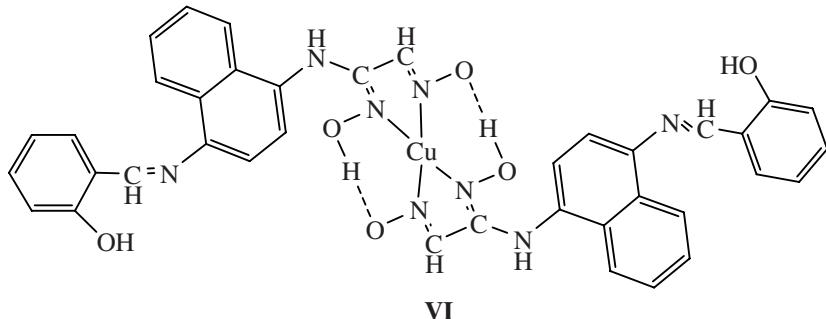
**Synthesis of  $\text{Co}_3(\text{H}_2\text{L})_2 \cdot 10\text{H}_2\text{O}$  complex (V).** A solution of 3 mmol of the metal salt  $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , 0.747 g] in 20 ml of distilled water was added to the solution of the ligand ( $\text{H}_2\text{L}$ , 2 mmol, 0.696g) in 20 ml of ethanol. The pH of the mixture was adjusted to 4.5–5.0 with the addition of 0.100 N NaOH solution. In

order to complete the precipitation the mixture was kept on a water bath at 25°C for 2 h. The complex formed was filtered off, washed with water, diethyl-ether, and cold ethanol, then dried under a vacuum at 70°C. Yield: 71%, mp >300°C, in the FAB-MS  $m/z$ : 1167.2 ( $M^+$ ).



**Synthesis of the  $\text{Cu}(\text{H}_2\text{L})_2$  complex (VI).** A solution of 1 mmol of the metal salt  $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , 0.199 g] in 20 ml of distilled water was added to the solution of the ligand ( $\text{H}_2\text{L}$ , 2 mmol, 0.696g) in 20 ml of ethanol. The pH of the mixture was adjusted to 4.5–5.0 with the addition of 0.100 N NaOH solu-

tion. To complete the precipitation the mixture was kept on a water bath at 25°C for 2 h. The complex formed was filtered off, washed with water, diethylether, and cold ethanol, then dried in a vacuum at 70°C. Yield: 55%, mp 195°C, in the FAB-MS  $m/z$ : 757.2 ( $M^+$ ).



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