

Synthesis of a Imine *vic*-Dioxime Ligand and Its Ni(II), Co(II), Cu(II) Complexes

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A novel imine *vic*-dioxime compound and its transition metal complexes were synthesized. The compound, N'-hydroxy-2-(hydroxyimino)-N-(4-(2,4,6-trihydroxybenzylideneamino)naphthalen-1-yl)acetimidamide (H₂L), has been derived from naphthalene as an imine oxime ligand. The ligand and their complexes were characterized FT-IR, UV, ¹H NMR, ¹³C NMR, MS, elemental analysis and conductometric measurements.

Key Words: Transition metal(II) complexes, Imines, *vic*-Dioximes, Conductometric measurements.

INTRODUCTION

The coordination chemistry of *vic*-dioximes is an intensive area of study and numerous transition metal complexes of these ligands have been investigated¹⁻⁵. The presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make vicinal dioximes amphoteric ligands which form corrin-type, square-planar, square-pyramidal or octahedral complexes with transition metal ion such as copper(II), nickel(II) and cobalt(II) as central atoms^{5,6}. More studies on these compounds concern liquid crystal, gas sensors and inhibitors for chemical warfare agents^{7,8}.

In this study, amphi-choloroglyoxime, anti-choloroglyoxime, 4-nitro-1-naphthylamine and FeO(OH) were prepared according to literature⁹⁻¹¹. Then, a novel imine *vic*-dioxime, N'-hydroxy-2-(hydroxyimino)-N-(4-(2,4,6-trihydroxybenzylideneamino)naphthalen-1-yl) acetimidamide (H₂L) has been synthesized from the materials obtained from the first stage. Finally, its Ni(II), Co(II), Cu(II) transition metal complexes were synthesized⁵.

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EXPERIMENTAL

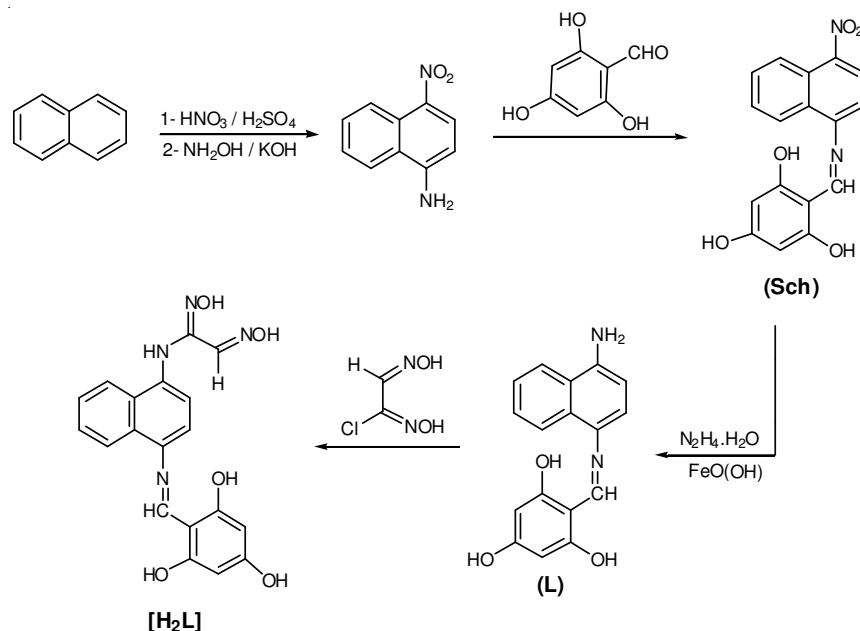
$C_2H_3O_2Cl_3$, Na_2CO_3 , $NH_2OH \cdot HCl$, KOH , $N_2H_4 \cdot H_2O$, $NaHCO_3$, C_2H_5OH , $NaOH$, $Ni(CH_3COO)_2$, $Cu(CH_3COO)_2$, $Co(CH_3COO)_2$, were obtained from Merck (Germany) and all of them were purified according to literature¹².

The carbon, hydrogen and nitrogen analyses were obtained using a Carlo Erba 1106 autoelemental analyzer. Jasco FT/IR-300 E Spectrometer was used for characterization for the functional groups. The electronic spectra in the 200-800 nm range were recorded in DMF on a Shimadzu UV-160 A spectrophotometer. Conductivities were measured in DMF using a LF330/SET conductivity Meter and were performed at 24 °C. Magnetic moments were measured by the Gouy method by using $Hg[Co(SCN)_4]$ as calibrant. 1H NMR and ^{13}C NMR spectra were obtained with a Bruker DPX-400, FT-NMR instrument with $CDCl_3$ as solvent. Mass spectra with chemical ionization were recorded on a AGILENT 1100 MSD instrument.

Synthesis of 2-((4-nitronaphthalen-1-ylimino)methyl)benzene-1,3,5-triol (Sch): 4-nitro-1-naphthylamine (5.64 g, 0.03 mol) synthesized as described previously¹⁰ dissolved in absolute ethanol (150 mL), was added with constant stirring to a solution 2,4,6-trihydroxybenzaldehyde (4.62 g, 0.03 mol) in 30 mL absolute ethanol. The mixture was allowed to stir magnetically and refluxed for 24 h. After cooling, resulting precipitate was filtered, recrystallized by absolute ethanol, washed several times with hexane and dried over calcium chloride under vacuum.

Synthesis of 2-((4-aminonaphthalen-1-ylimino)methyl)benzene-1,3,5-triol (L): 0.33 g $FeO(OH)$ as catalyst¹¹ was first activated in water for 0.5 h and was added to the solution of Sch (3.66 g, 0.011 mol in 120 mL absolute ethanol). Into this mixture, solution of hydrazinium hydroxide ($N_2H_4 \cdot H_2O$, 1.00 g in 20 mL absolute ethanol) was added dropwise for 5 min and refluxed for 5 h. Catalyst was filtered off after cooling the content of the flask to room temperature. Excess ethanol was removed under vacuum to give yellow solid. The product recrystallized by absolute ethanol, washed several times with cold hexane and dried over calcium chloride under vacuum.

Synthesis of N'-hydroxy-2-(hydroxyimino)-N-(4-(2,4,6-trihydroxybenzylideneamino)naphthalen-1-yl)acetimidamide (H₂L): A water solution of $NaHCO_3$ (0.39 g, 4.72 mmol) was added to a solution of L (0.70 g, 2.36 mmol in 10 mL absolute ethanol), then a solution of antichloroglyoxime (0.29 g, 2.36 mmol in 10 mL absolute ethanol) which is synthesized by the method described previously⁹ was added dropwise to the mixture at room temperature over 2 h. The mixture was stirred on a water bath at 60-70 °C for 5 h. The mixture was filtered and excess of ethanol was removed by evaporation through a rotary evaporator. The product was precipitated by the addition of ethanol. Obtained product was filtered off and dried in vacuum (**Scheme-I**).



Scheme-I

Synthesis of the Ni₃(H₂L)₂·4H₂O, Co₃(H₂L)₂·10H₂O and Cu(H₂L)₂ complexes: A solution of 0.196 mmol metal acetate salt in 10 mL distilled water were added to the 0.393 mmol solution of the ligand (H₂L 0.15 g) in 15 mL ethanol. The pH of the mixture was adjusted to 6.0-6.5 with the addition of 1 % NaOH solution. In order to complete the precipitation, the mixture was refluxed for 3 h before filtration. The complex formed was filtered off, washed with cold water and hexane, then dried in vacuum.

RESULTS AND DISCUSSION

The analytical data for the ligand and their metal complexes are listed in Table-1. The composition of the complexes are [M₃(H₂L)₂] for Ni and Co and M(H₂L)₂ for Cu. The schiff base ligand (H₂L) 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-2. In the spectra of the imine *vic*-dioxime ligand, bands at 211-266 nm are attributed to the benzene π - π^* transitions¹³⁻¹⁵. The bands at 321-432 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, since the imine nitrogen is involved in coordination with the metal ion.

TABLE-1
SOME ANALYTICAL DATA AND PHYSICAL PROPERTIES FOR
COMPOUNDS AND COMPLEXES OF H₂L

Compd. (m.w.)	m.f. (colour)	m.p. (°C) / Yield (%)	Mass spectra M ⁺ , m/z	Elemental analysis %: Found (Calcd.)		
				C	H	N
Sch (324.00)	C ₁₇ H ₁₂ N ₂ O ₅ (Yellow)	150 (55)	324	62.57 (62.96)	3.66 (3.73)	8.37 (8.64)
L (294.30)	C ₁₇ H ₁₄ N ₂ O ₅ (Orange)	128 (64)	294	69.01 (69.38)	4.50 (4.79)	9.41 (9.52)
H ₂ L (380.35)	C ₁₉ H ₁₆ N ₄ O ₅ (Dark-yellow)	177 (72)	380	59.43 (60.00)	4.09 (4.24)	14.56 (14.73)
Ni ₃ [H ₂ L] ₂ ·4H ₂ O (1122.91)	C ₄₂ H ₄₂ N ₈ Ni ₃ O ₁₈ (Yellow-green)	216* (83)	-	44.63 (44.92)	3.34 (3.77)	10.05 (9.98)
Co ₃ [H ₂ L] ₂ ·10H ₂ O (1231.72)	C ₄₂ H ₅₄ Co ₃ N ₈ O ₂₄ (White-green)	220* (84)	-	40.92 (40.95)	4.31 (4.42)	9.78 (9.10)
Cu[H ₂ L] ₂ (822.24)	C ₃₈ H ₃₀ CuN ₈ O ₁₀ (Gark-green)	205 (70)	-	55.21 (55.51)	3.84 (3.68)	12.78 (13.63)

*Decomposition points of corresponding molecule

TABLE-2
ELECTRONIC SPECTRAL AND MAGNETIC MOMENTS DATA OF THE
IMINE *vic*-DIOXIME LIGAND AND ITS METAL COMPLEXES

Compound	λ_{\max} (nm)	μ_{eff}
H ₂ L	429, 399 (s), 266, 247 (s), 211	-
Ni ₃ [H ₂ L] ₂ ·4H ₂ O	430, 361 (s), 321, 266, 247	2.48*
Co ₃ [H ₂ L] ₂ ·10H ₂ O	502 (s), 477, 47475, 233	3.61*
Cu[H ₂ L] ₂	432, 400, 364 (s), 334, 319, 279, 233	1.66

*For each metal ions; (s) = Shoulder.

The molar conductance values of the synthesized Ni(II), Co(II) and Cu(II) complexes are in the range 15 to 38 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in 10^{-3} M DMF solutions indicating the non-electrolytic nature of these compounds.

The tentative assignment of the most characteristic IR bands were observed and are given in Table-2. The vibration of the sterically hindered oxime groups of the free imine *vic*-dioxime ligand oxime (H₂L) are observed 3500-3400 cm^{-1} , respectively^{16,17}. When the spectra of the complexes are compared with those of the uncomplexed imine *vic*-dioxime ligand the $\nu(\text{C}=\text{N})$ band are shifted to lower frequency^{18,19}. This indicates that the imine nitrogen is coordinated to the metal ion. The spectra of the complexes show a few expected absorption bands 570-550 and 460-420 cm^{-1} ranges assigned to $\nu(\text{M}-\text{N})$ ^{18,20} and $\nu(\text{M}-\text{O})$ ¹⁹.

In order to understand the solution structure of the novel Sch, L and H₂L compounds, ¹H NMR spectra have been employed. The ¹H NMR assignments are listed in Table-3. For H₂L, the broad band (5H) observed

TABLE-3
INFRARED SPECTRAL DATA FOR COMPOUNDS AND COMPLEXES OF H₂L

Compound	O-H	C=N imine	C=N oxime	N-H	Ar(C-H)	Ar(C=C)	C-N	N-O	M-N	M-O
Sch	3520	1645	-	-	3070-3030	1450-1605	1154	985	-	-
L	3500	1640	-	3340-3300	3070-3030	1450-1605	1150	-	-	-
H ₂ L	3400-3500	1640	1625	3300	3070-3040	1450-1605	1150	970	-	-
Ni ₃ [H ₂ L] ₂ .4H ₂ O	3300 (H ₂ O)	1645	1630	-	3070-3045	1450-1605	1165	950	535	410
Co ₃ [H ₂ L] ₂ .10H ₂ O	3300 (H ₂ O)	1645	1630	-	3070-3040	1450-1605	1165	960	560	400
Cu[H ₂ L] ₂	3500	1645	1625	3290	3070-3035	1450-1600	1150	970	540	420

TABLE-4
¹H NMR SPECTRA OF THE COMPOUNDS AND ¹³C NMR SPECTRUM OF H₂L

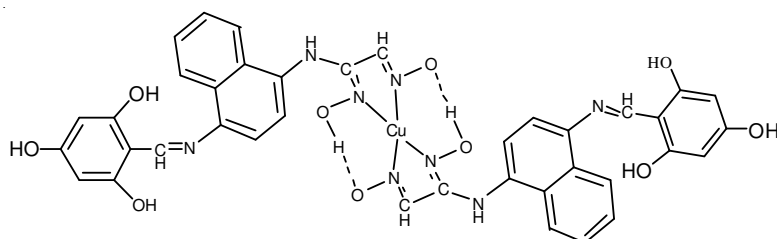
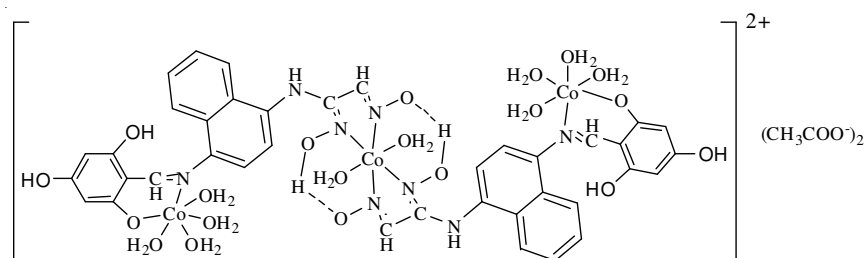
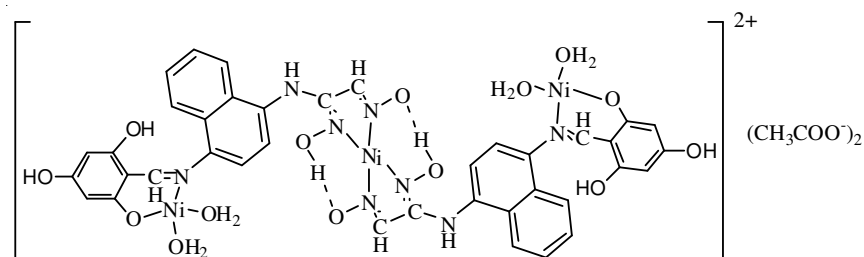
Compound	δ (ppm) (CDCl ₃)		Assignment
Sch ¹ H-NMR	15.2 (b, 3H)		Phenolic OH
	9.0 (s, 1H)		Ph-CH=N-Naf
L ¹ H-NMR	8.4 (d, 1H), 8.2 (d, 1H), 8.1 (d, 1H), 8.0 (d, 1H), 7.5 (d*d, 1H), 7.4 (d*d, 1H), 6.7 (s, 2H)		Aromatic ring (H)
	9.0 (s, 1H)		Ph-CH=N-Naf
	15.2 (b, 3H)		Phenolic OH
	4.0 (s, 2H)		NH ₂
H ₂ L ¹ H-NMR	12.0 (b, 2H)		=NOH
	9.0 (s, 1H)		Ph-CH=N-Naf
	8.4 (d, 1H), 8.2 (d, 1H), 8.1 (d, 1H), 7.9 (d, 1H), 7.5 (d*d, 1H), 7.4 (d*d, 1H), 6.7 (s, 2H)		Aromatic ring (H)
	6.1(s, 1H)		-CH=N-
	15.2 (b, 3H)		Phenolic OH
H ₂ L ¹³ C-NMR	3.6 (s, 1H)		NH
	162.0		Imine (C)
	160.2, 149.8		Oxime (C)
	163.6, 163.2, 142.5, 139.9, 130.7, 129.3, 128.1, 126.0, 125.1, 122.5, 119.4, 118.6, 105.3, 101.8		Aromatic (C)

between 12.0 ppm and 15.2 ppm are assigned =NOH and phenolic OH protons of ligand H₂L. The singlet (1H) observed at 9.0 ppm and 6.1 ppm are assigned to the protons of Ph-CH=N-Napht and -CH=N- the proton of the group, respectively. The multiplet (8H) observed at 8.4-6.7 ppm are assigned to the aromatic ring proton of the ligand H₂L. Furthermore, the singlet at 3.6 ppm in the ligand H₂L is attributed to the proton of NH group.

The ¹³C NMR spectrum of H₂L has showed a series of resonance peaks which are in accordance with the number of carbon atoms of the ligand (Table-3). In addition, the molecular ion peaks have been observed in mass spectra as based peaks (Table-4).

These result have showed that there are three metal ions in the structures of Ni(II) and Co(II) complexes and one metal ion in the structure of Cu(II) complex.

Finally, the following structures for the complexes have been proposed according to the spectral and analytical results.



Conclusion

In this study, synthesis of the novel imine *vic*-dioxime ligand containing additional phenolic OH groups to obtain the complexes with the appropriate transition metal ions such as Cu, Ni and Co in alcohol medium are reported. The addition of additional groups at the coordination system may enlarge the possibility of specific hetero-nuclear complexation and these complexes may also serve as models of relevance to bioinorganic chemistry such as metalloenzymes.

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