Synthetic and spectroscopic investigations of some transition metal complexes of hydroxy-oxime ligand

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N,N-Diacetyloximo-1,3-diamino-2-hydroxypropane reacts with metal(II) acetate yields complexes. The complexes were characterised by elemental analyses, IR, UV-VIS spectra, molar conductances, magnetic moments, DTA, and ESR measurements. The ESR spectrum of a solid copper(II) complex [LCu] H_2O, **(6)** at room temperature shows a broad signal, indicating spin exchange interactions take place between the copper(II) ions. However, in chloroform at 77K, the spectrum shows an axial type symmetry ($d_{x^2-y^2}$) with considerable covalent bond character. The ESR spectra of a doped complex **(7)** in the temperature range 243–244 K have been investigated.

Keywords: transition metal complexes, hydroxy-oxime ligand

In a recent contribution, we examined different physicochemical properties of transition metal complexes containing the oxime group, in particular, metal complexes of Schiff bases of the diacetyloxime.[1,2] In the present work, we report the synthesis and spectroscopic studies of the cobalt(II), nickel(II), copper(II) and manganese(II) complexes of N,N-diacetyloximo-1,3-diamino-2-hydroxypropane.

Results and discussion

The complexes are coloured solids, quite stable at room temperature and do not exhibit any decomposition after a long storage. The analytical and physical data (Table 1), spectral data (Tables 2 and 3) are compatible with the supposed structures (Fig. 1). The molar conductances in DMF (Table 1) indicate nonelectrolytic nature for the complexes except complex **(3)**.[3–5]

[H_2L] **(1)**

The IR spectrum of the ligand shows two ν(OH) bands, indicating the presence of two types of hydrogen bonded oxime groups. Thus, the higher frequency band (3580–3100 cm^{-1}) is associated with a weaker hydrogen bonding compared with the lower frequency band (2850–2300 cm^{-1}), of the relatively stronger hydrogen bonding. The ν(C=O) band of the ligand appears at 1660 cm^{-1}. The ν(C=N) vibrations (oxime and imine types) are located at 1588 cm^{-1} and 1622 cm^{-1} respectively. Two strong bands at 1028 and 1082 cm^{-1} are assigned to ν(NO). The ν(OH alcoholic) band appears at 3390 cm^{-1}. The electronic spectrum of the ligand in $CHCl_3$ shows absorption at 312 nm ($\in = 1.7 \times 10^3$ mol cm^{-1}), ascribed to intraligand electronic transitions. The ^1H NMR spectrum of the ligand in CD_3Cl shows a sharp singlet resonance at 2.29 ppm corresponding to the protons of methyl of acetyl groups and two at 2.36 and 2.55 ppm due to the protons of methyl groups attached to the imino-groups. The two methylene groups adjacent to imino-nitrogen groups give rise to peaks at 3.35 and 3.49 ppm respectively. The proton of –CH– appears at 4.12 ppm, however, the proton of the alcoholic OH group is observed at 5.50 ppm.[6,7] Also, the spectrum shows a peak at 11.52 ppm, due to the proton of the oxime group.[8] The DTA data show an endothermic peak at 158°C, corresponding to the melting point of the ligand.

Table 1 Analytical and physical data of the ligand and its metal complexes

Compound no./ formulation	Colour	DTA peaks(°C)		M.p.	Found (Calcd.)%						$\mu_{eff.}$ (BM)	Λ $\Omega^{-1}cm^2mol$	Yield /%
		Endo	Exo	(°C)	C	H	N	M					
(1),[H_2L] [$C_{13}H_{20}N_4O_5$]	Yellow	158		158	50.1 (50.0)	6.4 (6.4)	17.8 (17.9)	- -	-		Diamagnetic	6.1	87
(2),[LNi]H_2O [$C_{13}H_{20}N_4O_6Ni$]	Brown	80 175	280 520	175	40.3 (40.1)	5.2 (4.9)	14.5 (14.3)	15.2 (14.9)	-		Diamagnetic	7.0	95
(3), [LNi)Cr(salen)] NO_3H_2O [$C_{29}H_{34}N_7O_{11}NiCr$]	Dark brown	75	290 340 528 580	> 300	45.4 (45.0)	4.4 (4.3)	12.8 (12.7)	7.7 (7.6) Cr	6.8 (6.4) Ni		3.2	123	75
(4), [LCo] [$C_{13}H_{18}N_4O_5Co$]	Orange	182	280 525	182	42.3 (42.0)	4.9 (4.8)	15.2 (15.5)	16.0 (16.3)	-		2.15	15	93
(5), [$LCoTiCl_2$] [$C_{13}H_{18}N_4O_5Cl_2CoTi$]	Brown		325 530 565	>300	25.5 (25.2)	2.8 (2.7)	9.1 (9.2)	9.6 (9.8) Co	33.5 (33.6) Ti	11.6 (11.4) (Cl)	2.35	18.3	70
(6), [LCu].H_2O [$C_{13}H_{20}N_4O_6Cu$]	Brown	80 190	300 510	190	39.8 (39.7)	5.2 (4.8)	14.3 (14.4)	16.2 (16.0)	-		1.62	22	90
(8), [LMn].$2H_2O$ [$C_{13}H_{22}N_4O_7Mn$]	Brown	68 193	495	193	38.7 (38.9)	5.3 (5.2)	14.0 (13.9)	13.8 (13.9)			4.8	27	88

Table 2 IR spectral (cm^{-1}) assignment of the ligand and its metal complexes

Compound no.	Assignment ν(O–H)	ν(C=O)	ν(C=N)	ν(N–O)	ν(M–N)	(M–O)
(1)	3580–3100	1660	1622	1028	—	—
	2850–2300		1588	1082		
(2)	3630–3520	1660	1612	1168	570	—
			1575			—
(3)	3600–3320	1660	1612	1290	562	670
			1630			
			1537			
(4)	—	1670	1605	1180	560	—
			1570			
(5)		1665	1605	1165	555	570
			1555			
(6)	3250–3510	1665	1615	1165	550	—
			1572			
(8)	3600–3250	1660	1618	1168	520	—
			1570			

Table 3 Electronic spectra of the ligand and its metal complexes

Compound no.	Medium	λ max (nm)
(1)	Nujol	–
	$CHCl_3$	312nm ($\in$=1.7 × 10^3 mol cm^{-1}
(2)	Nujol	530, 490, 380
	$CHCl_3$	500, 450, 360
(3)	Nujol	515, 435, 332
	DMF	495, 420, 320
(4)	Nujol	530, 470, 365
	$CHCl_3$	500, 445, 350
(6)	Nujol	525, 495, 390
	$CHCl_3$	505, 465, 370
(8)	Nujol	515, 410, 365
	$CHCl_3$	505, 400, 350

[LNi] H_2O **(2)**

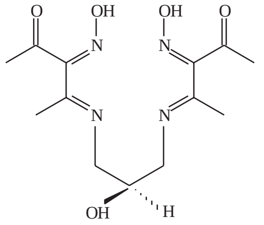
The IR spectrum of this complex reveals peaks at 1660 and 1168 cm^{-1}, due to the carbonyl and oxime groups, respectively.[9] The ν(C=N) appeared at 1612 cm^{-1} and the appearance of a band at lower frequency, 1575 cm^{-1} confirms the N-coordination of the oximato groups. The band at 1525 cm^{-1} is due to ν(C–OH). This complex was diamagnetic indicating square planar geometry.[10] The electronic spectrum in nujol mull shows bands at 530, 490 and 380 nm. However, in chloroform it displays bands at 500, 450 and 360 nm respectively (Table 3), assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1A_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions respectively of square planar geometry.[11,12] The DTA data (Table 1) show a broad endothermic peak at 80°C, assigned to loss of water of crystallisation. Another peak was observed at 175°C, corresponding to the melting point. A sharp exothermic peak at 280°C was attributed to a phase change. Finally, an exothermic peak was observed at 520°C, assigned to nickel oxide (NiO).

[(LNi)Cr(salen)]NO_3. H_2O **(3)**

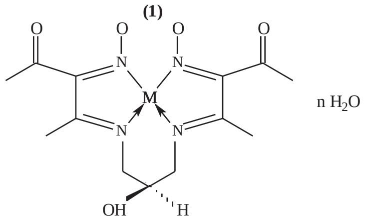
Complex **(2)** reacts with [Cr(salen)$(H_2O)_2$] NO_3 in ethanol to produce a new binuclear complex according to the following equation:

$$[Cr(salen)(H_2O)_2]\ NO_3 + [LNi]\ H_2O \rightarrow [(LNi)Cr(salen)]NO_3.H_2O + 2H_2O$$

The IR spectrum of the binuclear complex contains absorptions found in the IR spectra of both [Cr(salen)$(H_2O)_2$]NO_3 and [LNi]H_2O. Three bands centred at 1660, 1612 and 1630 cm^{-1}, are assigned to the carbonyl and imine stretches of the Schiff base and the imine groups of the salen ligand respectively. These three bands are unchanged from their positions in the original complexes. The significant IR spectral bands of the binuclear complex are 1537 and 1290 cm^{-1}, assigned to ν(C=N) of the oxime group and ν(N–O) stretches which are shifted from those in the original complexes, indicating that the dioxime oxygen atoms have been coordinated to the chromium atom. In addition, a medium band at 670 cm^{-1} is assigned to ν(Cr–O). The magnetic moment observed at room temperature is 3.2 B.M., which is slightly lower than the spin-only value indicating spin-exchange interactions take place. The electronic absorption data show addition bands in nujol mull at 332 and 515 nm and in DMF, bands at 320 and 495 nm. The former band may be attributed to the charge transfer transition and is thought to be d-π oximate in character.[13] The latter may be attributed to the d–d transition $^4A_2 \rightarrow {}^4T_1$ of six-coordinate chromium(III).[14] The DTA data (Table 1) show an endothermic peak at 75°C, corresponding to loss of water of crystallisation. Another exothermic peak at 290°C, is assigned to loss of the nitrate group. The product was stable to 340°C, when



(1)

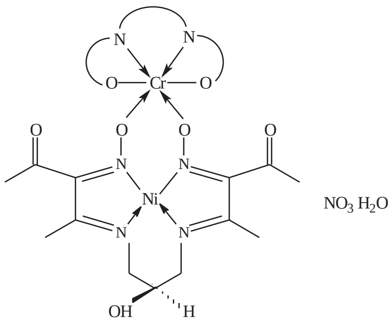


(2) M = Ni(II), n = H_2O

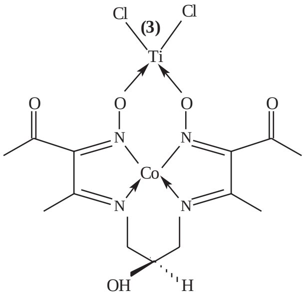
(4) M = Co(II), n = $0H_2O$

(6) M = Cu(II), n = H_2O

(8) M = Mn(II), n = $2H_2O$



(3)



(5)

Fig. 1

the organic constituents of the complex start decomposing, finally leaving the metal oxides at 528 and 580°C respectively.

[LCo] **(4)**

The suggested structure is based on the presence of carbonyl group at 1670 cm[1],[15,16] moreover, the presence of ν(NO) at 1180 cm^{-1}. The ν(C=N) appeared at 1605 cm^{-1}. Other bands appear at 1570 and 1528 cm^{-1} due to the ν(C=N) of the oximato and ν(C–OH) groups respectively. The magnetic moment was 2.15 B.M., indicating square planar geometry. The electronic spectrum in nujol mull consists of bands at 530, 470 and 365 nm, however, in chloroform it shows bands at 500, 445 and 350 nm (Table 3) due to the $^4T_{1g} \rightarrow {}^4T_{2g}$, $^4T_{1g} \rightarrow {}^4T_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) transitions respectively, of a square planar configuration.[11,15,17] The ESR spectrum of a solid complex at room temperature gives an isotropic signal (g_{iso}= 2.13), a characteristic of square planar geometry.[18] The DTA data (Table 1) show an endothermic peak at 182°C, corresponding to the melting point. Another exothermic peak at 280°C is assigned to a phase change. Finally the peak observed at 525°C is assigned to cobalt oxide (CoO).

[LCoTiCl₂] **(5)**

Titanium tetrachloride was added to the cobalt(II) complex, **(4)** in benzene. After addition of Zn/HCl in excess and reflux, a brown solid complex, **(5)** (Fig. 1) was produced. The elemental analyses (Table 1) revealed the formation of 1:1 ratio according to the following equation:

$$[\mathrm{LCo}] + \mathrm{TiCl_4} \xrightarrow[\text{benzene}\\ \text{Zn/HCl}]{\text{reflux in}} [\mathrm{LCoTiCl_2}] + 2\mathrm{HCl}$$

The magnetic moment was 2.35 B.M. The IR spectrum of the complex shows significant shifts in some of the characteristic bands as compared to the parent cobalt(II) complex, indicating the formation of a binuclear complex. The ν(C=O) appeared at 1665 cm^{-1} and the ν(NO) band was observed at 1165 cm^{-1}. The ν(C=N) of the oxime group appeared at 1555 cm^{-1} and the ν(TiCl) band appeared at 375 cm^{-1}. All these data suggest the formation of binuclear complex.[19,20] The electronic spectrum of the binuclear complex in nujol mull shows one broad band at 535 nm indicating square planar geometryfor the titinum ion[20] so, the specific assignment of the broad band is not possible. A second band observed at 410 nm, is due to charge transfer.[21] The DTA data (Table1) shows an exothermic peak 325°C, assigned to the thermal dissociation of coordinate chloride atoms. Other, exothermic peaks were observed at 530 and 565°C corresponding to metal oxides.

[LCu] H₂O **(6)**

In the case of the copper(II) complex, N-coordination of both oximato groups is proven by the presence of ν(NO) at 1165cm^{-1}, whereas the band at 1615 cm^{-1} is assigned to ν(C=N). The ν(C=N) of the oximato groups appears at 1572 cm^{-1}, however, the ν(C=O) was located at 1665 cm^{-1}. The magnetic moment is 1.62 B.M. The electronic spectrum in nujol mull shows bands at 525, 495 and 390 nm, however in chloroform, the bands appear at 505, 465 and 370 nm (Table 3) due to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions respectively, of a square planar geometry.[21] The DTA data of the complex (Table 1) show an endothermic peak at 80°C, attributed to water of crystallisation. Another peak at 190°C, corresponds to the melting point. Exothermic peaks at 300 and 510°C, are assigned to a phase change and the formation of copper oxide respectively. The ESR spectrum of a solid complex at room temperature gives a broad signal in the low field region which lacks hyperfine structure, indicating that spin-exchange interactions take place between the copper(II) ions[22] which is confirmed by the G value (Table 4).[23] The spectrum at 77K seems almost identical to that at room temperature, indicating that the geometry of the ligand around the copper(II) is not changed on lowering the temperature. However, the ESR spectrum in chloroform at 77K (Figure 2a) shows an axial type symmetry and the values $g_{11} > g_{\perp} > 2.04$ (Table 4), suggest a $d_{x^2-y^2}$ ground state with a square planar geometry.[23]

The complex shows an orbital reduction factor (K) = 0.9 (Table 4), indicating the covalent nature of the bonding.[24–27] It has been reported that, for an ionic environment $g_{11} \geq 2.3$, and for a covalent environment $g_{11} < 2.3$.[28] Theoretical work by Smith seems to confirm this view.[29] In this work, the complex shows $g_{11} < 2.3$, (Table 4), again, indicating a covalent bond character. Because the G value is less than 4, the ligand is strong field in character.[30] The g_{11}/A_{11} value (Table 4) indicates a square planar geometry for this complex.[30]

The in-plane σ-covalence parameter, $\alpha^2_{(cu)}$, was calculated using the expression given by Kivelson[28]

$$\alpha^2_{(cu)} = \left(\frac{A_{11}}{0.036}\right) + (g_{11} - 2.002) + \frac{3}{7}\ \{g_{\perp} - (2.002) + 0.04\}$$

The $\alpha^2_{(cu)}$ is 0.89 (Table 4) suggesting covalent bonding in this complex.[27] The copper(II) complex shows β_1^2 and β^2 values (Table 4) indicating a moderate degree of covalency in the in-plane and out-of-plane π-bondings.[27–31]

The orbital population for the complex is 83.4%, indicating a $d_{x^2-y^2}$ ground state.[32] The ESR spectra for a doped copper(II) complex **(7)** at 243 K and (77-4) K ranges are shown in Fig. 2(b) and (c). At 243 K, the spectrum shows an axial symmetry type with two g values, indicating a $d_{x^2-y^2}$ ground state and an essentially square-planar arrangement around the copper(II) ion.[29–30] The g_{11}/A_{11} value confirms a square-planar geometry. The ESR spectra for the doped complex **(7)** in the temperature range (243–244) K are shown in Figs 2 and 3. In this case, although the copper ion is coordinated to four nitrogen atoms as shown in Fig. 1, line broadening was detected but no nitrogen superhyperfine splitting was observed. The g_{11} values for the

Table 4 Experimental ESR parameters of the copper(II) complex (**6**) in chloroform at 77 K

Complex no.	g_{11}	$g_{\perp}$	g_{iso}	A_{11} (G)	$A_{\perp}$ (G)	A_{iso} (G)	G	g_{11}/A_{11} (cm)	$K_{\perp}^2$	K_{11}^2	K	$\alpha^2_{(cu)}$	β_1^2	β_1^2	ΔE_{xy} (cm^{-1})	ΔE_{xz} (cm^{-1})	2β (G)
(6)	2.24	2.069	2.13	200	28	85.3	3.5	107	0.71	0.88	0.90	0.89	0.80	0.98	19.802	21.505	-196.5

$g_{iso} = (g_{II} + 2g_{\perp})/3$,

$A_{iso} = (A_{11} + 2A_{\perp})/3$,

$$G = \frac{(g_{11} - 2)}{(g_{\perp} - 2)}$$

present complex show covalent bonding character in the temperature range (243–113) K. However, in the range (93–94) K, ionic bonding character was observed. The ESR parameters for a doped complex **(7)** at different temperatures are in Table 5. On lowering the temperature, the complex shows increased values of g_{11}, g_{11}/A_{11} and decreased values of A_{11} consistent with the presence of a distorted tetrahedral geometry. No change of the spectra was observed between 77K and 4K (Fig. 2c). These spectra are broader than at high temperatures. The spectrum of a doped complex at 77K shows an axial type ($d_{x^2-y^2}$) spectrum with ionic bond character. The g_{11} and A_{11}-values indicate a tetrahedral geometry around the copper(II) ion.[27–33]

A_{11} values, plotted against Δg_{11} in Fig. 4, indicate that the upper part of the line indicates square-planar symmetry, however, the lower part shows tetrahedral geometry in comparision with a Symon's Plot.[34]

[LMn] 2H$_2$O **(8)**

N-coordination of both of the oximato groups is proven by the presence of ν(N–O) at 1168 cm^{-1} whereas the higher frequency band at 1618 cm^{-1} is assigned to the ν(C=N) of the coordinated imino-nitrogen. The ν(C=O) is located at 1660 cm^{-1}, indicating that the oximato group must be coordinated to the metal ion through the oximino-nitrogen atoms. The ν(-OH) was observed at 1530 cm^{-1}. The band at 520 cm^{-1}, assigned to ν(Mn–N).[35] In all complexes, except **(4)** and **(5)**, a broad band appears in the 3630-3200 cm^{-1} range, (Table 2), due to the water molecules.[13] The magnetic moment was 4.8 B.M., indicating the presence of the Mn(II) ion.[36] The electronic spectrum in nujol mull shows bands at 515, 410 and 365 nm, however, in chloroform, it displays bands at 505, 400 and 350 nm (Table 3); the first band is attributed to the σ(N) → Mn(II) LMCT transition, the second bands may be attributed to the ligand field transitions, the higher intensity of the bands are due to intensity borrowing from the nearby charge-transfer band.[37] The ESR spectrum of a polycrystalline sample gives one broad isotropic signal centred at 2.09. The DTA data (Table 1) show endothermic peaks at 68 and 193°C, assigned to the loss of water of crystallisation and the melting point respectively. Another exothermic peak appears at 495°C, attributed to manganese oxide (MnO).

Table 5 ESR parameters for a doped copper(II) complex (**7**) at different temperatures

Temp (K)	g_{11}	$g_\perp$	g_{iso}	Δg_{11}	A_{11} (G)	G	g_{11}/A_{11} (cm)
243	2.201	2.024	2.083	0.199	177	8.4	121
223	2.215	2.035	2.095	0.213	167	6.1	128
193	2.235	2.050	2.112	0.233	153	5.0	140
173	2.250	2.060	2.123	0.248	143	4.2	150
153	2.264	2.070	2.135	0.262	134	3.8	160
133	2.277	2.080	2.146	0.275	125	3.5	171
113	2.292	2.090	2.157	0.290	115	3.2	174
93	2.306	2.100	2.169	0.304	105	3.1	204
77	2.320	2.131	2.194	0.318	96	2.4	223

$3g_{sio} = g_{11} + 2g_\perp$
$G = (g_{11} - 2) / (g_\perp - 2)$
$\Delta g_{11} = g_{11} - 2.0023$

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