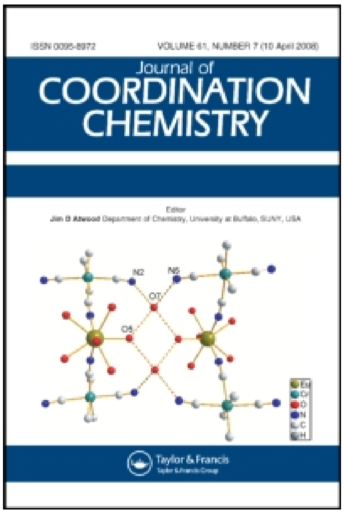

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Synthesis and formation of a new *vic*-dioxime complexes

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Synthesis and formation of a new *vic*-dioxime complexes

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In this study, *N*-(4-{[(2-ethyl-2-methyl-1,3-dioxolan-4-yl)methyl]amino}butyl)-*N*′-hydroxy-2-(hydroxyimino)ethanimidamide (L^1H_2) and *N*′-hydroxy-2-(hydroxyimino)-*N*-(4-{[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]amino}butyl)ethanimidamide (L^2H_2) were synthesized by the reaction of *N*-[(2-ethyl-2-methyl-1,3-dioxolan-4-yl)methyl]butane-1,4-diamine or *N*-[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]butane-1,4-diamine and *anti*-chloroglyoxime. Ligands form mononuclear complexes $[(LH)_2M]$ with a metal : ligand ratio of 1 : 2 with $M = Co(II)(H_2O)_2$, Ni(II) and Cu(II). Zn(II) forms complexes $[(LH)(H_2O)(Cl)Zn]$ with a metal : ligand ratio of 1 : 1. The Co(II) complexes of the ligands are proposed to be octahedral with water molecules as axial ligands, the Ni(II) and Cu(II) complexes are proposed to be square planar, and the complexes of Zn(II) are tetrahedral. A chloride ion and a water molecule are also coordinated to the Zn(II) ion. Structural assignments are supported by elemental analyses, IR, ^1H- and ^{13}C-NMR spectra, UV–Visible spectroscopy, molar conductivity, magnetic susceptibility measurements and thermogravimetric analyses (TGA).

Keywords: Synthesis of *vic*-dioxime complexes; Transition metal complexes

1. Introduction

Synthesis of various *vic*-dioximes and their transition metal complexes have been essential topics of research carried out in our laboratory [1–9]. High stability of the complexes prepared with *vic*-dioxime ligands has been extensively used for various purposes in organic, analytical, inorganic, bio, pigment, medical and industrial chemistry [10]. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make *vic*-dioximes amphoteric ligands which form corrin-type, square-planar, square-pyramidal or octahedral complexes with transition metal ions such as copper(II), nickel(II), cobalt(II) and cobalt(III) as central atoms. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure, which is stabilized by hydrogen bonding [11].

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vic-Dioximes and their derivatives are a very important class of ligands, forming complexes with transitions metals. Oxime/oximate metal complexes have been investigated since the early 1900s [12]. In general, oxime and dioxime derivatives are very important compounds in the chemical industry and in medicine. Technetium(V)- and copper(II)-containing *vic*-dioximes currently are used as cerebral and myocardial perfusion imaging agents [13]. Some oximes and their alkyl, oxyalkyl and amino derivatives have physiological and biological activity [14].

In the present article, we report the synthesis and characterization of a new *vic*-dioxime ligands and their mononuclear complexes with Co(II), Ni(II), Cu(II) and Zn(II) ions.

2. Experimental

2.1. *Materials*

The preparation of (*E,E*)-dichloroglyoxime has been described previously [15, 16]. All the reagents used were purchased from Merck or Fluka or Sigma Company and are chemically pure.

2.2. *Measurements*

Elemental analyses (C, H, N) were performed on a LECO-932 CHNSO elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR Spectrometer. Electronic spectra were obtained on a Shimadzu 1240 UV Spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temprature using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants. The melting points were determined on a Gallenkamp melting point apparatus. TGA curves were recorded on a Shimadzu TG-50 thermo balance.

2.3. *Preparation of the ligands (L^1H_2 and L^2H_2)*

A solution of *N*-[(2-ethyl-2-methyl-1,3-dioxolan-4-yl)methyl]butane-1,4-diamine (2.16 g, 0.01 mol) or *N*-[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]butane-1,4-diamine (2.64 g, 0.01 mol) in absolute ethanol (20 mL) was added drop-wise to a solution of *anti*-chloroglyoxime (1.23 g, 0.01 mol) in absolute ethanol (15 mL) with continuous stirring. $NaHCO_3$ (1.68 g, 0.02 mol) was added to the reaction mixture to neutralize liberated HCl. The reaction mixture was heated on a water bath at 50–60°C for 4 h, filtered and ethanol was removed by evaporation. The oily product was dissolved in absolute methanol (10 mL) and precipitated by diethyl ether (100 mL). The obtained product was filtered, washed with diethyl ether several times and dried in vacuum for 10 h. The compounds were found to be soluble in EtOH, MeOH, DMSO and DMF and insoluble in diethyl ether, *n*-hexane and benzene. L^1H_2: Characteristic ^{1}H-NMR (in DMSO-d_6): 11.71 (s, 1H, O–H), 10.10 (s, 1H, O–H), 8.00 (s, 1H, N=C–H), 5.48 (s, 2H, N–H), 4.55 (m, 1H, CH–O), 3.55 (m, 2H, CH_2–O), 2.61–3.17 (m, 6H, CH_2–NH), 1.39–1.51 (m, 6H, –CH_2), 0.87–1.31 (s, 6H, –CH_3); Characteristic ^{13}C-NMR (in DMSO-d_6): 146.19 (NH–C=N), 140.48 (H–C=N), 109.34 (>C<), 76.83 (CH–O), 67.45 (CH_2–O), 48.66 (CH_2–NH), 46.20 (CH_2–NH), 41.55 (CH_2–NH), 32.40 (–CH_2), 26.02 (–CH_2), 23.96 (–CH_2), 23.42 (CH_3), 8.31 (–CH_2CH_3).

L^2H_2: Characteristic ^{1}H-NMR (in DMSO-d_6): 10.95 (s, 1H, O–H), 9.90 (s, 1H, O–H), 7.75 (s, 1H, N=C–H), 7.20–7.60 (m, 5H, Arom-H), 6.45 (s, 2H, N–H), 4.00 (m, 1H, CH–O), 3.82 (m, 2H, CH_2–O), 2.63 (m, 6H, CH_2–NH), 1.84 (m, 4H, –CH_2), 1.65 (s, 3H, –CH_3); Characteristic ^{13}C-NMR (in DMSO-d_6): 151.20 (NH–C=N), 146.90 (H–C=N), 131.10 (Arom-C), 130.00 (Arom-C), 128.89 (Arom-C), 127.67 (Arom-C), 110.00 (>C<), 82.90 (CH–O), 76.50 (CH_2–O), 52.65 (CH_2–NH), 46.50 (CH_2–NH), 41.15 (CH_2–NH), 26.14 (–CH_2), 24.01 (–CH_2), 23.10 (CH_3).

2.4. *Preparation of the Co(II), Ni(II) and Cu(II) complexes*

A solution of metal salts (0.50 mmol) [$CoCl_2 \cdot 6H_2O$ (0.12 g), $NiCl_2 \cdot 6H_2O$ (0.12 g) and $CuCl_2 \cdot 2H_2O$ (0.09 g)] in ethanol (10 mL) was added to a hot 50°C solution of the ligands (1.00 mmol) [L^1H_2 (0.30 g) or L^2H_2 (0.35 g)] in absolute ethanol (15 mL). The pH dropped to around 3–4 and was raised to around 5–6 by addition of 1 M NaOH in ethanol. Every mixture was stirred for 4 h more at 50°C, filtered and the precipitate was washed with water, ethanol and diethyl ether and dried *in vacuum* at 60°C. $Ni(L^1H)_2$: Characteristic ^{1}H-NMR (in DMSO-d_6): 15.10 (s, 2H, O···H–O), 8.20 (s, 2H, N=C–H), 5.20 (s, 4H, N–H), 4.57 (m, 2H, CH_2–O), 3.56 (m, 4H, CH_2–O), 2.60–3.22 (m, 12H, CH_2–NH), 1.40–1.52 (m, 12H, –CH_2), 0.86–1.30 (s, 12H, –CH_3); Characteristic ^{13}C-NMR (in DMSO-d_6): 150.76 (NH–C=N), 142.26 (H–C=N), 109.33 (>C<), 76.84 (CH–O), 67.44 (CH_2–O), 48.65 (CH_2–NH), 46.21 (CH_2–NH), 42.83 (CH_2–NH), 32.39 (–CH_2), 26.04 (–CH_2), 23.94 (–CH_2), 23.41 (CH_3), 8.30 (–CH_2CH_3). $Ni(L^2H)_2$: Characteristic ^{1}H-NMR (in DMSO-d_6): 14.90 (s, 2H, O···H–O), 8.00 (s, 2H, N=C–H), 7.18–7.62 (m, 10H, Arom-H), 6.35 (s, 4H, N–H), 4.05 (m, 2H, CH_2–O), 3.80 (m, 4H, CH–O), 2.75 (m, 12H, CH_2–NH), 1.80 (m, 8H, –CH_2), 1.65 (s, 6H, –CH_3); Characteristic ^{13}C-NMR peaks are at (in DMSO-d_6): 155.13 (NH–C=N), 148.80 (H–C=N), 131.11 (Arom-C), 130.02 (Arom-C), 128.88 (Arom-C), 127.65 (Arom-C), 110.00 (>C<), 82.88 (CH–O), 76.51 (CH_2–O), 52.63 (CH_2–NH), 46.47 (CH_2–NH), 41.14 (CH_2–NH), 26.15 (–CH_2), 23.98 (–CH_2), 23.11 (CH_3).

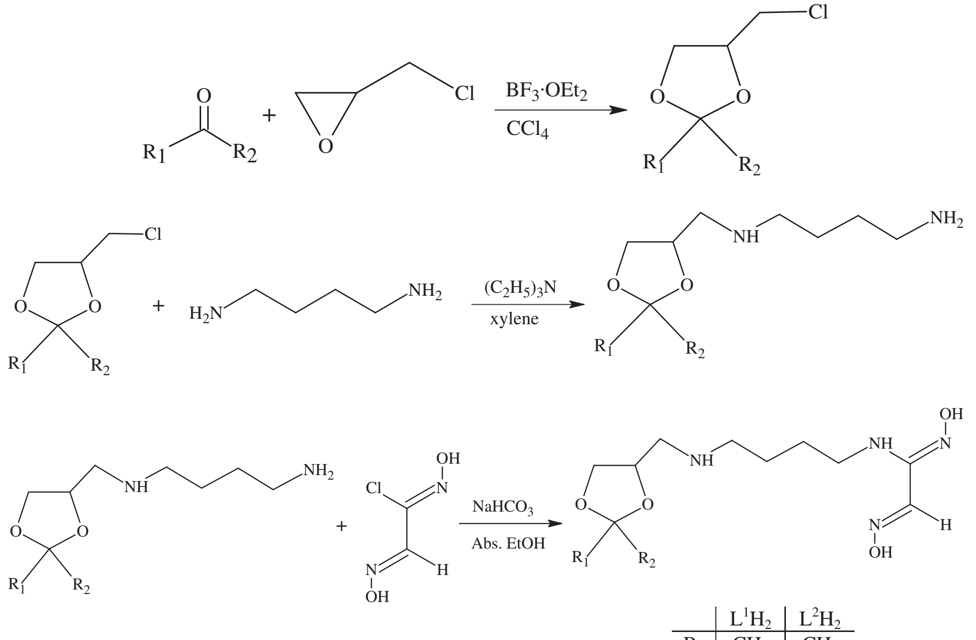
2.5. *Preparation of the Zn(II) complexes*

A solution of $ZnCl_2$ (0.14 g, 1.00 mmol) in absolute ethanol (20 mL) was added to a solution of ligand [L^1H_2 (0.30 g) or L^2H_2 (0.35 g)], dissolved in absolute ethanol (15 mL) by stirring on a water bath at 50°C for 2 h in order to complete precipitation. The solid complexes were filtered, washed with water, ethanol and diethyl ether and dried *in vacuum* at 60°C. $Zn(L^1H)(Cl)(H_2O)$: Characteristic ^{1}H-NMR (in DMSO-d_6): 10.30 (s, 1H, O–H), 8.31 (s, 1H, N=C–H), 5.16 (s, 2H, N–H), 4.56 (m, 1H, CH–O), 3.57 (m, 2H, CH_2–O), 3.32 (s, 2H, H_2O), 2.61–3.21 (m, 6H, CH_2–NH), 1.42–1.47 (m, 6H, –CH_2), 0.85–1.32 (s, 6H, –CH_3); Characteristic ^{13}C-NMR (in DMSO-d_6): 155.01 (NH–C=N), 143.66 (H–C=N), 109.34 (>C<), 76.82 (CH–O), 67.45 (CH_2–O), 48.66

(CH_2–NH), 46.19 (CH_2–NH), 41.99 (CH_2–NH), 32.41 (–CH_2), 26.03 (–CH_2), 23.96 (–CH_2), 23.41 (CH_3), 8.31 (–CH_2CH_3). Zn(L^2H)(Cl)(H_2O): Characteristic ^{1}H-NMR (in DMSO-d_6): 10.11 (s, 1H, O–H), 8.29 (s, 1H, N=C–H), 7.20–7.65 (m, 5H, Arom-H), 6.20 (s, 2H, N–H), 4.01 (m, 1H, CH–O), 3.80 (m, 2H, CH_2–O), 3.30 (s, 2H, H_2O), 2.60 (m, 6H, CH_2–NH), 1.82 (m, 4H, –CH_2), 1.63 (s, 3H, –CH_3); Characteristic ^{13}C-NMR (in DMSO-d_6): 159.20 (NH–C=N), 150.01 (H–C=N), 131.09 (Arom-C), 130.01 (Arom-C), 128.91 (Arom-C), 127.68 (Arom-C), 110.03 (>C<), 82.92 (CH–O), 76.51 (CH_2–O), 52.66 (CH_2–NH), 46.48 (CH_2–NH), 41.13 (CH_2–NH), 26.12 (–CH_2), 23.98 (–CH_2), 23.08 (CH_3).

3. Results and discussion

In this study, *N*-(4-{[(2-ethyl-2-methyl-1,3-dioxolan-4-yl)methyl]amino}butyl)-*N*′-hydroxy-2-(hydroxyimino)ethanimidamide (L^1H_2) and *N*′-hydroxy-2-(hydroxyimino)-*N*-(4-{[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]amino}butyl)ethanimidamide (L^2H_2) have been obtained in 61–65% yields by the reaction of *anti*-chloroglyoxime and *N*-[(2-ethyl-2-methyl-1,3-dioxolan-4-yl)methyl]butane-1,4-diamine or *N*-[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]butane-1,4-diamine in ethanol with excess of $NaHCO_3$ as buffer to neutralize HCl formed during the reaction. The diamines have been prepared from 4-(chloromethyl)-2-ethyl-2-methyl-1,3-dioxolane or 4-(chloromethyl)-2-methyl-2-phenyl-1,3-dioxolane and 1,4-diaminobutane as show in scheme 1. The structure of the ligands were determined by a combination of elemental analyses, IR, ^{1}H- and



	L^1H_2	L^2H_2
R_1	CH_3	CH_3
R_2	C_2H_5	Ph

Scheme 1. Structure of the ligands.

Table 1. Analytical and physical data of the ligands and their complexes.

							Calculated (Found) %		
Compounds	Formula (F.W.) g mol^{-1}	Color	Yield (%)	m.p. (°C)	μ_{eff}/atom (B.M.)	Λ_M^{a}	C	H	N
L^1H_2	$C_{13}H_{26}N_4O_4$ (302.43)	White	65	116	–	1.9	51.63 (51.96)	8.68 (9.00)	18.53 (18.92)
$[Co(L^1H)_2(H_2O)_2]$	$CoC_{26}H_{54}N_8O_{10}$ (697.81)	Brown	55	197	4.10	2.5	44.74 (44.88)	7.82 (7.81)	16.06 (15.93)
$[Ni(L^1H)_2]$	$NiC_{26}H_{50}N_8O_8$ (661.53)	Red	61	214	Dia	4.4	47.20 (46.84)	7.63 (8.01)	16.94 (17.30)
$[Cu(L^1H)_2]$	$CuC_{26}H_{50}N_8O_8$ (666.38)	Dark green	53	188	1.77	3.0	46.86 (47.17)	7.58 (7.19)	16.82 (17.31)
$[Zn(L^1H)(Cl)(H_2O)]$	$ZnC_{13}H_{27}ClN_4O_5$ (420.28)	Dark yellow	56	200	Dia	11.3	37.15 (36.79)	6.49 (6.77)	13.34 (13.68)
L^2H_2	$C_{17}H_{26}N_4O_4$ (350.47)	Dirty white	61	127	–	2.6	58.26 (57.88)	7.49 (7.86)	15.99 (16.37)
$[Co(L^2H)_2(H_2O)_2]$	$CoC_{34}H_{54}N_8O_{10}$ (793.89)	Brown	68	193	3.99	2.9	51.44 (51.80)	6.87 (7.22)	14.12 (13.79)
$[Ni(L^2H)_2]$	$NiC_{34}H_{50}N_8O_8$ (757.61)	Red	59	226	Dia	6.3	53.90 (54.25)	6.67 (6.99)	14.79 (15.16)
$[Cu(L^2H)_2]$	$CuC_{34}H_{50}N_8O_8$ (762.46)	Dark green	55	152	1.86	2.4	53.56 (53.95)	6.37 (5.99)	14.70 (14.95)
$[Zn(L^2H)(Cl)(H_2O)]$	$ZnC_{17}H_{27}ClN_4O_5$ (468.32)	Yellow	66	197	Dia	15.5	43.60 (43.94)	5.82 (5.68)	11.97 (12.36)

[a] Λ_M in (Ω^{-1} cm^2 mol^{-1}).

Table 2. Characteristic IR bands of the ligands and their complexes as KBr pellets (in cm^{-1}).

Compounds	ν(H_2O/O–H)	ν(N–O)	ν(C=N)	ν(O···H–O)
L^1H_2	3260–3370	990	1632	–
$[Co(L^1H)_2(H_2O)_2]$	3355–3500	980	1615	1706
$[Ni(L^1H)_2]$	–	981	1621	1735
$[Cu(L^1H)_2]$	–	975	1614	1721
$[Zn(L^1H)(Cl)(H_2O)]$	3362–3430	985	1620	–
L^2H_2	3250–3360	1000	1630	–
$[Co(L^2H)_2(H_2O)_2]$	3320–3510	990	1620	1720
$[Ni(L^2H)_2]$	–	970	1615	1725
$[Cu(L^2H)_2]$	–	995	1610	1720
$[Zn(L^2H)(Cl)(H_2O)]$	3240–3440	980	1620	–

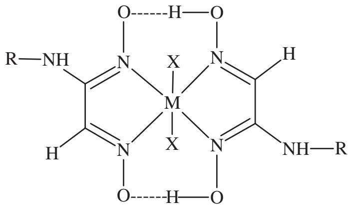
^{13}C-NMR spectroscopy, UV–Vis, magnetic susceptibility measurements, conductivity and thermogravimetric analyses (TGA) as shown in (tables 1 and 2).

The IR spectrum of the ligands and their mononuclear complexes were recorded in KBr pellets (table 2). For the ligands, the O–H, C=N and N–O stretching vibrations were observed around 3250–3370, 1630–1632 and 990–1000 cm^{-1}, respectively [7, 17]. In the IR spectrum of Co(II) complexes, the weak deformation vibration band assigned to the intramolecular hydrogen bond O···H–O bending vibration is observed around 1706–1720 cm^{-1}. The C=N stretch decreases from 1630–1632 cm^{-1} in the free ligands to 1615–1620 cm^{-1} in Co(II) complexes [1]. A lowering of the vibration frequency (relative to free ligands) of about 12–17 cm^{-1} for the C=N vibration in the H-bonded Co(II) complexes indicates coordination through the N atoms. For $[(L^1H)_2Co(H_2O)_2]$ and $[(L^2H)_2Co(H_2O)_2]$, coordinated H_2O molecules are identified by a broad OH absorption around 3500–3510 cm^{-1} with constant intensities after heating above 110°C for 24 h. The IR spectra of Ni(II) and Cu(II) complexes exhibit a C=N stretching vibration around 1610–1621 cm^{-1}. This vibration is at lower frequency than for the free ligands, attributable to N,N-chelation [3, 18]. A weak band around 1720–1735 cm^{-1} can be assigned to the intramolecular hydrogen bond O···H–O bending vibration [19]. The intensity of characteristic stretching and bending vibrations of the free ligands were shifted and lowered on complex formation, and new vibrational bands characteristic of the Ni(II) and Cu(II) complexes were observed. According to elemental analyses complexes with Zn(II) have a 1 : 1 metal : ligand ratio. In complexes with two of four coordination sites on the metal occupied by the N,O atoms of the *vic*-dioximes [2], the stretching band of C=N at 1630–1632 cm^{-1} in ligands are shifted to 1620 cm^{-1} for Zn(II) complexes. At the same time, the N–O band were moved to lower frequency (980–985 cm^{-1}) after complexation. These suggest that the ligand is coordinated through nitrogen and oxygen donors. A chloride ion and a water molecule are also coordinated to Zn(II). A broad band around 3430–3440 cm^{-1} was observed in the spectra of the complexes, due to the coordinated water [4, 20]. There is no O···H–O peak as expected for of complexes of formulas shown in figure 2.

In the ^{1}H-NMR spectrum of the ligands, two peaks were observed since the OH protons of this oxime are equivalent in the (E, E) form [21]. In the ligands, chemical shifts for =N–OH protons were observed around 9.90–11.71 ppm as singlets. Also, chemical shifts for –NH protons were observed around 5.48–6.45 ppm. These bands are easily identified by deuterium exchange. The N=C–H protons adjacent to the oxime groups were observed at 7.75–8.00 ppm. In the ^{13}C-NMR spectra, the C=NOH groups in the ligands show two peaks around 140.48–146.90 ppm. These values are in good agreement with reported values [22]. In the proton NMR spectrum of the diamagnetic Ni(II) complexes, there are no OH peaks belonging to the neighboring oxime group. The existence of intramolecular H bridging protons is observed by a new signal at lower field, 14.90–15.10 ppm, in addition to NH protons around 5.20–6.35 ppm, very near to the oxime group. Intramolecular hydrogen bonding O···H–O protons in Ni(II) observed around 14.90–15.10 ppm disappear after addition of D_2O [23, 24]. In the ^{1}H-NMR spectrum of the Zn(II) complex, the chemical shifts corresponding to N=C–H, NH, CH_2 and aromatic protons are observed at frequencies very near to those of the ligands. The Zn(II) complexes shows the presence of a N-coordinated oxime proton around 10.11–10.30 ppm [25]. ^{13}C-NMR spectra of the Ni(II) and Zn(II) complexes were recorded in DMSO-d_6. ^{13}C-NMR assignments are detailed in the experimental section. In the ^{13}C-NMR spectrum of Ni(II) complexes carbon resonances of the dioxime groups were observed around 142.26–155.13 ppm. In the ^{13}C-NMR spectrum of Zn(II) complexes azomethine carbon atoms are observed around 155.01–159.20 ppm.

The analytical and physical data of the complexes are presented in table 1. The ligands form mononuclear complexes with Co(II), Ni(II) and Cu(II) with a metal : ligand ratio of 1 : 2 but the Co(II) complexes have two coordinated water molecules, in addition to the two ligand molecules.

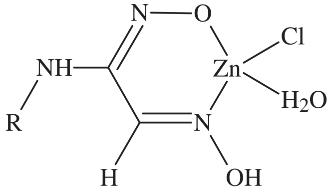
The electronic spectra of all compounds were recorded in DMSO. The $n \rightarrow \pi^*$ transitions associated with azomethine of oximes are found in the range *ca.* 280–285 nm. In the spectra of the complexes, the $n \rightarrow \pi^*$ transitions are shifted to higher energy. These results indicate that the nitrogen atoms of the oxime groups are coordinated to the metal ion [26]. In the complexes lower energy transitions can



M	Co(II)	Ni(II)	Cu(II)
X	H_2O	–	–

	L^1H_2	L^2H_2
R	$C_{11}H_{23}NO_2$	$C_{15}H_{23}NO_2$

Figure 1. Suggested structure of the octahedral and square-planar complexes of the ligands.



	L^1H_2	L^2H_2
R	$C_{11}H_{23}NO_2$	$C_{15}H_{23}NO_2$

Figure 2. Suggested structure of the tetrahedral complexes of the ligands.

also be observed in the 346–470 nm range corresponding to the d–d transitions. The electronic spectra of the Co(II) complexes shows two bands around 418 and 571 nm, which may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions. There are absorptions around 348–350 nm ascribed to metal-to-ligand charge transfer transitions [27]. In the diamagnetic Zn(II) complexes, transitions suggest a complex with tetrahedral geometry and support the proposal that H_2O and Cl groups are coordinated axially to Zn(II). The mononuclear Zn(II) complexes show an intense L–M (charge transfer) absorption at *ca.* 400 nm. The Ni(II) complexes are diamagnetic as expected for a d^8 electronic configuration. Whereas the Cu(II) and Co(II) complexes are paramagnetic and their magnetic susceptibility values are 1.77–1.86 and 3.99–4.10 B.M. respectively. According to these results, the Ni(II) and Cu(II) complexes are square-planar and the Co(II) complexes are octahedral [28]. The suggested structures of the complexes are shown in figure 1. The Zn(II) complexes are diamagnetic as expected for a d^{10} electronic configuration. To elucidate the structures of the complexes, elemental analyses IR, NMR and TGA have been used. The usual tetrahedral structures for Zn(II) complexes can be proposed, figure 2 [29].

The complexes are non-electrolytes as shown by their molar conductivities (Λ_M) in DMF [30], which are in the range 2.4–15.5 $\Omega^{-1}\,cm^2\,mol^{-1}$ (table 1).

The decomposition temperature and the weight losses of the complexes and the ligands were taken from the TGA data. The decomposition of ligands starts around 110°C and ends around 629–705°C. In the TGA curve of Co(II) complexes [calculated: 4.91%, found 5.16% for $(L^1H)_2Co(H_2O)_2$ and calculated: 4.53%, found 3.76% for $(L^2H)_2Co(H_2O)_2]$ weight loss was observed at 170°C. This shows that the complex contains two moles of water per molecule. In the TGA curve of the Zn(II) complexes [calculated: 4.28%, found 4.47% for $Zn(L^1H)(Cl)(H_2O)$ and calculated: 3.84%, found 4.33% for $Zn(L^2H)(Cl)(H_2O)]$ weight loss was observed around 140–155°C. This shows that the Zn(II) contains one coordinated water molecule. In addition, the thermal stability of all complexes increases in the order: $Ni < Cu < Co < Zn$. When the complexes are heated to higher temperatures, they decompose to give oxides of the MO type [31, 32].

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