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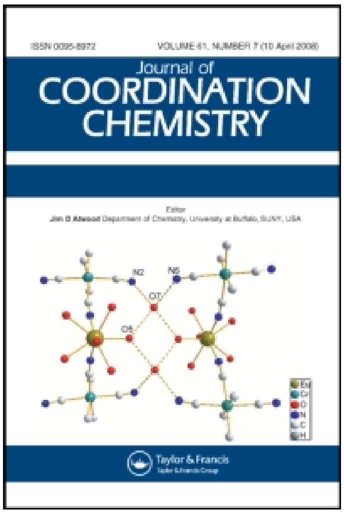

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Synthesis, spectroscopic and electrochemical studies of copper(II) and cobalt(II) complexes of three unsymmetrical <i>vic</i>-dioximes ligands

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Synthesis, spectroscopic and electrochemical studies of copper(II) and cobalt(II) complexes of three unsymmetrical *vic*-dioximes ligands

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Cobalt(II) and copper(II) complexes with three dioxime ligands cyclohexylamine-*p*-tolylglyoxime (L_1H_2), *tert*-butyl amine-*p*-tolylglioxime (L_2H_2) and *sec*-butylamine-*p*-tolylglyoxime (L_3H_2), have been prepared. The metal to ligand ratios of the complexes were found to be 1 : 2. The Cu(II) complexes of these ligands are proposed to be square planar; the Co(II) complexes are proposed to be octahedral with water molecules as axial ligands. Ligands and complexes are soluble in common solvents such as DMSO, DMF, $CHCl_3$ and C_2H_5OH. The ligands have been characterized by elemental analysis, IR, UV-VIS, ^1H NMR, ^{13}C NMR and thermogravimetric analysis (TGA). The complexes were characterized by elemental analysis, IR, UV-VIS, magnetic susceptibility measurements, thermogravimetric analysis (TGA) and electrochemistry. Electrochemical properties of metal complexes show quasi-reversible one-electron redox processes. However, $Co(L_1H)_2$ and $Cu(L_1H)_2$ complexes show another oxidation peak in the positive region. This single irreversible oxidation peak is caused by the cyclic ring of the ligand. Data also revealed that the electron transfer rates of metal complexes with L_1H_2 are higher than the other complexes.

Keywords: *vic*-Dioxime; Co(II) and Ni(II) complexes; Synthesis; Structures; Electrochemical properties

1. Introduction

The chemistry of oxime/oximato metal complexes has been investigated since preparation of nickel(II) dimethylglyoximato and recognition of the chelate five-membered character of this complex by Chugaev [1]. Oximes are widely recognized as versatile synthons for a variety of heterocycles [2]. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure, which is stabilized by hydrogen bonding [3]. When asymmetrical dioximes such as phenylglyoxime or methylglyoxime are employed as starting ligands, usually a mixture

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of *fac*- and *mer*-isomers was obtained. In a few cases one isomer could be isolated [4]. The synthetic chemistry of a MN_4 core containing *vic*-dioxime compounds has been described previously [5]. Metal-containing oxime complexes are utilized in medicine as well; technetium(V) and copper(II) complexes containing vicinal dioxime are currently used as cerebral and myocardial perfusion imaging agents [6].

Tas *et al.* have prepared *vic*-dioxime ligands, which have different substituents on their transition metal complexes [7]. Gok *et al.* have synthesized aza compounds attached to the dioxime group [8]. Other applications for these compounds concern liquid crystals [9], gas sensors [10] and inhibitors for chemical warfare agents [11].

We report here the synthesis and structural properties of three new *vic*-dioxime containing three new ligands (L_1H_2, L_2H_2 and L_3H_2) and mononuclear complexes with Cu(II) and Co(II). Electrochemistry of the mononuclear complexes has also been investigated.

2. Experimental

Anti-*p*-tolylchloroglyoxime was synthesized as described in the literature [12]. Cyclohexylamine, *tert*-butylamine and *sec*-butylamine (Fluka Chemical Company, Taufkirchen, Germany) and tetra-*n*-butylammonium perchlorate (n-Bu_4NClO_4, Fluka Chemical Company, Taufkirchen, Germany) were used as received.

Elemental analyses were carried out in the Laboratory of the Scientific and Technical Research Council of Turkey (TUBITAK). IR spectra were recorded on a Perkin-Elmer Spectrum RXI FT-IR Spectrometer as KBr pellets, ^{1}H NMR spectra were recorded on a Varian XL-200. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20°C) using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [13]. UV-VIS spectra were recorded on a Schimadzu 1601 PC. An EcoChemie Autolab-12 potentiostat with the electrochemical software package GPES 4.9 (Utrecht, The Netherlands) was used for voltammetric measurements. A three electrode system was used: a platinum wire counter electrode, an Ag/AgCl reference electrode and a 2 mm sized platinum disc electrode as working electrode. The working electrode was polished with 0.05 µm alumina prior to each experiment. Throughout the experiment oxygen-free nitrogen was bubbled through the solution for 10 min. Voltammetric experiments were performed at room temperature.

2.1. *Synthesis of the ligands L_1H_2, L_2H_2 and L_3H_2*

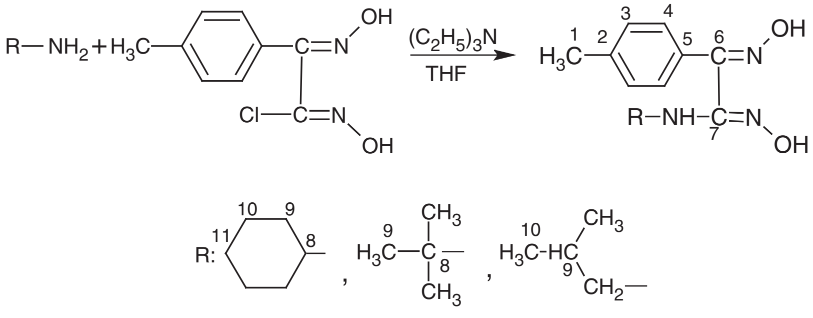
Anti-*p*-tolylchloroglyoxime was synthesized as described in the literature [12]. A solution of 15.8 mmol of cyclohexylamine, 15.8 mmol *t*-butylamine and 15.8 mmol secondarybutylamine in 30 cm^3 of absolute THF was added to a solution of 15.8 mmol of Et_3N in 10 cm^3 of absolute THF. This mixture was cooled to −15°C and kept at this temperature, and a solution of 15.8 mmol *anti*-*p*-tolylchloroglyoxime in 50 cm^3 absolute THF was added dropwise under a N_2 atmosphere with continuous stirring. The addition of the *anti*-*p*-tolylchloroglyoxime solution was carried out over 1.5 h. The mixture was stirred for 1 h more and the temperature raised to 20°C. Precipitated Et_3NHCl was filtered and the filtrate was evaporated to remove THF. The oily products were dissolved in 10 cm^3 of CH_2Cl_2 and 200 cm^3 of *n*-hexane were added to precipitate the compound. This process was then repeated several times. The products were filtered and dried in vacuum. The products are soluble in common solvents such as CH_2Cl_2, $CHCl_3$, Me_2CO, THF, EtOH and DMSO. L_1H_2 characteristic ^{13}C NMR chemical shift ($CDCl_3$, TMS, δ ppm): C_1 (35.16 and 34.78), C_2 (140.00), C_3 (126.67), C_4 (129.00), C_5 (133.93), C_6 (149.30), C_7 (148.67), C_8 (52.33), C_9 (25.51), C_{10} (25.07) and C_{11} (21.64 and 21.77); L_3H_2 characteristic ^{13}C NMR the chemical shift ($CDCl_3$, TMS, δ ppm): C_1 (31.10 and 31.06), C_2 (139.84 and 140.05), C_3 (127.47 and 126.73), C_4 (129.27 and 128.95), C_5 (130.61 and 130.00), C_6 (152.30), C_7 (149.03 and 148.85), C_8 (46.27), C_9 (50.99 and 50.48) and C_{10} (21.61–21.75 and 22.51–22.29).

2.2. *Synthesis of the cobalt(II) and copper(II) complexes*

0.5 mmol L_1H_2, 0.5 mmol L_2H_2 or 0.5 mmol L_3H_2 was dissolved in EtOH (25 cm^3). A solution (0.25 mmol) of the metal salt [$CoCl_2 \cdot 6H_2O$] or [$CuCl_2 \cdot 2H_2O$] in 10 mL of ethanol was added drop-wise with continuous stirring. The stirred mixture was heated at reflux for 1 h and maintained at this temperature. The pH of solutions was about 1.5–3.0 and was adjusted to 4.5–5.5 by the addition of a 1% NaOH solution in ethanol. After cooling to room temperature, the complexes were filtered and washed with hot water (3 × 5 mL), finally, washed with diethylether and dried at 90°C for 5 h. The products are soluble in solvents such as $CHCl_3$ and DMSO.

3. Results and discussion

The routes for the synthesis of L_1H_2, L_2H_2 and L_3H_2 are given in scheme 1. First, *anti-p*-tolylchloroglyoxime was synthesized as described in the literature [12]. Ligands (L_1H_2, L_2H_2 and L_3H_2), shown in figure 1, were prepared by reaction of cyclohexylamine, *tert*-butylamine or *sec*-butylamine with a suspension of *anti-p*-tolylchloroglyoxime in absolute THF with 15.8 mmol in solution of Et_3N(triethylamine) in absolute THF at −15°C. Excess Et_3N(triethylamine) was used to neutralize the HCl liberated in the reaction. The ligand has one cyclohexyl ring, one *p*-tolyl group and two oxime groups for L_1H_2, one *p*-tolyl group, one *tert*-group and two oxime groups for L_2H_2 and one *p*-tolyl group, one *sec*-group and two oxime groups



Scheme 1. The structure of L_1H_2, L_2H_2 and L_3H_2

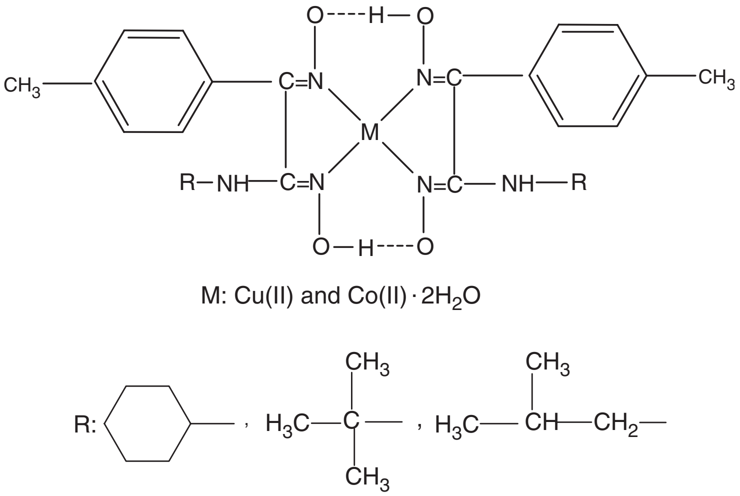


Figure 1. Structures of the Cu(II) and Co(II) complexes.

Table 1. The formulas, colors, melting points, yields, magnetic susceptibilities and elemental analyses of the ligands and complexes.

Compounds	Color	m.p. °C (dec.)	Yield (%)	μ_{eff} [BM]	Elemental analyses % calculated (Found) C	H	N
Ligand, L_1H_2	Pale Yellow	98	76	–	65.45 (65.20)	7.63 (8.03)	15.27 (15.12)
$Co(L_1H)_2 \cdot 2H_2O$	Brown	212	66	3.39	55.98 (56.00)	6.84 (6.95)	13.06 (12.80)
$Cu(L_1H)_2$	Dark Green	210	71	1.54	58.87 (58.50)	6.54 (6.71)	13.73 (13.82)
Ligand, L_2H_2	Pale Yellow	67	64	–	62.65 (62.42)	7.63 (8.15)	16.86 (16.50)
$Co(L_2H)_2 \cdot 2H_2O$	Brown	225	79	3.69	52.79 (52.54)	6.76 (6.95)	14.21 (14.60)
$Cu(L_2H)_2$	Dark Green	265	78	1.56	55.76 (56.00)	6.43 (6.95)	15.01 (14.80)
Ligand, L_3H_2	Pale Yellow	75	69	–	62.65 (62.90)	7.63 (8.12)	16.86 (16.69)
$Co(L_3H)_2 \cdot 2H_2O$	Dark Brown	207	66	3.76	52.79 (52.54)	6.76 (6.95)	14.21 (14.40)
$Cu(L_3H)_2$	Dark green	139	64	1.58	55.76 (55.54)	6.43 (6.75)	15.01 (14.95)

for L_3H_2. Mononuclear complexes have been synthesized from L_1H_2, L_2H_2 and L_3H_2 with salts of Cu(II) and Co(II) with a metal–ligand ratio of 1 : 2. The ligands coordinate by N,N′ atoms of vicinal dioximes. The cobalt(II) complex also has two coordinated waters. These *vic*-dioximes form mononuclear complexes [14, 15].

The formulas, colors, melting points, yields, magnetic susceptibilities and elemental analysis results of L_1H_2, L_2H_2 and L_3H_2 with their Cu(II) and Co(II) complexes are listed in table 1. The structural formulas were deduced by elemental analysis, IR,

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

Compounds	O–H	N–H	Aliph. C–H	O–H···O	N–O	C=N
Ligand, L_1H_2	3540–2557	3335	2930–2856	–	999	1647
$Co(L_1H)_2 \cdot 2H_2O$	3440–3078	3398	2928–2853	1716	967	1630
$Cu(L_1H)_2$	3680–3084	3365	2925–2853	1720	962	1613
Ligand, L_2H_2	3184	3350	2963–2867	–	999	1629
$Co(L_2H)_2 \cdot 2H_2O$	3463	–	2966–2865	–	958	1612
$Cu(L_2H)_2$	–	3399	2970–2859	–	973	1609
Ligand, L_3H_2	3351–3243	3388	2970–2872	–	994	1645
$Co(L_3H)_2 \cdot 2H_2O$	3268	3400	2964–2873	1724	972	1639
$Cu(L_3H)_2$	–	3357	2964–2870	1718	970	1641

Table 3. Characteristic UV-VIS bands of the ligands and complexes in $CHCl_3$, DMSO and C_2H_5OH.

Compounds	Solvents	Wavelength	λ max. (nm)	log ε (M^{-1} cm^{-1})			
Ligand, L_1H_2	C_2H_5OH	251(4.87)	257(2.99)	311(2.27)			
	$CHCl_3$	244(3.87)	272(3.68)	291(2.95)	307(2.24)		
$Co(L_1H)_2 \cdot 2H_2O$	C_2H_5OH	215(5.43)	239(5.38)	243(4.60)	259(4.20)	352(3.55)	459(2.72)
	$CHCl_3$	244(5.16)	271^s(4.90)	416^s(3.50)	634(2.66)		
$Cu(L_1H)_2$	DMSO	388(4.76)	391(3.85)	550^s(2.74)			
Ligand, L_2H_2	C_2H_5OH	252(4.26)	291(3.00)	307(2.28)			
	$CHCl_3$	243(4.52)	250(5.55)	260(4.37)	295(2.89)	314(21.7)	
$Co(L_2H)_2 \cdot 2H_2O$	DMSO	300(4.64)	697^s(2.28)				
	$CHCl_3$	246(6.22)	399(4.78)	488(4.11)			
$Cu(L_2H)_2$	DMSO	300(4.74)	383(4.61)	676^s(2.73)			
Ligand, L_3H_2	C_2H_5OH	251(5.07)	257(4.46)	293(2.95)	310(2.20)		
	$CHCl_3$	247(6.38)	252(5.68)	291(2.85)	343(2.12)		
$Co(L_3H)_2 \cdot 2H_2O$	C_2H_5OH	244(4.69)	257(4.52)	293(389)	459(3.16)	536(2.39)	
	$CHCl_3$	245(5.20)	268(4.48)	342(3.81)			
$Cu(L_3H)_2$	DMSO	393(4.54)	410^s(4.14)	670^s(2.68)			

s: shoulder.

Table 4. ^1H NMR spectra[a] of the ligands in $CDCI_3$ in δ (ppm).

Funct. group	L_1H_2	L_2H_2	L_3H_2
OH^a	–	–	–
Ar–CH_3	2.35 $(3H)^s$	2.2–2.4 $(3H)^t$	2.33 $(3H)^s$
Ar–CH–	7.1–7.13 $(2H)^d$ 7.26–7.64 $(2H)^d$	7.1–7.7 $(4H)^m$	7.53 and 7.55 $( )^d$, 7.64 and 7.66 $( )^d$, 7.09 and 7.11 $( )^d$, 7.19 and 7.25 $( )^d$ 4H
–CH	2.83 $(1H)^s$	–	2.91–3.10 $(1H)^b$
–CH_2	1.02 $(4H)^s$ 1.4–1.8 $(6H)^m$	–	1.13–1.31 $(2H)^m$
C–CH_3	–	1.1–1.4 $(9H)^m$	0.64–0.71 $(3H)^m$ 0.88–0.90 $( )^d$ and 0.96–0.98 $( )^d$ 3H
NH–	5.2 $(1H)^b$	5.3 $(1H)^b$	5.27 and 5.05 $(1H)^b$

m: multiplet, s: singlet, d: doublet, t: triplet, a: deuterium exchangeable, b: broad bands.

^1H NMR, ^{13}C NMR, UV-VIS spectroscopic and cyclic voltammetry. Additional analytical data are given in tables 1–5.

The interaction of the ligands L_1H_2, L_2H_2 and L_3H_2 with copper(II) salts yields complexes corresponding to the general formula $[M(L_xH)_2]$ and $[(L_xH)_2M \cdot 2H_2O]$ for cobalt(II).

Table 5. Voltammetric data for Co(II) and Cu(II) complexes.

Complex	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$^aE_{pa}$ (V)
$Co(L_1H)_2$	−1.27	−1.50	230	0.19
$Co(L_2H)_2$	−1.26	−1.57	310	
$Co(L_3H)_2$	−1.28	−1.55	270	
$Cu(L_1H)_2$	0.27	0.16	110	0.57
$Cu(L_2H)_2$	0.42	0.23	190	
$Cu(L_3H)_2$	0.23	0.10	120	

Supporting electrolyte = 0.05 M *n*-Bu_4NClO_4, Solvent = DMSO, $^aE_{pa}$ = Ligand based oxidation. Reference electrode = Ag/AgCl, Scan rate = 100 mV s^{-1}.

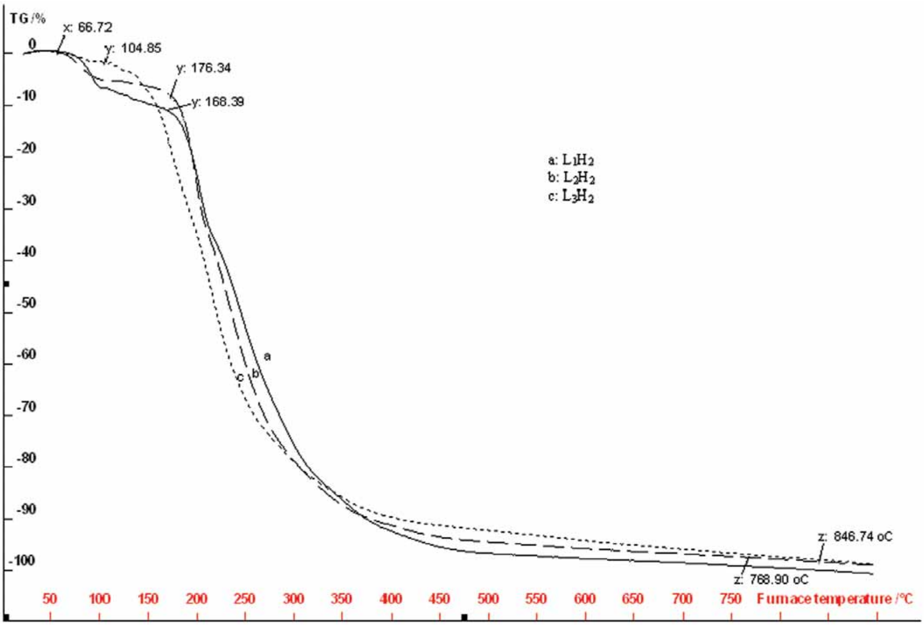


Figure 2. TGA curves of L_1H_2, L_2H_2 and L_3H_2 ligands.

3.1. *NMR results*

Although no chemical shifts were observed for =N–OH groups of oximes in the ^{1}H NMR spectra of L_1H_2, L_2H_2 and L_3H_2, the proton resonances support the structures (table 4).

In the ^{1}H NMR spectrum of L_1H_2, L_2H_2 and L_3H_2, the deuterium exchangeable NH is a singlet at $\delta = 5.2$, 5.3 and 5.27 and 5.05, respectively (table 4).

In the ^{13}C NMR spectrum of L_1H_2 the carbon resonances of oxime groups are observed at 149.30 (C_6) and 148.67 (C_7) ppm and for L_3H_2 at (152.30) C_6 and (149.03 and 148.85) C_7 ppm. For L_3H_2 (152.30) C_6 (149.03 and 148.85) C_7 ppm and all other carbon resonances are double indicating that L_3H_2 has a *cis–trans* isomerism [12]. The isomer ratio was found to be 64% *cis*-isomer and 36% *trans*-isomer from the ^{1}H NMR and ^{13}C NMR data (table 4).

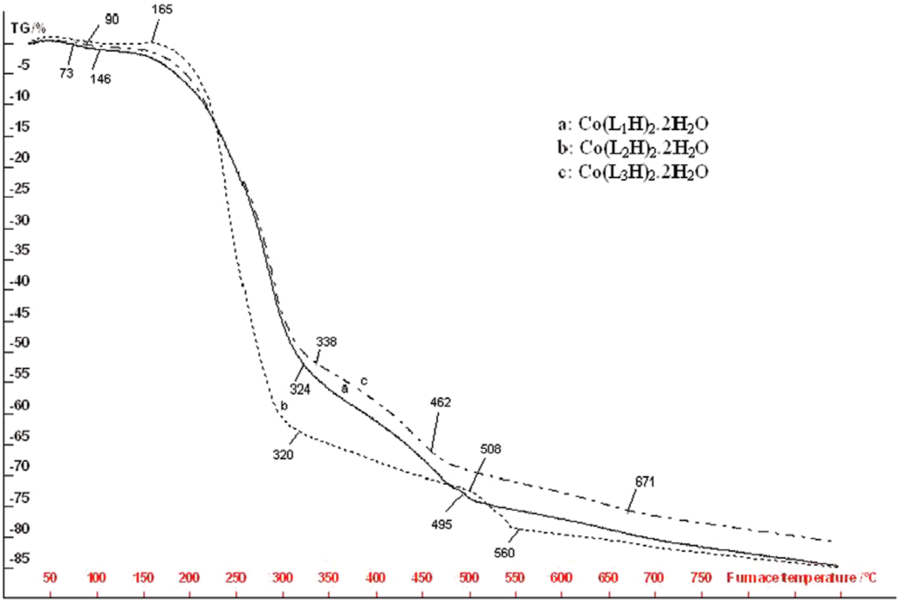


Figure 3. TGA curves of $Co(L_1H)_2 \cdot 2H_2O$, $Co(L_2H)_2 \cdot 2H_2O$ and $Co(L_3H)_2 \cdot 2H_2O$.

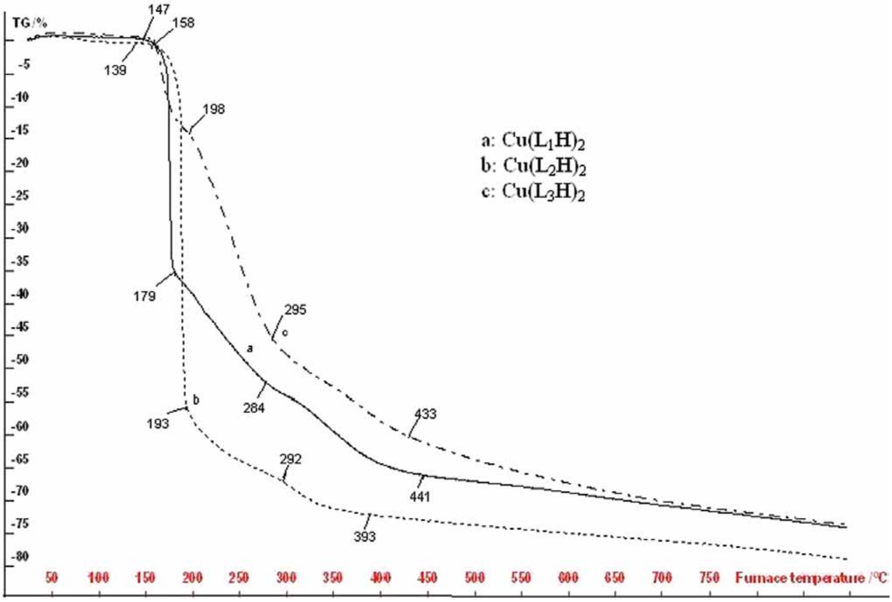


Figure 4. TGA curves of $Cu(L_1H)_2$, $Cu(L_2H)_2$ and $Cu(L_3H)_2$.

3.2. *IR results*

In the IR spectrum of L_1H_2, L_2H_2 and L_3H_2 (as KBr pellets) ν(OH) stretching absorption is observed at 3540–2557, 3184 and 3351–3243 cm^{-1}, respectively.

The ν(N–H) stretching vibrations are at 3335 $\mathrm{cm^{-1}}$ for L_1H_2, 3350 $\mathrm{cm^{-1}}$ for L_2H_2 and 3388 $\mathrm{cm^{-1}}$ for L_3H_2. The ν(C=N) and ν(N–O) vibrations are observed at 1647–994 $\mathrm{cm^{-1}}$ for L_1H_2, 1629–999 $\mathrm{cm^{-1}}$ for L_2H_2 and 1645–994 $\mathrm{cm^{-1}}$ for L_3H_2, which are in agreement with values reported for vicinal dioxime derivatives [16]. The IR spectra of the complexes were characterized by the appearance of very significant absorption band in the region 1724–1716 $\mathrm{cm^{-1}}$ due to ν(O–H···O) [17] and the shifts of ν(C=N) absorptions to lower energy [18]. Downward shifts (for L_1H_2, L_2H_2 and L_3H_2) of 34–6 $\mathrm{cm^{-1}}$ for the ν(C=N) absorption bands in the Cu(II) and Co(II) complexes indicate coordination through the N atoms [19]. The ψ(O–H) stretching band observed at 3540–2557, 3184 and 3351–3243 $\mathrm{cm^{-1}}$ in the IR spectrum of L_1H_2, L_2H_2 and L_3H_2 together with the existence of an H-bridge (O–H···O) near 1724–1716 $\mathrm{cm^{-1}}$ and the shifting of ν(C=N) and ν(N–O) stretching in IR spectra of the Cu(II) and Co(II) complexes provide support for MN_4-type coordination in the complexes. IR data of the ligands and complexes are given in table 2.

3.3. *UV-VIS results*

The UV-VIS spectra of the ligands (L_1H_2, L_2H_2 and L_3H_2) in $CHCl_3$ and C_2H_5OH showed three or four absorption bands between 244–311 nm for L_1H_2; three–five absorption bands between 243–314 nm for L_2H_2 and four absorption bands between 247–343 nm for L_3H_2. Between 215–676 nm the Cu(II) and Co(II) complexes in DMSO, $CHCl_3$ and C_2H_5OH showed absorption bands. The absorptions in the ultraviolet region are assignable to transitions involving ligands orbitals [20]. The bands below 459 nm have very high extinction coefficients and are almost certainly associated with intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ or charge–transfer transitions. In the electronic spectra of the ligands and their metal complexes, the wide range of bands seems to be due to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and d–d transitions and change-transfer transition arising from π electron interactions between the metal and ligand, either metal-to-ligand or ligand-to-metal electron transfer [21, 22]. The electronic spectra of Cu(II) complexes in DMSO show a broad band at 550 nm for $Cu(L_1H)_2$, 676 nm for $Cu(L_2H)_2$ and 670 nm for $Cu(L_3H)_2$ assigned to $^2E_g \rightarrow {}^2T_{2g}$ transitions, characteristic for square-planar geometry [23]. Weak d–d metal absorption bands were observed at 634 nm for $[Co(L_1H)_2 \cdot 2H_2O]$ in $CHCl_3$, 697 nm for $[Co(L_2H)_2 \cdot 2H_2O]$ in DMSO and 536 nm for $[Co(L_3H)_2 \cdot 2H_2O]$ in C_2H_5OH, respectively. Table 3 summarizes the UV data for ligands and complexes.

The cobalt(II) and copper(II) complexes are paramagnetic. Their magnetic susceptibilities are 3.39 BM for $Co(L_1H)_2 \cdot 2H_2O$, 3.69 BM for $Co(L_2H)_2 \cdot 2H_2O$, 3.76 BM for $Co(L_3H)_2 \cdot 2H_2O$, 1.54 BM for $Cu(L_1H)_2$, 1.56 BM for $Cu(L_2H)_2$ and 1.58 BM for $Cu(L_2H)_2$. The alternative chemical environments will give two (O–H···O) bridge protons in the *cis*-form. According to the above results, a square-planar geometry for the copper(II) complexes, and an octahedral geometry for the cobalt(II) complex are proposed [24, 25]. The UV-VIS spectrum of the Co(II) and Cu(II) complexes supports these structures because $\pi \rightarrow \pi^*$ and d–d transitions were observed, table 3. The suggested molecules of the complexes are shown in figure 1.

3.4. *Thermogravimetric measurements*

The thermal stability was investigated by TGA. The TGA curves, which were obtained under nitrogen between 20–900°C show the cobalt(II) complexes to be thermally stable to between 146°C with 339°C, whereas copper(II) complexes are thermally stable between 179°C with 198°C. The ligand decomposition starts at 168°C for L_1H_2, 176°C L_2H_2, 105°C for L_3H_2 and are completed at 847°C for L_2H_2 and L_3H_2 and 769°C for L_1H_2. The Co(II) and Cu(II) complexes decompose in three steps in the temperature ranges: 73–146, 146–324 and 324–495°C for $Co(L_1H)_2 \cdot 2H_2O$, 165–320, 320–508 and 508–560°C for $Co(L_2H)_2 \cdot 2H_2O$, 90–338, 338–462 and 462–671°C for $Co(L_3H)_2 \cdot 2H_2O$ with 147–179, 179–284 and 284–441°C for $Cu(L_1H)_2$, 139–193, 193–292 and 292–393°C for $Cu(L_2H)_2$, 158–198, 198–295 and 295–433 for $Cu(L_3H)_2$.

3.5. *Electrochemical studies*

Redox properties of the Co(II) and Cu(II) complexes were studied by cyclic voltammetry in dimethylsulfoxide (DMSO) containing 0.05 M tetra(*n*-butyl)ammonium perchlorate, using a 2 mm sized Pt disc electrode. The electrochemical data are summarized in table 5. The potentials are given versus Ag/AgCl reference electrode. The cyclic voltammogram of $Co(L_1H)_2$ exhibits a reduction peak at $E_{pc} = -1.50$ V and an associated re-oxidation peak at $E_{pa} = -1.27$ V. This redox couple is attributed to Co(II)/Co(I) as shown in figure 5. The peak separation for this couple is $\Delta E_p = 230$ mV. The anodic peak potential shifted to more positive potentials and the cathodic peak potential shifted to more negative potentials at higher scan rates. Therefore, the separation in the peak potentials increased gradually at faster scan rates. These data are indicative of a quasi-reversible one-electron redox process corresponding to the Co(II)/Co(I) couple [26]. The ratio of $Ip/v^{1/2}$ indicated that the electrochemical process is diffusion controlled [26]. $Co(L_1H)_2$ also exhibits an irreversible oxidation peak at ${}^{a}E_{pa} = 0.19$ V. This single oxidation peak may be attributed to the

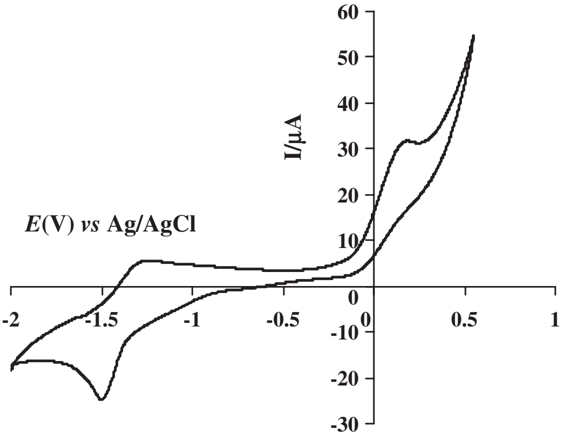


Figure 5. A cyclic voltammogram of 1.0×10^{-3} $Co(L_1H)_2$ in dimethylsulfoxide containing 0.05 M $n\text{-}Bu_4NClO_4$. Scan rate: 100 mV s^{-1}. Reference electrode: Ag/AgCl.

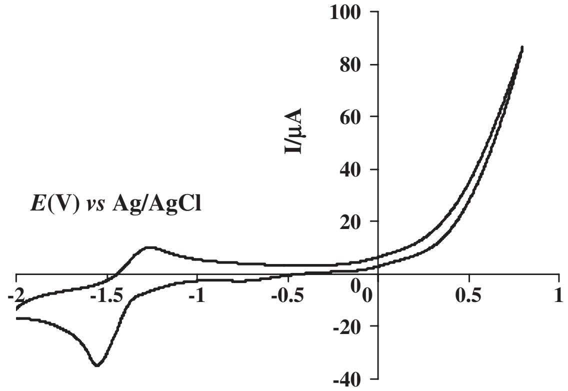


Figure 6. A cyclic voltammogram of 1.0×10^{-3} $Co(L_3H)_2$ in dimethylsulfoxide containing 0.05 M n-Bu_4NClO_4. Scan rate: $100\,mV\,s^{-1}$. Reference electrode: Ag/AgCl.

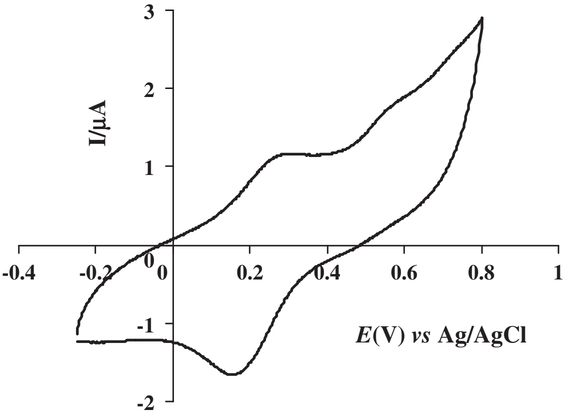


Figure 7. A cyclic voltammogram of 5.0×10^{-4} M $Cu(L_1H)_2$ in dimethylsulfoxide containing 0.05 M n-Bu_4NClO_4. Scan rate: $100\,mV\,s^{-1}$. Reference electrode: Ag/AgCl.

oxime of the ligand. In the reverse scan, no peaks are observed in the cathodic branch indicating that the oxidation of the oxime moiety is irreversible. The peak potential shifted to more positive potentials at faster scan rates, confirming the irreversibility of the oxime-based oxidation. Figure 6 shows a cyclic voltammogram of $Co(L_3H)_2$. As seen from table 5, the electrochemical properties of $Co(L_2H)_2$ and $Co(L_3H)_2$ are similar, both undergoing one-electron reduction/oxidation assigned to Co(II)/Co(I) couples. The separation in peak potentials clearly indicates that $Co(L_1H)_2$ has the highest electron transfer rate. However, no irreversible oxidation peaks are observed for $Co(L_2H)_2$ and $Co(L_3H)_2$ in the positive region. Figure 7 shows a cyclic voltammogram of $Cu(L_1H)_2$. The voltammogram exhibits a redox couple whose reduction occurs at $E_{pc} = 0.16\,V$ and oxidation at $E_{pa} = 0.27\,V$ assigned to quasi-reversible one electron charge transfer of Cu(II)/Cu(I) couple with a single irreversible oxidation peak at $E_{pa} = 0.57\,V$. The separation in the peak potentials for Cu(II)/Cu(I) couple is 110 mV. Diagnostic tests for copper(II) complexes indicated that the electrochemical

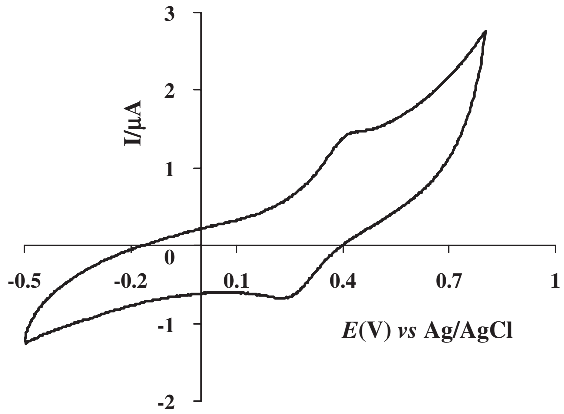


Figure 8. A cyclic voltammogram of 5.0×10^{-4} $Cu(L_2H)_2$ in dimethylsulfoxide containing 0.05 M n-Bu_4NClO_4. Scan rate: $100\,mV\,s^{-1}$. Reference electrode: Ag/AgCl.

behavior is also diffusion controlled. A cyclic voltammogram of $Cu(L_2H)_2$ is given in figure 8. The reduction peak occurs at $E_{pc} = 0.23\,V$ with an associated reoxidation peak at $E_{pa} = 0.42\,V$. The separation in the peak potentials is 190 mV indicating a quasi-reversible, one-electron process. No irreversible oxidation peaks were observed at positive potentials for the other two copper(II) complexes. Data also revealed that the electron transfer rate is higher for $Cu(L_1H)_2$ than the other two copper(II) complexes. A general conclusion for electrochemical properties of metal complexes is that all metal complexes show quasi-reversible one-electron redox processes. However, $Co(L_1H)_2$ and $Cu(L_1H)_2$ complexes show another oxidation peak in the positive region. This single irreversible oxidation peak is caused by the cyclic ring of the ligand. Data also revealed that the electron transfer rates of metal complexes with L_1H_2 are higher than the other metal complexes.

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