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Synthesis, characterization and electrochemical behaviour of some copper(II) complexes with linear and tripodal tetradentate ligands derived from Schiff bases

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Abstract—New copper(II) complexes $[Cu(H_2L)(H_2O)_n]Cl_2 \cdot xH_2O$ ($n = 0$ or 2) with linear and tripodal tetradentate ligands have been synthesized and characterized using elemental analysis, molar conductance, IR spectra, magnetic measurements, electronic and ESR spectra. The spectral studies support the binding of linear ligands with two N and two O donor sites to copper(II) ion, providing a square planar geometry and show also that tripodal ligands were coordinated to the metal ion by only one nitrogen atom, giving an arrangement of NO_3 donor groups, the other axial sites being occupied by the solvent. The ESR data indicate that the covalent character of the metal–ligand bonding in the copper(II) complexes increases with increasing electron donating effect of the ligand substituents R. From the results of cyclic voltammetry, it is shown that chelate structure and ligand geometry, steric bulk and electron donating effects of the ligand substituents are among the factors influencing the redox potentials of the complexes. © 1997 Elsevier Science Ltd

Keywords: copper(II) complexes; tetradentate ligands complexes; tripodal ligands complexes; synthesis; spectral studies; electrochemical behaviour.

In recent years, considerable interest has been developed in the coordination chemistry of copper(II) with Schiff base ligands in attempts to model the physical and chemical behaviour of biological copper systems [1–3].

It has been claimed that the functioning of copper metalloproteins related to electron transport is in some way dependent on the geometry of the coordination sphere and the electronic environment of the ligand [2–4].

In the present paper we report the synthesis of some copper(II) complexes with tetradentate N-alkylated ligands which are soluble in water, and we have determined the effects of substituents indirectly attached to the central ion, chelate structure and ligand geometry on the metal–ligand bonding character and on redox potentials of the complexes.

Based on the results obtained, tentative structures are proposed for the complexes.

EXPERIMENTAL

Analytical and physical measurements

The elemental microanalyses were carried out at the Central Service of Analysis, CNRS Vernaison (France). Chlorine and water of hydration were determined by conventional methods as described by Vogel [5]. Melting points were measured using a digital melting point apparatus IA 9000. The conductometric measurements were carried out with a CD 810 Tacussel conductivity meter. The IR spectra were recorded on a FTS-7 Biorad, Fourier transform infrared spectrometer using KBr disks. The ^1H NMR solution spectra in d_6-DMSO were recorded at 295 K on a Bruker

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AM 300 spectrometer with TMS as reference. The electronic absorption spectra in solution were recorded on a Perkin–Elmer Lamda 9 spectrometer using suprasil cells. Magnetic susceptibilities were obtained with a B-SU 10 Bruker magnetic balance using $Hg[Co(SCN)_4]$ as paramagnetic reference, and diamagnetic corrections were made using Pascal's constants. ESR spectra of copper(II) complexes were recorded at room temperature in the powder state and in $CHCl_3$ solution and at 77 K in the glass state with a E.9 X-band Varian spectrometer, using DPPH as a field marker.

Electrochemical measurements were recorded with a Princeton Applied Research model 273 potentiostat–galvanostat. Cyclic voltammograms were obtained using a SEFRAM-TGM.164 recorder. The working, counter and reference electrodes used were respectively a platinum wire, a platinum foil and a SCE (Saturated Calomel Electrode). The SCE was separated from the test solution by a bridge filled with the solvent and supporting electrolyte which was TBAP. The inert gas used was nitrogen. Coulometric measurements were made using a double circular platinum net as working electrode. The auxiliary and reference electrodes, the blank electrolyte solution and the inert gas were the same as in voltammetric measurements.

Materials

Dimethyl sulfoxide used for electrochemical measurements was dried by distillation over CaH_2 or by storing over 4-Å molecular sieves. All other chemical reagents and solvents used in the preparations were Fluka p.a. products and used without further purification.

Preparation of ligands

Linear ligands H_2L^{1-3} (Fig. 1). The ligands *N*,*N*′-bis(2-hydroxybenzyl)-1,2-diaminoethane (H_2L^1) *N*,*N*′-bis(2-hydroxyacetophenyl)-1,2-diaminoethane (H_2L^2) and *N*,*N*′-bis(2-hydroxypropiophenyl)-1,2-diaminoethane (H_2L^3), were prepared *via* $NaBH_4$ reduction [6] of their corresponding Schiff bases which have been synthesized according to the literature method through the ethylene diamine-aldehyde or ketone condensation [3].

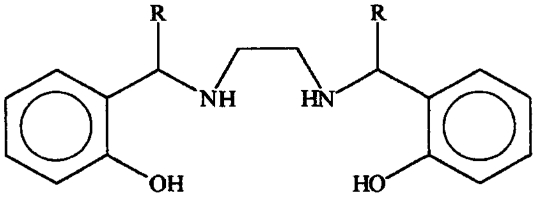

Fig. 1. Linear ligands. R = H: H_2L^1; R = CH_3: H_2L^2; R = C_2H_5: H_2L^3.

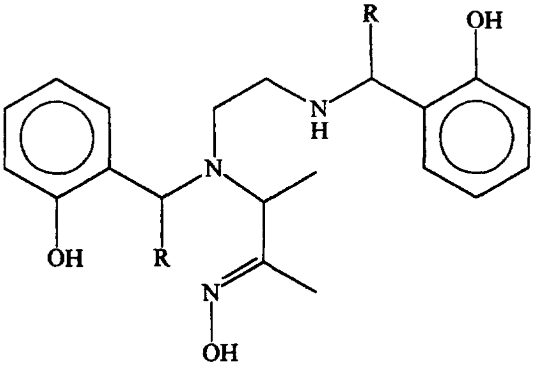

Fig. 2. Tripodal ligands. R = H: H_2L^4; R = CH_3: H_2L^5; R = C_2H_5: H_2L^6.

Tripodal ligands H_2L^{4-6} (Fig. 2). The ligands *N*,*N*-(2-hydroxybenzyl)-(3-butane-2-oxime)-*N*′-(2-hydroxybenzyl)-1,2-diaminoethane (H_2L^4), *N*,*N*-(2-hydroxyaceto-phenyl)-(3-butane-2-oxime)-*N*′-(2-hydroxyacetophenyl)-1,2-diaminoethane (H_2L^5) and *N*,*N*-(2-hydroxypropiophenyl)-(3-butane-2-oxime)-*N*′-(2-hydroxypropiophenyl)-1,2-diaminoethane (H_2L^6) were synthesized as follows:

2 mmoles of salicylaldehyde or 2-hydroxyacetophenone or 2-hydroxy-propiophenone were added with stirring to 50 cm^3 of methanolic solution of ethylenediamine (1 mmole) for the synthesis of H_2L^4, H_2L^5, H_2L^6, respectively. The bright yellow Schiff base began to form immediately, and stirring was continued for 1.5 h at room temperature. The pH was lowered to 5 with methanolic HCl solution, and $NaBH_4$ (2 mmoles) was slowly added. The reaction mixture was stirred at room temperature for 72 h, during which time the color faded to light yellow. 2,3-Butanedionemonoxime (1 mmole) was added. After the mixture was stirred at room temperature for 2 h, the pH was adjusted to 5. The solvent was removed and the residue was taken up to 20 cm^3 of water. This solution was extracted with CH_2Cl_2. The organic phase was concentrated *in vacuo* and the resulting residue was dried over P_2O_5, the CH_2Cl_2 was removed to yield a solid powder. All free ligands were characterized by microanalysis (Table 1), IR spectra (Table 2), and ^1H NMR (Table 3).

Preparation of complexes

An aqueous solution of $CuCl_2$, $2H_2O$ (1 mmole) was added dropwise to the ligand (1 mmole) dissolved in 10 cm^3 of a $EtOH\text{-}H_2O$ solution (25% by volume). The mixture was heated at 40°C with constant stirring until it was concentrated. The precipitate was filtered and washed successively with water and ethanol–water mixture (25% by volume), and finally dried at 80°C. All the complexes are stable at room temperature and soluble in water and in common organic solvents. The complexes were purified by recrystallization from dichloromethane.

Table 1. Characteristic and analytical data of the ligands and their copper(II) complexes

Compound	Colour	Yield (%)	M.p. (°C)	Found (Calc.) (%) C	H	N	M	Cl	H_2O^a	Ω^b in DMF
H_2L^1 $C_{16}H_{20}N_2O_2$	Off-white	80	109	70.2	6.9	9.9	—	—	—	—
				(70.6)	(7.3)	(10.3)				
H_2L^2 $C_{18}H_{24}N_2O_2$	Off-white	74	152	71.7	7.9	9.5	—	—	—	—
				(72.0)	(8.0)	(9.3)				
H_2L^3 $C_{20}H_{28}N_2O_2$	Off-white	70	156	72.7	8.2	9.0	—	—	—	—
				(73.2)	(8.5)	(8.5)				
H_2L^4 $C_{20}H_{27}N_3O_3$	Light yellow	64	116	66.8	7.8	12.2	—	—	—	—
				(67.2)	(7.5)	(11.7)				
H_2L^5 $C_{22}H_{31}N_3O_3$	Light yellow	68	158	68.9	8.0	11.4	—	—	—	—
				(68.6)	(8.0)	(10.9)				
H_2L^6 $C_{24}H_{35}N_3O_3$	Light yellow	54	162	69.5	8.9	9.8	—	—	—	—
				(69.7)	(8.5)	(10.2)				
1 $[Cu(H_2L^1)]Cl_2 \cdot H_2O$	Yellow green	18	117	44.8	5.3	6.8	15.3	16.3	4.0	120
				(45.2)	(5.2)	(6.6)	(15.0)	(16.7)	(4.2)	
2 $[Cu(H_2L^2)(H_2O)_2]Cl_2 \cdot 4H_2O$	Dark green	25	167	40.0	6.2	5.6	12.1	13.4	13.0	126
				(39.8)	(6.6)	(5.1)	(11.7)	(13.1)	(13.3)	
3 $[Cu(H_2L^3)(H_2O)_2]Cl_2 \cdot 2H_2O$	Dark green	30	185	44.4	7.1	5.6	11.4	13.4	6.4	133
				(44.9)	(6.7)	(5.2)	(11.8)	(13.3)	(6.7)	
4 $[Cu(H_2L^4)(H_2O)_2]Cl_2 \cdot H_2O$	Dark green	36	145	43.6	5.9	7.4	11.3	12.8	3.5	129
				(44.0)	(6.0)	(7.7)	(11.6)	(13.0)	(3.3)	
5 $[Cu(H_2L^5)(H_2O)_2]Cl_2 \cdot 3H_2O$	Dark green	30	179	42.9	6.5	6.6	10.0	12.1	8.4	122
				(43.3)	(6.7)	(6.9)	(10.4)	(11.6)	(8.8)	
6 $[Cu(H_2L^6)(H_2O)_2]Cl_2 \cdot 2H_2O$	Dark green	40	201	46.0	6.7	6.4	9.8	11.0	5.5	130
				(56.5)	(7.0)	(6.8)	(10.2)	(11.4)	(5.8)	

[a] Lattice water.

[b] In ohm^{-1} mol^{-1}.

RESULTS AND DISCUSSION

The analytical and physical data for the complexes are listed in Table 1. On the basis of analytical data the metal complexes are found to have 1 : 1 (metal–ligand) stoichiometry and some complexes are also associated with two molecules of water. The molar conductance values of the complexes in DMF at 10^{-3} M suggest that they are 1 : 2 electrolytes [7]. Unfortunately, we could not grow any single crystal suitable for X-ray crystallographic studies.

IR spectra

Important IR absorption frequencies of ligands and their complexes, along with their assignments, are listed in Table 2.

The IR spectra of complexes 1–6 exhibit an absorption in the region 3600–3000 cm^{-1}, with maxima at around 3400, 3300, 3200 and 3100 cm^{-1}. It is attributable to the simultaneous presence of lattice and coordinated water, NH amine group, OH phenolic group and OH oxime group (for complexes 3–6) [8–10]. This indicates the coordination of these groups to the metal ion without deprotonation, and they have undergone a shift to higher wavenumbers in the complexes.

The band assigned to ν(C=N) is shifted to lower frequency by 20 cm^{-1} in the complexes 4–6 [11–13]. The band assigned to ν(C—N) remains unaltered in the spectra of complexes 1–3, but it shows a shift of about 20 cm^{-1} towards the lower region in the complexes 4–6 [14]. The (C—O) band observed at 1030–1065 cm^{-1} in the IR spectra of ligands undergoes a slight shift of 10 cm^{-1} to high energies upon coordination [8,10]. The band originated from the N—O stretching vibration exhibits a shift of 20 cm^{-1} to the lower region in the complexes 4–6 [15].

The coordination mode of ligands is further supported by the appearance of ν(Cu—O) and ν(Cu—N) bands in the region 665–400 cm^{-1} [10,16].

The IR results show that the metal is coordinated through the nitrogen atom of the amine group and the oxygen atom of the phenolic group and besides through the oxygen atom of the oxime group for complexes 4–6 without any deprotonation of the ligand.

Electronic spectra

The electronic absorption spectra of Cu^{II} chelates recorded in DMSO solution exhibit prominent bands or shoulders in the range 14000–16200 cm^{-1} and 17000–18400 cm^{-1} and high intensity absorption in the region 25900–27400 cm^{-1} (Table 4). The first two

Table 2. Relevant IR data (cm^{-1}) of the ligands and complexes

Compound	ν(OH)^a	ν(OH)^a	ν(NH)	ν(OH)^c	ν(OH)^d	ν(C=N)	ν(C—N)	ν(C—O)	ν(N—O)	ν(M—O)^a	ν(M—O)^d	ν(M—O)^c	ν(M—N)
H_2L^1	—	—	3275s	3114w	—	—	1258s	1036s	—	—	—	—	—
H_2L^2	—	—	3295s	3061m	—	—	1265s	1030s	—	—	—	—	—
H_2L^3	—	—	3200sh	3100s	—	—	1263s	1030s	—	—	—	—	—
H_2L^4	—	—	3275s	3170m	3050m	1645m	1258s	1036m	1029w	—	—	—	—
H_2L^5	—	—	3295s	3130s	3054m	1620m	1265s	1050m	1030m	—	—	—	—
H_2L^6	—	—	3243sh	3128m	3070m	1593s	1269s	1065m	1040w	—	—	—	—
1	3400b	—	3312m	3233s	—	—	1260s	1040s	—	—	—	532w	415w
2	3400sh	3289w	3250sh	3128sh	—	—	1260s	1038m	—	565m	—	496w	457w
3	3400b	3314sh	3228m	3120w	—	—	1258sh	1042m	—	590m	—	484w	442w
4	3400sh	3371sh	3343m	3186m	3057w	1620s	1243w	1049m	1022m	669m	594m	500w	478w
5	3445s	3362s	3345s	3214m	3143sh	1597s	1244s	1071m	1020w	657m	592m	520w	500w
6	3400b	3286sh	3257m	3157sh	3100sh	1574m	1240s	1070m	1018m	628w	571w	514w	457w

s = strong; m = medium; b = broad; sh = shoulder; w = weak; a = aqua; c = phenolic; d = oxime

Table 3. ^{1}H NMR data of ligands

	CH$_3$			CH$_2$			CH					
Compound	1^a	2	3	4	5	6	7	8	C$_6$H$_4$	NH	OH	solvent
H$_2$L^1	—	—	—	2.80	—	3.90	—	—	6.70–7.00	7.10	7.40	CDCl$_3$
H$_2$L^2	—	—	1.50	2.80	—	—	—	3.90	6.70–7.10	—	—	DMSO-d
H$_2$L^3	—	—	1.40	2.00	2.20	—	—	3.40	6.70–7.00	7.10	7.30	CDCl$_3$
H$_2$L^4	1.80	2.10	—	2.90	—	3.80	7.30	—	6.50–6.90	—	—	DMSO-d
H$_2$L^5	1.90	2.10	3.10	3.80	—	—	7.40	4.20	6.90–7.20	8.40^b	8.40^b	CDCl$_3$
H$_2$L^6	1.40	2.10	2.90	3.10	3.40	—	7.40	4.30	6.80–7.20	9.50^b	9.50^b	CDCl$_3$

[a] 1 : OHNCCH$_3$; 2 : NCCH$_3$; 3 : R ; 4 : NCH$_2$; 5 : C$_2$H$_5$; 6 : CHR(R = H) ; 7 : NCH ; 8 : CHR.
[b] Broad signals.

Table 4. Magnetic and electronic spectral data of copper(II) complexes

Compound	μ_{eff}^{a}	Electronc transitions^b (ε)^c		
1	1.88	16 100 (510)	18 350 (640)	27 300 (6700)
2	1.92	15 750 (200)	18 000 (300)	26 650 (1000)
3	2.01	15 400 (270)	17 850 (360)	27 750 (1900)
4	1.96	16 000 (450)	18 200 (650)	27 000 (1600)
5	2.02	15 500 (400)	17 850 (600)	26 300 (4400)
6	1.97	14 300 (300)	17 100 (700)	26 000 (2250)

[a] Magnetic moment in Bohr magnetons.
[b] Wavenumber in cm^{-1}.
[c] Absorption molar coefficient in mol^{-1} l cm^{-1}.

regions correspond to the ligand field bands, the third one which has a higher intensity is due to the intra-ligand transition $\pi \rightarrow \pi^*$ [17]. The bands observed around 15 000 cm^{-1} and 18 000 cm^{-1} are reported to be characteristic of square planar or tetragonally distorted octahedral symmetry and are assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively [10,14,18].

Magnetic measurements

The room temperature magnetic moments of copper(II) chelates are in the range 1.88–2.02 BM (Table 4). These values are essentially due to spin only moment and are characteristic of square planar or tetragonally distorted octahedral symmetry around copper(II) [14,18]. The values are consistent with an orbitally non-degenerate ground state for the copper(II) and indicate that the complexes are mononuclear in nature [3,18].

Electron spin resonance spectra

The parameters $g_\parallel$, $g_\perp$ and $A_\parallel$, $A_\perp$ shown in Table 5 have been determined from experimental spectra of glass or polycrystalline samples. Three weak lines have been obtained in the cases of complexes 1,2,5,6 and the fourth line seems to be merged with the strong line. The values of $g_\parallel$ and $A_\parallel$ were determined from weak lines and $g_\perp$ from a strong line. Since the strong lines are not fully resolved, $A_\perp$ is calculated from the expression

$$A_0 = (A_\parallel + 2A_\perp)/3,$$

where A_0 is the isotropic hyperfine coupling constant obtained from the solution spectra. The results with g_0 are shown in Table 5.

The ESR spectra of all the complexes exhibit absorption typical for the mononuclear species and correspond to an axially elongated tetragonal stereochemistry. The trend $g_\parallel > g_\perp > g_e$ (2.0023) observed in these complexes shows that the unpaired electron is in the $d_{x^2-y^2}$ orbital of the copper(II) ion [19].

The present ESR results show that $g_\parallel$ is less than 2.3 in all the cases suggesting that the copper complexes are covalent in nature; they show also that $g_\parallel = 2.232$–2.260 which is in conformity with the presence of mixed copper–nitrogen and copper–oxygen bonds in these chelates [18].

The lowering of $A_\parallel$ values of the complexes 5,6 is probably an indication of the distortion of the copper environment.

The ESR spectra in CHCl$_3$ solution of the copper complexes consist of four hyperfine groups corresponding to $I_{Cu} = 3/2$ and splitting into five lines

Table 5. ESR spectral data and bonding parameters of copper(II) complexes

Complex	g_0	$A_0(Cu)10^4$ (cm^{-1})	$A_0(N)10^4$ (cm^{-1})	$g_\parallel$	$g_\perp$	g_{av}	$A_\parallel\ 10^4$ (cm^{-1})	$A_\perp\ 10^4$ (cm^{-1})	$\alpha^2\beta_1^2$	$\alpha^2\beta^2$	κ
1	2.130	39.6	7.0	2.232	2.092	2.138	100.3	9.3	0.560	0.997	0.246
2	2.114	42.0	7.0	2.237	2.093	2.141	93.3	16.3	0.558	0.990	0.255
3	2.121	44.3	7.0	2.242	2.090	2.140	—	—	0.557	0.949	0.261
4	2.088	42.0	7.0	2.233	2.093	2.140	—	—	0.558	0.999	0.254
5	2.078	42.0	7.0	2.240	2.094	2.142	88.0	18.6	0.557	0.992	0.256
6	2.092	46.6	7.0	2.260	2.095	2.150	70.0	35.0	0.556	0.959	0.277

each in the case of Cu—H_2L^{1-3} complexes (Fig. 3(a)) and into three lines in the complexes Cu—H_2L^{4-6} (Fig. 3(b)), although the first two are not so well resolved. The superhyperfine structure is attributable to interaction of the copper ion's unpaired electron with two nitrogen nuclei ($I_N = 1$) in complexes 1–3 and with one nitrogen nucleus in complexes 4–6.

The expressions for $g_\parallel$ and $g_\perp$ gave values of $\alpha^2\beta_1^2$ and $\alpha^2\beta^2$, where α and β_1 represent in-plane σ and π bonding, respectively, and β represents out-of-plane π bonding. The magnitudes of $\alpha^2\beta_1^2$ and $\alpha^2\beta^2$, which are a measure of the combined σ and π covalent bonding effects (see Table 5), lie between 1.0 and 0.25 which represent the values of 100% ionic and covalent character respectively. They are indicative of a considerable in-plane and very little out-of-plane covalent character of the metal–ligand bonding in the copper(II) complexes. In all the present complexes, $\alpha^2\beta_1^2$ and $\alpha^2\beta^2$ suggest that in-plane bonding is present.

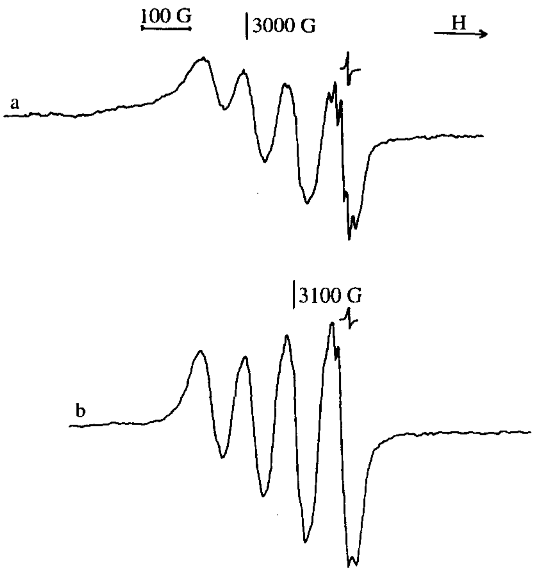

Fig. 3. ESR spectrum of (a) $[Cu(H_2L^1)]Cl_2$; (b) $[Cu(H_2L^4)(H_2O)_2]Cl_2$; in solution at room temperature.

By examining the trend of the $\alpha^2\beta_1^2$ and $\alpha^2\beta^2$ values obtained, it can be seen that the covalent character in the copper(II) complexes with the alkyl substituted ligands should increase in the order of substituents $H < CH_3 < C_2H_5$. This order satisfactorily correlates with electron density at the nitrogen donor atom which shows the same trend. Then the $\alpha^2\beta_1^2$ values for compounds 1–3 differ slightly from those for compounds 4–6. It can be concluded that a direct relation between the basicity of the amine and the character of bonding exists.

The values obtained for *K*, the Fermi contact hyperfine interaction (Table 5) are in good agreement with those estimated in the literature [18].

On the basis of the above results, the following schemes may be suggested for the complexes.

In complex 1 (Fig. 4) the ligand H_2L^1 is bonded to the copper ion through phenolic oxygens and amine nitrogens providing a square planar geometry.

For complexes 2 and 3 (Fig. 5) the ligands give a square planar arrangement of N_2O_2 donor groups around the copper ion. The other axial sites being occupied by water molecules.

In complexes 4–6, the environment of the copper ion is a distorted octahedron in which two *cis*-coordination sites are occupied by water molecules and the other by the tetradentate ligand. The construction of molecular models of complexes shows that the ligand gives several conformations. The most probable structure is represented by Fig. 6.

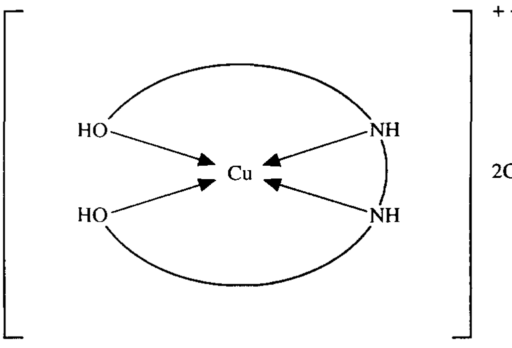

Fig. 4. Structural scheme of Cu-H_2L^1 complex.

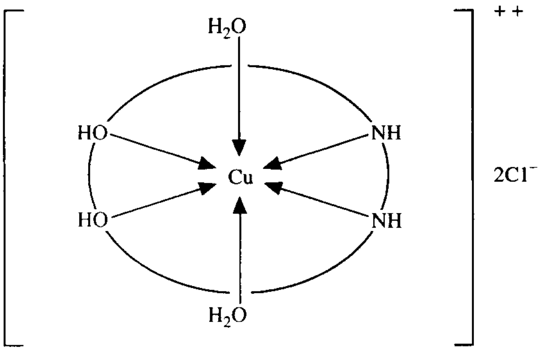

Fig. 5. Structural scheme of Cu-$H_2L^{2,3}$ complexes.

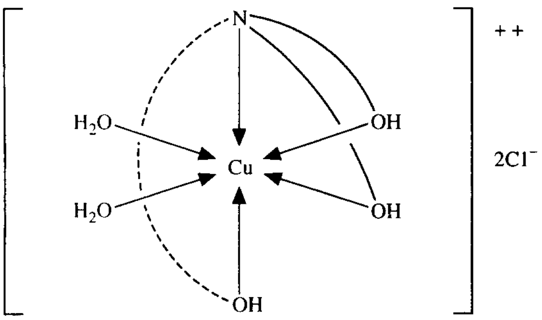

Fig. 6. Structural scheme of Cu-$H_2L^{4\text{–}6}$ complexes.

Cyclic voltammetry

The electrochemical behaviour of complexes 1–6 was investigated by cyclic voltammetry at a platinium electrode. Coulometric analysis indicates that each of the processes involves a one-electron transfer. Tripodal ligands $H_2L^{4\text{–}6}$ undergo one electron cathodic process which can be assigned to the reduction of the oxime group (Table 6).

The cyclic voltammogram of $CuCl_2$ compound shows two irreversible reduction processes (Table 6) and a single anodic peak at +0.640 V without any associated cathodic response. The electrochemical results on reduction of complexes 1–6 are summarized in Table 6.

In DMSO each complex shows two reductions at separate potentials, besides a reduction is observed in the limit of potential range studied (+0.7 V to −1.6 V) for the complexes 4–6. By comparing the cyclic voltammograms of complexes to those of ligands and that of $CuCl_2$—$6H_2O$ taken as reference, the first and the second reduction processes (see Fig. 7(a),(b)) should correspond to Cu(II/I) and Cu(I/0). The additional reversible reduction in the case of complexes 4–6 (Fig. 7(b)) could be assigned to ligand-centered reduction [1,20].

For all complexes, both metal centred electron-transfers are electrochemically irreversible, except for the first couple of 1. This results probably from a minimal change in the structure of the complex 1 (from square planar to tetrahedron) [1].

Table 6. Electrochemical data for reduction of ligands, $CuCl_2$ and Cu^{II} complexes[a] in 0.1 M TBAP in DMSO

Compound	E_{pc} (V)	E_{pa} (V)	ΔE(V)	$E_{1/2}$ (V)
H_2L^4	−1.600	−0.300	—	—
H_2L^5	−1.540	−0.240	1.300	−0.890
H_2L^6	−1.400	−0.260	1.140	−0.830
$CuCl_2$	−0.320	0.140	0.460	−0.090
	−0.960	−0.380	0.560	−0.670
1	−0.380	−0.280	0.100	−0.330
	−1.220	−0.800	0.420	−1.010
2	−0.680	0.100	0.780	−0.290
	−1.300	−0.360	0.940	−0.830
3	−0.660	0.140	0.800	−0.260
	−1.200	−0.400	0.800	−0.800
4	−0.600	0.180	0.780	−0.210
	−0.960	−0.300	0.660	−0.630
	−1.440	−1.120	0.320	−1.280
5	−0.620	0.160	0.780	−0.230
	−1.180	−0.360	0.820	−0.770
	−1.480	−1.180	0.300	−1.330
6	−0.630	0.120	0.750	−0.255
	−1.200	−0.380	0.820	−0.790
	−1.540	−1.220	0.320	−1.380

[a] Solute concentration = 10^{-3} M; scan rate = 100 mV/s; E_{pc} and E_{pa} are the cathodic and anodic peak potential, respectively; $\Delta E = E_{pa} - E_{pc}$; $E_{1/2} = 1/2\ (E_{pa} + E_{pc})$.

Further, in the negative potential range and on the cathodic scan, the first two waves shown by the cyclic voltammograms of complexes 2–6 are of poor or medium intensity. But on the reverse sweep, the anodic peaks related with the cathodic waves are intense. This indicates that on the cathodic reduction the electrode process is complicated by a chemical reaction [21].

More positive $E_{1/2}$ values were found for the complexes with tripodal ligands. The construction of molecular models of these complexes confirms that a tetrahedral structure is realized most easily with these ligands and consequently this causes an easier reduction of copper(II) to copper(I) [22].

The reduction potentials for the Cu(II/I) couple of complexes are sensitive to steric and electronic effects of the substituent R in the ligand. These potentials shift anodically on going from 1 to 3 and cathodically from 4 to 6.

The distortion of the unit CuN_2O_2 in complexes 1–3 increases on going from hydrogen to ethyl. This stabilizes copper(I) which favors a tetrahedral geometry [22]. In the complexes 4–6 with large size tripodal ligands which are more able to accommodate the larger copper(I) ion, the electron density on the copper ion increase from R = H to R = C_2H_5, this increases the difficulty to reduce the metal center [23].

The electrochemical results for oxidation of copper(II) complexes 1–6 showed one reversible couple

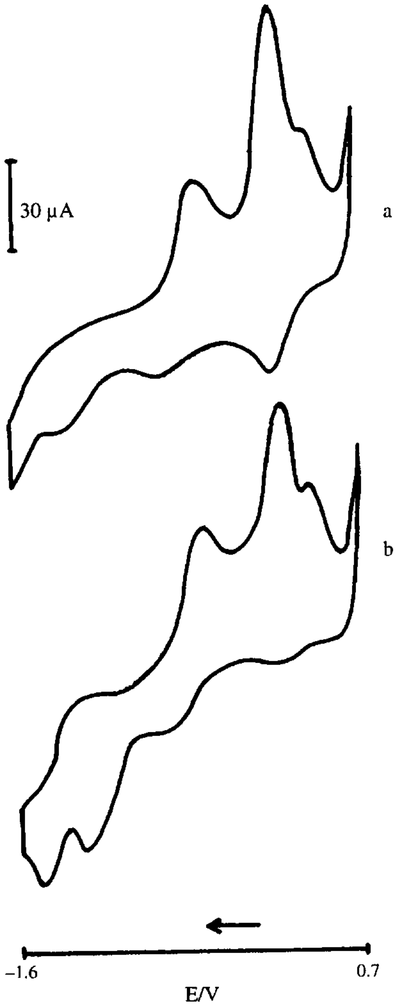

Fig. 7. Cyclic voltammograms for the complexes (a) $[Cu(H_2L^2)(H_2O)_2]Cl_2$; (b) $[Cu(H_2L^5)(H_2O)_2]Cl_2$; in DMSO (0.1 M TBAP); scan rate = 100 mV.

at around +0.260 volt *vs* SCE (the ratio i_p^{red}/i_p^{ox} is very close to one), assigned to Cu(III/II) charge transfer. This result indicates that the oxidation of copper(II) complexes is not so sensitive to electronic and size effects of ligands. This suggests that there is not a significant structural change between the oxidized ($3d^8$) and reduced ($3d^9$) species.

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