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Synthesis, spectra and electrochemical behaviour of biomimetic copper(II) complexes with CuN_5 and CuN_6 chromophores

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Abstract

The $Cu(ClO_4)_2$ complexes of the two pentadentate ligands, *N*-(2-hydroxyethyl)-*N,N',N'*-tris(benzimidazol-2'-ylmethyl)-1,2-ethanediamine and its 6'-methyl derivative and four sexadentate ligands, *N,N,N',N'*-tetrakis(benzimidazol-2'-ylmethyl)-1,2-ethanediamine, *N,N,N',N'*-tetrakis(benzimidazol-2'-ylmethyl)-1,2-cyclohexanediamine and their 6'-methyl derivatives have been isolated and studied. They are of the type $CuL(ClO_4)_2 \cdot nH_2O$ where $n=0$, 1. All the complexes exhibit two ligand field bands and the $\bar{\nu}_{max}$ and ϵ values are lower and higher, respectively, than the range known for CuN_4 chromophores. Compared to the latter they also have high $g_\parallel$, low $A_\parallel$ and high $g_\parallel/A_\parallel$ values. These spectral data are consistent with an appreciable displacement and/or tetrahedral twist of copper from the N_4 square plane of the complexes. The anchoring of a bulky benzimidazole moiety to *N,N'*-bis(benzimidazol-2-ylmethyl)-1,2-ethanediamine to incorporate a N-donor axial to the planar CuN_4 chromophore decreases CFSE and enhances the Cu^{II}–Cu^I redox potential. However, addition of two benzimidazole nitrogens to the N_4 ligand to obtain a CuN_6 chromophore, depresses the redox potential. Further, the fusion of a cyclohexyl ring into the above CuN_6 chromophore dramatically leads to elevation in $E_{1/2}$ with increase in reversibility. The introduction of a methyl group in the aromatic ring, far away from the redox centre, depresses $E_{1/2}$.

Keywords: Copper complexes; Multidentate ligand complexes; EPR spectra; Electrochemistry

1. Introduction

Although the biological roles of blue copper proteins are not yet fully understood, they are thought to function as electron carriers with the aid of interconversion between Cu^{II} and Cu^I states. The rather high redox potential of these proteins has been ascribed [1] to the coordination of copper to soft sulfur atoms and the trigonal geometry [2–6] of the 4–4 inner coordination sphere of the copper(II) ion forced by the protein superstructure which results in a small stereochemical reorganisation upon one electron addition. This has stimulated a great deal of work towards the characterisation of low molecular weight copper complexes with a coordination geometry similar to the active sites in these proteins. As histidine (imidazole) ligands are known [2,4] to constitute these active sites, we became interested in copper(II) complexes of synthetically accessible benzimidazole ligands.

In continuation of our work on copper(II) complexes of tri- [7] and tetradentate [8] benzimidazole ligands to understand the effect of bulky benzimidazole on structure and redox, we wish to add one (L2, L3) or two (L4, L5) (Scheme 1) benzimidazol-2-ylmethyl tentacles incapable of independent orientation to *N,N'*-bis(benzimidazol-2'-ylmethyl)-1,2-ethanediamine [8] (L1) to generate sterically constrained 'superstructure-like' tripodal or tetrapodal-like ligands, respectively, impose an unusual geometry around copper(II) and study the effect of such changes in ligand structure on spectra and redox behaviour. Such a study may help unravel the factors which lead to a minimal reorganisation barrier in biological redox systems. In fact, the X-ray crystal structure [9] of $[CuL4]^{2+}$ reveals a square-bicapped geometry around copper(II). Further, the fusion of cyclohexyl rings into L4 and L5 to construct L6 and L7 ligands is expected to lower the barrier for structural reorganisation and enhance the reversibility of the Cu^{II}–Cu^I couple. In this paper the preparation and spectroscopic and electrochemical properties of

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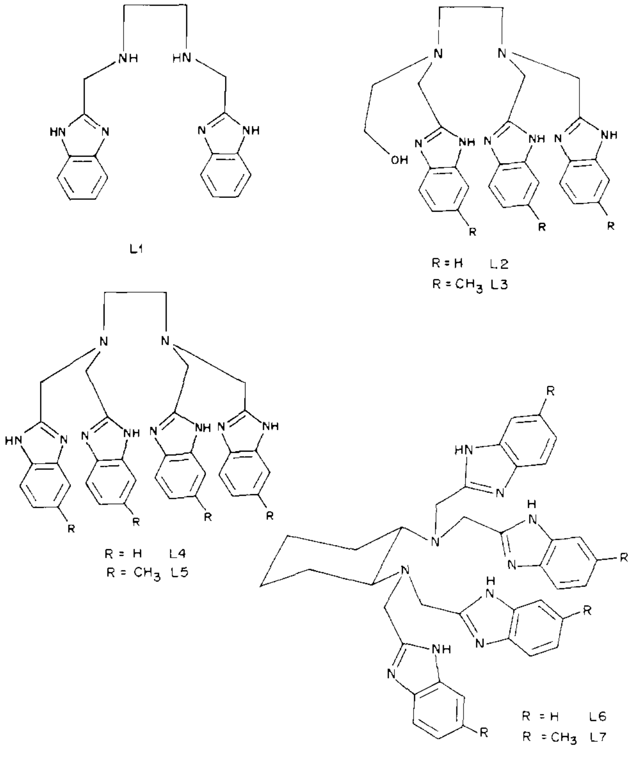

Scheme 1.

copper(II) perchlorate complexes of L2–L7 are discussed.

2. Experimental

2.1. Materials

$Cu(ClO_4)_2 \cdot 6H_2O$ and tetra-n-hexylammonium perchlorate were from G.F. Smith. Ethylenediamine tetraacetic acid (SDs, India), cyclohexane-1,2-diamine tetraacetic acid (Aldrich), and *N*-(2-hydroxyethyl)ethylenediamine triacetic acid (Aldrich) were used as received. 1,2-Diaminobenzene and 4-methyl-1,2-diaminobenzene were obtained from SISCO, India and Fluka, respectively, and used as received. Dry methanol was prepared by refluxing it with magnesium turnings and iodine and then distilling over $CaCl_2$.

2.2. Synthesis of ligands

N-(2-Hydroxyethyl)-*N*,*N*′,*N*′-tris(benzimidazol-2′-ylmethyl)-1,2-ethanediamine (L2) and *N*-(2-hydroxyethyl)-*N*,*N*′,*N*′-tris(6′-methylbenzimidazol-2′-ylmethyl)-1,2-ethanediamine (L3) were synthesised as reported in the literature [10]. *N*,*N*,*N*′,*N*′-Tetrakis(benzimidazol-2′-ylmethyl)-1,2-ethanediamine (L4) and *N*,*N*,*N*′,*N*′-tetrakis(6′-methylbenzimidazol-2′-ylmethyl)-1,2-ethanediamine (L5) were synthesised employing the procedure reported in the literature [11]. *N*,*N*,*N*′,*N*′-Tetrakis(benzimidazol-2′-ylmethyl)-1,2-cyclohexanediamine (L6) and *N*,*N*,*N*′,*N*′-tetrakis(6′-methylbenzimidazol-2′-ylmethyl)1,2-cyclohexanediamine (L7) were prepared as reported elsewhere [12].

2.3. Synthesis of complexes

$CuL4(ClO_4)_2$ and $CuL5(ClO_4)_2 \cdot H_2O$. These were obtained as reported in the literature [9,11].

$CuL2(ClO_4)_2$ and $CuL3(ClO_4)_2 \cdot H_2O$. To L2 (0.495 g, 1 mmol) or L3 (0.537 g, 1 mmol) dissolved in absolute methanol (25 ml) was added $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) dissolved in absolute methanol (10 ml) with stirring. The resulting green coloured solution was kept at room temperature for about 48 h. The green solid that precipitated was filtered off, washed with cold absolute methanol and dried under vacuum over P_4O_{10}. *Anal.* Calc. for $CuL2(ClO_4)_2$, $CuC_{28}H_{30}N_8O_9Cl_2$: C, 44.4; H, 4.0; N, 14.8; Cu, 8.4. Found: C, 44.6; H, 3.9; N, 14.8; Cu, 8.6%. Calc. for $CuL3(ClO_4)_2 \cdot H_2O$, $CuC_{31}H_{38}N_8O_{10}Cl_2$: C, 45.6; H, 4.7; N, 13.7; Cu, 7.8. Found: C, 45.8; H, 4.6; N, 13.6; Cu, 7.9%.

$CuL6(ClO_4)_2$ and $CuL7(ClO_4)_2 \cdot H_2O$. L6 (0.633 g, 1 mmol) or L7 (0.689 g, 1 mmol) was dissolved in warm absolute methanol (25 ml) and added with stirring to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) in absolute methanol (10 ml). Upon standing overnight a light blue crystalline or green solid was obtained and this was filtered off, washed with cold absolute methanol and dried under vacuum over P_4O_{10}. *Anal.* Calc. for $CuL6(ClO_4)_2$, $CuC_{38}H_{38}N_{10}O_8Cl_2$: C, 50.9; H, 4.3; N, 15.6; Cu, 7.1. Found: C, 50.9; H, 4.5; N, 15.8; Cu, 7.4%. Calc. for $CuL7(ClO_4)_2 \cdot H_2O$, $CuC_{42}H_{48}N_{10}O_9Cl_2$: C, 51.9; H, 5.0; N, 14.4; Cu, 6.5. Found: C, 51.5; H, 4.8; N, 14.6; Cu, 6.6%.

Caution! All the copper compounds reported in this work contain perchlorate anions. Although no accidents with the present perchlorates occurred during the experimental work for this article, it should be pointed out that perchlorates are hazardous because of the possibility of explosion.

2.4. Physical measurements

Elemental analyses were performed at CDRI, Lucknow, India. The copper content of the complexes was estimated by ethylenediaminetetraacetate titration after decomposing the complexes with a mixture of concentrated HNO_3 and concentrated H_2SO_4 and extracting with concentrated HCl (2 ml).

The IR spectra of the complexes were measured on a Shimadzu IR 435 spectrophotometer. The diffuse reflectance and methanol solution spectra were measured on a HITACHI U-3410 double beam UV/Vis/NIR spectrophotometer and EPR spectra were obtained on a Varian E 112 X-band spectrometer, calibrated with diphenylpicrylhydrazide (dpph). The spectra of the solid and solution were measured at ambient and liquid nitrogen temperatures. The values of $g_{\|}$ and $A_{\|}$ were calculated from 77 K and g_0/g_{av} and A_0/g_{av} from r.t. spectra.

Cyclic voltammetry and differential pulse voltammetry were performed on a platinum sphere electrode. A three-electrode cell configuration was used, the reference electrode being Ag(s)–$AgNO_3$ (0.01 M), $N(C_6H_{13})_4ClO_4$ (0.1 M) in acetonitrile. The temperature of the electrochemical cell was maintained at 25±0.2 °C by a cryocirculator (HAAKE D8 G). The solutions were deoxygenated by bubbling research grade nitrogen. The instrument utilised included a EG&G PAR 273 potentiostat/galvanostat. An IBM PS-2 computer with EG&G M270 software was employed to carry out the experiments and to acquire the data.

3. Results and discussion

The presence of an unsplit band around 1050 cm^{-1} in the IR spectra of all the present complexes suggests that ClO_4^- cannot possibly be coordinated to copper.

3.1. Electronic absorption spectra

The reflectance spectra of all the complexes display a broad ligand field band with a low energy shoulder (Table 1), suggesting a square-based geometry [13] around Cu(II). On dissolution in methanol the main feature is shifted to relatively higher energies with increased band separation (4600–5200 cm^{-1}) suggesting participation of the solvent in the coordination sphere. The average of energies of the bands in solution is much lower than the range (17 000–19 000 cm^{-1}) expected for a CuN_4 square environment [8,14–16]; this suggests the presence of strong axial interaction and/or tetrahedral distortion [17–19]. Thus, in the X-ray crystal structure [9] of $[CuL4]^{2+}$ is present a distorted bicapped square pyramidal geometry with four benzimidazole groups constituting the basal plane showing marked tetrahedral twist; the two tertiary nitrogens are involved in bicapped axial interaction. Obviously all the other CuN_6 complexes with ligand field spectra similar to $[CuL4]^{2+}$ would possess a similar bicapped square structure in the solid state. Structure 1(b) rather than 1(a) (Fig. 1) for the CuN_5 chromophore seems to be probable, as tertiary [20,21] nitrogen has been known to coordinate axially. Further, such tripodal-like ligands have been shown [21,22] to adopt square-based geometries. However, single crystal X-ray structures are needed to confirm such suggestions but attempts to grow good single crystals of complexes with CuN_5 chromophore were fruitless.

Table 1
Electronic absorption spectral data[a] for the Cu(II) complexes ($\tilde{\nu}_{max}$ (cm^{-1}) with ϵ (M^{-1} cm^{-1}) in parentheses)

Compound	Medium	Ligand field	Charge transfer
$[CuL2]^{2+}$	solid	14006 12300	
	MeOH	14492(103) 9302(40)	28818(sh)(594)
$[CuL3]^{2+}$	solid	14104 12195	
	MeOH	14906(111) 9497(32)	27027(sh)(541)
$[CuL4]^{2+}$	solid[b]	14104 12195	
	MeOH[b]	14205(147) 9597(36)	31153(877)
$[CuL5]^{2+}$	solid[c]	13908 12107	
	MeOH[c]	14306(126) 9200(35)	27778(sh)(706)
$[CuL6]^{2+}$	solid	13699 12300	
	MeOH	14306(141) 9497(59)	28818(sh)(872)
$[CuL7]^{2+}$	solid	13908 12195	
	MeOH	14492(149) 9497(50)	28818(sh)(1169)

sh = shoulder.
[a] Concentration, ≈ 1×10^{-3} M.
[b] Data consistent with ref. [9].
[c] Data consistent with ref. [11].

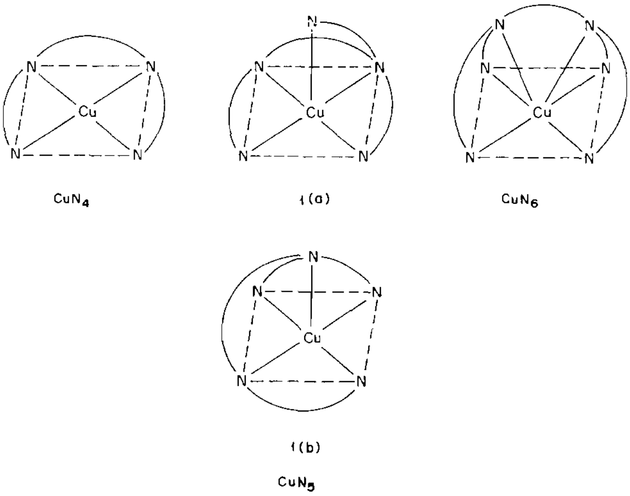

Fig. 1. Coordination structures of CuN_4, CuN_5 (a and b) and CuN_6 chromophores.

The band observed around 30 000 cm^{-1} for all the complexes in methanol has been assigned to the $N(\pi_{het}) \rightarrow Cu(II)$ charge transfer (CT) transition on the basis of its similarity to that exhibited by Cu(II): bzim (1:8) solution [8] and $CuL1(ClO_4)_2$ complexes [8].

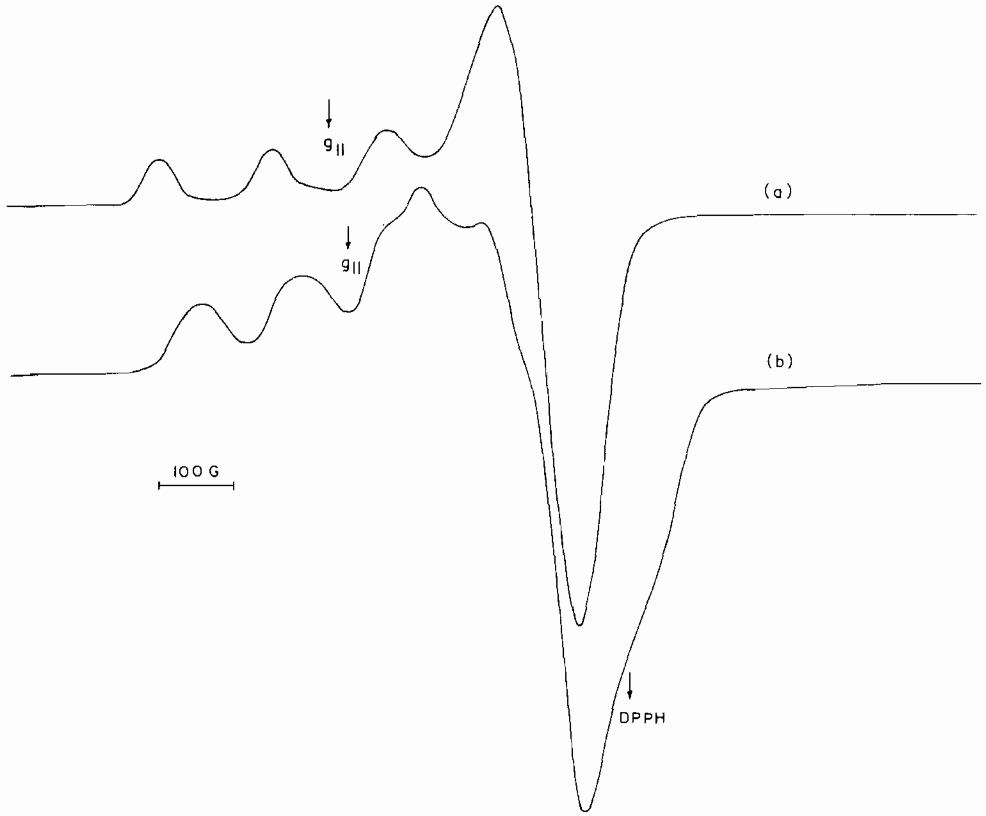

Fig. 2. (a) 77 K X-band EPR spectrum of $[CuL3]^{2+}$ in methanol:acetone (4:1 vol./vol.) glass. (b) 77 K X-band EPR spectrum of $[CuL6]^{2+}$ in methanol:acetone (4:1 vol./vol.) glass.

3.2. EPR spectra

The polycrystalline and frozen solution spectra (Fig. 2) of all the present complexes are clearly axial ($g_{\|} > g_{\perp} > 2.0$, Table 2) and suggest a $d_{x^2-y^2}$ ground state for Cu(II) in a square-based geometry. The $g_{\|}$ values for CuN_4 chromophores [8,14] are in the range 2.10–2.22. Since the values of $g_{\|}$ and $A_{\|}$ are known to increase and decrease, respectively, with increase [17,19] in either tetrahedral distortion or axial interaction, the relatively higher $g_{\|}$ values observed for the present complexes suggest the presence of tetrahedral and/or strong axial interaction, in line with electronic spectral results. Further, the $g_{\|}/A_{\|}$ quotient [23] ranges from 105 to 135 cm for square planar Cu(II) complexes and so an enhancement in the $g_{\|}/A_{\|}$ quotient would be expected on increasing the tetrahedral and/or axial interaction. Thus for the present square-pyramidal CuN_5 and bicapped square-pyramidal CuN_6 complexes and for Cu(II) bis(benzimidazolyl)-diaza complexes [8] the enhanced values of the $g_{\|}/A_{\|}$ quotient (140–178 cm, Table 2) represent, as expected, increasing axial interaction and/or tetrahedral distortion in the order $CuN_4 < CuN_5 < CuN_6$.

For all the present complexes the $g_{\|}$ values are almost the same but $A_{\|}$ varies dramatically ($128–162 \times 10^{-4}$ cm^{-1}). This is because the addend is a part of the ligand system and copper is pushed out of the N_4 equator; the latter results in a change in the orientation of the lone pair orbitals of the equatorial N-donor towards the $d_{x^2-y^2}$ orbital.

Table 2
Electron paramagnetic resonance spectral data[a] for the copper(II) complexes

Complex	Medium[b]	g_0/g_{av}	A_0/A_{av}	$g_{\|}$	$A_{\|}$	$g_{\|}/A_{\|}$
$[CuL2]^{2+}$	Pc	2.144	63	2.259	143	158
	solution	2.141	67	2.270	159	143
$[CuL3]^{2+}$	Pc	2.140	61	2.247	155	145
	solution	2.137	65	2.268	162	140
$[CuL4]^{2+}$	Pc[c]	2.153	75	2.264	168	135
	solution[c]	2.167	61	2.279	146	156
$[CuL5]^{2+}$	solution[d]	2.146	61	2.281	142	161
$[CuL6]^{2+}$	Pc	2.142	70	2.254	146	154
	solution	2.137	53	2.251	140	161
$[CuL7]^{2+}$	Pc	2.147	70	2.260	138	164
	solution	2.148	61	2.262	145	156

[a] Values determined as described in the experimental section; $A_{\|}$ values in 1×10^{-4} cm^{-1}; rhombic features are observed for most of the spectra.

[b] Pc = polycrystalline; methanol–acetone (4:1 vol./vol.) solution.

[c] Data consistent with Ref. [9].

[d] Data consistent with Ref. [11].

From the observed $A_{\parallel}$ values [7] of $CuL8(ClO_4)_2$ (L8 = N,N′-bis(benzimidazol-2-ylmethyl)-N-methylamine) (146×10^{-4} cm^{-1}) with a planar CuN_3O chromophore and $Cu(L9)_2(ClO_4)_2\cdot2H_2O$ (L9 = N,N-bis(benzimidazol-2-ylmethyl)amine] (180×10^{-4} cm^{-1}) with four benzimidazoles coordinated to Cu(II) in a square planar arrangement and a planar CuO_4 chromophore [24] (132×10^{-4} cm^{-1}), the contribution to $A_{\parallel}$ of four tertiary amine nitrogens has been calculated as 92×10^{-4} cm^{-1}, assuming an additive contribution to $A_{\parallel}$ by ligands in the equatorial plane only. The $A_{\parallel}$ value calculated for $Cu(L8)_2(ClO_4)_2$ using this value is in agreement with that observed [7]. For the present structures 1(a) and 1(b) the $A_{\parallel}$ values calculated similarly are 136 and 158×10^{-4} cm^{-1}, respectively. The latter value is strikingly very close to the observed value of 159×10^{-4} cm^{-1}, supporting structure 1(b), as discussed above.

For the present complexes no N-shf (superhyperfine) is observed, possibly because of the distorted tetragonal structure [17,25] and/or line broadening effects.

3.3. Redox behaviour

In the cyclic voltammograms of all the complexes obtained at the 50 mV s^{-1} scan rate, one reduction wave is observed in the potential range −0.43 to −0.65 V (Table 3) and the corresponding oxidation wave in the range −0.52 to −0.32 V. However, $[CuL7]^{2+}$ exhibits (Fig. 3) three oxidation processes at peaks B, C and D at scan rates 10–1000 mV s^{-1}. The current functions observed are consistent with one electron Cu^{II}–Cu^{I} redox process [8,14,16]. For all the complexes when the scan rate is increased, E_{pc} is shifted cathodically and E_{pa} anodically. The peak current ratio (i_{pa}/i_{pc}) is less than unity (unity for a reversible one electron redox process). The observations, together with the increase in ΔE_p with scan rate, are clearly diagnostic of a quasi-reversible electron transfer followed by an irreversible chemical reaction [26].

An analysis of the electrochemical data (Table 3) shows significant trends in redox potentials and reversibility. The addition of benzimidazole N-donor to the CuN_4 chromophore [8] leads to an increase in the Cu^{II}–Cu^{I} redox potential (20 mV); this is likely on account of the displacement of copper from the CuN_4 equator towards axial nitrogen, as evidenced by the increased $g_{\parallel}/A_{\parallel}$ value, and decreased CFSE [18] ($\bar{\nu}_{max}$ 16 200–14 000 cm^{-1}) and hence destabilisation of Cu^{II}. However, addition of one more benzimidazole N-donor as in $[CuL4]^{2+}$ depresses (60 mV) $E_{1/2}$ in spite of low CFSE and renders the redox irreversible, likely due to the rigid square-bicapped geometry [9] around Cu^{II}; however, for $[CuL5]^{2+}$ there is almost no change in $E_{1/2}$.

Fusion of a cyclohexyl ring into the CuN_6 chromophore as in $[CuL6]^{2+}$ and $[CuL7]^{2+}$ depresses $E_{1/2}$ (50, 110 mV) possibly due to strengthening of the Cu–N_{amine} bond by the electron-donating ability of the cyclohexylene group [27]. The introduction of an electron-releasing methyl group onto the benzimidazole ring, though far away from the redox centre, stabilises Cu^{II}, leading to a depression in $E_{1/2}$ (20–87 mV) but appears to decrease the reversibility (Fig. 4).

4. Conclusions

The present study leads to the conclusion that forced axial coordination of an N-donor to a planar CuN_4

Table 3
Electrochemical data[a] for Cu(II) complexes in methanol at 25 ± 0.2 °C

Complex	E_{pc} (V)	E_{pa} (V)	ΔE_p (mV)	$E_{1/2}$ (V)	$E_{1/2}$[b] (V)	i_{pa}/i_{pc}	i_{pc} (μA)
$[CuL1]^{2+}$	−0.476	−0.320 +0.194[c]	156	−0.398	−0.405 0.129	1.2	
$[CuL2]^{2+}$	−0.430	−0.324 +0.326[c]	106	−0.377	−0.369	0.8	25.8
$[CuL3]^{2+}$	−0.502	−0.320	182	−0.411	−0.447	0.9	21.0
$[CuL4]^{2+}$	−0.552				−0.429		26.1
$[CuL5]^{2+}$	−0.525	−0.375	150	−0.450	−0.449	0.8	24.2
$[CuL6]^{2+}$	−0.530	−0.440	90	−0.485	−0.476	0.6	31.0
$[CuL7]^{2+}$	−0.644	−0.524 −0.338[c] +0.252[c]	120	−0.584	−0.563	0.8	27.5

[a] Measured vs. non-aqueous silver reference electrode; add 0.544 V to convert to NHE. Scan rate: 50 mV s^{-1}. Supporting electrolyte: tetra-n-hexylammonium perchlorate (0.1 M). Under the present experimental conditions the ferrocenium–ferrocene couple was located at +0.644 V. Concentration 0.001 M in complex.

[b] Differential pulse voltammetry (DPV): scan rate, 1 mV s^{-1}, pulse height 50 mV.

[c] Additional anodic peak.

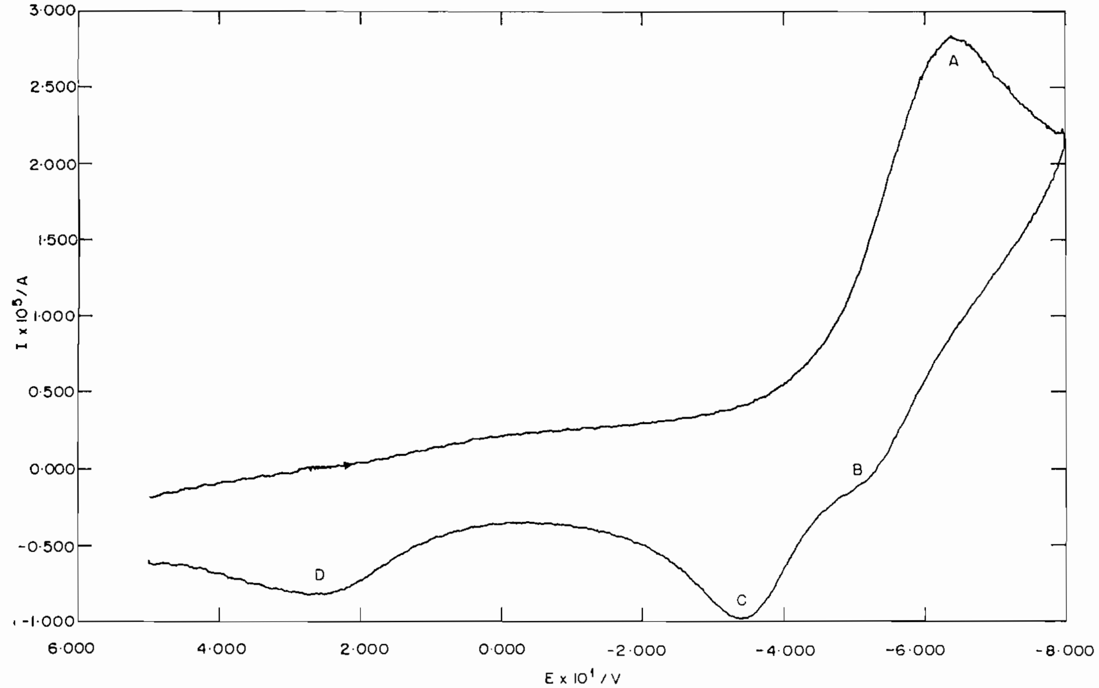

Fig. 3. Cyclic voltammogram of 0.001 M $[CuL7]^{2+}$ in methanol at 25 °C. Supporting electrolyte: 0.1 M $N(C_6H_{13})_4ClO_4$. Scan rate: 50 mV s^{-1}.

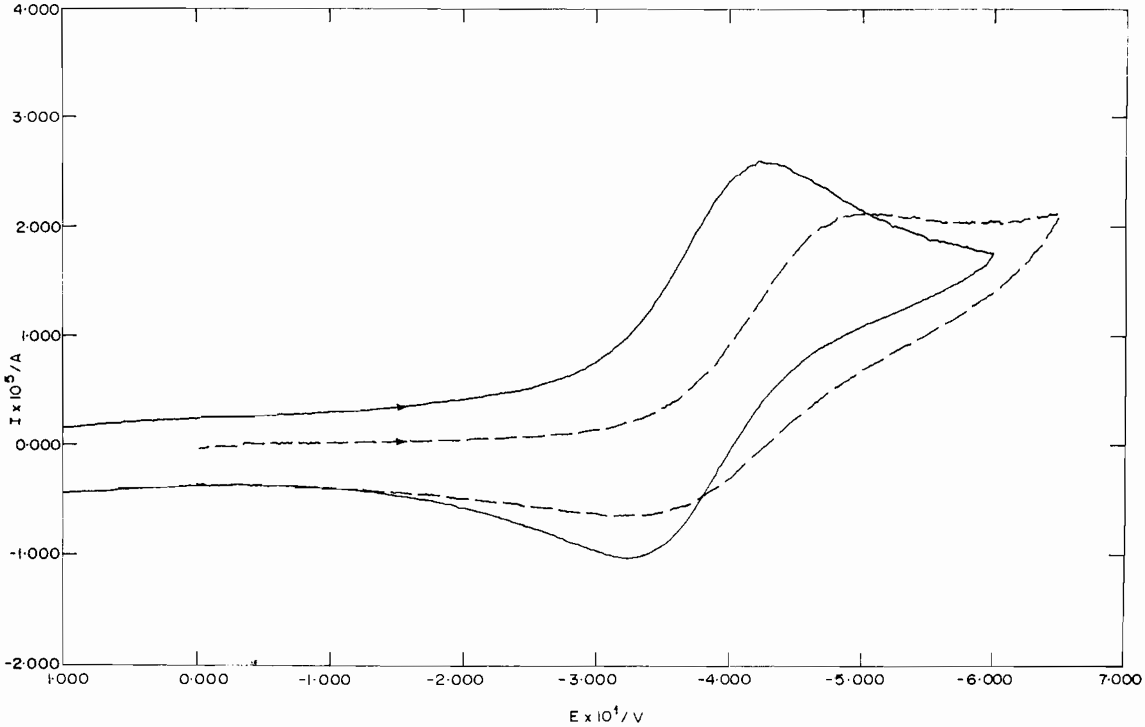

Fig. 4. Cyclic voltammograms of 0.001 M $[CuL2]^{2+}$ (——) and $[CuL3]^{2+}$ (– – –) in methanol at 25 °C. Supporting electrolyte: 0.1 M $N(C_6H_{13})_4ClO_4$. Scan rate: 50 mV s^{-1}.

chromophore displaces Cu^{II} out of the N_4 basal plane towards itself, decreases the CFSE and increases the Cu^{II}–Cu^{I} redox potential. However, the forced bicapped axial coordination of two tertiary N-donors to a planar CuN_4 chromophore results in an N_4 basal plane with a tetrahedral twist caused by intraligand repulsions in the solid state, decreases the CFSE and depresses the redox potential. Such forced coordinations of an axial donor to a square CuN_4 system, as may be achieved in the tertiary structure of a copper-containing protein, will significantly affect the redox potential of the redox centre in a fashion strongly dependent on the nature of the axial ligand.

In this regard it is worthy considering the optical and EPR spectroscopic properties of the present complexes. Out-of-plane displacement of and/or tetrahedral distortion around the copper ion as the structural origin for the low $\bar{\nu}_{max}$ as well as $A_{\parallel}$ values is in itself quite normal. Indeed, displacement of copper out of the basal plane towards the axial ligand in an otherwise square-pyramidal geometry appears to be the rule rather than the exception [14,28]. We have suggested that the $g_{\parallel}/A_{\parallel}$ quotient is a measure of not only tetrahedral distortion but also of such axial displacement from square planarity. In this regard it is interesting to note that unforced axial adduct formation by $Cu(cyclops)^+$ [14] does not lead to an enhanced value of this quotient. Such axial displacement (with or without tetrahedral twist) will allow the copper centre to adjust readily to the dissimilar geometric requirements normally associated with Cu^I and Cu^{II} oxidation states, which must be alternated rapidly on the time scale of enzyme redox chemistry.

Further, the fine-tuning of redox behaviour may be accomplished by incorporating suitable electronic and/or steric factors such as fusion of a cyclohexyl ring, methyl substitution, bulky benzimidazole etc. in the ligand environment in low molecular weight coordination compounds.

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References

[1] (a) J.A. Fee, *Struct. Bonding (Berlin), 23* (1975) 1, and refs. therein; (b) M.A. Augustin, J.K. Yandell, A.W. Addison and K.D. Karlin, *Inorg. Chim. Acta, L35* (1981) 55.

[2] P.M. Colman, H.C. Freeman, J.M. Guss, M. Murata, V.A. Norris, J.A.M. Ramshaw and M.P. Venkatappa, *Nature (London), 272* (1978) 319.

[3] J.M. Guss and H.C. Freeman, *J. Mol. Biol., 169* (1983) 521.

[4] E.T. Adman, R.E. Stenkamp, L.C. Sieker and L.H. Jensen, *J. Mol. Biol., 123* (1978) 35.

[5] E.N. Baker, *J. Mol. Biol., 203* (1988) 1071.

[6] K. Petratos, Z. Dauter and K.S. Wilson, *Acta Crystallogr., Sect. B, 44* (1988) 628.

[7] T. Pandiyan, M. Palaniandavar, M. Lakshminarayanan and H. Manohar, accepted for publication.

[8] T. Pandiyan, M. Palaniandavar, M. Lakshminarayanan and H. Manohar, *J. Chem. Soc., Dalton Trans.,* (1992) 3377.

[9] P.J.M.W.L. Birker, H.M.J. Hendriks, J. Reedijk and G.C. Verschoor, *Inorg. Chem., 20* (1981) 2408.

[10] J. van Rijn, *Ph.D. Thesis* (State University of Leiden), Leiden, Netherlands, 1985.

[11] H.M.J. Hendriks, P.J.M.W.L. Birker, J. van Rijn, G.C. Verschoor and J. Reedijk, *J. Am. Chem. Soc., 104* (1982) 3607.

[12] U. Sivagnanam, T. Pandiyan and M. Palaniandavar, *Indian J. Chem., 32B* (1993) 572.

[13] (a) E.D. Mekenzie, *J. Chem. Soc. A,* (1970) 3095; (b) P. Nagle, E.O. Sullivan, B.J. Hathaway and E. Muller, *J. Chem. Soc., Dalton Trans.,* (1990) 3399.

[14] A.W. Addison, M. Carpenter, L.K.M. Lau and M. Wicholas, *Inorg. Chem., 17* (1978) 1545.

[15] D.E. Nikles, M.J. Powers and F.L. Urbach, *Inorg. Chem., 22* (1983) 3210.

[16] A.W. Addison, M. Palaniandavar, W.L. Driessen, F. Paap and J. Reedijk, *Inorg. Chim. Acta, 142* (1988) 95.

[17] Y. Nonaka, T. Toku and S. Kida, *Bull. Chem. Soc. Jpn., 47* (1974) 312.

[18] H. Yokoi and A.W. Addison, *Inorg. Chem., 16* (1977) 1344.

[19] I. Adato and I. Eliezer, *J. Chem. Phys., 54* (1971) 1472.

[20] K.J. Oberhausen, R.J. O'Brien, J.F. Richardson and R.M. Buchanan, *Inorg. Chim. Acta, 173* (1990) 145.

[21] R. Uma, R. Viswanathan, M. Palaniandavar and M. Lakshminarayanan, *J. Chem. Soc., Dalton Trans.,* (1992) 3563.

[22] H.K. Baek and R.A. Holwerda, *Inorg. Chem., 22* (1983) 3452.

[23] U. Sakaguchi and A.W. Addison, *J. Chem. Soc., Dalton Trans.,* (1979) 600.

[24] D.X. West and M. Palaniandavar, *Inorg. Chim. Acta, 76* (1983) L149.

[25] (a) A.W. Addison, P.J. Burke, K. Henrick, T.N. Rao and E. Sinn, *Inorg. Chem., 22* (1983) 3645; (b) A.W. Addison, T.N. Rao, J. Reedijk, J.V. Rijn and G.C. Verschoor, *J. Chem. Soc., Dalton Trans.,* (1984) 1349.

[26] A.J. Bard and L.R. Faulkner, in *Electrochemical Methods: Fundamental Applications',* Wiley, New York, 1980, p. 218.

[27] Y. Kaifu, C.H. Len and C.S. Chung, *J. Chem. Soc., Dalton Trans.,* (1988) 2495.

[28] B.F. Hoskins and F.D. Whilland, *Coord. Chem. Rev., 9* (1972–1973) 365.