Influence of Chelate-ring Size and Number of Sulfur-donor Atoms on Spectra and Redox Behaviour of Copper(II) Bis(benzimidazolyl) Tetra- and Penta-thioether Complexes†

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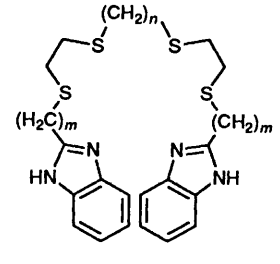
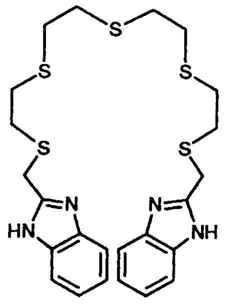
The linear quadridentate $R(CH_2)_mSCH_2CH_2S(CH_2)_nSCH_2CH_2S(CH_2)_mR$, where $m = 1$, $n = 2$ (L^1), or 3 (L^2), $m = 2$, $n = 2$ (L^3) or 3 (L^4), and the pentadentate $RCH_2(SCH_2CH_2)_4SCH_2R$ (L^5) (R = benzimidazol-2-yl) compounds formed 1:1 copper(II) perchlorate complexes. Some of the quadridentate compounds also formed complexes of the type $CuLX_2$ ($X = Cl^-$, NO_3^- or BF_4^-). All the complexes exhibited an absorption band around 30 000 cm^{-1} originating from a $S(\sigma)\rightarrow Cu^{II}$ charge-transfer transition. In solution the ClO_4^- and BF_4^- salts of $[CuL^1]^{2+}$ exhibit only one ligand-field band (14 800 cm^{-1}) while the other complexes show two bands ($\approx$11 000, 15 000–16 000 cm^{-1}). The polycrystalline EPR spectra of the former complexes are axial while those of the other complexes are rhombic. The cryogenic solution EPR spectra of the former complexes differ from those of the other complexes by exhibiting comparatively low $g_{\parallel}$ values and well resolved nitrogen superhyperfine structures. All these spectral features suggest a unique 'folded' geometry for the $[CuL^1]^{2+}$ complex. Among the tetrathioether complexes, the Cu^{II}–Cu^I redox potential increases with increase in the number of six-membered chelate rings, implying an increase in preference for the copper(I) over the copper(II) state. For copper(II) complexes of bis(benzimidazolyl) thioether ligands with all-five-membered chelate rings the potential increases with increase in the number of thioether donors.

The crystal structures of the electron-transfer blue proteins plastocyanin[1] and azurin[2] reveal that copper in the active sites is co-ordinated to two histidine nitrogen atoms, a methionine thioether and a cysteine thiolate. As the novel spectroscopic and redox properties[3,4] of these proteins are often associated with their unusual active-site geometry and copper–sulfur co-ordination, there has been continuing interest in copper(II) complexes of ligands containing biologically relevant thioether and (benz)imidazole nitrogen donors. A family of copper(II) complexes of bis(benzimidazolyl)-di-[5–8] and -trithia[9] ligands have been investigated. Among complexes with CuN_2S_2 chromophores, those involving the 555 and 656 chelate ring systems possess trigonal-bipyramidal geometry[5,7,10] while with the 565 chelate ring system[8] a geometry intermediate between trigonal bipyramidal and square-pyramidal is found. Recently the spectral and electrochemical behaviour of these complexes have been studied[9] in detail. It is now well known that thioether donors destabilise[11] the copper(II) state, elevating, while the incorporation of five-membered chelate rings depresses,[9] the Cu^{II}–Cu^{I} redox potentials. Studies on copper(II,I) complexes of bis(imidazolyl)dithia[12] and bis(benzimidazolyl)diaza[13] ligands illustrate the effect of bulky benzimidazole moieties on structures and spectra.

These observations prompted us to investigate systematically the effect of incorporating increasing numbers of sulfur-donor atoms, entailing different chelate-ring systems around copper(II), on the spectral and redox behaviour. In the present paper we describe the isolation and study of copper(II) complexes of bis(benzimidazolyl) ligands, with four (L^1–L^4) and five (L^5) thioether donor atoms and address the effect of the increasing number of thioether donors among complexes with all-five-membered chelate rings. Attempts are also made to infer the co-ordination geometries of these complexes from their ligand-field and EPR spectra in comparison with related complexes.



	n	m	
L^1	2	1	N_2S_4(55555)
L^2	3	1	N_2S_4(55655)
L^3	2	2	N_2S_4(65556)
L^4	3	2	N_2S_4(65656)



L^5 N_2S_5(555555)

Experimental

Materials.—Reagents were used as received from Fluka [$Cu(ClO_4)_2\cdot 6H_2O$, $Cu(BF_4)_2\cdot 6H_2O$], S. d. Fine-Chem pvt. Ltd., India ($CuCl_2\cdot 2H_2O$) and Merck, India (methanol, acetonitrile). Tetra-*n*-hexylammonium perchlorate (G. F.

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† *Non-SI unit employed:* G = 10^{-4} T.

Smith, USA) was recrystallised twice from aqueous ethanol. Methanol for electrochemistry was distilled over magnesium turnings.

Syntheses.—The ligands 1,12-bis(benzimidazol-2-yl)-2,5,8,11-tetrathiadodecane (L^1), 1,13-bis(benzimidazol-2-yl)-2,5,9,12-tetrathiatridecane (L^2), 1,14-bis(benzimidazol-2-yl)-3,6,9,12-tetrathiatetradecane (L^3), 1,15-bis(benzimidazol-2-yl)-3,6,10,13-tetrathiapentadecane (L^4) and 1,15-bis(benzimidazol-2-yl)-2,5,8,11,14-pentathiapentadecane (L^5) were synthesised as reported elsewhere.[14] The corresponding copper(II) perchlorate complexes were isolated as follows.

$CuL^1(ClO_4)_2$. A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol) in methanol (1 cm^3) was added with stirring to a methanolic solution (20 cm^3) of L^1 (0.47 g, 1 mmol) and then cooled. The complex obtained was filtered off, washed with cold methanol and dried over P_4O_{10} under vacuum. The complexes with L^2, L^4 and L^5 were prepared similarly. Some copper(II) complexes were isolated as chlorides, nitrates and tetrafluoroborates by starting from the respective copper(II) salt. The results of elemental analysis (Table 1) correspond to 1:1 complex formation.

CAUTION: some of the complexes contain perchlorate anion. Although no accidents occurred while handling these salts, care should be taken because of the possibility of explosion.

Physical Measurements.—Elemental analyses were performed at City University, London, MEDAC Ltd., Brunel University, Uxbridge, Middlesex and CDRI, Lucknow, India. The copper content was determined by atomic absorption. The diffuse reflectance and methanol solution spectra were measured on a Hitachi U-3400 double-beam UV/VIS/NIR spectrophotometer, infrared spectra as KBr pellets on a Shimadzu 435 spectrophotometer and EPR spectra on a Varian E-112 X-band spectrometer calibrated with diphenylpicrylhydrazyl (dpph). The values of g_0 and A_0 were measured at ambient temperature and $g_{\parallel}$ and $A_{\parallel}$ at 77 K; $A_{\perp}$ and $g_{\perp}$ were computed as $\frac{1}{2}(3A_0 - A_{\parallel})$ and $\frac{1}{2}(3g_0 - g_{\parallel})$ respectively.

Cyclic voltammetry and differential pulse voltammetry at a glassy carbon electrode were performed at 25 ± 0.2 °C. The temperature of the electrochemical cell was maintained by a cryocirculator (Haake D8 G). A three-electrode cell configuration was used; the reference electrode as Ag(s)–$AgNO_3$ (0.01 mol dm^{-3}), $N(C_6H_{13})_4ClO_4$ (0.1 mol dm^{-3}) in acetonitrile and the auxiliary electrode a platinum plate. The solutions were deoxygenated by bubbling research-grade nitrogen and an atmosphere of nitrogen was maintained over the solution during measurement. The apparatus utilised included a EG & G PAR 273 potentiostat. An IBM PS-2 computer with EG & G M270 software was employed to carry out the experiments and to acquire the data. Potentials were uncorrected for junction potentials.

Results and Discussion

All the copper(II) perchlorate complexes except $[CuL^3]^{2+}$ were isolated as crystalline solids and are stable. As $[CuL^3]^{2+}$ is very unstable possibly due to facile reduction[6] of Cu^{II} in the presence of ligand, physical measurements were therefore carried out on a freshly prepared solution containing $Cu(ClO_4)_2$ and L^3 in 1:1.1 ratio.

The infrared spectra of all the perchlorates show a strong band (ν_3) split into three components (1070, 1100 and 1140 cm^{-1}) suggesting[15] co-ordination of ClO_4^-. However, the forbidden ν_1 band which is allowed and appears around 900 cm^{-1} in lower symmetry is absent and a single sharp unsplit band is observed at 620 cm^{-1} (ν_4). This suggests that the unco-ordinated perchlorate is in an ionic form and that the splitting of ν_3 band may be due to ClO_4^- hydrogen bonded[16] to NH of the benzimidazole moiety. The tetrafluoroborate complexes also show a split ν_3 band around 1070 cm^{-1}, suggesting such hydrogen bonding rather than co-ordination of the anion.

Electronic Spectra.—The reflectance spectra of all the present complexes show either one broad or two well separated (> 3000 cm^{-1}) ligand-field bands in the visible region. In methanol solution noticeable differences in ligand-field features are observed (Table 2), implying structural changes, such as displacement of axially co-ordinated thioether, by solvent or anion. Thus in methanol solution both the ClO_4^- and BF_4^- salts of $[CuL^1]^{2+}$ exhibit only one ligand-field band, although they show different spectral features in the solid state. These spectral data suggest that the geometry[17,18] of the complexes is likely to be distorted octahedral rather than trigonal bipyramidal, both in solution and the solid state.

The $\tilde{\nu}_{max}$ values of all the complexes are in the same range as for bis(benzimidazolyl)-dithia and -trithia complexes[9,19] of copper(II), suggesting the presence of an equatorial CuN_2S_2 chromophore.[19,20] The ligand-field bands for $[CuL^1]^{2+}$ and $[CuL^4]^{2+}$ perchlorates are higher in energy than those for other perchlorates, suggesting that the all-five-membered chelate rings as in the former and the alternate six- and five-membered chelate rings in the latter provide the strongest ligand-field environment for Cu^{II}.

The intense band observed in the region 26 800–30 700 cm^{-1} for all the complexes is assigned to a $S(\sigma) \longrightarrow Cu^{II}$ charge-transfer (c.t.) transition.[19,21–24] Among the bis(benzimidazolyl) thioether complexes with all-five-membered chelate rings the ε_{max} values[9] of this band steadily increases with increase in the number of sulfur-donor atoms up to four but for five it decreases

Table 1 Analytical data * for $Cu^{II}L$ complexes

	Analysis (%)			
Complex	C	H	N	Cu
$CuL^1(ClO_4)_2 \cdot 2H_2O$	33.8 (34.2)	3.85 (3.90)	7.00 (7.25)	7.95 (8.20)
$CuL^1(BF_4)_2 \cdot 1.5H_2O$	35.5 (35.8)	3.85 (3.95)	7.10 (7.60)	8.30 (8.60)
$CuL^1(NO_3)_2 \cdot 0.5H_2O$	39.0 (39.4)	3.95 (4.05)	12.1 (12.5)	9.20 (9.45)
$CuL^1Cl_2 \cdot H_2O$	42.0 (42.1)	4.10 (4.50)	9.20 (8.95)	10.3 (10.1)
$CuL^2(ClO_4)_2 \cdot 2H_2O$	34.8 (35.1)	3.75 (4.10)	7.55 (7.10)	8.30 (8.05)
$CuL^2Cl_2 \cdot 2H_2O$	41.7 (41.9)	4.60 (4.90)	8.90 (8.50)	9.40 (9.65)
$CuL^4(ClO_4)_2$	38.9 (38.5)	3.90 (4.15)	7.55 (7.20)	8.35 (8.15)
$CuL^4(BF_4)_2 \cdot H_2O$	38.7 (38.9)	4.25 (4.45)	7.65 (7.25)	8.45 (8.25)
$CuL^4(NO_3)_2 \cdot 0.5H_2O$	41.8 (42.1)	4.30 (4.65)	11.4 (11.8)	8.65 (8.90)
CuL^4Cl_2	46.4 (46.1)	4.90 (4.95)	8.25 (8.60)	9.50 (9.75)
$CuL^5(ClO_4)_2 \cdot H_2O$	35.0 (35.4)	3.60 (3.95)	6.45 (6.85)	7.55 (7.80)
$CuL^5Cl_2 \cdot H_2O$	41.9 (41.9)	4.25 (4.70)	7.75 (8.15)	8.95 (9.25)

* Calculated values are within parentheses.

Table 2 Electronic spectral data of $Cu^{II}L$ complexes in methanol,[a] $\tilde{\nu}_{max}/cm^{-1}$ and $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ in parentheses

Complex	Medium	Ligand field	Charge transfer
$CuL^1(ClO_4)_2$	Solid	15 040	26 270
	MeOH	14 800 (175)[b]	28 400 (4230)
$CuL^1(BF_4)_2$	Solid	14 410	24 890
		15 980	
	MeOH	14 900 (177)[b]	28 470 (3690)
$CuL^1(NO_3)_2$	Solid	15 510	26 490
	MeOH	11 430 (177)	30 670 (2420)
		15 190 (234)	
CuL^1Cl_2	Solid	12 010	26 490
		14 590	
	MeOH	11 370 (231)	30 790 (2040)
		15 150 (301)	
$CuL^2(ClO_4)_2$	Solid	14 080	24 910
	MeOH	11 440 (200)	30 690 (2850)
		15 280 (190)	
CuL^2Cl_2	Solid	14 770	24 780
	MeOH	12 120 (483)	30 390 (3910)
		15 220 (380)	
$CuL^3(ClO_4)_2$[c]	MeOH	12 300 (143)	26 790 (1360)
		15 300 (286)	
$CuL^4(ClO_4)_2$	Solid	11 990	24 450
		16 250	
	MeOH	11 160 (256)	28 930 (3330)
		16 560 (271)	
$CuL^4(BF_4)_2$	Solid	16 490	24 170
	MeOH	12 130 (269)	28 940 (2520)
		16 660 (244)	
$CuL^4(NO_3)_2$	Solid	11 890	24 150
		15 910	
	MeOH	11 210 (267)	29 100 (3340)
		16 560 (247)	
CuL^4Cl_2	Solid	11 850	23 920
		16 330	
	MeOH	11 100 (289)	29 210 (2820)
		16 580 (279)	
$CuL^5(ClO_4)_2$	Solid	14 070	24 550
	MeOH	11 490 (270)	30 670 (2560)
		15 370 (258)	

[a] Concentration: $\approx 2 \times 10^{-3}$ mol dm^{-3}. [b] Unsymmetrical band. [c] 1:1 Solution of $Cu(ClO_4)_2$ and the ligand in methanol.

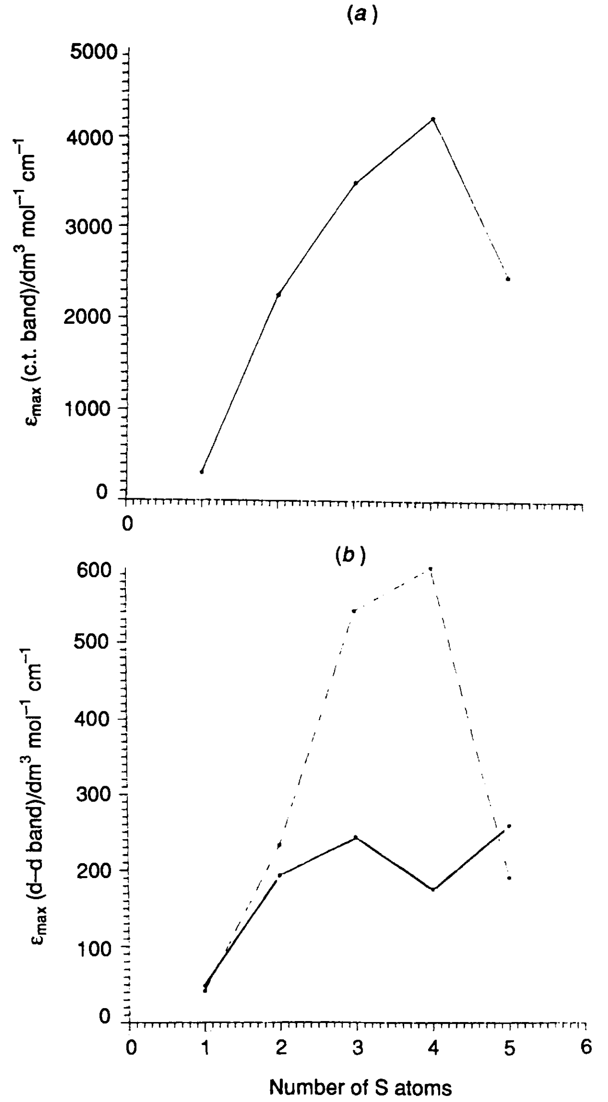


Fig. 1 (*a*) Plot of ε_{max} for the $S(\sigma)\rightarrow Cu^{II}$ band *vs.* the number of sulfur donor atoms in copper(II) complexes of bis(benzimidazol-2-yl) thioethers, with all-five-membered chelate-ring systems. (*b*) Calculated (——) and observed (– – – – –) ε_{max} values of the ligand-field bands *vs.* the number of sulfur-donor atoms in the same systems

[Fig. 1(*a*)]. It appears that this variation originates from structural changes imposed by the disposition or non-co-ordination of the thioether donors.

The modest enhancement of intensities for the visible band may be attributed to intensity borrowing[25] from the $S(\sigma)\rightarrow Cu^{II}$ c.t. band. Among the bis(benzimidazolyl) thioether copper(II) complexes with all-five-membered chelate-ring systems the relative intensities of the visible band, calculated using Jorgensen's equation,[26] parallel the observed variation in ε_{max} of the c.t. band [Fig. 1(*a*)] and this variation is in agreement with that observed for CuN_2S and CuN_2S_2 complexes[9] [Fig. 1(*b*)]. The lower value observed for CuN_2S_3 illustrates that the overlap of an axial thioether with the copper $d_{x^2-y^2}$ orbital is poor and confirms that its higher c.t. intensity is only structural in origin. Further, the ε_{max} value of $CuL^1(ClO_4)_2$ is much lower compared to those of the three other tetrathioether complexes, even though it has the highest ε_{max} value for the c.t. band. This may correspond to a structure (discussed below) and hence a *W* term[26] less favourable for intensity borrowing. Within the CuN_2S_4 perchlorates the significant variation in intensity of the ligand-field bands implies distortion and/or axial interaction affected by the chelate-ring size.

EPR Spectra.—The polycrystalline spectra of $CuL^1(ClO_4)_2$ and $CuL^1(BF_4)_2$ are axial while those of the other complexes are rhombic (Fig. 2). For the latter systems $g_{min} > 2.03$ (Table 3) and the *R* values $[=(g_2 - g_1)/(g_3 - g_2)]$ are < 1 indicating a predominantly $d_{x^2-y^2}$ ground state.[17,27] This is in contrast to copper(II) complexes of bis(benzimidazolyl) thioether ligands with CuN_2S_2 chromophores with d_{z^2} ground state in trigonal-bipyramidal geometry.[28,29] However, the frozen-solution spectra of all the complexes are axial ($g_{\parallel} > g_{\perp} > 2.0$), illustrating changes in structure on dissolution. The $g_{\parallel}$ (2.29–2.20), $g_{\perp}$ (2.09–2.04) and $A_{\parallel}[(140\text{–}130) \times 10^{-4}\ cm^{-1}]$ values of these complexes, except $[CuL^3]^{2+}$, are consistent with those reported for bis(benzimidazolyl)[5-9] and other thioether[25,30] complexes with CuN_2S_2 and CuN_2S_3 chromophores and lie in between the N_4 and S_4 delineators in the $g_{\parallel}:A_{\parallel}$ map,[31] supporting an equatorial N_2S_2 donor set as suggested by the electronic spectral data. The high $g_{\parallel}$ value observed for $[CuL^3]^{2+}$ illustrates that one or more thioether donors remain unco-ordinated[32] at 77 K. The $g_{\parallel}$ value is expected[31] to decrease and the $A_{\parallel}$ value to increase on increasing the number of co-ordinated sulfur atoms, but interestingly the reverse trend is observed on increasing the number of sulfurs from three to four to five, among all-five-membered chelate rings. This trend is similar to that in the ε_{max} values of $S(\sigma)\rightarrow Cu^{II}$ c.t. band, illustrating the influence of the axial interaction by sulfur. The values of the $g_{\parallel}/A_{\parallel}$ quotient (130–170 cm) of all the copper(II) complexes, except $[CuL^1]^{2+}$, are higher than the range (105–135 cm) expected for square-planar complexes.[31] This represents a highly distorted octahedral geometry caused by axial interaction, which is well known to raise[33] $g_{\parallel}$ and lower $A_{\parallel}$ values.

The nitrogen superhyperfine structure ($A_{\perp(N)} \approx 16$ G) in the perpendicular region is better resolved for $CuL^1(ClO_4)_2$ (Fig. 3) than for the $[CuL^2]^{2+}$ and $[CuL^5]^{2+}$ perchlorate complexes. The nine lines for the former may originate from the presence of two non-equivalent nitrogens or two equivalent nitrogens in the equatorial plane with the hyperfine structure complicated by the perpendicular features of copper.[34] We favour the latter explanation because in the parallel region only five lines corresponding to two equivalent nitrogens are observed (Fig. 3 inset). Further, the spectrum simulated assuming two equivalent nitrogens is identical with the observed one.

The above spectral discussion leads us to propose tentative structures (Fig. 4) for the present complexes. All of them contain the inferred CuN_2S_2 equatorial plane. The strong Cu–N_{bzim} bonds[35] would prefer to lie in the equatorial plane and the thioether donors would then be forced to occupy the other equatorial and axial sites or remain unbonded. One of the five thioether donors in $[CuL^5]^{2+}$ will not be permitted to form a bond to copper. Further, the observed $g_{\parallel}$ values are nearer to 2.28 rather than 2.31, which is characteristic of a *trans* rather than *cis* disposition of sulfur atoms in the CuN_2S_2 plane;[36] this is also supported by the symmetrical nature of the band at 30 000 cm^{-1}. Extensive studies[37] on cobalt(III) complexes of

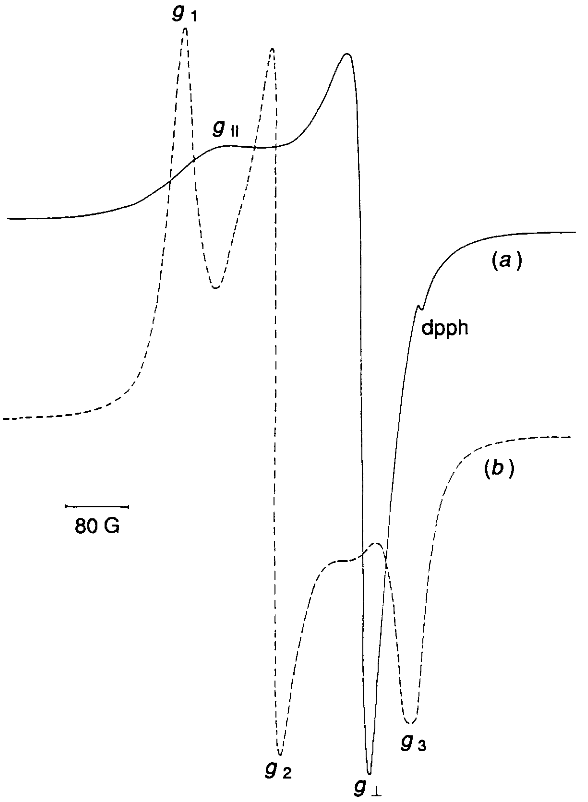


Fig. 2 Polycrystalline X-band EPR spectra at room temperature of $CuL^1(ClO_4)_2$ (——) and $CuL^4(ClO_4)_2$ (– – – –)

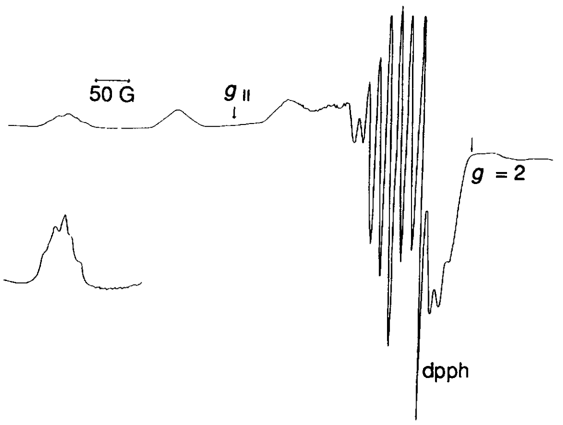
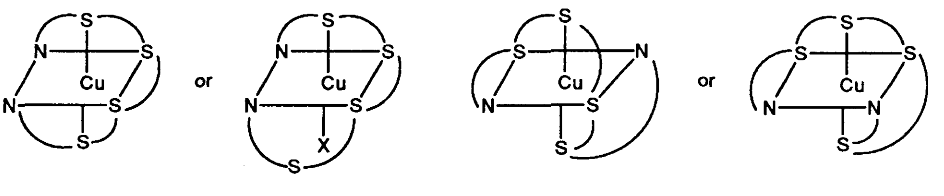


Fig. 3 X-Band EPR spectrum at 77 K of $CuL^1(ClO_4)_2$ in methanol–acetone solution

Table 3 EPR spectral data for $Cu^{II}L$ complexes

Complex	Medium	g_0	A_0[a]	$g_{\parallel}$	$A_{\parallel}$[a]	$g_{\perp}$
$CuL^1(ClO_4)_2$[b]	Powder	—	—	2.150	—	2.045
	MeOH–Me_2CO	2.099	66	2.184	167	2.057
$CuL^1(BF_4)_2$	Powder	—	—	2.155	—	2.043
	MeOH–Me_2CO	2.095	68	2.186	167	2.050
$CuL^1(NO_3)_2$	Powder	2.164, 2.099, 2.032	—	—	—	—
	MeOH–Me_2CO	2.096	49	2.208	124	2.040
CuL^1Cl_2	Powder	2.156, 2.075, 2.031	—	—	—	—
	MeOH–Me_2CO	2.118	59	2.198	135	2.078
$CuL^2(ClO_4)_2$	Powder	2.209, 2.131, 2.014	—	—	—	—
	MeOH–Me_2CO	2.150	50	2.242	134	2.104
CuL^2Cl_2	Powder	2.155, 2.065, 2.028	—	—	—	—
	MeOH–Me_2CO	2.120	61	2.197	131	2.082
$CuL^3(ClO_4)_2$[c]	MeOH–Me_2CO	2.079	68	2.412	122	1.913
$CuL^4(ClO_4)_2$	Powder	2.202, 2.116, 2.004	—	—	—	—
	MeOH–Me_2CO	2.112	64	2.198	138	2.069
$CuL^4(BF_4)_2$	Powder	2.204, 2.115, 2.006	—	—	—	—
	MeOH–Me_2CO	2.112	30	2.213	128	2.062
$CuL^4(NO_3)_2$	Powder	2.198, 2.120, 2.023	—	—	—	—
	MeOH–Me_2CO	2.113	30	2.288	140	2.026
CuL^4Cl_2	Powder	2.110	—	—	—	—
	MeOH–Me_2CO	2.112	59	2.195	135	2.071
$CuL^5(ClO_4)_2$	Powder	2.198, 2.120, 2.011	—	—	—	—
	MeOH–Me_2CO	2.110	28	2.242	143	2.044
CuL^5Cl_2	Powder	2.094	—	—	—	—
	MeOH–Me_2CO	2.110	61	2.276	169	2.027

[a] In 10^{-4} cm^{-1}. [b] Simulated values: $g_{\parallel}$ 2.250; $A_{\parallel}$ 154 × 10^{-4} cm^{-1}; $A_{\perp(N)}$ 15 × 10^{-4} cm^{-1}; $g_{\perp}$ 2.085. [c] Complex prepared *in situ*.



1 $[CuL^1]^{2+}$
X = anion

2 $[CuL^2]^{2+}$, $[CuL^3]^{2+}$, $[CuL^4]^{2+}$, $[CuL^5]^{2+}$

Fig. 4 Proposed geometries of copper(II) complexes of bis(benzimidazol-2-yl) tetra- and penta-thioether ligands

open-chain thioether ligands have established that a thioether donor linking two five-membered aliphatic chelate rings adopts a non-planar arrangement about the metal. A folded geometry has been observed for $CuL^6 \cdot 2H_2O$ (H_2L^6 = 2,5,8-trithianonane-1,9-dicarboxylic acid) and $[CuL^7{}_2]^{2+}$ [L^7 = bis(imidazol-2-ylmethyl) sulfide].[38,39] So $[CuL^1]^{2+}$ with all-five-membered chelate rings would be expected to display a 'folded' geometry* which is entirely different from those proposed for other complexes with one or more six-membered chelate rings. Such a unique and compact geometry reflects its distinct spectral features: (*i*) the position and intensity of the ligand-field band which are the highest and lowest respectively, compared to all other complexes; (*ii*) the $g_{\parallel}/A_{\parallel}$ quotient of 130 cm and (*iii*) the well resolved nitrogen superhyperfine structure. It is unfortunate that the present complexes do not yield single crystals suitable for X-ray diffraction, since such data would have helped considerably in clarifying much of the interpretation.

Redox Properties.—All the perchlorate complexes exhibit a well defined cathodic wave (0.250 to −0.050 V) and a corresponding anodic wave (0.180–0.580 V) (Fig. 5). The diffusion coefficients (Table 4) calculated from the slope of plots of i_{pc} *vs.* $v^{\frac{1}{2}}$ using the Randles–Sevcik equation[41] are typical of the Cu^{II}–Cu^{I} couple.[31] For all the present complexes the peak-current ratio (i_{pa}/i_{pc}) is nearer to unity, implying quasi-reversible electron transfer; but the $\Delta E_p{}^{\circ}$ values are greater than the Nernstian value ($\Delta E_p \approx 60$ mV) for a one-electron redox system. This clearly indicates considerable reorganisation of the co-ordination spheres during electron transfer, regardless of the precise mechanism. The $[CuL^1]^{2+}$ and $[CuL^4]^{2+}$ perchlorates exhibit much lower $\Delta E_p{}^{\circ}$ values than those of the other complexes, illustrating that the 'folded' geometry in $[CuL^1]^{2+}$ and six-membered chelate rings in $[CuL^4]^{2+}$ provide low reorganisational energy barriers during electron transfer.

Significant variation in Cu^{II}–Cu^{I} redox potentials (Table 4) is observed among the CuN_2S_4 perchlorates: $[CuL^2]^{2+}$ (55655) < $[CuL^1]^{2+}$ (55555) < $[CuL^4]^{2+}$ (65656) < $[CuL^3]^{2+}$ (65556). Six-membered rings present near the bzim moiety (in the CuN_2S_2 equator) elevate $E_{\frac{1}{2}}$ (240–176 mV), whereas that present at the middle of the ligands depresses $E_{\frac{1}{2}}$: $[CuL^2]^{2+}$ < $[CuL^1]^{2+}$ (168 mV) and $[CuL^4]^{2+}$ < $[CuL^3]^{2+}$ (103 mV). A similar increase in redox potential ($\approx$120 mV) representing progressive destabilisation of Cu^{II}, with increase in length of the bridging carbon chain, has been observed for copper(II) complexes of cyclic tetrathia[42] and open-chain N_2S_2 ligands.[43] Further, six-membered rings elevate or five-membered rings depress $E_{\frac{1}{2}}$, if π interaction[13] as in the present thioether chelates is important. This indicates that the redox potentials are affected both by the number and disposition of sulfur-donor atoms present. The redox potential of $CuL^1(ClO_4)_2$ decreases (25 mV) on the addition of an excess of Cl^- ions as tetraethylammonium chloride, illustrating that Cl^- ion may co-ordinate in solution by replacing possibly an axial thioether.

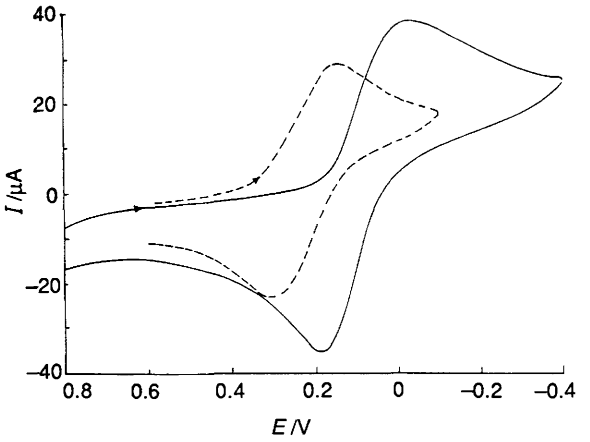


Fig. 5 Cyclic voltammograms of 1 mmol dm^{-3} $CuL^1(ClO_4)_2$ (– – – –) and $CuL^5(ClO_4)_2$ (——) in methanol [0.1 mol dm^{-3} $N(C_6H_{13})_4ClO_4$] at scan rate 50 mV s^{-1}

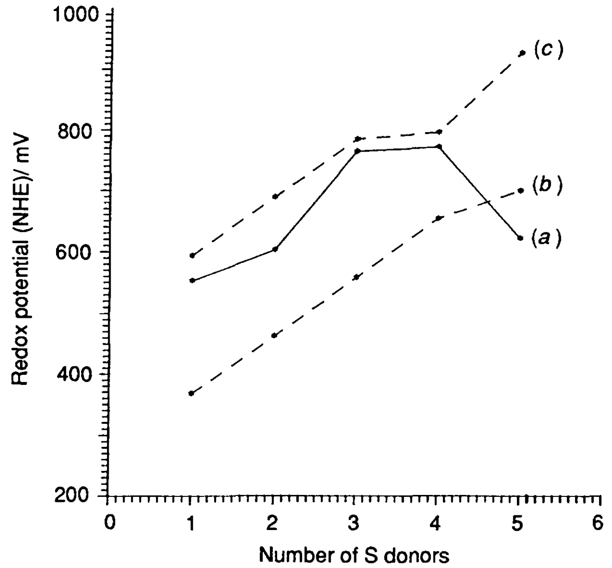


Fig. 6 Plots of $E_{\frac{1}{2}}$ *vs.* the number of sulfur-donor atoms for bis(benzimidazol-2-yl) thioether complexes of copper(II), with all-five-membered chelate-ring systems: (*a*) observed values and (*b*) and (*c*) empirically calculated values using Addison's and modified ΔE_L values respectively

A plot (Fig. 6) of the redox potentials of compounds containing only five-membered chelate-ring systems *vs.* the number of thioether donors reveals that the potential increases up to three, remains the same for four and then decreases for five

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* After the submission of this paper the crystal structures of nickel(II) complexes of pyridine analogues of N_2S_3 and $N_2S_4(L^1)$ ligands have been published. All contain the proposed 'folded' geometry with a *cis* disposition of the thioether donors in the equatorial plane. Increasing the number of thioether donors increases the positive character of $E_{\frac{1}{2}}$ of the Ni^{II}–Ni^{I} couple.[40]

Table 4 Electrochemical data[a] for the $Cu^{II}L(ClO_4)_2$ complexes

Complex	T/°C	E_{pc}/V	E_{pa}/V	ΔE_p/mV	$\Delta E_p{}^{\circ b}$/mV	$E_{\frac{1}{2}}$/V		i_{pa}/i_{pc}	10^6D/cm^2 s^{-1}	$10^3D\eta^d$/g cm s^{-2}
						CV	DPV[c]			
$[CuL^1]^{2+}$	25	0.146	0.308	162	120	0.227	0.215	1.0	1.2	0.8
	35	0.144	0.294	150		0.219	0.223	1.0		
	45	0.136	0.306	170		0.221	0.219	0.8		
$[CuL^2]^{2+}$	25	−0.110	0.228	338	268	0.059	0.081	1.1	2.7	1.9
	35	−0.042	0.218	260		0.088	0.095	1.1		
	45	0.010	0.198	188		0.104	0.105	1.0		
$[CuL^3]^{2+}$	25	0.236	0.570	334	210	0.403	0.435	1.1	1.0	0.7
	35	0.274	0.560	286		0.417	0.443	1.1		
	45	0.308	0.552	244		0.430	0.453	1.1		
$[CuL^4]^{2+}$	25	0.230	0.370	140	88	0.300	0.309	1.3	2.4	1.5
	35	0.226	0.386	160		0.306	0.311	1.3		
	45	0.234	0.388	154		0.311	0.325	1.2		
$[CuL^5]^{2+}$	25	−0.032	0.186	218	179	0.077	0.087	1.2	2.5	1.6
	35	−0.038	0.200	238		0.081	0.099	1.1		
	45	−0.016	0.214	230		0.099	0.109	0.8		

[a] Measured *vs.* non-aqueous silver reference electrode; add 544 mV to convert into normal hydrogen electrode (NHE). Scan rate 50 mV s^{-1}. Supporting electrolyte tetra-*n*-hexylammonium perchlorate (0.1 mol dm^{-3}). Complex concentration 1 mmol dm^{-3}. [b] $E_p{}^{\circ}$ is ΔE_p at zero i_{pc}. [c] Differential pulse voltammetry, scan rate 1 mV s^{-1}, pulse height 50 mV. [d] Kinematic viscosity (η)[9] 0.006 51 g cm^{-1} s^{-1}.

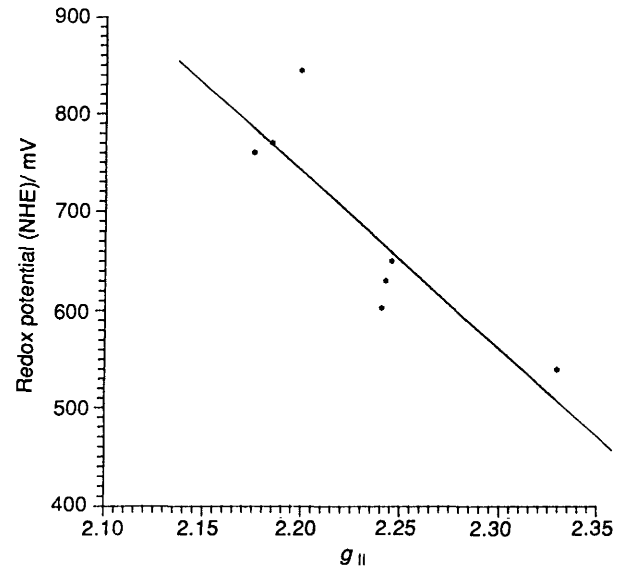

Fig. 7 Plot of $E_{\frac{1}{2}}$ (NHE) *vs.* $g_{\parallel}$ for copper(II) complexes of bis(benzimidazol-2-yl) thioether ligands

thioether donors. The observed regular increase is consistent with the empirical suggestion that each thioether donor elevates the potential by + 141 mV. However, the values calculated for the present complexes using Addison's ΔE_L parameters[44] (Fig. 6, ΔE_L is the donor atom contribution to redox potential) are lower than the adjusted values ($E_{adj} = E_{\frac{1}{2}} - E^{\circ}$; $E^{\circ} = 215$ mV in methanol[44]). This implies that the contribution by bulky bzim to $E_{\frac{1}{2}}$ is much higher[13] than that by pyridine or imidazole (ΔE_{het} + 52 mV[44]) and in fact a better agreement with the observed values is seen when a ΔE_{bzim} value of + 165 mV is used for the calculation. The values of $E_{\frac{1}{2}}$ calculated for $[CuL^5]^{2+}$ are higher than that observed, illustrating that one of the five thioethers is not co-ordinated. So it is obvious that the additivity in $E_{\frac{1}{2}}$ is applicable only to planar four-co-ordinated copper(II) complexes which on reduction form necessarily four-co-ordinated, probably tetrahedral copper(I) species.

Conclusion

The novel and distinct spectral and electrochemical behaviour of the CuN_2S_4 perchlorates with all-five-membered chelate rings is suggestive of a unique 'folded' geometry. The Cu^{II}–Cu^{I} redox potentials increase with decrease in energy of the $S(\sigma) \rightarrow Cu^{II}$ transitions.[25] An increase in the length of the bridging carbon chain among N_2S_4 complexes induces increased tetrahedral distortion and/or axial interaction and makes it easier to access[45] Cu^{I}. So $E_{\frac{1}{2}}$ is expected to increase with increase[33,46] in $g_{\parallel}$. However, a reverse trend is observed in the $g_{\parallel}$ *vs.* $E_{\frac{1}{2}}$ plot for all the present complexes and for complexes of bis(benzimidazolyl) polythioether ligands with all-five-membered chelate rings (Fig. 7). This leads us to conclude that the spectral properties and the high Cu^{II}–Cu^{I} redox potentials of all the present complexes are determined not only by distortion and/or axial interaction caused by both the chelate-ring structure and number of sulfur donors, but also by the axial/equatorial disposition of the sulfur donors. This is in contrast to planar copper(II) complexes of macrocyclic polythioether ligands, for which the effect of chelate-ring size is more important[47,48] than the number of sulfur-donor atoms in governing the redox potentials.

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