Facial Co-ordination in Bis[bis(benzimidazol-2-ylmethyl)-amine]copper(II) Perchlorate Dihydrate. Synthesis, Structure, Spectra and Redox Behaviour†

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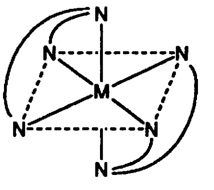
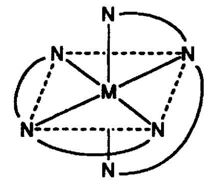
The 1 : 1 and 1 : 2 copper(II) complexes with the tridentate compound bis(benzimidazol-2-ylmethyl)amine (L^1) and its benzimidazole (L^2) and amine (L^3) *N*-methyl-substituted derivatives have been prepared and their spectroscopic properties studied. While the 1 : 1 complexes are of the type $CuLX_2{\cdot}nH_2O$ ($X = ClO_4^-$, NO_3^-, Cl^- or Br^-), the 1 : 2 complexes are of the type $CuL_2(ClO_4)_2{\cdot}nH_2O$ ($L = L^1$ or L^3, $n = 0$–4). In all these complexes L acts as a tridentate ligand with the amine nitrogen and both the benzimidazole nitrogens co-ordinating to Cu^{II}. The complex $[CuL^1_2][ClO_4]_2{\cdot}2H_2O$ crystallises in the monoclinic space group $P2_1/c$ with $a = 9.828(2)$, $b = 9.546(2)$ and $c = 19.906(2)$ Å and $\beta = 95.71(1)°$, for $Z = 2$. The *R* value is 0.0635 for 2180 significant reflections. The copper(II) ion has an elongated octahedral geometry with four equatorial benzimidazole and two long-distance axial amine N donors. The $Cu–N_{bzim}$ and $Cu–N_{amine}$ distances are 2.011(4) and 2.597(6) Å respectively. Factors favouring facial co-ordination of tridentate ligands are discussed. The 1 : 1 complexes involve meridional co-ordination of the ligands, with square-based geometry as revealed by ligand-field and EPR spectral properties. The NMe substitution as in $CuL^3(ClO_4)_2$ confers low $\tilde{\nu}_{max}$ and high $E_{\frac{1}{2}}$ for the $Cu^{II}–Cu^{I}$ couple. Most of the 1 : 1 complexes are less reversible but exhibit $E_{\frac{1}{2}}$ values more positive than those of the corresponding 1 : 2 complexes.

For the bis complex of a linear tridentate 3N ligand system three potential geometric isomers, *viz. fac* (**a**, **c**) and *mer* (**b**) are possible. However, the complexes $[Cu(dien)_2][NO_3]_2$ [1] and $[Cu(dien)_2]Br_2{\cdot}H_2O$ [2] (dien = diethylenetriamine) have been shown to exhibit only the *mer* isomer **b**. With bis(2-pyridylmethyl)amine (bpma) both of the *fac* isomers **a** and **c** but not the *mer* isomer **b** for the complexes $[M(bpma)_2]X_2$ [3] ($M = Mn^{II}$, Zn^{II} or Cd^{II}, $X = ClO_4^-$ or Cl^-) and only **a** for $[Fe(bpma)_2][ClO_4]_2$ have very recently been isolated.[4] However, $[Cu(bpma)_2]^{2+}$ has been shown[5] to exhibit two geometric isomers (**a**, **d**), interestingly, in the same unit cell. In order to impose facial co-ordination several tridentate tripodal-like 3N ligands[6] have been employed, the three-fold symmetry of which precludes geometric isomerism in the bis complexes. However, the steric requirements and symmetry of the novel ligand di-2-pyridylmethane (dpm) dictated that only two geometric isomers were possible, that is the facial *meso* (C_{2h}) or the *rac* (C_2), for the bis complexes of the first-row transition metals in various oxidation states, complexes of Fe^{II} and Co^{II} have been defined as *rac* isomers, those of Cu^{II} and Ni^{II} as *meso* isomers, by X-ray crystal structure analysis.[7]

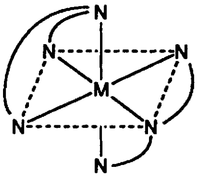
These observations prompted our interest in the co-ordination chemistry of the tridentate compound bis(benzimidazol-2-ylmethyl)amine (L^1) and its NMe derivatives (L^2, L^3). The ability to delocalise the electron density from the metal centre *via* π-back bonding and the steric bulk of the benzimidazolyl rings may be expected to influence the co-ordination geometry around Cu^{II}. Thus the $CuBr_2$ complex[8] of *N*,*N*′-bis(benzimidazol-2-ylethyl)ethylenediamine shows a planar CuN_4 chromophore with slight tetrahedral distortion. The 1 : 1 copper(II) complexes of L^2 and its homologues have been shown[9] to exhibit distorted octahedral/square pyramidal geometry and low $A_{\parallel}$ values. The present paper is concerned with the spectra and electrochemistry of the 1 : 1 and 1 : 2 complexes of L^1–L^3. The crystal structure determination of $[CuL^1_2][ClO_4]_2{\cdot}2H_2O$ is also reported.



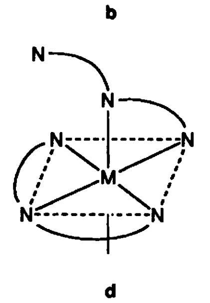
a



b



c



d

Experimental

Materials.—Reagents were used as received from G. F. Smith $[Cu(ClO_4)_2{\cdot}6H_2O]$, BDH, India $[Cu(NO_3)_2{\cdot}3H_2O$, $CuCl_2{\cdot}2H_2O$, $CuBr_2]$, SISCO, India (1,2-diaminobenzene, iminodiacetic acid, thiodiglycolic acid), Aldrich (*N*-methyliminodiacetic acid) and Kodak (*N*-methylbenzene-1,2-diamine dihydrochloride). Methanol for electrochemistry was distilled over magnesium turnings.

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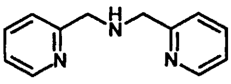
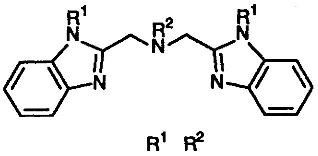
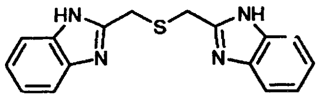
† *Supplementary data available* (No. SUP 57046, 3 pp.): ligand field and spectral parameters of related copper complexes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.
Non-SI unit employed: G = 10^{-4} T.



dpma



	R¹	R²
L¹	H	H
L²	Me	H
L³	H	Me



bbms

Synthesis of Ligands.—Bis(benzimidazol-2-ylmethyl)amine[9] (L^1), bis(1-methylbenzimidazol-2-ylmethyl)amine[10] (L^2), bis(benzimidazol-2-ylmethyl)methylamine[9] (L^3) and bis(benzimidazol-2-ylmethyl) sulfide[11] (bbms) were synthesised as reported.

Preparation of Complexes.—$CuL^1(ClO_4)_2$. To L^1 (0.277 g, 1 mmol) dissolved in methanol (20 cm^3) was added a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.370 g, 1 mmol) in methanol (5 cm^3). The blue complex obtained was collected, washed with small amounts of methanol and dried over P_4O_{10} under vacuum. Yield: 0.44 g (82%).

$CuL^1Cl_2{\cdot}2H_2O$. To L^1 (0.277 g, 1 mmol) dissolved in methanol (20 cm^3) was added a solution of $CuCl_2{\cdot}2H_2O$ (0.170 g, 1 mmol) dissolved in methanol (10 cm^3). The resulting blue solution was kept aside at room temperature for 1 d. The green crystals formed were collected, washed with small amounts of methanol and dried over P_4O_{10} in vacuum. Yield: 0.35 g (78%).

CuL^1Br_2. To L^1 (0.277 g, 1 mmol) dissolved in methanol (20 cm^3) was added a solution of $CuBr_2$ (0.244 g, 1 mmol) in methanol (10 cm^3). The resulting blue solution was rotaevaporated to small volume. The blue complex obtained was collected, washed with small amounts of methanol and dried over P_4O_{10} in vacuum. Yield: 0.42 g (83%).

$CuL^1_2(ClO_4)_2{\cdot}2H_2O$. A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.370 g, 1 mmol) in methanol (5 cm^3) was added to L^1 (0.554 g, 2 mmol) dissolved in methanol (10 cm^3). The light blue crystals obtained were collected, washed with methanol and dried over P_4O_{10} in vacuum. Yield: 0.68 g (80%).

A solution of the above complex (0.01 g) dissolved in methanol (10 cm^3) was allowed slowly to evaporate. The fine blue single crystals obtained were suitable for X-ray diffraction.

$CuL^1(NO_3)_2{\cdot}MeOH$. This was prepared as reported.[9] Yield: 85%.

$CuL^1_2(NO_3)_2$. Compound L^1 (0.554 g, 2 mmol) was dissolved in methanol (20 cm^3) and a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.256 g, 1 mmol) in methanol (10 cm^3) was added. The bluish green crystals obtained were collected, washed with methanol and dried over P_4O_{10} in vacuum. Yield: 0.56 g (75%).

$CuL^2(ClO_4)_2{\cdot}H_2O$. This was prepared by a similar procedure to that used for $CuL^1(ClO_4)_2$. Yield: 80%.

$CuL^2Br_2{\cdot}2H_2O$. To L^2 (0.305 g, 1 mmol) dissolved in methanol (20 cm^3) was added a solution of $CuBr_2$ (0.224 g, 1 mmol) in methanol (15 cm^3). The green compound was collected, washed with small amounts of methanol and dried over P_4O_{10} in vacuum. Yield: 0.49 g (86%).

$CuL^3(ClO_4)_2{\cdot}4H_2O$. This was prepared by a similar procedure to that used for $CuL^1(ClO_4)_2$. Yield: 80%.

Table 1 Elemental analyses of copper(II) complexes; calculated values in parentheses

	Analysis (%)			
Complex	C	H	N	Cu
$CuL^1(ClO_4)_2$	35.50	2.45	12.70	11.55
	(35.60)	(2.80)	(13.00)	(11.75)
$CuL^1Cl_2{\cdot}2H_2O$	42.60	3.95	15.50	14.10
	(42.90)	(4.30)	(15.65)	(14.20)
CuL^2Br_2	38.30	3.40	13.65	12.55
	(38.40)	(3.00)	(14.00)	(12.70)
$CuL^1(NO_3)_2{\cdot}MeOH$	41.05	3.70	19.45	12.65
	(41.10)	(3.85)	(19.75)	(12.80)
$CuL^1_2(ClO_4)_2{\cdot}2H_2O$	45.05	4.00	16.40	7.35
	(45.05)	(4.00)	(16.40)	(7.45)
$CuL^1_2(NO_3)_2$	51.45	4.10	22.35	8.45
	(51.80)	(4.05)	(22.65)	(8.55)
$CuL^2(ClO_4)_2{\cdot}H_2O$	37.20	3.65	12.00	11.15
	(36.90)	(3.60)	(11.95)	(10.85)
$CuL^2Br_2{\cdot}2H_2O$	38.40	3.55	12.25	11.05
	(38.55)	(3.40)	(12.50)	(11.35)
$CuL^3(ClO_4)_2{\cdot}4H_2O$	32.60	4.35	10.90	10.00
	(32.60)	(4.05)	(11.20)	(10.15)
$CuL^3_2(ClO_4)_2$	48.20	4.10	16.35	7.25
	(48.30)	(4.05)	(16.60)	(7.50)

The complex $CuL^3_2(ClO_4)_2$ was prepared similarly. Yield: 74%.

Elemental analyses for copper(II) complexes are given in Table 1.

CAUTION: Although no accident occurred with the present copper perchlorate complexes during the experimental work, it should be remembered that perchlorates are potentially explosive.

Physical Measurements.—Elemental analyses were performed at CDRI, Lucknow, India. The diffuse-reflectance and methanol solution spectra were measured on a Hitachi U-3400 double-beam UV/VIS-NIR spectrophotometer, EPR spectra on a Bruker or Varian E 112 X-band spectrometer calibrated with diphenylpicrylhydrazyl(dpph). The EPR spectra of polycrystalline samples were measured at ambient temperature. The values of g_0 and A_0 were measured at ambient temperature and $g_{\parallel}$ and $A_{\parallel}$ at 77 K for solutions of the complexes.

Cyclic voltammetry and differential-pulse voltammetry at a platinum-sphere electrode were performed at 25 ± 0.2 °C. A three-electrode cell configuration was used. The reference electrode was Ag(s)–$AgNO_3$ (0.01 mol dm^{-3}), tetrahexylammonium perchlorate (0.1 mol dm^{-3}) in acetonitrile. The temperature of the electrochemical cell was maintained 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 and an IBM PS-2 computer; EG & G M270 software was employed to carry out the experiments and to acquire the data.

Crystallographic Data Collection and Structure Analysis.—The compound $CuL^1_2(ClO_4)_2{\cdot}2H_2O$ on recrystallisation gave intense blue trapezoidal crystals. From oscillation and Weissenberg photographs the unit-cell dimensions were determined and the space group limited to *Pc*, *P2/c* or $P2_1/c$ of the monoclinic system. Of these the last was unambiguously determined by analysing the systematic absences on an Enraf–Nonius CAD4 Kappa geometry diffractometer using Mo-Kα radiation (λ 0.7107 Å).

The unit-cell parameters determined with the diffractometer were the same as those from oscillation and Weissenberg photographs. They were refined with 25 carefully centred reflections by least-squares procedures. Intensity data were collected by the ω–2θ scan technique and three standard

Table 2 Crystallographic data

Formula	$C_{32}H_{34}Cl_2CuN_{10}O_{10}$
M	853.14
Space group	$P2_1/c$
a/Å	9.828(2)
b/Å	9.546(2)
c/Å	19.906(2)
β/°	95.71(1)
U/Å^3	1858.3
Z	2
μ(Mo-Kα)/cm^{-1}	8.28
Crystal dimensions/mm	0.15 × 0.20 × 0.43
F(000)	874
D_c/g cm^{-3}	1.52
D_m/g cm^{-3}	1.53
T/K	293
θ range/°	1–27
No. of reflections measured	4760
No. of observed reflections [$F_o > 3\sigma(F_o)$]	2180
R	0.0635
R'	0.0681
Weighting scheme, w	$0.8952/\sigma^2(F + 0.007\,173F^2)$

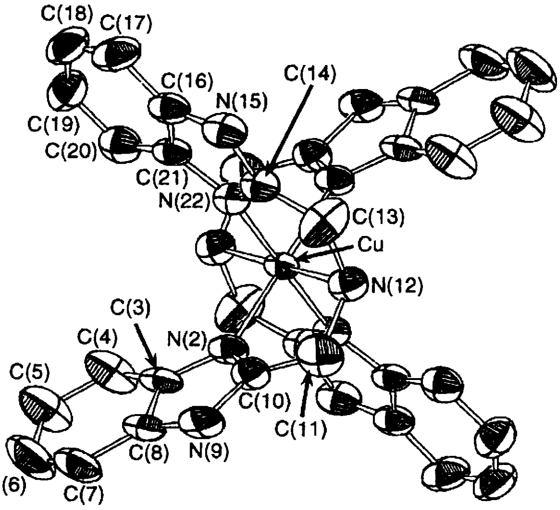


Fig. 1 An ORTEP drawing of the $[CuL^1_2]^{2+}$ cation showing the atom numbering and the thermal motion ellipsoids (50% probability level) for non-hydrogen atoms

reflections were monitored every 100; the latter showed good stability during the course of data collection. Details of the data collection and processing are presented in Table 2. The intensity data were subjected to Lorentz and polarisation corrections[12] but not absorption. The 2180 unique reflections with $I_o > 3\sigma(I_o)$ were used for structure analysis.

The structure was solved by conventional Patterson and Fourier methods. All the hydrogen atoms, except those belonging to the two lattice water molecules, were located from difference electron-density maps, but their positions were not refined. Their U values were fixed[13] at 0.05 Å. The final difference electron-density map revealed no peaks higher than 0.76 e Å^{-3} at ≈ 1.0 Å from the copper and chlorine positions.

The SHELX 76 of programs[13] was used for structure analysis and refinement and a DEC 1090 computer for calculations. Diagrams were drawn using the ORTEP II[14] program. The scattering factors for H, C, O, N and Cl were used as available[15] in the SHELX 76 program and for Cu they were taken from ref. 16 (anomalous dispersion corrections applied). The final atomic coordinates are collected in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 3 Atomic coordinates (× 10^4) of the non-hydrogen atoms of the complex $[CuL^1_2][ClO_4]_2 \cdot 2H_2O$

Atom	X/a	Y/b	Z/c
Cu	0	0	0
N(2)	−1858(4)	529(5)	246(3)
C(3)	−3034(6)	1055(5)	−140(3)
C(4)	−3362(7)	1175(7)	−824(4)
C(5)	−4598(7)	1764(8)	−1047(4)
C(6)	−5487(7)	2244(8)	−585(5)
C(7)	−5193(6)	2107(8)	86(5)
C(8)	−3950(6)	1476(6)	319(4)
N(9)	−3366(6)	1176(6)	937(4)
C(10)	−2128(6)	603(7)	886(3)
C(11)	−1195(8)	161(11)	1478(4)
N(12)	20(5)	−576(6)	1276(3)
C(13)	−72(9)	−2113(8)	1268(4)
C(14)	−626(6)	−2670(6)	606(3)
N(15)	−1239(6)	−3936(6)	524(4)
C(16)	−1628(6)	−4128(5)	−145(3)
C(17)	−2354(9)	−5198(7)	−495(5)
C(18)	−2642(12)	−5015(9)	−1166(5)
C(19)	−2242(11)	−3807(9)	−1501(5)
C(20)	−1526(9)	−2755(7)	−1147(4)
C(21)	−1210(6)	−2906(5)	−462(3)
N(22)	−583(5)	−2025(5)	26(3)
Cl	2481(2)	−4647(3)	−2107(1)
O(1)	219(2)	−411(1)	−149(6)
O(2)	296(2)	−448(2)	−145(1)
O(3)	144(3)	−418(3)	−169(1)
O(4)	261(2)	−370(2)	−262(1)
O(5)	206(2)	−317(2)	−248(1)
O(6)	310(3)	−443(4)	−264(1)
O(7)	133(2)	−554(2)	−237(1)
O(8)	212(3)	−580(3)	−241(1)
O(9)	95(4)	−472(4)	−200(2)
O(10)	302(3)	−619(3)	−205(1)
O(11)	404(3)	−449(3)	−224(2)
O(12)	385(4)	−490(3)	−182(2)
O(13)	556(2)	366(2)	718(1)
O(14)	499(4)	316(4)	699(2)
O(15)	604(3)	390(3)	729(1)

Chlorine atoms have been refined anisotropically, O(13), O(14) and O(15) correspond to one single disordered water oxygen. Coordinates of O atoms are × 10^3

Results and Discussion

Crystal Structure of $[CuL^1_2][ClO_4]_2 \cdot 2H_2O$.*—The ORTEP[14] view of the complex cation $[CuL^1_2]^{2+}$, also showing the atomic numbering scheme, is depicted in Fig. 1. The copper(II) is surrounded by two ligands, each acting in a tridentate manner. The nitrogen atom of the secondary amino group and two benzimidazole nitrogens are involved in the co-ordination. Relevant bond distances and angles are given in Table 4. The copper ion lies on a centre of symmetry, which implies that the two ligands are facially co-ordinated, with the two amine nitrogens in *trans* positions. The geometry of the complex ion is elongated octahedral and the equatorial plane is formed by the four benzimidazole nitrogens. The amino nitrogens are located at the axial positions at a rather long distance of 2.597(6) Å, obviously as a result of Jahn–Teller distortion. The equatorial N(2) and N(22) nitrogens are

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* A 1:2 perchlorate complex of the same ligand, $CuL^1_2(ClO_4)_2 \cdot 2H_2O \cdot 2MeOH$ has been reported[17] to crystallise in triclinic form. However, the limited nature of the refinement precluded a detailed characterisation or structure determination of the complex and no structural parameters were given.

Table 4 Selected bond lengths (Å) and angles (°) involving non-hydrogen atoms of $[\mathrm{CuL^1{}_2}]^{2+}$

Cu–N(2)	2.002(4)	Cu–N(12)	2.597(6)
Cu–N(22)	2.018(5)	N(2)–C(3)	1.415(7)
N(2)–C(10)	1.329(9)	C(3)–C(8)	1.404(10)
C(8)–N(9)	1.336(10)	N(9)–C(10)	1.347(9)
C(10)–C(11)	1.481(10)	C(11)–N(12)	1.476(10)
N(12)–C(13)	1.470(10)	C(13)–C(14)	1.474(10)
C(14)–N(15)	1.353(8)	C(14)–N(22)	1.313(8)
N(15)–C(16)	1.361(10)	C(16)–C(21)	1.407(8)
C(21)–N(22)	1.383(8)		
N(12)–Cu–N(22)	75.3(2)	N(2)–Cu–N(22)	88.1(2)
N(2)–Cu–N(12)	74.5(2)	Cu–N(2)–C(10)	121.5(4)
Cu–N(2)–C(3)	132.3(4)	N(2)–C(10)–N(9)	111.2(6)
N(9)–C(10)–C(11)	123.2(6)	N(2)–C(10)–C(11)	125.5(6)
C(10)–C(11)–N(12)	111.9(6)	Cu–N(12)–C(11)	103.8(4)
C(11)–N(12)–C(13)	115.3(6)	Cu–N(12)–C(13)	101.9(4)
N(12)–C(13)–C(14)	112.7(6)	C(13)–C(14)–N(22)	125.2(6)
C(13)–C(14)–N(15)	123.4(6)	N(15)–C(14)–N(22)	111.4(6)
C(14)–N(15)–C(16)	108.5(5)	N(15)–C(16)–C(21)	105.1(5)
C(20)–C(21)–N(22)	132.4(5)	C(16)–C(21)–N(22)	108.6(5)
C(14)–N(22)–C(21)	106.3(5)	Cu–N(22)–C(21)	132.3(4)
Cu–N(22)–C(14)	120.4(4)		

respectively 2.002(4) and 2.018(5) Å away from copper. The benzimidazole rings are planar and are twisted (inclined) relative to the $\mathrm{CuN_4}$ plane and the dihedral angle between them is 88.5°. Thus the $\mathrm{Cu{-}N_{bzim}}$ bond distances in the present complex fall in the range of those reported for copper(II) complexes of benzimidazole-containing ligands[8,9,11,18,19] and are similar to $\mathrm{Cu{-}N_{py}}$ bonds [1.986(5), 2.189(6) Å] in the pyridine analogue $[\mathrm{Cu(bpma)_2}][\mathrm{BF_4}]_2$.[5]

The $\mathrm{ClO_4^-}$ anions are not co-ordinated and exhibit static disorder in the crystal lattice. The pyrrole nitrogen N(15) of the benzimidazole ring and the amine N(12) are involved in hydrogen bonding, the former with O(1) and the latter with O(4) and O(7) of $\mathrm{ClO_4^-}$. The pyrrole nitrogen N(9) is also hydrogen bonded but to only one of the disordered lattice water molecules.

Much in contrast to the folded $\mathrm{L^1}$ ligand in the 1:2 chelate, the homologues of $\mathrm{L^3}$ is in meridional co-ordination in the equatorial plane of a highly distorted octahedral or square-pyramidal structure[8] in 1:1 nitrate complexes. The bite angle for the present complex is close to 90° as against 155–180° for 1:1 complexes. The mean planes of the two bases are almost coplanar in 1:1 nitrate complexes, while their dihedral angle is 88.5° for the present complex. The displacement of the N donor from the equatorial plane in the 1:1 complex to the axial position in the 1:2 complex is accompanied by a Cu–NH bond length increase of approximately 0.50 Å in the present case; however, no change occurs for the pyridine analogue [*mer* (**d**) ⟶ *fac* (**a**)]. A possible rationale[11] for the observed preference for equatorial positioning of the NH group in 1:1 complexes is the shortest and hence the strongest bond(s) formed by the primary and secondary amines, defining the equatorial *xy* plane, rather than one of them defaulting to a more weakly bound *z*-axial position (as in the 1:2 complex).

Table 5 Electronic absorption spectral data

		$10^{-3}\,\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ ($\varepsilon/\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$)	
Compound	Medium	Ligand field[a]	Charge transfer[b]
$\mathrm{CuL^1(ClO_4)_2}$	Solid	15.4	26.4
	MeOH	14.9 (154)	26.8 (sh) (280)
$\mathrm{CuL^1Cl_2{\cdot}2H_2O}$	Solid	14.6	25.7
	MeOH	14.4 (110)	28.9 (sh) (304)
$\mathrm{CuL^1Br_2}$	Solid	13.6, 17.1	26.9 (sh)
	MeOH	14.9 (60)	28.9 (sh) (420)
$\mathrm{CuL^1(NO_3)_2{\cdot}MeOH}$	Solid	14.2	26.2 (sh)
	MeOH	14.7 (81)	30.0 (sh) (250)
$\mathrm{CuL^1{}_2(ClO_4)_2{\cdot}2H_2O}$	Solid	14.1, 17.5	26.8 (sh)
	MeOH	15.0 (100), 12.1 (47)	32.0 (sh) (530)
$\mathrm{CuL^1{}_2(NO_3)_2}$	Solid	14.5	26.0
	MeOH	14.8 (123)	29.8 (sh) (355)
$\mathrm{CuL^2(ClO_4)_2{\cdot}H_2O}$	Solid	14.2	26.7
	MeOH	13.7 (400)	31.2 (sh) (575)
$\mathrm{CuL^2Br_2{\cdot}2H_2O}$	Solid	12.4	24.4 (sh)
	MeOH–MeCN	14.4 (180)	27.8 (sh) (1100)
$\mathrm{CuL^3(ClO_4)_2{\cdot}4H_2O}$	Solid	15.1	26.4 (sh)
	MeOH	14.6 (75)	34.4 (sh) (1550)
$\mathrm{CuL^3{}_2(ClO_4)_2}$	Solid	15.2, 17.2 (sh)	26.1 (sh)
	MeOH	14.6 (108)	34.4 (sh) (2050)
$[\mathrm{Cu(bbms)}]^{2+}$	MeOH	14.2 (54)	28.4 (328)
$[\mathrm{Cu(bbms)_2}]^{2+}$	MeOH	17.3 (58), 13.5 (109)	27.9 (374)

[a] $\approx 1 \times 10^{-2}$ mol dm^{-3}. [b] $\approx 1 \times 10^{-3}$ mol dm^{-3}; $\mathrm{N_{bzim}}(\pi) \longrightarrow \mathrm{Cu^{II}}$; refs. 8 and 23; sh = shoulder.

A similar facial co-ordination of bis(imidazol-2-ylmethyl) sulfide has been observed[20,21] but is due to the well known ability of co-ordinated thioether when linking two adjacent five-membered chelate rings to adopt a 'folded' geometry.[22] In all the 1:2 complexes of 3N and NSN ligands, with facial co-ordination the $\mathrm{Cu{-}N_{het}}$ bonds invariably occupy the equatorial position and vary from 1.910 to 2.189 Å. The $\mathrm{Cu{-}N_{amine}}$ and Cu–S distances are in the range 1.995–2.369 Å when the N or S donor lies in the equatorial plane and are longer [2.201(5)[5]–2.790(8) Å[20,21]] when it is in the axial position. For all these complexes the co-ordination geometry invariably becomes elongated octahedral while for $[\mathrm{Cu(dien)_2}]^{2+}$, in contrast, it is compressed octahedral[1,2] with meridional co-ordination of dien. Both structural types are the consequences of Jahn–Teller distortion and the structure of the ligand and the nature of the donor atoms are responsible for the large difference in structure.

Spectral Properties.—The reflectance and solution spectra of almost all the 1:1 perchlorates display a broad band in the range 13 700–15 400 cm^{-1} (Table 5). The *N*-methyl substitution at the secondary amine nitrogen as in $\mathrm{CuL^3(ClO_4)_2}$ leads to a red shift (1200 cm^{-1}) with a three-fold increase in intensity and a higher $g_\parallel$ and remarkably lower $A_\parallel$ values ($g_\parallel/A_\parallel$ quotient[24] 148 cm) (Table 6). This reflects the steric demand of the NMe group, which would change the orientation of the nitrogen lone-pair orbital towards the copper orbital, leading to a distorted $\mathrm{CuN_3O}$ square geometry.[9,25]

The polycrystalline spectrum of $\mathrm{CuL^1(NO_3)_2{\cdot}MeOH}$ is slightly rhombic, with the lowest *g* value not less than 2.03 as often found for copper(II) complexes with nitrogen- and oxygen-donor ligand systems with a d_{z^2} ground state.[26–29] The EPR parameters of $\mathrm{CuL^1Cl_2}$ are suggestive of a tetragonally distorted square-pyramidal environment, the equatorial plane comprising $\mathrm{CuL^1Cl}$ with the second $\mathrm{Cl^-}$ occupying the axial position as observed in the crystal structure[30] of a $\mathrm{CuLCl_2}$ complex. In frozen solution $\mathrm{CuL^1Br_2}$ displays an axial spectrum with nine superhyperfine lines ($|A| = 14$ G) on the perpendicular feature. As only five superhyperfine lines are expected for the two equivalent heterocyclic nitrogens in the equatorial plane, the additional lines may originate from copper and/or bromine hyperfine coupling. The polycrystalline EPR spectrum of $\mathrm{CuL^2Br_2}$, in contrast to that of $\mathrm{CuL^1Br_2}$ is inverted axial with $g_\parallel < g_\perp$ (Table 6) and a very low $G\ [= (g_\parallel - 2)/(g_\perp - 2)]$ value (1.12), suggesting a compressed square-pyramidal or a trigonal-bipyramidal geometry with a d_{z^2} ground state.[27,31]

The reflectance and solution spectra of $\mathrm{CuL^1{}_2(ClO_4)_2}$ contain two ligand-field bands (Table 5), as expected[27] for its

Table 6 Electron paramagnetic resonance spectral data[a] for copper complexes

Compound	Medium[b]	g_o/g_{av}	A_o	$g_\parallel$	$A_\parallel$	$g_\perp$[c]
$CuL^1(ClO_4)_2$	*d*			2.23	170	2.06
	MeOH–water	2.069	48	2.234	198	2.057
$CuL^1Cl_2\cdot2H_2O$	*d*			2.23		2.10
	MeOH–Me_2CO	2.122	70	2.245	163	2.097
CuL^1Br_2	*d*			2.28	165	2.07
	MeOH–Me_2CO	2.116	69	2.254	170	2.059
$CuL^1(NO_3)_2\cdot MeOH$	*d*	2.25, 2.09, 2.06				
	MeOH	2.133	79	2.269	165	2.073
$CuL^1{}_2(ClO_4)_2\cdot2H_2O$	*d*			2.20		2.07
	MeOH–Me_2CO	2.173	55	2.264	184	2.061
$CuL^1{}_2(NO_3)_2$	*d*	2.08	—			
	MeOH	2.167	66	2.314	201	2.094
$CuL^2(ClO_4)_2\cdot H_2O$	*d*			2.26		2.06
	MeOH–Me_2CO	2.076	60	2.258	162	2.065
$CuL^2Br_2\cdot2H_2O$	*d*			2.06		2.16
	MeOH–Me_2CO	2.142	65	2.221	189	2.063
$CuL^3(ClO_4)_2\cdot4H_2O$	*d*	2.06				
	MeOH–Me_2CO	2.149	42	2.268	140	2.084
$CuL^3{}_2(ClO_4)_2$	*d*	2.07				
	MeOH–Me_2CO		53	2.268	146	2.053

[a] Values determined as described in the Experimental section; *A* values in 10^{-4} cm^{-1}. [b] Methanol–acetone (4 : 1 v/v). [c] $g_\perp = \frac{1}{2}(3g_o - g_\parallel)$. [d] Polycrystalline.

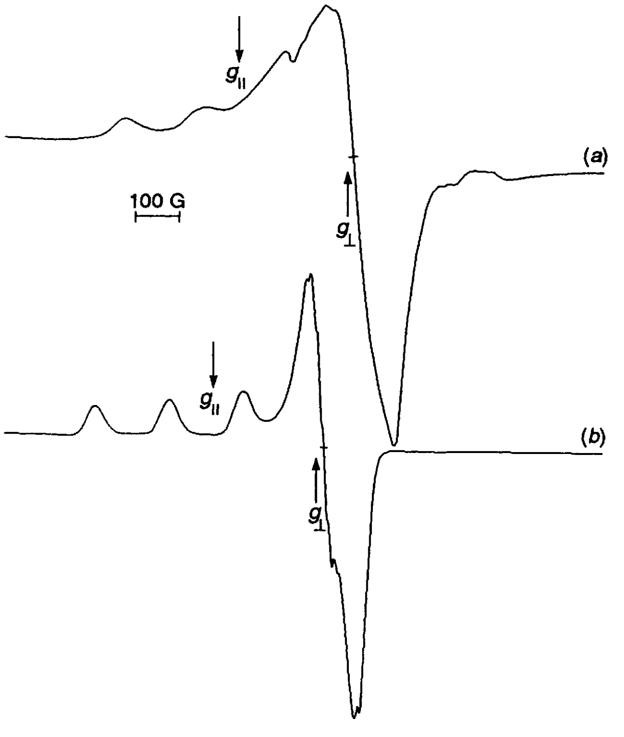

Fig. 2 The 77 K X-band EPR spectra of (*a*) $CuL^1(ClO_4)_2$ and (*b*) $CuL^1{}_2(ClO_4)_2$

elongated octahedral geometry revealed by the crystal structure. The ligand-field energies are similar to those of $[Cu(bbms)_2]^{2+}$ (Table 5) but lower than those observed for the analogous bis(imidazol-2-yl) thioether complexes.[20,21] These results imply that the N_4 (benzimidazole) donor set possesses a ligand field weaker than that of the N_4 (imidazole) donor set. The appearance and parameters of EPR spectra of the present 1 : 2 complexes (Fig. 2) are similar to those observed for planar CuN_4 chromophores constituted by four heterocyclic nitrogens.[32–36] The $g_\parallel$ and $A_\parallel$ values, though similar, are also significantly higher and lower respectively than those expected for a square-planar CuN_4 chromophore,[8] suggesting axial interaction by amine nitrogens. In contrast to $CuL^1{}_2(ClO_4)_2$, $CuL^3{}_2(ClO_4)_2$ shows only one low-energy visible band, low $A_\parallel$ values and no nitrogen superhyperfine lines. Since the sterically hindered NMe group is known[9] to change the orientation of its lone-pair orbital towards copper, we suspect that these results correspond to an entirely different structure [*mer* (**d**)].

Electrochemical Properties.—The Cu^{II}–Cu^{I} reduction potentials of the perchlorates (Table 7) follow the order $[CuL^2]^{2+} < [CuL^1]^{2+} < [CuL^3]^{2+}$, $[CuL^1{}_2]^{2+} < [CuL^3{}_2]^{2+}$. This reflects the stabilisation of Cu^{II} towards reduction by the electron-donating *N*-methyl group of benzimidazole and its destabilisation by the steric effect of the amine *N*-methyl group, as inferred from the electronic and EPR spectral parameters. The reduction potentials of $[CuL^1]^{2+}$ and $[CuL^1{}_2]^{2+}$ are more negative than those respectively of the 1 : 1 and 1 : 2 complexes of bbms; while the secondary amine nitrogen stabilises Cu^{II}, the thioether stabilises[9] Cu^{I}. Further, the 1 : 2 complexes are harder to reduce (60–120 mV) than are the 1 : 1 because of the change in co-ordination number.

Conclusion

The present investigation establishes that facial co-ordination results in weak axial interaction and leads to an elongated octahedral geometry, as seen in the copper(II) bis complex of bis(benzimidazol-2-ylmethyl)amine. This is in contrast to meridional co-ordination which leads to a strong axial interaction and hence a compressed octahedral geometry. Facial co-ordination appears to be facilitated when the terminal donor sites in the tridentate 3N ligand possess partial rigidity and hence reduced σ-donor as well as enhanced π-back-bonding ability (benzimidazole) or when the central donor is a soft one (thioether). On the other hand, meridional co-ordination is facilitated when primary amine nitrogens with strong σ-donor ability form the termini of the non-rigid ligand or when a ligand like 2,2′ : 6′,2″-terpyridine[37] or 2,6-bis(benzimidazol-2-yl)pyridine is available for planar co-ordination. Interestingly, when heterocyclic pyridine nitrogens with good σ- (but weaker than primary amine nitrogen) and π-bonding abilities form the termini both *mer* and *fac* isomers are possible. If the central nitrogen in the 3N ligand carries a methyl substituent as in L^3 it does not seem to favour the *fac* isomer.

It is well known[38] that as the axial interaction in copper(II) complexes increases, $\tilde{\nu}_{max}$ of the ligand-field spectral feature(s) decreases, $g_\parallel$ increases and $A_\parallel$ decreases. Thus, for the bis complexes of the present and other 3N and bis(imidazolyl) thioether ligands mentioned above, a plot of $\tilde{\nu}_{max}$ against the

Table 7 Electrochemical data[a] for the copper(II) complexes at 25 °C

Compound	E_{pc}/V	E_{pa}/V	ΔE_p/mV	$E'_{\frac{1}{2}}$/V	$E'_{\frac{1}{2}}{}^{b}$/V
$CuL^1(ClO_4)_2$	−0.390	—	—	—	−0.294
	—	0.268[c]	—		
CuL^1Cl_2	−0.500	—	—	—	−0.471[d]
		−0.082[c]			
$CuL^1(NO_3)_2$	−0.382	—	—	—	−0.307
		0.158[c]			
$CuL^1{}_2(ClO_4)_2$	−0.480	0.332	148	−0.406	−0.411
		−0.052[c]			
$CuL^2(ClO_4)_2$	−0.354	—	—	—	−0.311
$CuL^3(ClO_4)_2$	−0.310	−0.198	112	−0.254	−0.230
		0.206[c]			
$CuL^3{}_2(ClO_4)_2$	−0.350	−0.190	160	−0.270	−0.324
		0.162[c]			
$Cu(bbms)(ClO_4)_2$	0.026	0.186	160	0.106	0.103
$Cu(bbms)_2(ClO_4)_2$	−0.200	0.140	340	−0.030	0.063

[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, tetrahexylammonium perchlorate (0.1 mol dm^{-3}); complex concentration 1 mmol dm^{-3}. [b] Differential pulse voltammetry, scan rate 1 mV s^{-1}, pulse height 50 mV. [c] Additional anodic peak. [d] There is an additional peak at −0.331 V, which increases in intensity with increase in concentration of added NEt_4Cl.

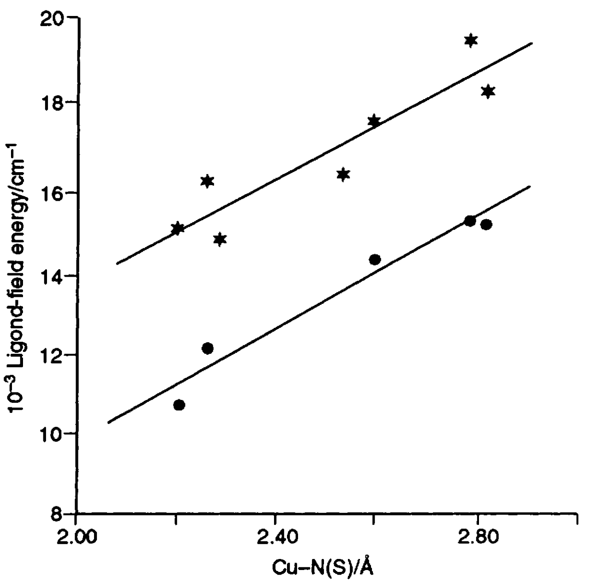

Fig. 3 Plot of $\tilde{\nu}_{max}$ *vs.* axial (longest) bond distance for copper(II) bis complexes of tridentate ligands

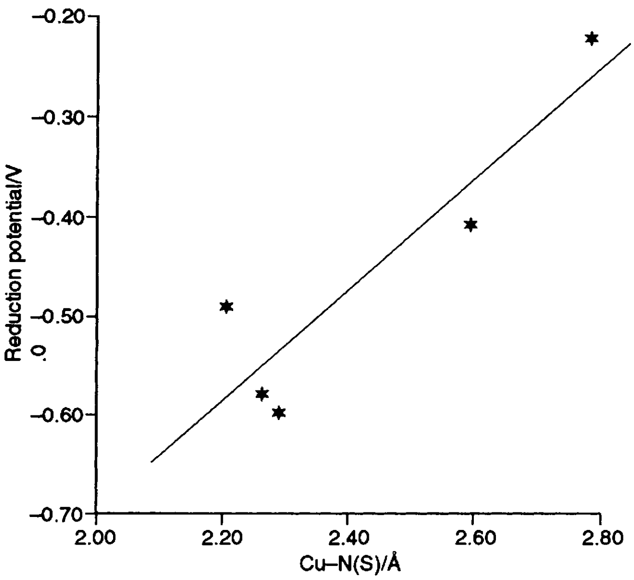

Fig. 4 Plot of Cu^{II}–Cu^{I} redox potential *vs.* axial (longest) bond distance for copper(II) bis complexes of tridentate ligands

measured axial (longest) bond distance (see SUP 57046) gives two straight lines which are almost parallel (Fig. 3). This implies that a stronger axial field (decreased axial distance) would lead to an increase in equatorial Cu–N distance,[23] resulting in a decrease in repulsion between the $d_{x^2-y^2}$ orbital and equatorial ligands and hence a regular decrease in the energy of this orbital; this facilitates the addition of the electrochemical electron into this orbital (where the hole resides), *i.e.* reduction is easier. Thus the Cu^{II}–Cu^{I} reduction potential would become increasingly positive with a decrease in the axial bond distance. However, the opposite trend is observed (Fig. 4); this is possibly because breakage of the axial bond would precede electron transfer to Cu^{II} with a six-co-ordinated geometry to give Cu^{I} with possibly a four-co-ordinated tetrahedral geometry, *i.e.* a weaker axial bond would facilitate bond dissociation and hence electron addition and make the reduction potential more positive. In contrast, $g_{\parallel}$ increases and $A_{\parallel}$ decreases (see SUP 57046) as the axial interaction becomes weaker for these complexes; however, it should be noted that the plots of $g_{\parallel}$ *vs.* $A_{\parallel}$ and of these spectral properties *vs.* Cu–X axial distance are not linear.

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