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Synthesis, structure, spectra and redox of Cu(II) complexes of chelating bis(benzimidazole)—thioether ligands as models for electron transfer blue copper proteins †

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The tridentate ligand 1,5-bis(benzimidazol-2-yl)-3-thiapentane (L^1) with N_2S donor set forms the complex $[Cu(L^1)(H_2O)Cl]Cl$ **1a** and the linear quadridentate ligand 1,8-bis(benzimidazol-2-yl)-3,6-dithiaoctane (L^2) with N_2S_2 donor set forms the complexes $[Cu(L^2)](ClO_4)_2\cdot 2H_2O$ **2a** and $[Cu(L^2)(NO_3)]NO_3$ **2b**. The linear pentadentate ligand 1,11-bis(pyrid-2-yl)-3,6,9-trithiaundecane (L^3) with N_2S_3 donor set forms the complex $[Cu(L^3)](ClO_4)_2$ **3**. The perchlorate complex $[Cu(L^4)](ClO_4)_2\cdot 2CH_3CN$ **4** of the pentadentate ligand, *N,N*-bis(benzimidazol-2-ylmethylthioethyl)methylamine (L^4) with N_3S_2 donor set has also been isolated. In **1a** Cu(II) is coordinated to the two benzimidazole nitrogens and thioether sulfur of the ligand L^1, a chloride ion and a water molecule. The coordination geometry around copper is intermediate between trigonal bipyramidal and square pyramidal geometries and is better described as trigonal bipyramidal distorted square based pyramidal (TBDSBP) with the sulfur and nitrogen atoms and the chloride ion in the equatorial positions and the oxygen of water in the apical position. The coordination geometry around copper(II) in **2b** is best described as trigonal bipyramidal, with both the thioether sulfur atoms [Cu–S(1), 2.529(5) and Cu–S(2), 2.438(6) Å] and one of the oxygen atoms of the nitrate ion [Cu–O(1), 2.066(13) Å] constituting the trigonal plane and both the benzimidazole nitrogens [Cu–N, 1.985(14) and 1.953(13) Å] occupying the axial positions. The bulky benzimidazole moieties of the ligand prevent the other nitrate ion from coordinating and favours trigonal bipyramidal geometry in spite of the presence of two six-membered chelate rings. In **4** the coordination plane of Cu(II) is comprised of two benzimidazole nitrogens, one thioether sulfur and *N*-methyl substituted amine nitrogen atom with the other thioether sulfur atom coordinated axially. The coordination geometry is best described as trigonal bipyramidal distorted square based pyramidal (TBDSBP). The ligand field and EPR spectra of **1a**, **2a** and **2b** are consistent with trigonal bipyramidal geometry in the solid state, whereas two ligand field bands in solution and an axial EPR spectrum in frozen solution were observed suggesting a change in coordination geometry to a square-based one on dissolution. The complexes **3** and **4** exhibit only one ligand field band in the solid state and axial EPR spectrum consistent with a square based geometry. All the complexes exhibit an intense $S(\sigma) \longrightarrow Cu(II)$ CT band in the range 330–380 nm and a high positive Cu^{II}/Cu^{I} redox potential.

Introduction

The active sites in blue copper proteins contain two histidine imidazoles and a cysteine thiolate coordinated to Cu(II) and a methionine thioether present at a long but bonding distance with a geometry closer to trigonal (bi)pyramidal.[1–3] They are in fact variable with subtle changes in their copper coordination geometry, which determine the spectral and redox properties of the proteins. Even though there is a possibility that the apical thioether ligand may control the rather high Cu^{II}/Cu^{I} redox potential of the proteins, its definite role still remains ambiguous.[4] So the synthesis and study of structure, spectra and redox properties of Cu(II) complexes as models for the proteins are essential to further address the structure/redox potential relationship.[5]

There is a growing interest in the Cu(II) complexes of tetradentate bis(benzimidazol-2-yl)dithioether ligands,[6–10] as they offer a CuN_2S_2 chromophore as in blue proteins. A remarkable feature of this class of complexes is that many of them possess a trigonal bipyramidal component while the corresponding 4-imidazolyl ligand complexes form a surprising number of ‘compressed’ octahedral structures[10,11] illustrating the importance of the bulky benzimidazole (bzim) moieties. Thus in the CuN_2S_2 complex [Cu(bbdh)Cl]Cl [bbdh = 1,6-bis(benzimidazol-2-yl)-2,5-dithiahexane][6] with a 555 chelate ring system a trigonal bipyramidal distorted square based pyramidal (TBDSBP)[12] geometry is observed. On adding a methylene group between the thioether sulfurs in this complex to obtain $[Cu(bmdhp)](ClO_4)_2$ [bmdhp, 1,7-bis(*N*-methylbenzimidazol-2-yl)-2,6-dithiahexane][8] the geometry becomes more trigonal bipyramidal distorted square based pyramidal (TBDSBP)[12] and significant changes in spectral and redox properties[13] are observed. So, it is of great interest to probe the consequences of enlarging the ligand by varying the chelate ring sizes on structure and spectral and redox properties of CuN_2S_2 complexes.

In the present report the consequences of incorporating one more methylene group between sulfur and benzimidazole donors in bbdh to generate the ligand 1,8-bis(benzimidazol-2-yl)-3,6-dithiaoctane (bbdo, L^2, Scheme 1) and removing one thioether sulfur donor from L^2 to obtain the ligand 1,5-

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† Dedicated to Professor P. Natarajan on the occasion of his sixtieth anniversary.

Electronic supplementary information (ESI) available: Fig. S1 showing the preliminary X-ray structure of the $[Cu(L^3)]^+$ cation, Figs. S2, S4 and S5 showing the cyclic and differential pulse voltammograms of complexes **1a**, **3** and **4** respectively and Fig. S3 showing the cyclic voltammograms of complexes **2a** and **2b**. See http://www.rsc.org/suppdata/dt/b1/b103511h/

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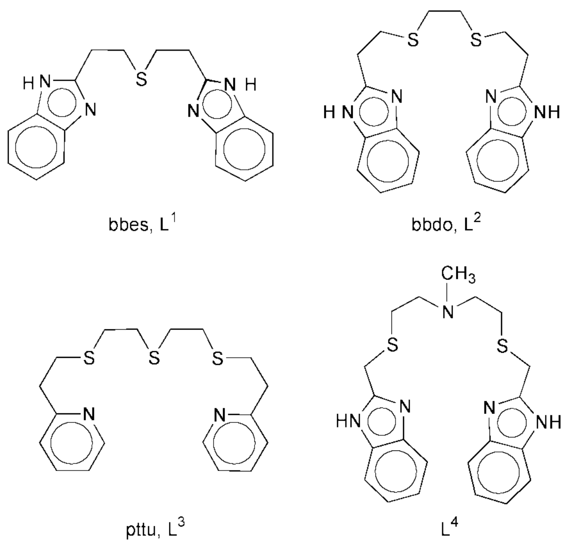

Scheme 1

bis(benzimidazol-2-yl)-3-thiapentane (bbes, L[1], Scheme 1) on the structure and spectral and electrochemical behaviour of their Cu(II) complexes are discussed. The present work also provides an opportunity to gain insight into the relative importance of the contributions from the coordination of thioethers[14–16] and the benzimidazole,[13,16,17] both of which are known to contribute to the positive Cu^{II}/Cu^{I} redox potential.

Addison *et al.* have studied Cu(II) complexes of linear N_2S_3 ligands containing pyridyl,[18] quinolyl[18] and benzimidazolyl[13] termini. Recently Liu *et al.* and Adhikary and Lucas have described the structure and properties of Cu(II) complexes of trithioether ligands containing substituted pyrazolyl[19] [1,9-bis(3,5-dimethyl-1-pyrazolyl)-2,5,8-trithianonane, pzttn], benzimidazolyl[19] [1,9-bis(3,5-benzimidazol-2-yl)-2,5,8-trithianonane, bzttn] and pyridyl[19,20] [(1,9-bis(pyrid-2-yl)-2,5,8-trithianonane, pttn] moieties. Recently we have described[17] the effect of incorporating increasing numbers of sulfur donors and varying chelate ring size on the structure and spectra of copper(II) complexes of bis(benzimidazol-2-yl)tetra- and pentathioether ligands. The present work deals with our attempt to understand the effect of ligand enlargement on the spectral and redox properties of the Cu(II) complex of the new ligand 1,11-bis(pyrid-2-yl)-3,6,9-trithiaundecane (pttu, L[3], Scheme 1) generated by addition of one more methylene group between pyridyl (py) and sulfur in pttn, which has also been isolated and investigated. Also we have enlarged the bbdh ligand by incorporating an amino nitrogen donor in between the two thioether sulfurs to obtain the ligand L[4] (Scheme 1) and its copper(II) complex and such a study would also enable us to understand the effect of the ligand enlargement and incorporating the third thioether sulfur on the spectral and electrochemical properties.

Experimental

Materials

$CuCl_2\cdot 2H_2O$, $Cu(NO_3)_2\cdot 3H_2O$ (BDH, India), bis(2-mercaptoethyl)sulfide, 1,2-ethanedithiol (Aldrich), $Cu(ClO_4)_2\cdot 6H_2O$, 3-chloropropionic acid, sodium borohydride and 2-vinylpyridine (Fluka), thionyl chloride (Ranbaxy, India) and 1,2-diaminobenzene, 3,3-thiodipropionic acid, thioglycolic acid and *N*-methyldiethanolamine (Sisco, India) were used as supplied. Tetra-*n*-hexylammonium perchlorate (THAP, G. F. Smith, USA) was recrystallised twice from aqueous ethanol. Tetra-*n*-butylammonium perchlorate was prepared by the addition of sodium perchlorate to a hot ethanol solution of tetra-*n*-butylammonium bromide (G. F. Smith, USA). The product was recrystallised from aqueous ethanol and tested for the absence of bromide. Methanol for electrochemistry was distilled over magnesium turnings and acetonitrile over P_4O_{10}.

Syntheses of ligands

The ligands 1,5-bis(benzimidazol-2-yl)-3-thiapentane (L^1)[21] and 1,8-bis(benzimidazol-2-yl)-3,6-dithiaoctane (L^2)[13] were synthesised as reported previously.

1,11-Bis(pyrid-2-yl)-3,6,9-trithiaundecane (L^3, pttu). The ligand pttu was prepared by adding 2-vinylpyridine (2.1 g, 20 mmol) slowly with stirring to bis(2-mercaptoethyl)sulfide (1.5 g, 10 mmol) and stirring continued for two hours. To the resulting solution was added water with stirring and the precipitate obtained was collected, recrystallised from aqueous ethanol and dried over P_4O_{10}. Yield, 67%, mp 63–65 °C. ^1H NMR (DMSO-d_6): δ 2.45 (s, 2 $-SCH_2CH_2S-$), 3.40 (t, $-SCH_2-$), 3.48 (t, $-CH_2py$), 7.54–7.69 (m, py-3,5 protons), 8.02 (m, py-4 protons) and 8.95 (d, py-6 protons). Found: C, 59.5; H, 6.73; N, 7.53. Calc. for $C_{18}H_{24}N_2S_3$: C, 59.3; H, 6.63; N, 7.68%.

***N*,*N*-Bis(benzimidazol-2-ylmethylthioethyl)methylamine (L^4).** *N*-Methyldiethanolamine (5.96 g, 0.05 mol) was suspended in dichloromethane (50 ml) and an excess of thionyl chloride (23.8 g, 2.0 mol) was added dropwise with constant stirring at 0 °C. The reaction mixture was refluxed for an hour and then cooled. The excess thionyl chloride was removed by adding a small amount of methanol, the bis(chloroethyl)-*N*-methylamine hydrochloride formed was collected and dried over $CaCl_2$ in vacuum. Sodium hydroxide (0.80 g, 20 mmol) and 2-mercaptomethylbenzimidazole[16] (4.02 g, 20 mmol) were combined in ethanol (50 ml) and the mixture stirred for 30 minutes under nitrogen. Then an ethanol solution (30 ml) of bis(chloroethyl)-*N*-methylamine hydrochloride (1.93 g, 10 mmol) was added to this and the resulting solution mixture was stirred for an hour and then refluxed for an hour. The pH of the resulting mixture was adjusted to 9.0 with sodium hydroxide solution. The volume of ethanol was reduced after treatment with charcoal, by rotary evaporation and 100 ml of water was added. The oily product obtained was used as such for the complex preparation without further purification.

Preparation of complexes

The complexes $[Cu(L^1)(H_2O)Cl]Cl$ **1a**, $[Cu(L^2)](ClO_4)_2\cdot 2H_2O$ **2a**,[13] $[Cu(L^2)(NO_3)]NO_3$ **2b** and $[Cu(L^3)](ClO_4)_2$ **3** and $[Cu(L^4)](ClO_4)_2\cdot 2CH_3CN$ **4** were obtained by adding the corresponding Cu(II) salt in methanol to a methanolic solution of the ligands in 1 : 1 mole ratio and then cooling the solutions. The products formed were filtered, washed with a small amount of cold methanol and the complex then dried over P_4O_{10}. Found: C, 43.42; H, 4.32; N, 11.78. Calc. for $C_{18}H_{20}N_4OSCl_2Cu$ (**1a**) C, 43.53; H, 4.24; N, 11.80%. Found: C, 37.5; H, 3.72; N, 8.75. Calc. for $C_{20}H_{22}S_2N_4O_8Cl_2Cu$ (**2a**) C, 37.2; H, 3.44; N, 8.69%. Found: C, 41.8; H, 3.96; N, 14.4. Calc. for $C_{20}H_{22}S_2N_6O_6Cu$ (**2b**) C, 42.1; H, 3.89; N, 14.7%. Found: C, 34.3; H, 3.91; N, 4.28. Calc. for $C_{18}H_{24}S_3N_2O_8Cl_2Cu$ (**3**) C, 34.5; H, 3.86; N, 4.47%. Found: C, 39.82; H, 4.21; N, 12.89. Calc. for $C_{25}H_{31}S_2N_7O_8Cl_2Cu$ (**4**) C, 39.71; H, 4.13; N, 12.97%. Single crystals of $[Cu(L^1)(H_2O)Cl]Cl$ **1a** suitable for X-ray diffraction were obtained on slow evaporation of the 1 : 1 water : acetonitrile solution of the complex. Single crystals of $[Cu(L^2)(NO_3)]NO_3$ **2b** suitable for X-ray structure analysis were obtained on slow evaporation of the methanolic solution obtained by mixing Cu(II) nitrate and the ligand in 1 : 1 ratio. Single crystals of $[Cu(L^4)](ClO_4)_2\cdot 2CH_3CN$ **4** suitable for X-ray diffraction were obtained on slow evaporation of the 1 : 1 acetonitrile : toluene solution of the complex.

Caution. During handling of the perchlorate salts of organic ligands care should be taken because of the possibility of

Table 1 Crystallographic data for the complexes $[Cu(L^1)(H_2O)Cl]Cl$ **1a**, $[Cu(L^2)(NO_3)]NO_3$ **2b** and $[Cu(L^4)](ClO_4)_2\cdot 2CH_3CN$ **4**

	1a	**2b**	**4**
Chemical formula	$C_{18}H_{20}N_4CuOSCl_2$	$C_{20}H_{22}N_6O_6S_2Cu$	$C_{23}H_{28}N_6O_8S_2Cl_2Cu$
M	474.88	570.10	715.07
Space group	$P\bar{1}$ (no. 2)	$P2_1/a$ (no. 14)	$P2_1/n$ (no. 14)
Crystal system	Triclinic	Monoclinic	Monoclinic
a/Å	9.466(3)	15.990(7)	10.9367(5)
b/Å	9.480(3)	13.706(4)	15.6280(6)
c/Å	11.519(2)	10.972(4)	17.6216(8)
α/°	75.880(18)		
β/°	81.362(18)	93.90(3)	100.9692(15)
γ/°	80.03(2)		
V/Å^3	981.1(4)	2399(2)	2956.8(2)
Z	2	4	4
T/°C	20	20	20
λ(Mo-Kα)/Å	0.71069	0.71069	0.71069
ρ_{calc}/g cm^{-3}	1.608	1.578	1.606
μ/mm^{-1}	1.508	1.134	1.117
$R[I > 2\sigma(I)]$	0.0487	0.0695	0.0680
$wR2$	0.1474	0.1336	0.1688

explosion. $[Cu(L^3)](ClO_4)_2$ led to an explosion during sample transfer in our laboratory.

Physical measurements

Elemental analyses were performed at City University, London. The solid state reflectance and the solution spectra in DMF, MeCN and MeOH were measured on a HITACHI U-3410 double beam UV-Vis-NIR spectrophotometer. EPR spectra were obtained on a JES-FE2XG X-band spectrometer, the field being measured using a NMR field meter. The values of g_o/g_{av} were measured at ambient temperature and $g_{\parallel}$ and $A_{\parallel}$ at 77 K. Cyclic voltammetry and differential pulse voltammetry were performed at 25.0 ± 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 being Ag(s)/$AgNO_3$ (0.01 M), tetra-*n*-hexylammonium perchlorate (THAP) (0.1 M) in acetonitrile. The $E_{1/2}$ and ΔE_p values observed under identical conditions for Fc/Fc$^+$ couple in methanol were 0.094 V and 96 mV respectively. The experimental solutions were deoxygenated by bubbling research grade nitrogen. The potentials were not corrected for the liquid junction. The instrument utilized included an EG&G PAR 273 potentiostat/galvanostat and an IBM PS-2 computer. EG&G M270 software (Princeton Applied Research, USA) was employed to carry out the experiments and to acquire the data.

Crystallographic data collection and structure analysis

Crystals of **1a**, **2b** and **4** showing sharp extinction under a polarising microscope were used for data collection with Enraf-Nonius-CAD4, Rigaku AFC-5 and Siemens three-circle diffractometers, respectively, with a CCD area detector using Mo-Kα radiation. The ω–2θ scan technique was used to record the intensity data for the crystals **1a** and **2b** and the ω scan technique was used for **4**. The data were corrected for Lorentz and polarisation but not for absorption effects. The details of data collection and structure analysis are given in Table 1. The structures were solved by direct methods.[22] The non-hydrogen atoms were located from the difference Fourier maps and further refined by the least-squares technique. All non-hydrogen atoms were refined anisotropically but in the case of crystal **2b**, due to the relatively low number of unique and observed reflections [$I > 2\sigma(I)$] and to maintain a reasonable data-to-parameter ratio, the non-hydrogen atoms other than ring carbons atoms were refined anisotropically, while the ring carbons (C1–C6 and C15–C20) were refined isotropically. In **1a**, the hydrogen atoms of water were located from the difference Fourier maps but their positions were not refined and their isotropic thermal parameter (U) values were fixed at 0.05 Å. The other hydrogen atoms were included in calculated positions and refined using a riding model. In the case of **2b** and **4**, all the hydrogen atoms were included in their calculated positions and refined using a riding model. All structure solutions[22] and refinement calculations were carried out using SHELXL-97[23] (**1a**, **4**) and SHELXL-93[24] (**2b**) crystallographic software packages. The molecular structures were drawn using ZORTEP.[25] Selected bond lengths and angles are given in Table 2.

CCDC reference numbers 156236, 156237 and 171722.

See http://www.rsc.org/suppdata/dt/b1/b103511h/ for crystallographic data for **1a** (156236) and **4** (156237) in CIF or other electronic format.

Results and discussion

The present ligands were synthesised according to known procedures which involve the Phillip's condensation of 1,2-diaminobenzene with the dicarboxylic acids dithiopropionic acid, mercaptoacetic acid and 4,7-dithiaoctane dicarboxylic acid to obtain respectively 1,5-bis(benzimidazol-2-yl)-3-thiapentane (L^1, bbes), mercaptoethylbenzimidazole and 1,8-bis(benzimidazol-2-yl)-3,6-dithiaoctane (L^2, bbdo). The tridentate ligand *N,N*-bis(benzimidazol-2-ylmethylthioethyl)-methylamine (L^4) and the acid 4,7-dithiaoctane dicarboxylic acid were synthesised by the nucleophilic substitution of the chlorides, *viz.* bis(2-chloroethyl)methylamine and chloropropionic acid by respectively mercaptomethylbenzimidazole and 1,2-ethanedithiol in the presence of alkali. Copper(II) complexes of these ligands were obtained by their reaction with equimolar amounts of the appropriate copper salt in methanol. All the complexes are soluble in common solvents like methanol, acetonitrile and dimethylformamide.

The electronic and EPR spectra of the complexes in solution are consistent with structural changes occurring on dissolution and reveal anion–copper interaction. The conductivity measurements of the complexes **1a** and **2b** in MeOH solution suggest that they exist as 1 : 1 electrolytes and those of **2a** and **4** in MeOH solution and **3** in CH_3CN solution suggest that they exist as 1 : 2 electrolytes. The benzimidazole and imidazole moieties have pK_a(HB$^+$) values[26] of 5.5 and 6.0 respectively suggesting that Cu–benzimidazole interaction in the complexes would duplicate the properties of Cu–imidazole interaction in proteins. The extra rigidity and bulk of benzimidazole relative to imidazole may be advantageous in attempts to mimic the constrained biological coordination environments in copper proteins. Thus the N_2S_2 ligand L^2 represents a good ligand

Table 2 Selected bond distances (Å) and angles (°)

$[Cu(L^1)(H_2O)Cl]Cl$ **1a**			
Cu(1)–S(1)	2.4201(12)	Cu(1)–O(1)	2.217(3)
Cu(1)–N(3)	1.969(3)	Cu(1)–N(1)	1.988(3)
Cu(1)–Cl(1)	2.3017(12)		
N(3)–Cu(1)–N(1)	176.64(13)	N(3)–Cu(1)–O(1)	87.87(13)
N(1)–Cu(1)–O(1)	92.28(14)	N(3)–Cu(1)–Cl(1)	91.56(10)
N(1)–Cu(1)–Cl(1)	91.33(10)	O(1)–Cu(1)–Cl(1)	118.11(11)
N(3)–Cu(1)–S(1)	91.09(10)	N(1)–Cu(1)–S(1)	85.56(10)
O(1)–Cu(1)–S(1)	94.32(10)	Cl(1)–Cu(1)–S(1)	147.53(5)
$[Cu(L^2)NO_3]NO_3$ **2b**			
Cu(1)–N(2)	1.953(13)	Cu(1)–N(3)	1.985(14)
Cu(1)–O(1)	2.066(13)	Cu(1)–S(2)	2.438(6)
Cu(1)–S(1)	2.529(5)		
N(2)–Cu(1)–N(3)	177.6(6)	N(2)–Cu(1)–O(1)	89.8(5)
N(3)–Cu(1)–O(1)	90.0(5)	N(2)–Cu(1)–S(2)	86.4(4)
N(3)–Cu(1)–S(2)	92.6(4)	O(1)–Cu(1)–S(2)	148.4(4)
N(2)–Cu(1)–S(1)	92.4(4)	N(3)–Cu(1)–S(1)	89.7(4)
O(1)–Cu(1)–S(1)	122.4(5)	S(2)–Cu(1)–S(1)	89.1(2)
$[Cu(L^4)](ClO_4)_2\cdot 2CH_3CN$ **4**			
Cu(1)–N(1)	1.982(6)	Cu(1)–S(2)	2.335(3)
Cu(1)–N(3)	1.993(6)	Cu(1)–S(1)	2.559(2)
Cu(1)–N(5)	2.118(6)		
N(1)–Cu(1)–N(3)	96.6(3)	N(1)–Cu(1)–N(5)	92.9(3)
N(3)–Cu(1)–N(5)	153.2(3)	N(1)–Cu(1)–S(2)	175.8(2)
N(3)–Cu(1)–S(2)	82.8(2)	N(5)–Cu(1)–S(2)	86.0(2)
N(1)–Cu(1)–S(1)	82.71(19)	N(3)–Cu(1)–S(1)	120.31(19)
N(5)–Cu(1)–S(1)	85.70(19)	S(2)–Cu(1)–S(1)	101.19(9)

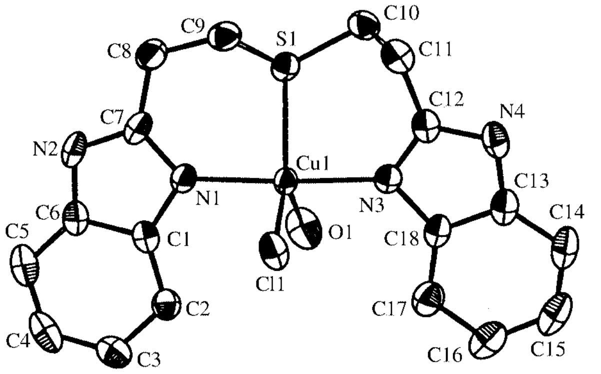

Fig. 1 ZORTEP drawing of $[Cu(L^1)(H_2O)Cl]Cl$ **1a** showing the atom numbering scheme and thermal motion ellipsoids (50% probability level) for the non-hydrogen atoms. The hydrogen atoms are omitted for clarity.

model with donors similar to those in blue copper proteins, with one of the weak thioether donors simulating the Cu–cysteinate interaction in the latter.

Description of the crystal structures of $[Cu(L^1)(H_2O)Cl]Cl$ 1a, $[Cu(L^2)(NO_3)](NO_3)$ 2b and $[Cu(L^4)](ClO_4)_2\cdot 2CH_3CN$ 4 and comparison with related structures

The ZORTEP views of **1a**, **2b** and **4** are illustrated in Figs. 1, 2 and 3 respectively, with atom numbering schemes shown. Selected bond lengths and angles are given in Table 2. In the complex cation of $[Cu(L^1)(H_2O)Cl]Cl$ **1a**, Cu(II) is located in an approximately trigonal bipyramidal geometry in which the equatorial positions are occupied by the sulfur atom of L^1, a chloride ion and the oxygen atom of water and the axial positions by the two benzimidazole nitrogen atoms [Cu–N(1), 1.988(3), Cu–N(3), 1.969(3) Å] with the N(1)–Cu(1)–N(3) angle of 176.64(13)° being close to the 'ideal' value of 180° which is usual for such systems.[27] However, as seen from the trigonality index[9] τ of 0.49 [$\tau = (\beta - \alpha)/60$ where β = N(1)–Cu(1)–N(3) = 176.64(13)° and α = Cl(1)–Cu(1)–S(1) = 147.53(5)°; for perfect square pyramidal and trigonal bipyramidal geometries the values of τ are zero and unity respectively], the coordination geometry around copper is intermediate between trigonal bipyramidal and square pyramidal geometries and is better described as trigonal bipyramidal distorted square based pyramidal (TBDSBP)[12] with copper displaced 0.587 Å above the N_2SCl coordination plane and towards the elongated apical oxygen atom. In the present complex only one of the counter-ions is coordinated, possibly due to the steric hindrance from

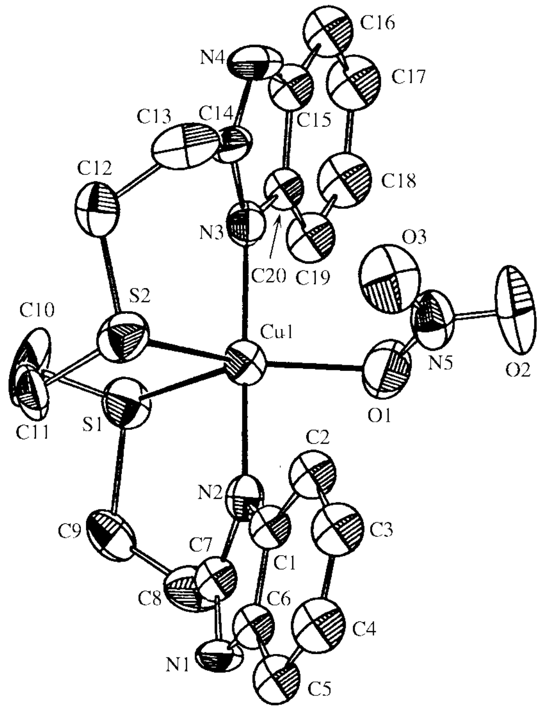

Fig. 2 ZORTEP drawing of $[Cu(L^2)(NO_3)]NO_3$ **2b** showing the atom numbering scheme and thermal motion ellipsoids (50% probability level) for the non-hydrogen atoms. The hydrogen atoms are omitted for clarity.

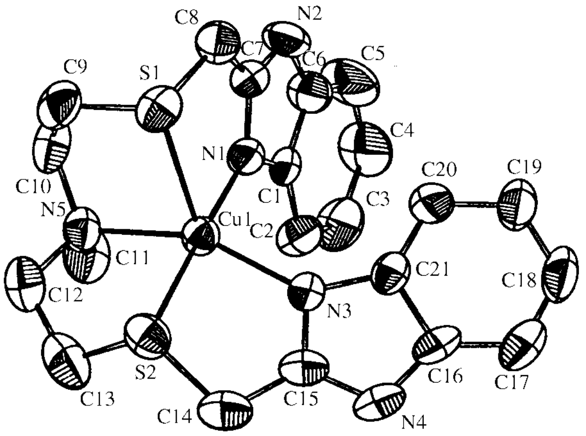

Fig. 3 ZORTEP drawing of $[Cu(L^4)](ClO_4)_2·2CH_3CN$ **4** showing the atom numbering scheme and thermal motion ellipsoids (50% probability level) for the non-hydrogen atoms. The hydrogen atoms and solvent molecules are omitted for clarity.

the bulky benzimidazole groups. Interestingly, the Cu–O and Cu–S distances [Cu–O(H_2O), 2.217(3), Cu–S, 2.4201(12) Å] in **1a** are longer than in $[Cu(L^1)(H_2O)(CH_3OH)]ClO_4$ **1b**[28] [Cu–S, 2.297, Cu–O(H_2O), 1.995 Å] obviously because of the increase in formal charge on **1a** by coordination of chloride. Both the hydrogens of the coordinated water molecule are hydrogen bonded to the uncoordinated chloride anion and both the benzimidazole hydrogens (–NH) are hydrogen bonded to coordinated chloride of the next molecule and so on.

The coordination geometry around copper(II) in $[Cu(L^2)(NO_3)](NO_3)$ **2b** is best described as trigonal bipyramidal, with both the thioether sulfur atoms and one of the oxygen atoms of the nitrate ion in the trigonal plane and both the benzimidazole nitrogens occupying the axial positions. The bulky benzimidazole groups on the ligand apparently prevent the other nitrate ion from coordinating. The thioether sulfur S2 is coordinated at a short distance [Cu–S(2), 2.438(6) Å] with the other at a rather long distance [Cu–S(1), 2.529(5) Å], revealing that the very symmetric ligand is coordinated in an asymmetric fashion, which is allowed by the flexibility of the Cu(II) coordination geometry. The Cu–S distances are similar to that in **1a** and those[6] in $[Cu(bbdh)Cl]^+$; however, they are longer than those[9] in $[Cu(bmdhp)(H_2O)]^{2+}$ on account of a decrease in formal charge on anion coordination to copper(II) in **2b**, as illustrated above for **1a**. It is also possible that the addition of a methylene group between the thioethers as in the bmdhp complex, rather than that between thioether and benzimidazole groups as in the present complex, leads to stronger coordination of thioethers. The $Cu–N_{bzim}$ distances [1.953(13), 1.985(14) Å] are in good agreement with those in **1a** and similar compounds.[6,8–10,27] The N(2)–Cu–N(3) angle of 177.6(6)° is close to the 'ideal' angle of 180°, whereas the S(1)–Cu–S(2) bond angle of 89.1(2)° is much smaller than the 'ideal' angle of 120°. The latter is a consequence of the limited bite of the ethylene bridge between the two sulfur atoms, as also found in $[Cu(bbdh)Cl]^+$. Based on the geometrical criteria already established,[29] the nitrate ion is considered to engage in a monodentate mode of coordination as evident from a Δd value of 0.6649 Å (>0.6 Å) and Δangle of 30.55° (>28°). The benzimidazole –NH is intermolecularly hydrogen-bonded to one of the oxygen atoms of the uncoordinated nitrate anion another oxygen atom of which is further hydrogen-bonded to –NH of benzimidazole of the next molecule and so on.

The trigonality index[9] τ for **2b** (0.49) illustrates that the coordination geometry is best described also as TBDSBP.[12] The geometry is distorted towards trigonal bipyramidal (with more constraint at copper) more than [Cu(bbdh)Cl]Cl (τ, 0.40), $[Cu(bmdhp)(H_2O)](ClO_4)_2$ (τ, 0.48) but less than $[Cu(bbtb)(H_2O)](ClO_4)_2$ [bbtb = 1,2-bis(benzimidazol-2-ylmethylthio)benzene][8] (τ, 0.64).[8] This illustrates that both the replacement of five-membered chelate ring(s) in $[Cu(bbdh)Cl]^+$ by six-membered one(s) and the fusion of a benzene ring between the thioether donors as in $[Cu(bbtb)]^{2+}$ lead to increased constraint at copper and enhanced distortion towards trigonality. Further, interestingly, the addition of a CH_2 group in between the two sulfur atoms lead to an equatorial disposition of both the sulfur atoms as in $[Cu(bmdhp)(H_2O)](ClO_4)_2$. A comparison of the present structure with that of its diamino analogue[30] *viz.* $[Cu(bbeda)]^{2+}$ [bbeda = *N,N′*-bis(benzimidazolyl-2-ylethyl)ethane-1,2-diamine], which possesses a square planar CuN_4 chromophore, suggests that the presence of Cu–S bond(s) is essential for distortion towards trigonal bipyramidal geometry. This is in conformity with the earlier observation[31] that π-bonding atoms confer on Cu(II) with ability to distort its coordination sphere toward a tetrahedral geometry even in the absence of steric forces. On the other hand, the pyridine analogue[32] of the present complex *viz.* $[Cu(pdto)(ClO_4)]^+$ [pdto = 1,8-bis(pyrid-2-yl)-3,6-dithiaoctane] possesses a square pyramidal structure (τ, 0.12). So it is evident that, in addition to coordinated thioethers, sterically hindered benzimidazole groups are required to confer on Cu(II) a geometry with considerable trigonal bipyramidal distortion.

The copper atom in $[Cu(L^4)](ClO_4)_2·2CH_3CN$ **4** is coordinated by two thioether sulfur atoms, two benzimidazole nitrogen atoms and the tertiary amine nitrogen atom. The value of the geometric parameter τ (0.38) indicates that the coordination geometry around copper(II) is best described as (TBDSBP)[12] with the corners of the square plane being occupied by one thioether sulfur atom (S2), two benzimidazole nitrogens and the tertiary amine nitrogen and the apical position by the other sulfur atom (S1). As in other bis(benzimidazolyl)dithioether systems, the sterically demanding benzimidazole groups prevent the sulfur and benzimidazole nitrogen atoms from lying in the same plane but still introduce trigonality in the coordination geometry around copper(II). The $Cu–N_{amine}$ bond [2.118(6) Å] is longer than the $Cu–N_{bzim}$ bond [1.982(6) and 1.993(6) Å],[6,8–10,27] as expected of the sp^3 and sp^2 hybridizations respectively of amine and benzimidazole nitrogen atoms. The basal Cu–S(2) distance [2.335(3) Å] is significantly shorter than the Cu–S(1) bond distance [2.559(2) Å]. The significant deviation of the S(1)–Cu–N(3) bond angle [120.31(19)°] from the ideal value of 90° illustrates the tendency of the ligand, because of all-five-membered chelate rings, to become folded, as also found in the $[Cu(pttn)]^{2+}$ and $[Cu(pzttn)]^{2+}$ complexes,[19,20] and also that of the N–Me group to become flexible like a thioether donor. The benzimidazole –NH is hydrogen-bonded to the uncoordinated perchlorate oxygen.

Spectral properties

An intense band observed in the range 330–380 nm for all the complexes is assigned to a S(σ)⟶Cu(II) charge transfer (CT) transition.[27,33] The solid state reflectance spectra of **1a**–**4** show two poorly resolved ligand field (LF) bands; however, in methanol or acetonitrile solutions two well separated (>3000 cm^{-1}) bands of almost equal intensity are observed suggesting that on dissolution[34,35] the complexes undergo a change from a geometry with a trigonal bipyramidal component,[36] as revealed in the X-ray crystal structures of **1a**, **2b** and **4**, to a square-derived geometry with considerable axial interaction. Further, the spectral features of **3** observed in the solid state and in solution are similar to those of $[Cu(pttn)]^{2+}$, which possesses a square based pyramidal distorted trigonal bipyramidal (SBPDTB)[12] geometry in its X-ray crystal structure,[19,20] and are consistent with a distorted square-based geometry. The chloro complex **1a** displays more intense ligand field bands at energies slightly higher than its perchlorate analogue[28] **1b**; however, the S(σ)⟶Cu(II) CT band energy is lower which is in line with the elongation of the Cu–S bond on chloride coordination. Ligand field and CT spectral titrations of **1b** with chloride ions (LiCl) reveal the coordination of two chloride ions to copper. These observations illustrate that the location of the CT band at very low energies in blue copper proteins may be partly due to strong copper(II)–cysteinate interaction.

The polycrystalline EPR spectra of **1a**, **2a** and **2b** are rhombic with three g values [lowest g <2.03, Table 3], which is consistent with the TBDSBP[12] coordination geometry observed in the X-ray crystal structures of **1a** and **2b**. The low values for g_1 with $R > 1$ [$R = (g_3 - g_2)/(g_2 - g_1)$] are characteristic of copper(II) complexes containing one or two thioether bonds and are consistent with the trigonal bipyramidal distorted geometry with a predominantly $d_{x^2-y^2}$ ground state.[34,37,38] The rhombic spectra of **2a** and **2b** are in contrast to the polycrystalline axial spectra of the analogous CuN_2S_2 complexes [Cu(bbdh)Cl]$^+$ and [Cu(bmdhp)(H$_2$O)]$^+$, both with lesser trigonal bipyramidal components in their geometries. Thus the spectral properties are in support of the description of the geometry of

Table 3 Spectral and electrochemical data for Cu(II) complexes

	Electronic spectra λ_{max}/nm (ε_{max}/M^{-1} cm^{-1})		EPR spectra[a]		Redox[d]			
Complex	LF	CT	Solid	Frozen solution	Solvent supporting electrolyte	$E_{1/2}$/V	ΔE_p/mV	$10^6 D$/cm^2 s^{-1}
	MeOH			MeOH				
[Cu(L^1)(H$_2$O)(CH$_3$OH)](ClO$_4$)$_2$ **1b**	695 (160)	327 (1740)		$g_{\parallel}$ 2.234				
	912 (128)	353 (1720)		$g_{\perp}$ 2.06 $A_{\parallel}$ 151				
+LiCl (excess)	694 (266)	312 (2420)						
	884 (352)	352 (2070)						
	Solid			MeOH	MeOH/THAP	0.110	92	4.5
[Cu(L^1)(H$_2$O)Cl]Cl **1a**	710	305	g_1 2.018	$g_{\parallel}$ 2.234				
	870	380	g_2 2.107	$g_{\perp}$ 2.014[b]				
	MeOH		g_3 2.194	$A_{\parallel}$ 153				
	680 (206)	305 (2206)						
	870 (150)	365 (2260)						
	H$_2$O							
	670 (155)	330 (1421)						
	900 (110)							
	Solid			MeOH	MeOH/THAP	0.299	82	2.5
[Cu(L^2)](ClO$_4$)$_2$ **2a**	625		g_1 2.009	$g_{\parallel}$ 2.227				
	900		g_2 2.214	$g_{\perp}$ 2.071				
	MeOH		g_3 2.207	$A_{\parallel}$ 146	H$_2$O/NaClO$_4$	0.483	127	1.2
	600 (220)	345 (2840)						
	890 (260)							
	MeCN							
	590 (220)							
	860 (210)							
	H$_2$O							
	600 (170)	340 (3760)						
	880 (190)	405 (1420)						
	Solid			MeOH	MeOH/THAP	0.263	90	2.5
[Cu(L^2)(NO$_3$)]NO$_3$ **2b**	640		g_1 2.029	$g_{\parallel}$ 2.210				
	870		g_2 2.134	2.241[c]				
	MeOH		g_3 2.185	$g_{\perp}$ 2.026	MeOH/NaNO$_3$	0.227	90	2.8
	605 (220)	345 (2300)	$A_{\parallel}$ 145					
	885 (220)			157[c]				
	MeCN			DMF				
	615 (160)	340 (3020)		$g_{\parallel}$ 2.210	CH$_3$CN/THAP	0.247	98	2.6
	890 (110)			2.215[c]				
				$g_{\perp}$ 2.071				
				$A_{\parallel}$ 145				
				131[c]				
	Solid			H$_2$O[b]	MeOH/THAP	0.364	84	3.7
[Cu(L^3)](ClO$_4$)$_2$ **3**	600		$g_{\parallel}$ 2.174	$g_{\parallel}$ 2.172				
	900		$g_{\perp}$ 2.031	$A_{\parallel}$ 170				
	H$_2$O				H$_2$O/NaClO$_4$	0.470	80	4.9
	600 (300)	380 (1910)						
	900 (120)							
	MeOH							
	610 (430)	380 (2540)						
	900 (110)							
	MeCN							
	615 (490)	380 (3280)						
	900 (100)							
	Solid			DMSO	CH$_3$CN/THAP	−0.039	94	1.4
[Cu(L^4)](ClO$_4$)$_2$·2CH$_3$CN **4**	870	337	$g_{\parallel}$ 2.175	$g_{\parallel}$ 2.193				
	615	416 (sh)	$g_{\perp}$ 2.053	$g_{\perp}$ 2.077				
	MeCN			$A_{\parallel}$ 172				
	620 (265)	332 (5520)						
	836 (120) sh							

[a] $A_{\parallel}$ values are in units of 10^{-4} cm^{-1}. [b] At least five N-shf lines are located on the perpendicular feature. [c] Minor species. [d] Measured *vs.* non-aqueous Ag/Ag$^+$ reference electrode for non-aqueous solvents (Add 544 mV to convert into NHE) and *vs.* SCE for aqueous solutions. Glassy carbon working electrode for complexes **1a** and **4** and Pt sphere for **2a**, **2b** and **3**. Scan rate 50 mV/s; concentration of the complexes 0.001 M.

2b as trigonal bipyramidal distorted square based pyramidal (TBDSBP).[12] The frozen solution spectrum of **1a** is axial supporting changes in structure on dissolution, inferred from electronic spectral studies. The $g_{\parallel}$ value of **1a** is higher than the perchlorate[28] **1b**, consistent with the higher constraint (higher τ) at copper in **1a**. The frozen solution spectrum of **2b** shows clearly resolved peaks in the $g_{\parallel}$ region, consistent with the superposition of spectra of three species. As the solution is diluted, the signals corresponding to solvated cupric ion grew in intensity relative to those of other species. On the addition of excess $NaNO_3$, the signals corresponding to the less abundant species with high $g_{\parallel}$ value decreased in intensity and a well-defined axial spectrum with a weak rhombic component for the other species tend to appear; however, the signals for solvated cupric ion still remain. A similar dissociative equilibrium involving ligand and solvent has been observed previously even in frozen methanol solution for other copper–thioether complexes,[7,19] the $g_{\parallel}$ values being in the same range as those observed for copper(II) thioether complexes.[9,18,27,33] The less abundant species, as it has a high $g_{\parallel}$ value, is likely to have at least one of the weakly coordinated thioethers replaced by solvent. In contrast to **2b**, the frozen solution spectrum of **2a** is axial and no dissociative equilibrium could be discerned. The $g_{\parallel}$ and $A_{\parallel}$ values (Table 3) are close to those observed for the more abundant species of **2b**.

The polycrystalline EPR spectra of **3** and **4** are clearly axial suggesting that the ground state is predominantly $d_{x^2-y^2}$.[34,38] The frozen solution spectra of **3** and **4** are also clearly axial (Fig. 4). The observed $g_{\parallel}$ and $A_{\parallel}$ values of **3** are similar to $[Cu(pdto)]^{2+}$ ($g_{\parallel}$, 2.176; $A_{\parallel}$, 174 × 10^{-4} cm^{-1})[32] with the N_2S_2 equatorial plane supporting the presence of a similar square-based coordination environment, suggested by electronic spectral studies. The $g_{\parallel}$ and $A_{\parallel}$ values of **4** are less than those for complexes with a CuN_4 chromophore ($g_{\parallel}$, 2.200; $A_{\parallel}$, 190–200 × 10^{-4} cm^{-1}). Further, the $A_{\parallel}$ rather than $g_{\parallel}$ value is very sensitive to the inclusion of thioether sulfur in the equatorial plane.

Electrochemistry

All the present complexes exhibit reversible to irreversible one-electron transfer involving Cu^{II}/Cu^{I} couple[9,39,40] (diffusion coefficients D, 1.2–4.9 × 10^{-6} cm^2 s^{-1}, Table 3). The value of ΔE_p in excess of 59 mV (for reversible one-electron transfer ΔE_p is 59 mV; for the Fc/Fc^+ couple of ferrocene in MeOH: $E_{1/2}$, 0.094 V; ΔE_p^0, 80 mV under identical conditions; ΔE_p^0 is ΔE_p extrapolated to zero scan rate) is considered to reflect the involvement of, apart from other factors, stereochemical reorganization accompanying electron transfer, which can be qualitatively understood from a comparison of the structures of the copper(II) and copper(I) forms of the present complexes. Thus the slightly higher ΔE_p and ΔE_p^0 values of **2a** and **2b** suggest that the differences expected in the structures of their Cu(I) and Cu(II) forms would be small and hence would imply lower structural reorganization energy involved during the heterogeneous electron transfer[41] which follows dissociation of weakly coordinated solvent/anion.

In contrast, upon one-electron transfer, the strongly bound chloride ion and a solvent molecule in **1a** with trigonal bipyramidal based geometry are displaced from the copper center to give possibly a T-shaped structure for the d^{10} Cu(I) ion, similar to that observed for its homologue[27] $[Cu(i\text{-Pr-bbes})]^+$. Further, assuming that N-*i*-Pr substitution in the homologue is only peripheral and does not influence the bond length, it may be noted that the decrease in coordination number from five to three is accompanied by enormous changes in bond angles, elongation of the Cu–S bond [2.469(9) Å] and a significant decrease in the $Cu–N_{bzim}$ bond distance [1.912(5) and 1.910(5) Å]. Such intricate structural changes, though difficult to verify in solution, account for the enhanced departure from electrochemical reversibility (ΔE_p^0, 88 mV) for **1a**. They are unlike those observed in blue copper proteins on electron transfer, which involve very small changes in geometry (bond lengths, <0.15 Å). The pentadentate ligand complexes $[Cu(L^3)]^{2+}$ **3** and $[Cu(L^4)]^{2+}$ **4**, both with square pyramidal structures as discussed above, are expected to undergo relatively less reversible electron transfer with the rupture of weak Cu–S or, most possibly, the terminal $Cu–N_{py}$ bonds as part of the structural reorganization to achieve a four coordinated pseudo-tetrahedral structure suitable for the copper(I) ion. In fact, as revealed in its preliminary X-ray crystal structure[42] $[Cu(L^3)]^+$ possesses a tetrahedral structure with a terminal $Cu–N_{py}$ bond dissociated. Thus the reversibility of the Cu^{II}/Cu^{I} couple appears to depend on bond-breaking of not only chelating ligands but also of coordinated anions and solvent.

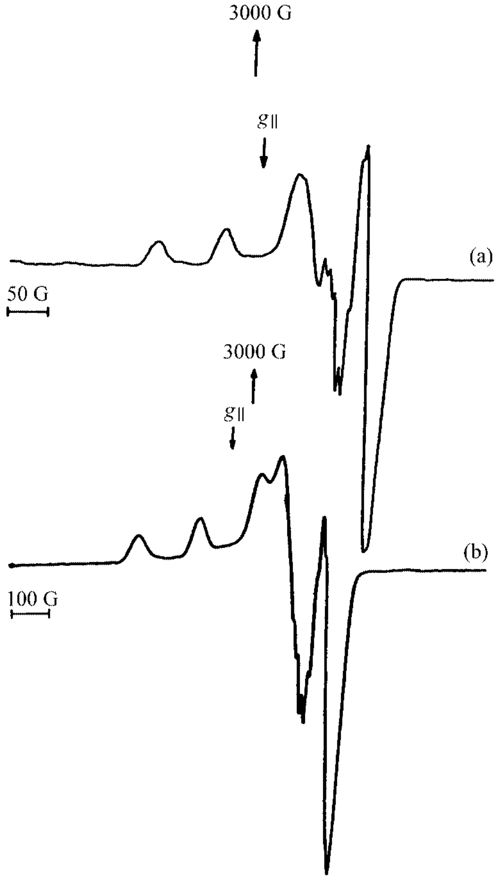

Fig. 4 EPR spectrum of **3** in aqueous solution (a) and **4** in DMSO solution (b) at 77 K.

The Cu^{II}/Cu^{I} redox potentials of **1a** and **2a** are higher than those of their amine analogues,[30,43] $[Cu(bba)]^{2+}$ and $[Cu(bbedo)]^{2+}$ (−0.294 V, −0.508 V *vs.* Ag/Ag^+ respectively), the latter with the same chelate ring sizes as **2a**. This suggests that the sulfur donor atom, by virtue of its greater π-acceptor ability, stabilizes Cu(I) with respect to the Cu(II) form more than the amino nitrogen. Thus the incorporation of a sulfur donor into L^1 to form the complex **2a**, and into L^2 to form copper(II) complexes of 1,9-bis(benzimidazol-2-yl)-2,5,8-trithianonane (bttn) and 1,11-bis(*N*-methylbenzimidazol-2-yl)-3,6,9-trithiaundecane (bmbtu), both with N_2S_3 donor sets, raises the redox potential (+0.23, +0.35 V *vs.* Ag/Ag^+)[44] whereas the addition of one amine nitrogen into **2b** to give **4** decreases the redox potential, as expected. Further, on incorporation of a third sulfur donor into $[Cu(pdto)]^{2+}$ to obtain **3** a rise in $E_{1/2}$ by 95 mV is expected,[45] which is in fair agreement with the observed rise of 108 mV; however, a similar rise in the $E_{1/2}$ of $[Cu(pttn)]^{2+}$, a homologue of **3** is only 25 mV. This clearly suggests that an increase in number of coordinated sulfur atoms from one to two to three increases the redox potential, while incorporation of a five-membered chelate ring decreases the redox potential.

The redox potentials of **1a** and **2b** are lower than their perchlorate complexes (**1b**, $E_{1/2}$, 0.110 V) and **2a** respectively; this is consistent with the stabilization of the Cu(II) form by chloride and nitrate ion coordination as evident from the above electronic and EPR spectral behaviour. In fact, addition of excess chloride (LiCl) to **1b** and use of $NaNO_3$ as supporting electrolyte for **2b** decreases the $E_{1/2}$ values significantly. This implies that the covalent copper(II)–cysteinate interaction in blue copper proteins would also lead to a decrease in Cu^{II}/Cu^{I} redox potential; however, the unusual distorted tetrahedral geometry for copper appears to offset this effect and raises the redox potential of the protein. Further, the $E_{1/2}$ values of both **2a** and **2b** are higher than their pyridine analogue $[Cu(pdto)]^{2+}$, obviously due to the bulky benzimidazole groups which confer distorted geometries as illustrated above. In fact, the $E_{1/2}$ value calculated for **2a** using Addison's ΔE_L parameters[45] (ΔE_{im}, 52 mV) is lower than the adjusted value [$E_{adj} = E_{exptl} - 0.215$ V (in methanol)].[45] This implies that the contribution by bulky benzimidazole to $E_{1/2}$ is much higher than that by pyridine or imidazole and thus a better agreement with the observed values is seen when a ΔE_{bzim} value[17] of +165 mV is used for calculating an $E_{1/2}$ of $[Cu(bbdh)]^{2+}$. The value of $E_{1/2}$ calculated for **2a**, however, is still lower (60 mV) than the observed one, illustrating that its copper(II) structure in solution may still possess significant trigonal bipyramidal distortion.[40] Among the bis(benzimidazolyl)dithioether complexes the $E_{1/2}$ value varies as $[Cu(bbdh)]^{2+}$ [13] < $[Cu(bmdhp)]^{2+}$ [13] < $[Cu(L^2)]^{2+}$ **2a** in methanol, suggesting that six-membered chelate rings[46,47] in the presence of π-donors increase the redox potential and that larger chelate rings can accommodate the pseudo-tetrahedral structure suitable for the Cu(I) state as expected.[20,41,48,49] Thus the incorporation of thioether donors or benzimidazole moieties or six-membered chelate rings and enlargement of the ligand backbone elevates the Cu^{II}/Cu^{I} redox potential by readily facilitating access to a pseudo-tetrahedral coordination geometry suitable for the Cu(I) oxidation state.

Conclusions

The CuN_2S_2 complexes exhibit a square-based geometry with enhanced trigonality, in spite of the presence of two ethylene bridges in between thioether and benzimidazole donors; this is interesting because the bis(pyridyl)dithioether and bis(benzimidazolyl)diamino analogues, which contain such bridges between –S– and pyridine and –NH– and benzimidazole respectively, possess square-based geometries with lesser trigonality. This is obviously because of geometric distortion induced by steric effects of the bulky benzimidazole groups, facilitated by coordinated thioethers. Further, the present study leads to the significant conclusion that in the solid state Cu(II) complexes of all tetradentate bis(benzimidazol-2-yl)dithioether ligands possess coordination geometries with the trigonality increasing with increase in number of six-membered chelate rings and with incorporation of fused benzene rings.[6,8] Similar to other members of its class, the present CuN_2S_2 complex has a solid state geometry which, because of its sensitivity to interactions with solvents and anions, tends to become square-based in solution. A water molecule or a halogenide or a relatively strongly coordinating anion like nitrate can be bound to copper(II) as the fifth ligand. The above variations in structures are reflected in their spectral and electrochemical behaviour and thus an enhanced redox potential expected of ligand enlargement is observed.

Incorporation of an amine donor into the CuN_2S_2 chromophore leads to the imposition of a square-derived geometry with a tendency towards ligand folding and decrease in redox potential. The replacement of pyridyl by a sterically demanding benzimidazolyl moiety and amino nitrogen by thioether and also the five-membered chelate rings, because of large constraints within the ligand, tend to impose a trigonal bipyramidal component in the coordination geometry. On the other hand, increasing the number of coordinated thioethers, though enhancing the redox potential, does not seem to exercise a preference for a geometry with enhanced trigonal distortion because of other influential factors like type of donor atoms and chelate ring size. Though we were successful in designing models with high redox potentials and decreased hyperfine splitting constants ($A_{||}$), the latter is only remotely comparable with that of blue copper proteins and the square-based structures and spectral properties are comparable only to the normal copper(II) species. Valid models for blue copper proteins may be constructed by incorporating bulky ligand moieties, six-membered chelate rings and a minimum of two sulfur donors *i.e.* N_2S_2 ligands.[46] Thus very recently success has been attained[50] in reproducing type I coordination geometry by characterising a Cu(II) complex with N_2S(thiolate)S(thioether) ligation; however, though relatively low $A_{||}$ values and a low energy S⟶Cu(II) LMCT band have been observed, the positive redox potential of the proteins is not reproduced. Moreover, a study on interaction of Cl^-, a stronger coordinating anion, with CuN_2S complexes with trigonal bipyramidal geometry may simulate the effect of strong cysteinyl sulfur coordination in increasing the Cu–thioether bond length and shifting the charge transfer band to lower energy. This result demands a further study on the interaction of this complex with heavily protected thiolates with an aim to isolate four-coordinate complexes with a geometry approaching that in blue copper proteins.

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