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### Copper(II) complexes of sterically hindered Schiff base ligands: Synthesis, structure, spectra and electrochemistry

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### Abstract

The synthesis, structure and spectral and redox behaviour of copper(II) complexes of sterically constrained  $N_3$ ,  $N_3S_2$  and  $N_2S_2$  ligands are described. The ligands 2,6-bis(2,4,6-trimethylphenyliminomethyl)pyridine (L1), 2,6-bis(2,6-diisopropylphenyliminomethyl)pyridine (L2), 2,6-bis(2-methylthiophenyliminomethyl)pyridine (L3), 1,3-bis(2-methylthiophenyliminomethyl)benzene (L4), 1,3-bis(2,4,6-trimethylphenyliminomethyl)benzene (L5) and 1,3-bis(2,6-diisopropyl-phenyliminomethyl)benzene (L6) have been synthesized. The 1:1 copper(II) complexes of L1–L5 have been isolated and characterized by spectral and electrochemical techniques. The X-ray crystal structure of the complex [Cu(L2)Cl<sub>2</sub>](2) has been successfully determined and is found to possess a distorted square pyramidal coordination geometry. The replacement of isopropyl groups in this complex by the less sterically demanding methyl groups as in [Cu(L1)Cl<sub>2</sub>] leads to a decreased geometric distortion. The complexes show relatively high positive redox potentials with a low reorganizational energy barrier for electron transfer involving the Cu(II)/Cu(I) couple. The redox cycle of the complexes 1 and 2 has been explained by assuming a square scheme. The spectral and electrochemical properties of CuN<sub>3</sub>S<sub>2</sub> and CuN<sub>2</sub>S<sub>2</sub> complexes generated by the incorporation of thioether sulfurs into L1/L2 and L4/L5, respectively, are also discussed. Both the complexes show positive redox potentials suggesting the coordination of at least one thioether sulfur to copper(II). The incorporation of a pyridine nitrogen donor into the CuN<sub>2</sub>S<sub>2</sub> complexes leads to higher LF field strengths but with lower absorptivities. The coordination of Cl<sup>-</sup> ions to the CuN<sub>3</sub>S<sub>2</sub> and CuN<sub>2</sub>S<sub>2</sub> complexes significantly alter the spectral and redox properties of the complexes. © 2005 Elsevier Ltd. All rights reserved.

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Keywords: Copper(II) complexes; X-ray structure; Tri- and pentadentate ligands; EPR spectra; Redox properties

### 1. Introduction

Copper compounds of chelating ligands incorporating pyridine, thioether, imidazole and imine donors have been of great interest in recent years. This is mainly because of their relevance to histidine coordinated copper proteins such as blue copper proteins, hemocyanin, tyrosinase, cytochrome c oxidase and laccase [1]. Very often better structural and functional models for metalloproteins have been prepared by altering the substituents of the ligands in order to match with the required spectral

properties of the metalloproteins [2]. As the function of a metalloprotein is closely related to the structure of its active site, i.e., the geometrical arrangement of the amino acid residues around copper, the objective of such studies include synthesizing ligands that contain donor atoms around copper in biomolecules so that the copper complexes resemble the overall structure of the active site [3]. Among the most extensively investigated ligands, macrocyclic amines, imines and thioethers deserve attention. Their flexibility, ease of preparation and capability of stabilizing unusual oxidation states of copper can explain their successful performance in mimicking the peculiar geometries around the metal, leading to very interesting spectroscopic properties [4]. Several Cu(II)

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complexes of bis(benzimidazolyl)-thioether donors with  $N_2S$  [5–7],  $N_2S_2$  [8–12] and  $N_2S_3$  [13–17] donor sets have been synthesized as models for the active sites in proteins and their structures, spectra and redox behaviour have been investigated with the goal of relating the electronic structure properties to the active site reactivity.

In our laboratory we have undertaken a systematic structural, spectroscopic and electrochemical study on a series of mononuclear copper(II) complexes of linear polydentate bis(benzimidazolyl)-thioether/amine/pyridine ligands [7,18–20] offering N and S donor atoms. The copper(II) complexes of nitrogen and sulfur containing Schiff base ligands have been demonstrated as valid models for blue copper proteins. Also, there is a continuing interest in investigating the relationship between the redox potentials and other electrochemical parameters and the spectral/geometrical parameters of Schiff base metal complexes, which could be the result of steric and electronic effects [21]. In this report, we describe the synthesis of copper(II) complexes of di-, tri-, tetraand pentadentate ligands (Scheme 1) containing heterocyclic N, imine N and thioether S donors with different and varying steric demands. The 3N ligands L1 and L2 have been designed as they have the ability to form copper(II) complexes in a meridional rather than facial coordination mode. Two thioether sulfur atoms have been incorporated into the 3N framework of L1/L2 to offer a  $N_3S_2$  donor set (L3). The ligand L4 has been synthesized to generate a novel CuN<sub>2</sub>S<sub>2</sub> coordination geometry with steric constraints, to help in understanding the role of the central pyridine nitrogen in L3. The 2N ligands L5 and L6 are sterically constrained to impose geometric distortions in bis-complexes of copper(II). The X-ray crystal structure of the copper(II) complex of L2 has been successfully determined. The spectral and electrochemical properties of the complexes have been studied and the results discussed.

### 2. Results and discussion

#### 2.1. Synthesis

A series of systematically varied ligands have been synthesized with the aim to understand the effect of ligand electronic and steric factors upon the structure and spectra of the copper(II) complexes. The ligands L1, L2 and L3 have been synthesized using the reported procedure with slight modifications, by condensing 2,6-pyridinedicarboxaldehyde [22] with 2,4,6-trimethylaniline, 2,6-diisopropylaniline and 2-(methylthio)aniline, respectively. The ligands L4, L5 and L6 have been obtained by the condensation of isophthalaldehyde with the corresponding sterically hindered anilines. The results of elemental analyses of L1-L6 were satisfactory and the <sup>1</sup>H and <sup>13</sup>C NMR confirmed the identity of the ligands. All the Schiff base ligands, except L6, readily form complexes on treating one or two equivalents of them with copper(II) salts in methanol at room temperature. The perchlorate complexes were synthesized in order to avoid the competing coordination of chloride ions to copper(II) in the presence of weakly coordinating thioether sulfur donors. Our attempt to synthesize  $[Cu(L6)_2]^{2+}$  was unsuccessful and no pure solid product could be isolated from the brown solutions obtained on mixing the ligand L6 and copper(II) perchlorate. The stoichiometries of the complexes were derived from elemental analysis and conductivity studies and that of complex 2 was confirmed by determining its X-ray crystal structure. The observed values of molar conductance suggest [23] that the complexes 1, 2 and 4a (30–60  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>) behave as neutral species, while the complexes 3–5 (160–205  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>) exist as 1:2 electrolytes in solution. The molar conductance  $(90 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1})$  of **3a** suggests that it behaves as 1:1 electrolyte in solution. The IR spectral data of the complexes support the coordination of the ligands to copper(II). The C=N  $(1700-1580 \text{ cm}^{-1})$  and C-S (L3, 690; L6,



685 cm<sup>-1</sup>) stretching vibrations of the ligands are shifted to lower frequencies (v(C=N), 1600–1470 cm<sup>-1</sup>; v(C-S), 645–635 cm<sup>-1</sup>) upon complex formation. The intense bands observed around 1095 and 625 cm<sup>-1</sup> for the perchlorate complexes are due to v(Cl-O) of uncoordinated perchlorate anions.

### 2.2. Description of the structure of $[Cu(L2)Cl_2]$ (2)

The ORTEP representation of the structure of the complex including the atom numbering scheme is shown in Fig. 1. The crystallographic data are given in Table 1 while the bond lengths and bond angles are collected in Table 2. The structure of the complex molecule involves a five-coordinate CuN<sub>3</sub>Cl<sub>2</sub> chromophore constituted by two imine (N9, N23) and one pyridine (N2) nitrogen of the tridentate ligand L2 and two chloride ions. The geometry around copper(II) is best described as distorted square pyramidal [24], as evident from the value of the trigonal index [11]  $\tau$  of 0.18 [ $\tau = (\beta - \alpha)/60$ , where  $\alpha = N2-Cu1-Cl36 =$  $160.42(5)^{\circ}$  and  $\beta = N23-Cu1-N9 = 149.63(7)^{\circ}$ ; for perfect square pyramidal and trigonal bipyramidal geometries the  $\tau$  values are zero and unity, respectively]. The N9, N23 and N2 nitrogen atoms of the meridionally coordinated L2 ligand and one of the chloride ions (Cl36) occupy the corners of the square plane. The other chloride ion (Cl37) is axially coordinated at an average angle of 99.43° to the CuN<sub>3</sub>Cl plane. The Cu-N<sub>pv</sub> (1.9523 Å) and Cu-N<sub>imine</sub> bond distances (2.1203, 2.1482 Å) fall in the range of values found for similar complexes [25,26]. The axial chloride ion is located at a distance (2.391 Å) longer than the equatorially located chloride ion (2.203 Å). The two phenyl rings are almost parallel to each other as in this arrangement the steric interaction between them is mini-

Table 1 Crystal data and structure refinement for the complex  $[Cu(L2)Cl_2]$  (2)

$\begin{array}{c} C_{31}H_{39}Cl_2CuN_3\\ 588.09\\ \text{orthorhombic}\\ P2_12_12_1\\ 11.0446(2)\\ 14.9386(2)\\ 18.7519(3)\\ 90.000\\ 20.000 \end{array}$
588.09 orthorhombic P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> 11.0446(2) 14.9386(2) 18.7519(3) 90.000
orthorhombic P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> 11.0446(2) 14.9386(2) 18.7519(3) 90.000
$\begin{array}{c} P2_{1}2_{1}2_{1}\\ 11.0446(2)\\ 14.9386(2)\\ 18.7519(3)\\ 90.000\\ \end{array}$
11.0446(2) 14.9386(2) 18.7519(3) 90.000
14.9386(2) 18.7519(3) 90.000
18.7519(3) 90.000
90.000
90.000
90.000
3093.89(9)
4
1.263
0.902
1236
7002/16/361
1.035
0.0303
0.0755

 ${}^{a} R = \sum ||F_{o}| - |F_{c}|| \sum |F_{o}|.$  ${}^{b} wR_{2} = \{\sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / \sum w[(F_{o}^{2})^{2}]\}^{1/2}.$ 

mized. Also, interestingly, the bulky isopropyl substituents on the phenyl rings are pushed away from the chloride ions and hence there is no steric clash between them.

### 2.3. Spectral properties

The solid-state reflectance spectra of all the complexes display either one broad or two poorly separated ligand-field bands  $(11900-15800 \text{ cm}^{-1})$  in the visible region, which is typical of Cu(II) located in a weakly tetragonal field [27]. On dissolution in methanol or acetonitrile no



Fig. 1. ORTEP drawing of  $[Cu(L2)Cl_2]$  (2) showing the atom numbering scheme and thermal motion ellipsoids (50% probability level). The hydrogen atoms are omitted for clarity.

Table 2 Selected Bond lengths (Å) and angles (°) for [Cu(L2)Cl<sub>2</sub>] (**2**)

8.000	) - L ( ) - 23( )
Cu(1)–N(2)	1.9523(16)
Cu(1)–N(23)	2.1203(16)
Cu(1)–N(9)	2.1482(17)
Cu(1)-Cl(36)	2.2033(5)
Cu(1)–Cl(37)	2.3905(6)
N(2)-Cu(1)-N(23)	77.39(6)
N(2)-Cu(1)-N(9)	77.44(7)
N(23)-Cu(1)-N(9)	149.63(7)
N(2)-Cu(1)-Cl(36)	160.42(5)
N(23)-Cu(1)-Cl(36)	96.82(5)
N(9)-Cu(1)-Cl(36)	101.25(5)
N(2)-Cu(1)-Cl(37)	93.66(5)
N(23)-Cu(1)-Cl(37)	101.93(5)
N(9)-Cu(1)-Cl(37)	96.36(5)
Cl(36)-Cu(1)-Cl(37)	105.88(2)

appreciable change in the ligand field bands is observed for the complexes 1, 2 and 4 (Table 3). However, noticeable changes in the ligand field features are observed for the complexes 3 and 5. For the complexes 1 and 2 two more absorption bands are observed at higher energies (1, 23900 and 26200 cm<sup>-1</sup>; **2**, 26300 and 28000 cm<sup>-1</sup>), which are presumably derived from nitrogen to copper(II) charge transfer (CT) transitions. Replacing the methyl groups in 1 by the more sterically demanding isopropyl groups, as in 2, would be expected to effect distortions in the copper(II) coordination geometry and hence lower the LF energy, but no significant spectral differences are observed. Obviously, the free rotation of the phenyl rings in the complexes (cf. above) minimize the steric constraints around copper(II), which is independent of the phenyl ring substituents and hence similar LF features are observed for 1 and 2. For complex 3, two ligand to metal charge transfer (LMCT) bands, characteristic of  $S(\sigma) \rightarrow Cu(II)$  and  $N(\pi) \rightarrow Cu(II)$  transitions, are observed (33200 and  $32700 \text{ cm}^{-1}$ ). Complex 4 in acetonitrile solution shows an absorption band  $(13500 \text{ cm}^{-1})$  with enhanced absorptivity  $(2340 \text{ M}^{-1} \text{ cm}^{-1})$  in the visible region, which may be attributed to intensity borrowing [28] from the  $S(\sigma) \rightarrow Cu(II)$ LMCT band, providing strong evidence for thioether coordination to copper(II) in solution. The noteworthy observation is that the LF band energy of 4 is lower than that of 3, with the absorptivity of 4 being 30-fold higher than that of **3** (Table 3). This suggests the presence of an axial interaction by solvent and/or distortion around copper(II) effected by the  $N_2S_2$  donor set of the L4 ligand, which is unfavourable for square planar coordination. The difference in electronic spectra of 3 and 4 in methanol solution indicates that complex 4 experiences partial or complete replacement of one or two weakly coordinated thioether donors by coordinating solvents. The chloride complex 4a exhibits a spectral pattern closely similar to 4, but with very low absorptivity (Table 3). The bis-complex 5, which does not have a pyridine donor as in L1-L3, exhibits a broad LF band around  $13900 \text{ cm}^{-1}$  with a shoulder around 18900 cm<sup>-1</sup>, implying a distorted square based

coordination geometry. This is expected as copper(II) complexes with a  $N_4$  donor set display a LF band in the range 14000–19000 cm<sup>-1</sup> [7,27].

The polycrystalline EPR spectra of complexes 2, 4a and 5 are isotropic while those of complexes 3 and 3a are axial. Interestingly, the complexes 1 and 4 show rhombic spectra with R values greater than unity  $[R = (g_3 - g_2)/(g_2 - g_1) =$ 1.2 (1); 1.1 (4), Table 3]. The rhombicity is more likely to arise from the interaction between differently oriented Cu(II) complexes rather than a  $d_{r^2}$  ground state for copper(II) in the solid state [29,30]. The cryogenic solution EPR spectra of all the complexes are axial  $[g_{\parallel} > g_{\perp} > 2.0,$  $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 3.0-4.5$ ], suggesting the presence of a  $d_{x^2-y^2}$  ground state for copper(II) located in square based geometries [31,32]. The complex  $[Cu(L2)Cl_2]$  (2) shows  $g_{\parallel}$  (2.254) and  $A_{\parallel}$  (133 × 10<sup>-4</sup> cm<sup>-1</sup>, Fig. 2) values, which are consistent with the 'CuN<sub>3</sub>Cl + Cl' chromophore as observed in the X-ray crystal structure. The complex  $[Cu(L)(H_2O)_2](ClO_4)_2.(H_2O)_2 \quad (L = bis(benzimidazol-2-yl)$ methylamine) [30] with the  $CuN_3O_2$  chromophore shows similar  $g_{\parallel}$  (2.268) and  $A_{\parallel}$  (140 × 10<sup>-4</sup> cm<sup>-1</sup>) values. However, copper(II) complexes of tridentate ligands with a CuN<sub>3</sub>Cl<sub>2</sub> coordination sphere, synthesized in our laboratory very recently [33], exhibit  $g_{\parallel}$  and  $A_{\parallel}$  values in the range 2.21–2.25 and  $179-184 \times 10^{-4}$  cm<sup>-1</sup>, respectively. Though the  $g_{\parallel}$  value of complex 2 falls within this range, the very low  $A_{\parallel}$  value observed indicates a large deviation from axial symmetry, which is evident from its crystal structure. It is interesting to compare the complexes 1 and 2, which are expected to have similar coordination geometries. On replacing isopropyl groups in **2** by methyl groups as in **1** the  $g_{\parallel}$ value decreases and the  $A_{\parallel}$  value increases suggesting a decrease in geometric distortion or axial interaction with copper(II). This is supported by the lower  $g_{\parallel}/A_{\parallel}$  quotient (131 cm) of complex 1, which falls in the range 105-135 cm, as expected [34] for square-planar copper(II) complexes. The  $g_{\parallel}$  and  $A_{\parallel}$  values of 2, which are higher and lower, respectively, than 1, suggest that the former possesses a coordination geometry distorted  $(g_{\parallel}/A_{\parallel}, 169 \text{ cm})$ more than 1 because of the sterically demanding isopropyl groups, rather than an axial interaction [35]. This is in contrast to the similar electronic spectral parameters of 1 and 2 suggesting the usefulness of EPR spectroscopy in detecting even small differences in coordination geometries.

The copper(II) complexes containing bis(benzimidazolyl)-thioether ligands [19] offering a N<sub>3</sub>S<sub>2</sub> donor set display  $g_{\parallel}$  and  $A_{\parallel}$  values in the range 2.24–2.29 and 138–  $187 \times 10^{-4}$  cm<sup>-1</sup>, respectively. Complex **3**, also with a N<sub>3</sub>S<sub>2</sub> donor set, exhibits a  $g_{\parallel}$  value of 2.249 and an  $A_{\parallel}$  value of  $140 \times 10^{-4}$  cm<sup>-1</sup> (Fig. 2). The relatively low  $A_{\parallel}$  value of complex **3** supported by the relatively low value of LF band energy indicates the presence of strong geometric distortion or strong axial interaction in the square-based coordination geometry. The EPR spectral features of **3a** are very similar to that of **3**; however, a lower  $g_{\parallel}/A_{\parallel}$  value is observed for **3a**. On replacing the pyridine ring in the L**3** complex by a benzene ring as in complex **4**, the  $g_{\parallel}$  (2.382) and  $A_{\parallel}$ 

Table 3 Electronic and EPR spectral data for the copper(II) complexes

Complexes	Electronic spectra <sup>a</sup> $\bar{\nu}_{max} \times 10^3 \text{ cm}^{-1} (\epsilon, \text{M}^{-1} \text{ cm}^{-1})$			EPR spectra <sup>b</sup>		
	Solid	Solution		Solid	Frozen solution	
$\left[Cu(L1)Cl_{2}\right](1)$	11.9 22.3	MeOH 12.2 (215) 23.9 (6070) 26.2 (6520) 34.1 (15770)		g <sub>3</sub> 2.243 g <sub>2</sub> 2.138 g <sub>1</sub> 2.052	$\begin{array}{c} \text{CH}_{3}\text{CN} \\ g_{\parallel} \ 2.192^{\circ} \\ A_{\parallel} \ 167 \\ g_{\perp} \ 2.091 \\ g_{\parallel}/A_{\parallel} \ 131 \end{array}$	
$\left[Cu(L2)Cl_2\right](\textbf{2})$	12.3 20.2	MeOH 12.1 (205) 26.3 (2885) 28.0 (3605) 34.6 (10600)		g <sub>ave</sub> 2.098	MeOH $g_{\parallel} 2.254$ $A_{\parallel} 133$ $g_{\perp} 2.084$ $g_{\parallel}/A_{\parallel} 169$	
[Cu(L3)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>3</b> )	13.5 22.6	MeOH 14.0 (135) 33.2 (10825) 32.7 (4000) 41.7 (20340)	CH <sub>3</sub> CN 14.5 (40) 29.4 (6165)	$\begin{array}{c} g_{\parallel} \ 2.211 \\ g_{\perp} \ 2.072 \end{array}$	CH <sub>3</sub> CN $g_{\parallel}$ 2.249 $A_{\parallel}$ 140 $g_{\perp}$ 2.082 $g_{\parallel}/A_{\parallel}$ 161	
[Cu(L3)Cl]Cl ( <b>3a</b> )	12.1 23.6	DMF 12.0 (215) 26.6 (10560) 32.6 sh 37.2 (35890)		$\begin{array}{c} g_{\parallel} \ 2.232 \\ g_{\perp} \ 2.084 \end{array}$	DMF $g_{\parallel} 2.242$ $A_{\parallel} 153$ $g_{\perp} 2.082$ $g_{\parallel}/A_{\parallel} 146$	
[Cu(L4)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>4</b> )	13.8 23.0	MeOH 13.5 (1105) 15.8 sh 28.0 (4095) 33.7 (6690)	CH <sub>3</sub> CN 13.5 (2340) 17.7 sh 26.4 (6025)	g <sub>3</sub> 2.266 g <sub>2</sub> 2.138 g <sub>1</sub> 2.019	$\begin{array}{c} {\rm CH_3CN^d} \\ g_{\ } \ 2.382 \\ {\cal A}_{\ } 148 \\ g_{\perp} \ 2.083 \\ g_{\ } / {\cal A}_{\ } \ 161 \end{array}$	
$\left[Cu(L4)Cl_2\right](\textbf{4a})$	13.6 22.8	MeOH 13.4 (400) 17.8 (840) 28.0 (5065) 33.9 (15330)		g <sub>ave</sub> 2.078	MeOH <sup>e</sup> $g_{\parallel} 2.485$ $A_{\parallel} 128$ $g_{\perp} 2.105$ $g_{\parallel} / A_{\parallel} 193$	
$[Cu(L5)_2(H_2O)](ClO_4)_2$ (5)	15.8 19.0	MeOH 13.9 (67) 18.9 sh 29.8 (6240)		g <sub>ave</sub> 2.072	CH <sub>3</sub> CN $g_{\parallel}$ 2.201 $A_{\parallel}$ 178 $g_{\perp}$ 2.069 $g_{\parallel}/A_{\parallel}$ 124	

 $^a$  Concentration,  $2 \times 10^{-3} \, M$  for ligand field and  $2 \times 10^{-5} \, M$  for ligand based transitions.

<sup>b</sup>  $A_{\parallel}$  in 10<sup>-4</sup> cm<sup>-1</sup>.

<sup>c</sup> The species  $[Cu(solvent)_4]^{2+}$  is also present  $(g_{\parallel} 2.418; A_{\parallel}, 148 \times 10^{-4} \text{ cm}^{-1}).$ 

<sup>d</sup> Values in methanol,  $g_{\parallel}$  2.408;  $A_{\parallel}$  134 × 10<sup>-4</sup> cm<sup>-1</sup>;  $g_{\perp}$  2.099.

<sup>e</sup> Values in DMF,  $g_{\parallel}$  2.404;  $A_{\parallel}$  131 × 10<sup>-4</sup> cm<sup>-1</sup>;  $g_{\perp}$  2.089.

 $(148 \times 10^{-4} \text{ cm}^{-1})$  values are enhanced (Table 3). This reveals the presence of a severely distorted square planar stereochemistry around copper(II) in 4 effected by the N<sub>2</sub>S<sub>2</sub> donor atoms, the geometrical disposition of which are unfavourable for square planar coordination around Cu(II).

### 2.4. Redox chemistry

The electrochemical data obtained in methanol or acetonitrile solution of the present complexes using TBAP as a supporting electrolyte are collected in Table 4. For all the complexes the one electron reduction peak  $(E_{\rm pc})$  corresponding to Cu(II) to Cu(I) reduction occurs in the potential range 0.508–0.208 V, with a directly associated reoxidation peak  $(E_{\rm pa})$  in the reverse scan, whose potential values fall within the range 0.702–0.296 V (Table 4). Further, the original Cu(II) complex species undergoing reduction are completely regenerated following electrochemical oxidation (the ratio of peak currents,  $i_{\rm pa}/i_{\rm pc} \sim 1.0$ , Table 4) suggesting a chemically reversible Cu<sup>II</sup>/Cu<sup>I</sup> couple. However, the value of the limiting peak-to-peak separation ( $\Delta E_{\rm p}$ , 86–226 mV) is higher than that for the Fc/Fc<sup>+</sup> couple ( $\Delta E_{\rm p}$ , 84 mV;  $E_{1/2}$ , 0.414 V) under identical conditions.



Fig. 2. X-band EPR spectra of the complexes  $[Cu(L2)Cl_2]$  (2) (a) in methanol/acetone and  $[Cu(L3)](ClO_4)_2$  (3) (b) and  $[Cu(L5)_2](ClO_4)_2$  (5) (c) in acetonitrile/acetone solution at 77 K.

Table 4 Electrochemical data<sup>a</sup> for the copper complexes at  $25 \pm 2$  °C in methanol solution

This suggests that the heterogeneous electron-transfer process in most of the present complexes is far from reversible and that on electron transfer considerable stereochemical reorganization of the coordination sphere occurs. However, quantitative conclusions on the extent of such reorganization are difficult to estimate [36]. Interestingly, the complexes 1 (Fig. 3) and 2 (Fig. 4(a)) have a minimal reorganizational energy barrier ( $\Delta E_p$ , 1, 88; 2, 86; Fc/ Fc<sup>+</sup>, 84 mV) indicating that the structural reorganization between the two oxidation states is minimum and hence electron transfer in these complexes is facile. It is relevant to note that in naturally occuring electron transfer copper proteins the redox is facile because of minimal structural changes between the redox pairs.

Complex 2 exhibits a one electron reduction at 0.268 V and the corresponding oxidation occurs at 0.348 V. Interestingly, an additional anodic peak at 0.484 V is observed (Fig. 4(a)), which can be explained by assuming a square scheme (Scheme 2). As the conductance of 2 is  $30 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$  it is probable that the complex is present as a [CuLCl]<sup>+</sup> species. The additional peak may arise from the oxidation of a trigonal planar (tp) Cu(I) species. Thus, when the scan rate is increased from 50 to 500 mV the additional peak grows in height suggesting that at higher scan rates the tp Cu(I) species is preferentially formed immediately on reducing the square planar (sp) [CuLCl]<sup>+</sup> species. Further, on addition of Cl<sup>-</sup> ions (LiCl), the height of the additional anodic peak decreases illustrating that the tp Cu(I) species combine with the Cl<sup>-</sup> ion to form a tetrahedral Cu(I) species, decreasing its concentration. It may be noted that the tp Cu(II) species corresponding to the tp Cu(I) species could not be detected, obviously because the isopropyl substituents on the phenyl rings in the Cu(II) species would be brought closer to exhibit strong steric clashes leading to

Compound	$E_{\rm pc}$ (V)	$E_{\mathrm{pa}}\left(\mathrm{V} ight)$	$\Delta E_{\rm p} ({\rm mV})^{\rm b}$	$E_{1/2}$ (V)		$i_{\rm pa}/i_{\rm pc}$	$10^6 D \ (\mathrm{cm}^2 \mathrm{s}^{-1})$
				CV	DPV <sup>c</sup>		
$[Cu(L1)Cl_2](1)$	0.208	0.296	88	0.252	0.274	0.9	12.3
+ LiCl	0.391	0.492	101	0.442	0.436	0.9	12.3
	0.400	0.502	102	0.451	0.474	1.0	
	0.200	0.310	110	0.255	0.266	0.8	8.9
$[Cu(L2)Cl_2]$ (2)	0.262	0.348 <sup>d</sup>	86	0.305	0.316	0.8	1.1
+ LiCl	0.252	0.360	108	0.306	0.314	1.0	8.0
$[Cu(L3)](ClO_4)_2$ (3)	0.338	0.452	114	0.395	0.414	1.3	0.8
[Cu(L3)Cl]Cl(3a)	0.290 <sup>e</sup>	0.516	226	0.403	0.398	1.1	3.0
+ LiCl	0.164	0.510	346	0.337	0.326	1.3	2.7
$[Cu(L4)](ClO_4)_2$ (4)	0.508	0.702	194	0.605	0.592	1.1	2.4
$[Cu(L4)Cl_2]$ (4a)	0.230	0.548	318	0.389	$0.500^{f}$	0.8	13.5
+ LiCl	0.420	0.510	90	0.465	0.490	1.1	5.4
[Cu(L5) <sub>2</sub> (H <sub>2</sub> O)](ClO <sub>4</sub> ) <sub>2</sub> (5)	0.380	0.496	116	0.438	0.432	0.9	3.8

<sup>a</sup> Measured on a Pt working electrode vs. a non-aqueous Ag/Ag<sup>+</sup> reference electrode; add 544 mV [300 mV, Ag/Ag<sup>+</sup> to SCE; +244 mV, SCE to SHE] to convert to standard hydrogen electrode (SHE); Fc/Fc<sup>+</sup> couple in CH<sub>3</sub>CN,  $E_{1/2}$ , 0.414 V (CV); 0.401 V (DPV); scan rate 50 mV s<sup>-1</sup>; supporting electrolyte, tetra-*N*-butylammonium perchlorate (0.1 mol dm<sup>-3</sup>); complex concentration, 1 mmol dm<sup>-3</sup>.

<sup>b</sup>  $\Delta E_{\rm p}$  at 50 mV s<sup>-1</sup> scan rate.

<sup>c</sup> Differential pulse voltammetry, scan rate 1 mV s<sup>-1</sup>; pulse height 50 mV.

<sup>d</sup> Additional anodic peak appears at 0.484 V. Cathodic peak does not apppear at high scan rate.

<sup>e</sup> Values in DMF.

<sup>f</sup> Additional peak at 0.316 V.



Fig. 3. Cyclic (a) and differential pulse (b) voltammograms of 0.001 M complex  $[Cu(L1)Cl_2](1)$  before (----) the addition of excess LiCl in methanol solution at 25 °C at 0.05 V s<sup>-1</sup> scan rate.

its destability. Thus, in the X-ray structure of the tp Cu(I) complex [Cu(bbtmp)](NO<sub>3</sub>) [bbtmp = 2.6-bis (benzimidazol-2'-ylthiomethyl)pyridine] the benzimidazole rings are closer to each other than in the corresponding tetrahedral [Cu(bbtmp)Cl] species [17]. From the difference in  $E_{pa}$  values  $(\Delta E_{\rm pa})$  for the oxidation of the two Cu(I) species, the  $\Delta E_{1/2}$ values for the redox of [Cu(L2)Cl] and  $[Cu(L2)]^+$  species was estimated assuming reversibility, from which the  $K_1/$  $K_2$  value was calculated [37] as  $7.9 \times 10^{-3}$ . The magnitude of  $K_1/K_2$  illustrates that the tp Cu(II) species rather than the tp Cu(I) species readily combines with Cl<sup>-</sup> ions leading to the non-detection of the tp Cu(II) species. Similarly, the tp Cu(I) species shows a reluctance to bind to the Cl<sup>-</sup> ion illustrating the above observation that the tp Cu(I) species are directly formed from square planar [Cu(L2)Cl]<sup>+</sup> species on reduction. The decreased steric constraints in the tp Cu(II) species of 1 leads to its detection in the CV ( $E_{pc}$ , 0.391 V), in contrast to 2. Similarly, the tp Cu(I) species for 1 will be more stable than that for 2 and hence combine with Cl<sup>-</sup> less strongly  $(K_1/K_2, 1.8 \times 10^{-3}, \text{ calculated from the two})$ 

 $E_{1/2}$  values (Table 4) obtained from differential pulse voltammetry (DPV)). As for **2**, an increase in scan rate leads to the formation of more tp Cu(I) species, as seen from the increase in height of the additional anodic peak with increase in scan rate. The tp Cu(II) species of **1** is more stable because the steric clash between the two phenyl rings carrying the methyl groups is less compared to the corresponding tp Cu(II) species of **2** and hence its detection in the CV.

Complex 3, bearing a CuN<sub>3</sub>S<sub>2</sub> coordination sphere, shows a positive redox potential of 0.395 V (Fig. 4(b)). The incorporation of two sulfur atoms into 1 as in complex 3 leads to a Cu(II)/Cu(I) redox potential higher than 1/2 suggesting the involvement of thioether coordination in 3 [38]. The higher  $E_{1/2}$  value (0.403 V) observed for the chloro complex 3a is almost the same as for 3 but, interestingly, the  $\Delta E_p$  value of complex 3a (226 mV) is higher than 3 (114 mV). This suggests that the chloride ion coordinates to copper(II), as shown by the lower conductance (90  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>) of 3a. Further, the addition of excess LiCl shifts the cathodic peak to a more



Fig. 4. Cyclic (——) and differential pulse (----) voltammograms of the complexes  $[Cu(L2)Cl_2](2)$  (a) and  $[Cu(L3)](ClO_4)_2$  (3) (b) and methanol solution at 25 °C at 0.05 V s<sup>-1</sup> scan rate.

negative value confirming the coordination of the chloride ion to copper(II), which renders the reduction more difficult.

The complexes 4 and 4a display redox potentials higher than complexes 3 and 3a, which is expected with the incorporation of hard N donors into the CuN<sub>2</sub>S<sub>2</sub> coordination sphere of 4 and 4a. An interesting electrochemical behaviour was observed for the chloro complex 4a, which undergoes reduction at a very low positive potential of 0.230 V with a shoulder around 0.438 V. The high  $\Delta E_p$  value (318 mV) and the observation of two waves in DPV at different potentials suggest the coordination of Cl<sup>-</sup> ion as illustrated above for 2. A well-defined CV with a low  $\Delta E_p$  value of 90 mV was obtained after the addition of excess of LiCl, supporting the dissociation of chloride ions as proposed above. It should be noted that all these proposals are only speculative in the absence of crystal structures of the complexes. The bis-complex 5 also exhibits positive re-



dox potentials (0.438 V) because of the bulky *N*-phenyl groups, which would favour the formation of tetrahedral copper(I) species more than complex 1, which may be

due to the presence of hard N donors in the latter complex as discussed above. The high redox potential (0.592 V versus  $Ag/Ag^+$ ) for the Cu(II)/Cu(I) couple of complex 4 may be attributed to tetrahedral distortion from a regular square-based geometry.

### 3. Conclusions

The distinct spectral and electrochemical behaviour of copper(II) complexes of five sterically hindered Schiff base ligands have been studied. The 1:1 copper(II) complex of 2,6-bis(2,6-diisopropylphenyliminomethyl)pyridine adopts a distorted square pyramidal geometry. The replacement of isopropyl groups in this complex by the less sterically demanding methyl groups leads to a similar coordination geometry as revealed by their similar spectral and electrochemical features. However, the redox potential of the isopropyl complex is higher than the methyl complex, which is consistent with the higher  $g_{\parallel}$  value [39] of the former complex, illustrating the importance of sterically demanding isopropyl groups in distorting the coordination geometry around copper(II). Further, the interaction of a thiolate moiety with the methyl/isopropyl complexes would be expected to generate a Cu(I) trigonal pyramidallike or tetrahedral-like coordination geometry, which would be a better copper(II) model for the active sites of electron transfer copper proteins. Thus, Holland and Tolman [40] have recently reported four-coordinate copper(II) complexes with a thiolate and thioether containing chelating ligand and a bidentate β-diketiminate as an auxiliary ligand and these complexes are believed to be close structural mimics for the type I copper proteins. However, these complexes fail to reproduce the positive redox potential of the blue copper proteins.

The copper(II) complexes of sterically constrained ligands providing  $N_3S_2$  and  $N_2S_2$  donor sets, which are unfavourable for square planar coordination, have also been synthesized and characterized. The spectral and electrochemical properties of these complexes suggest the presence of thioether coordination in solution. The incorporation of a pyridine nitrogen donor into the  $CuN_2S_2$  complexes leads to a higher LF band energy but with lower absorptivity, suggesting lesser distortion in the coordination sphere. Both the  $CuN_3S_2$  and  $CuN_2S_2$  complexes show positive redox potentials suggesting the coordination of at least one thioether sulfur. The bis-complex of a sterically hindering bidentate ligand also shows a positive redox potential suggesting that the distortion in the coordination sphere is significantly large.

### 4. Experimental

### 4.1. Materials

Copper(II) chloride dihydrate, copper(II) perchlorate hexahydrate, 2,6-pyridinedimethanol, 2,4,6-trimethylaniline, 2,6-diisopropylaniline, selenium dioxide (Aldrich), isophthaladehyde (Lancaster) were used without further purification.

### 4.2. Synthesis of ligands

# *4.2.1. 2,6-Bis(2,4,6-trimethylphenyliminomethyl)pyridine* (*L1*)

2,6-Pyridinedicarboxaldehyde (0.68 g, 5.0 mmol) and 2,4,6-trimethylaniline (1.35 g, 10.0 mmol) were refluxed [26] in methanol (25 mL) for 2 h over molecular sieves (4 Å). The reaction mixture was filtered while hot. The yellow crystals of L1 (1.64 g, 89%) obtained upon cooling the reaction mixture were filtered off and dried. *Anal.* Calc. for C<sub>25</sub>H<sub>27</sub>N<sub>3</sub>: C, 81.3; H, 7.4; N, 11.4. Found: C, 81.4; H, 7.5; N, 11.4%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ , ppm 8.39 (s, 2H, *HC*=N), 8.38 (d, *J* = 7.8, 2H, *HPy*), 7.97 (t, *J* = 7.6, 1H, *HPy*), 6.91 (s, 4H, *HPh*), 2.30 (s, 6H, *H*<sub>3</sub>C–PhC<sub>4</sub>), 2.16 (s, 12H, *H*<sub>3</sub>C–PhC<sub>2</sub>). <sup>13</sup>C NMR (CDCl3, 100 MHz):  $\delta$ , ppm 163.6 (*CH*=N), 155.0, 148.2, 137.7, 134.0, 129.3, 127.2, 123.0 (*CPy*, *CPh*), 21.2 (*CH*<sub>3</sub>–C<sub>4</sub>), 18.7 (*CH*<sub>3</sub>–C<sub>2</sub>). IR (KBr): *v*, cm<sup>-1</sup> 2971s, 2914s, 2914s, 1640vs, 1481s, 1205vs, 1140s, 835s, 733s.

## *4.2.2. 2,6-Bis(2,6-diisopropylphenyliminomethyl)pyridine* (*L2*)

The ligand L2 was synthesized by the reported procedure [41]. To a solution of 2,6-pyridinedicarboxaldehyde (0.68 g, 5.0 mmol) in ethanol (25 mL) were added 2.6-diisopropylaniline (1.77 g, 10.0 mmol) and one drop of glacial acetic acid, and the resulting mixture was refluxed over molecular sieves (4 Å). After 24 h the reaction mixture was filtered and the ligand (1.78 g, 78%) was obtained upon cooling. Anal. Calc. for C<sub>31</sub>H<sub>39</sub>N<sub>3</sub>: C, 82.1; H, 8.7; N, 9.3. Found: C, 81.5; H, 8.9; N, 9.5%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ , ppm 8.41 (d, J = 7.8, 2H, HPy), 8.39 (s, 2H, HC=N), 8.01 (t, J = 7.8, 1H, HPy), 7.21-7.10 (m, 6H, HPh), 3.00 (sep, 10.1) $J = 6.8, 4H, HC(H_3C)_2$ , 1.20 (d,  $J = 6.8, 24H, (H_3C)_2C$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ, ppm 162.8 (CH=N), 154.6, 148.4, 137.5, 137.3, 124.7, 123.2, 122.9 (CPy, CPh), 28.1 (CH(H<sub>3</sub>C)<sub>2</sub>), 23.6 ((CH<sub>3</sub>)<sub>2</sub>C). IR (KBr): v, cm<sup>-</sup> 3065w, 2961vs, 1585vs, 1566w, 1456w, 1319s, 1184s, 748s.

### 4.2.3. 2,6-Bis(2-methylthiophenyliminomethyl)pyridine (L3)

A mixture of 2,6-pyridinedicarboxaldehyde (0.68 g, 5.0 mmol) and 2-(methylthio)aniline (1.47 g, 10.5 mmol) were refluxed in benzene (20 mL) for 36 h. The reaction mixture was filtered under hot conditions. Fine yellow crystals of **L3** (1.16 g, 62%) were obtained on recrystallization in benzene, which was filtered off and dried. *Anal.* Calc. for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>S<sub>2</sub>: C, 66.8; H, 5.1; N, 11.1. Found: C, 66.9; H, 5.1; N, 11.2%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ , ppm 8.63 (s, 2H, *HC*=N), 8.41 (d, *J* = 7.8, H, *HP*y), 7.95 (t, *J* = 7.8, 1H, *HP*y), 7.36–7.11 (m, 8H, *HP*h), 2.49 (s, 6H, *H*<sub>3</sub>C). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ , ppm 159.7 (*C*H=N), 154.7, 147.8, 137.5, 135.1, 127.5, 125.4, 124.7, 123.6, 117.5 (*CP*y, *CP*h), 14.9 (*CH*<sub>3</sub>). IR (KBr): *v*, cm<sup>-1</sup> 3050w, 2978w, 2913s, 1619vs, 1570w, 1468s, 1331s, 800s, 724vs.

### 4.2.4. 1,3-bis(2-methylthiophenyliminomethyl)benzene (L4)

The ligand L4 was synthesized by the same method adopted for L3, using isophthalaldehyde (0.67 g, 5.0 mmol). The yellow solid precipitated was filtered off and dried (1.43 g, 76%). *Anal.* Calc. for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub>: C, 70.2; H, 5.4; N, 7.4. Found: C, 70.2; H, 5.3; N, 7.5%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ , ppm 8.50 (s, 2H, *HC*=N), 8.41 (s, 1H, *HPh*), 8.14 (d, *J* = 7.8, 1H, *HPh*), 8.13 (d, *J* = 7.6, 1H, *HPh*), 7.59 (t, *J* = 7.6, 1H, *HPh*), 7.24–7.03 (m, 6H, *HPh*), 7.01 (d, *J* = 7.6, 2H, *HPh*), 2.48 (s, 6H, *H*<sub>3</sub>C). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ , ppm 159.3 (*C*H=N), 148.9, 136.9, 134.3, 131.5, 130.2, 129.4, 126.8, 125.4, 124.7, 117.7 (*CPh*), 14.9 (*C*H<sub>3</sub>). IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3050w, 2978w, 2905w, 1614vs, 1570s, 1466s, 1436s, 1351s, 1268s, 1071s, 804s, 754vs, 691s.

# *4.2.5. 1,3-bis(2,4,6-trimethylphenyliminomethyl)benzene* (*L5*)

The ligand L5 was prepared by refluxing isophthalaldehyde (0.67 g, 5.0 mmol) and 2,4,6-trimethylaniline (1.42 g, 1.42 g)10.5 mmol) in benzene (20 mL) for 36 h over molecular sieves (4 Å). The reaction mixture was filtered and the solvent removed under vacuum. The excess amine was evaporated on warming gently under high vacuum. The <sup>1</sup>H NMR spectrum of the residue showed that the product was sufficiently pure (1.62 g, 88%). Anal. Calc. for C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>: C, 84.7; H, 7.7; N, 7.6. Found: C, 84.8; H, 7.7; N, 7.7%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ, ppm 8.36 (s, 1H, HPh), 8.31 (s, 2H, HC=N), 8.10 (d, J = 7.6, 1H, *H*Ph), 8.09 (d, J = 7.8, 1H, *H*Ph), 7.63 (t, J = 7.6, 1H, HPh), 6.91 (s, 4H, HPh), 2.31 (s, 6H, H<sub>3</sub>C-C<sub>4</sub>), 2.15 (s, 12H,  $H_3$ C–C<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ , ppm 162.1 (CH=N); 148.6, 136.9, 133.3, 130.9, 129.4, 128.9, 128.8, 127.1 (CPh), 20.9 (CH<sub>3</sub>-C<sub>4</sub>), 18.4 (CH<sub>3</sub>-C<sub>2</sub>).

# *4.2.6. 1,3-bis(2,6-diisopropylphenyliminomethyl)benzene* (*L6*)

The ligand **L6** was prepared using the method adopted for **L5**. After the evaporation of the solvent the solid obtained was washed with hexane to yield **L6** (1.89 g, 83%). *Anal.* Calc. for C<sub>32</sub>H<sub>40</sub>N<sub>2</sub>: C, 84.9; H, 8.9; N, 6.2. Found: C, 85.0; H, 9.0; N, 6.2%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ , ppm 8.36 (s, 1H, *H*Ph), 8.32 (s, 2H, *HC*=N), 8.15 (d, J = 7.8, 1H, *H*Ph), 8.14 (d, J = 7.6, 1H, *H*Ph), 7.68 (t, J = 7.6, 1H, *H*Ph), 7.21–7.15 (m, 6H, *H*Ph), 3.02 (sep, J = 6.8, 4H, *HC*(*H*<sub>3</sub>C)<sub>2</sub>), 1.21 (d, J = 6.8, 24H, (*H*<sub>3</sub>C)<sub>2</sub>C). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ , ppm 161.8 (*CH*=N); 149.4, 137.9, 137.2, 131.5, 129.9, 129.5, 124.8, 123.5 (*C*Py, *C*Ph), 28.4 (*CH*(H<sub>3</sub>C)<sub>2</sub>), 23.9 ((*CH*<sub>3</sub>)<sub>2</sub>C). IR (KBr): v, cm<sup>-1</sup> 3057w, 2964vs, 2869s, 1636vs, 1581s, 1456w, 1361s, 1321s, 1147s, 840s, 762vs, 692s.

### 4.3. Synthesis of copper(II) complexes

The copper(II) complexes 1–4 of the ligands L1–L4 were prepared by adding the corresponding copper(II) salt in methanol to a methanolic solution of the ligand in a 1:1 mole ratio. The volume of the solvent was reduced by rotary evaporation and then cooled. The product formed was filtered off, washed with small amounts of cold methanol and then dried under vacuum. Single crystals of  $[Cu(L2)Cl_2](2)$  suitable for X-ray diffraction were obtained by diffusion of ether vapour into an acetonitrile solution of 2. The complex 5 was obtained by mixing the ligand L5 and copper(II) perchlorate hexahydrate in a 2:1 (ligand:metal) mole ratio.

 $[Cu(L1)Cl_2](1)$ . Yield: 86% (0.43 g). Anal. Calc. for  $C_{25}H_{27}N_3Cl_2Cu$ : C, 59.6; H, 5.4; N, 8.3. Found: C, 59.6; H, 5.5; N, 8.4%.

 $[Cu(L2)Cl_2](2)$ . Yield: 88% (0.52 g). Anal. Calc. for  $C_{31}H_{39}N_3Cl_2Cu$ : C, 63.3; H, 6.7; N, 7.1. Found: C, 63.4; H, 6.7; N, 7.2%.

 $[Cu(L3)](ClO_4)_2(3)$ . Yield: 91% (0.58 g). Anal. Calc. for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>8</sub>S<sub>2</sub>Cl<sub>2</sub>Cu: C, 39.4; H, 2.9; N, 6.6. Found: C, 39.5; H, 3.0; N, 6.7%.

[Cu(L3)Cl]Cl(3a). Yield: 76% (0.39 g). Anal. Calc. for  $C_{21}H_{19}N_3S_2Cl_2Cu$ : C, 49.3; H, 3.7; N, 8.2. Found: C, 49.3; H, 3.8; N, 8.3%.

 $[Cu(L4)](ClO_4)_2(4)$ . Yield: 63% (0.40 g). Anal. Calc. for  $C_{22}H_{20}N_2O_8S_2Cl_2Cu$ : C, 41.4; H, 3.2; N, 4.4. Found: C, 42.4; H, 3.4; N, 4.4%.

 $[Cu(L4)Cl_2](4a)$ . Yield: 82% (0.42 g). Anal. Calc. for  $C_{22}H_{20}N_2S_2Cl_2Cu$ : C, 51.7; H, 3.9; N, 5.5. Found: C, 51.8; H, 4.0; N, 5.5%.

 $[Cu(L5)_2(H_2O)](ClO_4)_2(5)$ . Yield: 62% (0.39 g). Anal. Calc. for C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>8</sub>Cl<sub>2</sub>Cu: C, 48.1; H, 4.7; N, 4.3. Found: C, 48.1; H, 4.8; N, 4.3%.

### 4.4. Data collection and structure refinement

Single crystals of  $[Cu(L2)Cl_2]$  were chosen for X-ray data collection after careful examination under an optical microscope. The X-ray diffraction intensities were measured by  $\omega$  and  $\phi$  scans using a Nonius Kappa CCD four-circle diffractometer fitted with a CCD area detector and a graphite monochromator for the Mo K $\alpha$  radiation. The unit cell parameters and the orientation matrix of the crystal were determined using all data. Data reduction was performed using the DENZO program [42], and a semi-empirical multi-scan absorption correction was applied using the program SORTAV [43]. The structures were solved by direct methods using the SHELXS-97 program [44] and refined by the full-matrix least-squares method on  $F^2$  using SHELXL-97 [45]. While three of four isopropyl groups showed slightly higher thermal parameters, indicative of librational motion, in only one of those were the ellipsoids large enough to merit a disorder model. This was refined over two equally occupied orientations, C(33A)-C(35A) and C(33B)-C(35B). All disordered C-C bond lengths were restrained to 1.53(2) A, and nonbonded 1,3-C···C distances between methyl groups on each disordered orientation to 2.50(2) Å. All non-H atoms except the disordered C atoms were refined anisotropically, while all sp<sup>2</sup>-H atoms were placed in calculated positions and refined using a riding model. Methyl H atoms were treated as idealised groups with freely refined torsions about their C–C bonds.

### 5. Supplementary data

Full crystallographic data for **2** are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 255046.

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