



# Copper(II) complexes of new tetradentate NSNO pyridylthioazophenol ligands: synthesis, spectral characterization and crystal structure

Pulak K. Dhara <sup>a</sup>, Sadhan Pramanik <sup>a</sup>, Tian-Huay Lu <sup>b</sup>, Mike.G.B. Drew <sup>c</sup>,  
Pabitra Chattopadhyay <sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, The Burdwan University, Golapbag, Burdwan 713104, W.B., India

<sup>b</sup> Department of Physics, National Tsing Hua University, Hsinchu 300, Taiwan, ROC

<sup>c</sup> Department of Chemistry, Reading University, Reading RG 66AD, Berks, UK

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## Abstract

Copper(II) complexes of a series of new tetradentate NSNO ligands were synthesized and characterized spectroscopically. The ligands were also characterized by elemental analyses, IR, <sup>1</sup>H NMR, FAB-MS and UV–Vis spectroscopy. The solid-state structures of two complexes **2a** and **4a** were established by X-ray crystallography. The geometry about the copper ion of the complexes is dependent on the counter anion of the copper salt used. The five-coordinated copper ion is distorted square pyramidal when SCN<sup>−</sup> or Cl<sup>−</sup> ligate with the copper(II) ion, occupying the equatorial position, whereas the geometry about the four-coordinated copper ion is square planar when the counter anion is perchlorate. The electronic spectra of **2** and **3** in methanol show that the distortion of square pyramidal towards trigonal bipyramidal geometry about the copper ion of the complexes in solution is dependent on the presence of the electron withdrawing group. All the complexes exhibit a band for S(σ) → Cu(II) charge transfer (LMCT) in the range of 380–394 nm. The EPR spectra of complexes **2** and **3** are consistent with the fact that the unpaired electron is predominantly in the d<sub>x<sup>2</sup>−y<sup>2</sup></sub> orbital as g<sub>||</sub> > g<sub>⊥</sub>. The redox behavior of all the complexes in methanol was studied by CV using TBAP as the supporting electrolyte.

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**Keywords:** Copper(II) complex; Pyridylthioazophenol ligands; Crystal structure

## 1. Introduction

The coordination chemistry of transition metal complexes involving nitrogen and sulfur donor ligands has been the cynosure among chemists during recent years due to the application of these chelates in modelling of biomolecules, in the field of chemical and biological reactivity and nuclear medicine. The potential role played by copper ions, being present in the active sites

of a large number of metalloproteins having the CuN<sub>2</sub>S<sub>2</sub> chromophore [1], has stimulated efforts to design new ligand frames having nitrogen–sulfur donor sets and characterize copper complexes as models for providing a better understanding of the biological system [2]. It has been found that copper(II) chelates, especially of nitrogen–sulfur ligand frames, have antineoplastic activities and interactions with biological systems [3]. Considerable attention has been directed towards the synthesis of copper(II) chelates, especially of nitrogen–sulfur containing ligands, in search of nuclear medicine [4] and anticancer agents present in the hypoxic cell [5]. Again, current research shows that the involvement of both the

\* Corresponding author. Tel.: +913422558339; fax: +913422530452.

E-mail address: [pabitracc@yahoo.com](mailto:pabitracc@yahoo.com) (P. Chattopadhyay).

sulfur-to-copper charge transfer (LMCT) and the copper d–d band in the photosensitization process lead to an efficient DNA cleavage [6].

Herein, we have synthesized three sets of copper(II) complexes of a series of new tetradentate NSNO ligands using different copper(II) salts. In this paper, we present an account on copper(II) complexes of pyridylthioazophenol ligands. The present contribution aims to study the structural chemistry of the copper(II) complexes of the new ligands and the change of the geometry about the copper ion due to the presence of the anions ( $\text{Cl}^-$ ,  $\text{SCN}^-$  and  $\text{ClO}_4^-$ ) in the copper salts. The complexes **2** and **3** are five-coordinated inner metallic complexes where the fifth coordination number is satisfied by  $\text{NCS}^-$  or  $\text{Cl}^-$  being present in the equatorial position and the borderline base pyridine-N of the tetradentate (NSNO) ligands are in the axial site of the distorted square pyramidal geometry. In the cationic copper(II) pyridylthioazophenol complexes (**4**), the counteranion is perchlorate and the geometry about the copper ion is square planar.

## 2. Experimental

### 2.1. Materials

All the reagents were obtained from commercial sources and used without further purification. Copper(II) thiocyanate was obtained by adding a saturated solution of potassium thiocyanate to a solution of copper(II) chloride in methanol, followed by removing the precipitate of KCl by filtration. Tetra-*n*-butylammonium perchlorate was prepared by the addition of sodium perchlorate to a hot solution of tetra-*n*-butylammonium bromide (Aldrich). The product was recrystallized from aqueous ethanol and tested for the absence of bromide. Solvents were distilled from an appropriate drying agent [7].

### 2.2. Physical measurements

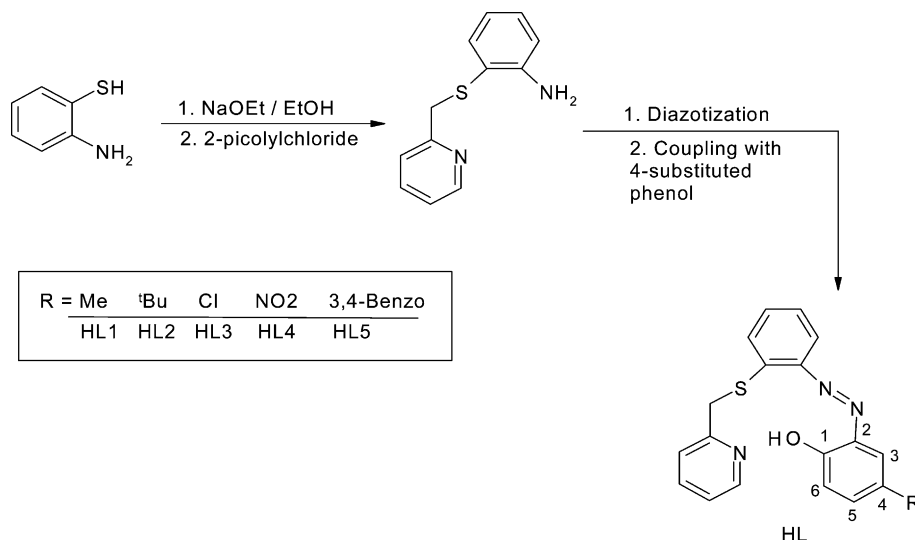
The  $^1\text{H}$  NMR spectra were obtained on a Bruker AC300 spectrometer with chemical shifts reported in  $\delta$  values relative to the residual solvent resonance of  $\text{CDCl}_3$ . IR spectra were obtained on a JASCO FT-IR model 420 spectrometer using KBr disks, UV–Vis on a JASCO UV–Vis/NIR model V-570 spectrometer and mass spectra on a VG system, model 70-250S spectrometer. Microanalyses were performed with the use of a Perkin–Elmer 2400 CHN elemental analyzer and copper analysis was carried out by the iodometric titration method [8]. Molar conductance ( $A_M$ ) were measured in a systronics conductivity meter 304 model using  $\sim 10^{-3}$  M solutions in MeOH. Magnetic moments ( $\mu$ , BM) were

obtained from vibrating sample magnetometer PAR 155 model. X-band EPR spectra were taken on a Bruker spectrometer with a variable temperature liquid nitrogen cryostat at NTHU, Hsinchu, Taiwan. The values  $g_{\text{II}}$  and  $A_{\text{II}}$  were measured at 77 K. Electrochemical measurements were made with a computer controlled EG&G PAR model 270 VERSTAT electrochemical instrument using Ag/AgCl electrodes. All measurements were made at 298 K in dry MeOH with  $[\text{Bu}_4\text{N}]\text{ClO}_4$  as the supporting electrolyte. The experimental solutions were deoxygenated by bubbling with research grade dinitrogen. The reported potentials are uncorrected for junction potential.

### 2.3. Syntheses of the ligands (HL)

The syntheses of the ligands were carried out following the common procedure of coupling different *para*-substituted phenols with the diazotized 2-(2-pyridylmethylthio)-aniline (Scheme 1). The procedure for the synthesis of 2-hydroxy-4-methyl-2'-(2-picolyl-thio)azobenzene (HL1) is as follows.

At first 2-(2-pyridylmethylthio)-aniline was synthesized following the reported procedure [9]. Then the preparation of 2-(2-pyridylmethylthio)-phenylazo-(4-methyl)-phenolate was carried out. The details are given as follows for **1a**. To an alkaline solution of *p*-cresol (1.0 g, 9.3 mmol) at 5 °C was added a diazotized solution of 2-(2-pyridylmethyl-thio)-aniline (2.0 g, 9.3 mmol) dropwise with continuous stirring. The temperature was controlled at ice-cold conditions. The resulting solution was acidified and the pH was controlled between 6 and 7. The red colored compound so precipitated was filtered and washed with water. Finally the pure recrystallized compound was obtained from ethanol-water. The yield was 65%. The yield of the other ligands varied from 50% to 68% following a similar method. *Anal.* Calc. for **1a**: C, 68.06; H, 5.07; N, 12.53. Found: C, 68.83; H, 4.96; N, 12.74%. Calc. for **1b**: C, 70.02; H, 6.10; N, 11.14. Found: C, 69.63; H, 5.98; N, 11.54%. Calc. for **1c**: C, 60.76; H, 3.94; N, 11.81. Found: C, 60.23; H, 3.81; N, 11.99%. Calc. for **1d**: C, 59.01; H, 3.82; N, 15.30. Found: C, 58.75; H, 3.75; N, 15.48%. Calc. for **1e**: C, 71.16; H, 4.58; N, 11.32. Found: C, 70.92; H, 4.47; N, 11.56%; m.p.(°C): **1a**:  $87 \pm 1$ , **1b**:  $167 \pm 1$ , **1c**:  $118 \pm 1$ , **1d**:  $75 \pm 1$ , **1e**:  $159 \pm 1$ ;  $^1\text{H}$  NMR  $\delta$  (ppm) (in  $\text{CDCl}_3$ ): **1a**: 12.58(s, 1H), 8.52(d, 1H), 7.82–6.96 (m, 10H), 4.31(s, 2H), 2.31(s, 3H); **1b**: 12.61(s, 1H), 8.54(d, 1H), 7.78–7.01 (m, 10H), 4.83(s, 2H), 1.40(s, 9H); **1c**: 12.54(s, 1H), 8.50(d, 1H), 7.91–6.75 (m, 10H), 4.45(s, 2H); **1d**: 12.61(s, 1H), 8.54(d, 1H), 8.01–6.96 (m, 10H), 4.50(s, 2H); **1e**: 12.61(s, 1H), 8.51(d, 1H), 7.72–6.23 (m, 13H), 4.48(s, 2H); FAB-MS (FAB<sup>+</sup>,  $[\text{M}+\text{H}]^+$ ): **1a**: 336.11, **1b**: 378.15, **1c**: 356.06, **1d**: 367.10, **1e**: 372.12.



Scheme 1. Synthetic procedure for the ligands.

#### 2.4. Syntheses of Cu(II) complexes of the ligands (HL)

The preparation follows a common procedure. To a methanolic solution (15 mL) of **1a** (0.335 g, 1.0 mmol) the corresponding copper salt (1.0 mmol) solution was added dropwise and the resulting solution stirred for a period of 3 h for **2a**, 2 h for **3a** and 4 h for **4a**. The solution was dried at ambient temperature. The product was collected by washing with cold MeOH–H<sub>2</sub>O and dried. The pure reddish-violet colored crystallized product was obtained from dichloromethane. Yield: 80–85%. *Anal.* Calc. for **2a**: C, 52.66; H, 3.69; N, 9.70; Cu, 14.67. Found: C, 52.01; H, 3.59; N, 9.91; Cu, 14.21%. Calc. for **2b**: C, 55.58; H, 4.63; N, 8.84; Cu, 13.36. Found: C, 55.28; H, 4.50; N, 8.97; Cu, 12.98%. Calc. for **2c**: C, 47.63; H, 2.87; N, 9.26; Cu, 14.00. Found: C, 48.01; H, 2.93; N, 9.31; Cu, 13.67%. Calc. for **2d**: C, 46.55; H, 2.80; N, 12.07; Cu, 13.68. Found: C, 46.76; H, 2.78; N, 12.19; Cu, 13.90%. Calc. for **2e**: C, 56.29; H, 3.41; N, 8.96; Cu, 13.54. Found: C, 55.98; H, 3.32; N, 8.98; Cu, 13.39%. Calc. for **3a**: C, 52.69; H, 3.51; N, 12.29; Cu, 13.94. Found: C, 52.12; H, 3.44; N, 12.51; Cu, 13.39%. Calc. for **3b**: C, 55.48; H, 4.42; N, 11.25; Cu, 12.76. Found: C, 55.98; H, 4.30; N, 11.77; Cu, 12.18%. Calc. for **3c**: C, 47.90; H, 2.73; N, 11.76; Cu, 13.34. Found: C, 48.12; H, 2.83; N, 11.99; Cu, 13.69%. Calc. for **3d**: C, 46.86; H, 2.67; N, 14.39; Cu, 13.05. Found: C, 47.01; H, 2.81; N, 14.89; Cu, 12.79%. Calc. for **3e**: C, 56.15; H, 3.25; N, 11.39; Cu, 12.92. Found: C, 56.28; H, 3.30; N, 11.58; Cu, 12.39%. Calc. for **4a**: C, 45.87; H, 3.22; N, 8.45; Cu, 12.78. Found: C, 46.03; H, 3.10; N, 8.71; Cu, 12.81%. Calc. for **4b**: C, 48.98; H, 4.08; N, 7.79; Cu, 11.78. Found: C, 48.89; H, 4.06; N, 7.62; Cu, 11.57%. Calc. for **4c**: C, 41.74; H, 2.51; N, 8.11; Cu, 12.27. Found: C, 41.95; H, 2.63; N, 7.95; Cu, 12.25%. Calc. for **4d**:

C, 40.90; H, 2.46; N, 10.60; Cu, 12.03. Found: C, 40.64; H, 2.51; N, 10.79; Cu, 11.79%. Calc. for **4e**: C, 49.53; H, 3.00; N, 7.88; Cu, 11.91. Found: C, 50.04; H, 2.88; N, 7.78; Cu, 11.51%.

#### 2.5. X-ray crystal structure analysis

Single crystals suitable for X-ray work of **2a** were grown by slow evaporation of a solution of the complex **2a** in methanolic:toluene (1:2) at ambient temperature while **4a** was grown by slow diffusion of hexane into a benzene solution of the complex at 298 K. A suitable single crystal of the complex **2a** was mounted on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was also employed using the SAINT program. A total of 10601 [unique data = 4107;  $R_{\text{int}} = 0.032$ ] reflections were measured and 2876 reflections were assumed observed the applying the condition  $I > 2\sigma(I)$ . The structure was solved by Patterson syntheses, followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on  $F^2$  were carried out using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms in all cases. Hydrogen atoms were constrained to ride on the respective carbon atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of their parent atom. The refinement converged to residual indices  $R = 0.0390$ ;  $wR_2 = 0.0927$  with  $I > 2\sigma(I)$ . The final difference Fourier map showed the maximum and minimum peak heights at 0.43 and  $-0.27$  e Å<sup>-3</sup>, respectively, having no chemical significance. Complex neutral atom scattering factors [10a] were used throughout. All calculations were carried

out using SHELXS-93 [10b], SHELXL-97 [10c], PLATON-99 [10d] and ORTEP3 [10e] programs. Data of **4a** were measured with Mo K $\alpha$  radiation using the MARresearch Image Plate System. The crystal was positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the xDS program [11a] to provide 2593 independent reflections. The structure was solved using direct methods with the SHELX-86 program [11b]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An empirical absorption correction was applied using DIFFABS [11c]. The structure was refined on  $F^2$  using SHELXL [11d] with  $I > 2\sigma(I)$ .

### 3. Result and discussions

#### 3.1. Synthesis

The ligands 2-(2-pyridylmethylthio)-phenylazo-(4-methyl)phenolates (**1**) were prepared by coupling 4-substituted-phenols with the diazonium ion obtained from 2-(2-pyridylmethylthio)-aniline, which was synthesized from 2-aminothiophenol by reacting it with 2-picolychloride in presence of a base at the first step. This series of organic moieties act as tetradentate NSNO ligands which are interesting chelators due to the presence of hard donor azo-N and phenolate-O, borderline base pyridine-N and soft thioether S donor centres. The ligands have been spectroscopically characterized. The copper(II) complexes of these ligands were obtained by their reaction with equimolar amounts of the appropriate copper salts in methanol. All the complexes are soluble in common organic solvents.

#### 3.2. Structures of the Cu(II) complexes (**2a** and **4a**)

The ORTEP views of **2a** and **4a** are illustrated in Figs. 1 and 2, respectively, with the atom numbering schemes shown. The selected bond distances and angles are listed in Tables 1 and 2, respectively. The crystal of **2a** is of the monoclinic system with the space group  $P2_1/n$ . In this monomeric complex **2a**, the copper center is bonded to a tetradentate monobasic NSNO donor pyridylthioazophenolate organic moiety (L1) and a monodentate chloride ligand. The coordination geometry is distorted square pyramidal with two nitrogen, one oxygen and chlorine donor atoms occupying the basal plane. The pyridinic N(1) shows the axial contact at a long distance of 2.2194 (18) Å. The axial Cu–N(1) bond distance (2.2194 (18) Å) is longer than the equatorial Cu–N(2) (1.980 (2) Å) due the geometric position as

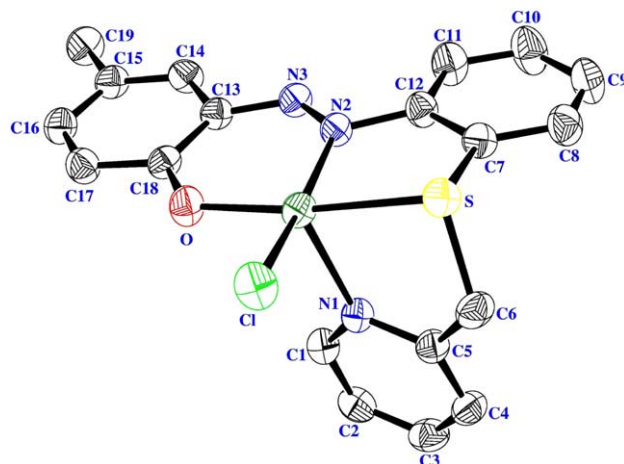


Fig. 1. Solid-state structure of [Cu(L1)Cl] (**2a**) showing the atom labelling scheme.

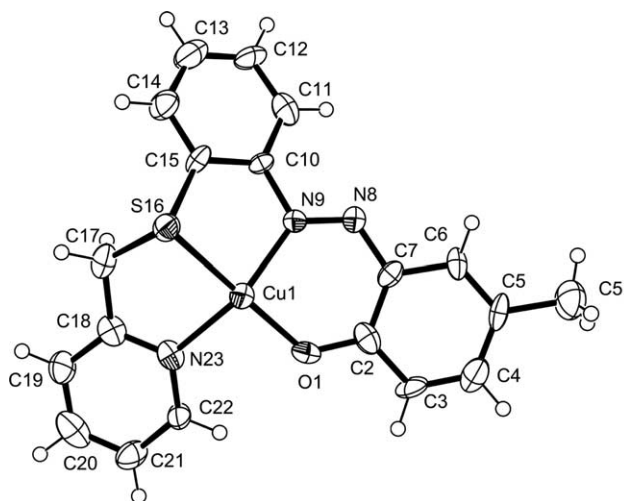


Fig. 2. An ORTEP view of the cation of the complex **4a** with thermal ellipsoids at the 50% probability level and the atom numbering scheme.

usual. The Cu–Cl bond distance is 2.2973(9) Å. The thioether sulfur S is strongly coordinated with copper, being present in the basal plane, and the Cu–S bond distance of 2.3360(8) Å is shorter than axial [12] and moderate in comparison to the usually observed basal Cu–S bond distances in pentacoordinated copper complexes [13]. The structure of **2a** is almost regular square pyramidal as seen from the trigonality index [14]  $\tau$  of only 0.116 [ $\tau = (\beta - \alpha)/60$  where  $\beta = \text{O–Cu–S} = 172.95(6)^\circ$  and  $\alpha = \text{N2–Cu–Cl} = 165.99(7)^\circ$ ].

In the complex cation of [Cu(L1)]ClO<sub>4</sub> (**4a**), Cu(II) is located in the centre of a square planar environment and the metal atom is bonded to four atoms of the ligand. Here, both coordinating N atoms are at equivalent distances whereas this fact is different in the case of **2a**. The distortion from square planar geometry to tetrahedral geometry is also observed as distances from the donor atoms to the square plane are –0.29, 0.29, –0.27, 0.28



Table 1  
Summarized crystallography data for **2a** and **4a**

	<b>2a</b>	<b>4a</b>
Empirical formula	C <sub>19</sub> H <sub>16</sub> ClCuN <sub>3</sub> O <sub>5</sub> S	C <sub>19</sub> H <sub>16</sub> ClCuN <sub>3</sub> O <sub>5</sub> S
Formula weight	433.42	497.40
Crystal system	monoclinic	monoclinic
Space group	<i>P2<sub>1</sub>/n</i>	<i>C2/c</i>
<i>a</i> (Å)	9.8658(9)	26.15(3)
<i>b</i> (Å)	8.6589(8)	12.047(15)
<i>c</i> (Å)	21.6344(19)	14.179(15)
$\alpha$ (°)	90.00	90.00
$\beta$ (°)	99.224(2)	117.000(10)
$\gamma$ (°)	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	1824.3(3)	3981(8)
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.578	1.660
<i>Z</i>	4	8
Radiation wavelength $\lambda$ (Å)	0.71073	0.71073
<i>F</i> (000)	884	2024
<i>T</i> (K)	293	293
$\theta$ (°)	1.9–28.2	2.22–25.98
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	1.471	1.471
Number of reflections (total)	10601	5738
Number of reflections (granted)	4107	2593
Observed data ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	2876	1914
<i>R</i>	0.0390	0.1036
<i>wR</i>	0.0927	0.1347

Table 2  
Selected bond distances (Å) and bond angles (°) for **2a** and **4a**

	<b>2a</b>	<b>4a</b>		
<i>Bond distances</i>				
Cu–O	1.9031(19)	Cu–O1	1.860(9)	
Cu–N2	1.980(2)	Cu–N9	1.949(9)	
Cu–N1	2.2194(18)	Cu–N23	1.984(10)	
Cu–S	2.3360(8)	Cu–S16	2.295(4)	
O–C18	1.295(3)	O1–C2	1.321(14)	
N3–C13	1.359(3)	C7–N8	1.388(15)	
N2–N3	1.283(3)	N8–N9 (azo)	1.267(12)	
N2–C12	1.440(4)	N9–C10	1.420(15)	
S–C7	1.776(3)	C15–S16	1.799(13)	
S–C6	1.812(3)	S16–C17	1.852(13)	
Cu–Cl	2.2973(9)	C18–N23	1.353(15)	
C1–N1	1.331(3)	C22–N23	1.340(16)	
<i>Bond angles</i>				
N1–Cu–S	81.80(6)	O1–Cu–N9	93.5(4)	
N1–Cu–N2	92.61(9)	O1–Cu–N23	96.9(4)	
N1–Cu–Cl	98.95(6)	N9–Cu–S16	87.7(3)	
N1–Cu–O	104.97(8)	N23–Cu–S16	86.2(3)	
N2–Cu–S	85.96(7)	O1–Cu–S16	168.0(3)	
N2–Cu–O	91.71(9)	N9–Cu–N23	157.8(4)	
N2–Cu–Cl	165.99(7)	C2–O1–Cu	123.7(8)	
Cl–Cu–S	87.89(3)	N8–N9–Cu	128.1(8)	
Cl–Cu–O	92.89(6)	N9–N8–C7	121.1(10)	
O–Cu–S	172.95(6)	C10–N9–Cu	114.5(7)	
N3–N2–Cu	128.79(18)	C15–S16–Cu	92.9(4)	
C6–S–Cu	97.68(9)	C17–S16–Cu	92.3(4)	

Å for O(1), N(9), S(16) and N(23), respectively, the copper atom being  $-0.07$  Å from this plane. The perchlorate ion has no close contact to the copper atom.

Both complexes are monomeric but all the corresponding Cu–O, Cu–N and Cu–S distances of **4a** are significantly shorter than those of **2a**. It may be due to the increase in formal charge on **2a** by coordination of chloride and the difference in geometry of the complexes. The Cu–N(pyridinic) distance in **4a** is shorter than that of **2a** by ca. 0.24 Å. This Cu–N bond in **2a** is axial and not in the same plane as the other donor atoms of the ligand, which is different from that in **4a**. This difference in bond lengths for the same ligand frame is due to the flexibility of the Cu(II) coordination geometry.

### 3.3. Spectral properties

The ligands **1** exhibit medium intense IR bands at  $\sim 3300$  cm<sup>-1</sup> (O–H of H bonded phenolic OH) [15] which is absent in all the complexes. This indicates coordination of oxygen to the metal centre [16]. The  $\nu_{\text{N}=\text{N}}$  mode of the free ligand (1495–1505 cm<sup>-1</sup>) is shifted to lower to wave numbers ( $\Delta \sim 20$ –30 cm<sup>-1</sup>) in the complexes, suggesting coordination of the metal ions to the azo function [17]. The  $\nu_{\text{N}=\text{N}}$  band is observed at 1465–1478 cm<sup>-1</sup> for all the complexes. In addition to this  $\nu_{\text{C}-\text{S}}$  at 790 cm<sup>-1</sup> for the ligands shifts to 760 cm<sup>-1</sup> for the complexes. Thiocyanato complexes **3** show a characteristic band in the range of 2050–2060 cm<sup>-1</sup> indicating the presence of N-bonded NCS groups [18]. Infrared spectra of the complexes **4** exhibit an intense band at approximately 1090 cm<sup>-1</sup> along with a weak band at 625 cm<sup>-1</sup> which have been assigned to  $\nu(\text{ClO}_4^-)$ . The conductivity measurements of complexes **2** and **3** in methanolic solution show the conductance in the range of 9–20  $\Lambda_0$  mol<sup>-1</sup> cm<sup>-1</sup> and those of **4** in MeOH are 89–102  $\Lambda_0$  mol<sup>-1</sup> cm<sup>-1</sup>. The values suggest that the complexes **2** and **3** exist as non-electrolytes and **4** as having 1:1 electrolytic nature in the solution state. Magnetic susceptibility data reveal spin-only values for all the copper complexes as the values are very close to 1.73 BM (in the range of 1.72–1.92 BM).

#### 3.3.1. Electronic spectra

The electronic absorption spectra of the azo ligands and their complexes were recorded at room temperature using MeOH as the solvent, and the results are shown in Table 3. The spectra of the free ligands and the complexes exhibit transitions at lower than 400 nm corresponding to intramolecular  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions [19]. In the case of the complexes, a band around 390 nm is assignable to the S( $\sigma$ )  $\rightarrow$  Cu(II) charge transfer (LMCT) transition [6,20]. The copper(II) complexes are characterized by a rather broad d–d absorption band in their solution electronic spectra; often a low- or high-energy shoulder is also present or, occasionally, two distinct absorption maxima are observed. In many cases it has been shown that the presence of a single d–d band with a high energy shoulder

Table 3  
UV–Vis spectral, electrochemical and EPR data

Compound	$\lambda$ nm ( $\epsilon$ ) ( $\epsilon$ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )	Electrochemical data $E^{o'}$ , mV ( $\Delta E_p$ , mV) [ $E_{pa}$ , mV $E_{pc}$ , mV]	EPR data		
			$g_{\parallel}$	$A_{\parallel}$ (G)	$g_{\perp}$
<b>1a</b>	206 (23385), 254 (11449), 326 (11871), 410 (7244), 458 (3981)				
<b>1b</b>	218 (24231), 252 (12658), 327 (10993), 408 (8012), 456 (3896)				
<b>1c</b>	210 (19952), 251 (10272), 320 (17102), 410 (7562), 472 (4265)				
<b>1d</b>	212 (21158), 236 (11322), 324 (8325), 412 (5822), 486 (3912)				
<b>1e</b>	212 (24271), 260 (12358), 308 (10986), 410 (4375), 494 (8522)				
<b>2a</b>	206 (24268), 260 (11415), 344 (11896), 392 (3854), 528 (6115), 708 (268), 852 (sh, 133)	–65 (150) [10, –140]	2.229	164	2.054
<b>2b</b>	218 (24550), 258 (13381), 346 (16544), 392 (5825), 528 (8182), 708 (270), 850 (sh, 111)	65.8 (148.3) [140, –8.3]	2.234	166	2.060
<b>2c</b>	210 (16886), 260 (9837), 338 (7124), 386 (2967), 528 (4051), 718 (218), 844 (sh, 128)	142.5 (93) [188, 95]	2.230	160	2.052
<b>2d</b>	216 (19982), 262 (10785), 330 (7253), 390 (2598), 528 (3925), 736 (186), 824 (193)	177 (96) [225, 129]	2.221	154	2.052
<b>2e</b>	216 (23245), 258 (16284), 344 (4099), 386 (5127), 528 (8542), 700 (261), 896 (sh, 106)	57.7 (150.6) [133, –17.6]	2.237	168	2.058
<b>3a</b>	206 (22931), 260 (7528), 346 (7531), 394 (2654), 528 (3804), 710 (198), 876 (sh, 97)	–13 (120) [47, –73]	2.231	167	2.040
<b>3b</b>	218 (26822), 258 (17102), 346 (15164), 392 (5165), 528 (8012), 710 (278), 875 (sh, 95)	50 (178) [139, –39]	2.232	172	2.041
<b>3c</b>	208 (17089), 260 (10181), 344 (7201), 392 (3012), 528 (4212), 722 (172), 838 (sh, 92)	130 (108) [184, 76]	2.227	165	2.043
<b>3d</b>	216 (19876), 262 (11108), 330 (7203), 390 (2501), 530 (4125), 730 (140), 820 (138)	165 (134) [232, 98]	2.217	158	2.037
<b>3e</b>	216 (22956), 262 (16203), 338 (4322), 386 (5203), 530 (8433), 714 (201), 912 (sh, 65)	62 (156) [140, –16]	2.238	173	2.045
<b>4a</b>	206 (29604), 260 (14038), 300 (9583), 346 (13671), 390 (5334), 530 (6890), 704 (317)	15 (210) [120, –90]			
<b>4b</b>	216 (25989), 261 (17223), 346 (15003), 390 (5324), 530 (8245), 706 (320)	69 (162) [150, –12]			
<b>4c</b>	208 (17522), 260 (10036), 342 (7112), 392 (4258), 530 (4549), 704 (318)	120 (96) [168, 72]			
<b>4d</b>	216 (19509), 262 (10798), 338 (6978), 391 (3122), 536 (5423), 708 (309)	152.5 (101) [203, 102]			
<b>4e</b>	216 (23203), 258 (16722), 339 (3949), 380 (5344), 536 (8738), 706 (321)	63 (140) [133, –7]			

is typical of a trigonal bipyramidal stereochemistry for copper, whereas an absorption with a low energy shoulder indicates a square pyramidal geometry [21].

On the basis of the above criterion, the observed data of **2** and **3** suggest that the distortion of square pyramidal towards trigonal bipyramidal about the copper ion of the complexes in solution is maximum in case

of the complexes **2d** and **3d**. Here, complexes **2d** and **3d** in methanol exhibit two bands of nearly equal intensity between 730 and 824 nm, this pattern suggests that the geometry about the copper ion in solution is between square pyramidal and trigonal bipyramidal. In the case of the complexes **4**, only one broad d–d absorption band around 705 nm and an intense band at 528 nm demon-

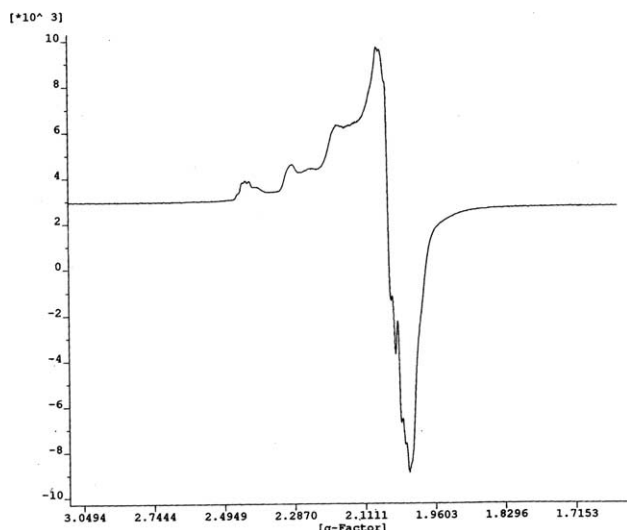


Fig. 3. EPR spectra of [Cu(L1)Cl] (**2a**) in MeOH at 77 K.

strates the square planar geometry around the copper ion.

### 3.3.2. EPR spectra

EPR spectra of the cupric complexes **2** and **3** have been recorded in MeOH at 300 and 77 K. The data are tabulated in Table 3 and one representative spectra of **2a** is shown in Fig. 3. However, the complexes in the frozen state at 77 K show well-resolved peaks of low intensities in the low-field region and an intense peak in the high field region. No band corresponding to the  $M_s = +2$  transition was observed in the spectra, ruling out any Cu–Cu interaction. The complexes **2** and **3** appear to exhibit axial spectra of square pyramidal species with  $g_{\parallel}$  varying from 2.217 to 2.238 and  $A_{\parallel}$  having a range from  $154 \times 10^{-4}$  to  $173 \times 10^{-4} \text{ cm}^{-1}$ . The result are in general agreement with the solution electronic spectra, which also suggest the existence of distorted square pyramidal geometries with more distortions in the complexes **2d** and **3d**. From the observed  $g$ -tensor values of the Cu(II) complexes it is clear that  $g_{\parallel} > g_{\perp}$  which dictate that in complexes **2** and **3** the unpaired electron is predominantly in the  $d_{x^2-y^2}$  orbital [22] giving  $^2B_{1g}$  as the ground state.

### 3.4. Electrochemistry

Redox properties of the complexes were examined by cyclic voltametry using a Pt-disk working electrode and a Pt-wire auxiliary electrode in dry MeOH and in the presence of  $[n\text{-Bu}_4\text{N}]\text{ClO}_4$  as the supporting electrolyte. The potentials (Table 3, Fig. 4) are expressed with reference to Ag/AgCl electrodes. In solution all compounds displayed a quasi-reversible voltammogram having  $i_{pc}/i_{pa} \approx 1$  in the range from  $-65$  to  $177$  mV with  $\Delta E = 96$ – $210$  mV. The influence of the substituents in the ligands is apparent from the data.

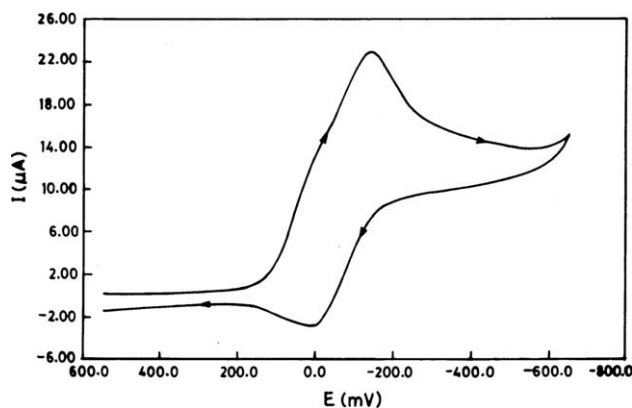


Fig. 4. CV diagram of [Cu(L1)Cl] (**2a**) in MeOH.

## 4. Supporting material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 229572 and 224745 for compounds **2a** and **4a**, respectively. Copies of this information are available free of charge on request from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.ac.uk or www:<http://www.ccdc.cam.ac.uk>).

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