

# Axial versus equatorial coordination of thioether sulfur: Mixed ligand copper(II) complexes of 2-pyridyl-*N*-(2'-methylthiophenyl)-methyleneimine with bidentate diimine ligands

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## Abstract

The synthesis, structure and spectral and redox properties of the copper(II) complexes [Cu(pmtpm)Cl<sub>2</sub>] (**1**) and [Cu(pmtpm)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**6**), where **pmtpm** is the linear tridentate ligand 2-pyridyl-*N*-(2'-methylthiophenyl)methyleneimine containing a thioether and two pyridine donors, are described. Also, the mixed ligand complexes [Cu(pmtpm)(diimine)](ClO<sub>4</sub>)<sub>2</sub> (**2-5**), where the diimine is 2,2'-bipyridine (**bpy**) (**2**), 1,10-phenanthroline (**phen**) (**3**), 2,9-dimethyl-1,10-phenanthroline (**2,9-dmp**) (**4**) or dipyrido-[3,2-d:2',3'-f]-quinoxaline (**dpq**) (**5**), have been isolated and studied. The X-ray crystal structures of the complexes **1**, [Cu(pmtpm)(2,9-dmp)](ClO<sub>4</sub>)<sub>2</sub> **4** and **6** have been successfully determined. The complex **1** possesses a trigonal bipyramidal distorted square based pyramidal (TBDSBP) coordination geometry in which three corners of the square plane are occupied by two nitrogens and thioether s of **pmtpm** ligand and the remaining equatorial and the axial positions by two chloride ions. The complex **4** contains a CuN<sub>4</sub>S chromophore also with a TBDSBP coordination geometry in which two nitrogens and the thioether sulfur of **pmtpm** ligand occupy three corners of the square plane. One of the two nitrogens of 2,9-dmp ligand is equatorially coordinated and the other axially to copper. On the other hand, the complex **6** is found to possess a square based pyramidal distorted trigonal bipyramidal (SPDTBP) coordination geometry. The CuN<sub>2</sub>S trigonal plane in it is comprised of the pyridine and imine nitrogens and the thioether sulfur of the **pmtpm** ligand. The pyridine nitrogens of the ligand occupy the axial positions and the second thioether sulfur remains uncoordinated. On long standing in acetonitrile solution the mixed ligand complexes **2** and **3** undergo ligand disproportionation to provide the corresponding bis-complexes of bpy and phen, respectively, and **6**. The electronic and EPR spectral parameters and the positive redox potential of complex **4** are consistent with the equatorial location of the thioether sulfur in the square-based coordination geometry around copper(II). On the other hand, the higher *g*<sub>||</sub> and lower *A*<sub>||</sub> values and lower *E*<sub>1/2</sub> values for the complexes **2**, **3** and **5** are consistent with the axial coordination of the thioether sulfur. Also, the Cu(II)/Cu(I) redox potentials increase with increase in number of aromatic rings of the diimine ligand. The steric and electronic effects of the bidentate diimine ligands in orienting the thioether coordination to axial or equatorial position are discussed.

**Keywords:** Copper(II) complexes; X-ray structures; Tridentate N<sub>2</sub>S ligand; Diimine ligands; Thioether coordination; EPR spectra; Redox chemistry

## 1. Introduction

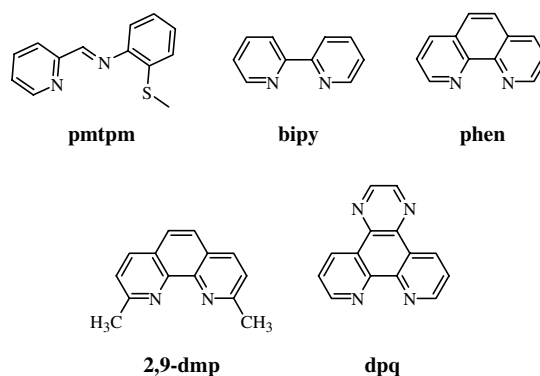
There is continuing interest in coordination complexes of copper(II) with various combinations of heterocyclic nitrogen, thiolate and thioether donors [1–5], because of the coordination of copper to two histidine nitrogen atoms

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and cysteine and methionine sulfur atoms in the electron transfer blue copper proteins [6,7]. Several attempts have been made to replicate some of the structural, electronic and electrochemical features of these proteins by simulating their active sites in synthetic complexes [1,8,9]. Complexes containing sterically constrained as well as synthetically accessible pyridine, benzimidazole and thioether donors have been investigated. The X-ray crystal structures of both Cu(II) and Cu(I) forms (square pyramidal and tetrahedral, respectively) of the chelating  $N_2S_2$  ligand 1,8-bis(pyrid-2-yl)-3,6-dithiaoctane have been reported by Brubaker et al. [10]. Using a hindered tripodal pyrazolyl ligand a group of Cu(II) thiolate complexes have been reported [11,12] as blue protein models and one of the Cu(II) complexes,  $[Cu(Cl)(HB(3,5-i-Pr_2pz)_3)]$  with tetrahedral geometry exactly mimics the spectral properties of the blue site in  $CH_2Cl_2$  solution. There was much interest in the copper(II) complexes of tetradentate bis(benzimidazol-2-yl)-dithioether ligands [13–18]; the thiolate group being substituted by an extra thioether donor, they offer a  $CuN_2S_2$  chromophore as in blue proteins. A series of Cu(II) complexes with  $N_2S_2$  ligands (S, thioether; N, pyridyl, pyrazolyl, benzimidazolyl) as type I models [13–16,19,20] were isolated and studied. 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 [3,4,21,22] offering N and S donor atoms. Studies on models for the active sites in these proteins have revealed that low symmetry, tetrahedral distortion caused by bulky ligands, thioether coordination and  $\pi$ -bonding can all contribute [23] to high redox potentials as in the blue proteins. However, only very few attempts [4,21] have been made to synthesize copper(II) complexes containing thioether donors in the axial position. Such studies are very important as the axially coordinated thioether donor in trigonal (bi)pyramidal active site geometries in blue copper proteins are suggested to confer highly positive Cu(II)/Cu(I) redox potentials and hence it is involved in facile electron transfer in biological processes.

As it is difficult to incorporate all the donor atom types into one ligand [24], we are attempting to design mixed-ligand complexes containing biomimetic donors. In the present investigation we have chosen the tridentate ligand 2-pyridyl-*N*-(2'-methylthiophenyl)methyleneimine (**pmtpm**) containing thioether and pyridine donors (Scheme 1) as the primary ligand. On complexation with copper(II), tridentate ligands with a thioether sulfur donor often results in five coordinate complexes due either to coordination of solvent molecules or of counter ions [25,26]. A higher coordination number may be achieved by incorporating bidentate chelating agents (Scheme 1) as secondary ligands, which would be expected to force the weakly coordinating sulfur donor of the primary ligand to the axial position. The chelating diimine ligands 2,2'-bipyridine (**bpy**), 1,10-phenanthroline (**phen**), 2,9-dimethyl-1,10-phenanthroline



Scheme 1.

(**2,9-dmp**) and dipyrido-[3,2-d:2',3'-f]-quinoxaline (**dpq**) [27] have been used as secondary ligands to prepare mixed ligand complexes of the type  $[Cu(pmtpm)(diimine)](ClO_4)_2$ . In this report, the preparation and spectroscopic and electrochemical properties of the mixed ligand copper(II) complexes are discussed. The involvement of secondary ligands in determining the axial coordination of thioether is probed. The bidentate diimines are expected to force the thioether donor either to axial or equatorial position. The crystal structures of three of the complexes have been determined to understand the coordination preference of the thioether donor.

## 2. Experimental

### 2.1. Materials

Copper(II) chloride dihydrate, copper(II) perchlorate hexahydrate, pyridine-2-carboxaldehyde, 2-(methylthio)aniline (Aldrich), 2,2'-bipyridine, 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline (Merck) were used without further purification.

### 2.2. Synthesis of 2-pyridyl-*N*-(2'-methylthiophenyl)-methyleneimine (**pmtpm**)

The ligand was synthesized by modifying the literature procedure [28]. 2-(Methylthio)aniline (0.70 g, 5.0 mmol) and pyridine-2-carboxaldehyde (0.54 g, 5.0 mmol) were refluxed in benzene (20 mL) for 24 h over molecular sieves. The reaction mixture was filtered and the solvent was evaporated. The crude product was recrystallized from benzene/hexane. The yellow crystals of **pmtpm** (0.82 g, 72%) obtained was filtered off and then dried in vacuum.

$^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 8.70 (dq,  $J$  = 4.8, 1.0, 1H, *H*Py); 8.57 (s, 1H, *H*C=N); 8.33 (dt,  $J$  = 7.8, 1.0, 1H, *H*Py); 7.81 (tq,  $J$  = 7.8, 1.8, 1H, *H*Py); 7.38–7.35 (m, 1H, *H*Py); 7.28–7.16 (m, 3H, *H*Ph); 7.08 (dd,  $J$  = 7.8, 1.3, 1H, *H*Ph); 2.47 (3H,  $H_3C$ ).

$^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 160.7 (*H*C=N); 155.1, 150.0, 148.3, 137.1, 135.2, 128.8, 125.7, 125.6, 124.9, 122.4, 117.8 (*C*Py and *C*Ph); 15.2 ( $H_3C$ ).

MS (FAB): 229 (100,  $M^+ + 1$ ); 228 (14,  $M^+$ ); 181 (34); 136 (19); 93 (10).

IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3057w, 2978s, 2898w, 1622vs, 1564s, 1471vs, 1361s, 1435vs, 1342s, 1197s, 1067s, 991s, 781s, 742s, 692s.

EA (calculated values are in parenthesis for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{S}$ ): C, 68.40 (68.39); H, 5.33 (5.30); N, 12.30 (12.27).

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

The complex **1** was prepared by adding copper(II) chloride in methanol to a methanolic solution of the ligand in 1:1 mole ratio. The volume of the solvent was decreased under reduced pressure. The solid product formed upon cooling was filtered off, washed with small amounts of cold methanol and then dried under vacuum. Single crystals of  $[\text{Cu}(\text{pmtpm})\text{Cl}_2]$  (**1**) suitable for X-ray diffraction were grown from acetonitrile solutions by slow evaporation. The mixed ligand complexes  $[\text{Cu}(\text{pmtpm})(\text{diimine})](\text{ClO}_4)_2$  (**2-5**), where the diimines are 2,2'-bipyridine (**bpy**) (**2**), 1,10-phenanthroline (**phen**) (**3**), 2,9-dimethyl-1,10-phenanthroline (**2,9-dmp**) (**4**) and dipyrido-[3,2-d:2',3'-f]-quinoxaline (**dpq**) (**5**), were isolated by mixing equimolar amounts of **pmtpm** (0.23 g, 1.0 mmol) and the diimine ligands (1.0 mmol) in methanol and then adding to copper(II) perchlorate hexahydrate (0.37 g, 1.0 mmol) in methanol. The products obtained were filtered off and dried. The complex **6** was obtained by mixing the corresponding ligand and copper(II) perchlorate hexahydrate in 2:1 molar ratio. Single crystals of the complexes **4** and **6** were obtained from diffusion of ether vapour into acetonitrile solution of the complexes. The elemental analysis for the complexes was satisfactory.

### 2.4. Data collection and structure refinement

For the complex **1**, preliminary cell dimensions and the crystal system were determined and the data were collected at 105 K. The X-ray data for the complex **1** was collected in a four-circle Enraf-Nonius Kappa CCD X-ray diffractometer and graphite monochromatized Mo  $K\alpha$  radiation was used. The data collection was done using COLLECT software [29]. The data reduction was performed using DENZO/SCALEPACK program. The structure was solved by direct method using SIR-92 program [30] and then refined using CRYSTALS [30]. The non-hydrogens were refined anisotropically. Crystal data and additional details of the data collection and refinement of the structure are presented in Table 1.

Suitable single crystals of **4** and **6** were obtained as dark green blocks or rods. The intensity data were collected at 173 K on a Stoe Mark II-Image Plate Diffraction System [31] equipped with a two-circle goniometer using Mo  $K\alpha$  graphite monochromated radiation. The structures were solved by direct methods using SHELXS-97 program [32]. The refinement and all further calculations were carried out using SHELXL-97 [32]. The H-atoms were fixed at calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on  $F^2$ . An empirical absorption correction was applied using the DELREFABS routine in PLATON [33]; transmission factors:  $T_{\text{min}}/T_{\text{max}} = 0.321/0.753$  (**4**);  $0.773/0.944$  (**6**). In complex **4**, a region of disordered solvent was squeezed out using the SQUEEZE routine in PLATON [33]; 113 electrons for a volume of  $448 \text{ \AA}^3$  per unit cell, which was equated to  $0.5\text{CH}_3\text{CN}$  and  $0.25\text{H}_2\text{O}$  per molecule of the complex. The molecule **6** crystallizes with 1.5 molecules of water of

Table 1  
Crystal data and structure refinement for complexes **1**, **4** and **6**

Compound	<b>1</b>	<b>4</b>	<b>6</b>
Empirical formula	$\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{CuN}_2\text{S}$	$\text{C}_{28}\text{H}_{26}\text{Cl}_2\text{CuN}_{4.5}\text{O}_{8.25}\text{S}$	$\text{C}_{26}\text{H}_{27}\text{Cl}_2\text{CuN}_4\text{O}_{9.50}\text{S}$
Formula weight	362.77	724.03	746.08
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
$a$ (Å)	8.4595(1)	17.8374(8)	43.461(5)
$b$ (Å)	10.7375(1)	11.9491(8)	7.6405(4)
$c$ (Å)	15.5275(2)	15.1483(8)	21.951(2)
$\beta$ (°)	92.7907(7)	98.252(4)	119.496(8)
$V$ (Å <sup>3</sup> )	1408.75(3)	3195.3(3)	6344.3(10)
$Z$	4	4	8
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.710	1.505	1.562
Absorption coefficient ( $\text{mm}^{-1}$ )	2.060	0.972	1.047
$F(000)$	732	1482	3056
Data/restraints/parameters	3401/0/221	5918/0/391	5633/0/403
Goodness-of-fit on $F^2$	1.080	1.073	0.953
Final $R$ indices [ $I > 2\sigma(I)$ ]			
$R^a$	0.0219	0.1086	0.0732
$wR^b$	0.0243	0.3008	0.1292

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum w[(F_o^2)]} \right\}^{1/2}$$

crystallization, one of which is disordered over two positions. The two perchlorate anions are also disordered. The perchlorate anions in both the molecules found to be disordered and reflected in the high  $R$ -values.

### 3. Results and discussion

#### 3.1. Synthesis

The ligand 2-pyridyl- $N$ -(2'-methylthiophenyl)methyleneimine (**pmtpm**) has been synthesized by the reported [28] procedure with slight modifications. The ligand shows IR spectral bands around 1620 and 690  $\text{cm}^{-1}$ , which are assigned, respectively, to C=N and C-S stretching vibrations. It readily forms a complex with copper(II) chloride as revealed from the decrease in  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}-\text{S})$  vibrations of the ligand from 1620 to 1592 and 690–645  $\text{cm}^{-1}$ , respectively. The stoichiometry of the complex was determined as  $[\text{Cu}(\text{pmtpm})\text{Cl}_2]$  by elemental analysis and was confirmed by X-ray crystallographic studies. The mixed ligand complexes  $[\text{Cu}(\text{pmtpm})(\text{diimine})](\text{ClO}_4)_2$  (**2–5**), where the diimines are 2,2'-bipyridine (**bpy**) (**2**), 1,10-phenanthroline (**phen**) (**3**), 2,9-dimethyl-1,10-phenanthroline (**2,9-dmp**) (**4**) and dipyrido-[3,2-d:2',3'- $f$ ]-quinoxaline (**dpq**) (**5**), were prepared by the addition of a methanolic solution of **pmtpm** and an equivalent amount of the bidentate diimine chelating ligands to a methanolic solution of copper(II) perchlorate hexahydrate. All the complexes display  $\text{S}(\sigma) \rightarrow \text{Cu}(\text{II})$  ligand to metal charge transfer (l.m.c.t.) absorption band in the region 335–350 nm and show IR absorptions between 1590 and 1600  $\text{cm}^{-1}$  for  $\nu(\text{C}=\text{N})$ . This primarily indicates the coordination of the tridentate ligand **pmtpm** to copper(II) through thioether sulfur. ESI mass spectra of the complexes **2**, **3** and **5** were recorded in acetonitrile solution. The molecular ion peaks of the complexes **2** ( $m/z$ , 547.7,  $\{[\text{Cu}(\text{pmtpm})(\text{bpy})](\text{ClO}_4)\}^+$ ), **3** ( $m/z$ , 571.7,  $\{[\text{Cu}(\text{pmtpm})(\text{phen})](\text{ClO}_4)\}^+$ ) and **5** ( $m/z$ , 625.9,  $\{[\text{Cu}(\text{pmtpm})(\text{dpq})](\text{ClO}_4)\}^+$ ) suggest the clean formation of the mixed ligand complexes (cf. supporting information). It is to be mentioned that no mass peaks were observed for the formation of either bis(diimine) complex or **6**. The stoichiometry of the complexes was derived from elemental analysis and was confirmed by X-ray crystal structure for the complexes **4** and **6**. The X-ray quality single crystals of **4** and **6** were obtained by diffusing diethyl ether into an acetonitrile solution of the complex. Attempts were made to crystallize the complexes **2** and **3** by vapour diffusion of diethyl ether into the complex solution in acetonitrile. However, from the solutions of **2** and **3**, green and blue crystals were isolated. The green crystals of both the complexes were found to have the same unit cell parameters as that of complex **6**. The X-ray structure analysis of blue crystals obtained from **2** and **3** indicates the formation of  $[\text{Cu}(\text{bpy})_2](\text{ClO}_4)_2$  and  $[\text{Cu}(\text{phen})_2](\text{ClO}_4)_2$ , respectively (cf. supporting information). It is obvious that the complexes **2** and **3** undergo ligand disproportionation when kept for recrystallization in aceto-

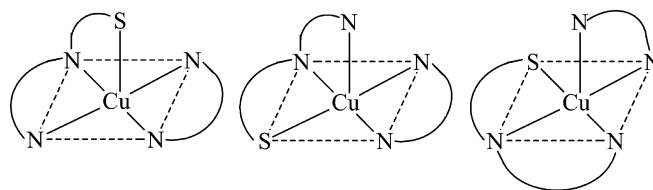


Fig. 1. Possible coordination modes of tridentate **pmtpm** ligand in the presence of bidentate chelating ligands in mixed ligand complexes with square-based copper(II) geometry.

nitrile solution for a long time. The present observation is an example for (symbiotic) tendency of compounds to be symmetrically substituted rather than to have mixed substituents. The mixed ligand complexes were synthesized with an aim to understand the role of bidentate chelating ligands in determining the coordination preferences that is axial versus equatorial ligation of the thioether ligand **pmtpm**. The facial coordination or folded geometry of the tridentate ligand **pmtpm** leads to a square pyramidal geometry with either axial or equatorial thioether ligation (Fig. 1). On the other hand, the meridional coordination would result in equatorial ligation of thioether donor of the ligand.

#### 3.2. Description of the structures of $[\text{Cu}(\text{pmtpm})\text{Cl}_2]$ (**1**), $[\text{Cu}(\text{pmtpm})(2,9\text{-dmp})](\text{ClO}_4)_2$ (**4**) and $[\text{Cu}(\text{pmtpm})_2](\text{ClO}_4)_2$ (**6**)

The X-ray crystallographic investigation of a single crystal of the complex  $[\text{Cu}(\text{pmtpm})\text{Cl}_2]$  (**1**) provided the molecular structure shown in Fig. 2. Selected bond distances and bond angles are presented in Table 2. The complete list of bond distances, bond angles, atomic coordinates, anisotropic thermal parameters and hydrogen bonding interactions for the complexes **1**, **4** and **6** are presented in supporting information. The coordination geometry around copper(II) is best described as trigonal bipyramidal distorted square based pyramidal (TBDSBP) [34], as revealed by the magnitude of the trigonality index [16]  $\tau$  of 0.07 [ $\tau = (\beta - \alpha)/60$ , where  $\alpha = \text{N1}-\text{Cu1}-\text{S1} = 162.50(4)^\circ$  and  $\beta = \text{N2}-\text{Cu1}-\text{Cl1} = 158.03(4)^\circ$ ; for perfect square pyramidal and trigonal bipyramidal geometries the  $\tau$  values are zero and unity, respectively]. The three corners of the square plane are occupied by the pyridine (N1), imine (N2) nitrogen atoms, the thioether sulfur (S1) of the meridionally bound **pmtpm** ligand and one of the two chloride ions; the axial position is occupied by the other chloride ion. Copper is displaced 0.307 Å above the  $\text{N}_2\text{SCl}$  least square plane towards the axially coordinated  $\text{Cl}^-$  ion. The  $\text{Cu}-\text{N}_{\text{py}}$  and  $\text{Cu}-\text{N}_{\text{imine}}$  distances fall within the ranges expected ( $\text{Cu}-\text{N}_{\text{py}}$ , 2.00–2.11 [35,36];  $\text{Cu}-\text{N}_{\text{imine}}$ , 2.09–2.45) [37,38]. The  $\text{Cu}-\text{S}(\text{thioether})$  bond length (2.338 Å) is typical of equatorially bound thioether sulfur [4,5,25]. The dihedral angle made by  $\text{N2}-\text{Cu1}-\text{N1}$  and  $\text{S1}-\text{Cu1}-\text{Cl1}$  planes is  $24.0^\circ$ . It is interesting to compare the present structure with the perchlorate analogue  $[\text{Cu}(\text{pmtpm})$

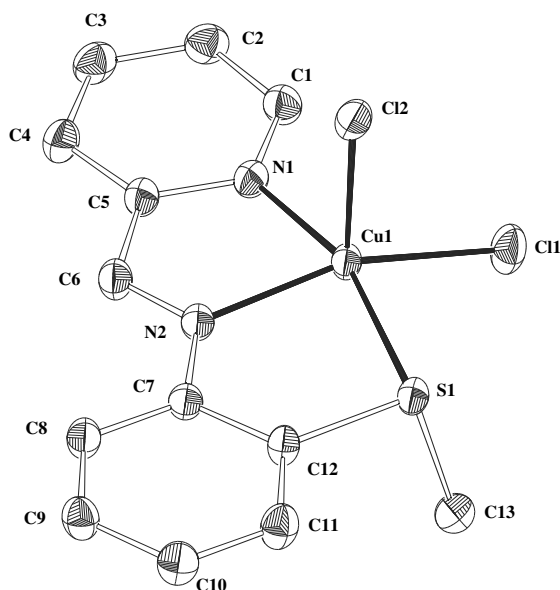


Fig. 2. ORTEP drawing of **1** showing the atom numbering scheme and thermal motion ellipsoids (50% probability level). The hydrogen atoms are omitted for clarity.

(H<sub>2</sub>O)(ClO<sub>4</sub>)<sub>2</sub>·(H<sub>2</sub>O) (**1a**) reported [39] earlier, which possesses, interestingly, a distorted octahedral geometry with ‘4+2’ coordination, thus belonging to Jahn–Teller elongated pseudo-octahedral examples. All the bond lengths in **1a** (Cu–S, 2.320 Å; Cu–N<sub>py</sub>, 2.000 Å; Cu–N<sub>imine</sub>, 1.943 Å) are considerably shorter than in **1** (Table 2), obviously because of the increase in positive charge on copper(II) by the replacement of the strongly coordinated chloride ions in [Cu(pmtpm)Cl<sub>2</sub>] by two ClO<sub>4</sub><sup>−</sup> to give **1a**.

An ORTEP view of complex **4** is illustrated in Fig. 3 with atom numbering scheme. The selected bond lengths and bond angles are collected in Table 2. The structure consists of a discrete five-coordinate complex cation, in which the tridentate ligand **pmtpm** is coordinated meridionally to copper(II) and **2,9-dmp** in a *cis* bidentate fashion.

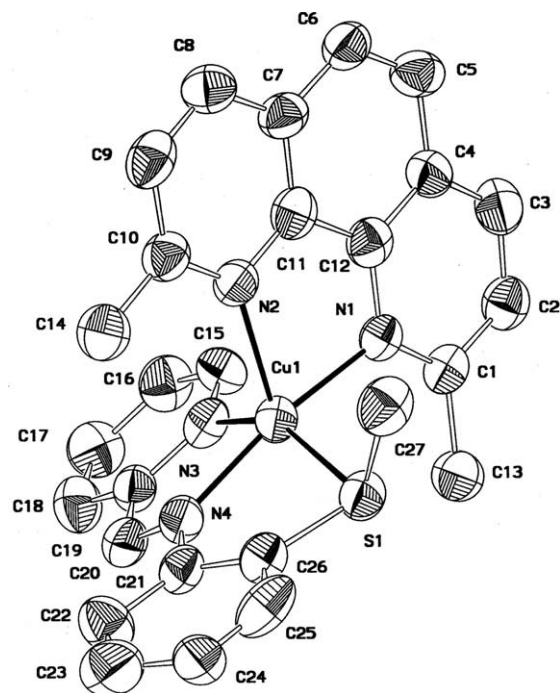


Fig. 3. ORTEP drawing of **4** showing the atom numbering scheme and thermal motion ellipsoids (50% probability level). The hydrogen atoms, perchlorate anions and solvent molecules are omitted for clarity.

The two perchlorates remain uncoordinated. The trigonality index [16]  $\tau$  (0.26) for **4** illustrates that the coordination geometry is best described as trigonal bipyramidal distorted square based pyramidal (TBDSBP) [34]. The corners of the plane in the coordination geometry is occupied by the pyridine nitrogen (N3), imine nitrogen (N4) and thioether sulfur (S1) atoms of the ligand **pmtpm** and one of the nitrogen (N1) atoms of **2,9-dmp** ligand and the axial position is occupied by the other nitrogen atom (N2) of **2,9-dmp**. The Cu–N<sub>py/imine</sub> and Cu–S<sub>thioether</sub> distances observed fall within the ranges, respectively, 1.94–2.11 [35,36] and

Table 2  
Selected bond lengths (Å) and angles (°) for **1**, **4** and **6**

Compound <b>1</b>		Compound <b>4</b>		Compound <b>6</b>	
Cu(1)–N(1)	2.0218(11)	Cu(1)–N(4)	1.963(8)	Cu(1)–N(4)	1.952(5)
Cu(1)–N(2)	2.0084(11)	Cu(1)–N(1)	1.998(7)	Cu(1)–N(1)	1.954(5)
Cu(1)–S(1)	2.3380(4)	Cu(1)–N(3)	2.056(8)	Cu(1)–N(3)	2.007(5)
Cu(1)–Cl(1)	2.2511(4)	Cu(1)–N(2)	2.181(8)	Cu(1)–N(2)	2.153(6)
Cu(1)–Cl(2)	2.4394(4)	Cu(1)–S(1)	2.372(3)	Cu(1)–S(2)	2.4306(19)
N(1)–Cu(1)–N(2)	80.44(5)	N(4)–Cu(1)–N(1)	167.4(3)	N(4)–Cu(1)–N(1)	176.2(2)
N(1)–Cu(1)–S(1)	162.50(4)	N(4)–Cu(1)–N(3)	80.5(3)	N(4)–Cu(1)–N(3)	81.5(2)
N(2)–Cu(1)–S(1)	84.06(3)	N(1)–Cu(1)–N(3)	92.5(3)	N(1)–Cu(1)–N(3)	100.7(2)
N(1)–Cu(1)–Cl(1)	98.15(4)	N(4)–Cu(1)–N(2)	110.8(3)	N(4)–Cu(1)–N(2)	101.5(2)
N(2)–Cu(1)–Cl(1)	158.03(4)	N(1)–Cu(1)–N(2)	81.1(3)	N(1)–Cu(1)–N(2)	80.2(2)
S(1)–Cu(1)–Cl(1)	93.178(14)	N(3)–Cu(1)–N(2)	105.2(3)	N(3)–Cu(1)–N(2)	117.0(2)
N(1)–Cu(1)–Cl(2)	98.12(4)	N(4)–Cu(1)–S(1)	83.3(2)	N(4)–Cu(1)–S(2)	80.57(16)
N(2)–Cu(1)–Cl(2)	96.11(4)	N(1)–Cu(1)–S(1)	98.5(2)	N(1)–Cu(1)–S(2)	95.92(17)
S(1)–Cu(1)–Cl(2)	91.540(14)	N(3)–Cu(1)–S(1)	151.7(2)	N(3)–Cu(1)–S(2)	143.61(18)
Cl(1)–Cu(1)–Cl(2)	105.756(16)	N(2)–Cu(1)–S(1)	102.3(2)	N(2)–Cu(1)–S(2)	97.49(15)

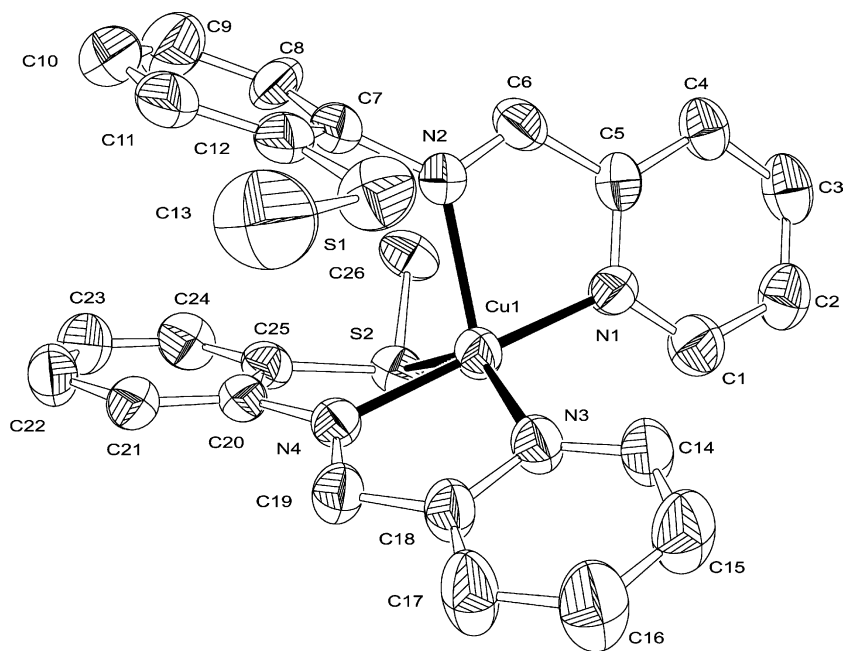


Fig. 4. ORTEP drawing of **6** showing the atom numbering scheme and thermal motion ellipsoids (50% probability level). The hydrogen atoms, perchlorate anions and solvent molecules are omitted for clarity.

2.31–2.76 Å [37] observed earlier. The N1–Cu1–N4 and N3–Cu1–S1 bond angles are 167.4° and 151.7°, respectively, which are far away from the ‘ideal’ value of 180° indicating severely distorted coordination geometry around copper(II). The molecular structure of **6** is shown in Fig. 4 together with the atom numbering scheme. The complex molecule crystallizes in the monoclinic space group  $C2/c$  and is found to possess a  $CuN_4S$  coordination sphere around copper(II). The copper atom is bonded to two Schiff base ligands, one of them acting as a tridentate chelating  $N_2S$  ligand and the other as a bidentate chelating ligand with its sulfur at a non-bonding distance. The pyridine and imine nitrogens are coordinated *cis* to each other giving a meridional coordination of the ligand around copper(II). The coordination geometry around copper(II) is described as square pyramidal distorted trigonal bipyramidal (SPDTBP) with the  $\tau$  value of 0.54. The pyridine nitrogen (N3), the imine nitrogen (N2) and the thioether sulfur (S2) of the ligand **pmtpm** occupy the corners of the trigonal plane while the pyridine nitrogens (N1, N4) occupy the axial positions. The Cu– $N_{py}$  (2.007, 1.954 Å) and Cu–S (2.430 Å) bond distances are significantly different from those of complex **1**. It appears that the strong coordination of pyridine (N1, N3) and imine (N2, N4) nitrogens elongates the Cu–S bond in **6** more significantly than in **1** and **4**.

A comparison of the bond distances and bond angles of compounds **1** and **4** helps us to understand the effect of incorporating the secondary ligand **2,9-dmp** on the basic structure of **1**. The structural index  $\tau$ , which is a measure of trigonal distortion, is 0.07 for **1** indicating an almost square-based geometry. The replacement of the two chloride ions in **1** by **2,9-dmp** and **pmtpm** as in **4** and **6**, respec-

tively, enhances the trigonal distortion and steric constraint at copper, as revealed by the increase in  $\tau$  values to 0.26 (**4**) and 0.54 (**6**) from 0.07. Also in complex **4**, the Cu– $N_{py}$  and Cu– $S_{thioether}$  bond distances increase because the two terminal donor atoms of **pmtpm** ligand are located very near to the sterically hindered methyl groups of **2,9-dmp** ligand. This increase is compensated by a stronger coordination of the central imine nitrogen of **pmtpm** ligand. It would be also interesting to compare the present structure with that of the analogous mixed ligand complex  $[Cu(L)(2,9-dmp)]ClO_4$  (**7**) (HL = 2-(methylthio)phenylsalicylaldimine) reported [37] recently. The complex **7** also possesses a square based coordination geometry but with a  $\tau$  value of 0.20 indicating a geometric distortion towards trigonal bipyramidal but lower than **4**. The replacement of the pyridine nitrogen in **4** by the strongly coordinating phenolate donor as in **7** leads to weaker coordination of **2,9-dmp** as revealed by the longer Cu– $N_{dmp}$  distances (2.060, 2.212 Å) in **7**. This illustrates that the coordination of the sterically demanding **2,9-dmp** ligand enforces enhanced trigonal constraint at copper in **4**. The stronger coordination of **2,9-dmp** in **4** and **7** results in a longer Cu–S bond distance (**4**: 2.372; **7**: 2.352 Å).

### 3.3. Spectral properties

The reflectance spectra of all the complexes exhibit a broad low energy ligand field (LF) band in the region 13400–16200  $cm^{-1}$  (Table 3) suggesting a square based geometry [40] around copper(II), which is consistent with the observed X-ray crystal structures of **1**, **4** and **6**. The high energy band in the region 21800–26000  $cm^{-1}$  may originate from the coordinated thioether to metal charge

Table 3  
Electronic and EPR spectral data for the complexes **1–6**

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
[Cu(pmtpm)Cl <sub>2</sub> ] ( <b>1</b> )	13.4	CH <sub>3</sub> CN 13.8 (60)	$g_{\parallel}$ 2.202	CH <sub>3</sub> CN $g_{\parallel}$ 2.218
	26.0	30.1 (11 340)	$g_{\perp}$ 2.041	$A_{\parallel}$ 163
		36.5 (6255)		$g_{\perp}$ 2.067
		42.0 (8385)		$g_{\parallel}/A_{\parallel}$ 136
[Cu(pmtpm)(bpy)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>2</b> )	15.2	MeOH 15.2 (130)	$g_3$ 2.133	CH <sub>3</sub> CN $g_{\parallel}$ 2.255
	21.8	28.3 (4970)	$g_2$ 2.064	$A_{\parallel}$ 174
	26.4	32.1 (16 735)	$g_1$ 1.989	$g_{\perp}$ 2.064
		33.4 (19 4 80)		$g_{\parallel}/A_{\parallel}$ 130
[Cu(pmtpm)(phen)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>3</b> )	15.6	MeOH 15.3 (150)	$g_{\parallel}$ 2.212	CH <sub>3</sub> CN $g_{\parallel}$ 2.274
	22.2	29.1 (6570)	$g_{\perp}$ 2.062	$A_{\parallel}$ 164
	26.6	33.7 (15 650)		$g_{\perp}$ 2.072
		37.2 (25 270)		$g_{\parallel}/A_{\parallel}$ 139
[Cu(pmtpm)(2,9-dmp)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>4</b> )	15.5	CH <sub>3</sub> CN 15.3 (55)	$g_3$ 2.171	CH <sub>3</sub> CN $g_{\parallel}$ 2.187
	21.8	30.0 (10 870)	$g_2$ 2.109	$A_{\parallel}$ 162
	25.7	34.0 (17 555)	$g_1$ 2.047	$g_{\perp}$ 2.067
				$g_{\parallel}/A_{\parallel}$ 135
[Cu(pmtpm)(dpq)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>5</b> )	15.8	CH <sub>3</sub> CN 15.5 (65)	$g_{\parallel}$ 2.230	CH <sub>3</sub> CN $g_{\parallel}$ 2.288
	22.6	29.9 (2380)	$g_{\perp}$ 2.107	$A_{\parallel}$ 172
		33.7 (5030)		$g_{\perp}$ 2.103
		38.9 (14 830)		$g_{\parallel}/A_{\parallel}$ 133
[Cu(pmtpm) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ( <b>6</b> )	16.2	CH <sub>3</sub> CN 15.8 (220)	$g_{\text{ave}}$ 2.078	CH <sub>3</sub> CN $g_{\parallel}$ 2.201
	22.3	23.4 (4160)		$A_{\parallel}$ 178
	26.5	30.2 (26 760)		$g_{\perp}$ 2.069
		35.5 (28 080)		$g_{\parallel}/A_{\parallel}$ 124

<sup>a</sup> 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  $10^{-4} \text{ cm}^{-1}$ ; a minor species is also present ( $g_{\parallel}$ , 2.207;  $A_{\parallel}$ ,  $161 \times 10^{-4} \text{ cm}^{-1}$ ).

transfer (l.m.c.t.) transition involving the ligand **pmtpm**. In methanol or acetonitrile solution all the complexes show a single ligand field band with  $\bar{\nu}_{\max}$  value in the range 13 800–15 800  $\text{cm}^{-1}$  typical of copper(II) in a weakly tetragonal field [40]. Most of the complexes do not show any change in position of the ligand field band on dissolution suggesting a negligible change in coordination geometry of the complexes on dissolution.

On going from **1** to **2–6**, the LF band is blue shifted to 15 200–15 800  $\text{cm}^{-1}$  obviously due to incorporation of two more nitrogen donors of diimine ligands in the coordination sphere. The high  $\epsilon$  value (11 340  $\text{M}^{-1} \text{ cm}^{-1}$ ) of the l.m.c.t. band at 30 100  $\text{cm}^{-1}$  of **1** suggests the strong equatorial coordination of the thioether donor as observed in the X-ray crystal structure. This band is shifted to lower energy (23 400–30 000  $\text{cm}^{-1}$ ) in complexes **2–6** on account of change in the coordination sphere effected by the coordination of the secondary diimine ligands. It is remarkable that the intensity of the l.m.c.t. band in the 2,9-dmp complex **4** is almost twice that of the complexes **2** (**bpy**), **3** (**phen**)

and **5** (**dpq**). This is consistent with the equatorial coordination of thioether sulfur in **4** evident in its X-ray crystal structure. On the other hand, the thioether is located in the equatorial position in the X-ray crystal structure of [Cu(L)(2,9-dmp)]<sup>+</sup> (**7**) [37] but in the axial position in the analogous [Cu(L)(phen)]<sup>+</sup> and [Cu(L)(dpq)]<sup>+</sup> complexes at exceptionally longer distance of 2.765 and 2.788 Å, respectively. So it is obvious that a variation in the steric and electronic properties of the diimine ligands dictates whether the thioether sulfur should occupy the axial or equatorial position. Interestingly, in complex **6** there are two  $S(\sigma) \rightarrow \text{Cu(II)}$  l.m.c.t. bands around 23 400 and 30 200  $\text{cm}^{-1}$  with the latter being much more intense than the former. It appears that the uncoordinated sulfur weakly interacts with copper(II) ion in solution.

The ambient temperature polycrystalline EPR spectrum of complex **6** is isotropic, while those of complexes **1**, **3** and **5** are axial. The complexes **2** and **4** show rhombic spectra (Fig. 5) with three  $g$  values and the  $R$  values [ $R = (g_3 - g_2)/(g_2 - g_1)$ ] of 0.9 (**2**) and 1.0 (**4**) indicate the

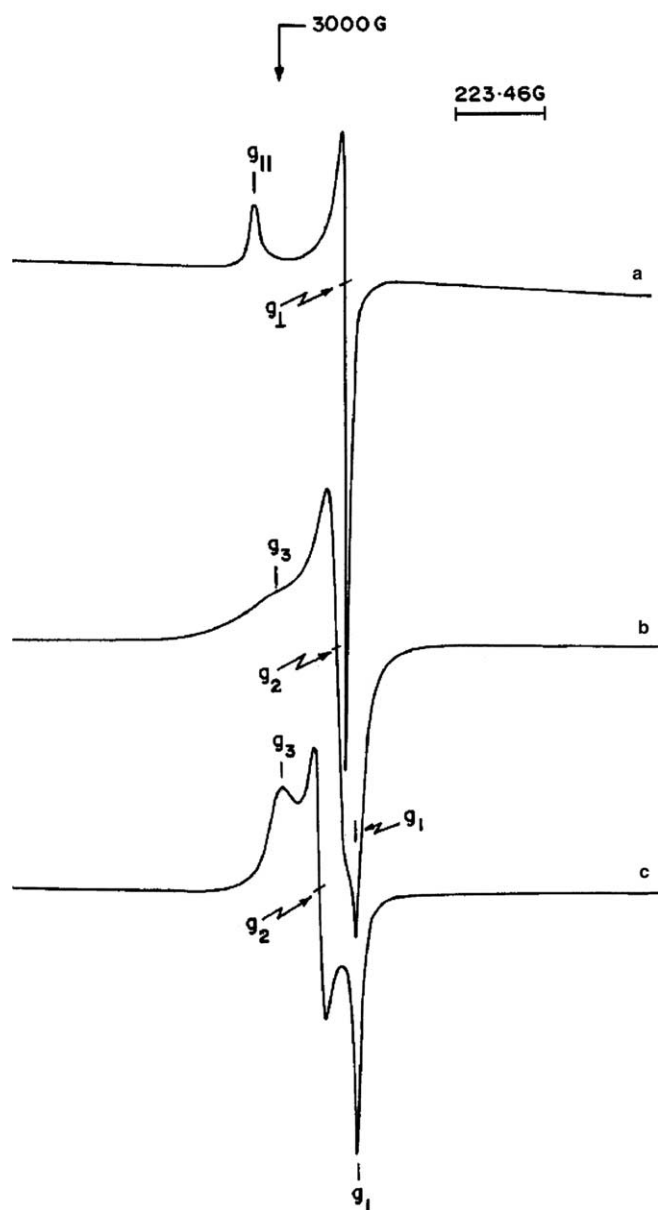


Fig. 5. X-band Polycrystalline EPR spectra of the complexes **1** (a), **2** (b) and **4** (c).

presence of a  $d_{z^2}$  ground state in the solid state [41]. The cryogenic solution EPR spectra (Fig. 6) of all the complexes are clearly axial [ $g_{\parallel} > g_{\perp} > 2.0$ ,  $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 2.9 - 4.4$ ], which is diagnostic of a  $d_{x^2-y^2}$  ground state for copper(II) located in square based environment [42,43]. The  $g_{\parallel}$  (2.19–2.29) and  $A_{\parallel}$  ( $162-178 \times 10^{-4} \text{ cm}^{-1}$ ) values lie in the range typical for copper(II) complexes of N and S containing ligands [18,22,37,44]. Further, the analogous complexes reported by Chakravarty et al. [37] bearing  $\text{N}_3\text{OS}$  coordination around copper(II) display  $g_{\parallel}$  values (2.16–2.23) slightly lower than the present complexes due to the presence of stronger oxygen coordination in the former complexes. The values of  $g_{\parallel}/A_{\parallel}$  quotient (124–139 cm) for all the present complexes are within the range (105–

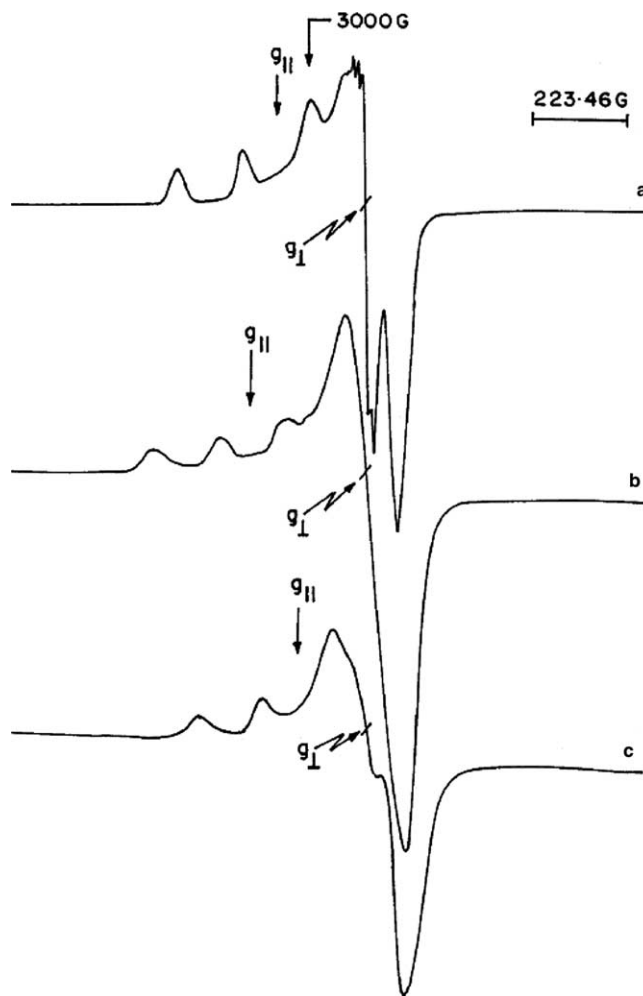


Fig. 6. X-band EPR spectra of the complexes **1** (a), **2** (b) and **4** (c) in acetonitrile/acetone glass at 77 K.

135 cm) expected for copper(II) complexes with perfectly square based geometry [22,45].

In general, copper(II) complexes possessing a  $\text{N}_4$  donor set exhibit  $g_{\parallel}$  and  $A_{\parallel}$  values in the range 2.21–2.26 and  $175-200 \text{ cm}^{-1}$ , respectively. The inclusion of sulfur in square planar coordination geometry decreases the  $g_{\parallel}$  values [45]. Thus, the complex **4** having strong equatorial thioether coordination as revealed in its X-ray crystal structure displays a lower  $g_{\parallel}$  value of 2.187 (Fig. 6(c)). On the other hand, the complexes **2**, **3** and **5**, which are expected to possess a coordination geometry similar to **4**, exhibits  $g_{\parallel}$  values (2.255–2.288) higher than complex **4**. This reveals that the thioether donor in these complexes is either coordinated weakly or may be located in the axial position. Thus, EPR spectroscopy is very useful in diagnosing axial/equatorial coordination mode of thioether. Also, complex **1** exhibits (Fig. 5(a)) a  $g_{\parallel}$  value (2.218) less than **2**, **3** and **5**, which is consistent with the equatorial coordination of thioether sulfur observed in the X-ray crystal structure. All these observations are supported by the l.m.c.t. spectral features of the complexes.



### 3.4. Redox chemistry

The electrochemical data of all the complexes obtained in methanol or acetonitrile solution using TBAP as supporting electrolyte are presented in Table 4. Typical cyclic (CV) and differential pulse voltammograms (DPV) of the complexes obtained by using a Pt working electrode and Ag/AgCl reference electrode are presented in Figs. 7 and 8. For all the mixed ligand complexes the reduction wave ( $E_{pc}$ , 0.132–0.342 V versus Ag/Ag<sup>+</sup>) corresponding to Cu(II) to Cu(I) reduction is obtained. During the reverse scan the oxidation of Cu(I) to Cu(II) occurs in the potential range 0.218–0.436 V (Table 4). All the present copper(II) complexes exhibit electrochemically and chemically reversible Cu<sup>II</sup>/Cu<sup>I</sup> redox behaviour, as evident from the linearity of the plots of  $i_{pc}$  versus  $v^{1/2}$  ( $D$ , 2.6–10.1 × 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup>) and from the observed values of the ratio of peak currents ( $i_{pa}/i_{pc}$  ~ 1.0, Table 4), respectively. However, the value of the limiting peak-to-peak separation ( $\Delta E_p$ , 86–194 mV), which is almost the same or higher than that for the Fc/Fc<sup>+</sup> couple ( $\Delta E_p$ , 84 mV;  $E_{1/2}$ , 0.414 V) under identical conditions. This suggests that the heterogeneous electron-transfer process in most of the complexes involves considerable stereochemical reorganization [46] of the coordination sphere. Thus, interestingly, the complexes **1** (86 mV) and **4** (94 mV) have relatively low  $\Delta E_p$  values indicating that the structural reorganization between their copper(II) and copper(I) species is minimal leading to a facile heterogeneous electron transfer, possibly due to the flexible equatorial thioether coordination. In contrast, the mixed ligand complexes **2**, **3** and **5** suggested to have axial thioether sulfur and the bis-complex **6** (Fig. 7) undergo less reversible heterogeneous electron transfer than complexes **1** and **4**. A departure from the electrochemical reversibility in the complexes thus means higher structural reorganization accompanying one electron transfer.

There are certain other noteworthy features of the redox chemistry, which deserve attention. The complexes **2–6** show positive Cu(II)/Cu(I) redox potentials (0.20–0.39 V versus Ag/Ag<sup>+</sup>, Table 4) higher than [Cu(pmtpm)Cl<sub>2</sub>] (0.175 V) indicating that inclusion of the 2N chelating ligands tend

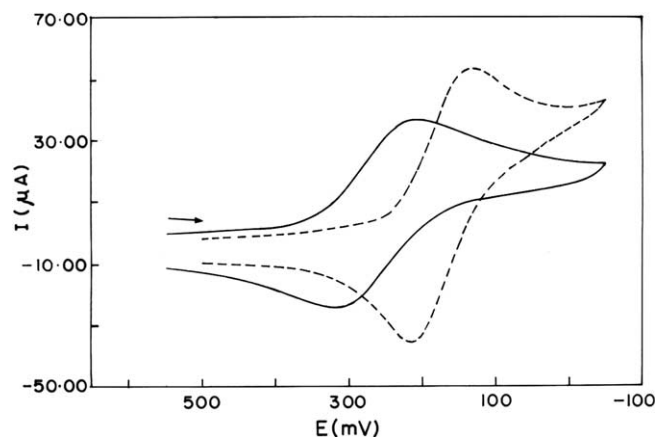


Fig. 7. Cyclic voltammograms of the complexes **1** (-----) and **6** (—) in methanol solution at 25 °C at 0.05 V s<sup>-1</sup> scan rate.

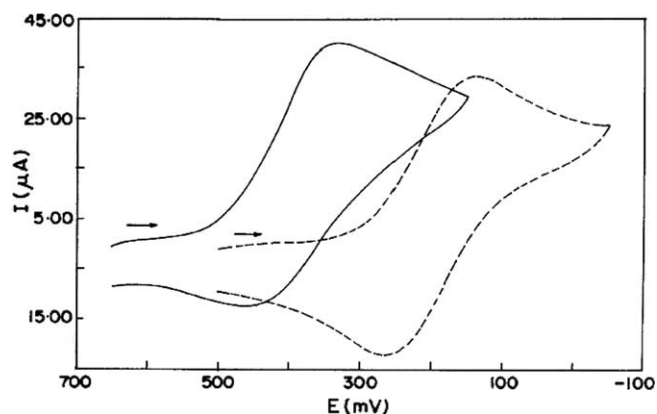


Fig. 8. Cyclic voltammograms of the complexes **2** (-----) and **4** (—) in methanol solution at 25 °C at 0.05 V s<sup>-1</sup> scan rate.

to destabilize copper(II) [47] by being involved in  $\pi$ -delocalization of electron density from copper. It is possible that the geometrical distortion induced by the sterically hindering 2N ligands would also contribute substantially to the stability of copper(II) oxidation state (cf.  $\tau$  values, **1**, 0.07; **4**, 0.26). Further, the redox potentials among the mixed ligand complexes of diimine ligands follow the order **bpy** <

Table 4  
Electrochemical data<sup>a</sup> for the copper complexes at 25 ± 2 °C

Compound	$E_{pc}$ (V)	$E_{pa}$ (V)	$\Delta E_p$ (mV) <sup>b</sup>	$E_{1/2}$ (V)		$i_{pa}/i_{pc}$	$10^6 D$ (cm <sup>2</sup> s <sup>-1</sup> )
				CV	DPV <sup>c</sup>		
[Cu(pmtpm)Cl <sub>2</sub> ] ( <b>1</b> )	0.132	0.218	86	0.175	0.190	1.1	10.1
[Cu(pmtpm)(bpy)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>2</b> )	0.138	0.260	122	0.199	0.214	1.1	3.4
[Cu(pmtpm)(phen)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>3</b> )	0.156	0.268	112	0.212	0.228	1.0	4.2
[Cu(pmtpm)(2,9-dmp)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>4</b> )	0.342	0.436	94	0.389	0.406	0.8	5.7
[Cu(pmtpm)(dpq)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>5</b> )	0.318	0.422	104	0.370	0.380	1.1	2.6
[Cu(pmtpm) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ( <b>6</b> )	0.208	0.320	112	0.264	0.282	1.1	4.9

<sup>a</sup> Measured vs. 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),  $\Delta E_p$ , 84 mV; scan rate 50 mV s<sup>-1</sup>; supporting electrolyte, tetra-*N*-butylammonium perchlorate (0.1 mol dm<sup>-3</sup>); complex concentration, 0.001 mol dm<sup>-3</sup>.

<sup>b</sup>  $\Delta E_p$  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.

**phen**  $\ll$  **dpq**  $<$  **2,9-dmp**. The order may be explained on the basis of electronic and steric factors. On going from **bpy** to **phen** to **dpq** the number of aromatic rings involved in  $\pi$ -delocalization of electrons involving copper increases and hence the higher redox potentials for the complexes and also the trend observed. The **2,9-dmp** complex shows the highest positive redox potential in this series, which is consistent with the location of the thioether sulfur in the equatorial position due to the steric hindrance to coordination of the nitrogen donors by the two methyl groups at 2 and 9 positions on the phen ring.

#### 4. Conclusions

The X-ray crystal structure of 1:1 copper(II) complex of the tridentate ligand **pmtpm** offering an  $N_2S$  donor set possesses a distorted square pyramidal geometry with equatorially coordinated thioether sulfur. Mixed ligand complexes of the type  $[Cu(pmtpm)(diimine)]^{2+}$ , where diimine is 2,2'-bipyridine (**bpy**), 1,10-phenanthroline (**phen**), 2,9-dimethyl-1,10-phenanthroline (**2,9-dmp**) and dipyrido-[3,2-d:2',3'-f]-quinoxaline (**dpq**), have been obtained. The X-ray crystal structure of  $[Cu(pmtpm)(2,9-dmp)]^{2+}$  reveals a square pyramidal  $CuN_4S$  coordination geometry, interestingly, with equatorially ligated thioether sulfur. The electronic and EPR spectral and redox properties of the mixed ligand **2,9-dmp** complex are interestingly different from those of **bpy**, **phen** and **dpq** complexes suggesting that the latter complexes with distorted square based geometries for  $CuN_4S$  chromophore contain an axially coordinated thioether sulfur. It is likely that the phen ring nitrogens sterically hindered by 2,9-dimethyl substituents coordinate to copper(II) weakly and one of them default to the axial position. On the other hand, the strongly coordinating nitrogens of **bpy**, **phen** and **dpq** favour the location of the weakly coordinating sulfur in the axial position. The mixed ligand complexes of **bpy** and **phen** undergo disproportionation to form bis-complexes of **bpy** and **phen**, respectively, and the bis-**pmtpm** complex. Interestingly, all the complexes exhibit high  $Cu(II)/Cu(I)$  positive redox potentials, which approximate to those of blue copper proteins. Further, the redox potential of 2,9-dmp complex is higher than all other diimine complexes, which is consistent with the presence of equatorially coordinated thioether sulfur. Thus, it is remarkable that the diimine ligands can be suitably tailored to orient the Cu–thioether bond in the axial direction so as to obtain close synthetic mimics for the copper proteins.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.09.062.

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