

An Unusual Cu(II) Mediated C–N Single Bond Cleavage of Pentacoordinating N₄S Ligands: Control of Copper Coordination Geometry by Modified Ligand Structure

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Complexation of copper(II) with penta-coordinated N₄S ligands in alcohols proceeded through unusual reaction paths involving C–N bond cleavage process. The products are square planar compound with a modified ligand structure that includes an alkoxy group provided by the solvent. The complexes are characterized by single crystal XRD, elemental analyses, IR, UV-visible and EPR spectroscopic techniques. Cyclic voltammetry shows Cu(II)/Cu(I) reduction becomes more difficult with the increase in donor strength of alkoxy group.

Keywords: Copper(II) complex, Crystal structure, ESR spectra, Cyclic voltammetry

INTRODUCTION

The flexibility in the ligand framework of N₄S ligands *viz.* Hmmpcd and Hmmeed offers interesting variation in their coordination mode [1-5]. With Zn(II) and Co(II) ions, the complexes formed have trigonal bipyramid (TBP) geometry [1,5] with ligand structure remaining intact. In the case of Ni(II) and Pd(II) however, the situation is not that straightforward. The ligand molecules undergo alcoholysis reaction through metal-induced activation of an otherwise unreactive C–N single bond, forming square planar complexes [2-4]. Thus two distinct types of coordination patterns emerge out for these ligands depending upon whether the metal ion in question prefers a geometry with a triangular base (Zn²⁺ and Co²⁺ ions) or a square one (as in Ni²⁺ and Pd²⁺).

Because of the plasticity effect [6], Cu(II) in pentacoordination can adopt a wide range of distorted geometries, intermediate between the idealized square pyramidal ($\tau = 0$) and trigonal bipyramidal ($\tau = 1$) extremes, τ being a structural indexing parameter [7]. Cu(II) complexes of the present set of N₄S ligands show interesting structural diversity with the associated steric bulks of the ligands. While [Cu(mmpcd)]ClO₄ (mmpcd = methyl 2-aminocyclopent-1-ene-1-dithiocarboxylate with pendent pyrazolyl groups (Me₂pzCH₂)₂NC₂H₃RNHC₅H₆CSSCH₃; R = CH₃) has a distorted square pyramidal geometry ($\tau = 0.26$) [1], corresponding product with the ligand HL₁ shows two distinct

structural forms, one with TBP ($\tau = 0.62$) and the other with square pyramidal ($\tau = 0.24$) geometry with varying degrees of distortions. The observation of a square base geometry for copper(II), has prompted us to examine their reactivity pattern in alcohols as substrates.

In this study, the coordination chemistry of Cu(II) with the aforesaid N₄S ligands has been reported. Interesting variations in the reactivity pattern are observed depending upon the preparative conditions used, leading to C–N single bond activation of the coordinated ligands, followed by alcoholysis as observed with the *d*⁸ ions under identical situation [2-4].

EXPERIMENTAL

Details of the elemental analyses, IR, UV/vis and room temperature magnetic measurements are as described earlier [5]. X-band EPR spectra at room temperature (298 K) as well as in the frozen state (77 K) in acetonitrile/toluene mixture (1:4 v/v) were recorded on a JEOL-JES RE3X instrument coupled with ESPRIT 330 data processing system. For measurements at room temperature in acetonitrile, a flat quartz cell was used.

Electrochemical measurements were done with a Bioanalytical system model 100 B/W workstation. Cyclic voltammograms were recorded at 25 ± 1 °C in dry acetonitrile under purified dinitrogen using platinum working and auxiliary electrodes and 0.1 M TBAP as the supporting electrolyte; potentials are

referenced to the Ag/AgCl electrode. Bulk electrolyses were carried out using a Pt-gauze working electrode. The ferrocene/ferrocenium (Fc/Fc⁺) couple was used as internal standard [8].

Synthesis: Caution[†] Perchlorate salts of metal complexes are potentially explosive [9]. Complexes reported in this article were isolated in small quantities and handled with care.

The ligand Hmmpcd was prepared following a reported method [1] and HL₁ as described elsewhere. [Cu(CH₃CN)₄]-ClO₄ was prepared following a reported method [10]. Reagent grade solvents, dried and distilled by standard methods [11], were used in all cases. All other chemicals were reagent grade, available commercially and used as received. Unless stated otherwise all manipulations in the following preparations were carried out under an atmosphere of purified dinitrogen.

Synthesis of [Cu(mmpcd)]ClO₄ (1a): To a stirred solution of compound **2a** (30 mg, 0.05 mmol) in acetonitrile (15 mL) was added large excess of 3,5-dimethylpyrazole (25 mg, 0.26 mmol). The resulting brown solution was heated at reflux for about 3 h during which time the colour of solution turned to green from its initial brown shade. The solution was cooled to room temperature, concentrated to about 5 mL volume by rotary evaporation and layered with Et₂O at 0 °C, where upon dark green crystals of the compound deposited overnight. The product was collected and recrystallized from CH₃CN/Et₂O. Yield: 10 mg (34 %).

Synthesis of [CuL₁]BPh₄ (1b) (method A): To a stirred solution in CH₃CN (15 mL) of HL₁ (0.19 g, 0.5 mmol) was added slowly a solution of [Cu(CH₃CN)₄]ClO₄ (0.17 g, 0.5 mmol), also taken in the same solvent (10 mL) and stirred for 1 h to get a red-brown solution. It was then exposed to atmospheric oxygen and stirred further for about 2 h. A green solution obtained at this stage was filtered. The filtrate volume was reduced to about 10 mL by rotary evaporation, combined with NaBPh₄ (0.2 g) and finally layered with Et₂O. Storage at 0 °C for an overnight period yielded dark green crystalline solids. These were collected by filtration, washed with cold Et₂O, dried *in vacuo* and finally recrystallized from CH₃CN/Et₂O. Yield: 0.17 g (45%). Anal. calcd. (found) % for C₄₂H₄₅N₆S₂CuB: C, 65.34 (65.40); H, 5.83 (5.80); N, 10.89 (10.98). IR (KBr disc; cm⁻¹): ν(C–C), 1580 s; ν(C–N)/pyrazole ring, 1520 m; ν(C–N + C–C), 1450 vs; ν(BPh₄⁻), 710 and 740 s. UV-vis (CH₃CN), λ_{max}/nm (ε_{max}/mol⁻¹ cm²): 574 (210); 391 (6000); 352 (20300); 292 (12500). μ_{eff}: 1.67 μ_B.

Method B: A solution of compound **2b** (30 mg, 0.06 mmol) containing large excess of pyrazole (20 mg, 0.3 mmol) in acetonitrile (15 mL) was heated at reflux for 3 h when a green solution was obtained. It was filtered and to the filtrate NaBPh₄ (25 mg) was added. Storage at 0 °C after layering with diethyl ether afforded green microcrystalline product. The product was collected by filtration and recrystallized from CH₃CN/Et₂O. Yield: 13 mg (28 %).

Synthesis of [Cu,ZnL₁]BPh₄: Complexes [ZnL₁]BPh₄ (0.12 g, 0.16 mmol) and compound **1b** (6.5 mg, 0.008 mmol) were dissolved in acetone (25 mL) with stirring. The stirring was continued for 15 min. The solution was then concentrated to about 10 mL volume by rotary evaporation and layered with *n*-hexane. Upon storage at 0 °C overnight afforded greenish-yellow solid. The compound was collected by filtration and

recrystallized from acetone/*n*-hexane mixture. Yield: 85 mg. The copper content (~3.7 mol %) was estimated spectrophotometrically by measuring the absorbance of the solution at 574 nm in CH₃CN.

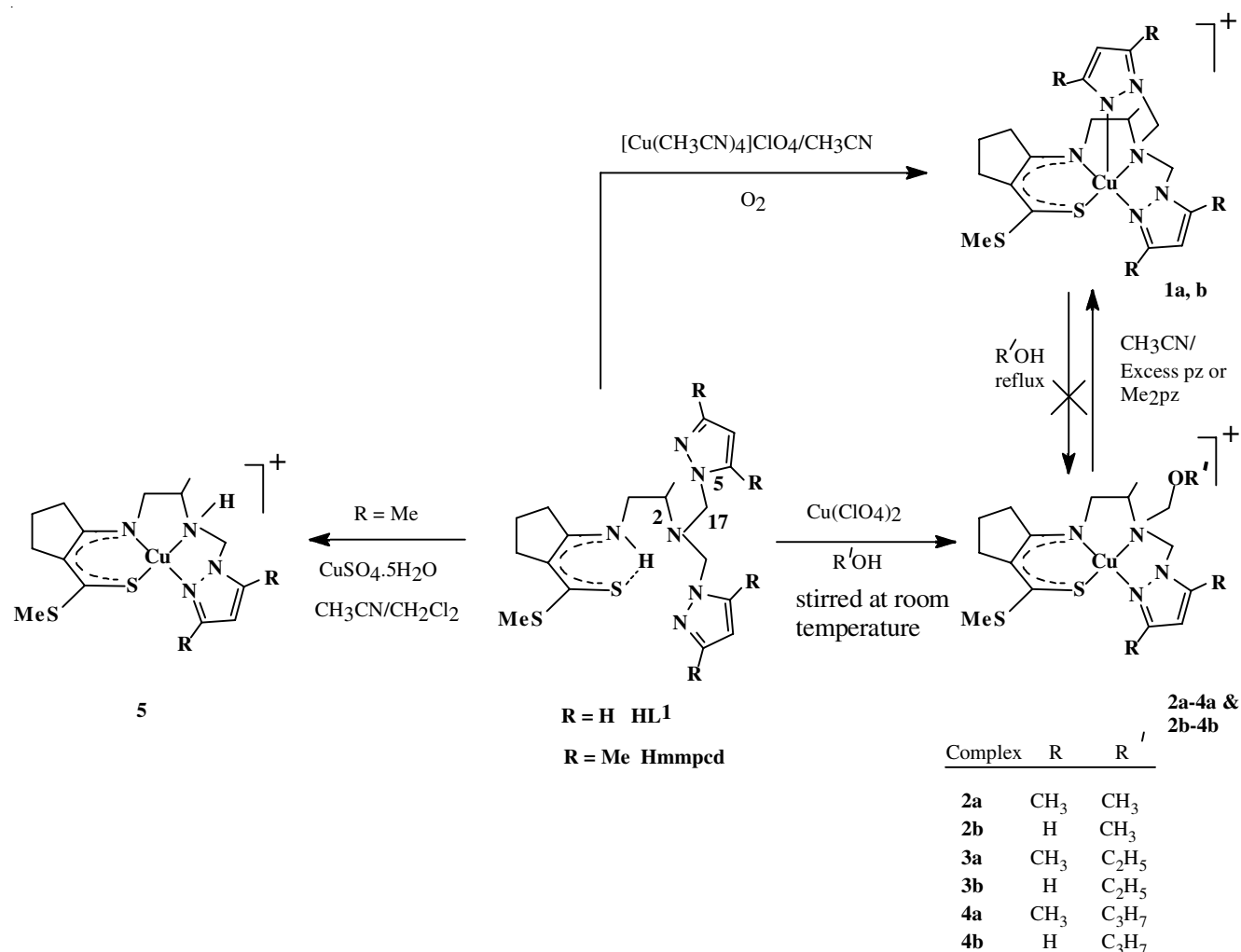
Synthesis of [Cu(N₃S)CH₂OMe]ClO₄ (2a): To a solution of Hmmpcd (0.22 g, 0.5 mmol) in methanol (15 mL) was added with stirring a methanolic solution of Cu(ClO₄)₂·6H₂O (10 mL) taken in equimolar quantity (0.18 g, 0.5 mmol). During this and subsequent syntheses, the parent N₃S ligands undergo C–N bond cleavage as depicted in **Scheme-I**. The colour of reaction mixture was changed immediately to brown from which microcrystalline solid began to appear within a few minutes. The stirring was continued for about 2 h to ensure complete precipitation. The product was collected by filtration, washed with cold ether and finally dried *in vacuo*. The compound was recrystallized from CH₃CN/Et₂O. Yield: 0.18 g (68 %). Anal. calcd. (found) % for C₁₈H₂₉N₄S₂CuClO₅: C, 39.7 (39.9); H, 5.33 (5.26); N, 10.29 (10.48). IR (KBr disc, cm⁻¹): ν(C–C), 1571 s; ν(C–N)/pyrazole ring, 1550 s; ν(C–N + C–C), 1467 s; ν_{as}(Cl–O), 1096 s; ν(O–Cl–O), 623 s. UV-vis (CH₃CN), λ_{max}/nm (ε_{max}/mol⁻¹ cm²): 780 (60); 550 (340); 383 (7200); 349 (19400); 290 (11600). μ_{eff}: 1.68 μ_B.

Synthesis of [Cu(N₃S)CH₂OMe]ClO₄ (2b): To a solution of HL₁ (0.19 g, 0.5 mmol) taken in methanol (15 mL) was added with stirring a methanolic solution (10 mL) of Cu(ClO₄)₂·6H₂O taken in equimolar amount (0.18 g, 0.5 mmol). The colour of the solution turned brown and precipitation of a compound began. The stirring was continued for about 2 h. The product obtained was filtered, washed with cold ether and finally dried *in vacuo*. The compound was recrystallized from acetonitrile. Yield: 0.19 g (72 %). Anal. calcd. (found) % for C₁₆H₂₅N₄S₂CuClO₅: C, 37.21 (37.77); H, 4.84 (4.62); N, 10.85 (11.21). IR (KBr disc, cm⁻¹): ν(C–C) + ν(C–N)/pyrazole ring, 1562 m; ν(C–N + C–C), 1452 s; ν_{as}(Cl–O), 1097 s; δ(O–Cl–O), 624 m. UV-vis (CH₃CN), λ_{max}/nm (ε_{max}/mol⁻¹ cm²): 794 (50); 514 (290); 385 (7200); 343 (20800); 290 (10800). μ_{eff}: 1.68 μ_B.

Synthesis of [Cu(N₃S)CH₂OEt]ClO₄ (3a): This compound was prepared following a similar procedure as for compound **2a** except that the solvent used here is EtOH. The modified forms of the ligands are represented by their respective donor atoms set. Yield: 0.12 g (44 %). Anal. calcd. (found) % for C₁₉H₃₁N₄S₂CuClO₅: C, 40.86 (40.92); H, 5.55 (5.35); N, 10.04 (10.45). IR (KBr disc, cm⁻¹): ν(C–C), 1560 s; ν(C–N)/pyrazole ring, 1540 s; ν(C–N + C–C), 1460 s; ν_{as}(Cl–O), 1090 s; ν(O–Cl–O), 625 s. UV-vis (CH₃CN), λ_{max}/nm (ε_{max}/mol⁻¹ cm²): 764 (44); 551 (340); 384 (7700); 346 (20800); 290 (12300). μ_{eff}: 1.76 μ_B.

Synthesis of [Cu(N₃S)CH₂OEt]ClO₄ (3b): The same procedure as that for the synthesis of compound **2b** was followed using EtOH as solvent. Yield: 0.14 g (52%). Anal. calcd. (found) % for C₁₇H₂₇N₄S₂CuClO₅: C, 38.49 (39.08); H, 5.09 (4.48); N, 10.57 (11.34). IR (KBr disc, cm⁻¹): ν(C–C) + ν(C–N)/pyrazole ring, 1574 m; ν(C–N + C–C), 1470 s, 1460 s; ν_{as}(Cl–O), 1084 s; ν(O–Cl–O), 623 s. UV-vis (CH₃CN), λ_{max}/nm (ε_{max}/mol⁻¹ cm²): 788 (50); 518 (290); 385 (7000); 342 (21100); 290 (11100). μ_{eff}: 1.68 μ_B.

Synthesis of [Cu(N₃S)CH₂OPrⁿ]BPh₄ (4a): This compound was prepared following a procedure similar to compound



Scheme-I

2a except that *n*-PrOH was used as solvent. The precipitated brown compound was dissolved in acetone (15 mL) and 0.2 g of NaBPh₄ was added. The solution volume was reduced to about 5 mL by rotary evaporation, layered with pet. ether (40–60 °C) and finally allowed to stand in a refrigerator (0 °C) for an overnight period to get brown crystalline compound. Yield: 0.14 g (34 %). Anal. calcd. (found) % for C₄₄H₅₃N₄S₂CuOB: C, 66.73 (66.47); H, 6.70 (6.54); N, 7.07 (6.97). IR (KBr disc, cm⁻¹): ν(C–C), 1560 s; ν(C–N)/pyrazole ring, 1530 m; ν(C–N + C–C), 1470 s, 1460 s; ν(BPh₄⁻), 710, 740 s. UV-vis (CH₃CN), λ_{max}/nm (ε_{max}/mol⁻¹ cm²): 760 (85); 523 (380); 387 (6850); 346 (17700); 290 (11900). μ_{eff}: 1.75 μ_B.

Synthesis of [Cu(N₃S)CH₂OPr]⁺BPh₄⁻ (4b): This compound was prepared following a methodology similar to the one adopted for compound **2b** except that the solvent used here was *n*-PrOH. The brown compound precipitated was dissolved in CH₃CN (15 mL) and combined with NaBPh₄ (0.2 g). The solution volume was reduced by rotary evaporation to about 5 mL. Brown crystalline product was obtained by layering diethyl ether carefully over the acetonitrile solution of compound at 0 °C. Yield: 0.15 g (38 %). Anal. calcd. (found) % for C₄₂H₄₉N₄S₂CuOB: C, 66.03 (66.16); H, 6.42 (6.41); N, 7.34 (7.70). IR (KBr disc, cm⁻¹): ν(C–C) + ν(C–N)/pyrazole ring, 1579 s, 1572 s; ν(C–N + C–C), 1453 s; ν(BPh₄⁻), 708, 735 s. UV-vis (CH₃CN),

λ_{max}/nm (ε_{max}/mol⁻¹ cm²): 780 (50); 522 (255); 384 (6700); 343 (19650); 288 (11350). μ_{eff}: 1.84 μ_B.

Synthesis of [Cu(N₃S)H]⁺ClO₄⁻ (5): To a slurry of copper sulfate (0.13 g, 0.5 mmol) in CH₃CN (1 mL) was added dropwise with stirring a solution of Hmmpcd (0.22 g, 0.5 mmol) in CH₂Cl₂ (20 mL). The stirring was continued for 1 h, when a clear brown solution was obtained. To this, 0.1 g of NaClO₄ was added and after an additional 10 min of stirring, the solution was filtered. The filtrate volume was reduced under vacuum to 2 mL, layered with diethyl ether and finally stored in a refrigerator at 4 °C for an overnight period to get brown crystalline solids. The product was finally crystallized from methanol. Yield: 0.05 g (22 %). Anal. calcd. (found) % for C₁₆H₂₅N₄S₂CuClO₄: C, 38.40 (38.63); H, 5.00 (4.69); N, 11.2 (11.09). IR (KBr disc, cm⁻¹): ν(C–C), 1570 s; ν(C–N)/pyrazole ring, 1545 s; ν(C–N + C–C), 1460 s; ν_{as}(Cl–O), 1100 s; ν(O–Cl–O), 620 s. UV-vis (CH₃CN), λ_{max}/nm (ε_{max}/mol⁻¹ cm²): 745 (50); 539 (290); 384 (8160); 340 (17050); 290 (10900). μ_{eff}: 1.78 μ_B.

Diffraction quality crystals of compound **1b** were grown by slow diffusion of diethyl ether into acetonitrile solution of the compound. A similar diffusion process was followed for compound **4a** using *n*-hexane/acetone as the solvent combination. Crystals of compounds **2a** and **5** were obtained by slow evaporation at 4 °C of acetonitrile and methanol solution of

the compounds, respectively. A suitable crystal of compound **1b** (dark blue, $0.18 \times 0.82 \times 0.34$ mm) was glued to the end of a thin glass fiber and transferred to a Siemens P4/S diffractometer equipped with graphite monochromatized MoK_α ($\lambda = 0.71073$ Å) radiation. Cell dimensions and an orientation matrix were obtained from a least-squares refinement of the setting angles of 25 accurately centred reflections. The structure was solved by direct methods using the SHELXL package [12]. Neutral atom scattering factors were used [13] with corrections for real and imaginary anomalous dispersion [14]. The structure was refined by full-matrix least-squares methods based on F^2 using SHELXL-96 [15] and using all unique data. Non-hydrogen atoms were refined anisotropically while hydrogen atoms were located in difference Fourier syntheses and refined isotropically.

Crystals of compound **2a** (red plate, 0.09 mm \times 0.45 mm \times 0.46 mm), compound **4a** (brown-red block, 0.18 mm \times 0.32 mm \times 0.57 mm) and compound **5** (dark red-brown block, 0.13 mm \times 0.19 mm \times 0.40 mm) were mounted on glass fibers. The orientation parameters and cell dimensions were obtained from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the ranges $13^\circ \leq \theta \leq 15^\circ$, $11.2^\circ \leq \theta \leq 12.6^\circ$ and $12.1^\circ \leq \theta \leq 14.7^\circ$ for compounds **2a**, **4a** and **5**, respectively. Table-1 contains a summary of relevant crystal data and final residuals. The centric distribution of intensities indicated the space group $P-1$ for compounds **2a** and **5**. The systematic absences indicated the space-group to be $P2_1/n$ for compound **4a**. Absorption corrections based on azimuthal scans (ψ scans) for compound **2a** or on the basis of isotropically refined structure [16] (for compound **4a**) were applied. Absorption corrections were not applied for compound **5**. For compounds **2a** and **5**, Patterson analysis (DIRDIF [17]) gave the positions of the non-hydrogen atoms. All hydrogen atoms were subsequently located and refined. For compound **4a**, however, a SIR92 E-map [18] showed all the non-hydrogen atoms. Hydrogen atoms were included at positions recalculated after each cycle of refinement [$B(\text{H}) = 1.2B_{\text{eq}}(\text{C})$; $d(\text{C-H}) = 0.95$ Å]. The anion appeared to be distorted in compound **2a**

as five oxygen sites O(2) to O(6) around the Cl atom were found; O(5) and O(6) were refined [O(6) isotropically] with occupancy factor 0.7 and 0.3, respectively. Refinements were based on F^2 . The final difference syntheses were featureless except for compound **2a** with several peaks upto 0.5 eÅ^{-3} near the Cl atom, arising from disorder, which could not be satisfactorily modelled. The TEXSAN program suite [19] incorporating complex scattering factors was used in all calculations. The copper(I) precursor compound in the solid state cannot be isolated [20].

RESULTS AND DISCUSSION

Penta-coordinated ligands HL_1 and Hmmpcd show interesting variations in their coordination mode when allowed to react with different copper ion precursors under diverse reaction conditions. Results are summarized in **Scheme-I**. Attempts to prepare the pentacoordinated compound **1b** by a metathetical reaction involving equimolar quantities of the ligand HL_1 and copper(II) perchlorate hexahydrate have been unsuccessful due to reducing nature of ligand [2], leading to a brown intractable solid of unknown composition. This has prompted us to look for an alternative strategy that involve synthesis of a red brown copper(I) precursor compound in the initial stage [20], followed by its aerial oxidation to the desired green copper(II) product. As revealed from X-ray crystal structure analysis, the asymmetric units of compound **1b** are two independent molecules, present in 1:1 molecular proportion in the unit cell. One of these has a trigonal bipyramid (TBP) structure, while the other has a square pyramidal geometry.

Earlier reports [2-4] have confirmed that nickel(II) and palladium(II) complexes with preference for square base geometry, appear to promote the solvolytic cleavage of a C-N single bond of the coordinated N_4S ligands in alcohols as solvent. These observations have led us to repeat this alcoholysis reaction with copper(II) which can also wrap up the N_4S ligands generating tetragonal geometry. The products **2a-4a** and **2b-4b** are all brown crystalline solids obtained at room temperature by stirring a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with the N_4S ligands in

TABLE-1
SUMMARY OF X-RAY CRYSTALLOGRAPHIC DATA

	Compound 1b	Compound 2a	Compound 4a	Compound 5
Composition	$\text{C}_{42}\text{H}_{45}\text{BCuN}_6\text{S}_2$	$\text{C}_{18}\text{H}_{29}\text{ClCuN}_4\text{O}_5\text{S}_2$	$\text{C}_{44}\text{H}_{53}\text{BCuN}_4\text{OS}_2$	$\text{C}_{16}\text{H}_{25}\text{ClCuN}_4\text{O}_4\text{S}_2$
Formula wt	772.31	544.57	792.4	500.5
Space-group	$P2_1$	$P-1$	$P2_1/n$	$P-1$
a (Å)	9.9876(6)	9.3640(13)	9.263(2)	7.0613(10)
b (Å)	29.3261(19)	10.5392(8)	15.030(3)	9.6302(7)
c (Å)	13.1924(13)	12.1567(18)	29.464(5)	15.4917(15)
α (°)	90	84.651(10)	90	101.91(1)
β (°)	92.897(7)	76.137(12)	90.24(2)	90.05(1)
γ (°)	90	85.319(9)	90	92.31(1)
V (Å) ³	3859.1(5)	1157.5(3)	4102(2)	1029.9(3)
Z	4	2	4	2
d_{calc} , (g cm ⁻³)	1.329	1.562	1.283	1.614
Temp. (°C)	20	22	22	23
λ (Å)	0.71073	0.71073	0.71073	0.71073
μ (cm ⁻¹)	7.13	12.8	6.7	14.2
R^a	0.0557	0.045	0.088	0.035
R_w^b	0.1552	0.053	0.071	0.040

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

alcohols as solvent. This is unlike the corresponding Ni(II) complexes [2] for which more drastic reaction conditions are needed in higher alcohol solvents. Compounds **2a-4a** and **2b-4b** are all mononuclear square-planar copper(II) complexes with N₃S chromophore and a pendant arm that accommodates the alkoxy group provided by the R'OH solvent (R' = Me, Et and *n*-Pr) (**Scheme-I**).

When complex **2a** (or **2b**) is refluxed in acetonitrile for about 3 h in the presence of excess 3,5-dimethylpyrazole (or pyrazole), the initial brown colour of solution is changed to green, leading to the isolation of green product **1a** (or **1b**) formed by a simple condensation type of reaction (**Scheme-I**). Identity of the product was established from their overlapping IR spectra and elemental analyses. The pentacoordinated compounds once formed are incapable of undergoing further alcoholysis reaction even under refluxing condition. That establishes the thermodynamic stability of complexes **1a** and **1b** over the alcoholysis products **2a-4a** and **2b-4b**, which are only formed by a kinetically controlled pathway in alcohol.

When hydrated copper sulfate is used as the metal ion precursor, the reaction with Hmmpcd in CH₃CN/CH₂Cl₂ solvent mixture at room temperature takes a new course and the product obtained is yet another brown crystalline solid (**5**) with N₃S chromophore but this time, formed by the cleavage of different C–N bond of the coordinated ligand (**Scheme-I**). Unlike the alcoholysis reaction, in which the bond cleavage takes place at the C(17)–N(5) bond (**Scheme-I**) involving the methylene carbon and a pyrazolyl nitrogen atom, the bond rupture during the formation of compound **5** occurs at the C(17)–N(2) bond involving the methylene carbon and the tertiary nitrogen atom. We are at this stage not quite confident to comment on the mechanisms of these C–N bond cleavage reactions.

All the complexes are air stable solids with green (**1a**, **1b**) or intense brown colour (**2a-4a**, **2b-4b** & **5**) and have varying degrees of solubilities in common organic solvents. In solutions, however, decompositions take place only on prolonged standing in the air. Use of dry and freshly distilled solvents, thoroughly purged with purified dinitrogen can check such decomposition.

Infrared spectra of the complexes have several prominent features characteristic of the coordinated N₄S ligand framework as noted earlier [1]. Important among these are due to $\nu(\text{C–N})$ /pyrazole ring and $\nu(\text{C–N} + \text{C–C})$ /cyclopentene moiety appearing at about 1550 and 1460 cm^{–1} region. Compound **5** also has a medium intensity band at 3210 cm^{–1} attributable to $\nu(\text{N–H})$ vibrations, confirming the removal of a CH₂(Me₂pz) arm from the coordinated Hmmpcd. Two strong sharp bands appearing about 1100 and 625 cm^{–1} are due to ionic perchlorate [21] and those at about 710 and 740 cm^{–1} belonged to $\nu(\text{BPh}_4^-)$.

Crystal and molecular structure: The asymmetric unit of compound **1b** contains two independent molecules one with a square pyramidal ($\tau = 0.24$) structure while the other with a TBP ($\tau = 0.62$) geometry. Figs. 1 and 2 display the ORTEP views of these independent molecules. Selected bond lengths and bond angles are given in Table-2. The Cu–N(1), Cu–S(1), Cu–N(2) distances in the two molecules are nearly identical: Cu1–N1A, 1.933 Å (Cu2–N1B, 1.927 Å); Cu1–S1A, 2.227 Å (2.234 Å); Cu1–N2A, 2.147 Å (2.138 Å) where Cu1 and Cu2

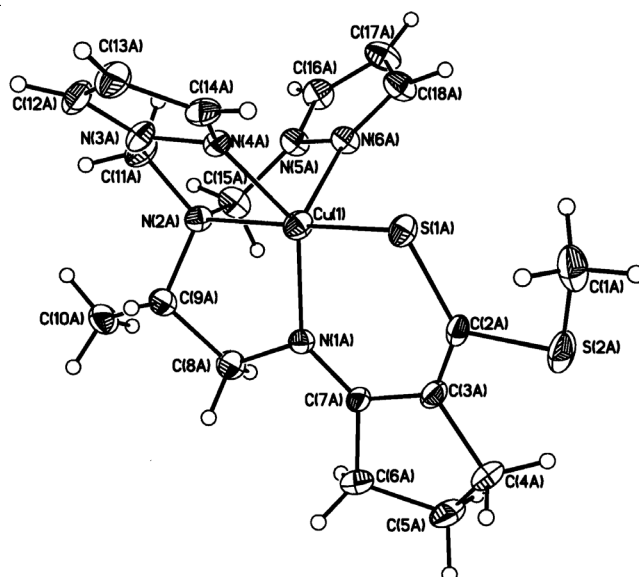


Fig. 1. ORTEP view of one of the two independent molecules of compound **1b** with TBP geometry

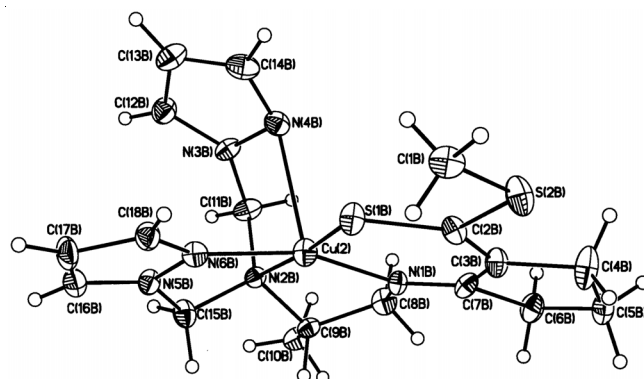


Fig. 2. ORTEP view of the structure of second independent molecule of compound **1b** with square planar geometry

TABLE-2
SELECTED BOND DISTANCES (Å) AND
ANGLES (°) OF COMPOUND **1b**

	Compound 1b (SP)	Compound 1b (TBP)
Cu–S(1)	2.234(2)	2.227(3)
Cu–N(1)	1.927(7)	1.933(7)
Cu–N(2)	2.138(7)	2.147(7)
Cu–N(4)	2.538	2.205(8)
Cu–N(6)	1.963(8)	2.248(8)
S(1)–Cu–N(1)	99.0(2)	98.2(2)
S(1)–Cu–N(2)	174.9(2)	175.6(2)
S(1)–Cu–N(4)	99.5	94.7(2)
S(1)–Cu–N(6)	94.0(2)	106.6(2)
N(1)–Cu–N(2)	86.1(3)	83.5(3)
N(1)–Cu–N(4)	106.2	138.2(3)
N(1)–Cu–N(6)	160.4(3)	112.8(3)
N(2)–Cu–N(4)	78.4	81.4(3)
N(2)–Cu–N(6)	81.2(3)	76.3(3)
N(4)–Cu–N(6)	86.0	101.0(3)

SP = square-pyramidal, TBP = trigonal bipyramid

represent the copper sites in TBP and square pyramidal molecules, respectively. The remaining pair of Cu–N distances, both due to the flexible pyrazolyl arms of ligands, show interesting variations as we go from one structure to the other.

Thus, the distance due to N(4) nitrogen which occupies an axial position in the square pyramidal structure (Cu2-N4B, 2.538 Å) is elongated by 0.513 Å compared to the corresponding distance (Cu1-N4A, 2.025(8) Å) in the TBP structure in which the N4 atom is in a basal position (Fig. 1). The second pyrazolyl nitrogen atom N6 which occupies a basal position in both the molecules, the Cu1-N6A distance (2.248(8) Å) is longer by 0.285 Å in the TBP structure compared to the corresponding distance (Cu2-N6B, 1.963(8) Å) in the square pyramidal one. Thus a remarkable flexibility in the ligand backbone due to the presence of a pair of pyrazolyl arms, has made it possible for the ligand L_1^- to adopt two distinct pentacoordinating geometries around copper in complex **1b**.

X-ray crystallographic analyses of the complexes **2a**, **4a** and **5** have enabled us to provide confirmatory evidences in favour of the ligand breakdown processes as described in **Scheme-I**. Thus in the complexes **2a** and **4a**, one of the pyrazolyl arms of the ligand Hmmpcd is modified by the presence of an alkoxy group provided by the solvent, while in compound **5**, a complete detachment of a $\text{CH}_2\text{Me}_2\text{pz}$ arm is observed. The products obtained have square planar geometry involving N_3S chromophore with varying degrees of tetrahedral distortions.

Fig. 3 displays the thermal ellipsoid plots for these complexes. Their selected metric parameters are given in Table-3. Compounds **2a** and **5** crystallize in triclinic space group $P-1$ with two molecules per unit cell, while compound **4a** has the monoclinic space group $P2_1/n$ with four molecules accommodated in the unit cell. The basic structural features are almost identical in these compounds. The S(1), N(1), N(2) and N(3) atoms of the modified ligand forms define the square planes around the Cu centers. The dihedral angles between the planes comprising N1-Cu-S1 and N2-Cu-N3 atoms show appreciable change from 8.8° (**5**) to 18.0° (**4a**) via 10.9° (**2a**) with the increase in steric bulk of the appended arm associated with the N2 atom. The Cu-N distances in these molecules are disparate with Cu-N2 bonds lying *trans* to Cu-S1 direction having the largest distances (2.024(3)-2.108(3) Å). The Cu-N1 bond lengths (1.935(3)-1.945(2) Å) on the other hand, are the least among these which is as expected considering N1 being the site of deprotonation of the ligands. The Cu-S distances in these compounds (2.207(1)-2.218(2) Å) are close to the range 2.174(4)-2.242(1) Å reported for the Cu(II)-thiolate distances in

biologically relevant molecules [22,23]. Also the C2-S1 bond lengths are in the range 1.711(4)-1.714(3) Å, giving indication that the S1 atoms in these molecules are an electronic analogous of thiolate functionality [24,25], a feature already documented for analogous ligand molecules with dithiocarboxylate functionality [1,26]. The *trans* angle N1-Cu-N3 in these molecules (162.4(1)-163.45(9)°) show maximum departure from linearity due to the restricted bite angle of the ligands. Sum of the *cis* angles around copper is close to 360° in all cases, giving evidence in favour of metal atom being seated right onto the basal plane.

TABLE-3
SELECTED BOND DISTANCES (Å) AND
ANGLES (°) FOR COMPOUNDS **2a**, **4a** AND **5**

	Compd. 2a	Compd. 4a	Compd. 5
Cu-S(1)	2.207(1)	2.218(2)	2.217(1)
Cu-N(1)	1.935(3)	1.941(6)	1.945(2)
Cu-N(2)	2.108(3)	2.111(5)	2.024(3)
Cu-N(3)	2.002(3)	2.004(6)	2.012(2)
C(2)-S(1)	1.711(4)	1.713(7)	1.714(3)
S(1)-Cu-N(1)	98.16(9)	97.8(2)	97.74(7)
S(1)-Cu-N(2)	173.30(9)	177.1(2)	173.9(1)
S(1)-Cu-N(3)	96.57(9)	96.6(2)	97.53(6)
N(1)-Cu-N(2)	85.0(1)	85.1(2)	84.03(9)
N(1)-Cu-N(3)	162.4(1)	162.5(3)	163.45(9)
N(2)-Cu-N(3)	81.3(1)	80.5(2)	81.44(9)

Electronic spectroscopy: In the visible region, spectrum of compound **1b** in acetonitrile contains a single *d-d* band at 574 nm (ϵ , 210 mol⁻¹ cm²) which is diagnostic of a distorted square pyramidal structure [27,28]. Thus contrary to the solid state structure as revealed from X-ray analysis, compound **1b** in solution exists predominantly in the square pyramidal form. Spectral features of the remaining compounds (**2a-5**) are grossly identical, each involving a couple of *d-d* bands. A representative spectrum (**2b**) displayed in Fig. 4, which reveals bands at 794 (ϵ , 50 mol⁻¹ cm²) and 514 nm (ϵ , 290 mol⁻¹ cm²) corresponding to transitions $d_{z^2} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, respectively as expected for square planar complexes [29]. The more intense band (ϵ , 6000-8000 mol⁻¹ cm²) appearing in the near-UV region (390-380 nm) for all these complexes is indicative of a charge transfer transition, probably originating from S(π) \rightarrow Cu(II) charge transfer [30]. All the remaining bands in the UV region are due ligand internal transitions.

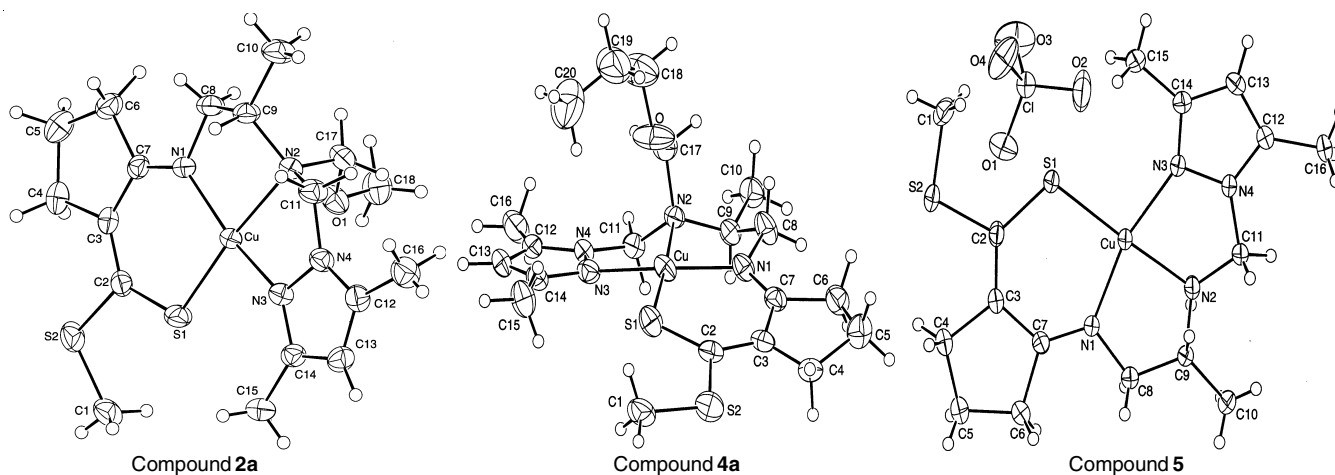


Fig. 3. ORTEP plot and atom numbering scheme for compounds **2a**, **4a** and **5**

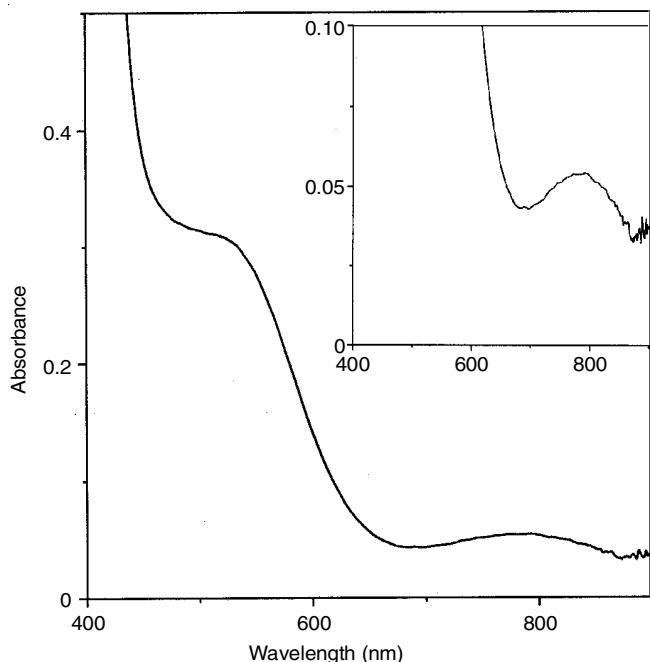


Fig. 4. Electronic absorption spectrum of compound **2b** in acetonitrile. The inset shows the *d-d* band at 794 nm

Magnetic susceptibility and EPR spectra: The magnetic moments and EPR parameters of the complexes are summarized in Table-4. At room temperature, the powdered polycrystalline samples have spin-only moments lying within the range 1.68–1.78 B.M., consistent with an $S = 1/2$ paramagnet and indicating that the orbital angular momentum here is effectively quenched by the low symmetry ligand field surrounding the central metal ion.

X-band EPR spectra of the complexes were recorded at room temperature (298 K) as well as in the frozen state (77 K) in acetonitrile/toluene (1:4 v/v) medium. At room temperature, EPR spectra of all the complexes in solution reveal well resolved four-line patterns, characteristic of an unpaired electron being coupled to copper nuclear spin ($^{63,65}\text{Cu}$, $I = 3/2$). A representative spectrum (compound **1b**) with $\langle g \rangle = 2.085$ and $\langle A \rangle = 69.4 \times 10^{-4} \text{ cm}^{-1}$ is shown in Fig. 5a.

In the frozen glass (77 K), the spectrum of compound **1b** (Fig. 5b) shows axial anisotropy with rhombical distortions [31]. The observed parameters g_{\parallel} (2.16) $>$ g_{\perp} (2.05) with $A_{\parallel} = 182.3 \times 10^{-4} \text{ cm}^{-1}$ are diagnostic of a pseudotetragonal site

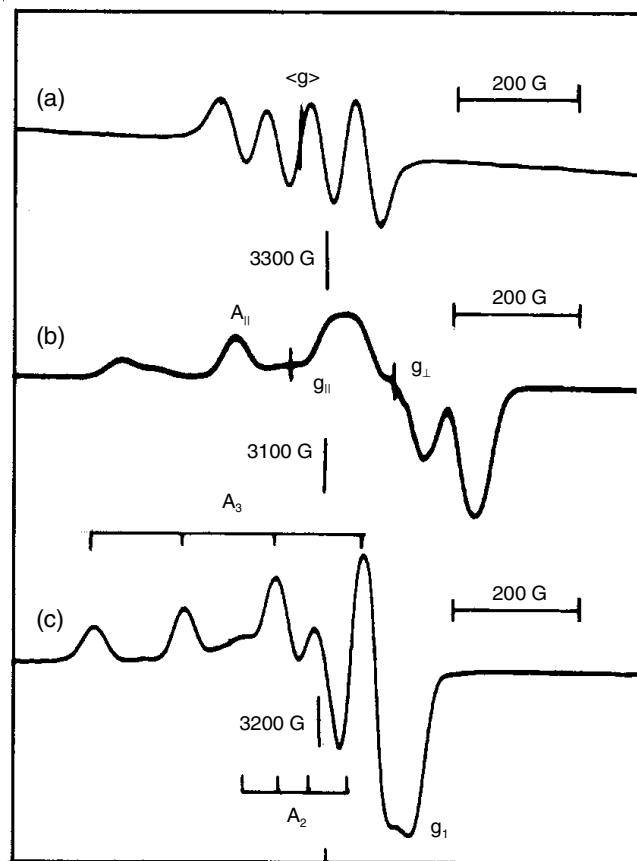


Fig. 5. X-band EPR spectra of compound **1b** in acetonitrile/toluene (1:4 v/v) solution: (a) at 298 K (b) at 77 K and (c) as polycrystalline powder at 77 K doped (3.7%) into $[\text{ZnL}_1]\text{ClO}_4$ host

symmetry for the Cu(II) center in compound **1b** [27,32]. A further close look at this spectrum reveals some additional signals in the lower field region and an overall broad feature which appear to suggest a minor contribution from the TBP structure of compound **1b** as also indicated by the electronic spectral studies (*vide supra*). When compound **1b** is doped into its zinc(II) counterpart ($[\text{ZnL}_1](\text{ClO}_4)$ which has a TBP structure [33], the EPR spectrum of doped polycrystalline sample (containing 3.7 mol % of Cu^{2+}) shows a typical rhombic pattern (Fig. 5c) with reasonably well resolved hyperfine structures for the higher g components: $g_3 = 2.16$ ($A_3 = 142.9 \times 10^{-4} \text{ cm}^{-1}$); $g_2 = 2.09$ ($A_2 = 52.04 \times 10^{-4} \text{ cm}^{-1}$) together with the unresolved

TABLE-4
MAGNETIC MOMENTS AND EPR DATA FOR THE COPPER(II) COMPLEXES

Complex	μ_{eff}^a/μ_B	$\langle g \rangle^b$	$10^4 \langle A \rangle^b (\text{cm}^{-1})$	$g_{\parallel}^c (g_3)$	$g_{\perp}^d (g_1, g_2)$	$10^4 A_{\parallel}^c (10^4 A_3) (\text{cm}^{-1})$	$10^4 A_{\perp}^d (10^4 A_2) (\text{cm}^{-1})$
1b	1.67	2.085	69.43	2.160 2.16 ^c	2.050 2.09 ^c , 1.979 ^c	182.3 142.9 ^c	12.99 52.04 ^c
2a	1.68	2.079	84.86	2.156	2.040	188.0	33.29
2b	1.68	2.076	86.38	2.147	2.041	190.4	34.37
3a	1.76	2.079	84.67	2.154	2.042	189.6	32.20
3b	1.68	2.075	85.62	2.150	2.038	190.3	33.28
4a	1.75	2.080	84.98	2.158	2.041	189.9	32.52
5	1.78	2.077	84.68	2.158	2.037	194.3	29.87

^aMeasured at room temperature with powdered polycrystalline samples. ^bFrom room temperature spectra in acetonitrile/toluene (1:4 v/v) solution.

^cFrom frozen solution (77 K) spectra. ^dCalculated from the equation $\langle g \rangle = 1/3[g_{\parallel} + 2g_{\perp}]$ and $\langle A \rangle = 1/3[A_{\parallel} + 2A_{\perp}]$. ^eFrom polycrystalline doped (3.7 % Cu/Zn) sample.

lowest g component ($g_{\parallel} = 1.98$). Almost a similar rhombic pattern has been reported for 1 % copper(II)-doped [Zn(dien)(bipy)]-(NO₃)₂ complex [34] in which the guest and the host molecules are isostructural, both having TBP structures. The results thus provide strong evidence in favour of ligand HL₁ being flexible enough to adopt both TBP and square pyramidal geometry around copper as confirmed by the results of X-ray crystallography.

EPR spectra of square planar complexes (**2a-5**) are nearly identical. In the frozen glass (acetonitrile/toluene, 1:4 v/v, 77 K), the spectrum of compound **3b** is shown in Fig. 6 as a representative which reveals an axial anisotropy and is only sufficiently resolved to extract the parameters $g_{\parallel} = 2.15$ and $A_{\parallel} = 190.3 \times 10^{-4} \text{ cm}^{-1}$. Almost a similar spectral pattern has been reported recently for Cu(II)-peptide complexes with comparable tetrahedrally distorted square planar geometry [35]. These parameters along with the room temperature data ($\langle g \rangle$ and $\langle A \rangle$) are used to calculate the perpendicular components of g -anisotropies using appropriate equations (Table-4). The observed trend $g_{\parallel} > g_{\perp} > 2.0$ is indicative of a $d_{x^2-y^2}$ orbital ground state in agreement with the square planar environment of copper [36]

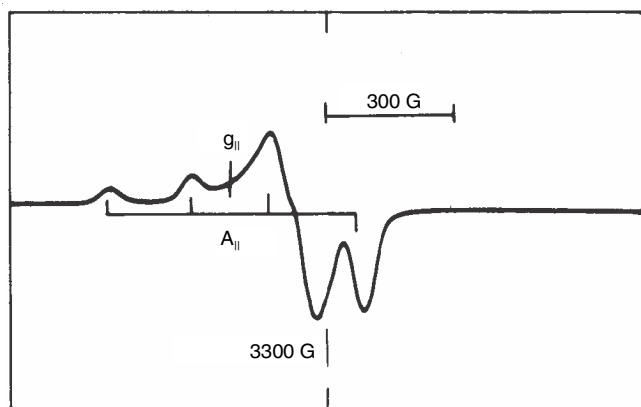


Fig. 6. X-band EPR spectrum at 77 K of compound **3b** in acetonitrile/toluene (1:4 v/v) solution

Electrochemistry: The redox activity of the complexes has been studied by cyclic voltammetry in acetonitrile using a platinum working electrode and the results are summarized in Table-5. All the complexes have nearly identical voltammetric features.

TABLE-5
ELECTROCHEMICAL DATA^a FOR THE
MONONUCLEAR Cu(II) COMPLEXES

Complex	Cu(II)/Cu(I)		Cu(II)/Cu(III)	
	$E_{1/2}^b$ (mV)	ΔE_p^c (mV)	i_{pc}/i_{pa}	E_{pa}^b (mV)
1b	-256	67	0.95	+1082
2a	-182	81	1.00	+1124
2b	-200	75	0.92	+1148
3a	-197	70	1.00	+1118
3b	-213	81	0.90	+1151
4a	-200	72	0.83	+1137
4b	-225	75	0.88	+1155
5	-341	66	0.92	+1095

^aSolvent: acetonitrile; Supporting electrolyte: TBAP (0.1 M); Solute concentration: about 10^{-3} M; Working electrode: platinum. ^bPotentials are vs. Ag/AgCl and estimated by cyclic voltammetry at a scan rate of 100 mV s^{-1} . $E_{1/2} = 0.5 (E_{pc} + E_{pa})$. ^c $\Delta E_p = E_{pc} - E_{pa}$

A representative voltammogram for compound **3b** is shown in Fig. 7 in the potential range -0.6 to $+1.6 \text{ V}$ vs. Ag/AgCl reference. The compound displays a nearly reversible reduction (ΔE_p , 81 mV; i_{pc}/i_{pa} , 0.90 at 100 mV s^{-1}) at $E_{1/2} = -0.21 \text{ V}$ and an irreversible oxidation process at $E_{pa} = +1.15 \text{ V}$. Comparison with ferrocenium/ferrocene (Fc⁺/Fc) couple (ΔE_p , 70 mV; i_{pc}/i_{pa} , 1.0 at 100 mV s^{-1}) as an internal standard [8] suggests these processes to be monoelectronic [37] as represented by eqn. 1 involving three copper oxidation states. Exhaustive electrolyses past the reduction process (E_w set at -0.25 V) have confirmed the monoelectron ($n = 1.0 \pm 0.15$) stoichiometry for this couple, while for the oxidation process, results are inconclusive due to constant coulomb counts. Nevertheless, the monoelectronic nature of the later process has been established by normal pulse voltammetric (NPV) experiments which showed identical current heights for both the electron-transfer processes as displayed in Fig. 8.

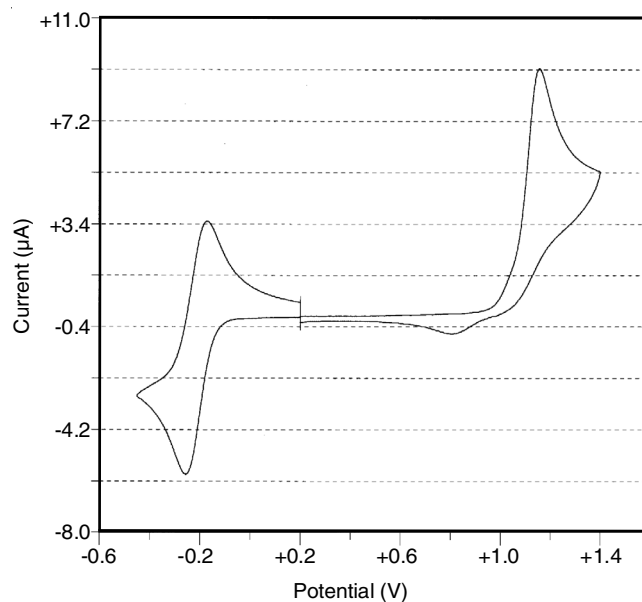
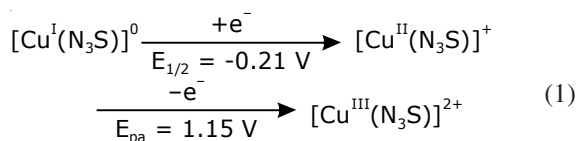


Fig. 7. Cyclic voltammogram of compound **3b** in 0.1 M TBAP/CH₃CN at a platinum electrode (100 mV s^{-1} scan rate)

A careful scrutiny of Table-5 reveals some interesting trends in the redox potential values of Cu(II)/Cu(I) couples of these complexes. Although compounds **2a-5**, all have identical donor atoms (N₃S) set around the Cu(II) center, they show considerable negative shift (by about 160 mV) in potential as one goes from **2a** to **5**. Compound **5** with almost a planar geometry (dihedral angle 8.8°(5)) is more difficult to reduce ($E_{1/2} = -0.34 \text{ V}$) than its counterparts **2a-4a** and **2b-4b** ($E_{1/2}$ range -0.18 to -0.22 V) with geometries distorted more towards tetrahedral. This is however, not unexpected, considering the preference of copper(I) for tetrahedral geometry [38,39]. Again in the series **2a-4a**, the Cu(II)/Cu(I) reduction becomes more difficult ($E_{1/2}$ more negative) in going from **2a** to **4a** when the geometry around copper becomes more towards tetrahedral. This is contrary to the expectation mentioned earlier that copper(II) in tetrahedral

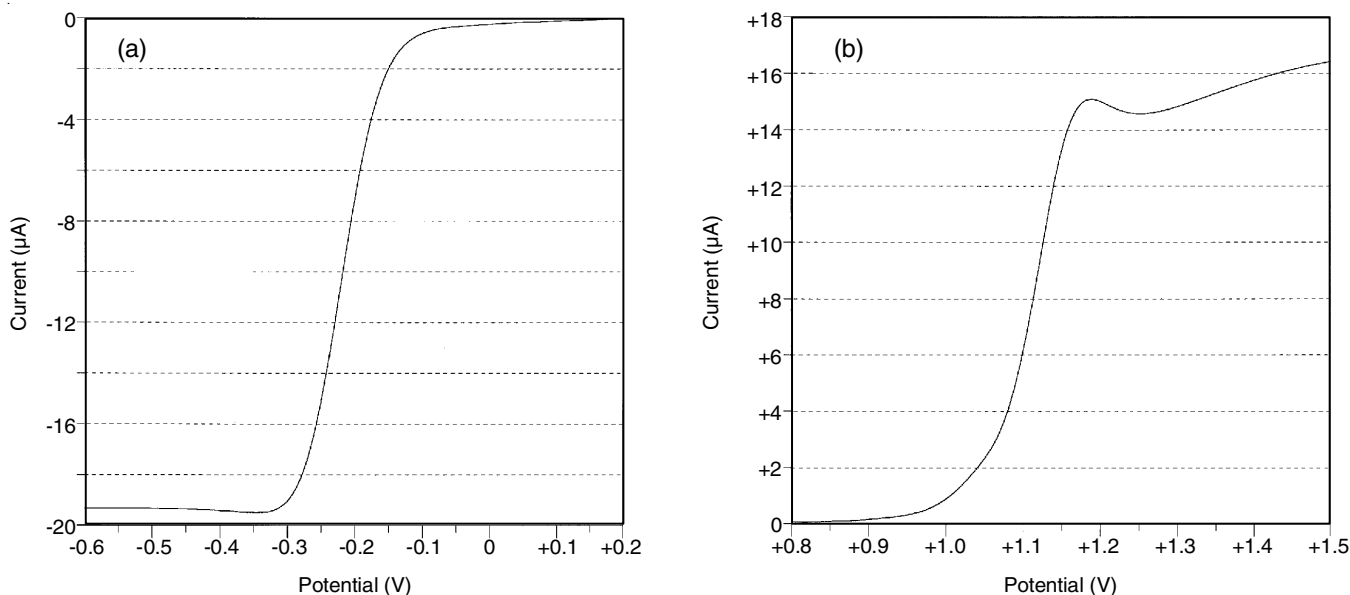


Fig. 8. Normal pulse voltammogram of compound **3b**: (a) for the reduction (Cu(II)/Cu(I)) process (E_w , -0.22 V); and (b) for the oxidation (Cu(II)/Cu(III)) process (E_w , 1.11 V); working electrode: platinum; scan rate: 10 mV s^{-1} ; solvent: acetonitrile

geometry favours the Cu(II)/Cu(I) reduction [38,39]. This unusual trend is due to the weak coordination of alkoxy group to the Cu(II) center in solution which makes the metal center electronically richer in going from **2a** to **4a** with the increase in donor strength of alkoxy group.

Conclusion

Metal induced activation of carbon-nitrogen multiple bond is well documented [40]. Not much is however, known about similar activation of C–N single bond except a few reports [41–43] involving oxidative dealkylation of amines. Results reported in this segment describe the copper(II) induced activation of an otherwise unreactive C–N single bond of pentacoordinating N₄S ligands in alcohols as solvent. The products (**2a–4b**) obtained using copper(II) perchlorate hexahydrate as the metal ion precursor are all tetrahedrally distorted four coordinated planar Cu(II) complexes with a pendant arm that accommodates the alkoxy group provided by the solvents. This distortion towards tetrahedral geometry becomes more prominent with bulky alkoxy group. Compounds **2a–4b** can take up pyrazolyl moiety to generate the pentacoordinated product **1b** by a condensation reaction in acetonitrile. Once formed, compound **1b** does not undergo further alcoholysis even after prolonged reflux in alcohol. With copper(II) sulfate as the metal ion precursor, the product is a square planar compound (**5**), obtained by the complete detachment of a pyrazolyl arm from the ligand framework, but this time from a different C–N bond cleavage. All these copper(II) complexes undergo a reversible Cu(II)/Cu(I) reduction, the $E_{1/2}$ values for which follow a trend that provides evidence in favor of alkoxy group coordination to the Cu(II) center in solution.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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