

Synthesis and spectral characterization of some mixed ligand complexes of Cu^{II} containing NNS and NN/NO/OO chelating ligands

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Abstract : Cu(NN'S)Cl₂ (NN'S : 1-alkyl-2-{*o*-thioalkyl}phenylazo}imidazole) reacts with some bidentate chelating ligands like, N,N (2,2'-bipyridine, 1,10-phenanthroline), N,O (oxine, picolinic acid) and O,O (salicylic acid, oxalic acid) to prepare mixed ligand complexes, [Cu(NN'S)(N,N)](ClO₄)₂, [Cu(NN'S)(N,O)](ClO₄) and [Cu(NN'S)(O,O)]. The complexes are characterized by the elemental analysis, Mass, molar conductance measurements, magnetic moment data. Penta-coordinated distorted square pyramidal structure is supported by spectral studies (FT-IR, UV-Vis). The cyclic voltammetric measurements and EPR spectral studies assign Cu^{II} redox state. DFT and TD-DFT computation have been carried out of representative complex to explain spectral and redox properties.

Keywords : Copper(II)-thioalkyl-arylazoimidazole, mixed ligand complexes, spectra, electrochemistry, magnetic data, DFT.

Introduction

Imidazole is a ubiquitous ligand in chemical and biological molecules^{1,2}. Imidazolyl motif having S-donor centre in a chelated environment with additional N and/or O donors in a molecule has become an interesting ligand in the development of coordination chemistry of transition metal complexes^{3,4}. Thioether donors destabilize +2 redox state of copper, nickel elevating the M(II) → M(I) redox potentials⁵ and are useful in hydrogenase and CO oxidoreductase enzymes. We have designed a ligand containing imidazolyl-N and thioether-S donor centres along with an azo-N donating centre in 1-alkyl-2-{*o*-thioalkyl}phenylazo}imidazole (SRaaiNR'), a potential tridentate imidazolyl-N, azo-N and thioether-S ligand^{6,7}. They may act as monodentate imidazolyl-N⁸; bidentate imidazolyl-N, azo-N chelators⁷. In this article we describe the ternary complexes of copper(II) with SRaaiNR' and group of N,N (2,2'-bipyridine (bpy), 1,10-phenanthroline (phen)); N,O (oxine, picolinic acid (pic)) and O,O-ligands (salicylic acid (salc), oxalic acid (ox)). The mixed ligand complexes are characterized by spectroscopic, magnetic and electrochemical techniques. DFT computation of optimized geometry has been used to explain the electronic and redox properties of the complexes.

Experimental

Materials and methods :

CuCl₂·2H₂O, 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 2-picolinic acid (pic), salicylic acid (H₂salc), oxalic acid (H₂ox), picolinic acid (Hpic), 8-hydroxyquinoline (Hoxine), *o*-(amino)thiophenol, methyl iodide (MeI), ethyl iodide (EtI) were purchased from E. Merck, India. Cu(NN'S)Cl₂ complexes were prepared from CuCl₂·2H₂O⁹. Solvents were used after drying. All experiments were carried out under N₂ atmosphere. The syntheses of the ligands were carried out following common procedure⁹ of coupling *o*-(thioalkyl)phenyldiazonium ion (obtained by diazotization of *o*-(thioalkyl)aniline) with imidazole at pH 7 followed by N(1)-alkylation using alkyl iodide in presence of NaH in dry THF under dry and inert condition.

Microanalyses (C, H, N) were determined using Perkin-Elmer 2400 CHNO/S elemental analyzer. Spectroscopic measurements were carried out using the following instruments : UV-Vis spectra, Perkin-Elmer UV-Vis Spectrometer model Lambda 25; IR spectra (KBr disk, 4000–400 cm⁻¹), Perkin-Elmer FT-IR Spectrometer model Spectrum RX1. Room temperature magnetic moment was measured using Magnetic Susceptibility Balance, Sherwood

Scientific, Cambridge, UK. Molar conductance (Λ_M) was measured in a Systronics conductivity meter 304 model using *ca.* 10^{-3} M solutions in MeOH. Electrochemical measurements were performed using computer-controlled CH Instruments with Pt-disk electrodes. All measurements were carried out under nitrogen environment at 300 K with reference to Ag/AgCl in acetonitrile using $[\text{nBu}_4\text{N}][\text{ClO}_4]$ as supporting electrolyte. The reported potentials were uncorrected for junction potential. EPR spectra were recorded from 0 to 10000 Gauss at 300 K with an X-band (9.15 GHz) Varian E-9 spectrometer.

Synthesis of complexes :

$[\text{Cu}(\text{SMeaiNMe})(\text{bpy})](\text{ClO}_4)_2$ (**1a**) :

To MeOH (15 mL) solution of $\text{Cu}(\text{SMeaiNMe})\text{Cl}_2$ (0.4 g or 1.09 mmol) 2,2'-bipyridine (bpy) (0.17 g or 1.09 mmol) was added and stirred for 2 h in air. Aqueous solution (2 mL) of NaClO_4 (saturated) was added and dark brown colored crystalline product was found after slow evaporation of the reaction mixture. The product was then washed with cold water followed by methanol-water (1 : 1, v/v) and dried in vacuum over CaCl_2 . Methanol solution of the product was slowly evaporated to allow for crystallization. Yield was 60% with reference to parent complex, $\text{Cu}(\text{SMeaiNMe})\text{Cl}_2$.

All the complexes of the series, **1-4**, were prepared by the same procedure. The yield varied from 50–65%.

Microanalytical data : Anal. (Calcd. %) for $[\text{Cu}(\text{SMeaiNMe})(\text{bpy})](\text{ClO}_4)_2$ (**1a**) $\text{C}_{21}\text{H}_{20}\text{N}_6\text{O}_8\text{Cl}_2\text{SCu}$: C, 38.70 (38.75); H, 3.03 (3.09); N, 12.96 (12.92); Mass (*m/z*), 650.85. For $[\text{Cu}(\text{SEtaaiNEt})(\text{bpy})](\text{ClO}_4)_2$ (**1b**) $\text{C}_{23}\text{H}_{24}\text{N}_6\text{O}_8\text{Cl}_2\text{SCu}$: C, 40.75 (40.69); H, 3.45 (3.56); N, 12.46 (12.38); Mass (*m/z*), 678.90. For $[\text{Cu}(\text{SMeaiNMe})(\text{phen})](\text{ClO}_4)_2$ (**2a**) $\text{C}_{23}\text{H}_{20}\text{N}_6\text{O}_8\text{Cl}_2\text{SCu}$: C, 40.82 (40.93); H, 3.08 (2.99); N, 12.44 (12.46); Mass (*m/z*), 674.87. For $[\text{Cu}(\text{SEtaaiNEt})(\text{phen})](\text{ClO}_4)_2$ (**2b**) $\text{C}_{25}\text{H}_{24}\text{N}_6\text{O}_8\text{Cl}_2\text{SCu}$: C, 42.60 (42.71); H, 3.33 (3.44); N, 11.90 (11.96); Mass (*m/z*), 702.92. For $[\text{Cu}(\text{SMeaiNMe})(\text{pic})](\text{ClO}_4)$ (**3a**) $\text{C}_{17}\text{H}_{16}\text{N}_5\text{O}_4\text{ClSCu}$: C, 39.30 (39.39); H, 3.14 (3.10); N, 13.40 (13.49); Mass (*m/z*), 517.18. For $[\text{Cu}(\text{SEtaaiNEt})(\text{pic})](\text{ClO}_4)$ (**3b**) $\text{C}_{19}\text{H}_{20}\text{N}_5\text{O}_4\text{ClSCu}$: C, 41.75 (41.79); H, 3.60 (3.69); N, 12.73 (12.80); Mass (*m/z*), 545.17. For $[\text{Cu}(\text{SMeaiNMe})(\text{oxine})](\text{ClO}_4)$ (**4a**) $\text{C}_{20}\text{H}_{18}\text{N}_5\text{O}_5\text{ClSCu}$: C, 44.48 (44.50); H, 3.30 (3.29); N, 12.98 (13.03); Mass

(*m/z*), 539.12. For $[\text{Cu}(\text{SEtaaiNEt})(\text{oxine})](\text{ClO}_4)$ (**4b**) $\text{C}_{22}\text{H}_{22}\text{N}_5\text{O}_5\text{ClSCu}$: C, 46.61 (46.59); H, 3.84 (3.90); N, 12.20 (12.30); Mass (*m/z*), 567.18. For $[\text{Cu}(\text{SMeaiNMe})(\text{ox})](\text{5a})$ $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_4\text{SCu}$: C, 40.68 (40.70); H, 3.09 (3.10); N, 14.59 (14.60); Mass (*m/z*), 383.05. For $[\text{Cu}(\text{SEtaaiNEt})(\text{ox})](\text{5b})$ $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_4\text{SCu}$: C, 43.67 (43.69); H, 3.89 (3.90); N, 13.58 (13.60); Mass (*m/z*), 411.07. For $[\text{Cu}(\text{SMeaiNMe})(\text{salc})](\text{6a})$ $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_3\text{SCu}$: C, 50.02 (50.06); H, 3.90 (3.91); N, 12.97 (12.98); Mass (*m/z*), 431.07. For $[\text{Cu}(\text{SEtaaiNEt})(\text{salc})](\text{6b})$ $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_3\text{SCu}$: C, 52.20 (52.23); H, 4.33 (4.35); N, 12.15 (12.19); Mass (*m/z*), 459.18.

Computational study :

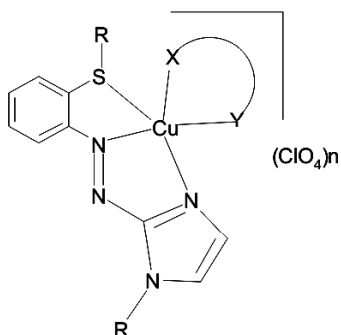
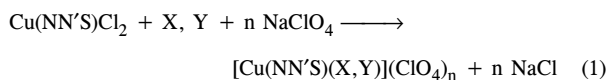
Two molecules, $[\text{Cu}(\text{SMeaiNMe})(\text{bpy})](\text{ClO}_4)_2$ (**1a**) and $[\text{Cu}(\text{SMeaiNMe})(\text{oxine})](\text{ClO}_4)$ (**4a**) were used to optimize their geometries and the calculations of molecular functions were executed by using GAUSSIAN-03 program package¹⁰. Hybrid DFT-B3LYP functional was used throughout the calculations¹¹. For C, H, N and O the 6-31G(d) basis set were assigned. Los Alamos effective core potential plus double zeta (LanL2DZ)¹² basis set along with the corresponding pseudo potential without any symmetry constrain for Cu and S were used. The vibrational frequency calculation was also performed for both the complexes to ensure that the optimized geometries represent the local minima and there are only positive Eigen values. To assign the low lying electronic transitions in the experimental spectra, TD-DFT calculations of the complexes were done. We computed the lowest 25 singlet-singlet transition in methanol using the conductor-like polarizable continuum model and results of the TD-DFT calculations was qualitatively very similar. Gauss Sum¹³ was used to calculate the fractional contributions of various groups to each molecular orbital.

Results and discussion

Synthesis and formulation of the complexes :

The $\text{Cu}(\text{NN}'\text{S})\text{Cl}_2$ are prepared by reported procedure⁹. Three different series of bidentate ligands (donor centres are abbreviated X,Y) such as N,N (2,2'-bipyridine (bpy), 1,10-phenanthroline (phen)); N,O (oxine, picolinic acid (pic)) and O,O (oxalic acid (ox), salicylic acid (salc)). To MeOH solution of $\text{Cu}(\text{NN}'\text{S})\text{Cl}_2$ bidentate ligand (X,Y) in the same solvent is added and stirred for 2 h in air.

Aqueous solution of NaClO_4 (saturated) is added and dark colored crystalline product (eq. (1)) is precipitated after slow evaporation of reaction mixture. The product was then recrystallised from methanol solution by slow evaporation.



$\text{X} = \text{Y} = \text{N}, \text{N}$ (bpy, **1**; phen, **2**) and $n = 2$; $\text{X} = \text{N}, \text{Y} = \text{O}$ (pic, **3**; oxine, **4**) and $n = 1$; $\text{X} = \text{Y} = \text{O}, \text{O}$ (ox, **5**; salc, **6**) and $n = 0$.

$[\text{Cu}(\text{SMeaaiNMe})(\text{bpy})](\text{ClO}_4)_2$ (**1a**); $[\text{Cu}(\text{SEtaaiNEt})(\text{bpy})](\text{ClO}_4)_2$ (**1b**); $[\text{Cu}(\text{SMeaaiNMe})(\text{phen})](\text{ClO}_4)_2$ (**2a**); $[\text{Cu}(\text{SEtaaiNEt})(\text{phen})](\text{ClO}_4)_2$ (**2b**); $[\text{Cu}(\text{SMeaaiNMe})(\text{pic})](\text{ClO}_4)$ (**3a**); $[\text{Cu}(\text{SEtaaiNEt})(\text{pic})](\text{ClO}_4)$ (**3b**); $[\text{Cu}(\text{SMeaaiNMe})(\text{oxine})](\text{ClO}_4)$ (**4a**); $[\text{Cu}(\text{SEtaaiNEt})(\text{oxine})](\text{ClO}_4)$ (**4b**); $[\text{Cu}(\text{SMeaaiNMe})(\text{ox})](\text{5a})$; $[\text{Cu}(\text{SEtaaiNEt})(\text{ox})](\text{5b})$; $[\text{Cu}(\text{SMeaaiNMe})(\text{salc})](\text{6a})$; $[\text{Cu}(\text{SEtaaiNEt})(\text{salc})](\text{6b})$.

Scheme 1. The complexes, $[\text{Cu}(\text{SRaaiNR}')(\text{X},\text{Y})]$, synthesized and characterized in this work.

The crystals those are isolated from synthetic mixture or separately by slow evaporation are not of good quality to diffract X-rays for structural analysis. So the characterization has been done by the elemental analysis, molar conductance measurements, magnetic moment data, spectral studies (FT-IR, UV-Vis, Mass), cyclic voltammetric measurements and EPR spectral studies. The complexes are soluble in methanol, ethanol, chloroform, dichloromethane and acetonitrile but insoluble in hexane, benzene, and toluene. The complexes **1** and **2** show 1 : 2 molar conductivity ($\Lambda_M = 160\text{--}170 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$ in MeOH) and the complexes **3** and **4** show 1 : 1 molar conductivity ($\Lambda_M = 90\text{--}100 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$ in MeOH) while the complexes **5** and **6** are non-conducting in methanol/acetonitrile solution. The bulk magnetic moment shows that the complexes are of one electron paramagnetism (1.8–2.0 B.M.) (Table 1).

The spectral studies :

Infrared spectra of the mixed ligand complexes, $[\text{Cu}(\text{SRaaiNR}')(\text{X},\text{Y})]^{n+}$, exhibit $\nu(\text{N}=\text{N})$ and $\nu(\text{C}=\text{N})$ at $1420\text{--}1430$ and $1575\text{--}1580 \text{cm}^{-1}$ respectively, and is red shifted by 10cm^{-1} compared to the results of free ligand. This supports coordination of azo-N and imine-N to Cu^{II} (Table 2). The coordination of the bidentate ligands are supported by additional peaks. In case of $[\text{Cu}(\text{SRaaiNR}')(\text{pic})]$ (**3**), $[\text{Cu}(\text{SRaaiNR}')(\text{salc})]$ (**6**), additional peaks are observed at $1640\text{--}1648 \text{cm}^{-1}$ which is assigned to $\nu(\text{C}=\text{O})$ of coordinated carboxylic group¹⁴. $[\text{Cu}(\text{SRaaiNR}')(\text{ox})]$ (**5**), derivatives also show high intense broad band at $1650\text{--}1660 \text{cm}^{-1}$ correspond to $\nu(\text{COO})$. The complexes with catechol and oxin ligands exhibit $\nu(\text{C}-\text{O})(\text{phenolic})$ at about 1100 to 1140cm^{-1} ¹⁴.

The electronic spectra of the mixed ligand complexes were collected in MeOH solution. The electronic spectra exhibit multiple high intense transitions ($\epsilon \sim 10^4 \text{M}^{-1} \text{cm}^{-1}$) in $500\text{--}240 \text{nm}$ along with a weak intensity band at $630\text{--}750 \text{nm}$ ($\epsilon \sim 200 \text{M}^{-1} \text{cm}^{-1}$). The spectra are compared with that of free ligand and $\text{Cu}(\text{NN}'\text{S})\text{Cl}_2$, under identical condition. Intra-ligand charge transferences $n\text{--}\pi^*$ and $\pi\text{--}\pi^*$ appear at $350\text{--}385$ and $240\text{--}280 \text{nm}$ respectively. Other transitions at $630\text{--}750$, $400\text{--}425$, $450\text{--}480 \text{nm}$ are new and only observed in the complexes and considerably shifted from that of starting complex, $\text{Cu}(\text{NN}'\text{S})\text{Cl}_2$ (Table 1, Fig. 1). Besides, the ligands thioalkylazoimidazoles possess a thioalkyl ($-\text{SR}$) reducing center. Copper(II) complexes containing coordinated $-\text{SR}$ group(s) exhibit strong S (thioether) $\longrightarrow \text{Cu}^{\text{II}}$ LMCT band. Copper(II)-azoheterocycles^{15–18} exhibit strong MLCT transition involving $d(\text{Cu}) \longrightarrow \pi^*(\text{arylazoheterocycle})$ because of efficient π -acidity of the ligands. On comparing with copper(II)-1-alkyl-2-(arylamino)imidazoles¹⁹, pyridylthioazophenolates²⁰ and other pyridylthioether^{21,22} based N,S donor ligands we may assign the transitions $450\text{--}480 \text{nm}$ as MLCT [$d(\text{Cu}) \longrightarrow \pi^*(\text{azoimidazole})$] and $400\text{--}425 \text{nm}$ LMCT (S $\longrightarrow \text{Cu}^{\text{II}}$) transitions MLCT transition. On comparing with spectral data of $\text{Cu}(\text{NN}'\text{S})\text{Cl}_2$ it is clear that the MLCT and LMCT bands have significantly influenced by the coligands⁹. Very weak absorption at $630\text{--}750 \text{nm}$ ($\epsilon \sim 200 \text{M}^{-1} \text{cm}^{-1}$) is undoubtedly a d-d transition²³.

Electrochemistry :

Cyclic voltammetry (CV) shows reductive response at

Table 1. UV-Vis spectral, cyclic voltammetric and magnetic moment data

Compds.	UV-Vis spectra ^a λ_{\max} (nm) [$10^{-3} \times \epsilon$ (dm ³ mol ⁻¹ cm ⁻¹)]	Cyclic voltammetric data ^c			μ (B.M.)
		E (V) (ΔE_p (mV))			
		Cu ^{II/I}	Cu ^{I/0}	Ligand reduction	
[Cu(SMeaaiNMe)(bpy)](ClO ₄) ₂ (1a)	684(0.05), 473(3.5), 413(6.8), 356(12.5), 242(14.3)	0.38 (150)	-0.28	-0.45(140) -1.14	1.92
[Cu(SETaaiNEt)(bpy)](ClO ₄) ₂ (1b)	685(0.12), 470(3.40), 394(14), 381(16), 248(9.7)	0.29 (150)	-0.24	-0.34(100) -1.08	1.87
[Cu(SMeaaiNMe)(phen)](ClO ₄) ₂ (2a)	692(0.05), 470(4.1), 423(6.1), 359(11.8), 295(10.6)	0.28 (150)	-0.29	-0.50(160) -1.34	1.88
[Cu(SETaaiNEt)(phen)](ClO ₄) ₂ (2b)	690(0.12), 470(4.5), 425(7.2), 359(12.0), 293(9.5)	0.28 (150)	-0.28	-0.52(160) -1.34	1.87
[Cu(SMeaaiNMe)(pic)](ClO ₄) (3a)	675(0.06), 459(2.36), 362(6.0), 257(9.47)	0.29 (140)	-0.28	-0.39(130) -1.07	1.88
[Cu(SETaaiNEt)(pic)](ClO ₄) (3b)	690(0.06), 474(3.80), 369(7.75), 258(8.85)	0.32 (150)	-0.28	-0.39(130) -1.07	1.87
[Cu(SMeaaiNMe)(oxine)](ClO ₄) (4a)	740(0.12), 471(4.5), 405(6.0), 365(7.5), 256(6.9)	0.29 (140)	-0.28	-0.40(130) -1.34	1.92
[Cu(SETaaiNEt)(oxine)](ClO ₄) (4b)	735(0.12), 470(4.5), 405(6.0), 360(7.5), 250(6.7)	0.30 (150)	-0.28	-0.40(130) -1.34	1.87
[Cu(SMeaaiNMe)(ox)] (5a)	630(0.22), 464(1.12), 365(3.5), 249(5.0)	0.30 (150)	-0.24	-0.44(150) -1.35	1.88
[Cu(SETaaiNEt)(ox)] (5b)	632(0.20), 465(1.10), 364(3.3), 244(4.2)	0.32 (150)	-0.25	-0.44(150) -1.35	1.87
[Cu(SMeaaiNMe)(salc)] (6a)	670(0.17), 470(5.3), 445(6.0), 380(6.0), 248(5.75)	0.32 (150)	-0.25	-0.40(130) -1.34	1.90
[Cu(SETaaiNEt)(salc)] (6b)	672(0.18), 474(5.4), 445(6.0), 381(6.0), 247(5.70)	0.32 (150)	-0.25	-0.40(130) -1.34	1.89

^aSolvent, MeOH. ^cSolvent, MeCN; working electrode, Pt-disk milli electrode, Pt-wire auxiliary, Ag/AgCl reference; supporting electrolyte [nBu₄N][ClO₄]; scan rate 0.05 V s⁻¹, potential $E_{1/2} = 0.5(E_{pa} + E_{pc})$, $\Delta E_p = |E_{pa} - E_{pc}|$, mV; E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential. ^d E_{pc} . ^e E_{pa} .

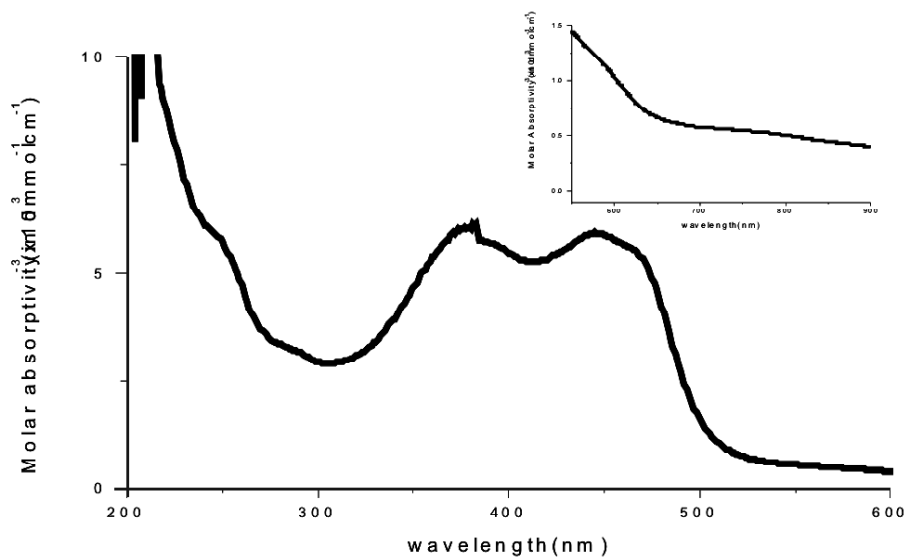


Fig. 1. UV-Vis spectra of [Cu(SMeaaiNMe)(salc)] (**6a**).

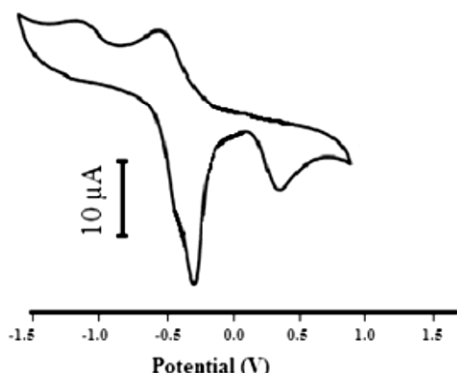


Fig. 2. Cyclic voltammogram of $[\text{Cu}(\text{SEtaaiNEt})(\text{bpy})]^{2+}$ (**1a**) in MeCN.

about 0.3 V versus Ag/AgCl along with three reductive responses at negative side (Table 1, Fig. 2). On comparing with CV of $\text{Cu}(\text{NN}'\text{S})\text{Cl}_2$ we may conclude that the couple is due to the reduction of Cu^{II} to Cu^{I} . Because of better π -acidity of bidentate coligands than 2Cl^- the redox couple is shifted to more positive side. Three quasireversible couples at about -0.4, -0.8 and -1.3 V are the description electron accommodation in the chelated ligands. Free ligand does not show any oxidation but irreversible reductive responses appear at < -1.0 V. On scanning to negative direction at potential < -0.6 V and reversal of direction shows upsurge of current at av. -0.3 V which refers to $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple. The increment of current density may be due to reoxidation of adsorbed Cu (metallic) on the electrode surface which has been produced upon reduction of Cu^{I} at highly negative potential. The current height to $\text{Cu}^{\text{I}}/\text{Cu}^{\text{0}}$ couple increases gradually. The peak-to-peak separation of the redox couple at positive to the reference electrode (~ 0.2 V) is also dependent on the scan rate and, increases from 120 mV at 10 mV s^{-1} to 600 mV at 1000 mV s^{-1} . At slow scan rates ($10\text{--}50 \text{ mV s}^{-1}$) ΔE_p remains almost constant. This observation suggests low heterogeneous electron-transfer rate constant which has been influenced by the applied potential. In general, the electrochemical reduction of copper(II) complexes is associated with change in coordination geometry. Solution structure of copper(II) complex shows square pyramidal or trigonal bipyramidal which upon reduction may change to tetrahedral geometry via bond rupture and bond formation. Bond reorganization energy should reasonably be high due to fast change in Cu-S bond length which will be longer in Cu^{II} than Cu^{I} ^{21,24}. Two quasireversible couples at -0.8 and -1.3 V may assign to azo reduction $[-\text{N}=\text{N}-]/[\text{N}=\text{N}-]^-$ and $[-\text{N}=\text{N}-]^-/[-\text{N}-\text{N}-]^-$ respectively (Table 1).

EPR studies :

Polycrystalline spectra of $[\text{Cu}(\text{NN}'\text{S})(\text{X},\text{Y})](\text{ClO}_4)_n$ at room temperature (298 K) are weakly resolved. The low resolution of polycrystalline spectra is usual where copper centers are relatively closer together, the hyperfine splitting are poor due to paramagnetic charge narrowing. However, the resolution is better in solution; therefore, the spectra at 77 K were used to determine the EPR parameters. The frozen solution spectra show better signal resolution that can be attributed to a single species. The EPR spectra of Cu^{II} complexes provide information about hyperfine and superhyperfine structures which helps in defining the geometry and distortion of the complexes. The complexes show usual four line (^{63}Cu , $I = 3/2$) EPR spectra and are anisotropic at higher magnetic field. The three peaks of low intensity in the weaker field are considered to originate from the g_{\parallel} component and A_{\parallel} lies $155\text{--}175 \times 10^{-4} \text{ cm}^{-1}$. The calculated g_{\parallel} and g_{\perp} values for these complexes were 2.21–2.42 (g_{\parallel} : 2.21 (**1a**), 2.32 (**1b**), 2.28 (**2a**), 2.42 (**2b**), 2.22 (**3a**), 2.33 (**3b**), 2.32 (**4a**), 2.22 (**4b**), 2.41 (**5a**), 2.22 (**5b**), 2.31 (**6a**), 2.21 (**6b**)) and 2.01–2.14 (g_{\perp} : 2.01 (**1a**), 2.05 (**1b**), 2.13 (**2a**), 2.10 (**2b**), 2.11 (**3a**), 2.01 (**3b**), 2.02 (**4a**), 2.13 (**4b**), 2.01 (**5a**), 2.02 (**5b**), 2.01 (**6a**), 2.02 (**6b**)). The relation $g_{\parallel} > g_{\perp} > 2.0023$ agrees with the ground state configuration of $d_{x^2-y^2}$. The superhyperfine coupling constant A_{\perp} average to $16 \times 10^{-4} \text{ cm}^{-1}$ and is in the range of Cu-N interaction¹⁹. For CuN_2 coordination there will be (2.2 + 1) 5 responses and they are observed, indeed (Fig. 3).

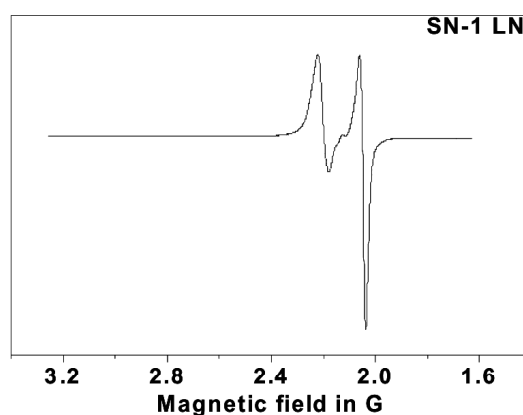


Fig. 3. EPR spectrum of $[\text{Cu}(\text{SEtaaiNEt})(\text{pic})](\text{ClO}_4)$ (**3b**) in MeOH at liquid nitrogen temperature.

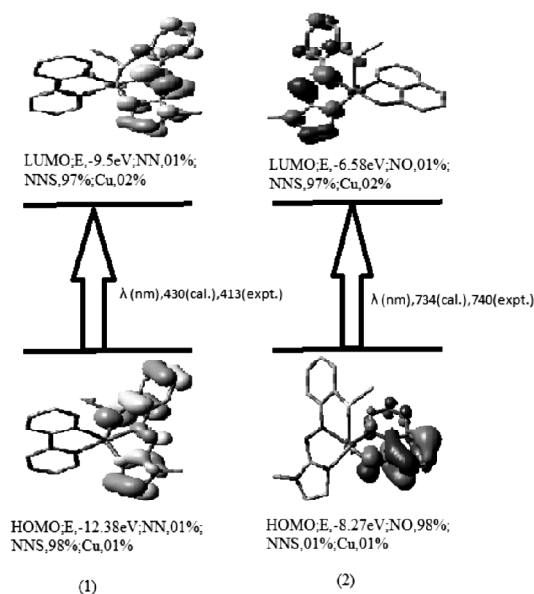


Fig. 4a. HOMO-LUMO electronic transitions considering α -molecular orbitals (1) for $[\text{Cu}(\text{SMeaiiNMe})(\text{bpy})]^{2+}$ (**1a**) and (2) for $[\text{Cu}(\text{SMeaiiNMe})(\text{oxine})]^+$ (**4a**).

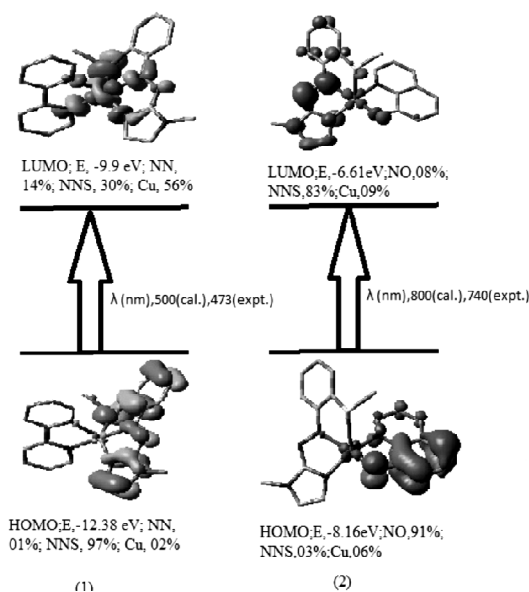


Fig. 4b. HOMO-LUMO electronic transitions considering β -molecular orbitals (1) for $[\text{Cu}(\text{SMeaiiNMe})(\text{bpy})]^{2+}$ (**1a**) and (2) for $[\text{Cu}(\text{SMeaiiNMe})(\text{oxine})]^+$ (**4a**).

Theoretical explanation :

Theoretically generated structures of $[\text{Cu}(\text{SMeaiiNMe})(\text{bpy})]^{2+}$ (**1a**) and $[\text{Cu}(\text{SMeaiiNMe})(\text{oxine})]^+$ (**4a**) are used to calculate composition and energy of the functions. These are used to explain the electronic properties of the complexes. The orbital energies along with contributions from the ligands and metal are given in Supplementary Materials Tables S1 and S2. Fig. 4 depicts HOMO-LUMO electronic transitions considering α and β -molecular orbitals respectively.

The HOMO of **1a** is constituted by Cu (01%), SMeaiiNMe (98%) and bpy (01%) while HOMO-1, HOMO-2 etc. are mainly contributed from SMeaiiNMe (>95%). In $[\text{Cu}(\text{SMeaiiNMe})(\text{oxine})]^+$ (**4a**) the HOMO and other occupied MOs (except HOMO-1) are mainly coming from oxine (>90%) and unoccupied MOs (except LUMO+1) are contributed from SMeaiiNMe (>80%). The calculated transitions are grouped in Supplementary Materials Table S2. The intensity of these transitions has been assessed from oscillator strength (f). In **1a** the visible region (400–570 nm) transitions are assigned to HOMO-3→LUMO, HOMO→LUMO etc. The calculated transitions at 470–570 nm are weak (f , 0.01) and are assigned to admixture of MLCT (metal-to-ligand charge transfer) and ILCT (intraligand charge transfer). An intense band is calculated at 430 nm (f , 0.47) which is an ILCT band (Table 2).

Cyclic voltammetric behaviour of the complexes are readily accountable from DFT calculation. Unoccupied MOs are significantly dominated by azoimine function, thus reduction may refer to electron accommodation at azo dominated orbital of the ligand. So the assignment, azo reductions are justified. The LUMO and other unoccupied MOs are SMeaiiNMe dominated (>95%), so reduction is as usual, $-\text{N}=\text{N} - + e \longrightarrow -\text{N}=\text{N}^-$.

Table 2. Theoretical (TD-DFT) UV-Vis spectral data (in MeOH)

Comps.	Considering α -molecular orbitals, λ_{max} (in nm) (f)	Considering β -molecular orbitals, λ_{max} (in nm) (f)
$[\text{Cu}(\text{SMeaiiNMe})(\text{bpy})]^{2+}$ (1a)	467(0.16), 435(0.47), 383(0.09), 290(0.21), 287(0.03), 244(0.14)	492(0.02), 467(0.16), 435(0.47), 383(0.09), 290(0.21), 244(0.14)
$[\text{Cu}(\text{SMeaiiNMe})(\text{oxine})]^+$ (4a)	528(0.08), 465 (0.12), 415(0.18),	583(0.02), 515(0.06), 465(0.12), 408(0.24), 395(0.04), 249(0.53)

Conclusion

The synthesis and characterization of ternary complexes of copper(II), [Cu(SRaaNR')(X,Y)]ClO₄, are described. Because of thioether coordination (RS→Cu^{II}) the metal centre becomes susceptible to reduction to Cu^I and has been observed in cyclic voltammetry. EPR spectra of the complexes support ground state configuration of $d_{x^2-y^2}$.

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Appendix A

Supplementary data :

Fig. S1 contains optimized structures of **1a** and **4a**. Fig. S2 contains Mass spectra of **6a**. The orbital energies along with contributions from the ligands, metal and the calculated transitions are given in Supplementary Materials Table S1(A-C), and S2(A-C). Table S3 contains FTIR spectral data and conductance measurements.

References

- H. Sigel (ed.), "Metal Ions in Biological Systems", M. Decker, New York, Different volumes.
- (a) S. Belanger and A. L. Beauchamp, *Inorg. Chem.*, 1996, **35**, 7836; (b) J. C. Lockhart and D. D. Reshton, *J. Chem. Soc., Dalton Trans.*, 1991, 2633.
- (a) A. C. van Steenbergen, E. Bouwman, R. A. G. de Graft, W. L. Driessen, J. Reedijk and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 1990, 3175; (b) R. Bastida, S. Gongalez, T. Rodriguez, A. Sousa and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1990, 3643; (c) M. R. Malachonsk, M. Adams, N. Elia, A. L. Rheingold and R. S. Kelly, *J. Chem. Soc., Dalton Trans.*, 1999, 2177; (d) L. Casella, M. Gullotti and R. Vigato, *Inorg. Chim. Acta*, 1986, **124**, 121.
- (a) M. E. Hossain, M. N. Alam, M. A. Ali, M. Nazimuddin, F. E. Smith and R. C. Hynes, *Polyhedron*, 1996, **15**, 973; (b) J. C. Liu, S. Xi, L. F. Wang, F. Y. He and X. Y. Huang, *Polyhedron*, 1996, 15.
- B. C. Westerby, K. L. Juntunen, G. H. Leggett, V. B. Ptt, M. J. Koenigbauer, M. D. Rurgett, M. J. Jascher, L. A. Ochry-mowycz and D. B. Rorabacher, *Inorg. Chem.*, 1991, **30**, 2109.
- S. Nandi, D. Bannerjee, J.-S. Wu, T.-H. Lu, A. M. Z. Slawin, J. D. Woollins, D. John, J. Ribas and C. Sinha, *Eur. J. Inorg. Chem.*, 2009, **26**, 3972.
- S. Nandi, D. Bannerjee, P. Datta, T.-H. Lu, A. M. Z. Slawin and C. Sinha, *Polyhedron*, 2009, **28**, 3519.
- S. Saha (Halder), B. G. Chand, J.-S. Wub, T.-H. Lu, P. Raghavaiah and C. Sinha, *Polyhedron*, 2009, **28**, 3519
- D. Bannerjee, U. S. Ray, Sk. Jasimuddin, J.-C. Liou, T.-H. Lu and C. Sinha, *Polyhedron*, 2006, **25**, 1299.
- Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery (Jr.), T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomas, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukud, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, P. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- B3LYP : A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- LanL2DZ : P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.
- N. M. O'Boyle and J. G. Vos, GaussSum 1.0, Dublin City University, Dublin, Ireland, 2005.
- K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Part B, 'Applications in Coordination, Organometallic, and Bioinorganic Chemistry', 6th ed., Wiley, New York, 2008.
- W. Kaim and B. Schwederski, "Bioinorganic Chemistry, Inorganic Elements in the Chemistry of Life", John Wiley & Sons, Chichester-New York-Brisbane-Toronto-Singapore, 1994, p. 22 and p. 196.
- P. M. Bush, J. P. Whitehead, C. C. Pink, E. C. Gramm, J. L. Eglin, S. P. Watton and L. E. Pence, *Inorg. Chem.*, 2001, **40**, 1871 and references therein.
- T. K. Misra, D. Das and C. Sinha, *Polyhedron*, 1997, **16**, 4163.
- T. K. Misra, D. Das and C. Sinha, *Indian J. Chem.*, 1998, **37A**, 741.

19. U. S. Ray, D. Bannerjee, G. Mostafa, T.-H. Lu and C. Sinha, *New J. Chem.*, 2004, **28**, 1432 and references therein.
20. P. K. Dhara, S. Pramanik, T.-H. Lu, M. G. B. Drew and P. Chattopadhyay, *Polyhedron*, 2004, **23**, 2457.
21. S. Torelli, C. Belle, C. Philouze, J.-L. Pierre, W. Rammal and E. Saint-Aman, *Eur. J. Inorg. Chem.*, 2003, 2452.
22. B. Adhikari and C. R. Lucas, *Inorg. Chem.*, 1994, **33**, 1376.
23. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1984.
24. E. A. Ambundo, M.-V. Deydier, A. J. Grall, N. Aguera-Vega, L. T. Dressel, T. H. Cooper, M. J. Heeg, L. A. Ochymowycz and D. B. Rorabacher, *Inorg. Chem.*, 1999, **38**, 4233.