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Copper(II) complexes of tetradentate N2S2 donor sets: Synthesis, crystal structure characterization and reactivity

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ABSTRACT

Two mononuclear and one dinuclear copper(II) complexes, containing neutral tetradentate NSSN type ligands, of formulation [Cu^{II}(L¹)Cl]ClO₄ (1), [Cu^{II}(L²)Cl]ClO₄ (2) and [Cu^{II}₂(L³)₂Cl₂](ClO₄)₂ (3) were synthesized and isolated in pure form [where L¹ = 1,2-bis(2-pyridylmethylthio)ethane, L² = 1,3-bis(2-pyridylmethylthio)propane and L³ = 1,4-bis(2-pyridylmethylthio)butane]. All these green colored copper(II) complexes were characterized by physicochemical and spectroscopic methods. The dinuclear copper(II) complex 3 changed to a colorless dinuclear copper(I) species of formula [Cu^I₂(L³)₂](ClO₄)₂,0.5H₂O (4) in dimethylform-amide even in the presence of air at ambient temperature, while complexes 1 and 2 showed no change under similar conditions. The solid-state structures of complexes 1, 2 and 4 were established by X-ray crystallography. The geometry about the copper in complexes 1 and 2 is trigonal bipyramidal whereas the coordination environment about the copper(I) in dinuclear complex 4 is distorted tetrahedral.

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1. Introduction

The potential role played by copper ions in the active sites of a large number of metalloproteins has stimulated efforts to design and characterize copper complexes as models for providing better understanding of biological systems and for assisting in the development of new homogeneous catalysts for selective oxidation. Particularly, the coordination chemistry and reactivity of copper complexes involving nitrogen–sulfur donor ligands has received considerable attention as models [1]. In particular the CuN₂S₂ chromophore is present in blue copper proteins such as plastocyanine [2] and copper(II) chelates of SNNS ligands have been found to have antineoplastic activities and to interact with biological systems [3].

Pursuing our continuous interest on nitrogen–sulphur polydentate chelators [4] and in addition of the importance of nitrogen– sulphur donor sets in the coordination chemistry of copper complexes, herein we report an account on the coordination properties of three neutral tetradentate ligands containing two pyridyl-N and two thioether-S donors. The mononuclear complexes **1** and **2** show penta-coordinated copper(II) ion with distorted trigonal bipyramid coordination geometry and the trigonality index (τ) of the solid-state structure increases (from 0.619 to 0.716) with the number of carbon atoms in the backbone of the ligands. The penta-coordinated copper(II) in the dinuclear green colored complex (**3**) is reduced to tetra-coordinated copper(I) species with concomitant change of color (colorless (**4**)) in dimethylformamide (DMF) even in the presence of air at ambient temperature within few days, while other complexes **1** and **2** show no change after several days. The single crystal X-ray structural analysis of **1**, **2** and **4** are discussed and compared.

2. Experimental

2.1. Materials and physical measurements

All chemicals and reagents were obtained from commercial sources and used as received, unless otherwise stated. Tetra-*n*-butylammoniumperchlorate was prepared by addition of sodium perchlorate to a hot solution of tetra-*n*-butylammoniumbromide (Aldrich). The product was recrystallized from aqueous ethanol and tested for the absence of bromide. Solvents were distilled from an appropriate drying agent [5].

The C, H, N elemental analyses were performed on a Perkin Elmer model 2400 elemental analyzer. Copper analysis was carried out by Varian atomic absorption spectrophotometer (AAS) model-AA55B, GTA using graphite furnace. Electronic absorption spectra were recorded on a JASCO UV-Vis/NIR spectrophotometer model V-570 in the range of 1100–200 nm. IR spectra were obtained by JASCO FT-IR spectrometer model 460 *plus* using KBr disk. ¹HNMR spectra were recorded on a Bruker AC300 spectrometer





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using TMS as an internal standard in CDCl₃. The room temperature magnetic susceptibility measurements were performed by using a vibrating sample magnetometer PAR 155 model. Molar conductance $(\Lambda_{\rm M})$ were measured in a systronics conductivity meter 304 model using $\sim 10^{-3}$ mol L⁻¹ solutions in acetonitrile. The measurement of pH of the reaction mixture was done with a systronics digital pH meter (Model 335). The separation and detection of the species in the reaction mixture were carried out using the hyphenated GC-MS system (Schimadzu, model GCMS-QP5050A). Electrochemical measurements were recorded on a computer controlled EG & G PAR model 270 VERSTAT electrochemical instruments using Ag/AgCl electrodes with TBAP as supporting electrolyte. All the measurements were made at 298 K with acetonitrile as solvent for complexes **1** and **2** and dimethylformamide for 3, using a concentration ca. 10^{-3} – 10^{-4} M purged with dry nitrogen for 3–4 min in order to remove dissolved oxygen.

2.2. Preparation of the ligands

The syntheses of the ligands were carried out following the reported procedure [6] with slight modification. A common procedure has been performed to obtain the ligands. The procedure for the preparation of 1,2-bis(2-pyridylmethylthio)ethane, (L¹) is here described. An ethanolic solution of 2-picolyl chloride, hydrochloride (1.64 g, 10.0 mmol) was added to 1,2-ethandithiol (0.47 g, 5.0 mmol) in dry ethanol containing sodium ethoxide (0.46 g 20.0 mmol) at low temperature (0-5 °C). Then this mixture was allowed to stir at room temperature for 0.5 h and then it was refluxed for 2 h. The mixture was cooled to room temperature, water was added and finally the ethanol was off by rotary evaporator. The product was extracted into dichloromethane and dried by using NaHSO₃. The product, 1,2-bis(2-pyridylmethylthio)ethane (L¹) was obtained as a yellow oil by removing the dichloromethane by rotary evaporator. The other products were also obtained as liquids. Finally the products were verified by ¹H NMR spectroscopy.

2.3. Preparation of the copper(II) complexes

The copper(II) complexes were synthesized following a common procedure as described below, using copper(II) perchlorate hexahydrate and the respective organic compounds in equimolar ratio. For complex **1**, L^1 (276.0 mg, 1.0 mmol), for complex **2**, L^2 (292.0 mg, 1.0 mmol) and for complex **3**, L^3 (306.0 mg, 1.0 mmol) were mixed with 1.0 mmol of copper(II) perchlorate hexahydrate, and the mixture was stirred for 4 h in methanol. Then sodium chloride (1.0 mmol) was added to the resulting mixture and stirred for another 1 h at room temperature. The green coloured complexes were precipitated out and the solid complexes were filtered, washed with water, cold methanol and dried in vacuo. Yield: 84–85%.

[Cu(L¹)Cl]ClO₄ (1): *Anal.* Calc. for C₁₄H₁₆Cl₂CuN₂O₄S₂: C, 35.37; H, 3.37; N, 5.90, Cu, 13.37. Found: C, 35.52; H, 3.46; N, 5.74, Cu, 13.21%. IR0020(cm⁻¹): $\nu_{C=N}$, 1476; ν_{C-S} , 758; ν_{ClO_4} , 1090 and 621. Magnetic moment (μ , B.M.): 1.81. Conductivity (Λ_0 , Ω^{-1} cm² mol⁻¹) in acetonitrile: 145.

[Cu(L²)Cl]ClO₄ (**2**): *Anal.* Calc. for C₁₅H₁₈Cl₂CuN₂O₄S₂: C, 36.82; H, 3.68; N, 5.73, Cu, 12.99. Found: C, 37.22; H, 3.77; N, 5.81, Cu, 13.11%. IR (cm⁻¹): $v_{C=N}$, 1465; v_{C-S} , 758; v_{ClO4} , 1088 and 624. Magnetic moment (μ , B.M.): 1.79. Conductivity (Λ_0 , Ω^{-1} cm² mol⁻¹) in acetonitrile: 140.

[Cu₂(L³)₂Cl₂](ClO₄)₂ (**3**): *Anal.* Calc. for C₃₂H₄₀Cl₄Cu₂N₄O₈S₄: C, 38.18; H, 3.98; N, 5.57, Cu,12.63. Found: C, 37.82; H, 4.02; N, 5.79, Cu, 12.47%. IR (cm⁻¹): $\nu_{C=N}$, 1478; ν_{C-S} , 760, ν_{ClO4} , 1088 and 622. Magnetic moment (μ , B.M.): 1.45 per Cu atom. Conductivity (Λ_0 , Ω^{-1} cm² mol⁻¹) in DMF: 150.

2.4. Preparation of the copper(I) complex of 1,4-bis(2-pyridylmethylthio)butane (**4**)

The solution of complex **3** in DMF was stirred for 1 h at room temperature in presence of air. After few days, the colorless single crystals of complex **4** were collected by slow evaporation of this solution

 $[Cu_2(L^3)_2](ClO_4)_2, 0.5H_2O$ (4): Anal. Calc. for $C_{32}H_{41}Cl_2Cu_2$. $N_4O_{8.5}S_4$: C, 40.68; H, 4.34; N, 5.93, Cu, 13.45. Found: C, 40.01; H, 4.21; N, 5.88; Cu, 13.34%. IR (cm⁻¹): $\nu_{C=N}$, 1479; ν_{C-S} , 758; ν_{ClO4} , 1092 and 623.

2.5. X-ray crystal structure analysis

Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of acetonitrile solutions of complex **1** and **2** at ambient temperature, while crystals of complex **4** were obtained from dimethylformamide solution of copper(II) complex **3** by slow evaporation at room temperature in presence of air.

Crystal data and details of data collections and refinements for the structures reported are summarized in Table 1. Diffraction data of **1** and **2** were collected at 150(2) K on Oxford Diffraction X-Calibur CCD System, data collection of **4** were carried out, at room temperature, on a Nonius DIP-1030H system, by using Mo K α radiation, $\lambda = 0.71073$ Å in both cases. Cell refinement, indexing and scaling of all the data sets were performed using programs Crys Alis [7], Denzo and Scalepack [8]. All the structures were solved by direct methods and subsequent Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections [9]. A residual in the difference Fourier map of **4**, located on a two-fold axis, was assigned to a water oxygen with occupancy 0.25. The contribution of hydrogen atoms at calculated positions were included in final cycles of refinement. All the calculations were performed using the WinGX System, Ver 1.70.01 [10].

3. Result and discussion

3.1. Synthesis and characterization

The organic compounds (L) were synthesized by the reaction of the respective alkyl dithiol compound with 2-picolyl chloride in

 Table 1

 Crystal data and details of refinements for 1, 2 and 4

	1	2	$\textbf{4.0}\cdot 5H_2O$
Empirical formula	$C_{14}H_{16}Cl_2CuN_2O_4S_2$	$C_{15}H_{18}Cl_2CuN_2O_4S_2$	C ₃₂ H ₄₁ Cl ₂ Cu ₂ N ₄ O _{8.5} S ₄
Formula weight	474.85	488.87	943.91
Crystal system	triclinic	monoclinic	orthorhombic
Space group	\overline{P}	P21/a	Iba2
a (Å)	8.2345(9)	8.5188(5)	20.331(4)
b (Å)	10.2758(10)	24.783(3)	21.310(4)
c (Å)	12.1620(11)	9.0438(12)	9.988(3)
α(°)	109.456(9)	90.00	90.00
β (°)	96.603(8)	92.586(7)	90.00
γ (°)	111.400(9)	90.00	90.00
Volume (Å ³)	870.03(15)	1907.4(3)	4327.3(18)
Ζ	2	4	4
ρ_{calc} (g/cm ³)	1.813	1.702	1.449
F(000)	482	996	1940
θ Range (°)	2.74-30.00	2.40-30.00	2.97-25.02
μ (Mo K α) (mm ⁻¹)	1.825	1.668	1.349
Independent reflections	4824	5519	3598
Reflections with $l > 2\sigma(l)$	3343	2129	2454
R_1	0.0570	0.0418	0.0664
wR ₂	0.1469	0.0760	0.1728
Goodness-of-fit	1.028	0.764	0.975



Scheme 1. Ligands and the reaction procedure.

presence of sodium ethoxide. These organic moieties have been confirmed by ¹H NMR spectral analyses. The five coordinated Cu(II) complexes with NSSN donor centers of these ligands and one chloride ion (1, 2 and 3) were obtained in good yield from the reaction of copper(II) perchlorate with equimolar amounts of the respective organic moieties in the methanol medium followed by the addition of aqueous sodium chloride solution at ambient temperature according to Scheme 1. Here, the sequence of the addition of anions along with Cu(II) ions to the ligand solutions is crucial. In the preparation of the complexes, it was found that the identity of the anion used was important. Thus the present complexes were obtained only when copper(II) perchlorate was used. A different series of copper(II) complexes were formed containing the decomposed product of these organic moieties and precipitated out from the reaction mixture when the organic moieties were allowed to react with copper(II) chloride in the first step. Characterization of these copper(II) complexes is in progress.

Here both monomeric **1** and **2** complexes are soluble in acetonitrile and DMF but sparingly soluble in methanol, ethanol and dichloromethane, while **3** is dimeric and soluble in DMF. At room temperature the magnetic moment (μ) of **1** and **2** is 1.81 and 1.79 B.M., respectively, while for **3** it is 1.40 B.M. per copper atom. The conductivity measurement of complexes **1** and **2** in acetonitrile shows the conductance values of 145 and 140 Λ_0 mol⁻¹ cm ⁻¹ respectively and while that of **3** in DMF is 150 Λ_0 mol⁻¹ cm⁻¹ at 300 K. These values suggest that complexes **1** and **2** exist as 1:1 electrolytes and **3** as a 1:2 electrolyte in solution.

3.2. Structures of the Cu(II) complexes 1 and 2

The ORTEP views of **1** and **2** with the atom numbering schemes are illustrated in Figs. 1 and 2, respectively, and a selection of bond distances and angles are listed in Table 2. In both mononuclear complexes, the copper center is coordinated by the tetradentate donor organic moiety and by a monodentate chloride ligand, but with a different geometrical disposition of the NSSN ligand in **1** and **2**. In fact, the highly distorted trigonal bipyramidal geometry about copper (II) shows axial positions occupied by the pyridyl-N donors in **1**, with chlorine and both thioether sulphur in the equatorial plane. On the other hand, in **2**, a pyridyl-N and a thioether-S reside at the axial positions, the equatorial plane consisting of the chlorine, the other pyridyl-N and thioether-S atoms. The almost



Fig. 1. ORTEP view of the cation in $[Cu(L^1)Cl]ClO_4(1)$ with labeling scheme.

trigonal bipyramid geometry present in complexes **1** and **2** is demonstrated by the trigonality index [11] τ of 0.619 and 0.716, respectively.

Coordination bond angles listed in Table 2 indicate large variation from the ideal geometry, especially for the atoms in the equatorial plane, indicating the strained suffered by the ligand coordinating the metal ion. In **1**, both axial bond distances Cu-N1 and Cu-N2 are comparable with their s.u. (2.006(3) and 1.994(3) Å, respectively), but in **2**, the axial Cu-N2 bond length (1.992(3) Å) is significantly shorter than the equatorial one (Cu-N1 of 2.076(3) Å) as the two pyridyl-N donors occupy different positions in the copper coordination sphere. It is worth noting that the Cl atom, located in equatorial position both in **1** and **2**, shows Cu-Cl bond length of 2.270(1) Å in **1**, and significantly longer in **2** (2.441(1) Å). The trend in Cu-Cl bond lengths follows



Fig. 2. ORTEP view of the molecular cation in $[{\rm Cu}(L^2){\rm Cl}]{\rm ClO}_4$ (2) with labeling scheme.

 Table 2

 Selected bond distances (Å) and bond angles (°) for 1, 2 and 4

	1	2		4
Bond distances				
Cu-S(1)	2.387(1)	2.274(1)	Cu-S(1)	2.344(2)
Cu-S(2)	2.486(1)	2.287(1)	Cu-S(2')	2.402(3)
Cu-N(1)	2.006(3)	2.076(3)	Cu-N(1)	2.032(6)
Cu-N(2)	1.994(3)	1.992(3)	Cu-N(2')	2.008(6)
Cu-Cl(1)	2.270(1)	2.441(1)		
Bond angles				
S(1)-Cu-S(2)	91.45(3)	92.94(4)	S(1)-Cu-S(2')	119.47(8)
N(1)-Cu-N(2)	172.57(12)	100.85(11)	N(1)-Cu-N(2')	129.2(2)
N(1)-Cu-S(1)	84.58(9)	81.98(8)	N(1)-Cu-S(1)	85.88(16)
N(1)-Cu-S(2)	92.03(9)	131.57(8)	N(1)-Cu-S(2')	118.08(17)
N(2)-Cu-S(1)	89.64(9)	174.52(8)	N(2')-Cu-S(1)	123.48(17)
N(2)-Cu-S(2)	83.44(9)	81.66(8)	N(2')-Cu-S(2')	84.88(17)
Cl(1)-Cu-S(1)	135.41(4)	89.32(3)		
Cl(1)-Cu-S(2)	132.99(4)	120.05(3)		
N(1)-Cu-Cl(1)	95.53(9)	108.07(7)		
N(2)-Cu-Cl(1)	91.86(9)	94.22(8)		

Symmetry code in **4** (') -x + 1, -y + 1, z.

a reverse order with respect to the Cu–S bond distances (Table 2), which average to 2.436 Å in **1** and 2.280 Å in **2**. The Cu–Cl distance in **1** is within the range found in complexes $[Cu(L)Cl]^+$ [12], where L ligand is close comparable to L¹ by replacing pyridine by imidazolyl rings. Thus the addition of a methylene group inside the ligand leads to different donor atom arrays in **1** and **2** with a significant change in the structural geometry, likely attributable to steric constraint. This feature has been already observed by Reedijk for analogous NSSN ligands containing imidazolyl rings [11,12].

3.3. Reactivity of 3 and structure of the Cu(I) complex 4

A colourless dinuclear copper(I) complex of formula $[Cu_2^1(L^3)_2](ClO_4)_2$, 0.5H₂O (**4**) was obtained from the solution of copper(II) complex (**3**) in DMF at ambient temperature in presence of air or in nitrogen atmosphere. On the other hand, the monomeric copper(II) complexes **1** and **2** in DMF showed no change *via* this type of reduction in nitrogen atmosphere even at elevated

temperature. Here, 1,4-bis(2-pyridylmethylthio)butane (L^3) plays key role in DMF as no change has been observed in case of **1** and **2** under the same condition. This behavior is quite different from the observations where the ligand itself behaved as reducing agent [13,14].

Here, at the first step, DMF was hydrolysed in presence of the dimeric copper(II) complex (**3**) and in this reaction, formic acid and dimethylamine are formed as the hydrolytic products of DMF. Then formic acid as reducing agent, reacts with $[Cu_2^{-II}(L^3)_2Cl_2](ClO_4)_2$ (**3**) to produce $[Cu_2^{-I}(L^3)_2](ClO_4)_2$ (**4**), CO₂ and HCl. The other hydrolytic product dimethylamine reacts with HCl to form $[Me_2NH_2]Cl$. The proposed path was established following the pH decreasing of the reaction mixture associated with a colour change from blue to colourless. This observation indicates that the production of H⁺ takes place in the reaction mixture and after 24 h, the pH of the solution remained unaltered. The steps of the reactions are as follows:

$$\begin{split} & 2\text{Me}_2\text{NCHO} + 2\text{H}_2\text{O} \to 2\text{HCOOH} + 2\text{Me}_2\text{NH} \\ & 2\text{HCOOH} + [\text{Cu}_2^{\text{II}}(\text{L}^3)_2\text{Cl}_2]^{2+} \to 2\text{CO}_2 + [\text{Cu}_2^{\text{I}}(\text{L}^3)_2]^{2+} + 2\text{HCl} \\ & 2\text{Me}_2\text{NH} + 2\text{HCl} \to 2 \text{ [Me}_2\text{NH}_2\text{]Cl} \end{split}$$

 $2\text{Me}_{2}\text{NCHO} + [\text{Cu}_{2}^{\text{II}}(\text{L}^{3})_{2}\text{Cl}_{2}]^{2+} + 2\text{H}_{2}\text{O} \rightarrow 2\text{CO}_{2} + [\text{Cu}_{2}^{\text{I}}(\text{L}^{3})_{2}]^{2+} + 2 [\text{Me}_{2}\text{NH}_{2}]\text{Cl}$

The presence of the HCOOH and $[Me_2NH_2]Cl$ was confirmed through GC–MS by injecting the reaction mixture into GC and detecting by mass spectrometry. Again the presence of chloride ion in the reaction mixture was confirmed as we got the precipitation of AgCl by adding a silver nitrate solution and the production of CO₂ was detected using saturated Ca(OH)₂ solution. The complex **4** was characterized by physicochemical tools and the molecular structure was established by single-crystal X-ray crystallography.

The reduction of the other copper(II) complexes (**1** and **2**) was observed when these species were allowed to react with formic acid but the first step of hydrolysis in DMF was not observed.

An ORTEP view of the cation of **4** with the atom numbering scheme is illustrated in Fig. 3, while a selection of bond distances and angles is listed in Table 2. The crystal structure consists of dinuclear complexes, located about a crystallographic two fold axis, and perchlorate anions. Thus the flexible NSSN ligand acts as a bis chelating agent towards the symmetry related metal ions which are separated by 8.089(2) Å. The copper exhibits a highly distorted tetrahedral coordination geometry, as evident from the coordination bond angles reported in Table 2. The Cu-S bond lengths are 2.344(2) and 2.402(3) Å, within the range measured in 1 and 2, while the Cu-N distances are 2.032(6) and 2.008(6) Å. The chelating angles N-Cu-S (85.88(6) and 84.88(7)°) are comparable to those observed in 1 (84.58(9), 83.44(9)°), but larger than the values of $2(81.98(8), 81.66(8)^\circ)$, likely induced by the different coordination geometry in the latter species. The torsion angle of 162.6(9)° along the alkyl C atoms (anti conformation) indicates no strain in ligand L^3 .

3.4. Spectral properties

Infrared spectra of all the complexes **1–4** exhibit an intense band at approximately 1090 cm^{-1} along with a weak band at 624 cm⁻¹, which have been assigned to $v_{s(CIO4)}$ and $v_{as(CIO4)}$ respectively. The $v_{C=N}$ band is observed at 1465–1478 cm⁻¹ for all the complexes, in addition to the v_{C-S} at 760 cm⁻¹.

The electronic absorption spectra of the complexes **1**, **2** and **3** were recorded at room temperature using acetonitrile (for **1** and **2**) and dimethylformamide (for **3**) as solvent and the data has been



Fig. 3. ORTEP drawing of the molecular cation in $[Cu_2(L^3)_2](ClO_4)_2 \cdot 0.5H_2O$ (4) with labeling scheme of the crystallographic independent atoms.

tabulated in Table 3. All the spectra exhibit a band around 360 nm assignable to the $S(\sigma) \rightarrow Cu(II)$ charge transfer (LMCT) transition [15] along with the transition at high energy region corresponding to intramolecular $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [16]. A characteristic d-d absorption band (above 640 nm) has been also observed in the electronic spectra of these complexes. In the electronic spectra of complex **2**, a high-energy shoulder at 626 nm along with the characteristic d-d band at 667 nm is present and this result emphasizes that the stereochemistry of the complex **2** in the solution state shows a typical trigonal bypyramidal geometry, as in many cases it has been shown that the presence of a single d–d band with high energy (low wave length) shoulder is typical of this stereochemistry for copper [17].

3.5. Electrochemistry

Redox properties of complexes **1**, **2** and **3** were examined by cyclic voltammetry using a Pt-disk working electrode and a Pt-wire auxiliary electrode in dry MeOH and in presence of $[n-Bu_4N]ClO_4$ as supporting electrolyte. The potentials (Table 3) are expressed with reference to Ag/AgCl electrodes. In solution all compounds displayed a quasi-reversible voltammogram having $i_{pc}/i_{pa} \approx 1$ in the range of -340 mV to -387 mV with $\Delta E = 132-294$ mV. Only one quasi-reversible Cu(II)/Cu(I) redox couple at negative potential was observed and it indicates that the similar chemical environment of the two copper ions in dinuclear complex **3** towards the electrochemical properties.

Table 3				
UV-Vis	spectral	and	electrochemical	data

Compound	$\lambda \operatorname{nm}(\varepsilon)$ (ε , dm ³ mol ⁻¹ cm ⁻¹)	Electrochemical data ^b $E^{o'}$, mV (ΔE_{p} , mV) (E_{pa} mV E_{pc} mV)
1	212 (s, 9,322), 261 (s, 8,442), 364 (s, 3,076), 672 (b, 238),	-340 (294) (-193, -487)
2	210 (s, 11,061), 257 (s, 8,302), 359 (s, 3,045), 626 (sh, 122), 667 (b, 249)	-387 (132) (-321, -453)
3	210 (s, 12,227), 258 (s, 8,432), 362 (s, 3,971), 646 (b, 316)	-378 (182) (-287, -469)

^a 1 and 2 in acetonitrile, 3 in DMF.

^b Scan rate of 100 mV s⁻¹.

4. Conclusion

Here, three tetradentate N_2S_2 neutral ligands (where L^3 is hitherto new) have been used to synthesize copper(II) complex having CuN_2S_2 chromophore. The addition of methylene group inside the ligand backbone leads to a significant change in the structural geometry and the chemistry of the organic moieties with copper. When the four methylene groups are present between the thioether-S donor atoms (in case of L^3), the chemistry of L^3 with copper is different from that of L^1 and L^2 . The reduction of copper(II) in **3** resulted a new colorless dinuclear copper(I) complex of formula $[Cu_2^l(L^3)_2](ClO_4)_2$, 0.5H₂O (**4**) in DMF at ambient temperature in presence of air, where the complex **3** plays a key role in DMF as the complex is dimeric complex of L^3 . On the other hand, the monomeric copper(II) complexes **1** and **2** in DMF showed no change *via* this type of reduction in nitrogen atmosphere even at elevated temperature.

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Appendix A. Supplementary material

CCDC 694636, 694637 and 694638 contain the supplementary crystallographic data for **1**, **2** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2008.08.004.

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