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Cu(II) complexes with square pyramidal (N₂S)CuCl₂ chromophore: Jahn–Teller distortion and subsequent effect on spectral and structural properties

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ABSTRACT

One monomeric neutral Cu(II) complex [(pmtpm)CuCl₂] (1) is reported by Lindoy and Livingstone [8]. Two new complexes namely, μ -Cl bridged binuclear Cu(II) complex [{(pmtpm)Cu(Cl)}₂ μ -Cl](ClO₄) (2) and a bis μ -Cl bridged binuclear Cu(II) complex [{(pmtpm)Cu}₂(μ -Cl)₂](ClO₄)₂ (3) derived from a tridentate Schiff base ligand, 2-*pyridyl*-*N*-(2'-*methylthiophenyl*)*methyleneimine* (pmtpm) were synthesized and characterized by various spectroscopic methods and by X-ray crystallography. (N₂S)CuCl₂ chromophore(s) of distorted square pyramidal coordination geometries around Cu(II) ion(s) have been observed for all the complexes 1–3. The equatorial sites of the square plane comprise two N and a thioether S donor atoms of the pmtpm ligand as well as one Cl⁻ ion (terminal in 1 and 2, and bridging in 3) while the remaining axial site is occupied by a terminal Cl⁻ ion (for 1) or a bridging Cl⁻ ion (for 2 and 3). The equatorial Cu-Cl distances [1: 2.4394(4) Å, 2: 2.5597(9) Å, 3: 2.7037(12) Å]. The correlation of an axial Cu-Cl bond elongation with a lower g_{||} value in the solid state EPR spectrum and a blue shifted ligand field transition in the solid and solution phase absorption spectrum has been observed.

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1. Introduction

The Jahn-Teller effect is commonly encountered in octahedral complexes of the transition metal ions with a d^9 , $d^7(low-spin)$ and d^4 (high-spin) electronic configuration [1]. As the Cu(II) ion has a d⁹ electronic configuration $(t_{2g}^6 e_g^3)$, the Jahn–Teller effect is found to be very often and prominent in case of octahedral Cu(II) complexes [2]. A long list of such Cu(II) complexes with a variety of coordination environment (CuO₆, CuN₆, CuS₆, CuN₄O₂, CuO₄N₂, and other) have been reported by Malcolm A. Halcrow [3] (see the Supporting information of Ref. [3]). The existence of pseudo or a second order Jahn-Teller effect is also known for the pentacoordinated Cu(II) complexes where the two limiting geometries such as square pyramidal (SP) or trigonal bipyramidal (TBP) is possible [4] depending on the nature of the ligand and its ligator atoms. In these two limiting geometries the non-degenerate ground electronic state is associated with a low lying degenerate excited state and the distortion of symmetry will result in mixing of the ground and excited states to lower down as a whole the energy of the ground state. The trigonal bipyramidal geometry is less stable than the square pyramidal one due to pseudo Jahn-Teller coupling; and the pseudorotation between these two limiting molecular structures have been studied by Reinen and Atanasov [4b]. Examples of penta-coordinated Cu(II) complexes are known with (CuN₅) [5a and b], (CuN₄O) [5c], (CuN₃O₂) [6] coordination environment where axial elongation is structurally evident. In fact, quite a large number of such Cu(II) complexes (penta or hexa-coordinated) are reported as a single complex only where the Jahn–Teller effect has been invoked to explain the elongation of axial bond(s) in an octahedral, square pyramidal or trigonal bipyramidal geometry. But with a single compound it is not possible to observe the changes of spectral properties due to this Jahn–Teller effect, unless otherwise a proper series of complexes with same coordination environment containing the same ligands are known. Such series of complexes will enable one to correlate unambiguously the spectral data with the extent of Jahn–Teller distortion observed.

Literature survey of the chloro ligated Cu(II) complexes reveal at least two such series of complexes [7]. D. Reinen and coworkers have reported a series of square pyramidal Cu(II) complexes of the general formula Cu(terpy) $X_2 \cdot nH_2O$ (where $X = CI^-$, Br^- , I^- , NO_2^- , NO_3^- , F^- ; and terpy = terpyridine) where the second order Jahn–Teller effect has been well established for the two chloro ligated compounds [7a] such as Cu(terpy)Cl₂ and Cu(terpy)Cl₂·H₂O. Here a water molecule as a solvent of crystallization, affects the crystal structure, with the consequence of a more pronounced elongation of the Cu–Cl bond relative to that of the other complex. The UV–Vis and EPR spectral properties of these two complexes are

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Scheme 1. Chem draw structure of the tridentate Schiff base ligand

also reported. Inspecting the other series of Cu(II) complexes with a differing tridentate nitrogen donor ligand, bis(2-pyridylmethyl)amine, having N₃Cl₂ coordination zone [7b] around the Cu(II) ion, only structural data have been published. In this paper, we report the synthesis, structure and spectral properties (solid and solution phase UV–Vis, EPR) including redox chemistry of two new binuclear Cu(II) complexes [{(pmtpm)Cu(Cl)}₂µ–Cl](ClO₄) (**2**) and [{(pmtpm)Cu}₂(µ–Cl)₂](ClO₄)₂ (**3**) derived from a tridentate Schiff base ligand, 2-*pyridyl-N*-(2'-*methylthiophenyl)methyleneimine*, pmtpm (Scheme 1). These complexes and a reported mononuclear Cu(II) complex [(pmtpm)CuCl₂] (**1**) with the same N₂SCuCl₂ chromophore [8c] comprises a series, where the correlation between the spectral properties and the extent of Jahn–Teller distortion could be studied.

2. Experimental

2.1. Materials

Pyridine-2-carboxaldehyde, 2-(methylthio)aniline, sodium perchlorate (NaClO₄), Ag₂O (Aldrich) were purchased and used without further purification. Anhydrous CuCl₂ was prepared from CuCl₂·2H₂O (Aldrich) following the reported procedure [9]. (Ag-ClO₄)₂·C₆H₆ has been prepared by reacting Ag₂O with HClO₄ then recrystallizing from benzene. Solvents used for spectroscopic studies and for synthesis were purified and dried by standard procedures before used [10].

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

The ligand has been synthesized by modifying the reported procedures [11,8c]. To a solution of pyridine-2-carboxaldehyde (1.0 g, 9.33 mmol) in 15 ml of freshly distilled methanol was added a methanolic solution (15 mL) of 2-(methylthioaniline) (1.299 g, 9.33 mmol) and refluxed under N₂ for 6 h. Solvent removal afforded a thick yellow oil that was dissolved in 70 mL chloroform and washed successively with distilled water, brine solution and finally with distilled water. The organic layer separated was then dried over anh Na₂SO₄ for 1 h, filtered and solvent was removed completely. The yellow oil kept at 4 °C for overnight to get a yellow solid. The solid was then recrystallized from diethyl ether that afforded yellow block/needle shaped crystals of the ligand pmtpm after a day (yield: 1.80 g, ca. 84%).

IR (KBr, v_{max}/cm^{-1} , selected peaks): 1622vs (C=N), 693 m (C–S). ¹H NMR (300 MHz, CDCl₃): δ 8.70 (1H, d, pyridine proton adjacent to N), 8.57 (1H, s, HC=N), 8.33 (1H, d, pyridine proton), 7.81 (1H, t, pyridine proton), 7.37 (1H, t, pyridine proton), 7.28–7.16 (3H, m, phenyl ring proton), 7.08 (1H, d, phenyl ring proton), 2.47 (3H, t, methyl group of S–Me).

2.3. Synthesis of $[{(pmtpm)Cu(Cl)}_2\mu$ -Cl](ClO₄) (2)

To a yellow solution of the ligand pmtpm (1 g, 4.38 mmol) in 150 mL of a mixed solvent $CH_2Cl_2/MeOH$ (2:1 v/v) was added a

methanolic solution (30 mL) of anh CuCl₂ (0.59 g, 4.38 mmol). A dark green color develops to which solid NaClO₄ (1.07 g, 8.73 mmol) was added. The reaction mixture was stirred for 2 h then kept undisturbed for slow evaporation. Within a day dark green needle shaped crystals obtained was filtered off and washed with cold MeOH, ether and dried under vacuum (yield: 1.3 g, ca 75%). *Anal.* Calc. for C₂₆H₂₄N₄S₂Cl₄O₄Cu₂: C, 39.55; H, 3.06; N, 7.10. Found: C, 39.52; H, 3.01; N, 7.02%. IR (KBr, cm⁻¹, selected peaks): 1596s imine C=N), 1100vs and 623 ClO₄), 646 C–S). Molar conductance, $A_{\rm M}$ (MeCN, 298 K) = 130 Ω^{-1} cm² mol⁻¹. Absorption spectrum (in MeCN) [$\lambda_{\rm max}$, nm (ε dm³ mol⁻¹ cm⁻¹]: 752(260), 333(28 000), 275sh (19 860), 227(32 080). ESI-MS (positive ion mode, MeCN): m/z 688.64 ([{(pmtpm)CuCl}₂Cl]⁺, 25%), 325.81 ([{(pmtpm)CuCl}₂]²⁺, 100).

2.4. Synthesis of $[(pmtpm)Cu]_2(\mu-Cl)_2](ClO_4)_2$ (3)

To a methanolic suspension/solution (10 mL) of **2** (0.1 g)0.126 mmol) was added drop wise a solution of $(AgClO_4)_2 \cdot C_6 H_6$ (0.062 g, 0.252 mmol) in 5 mL MeOH. The reaction mixture was refluxed for 2 h. White precipitate of AgCl was formed. After cooling the reaction mixture to room temperature AgCl was filtered off through celite pad using a G-4 frit and filtrate was kept for slow evaporation that affords green needle shaped crystals of 3 (yield: 0.11 g, ca 65%). Anal. Calc. for C₂₆H₂₄N₄S₂Cl₄O₄Cu₂: C, 36.59; H, 2.83; N, 6.56. Found: C, 36.53; H, 2.81; N, 6.51%. IR (KBr, cm⁻¹, selected peaks): 1594vs imine C=N); 1145vs, 1080vs and 624w 646w C–S). Molar conductance, $\Lambda_{\rm M}$ (MeCN, ClO₄), 298 K) = 245 Ω cm² mol⁻¹. Absorption spectrum in MeCN [λ_{max} , nm (ε dm³ mol⁻¹ cm⁻¹: 657(190), 333(24 500), 275sh (23 900), 229(37 800). ESI-MS (positive ion mode, MeCN): m/z 325.83 $([{(pmtpm)CuCl}_2]^{2+}, 100\%).$

Caution: Perchlorate salts are potentially explosive and should be handled with small quantities and care. We did not encounter any difficulties during the work.

2.5. Physical measurements

The Fourier transform infrared spectra of the ligand and the complexes were recorded on a Thermo Nicolet iS10 spectrophotometer using KBr pellet in the range 4000–400 cm⁻¹. The solid state diffuse reflectance spectra and the solution phase electronic spectra were recorded on a Shimadzu UV-2401 PC and on an Agilent 8453 diode array spectrophotometer, respectively. Elemental analyses were carried out on a Perkin–Elmer 2400 series-II CHNS Analyzer. Electron paramagnetic resonance (EPR) spectrum of **2** and **3** were recorded on the polycrystalline samples as well as in MeCN solution with an X-band JEOL-JES-200 spectrometer at 298 K and 77 K. Mass spectra of **2** and **3** were recorded on Micromass Q-Tof microTM. ¹H NMR spectrum of pmtpm has been recorded on Bruker DPX-300. Solution conductivity and redox potentials were measured using Eutech CON-510 and CHI 1120A potentiometer, respectively.

2.6. Data collection and structure refinement

Diffraction intensities for the two complexes **2** and **3** were collected at 150(2) K using a Bruker Smart APEX II CCD area detector with Mo K α radiation (λ = 0.71073 Å). The cell refinement, indexing and scaling of the data set were carried out using APEX2 v2.1-0 programme [12]. Both structures were solved by direct methods with SHELXS [13a], and refined by full-matrix least square based on F^2 with SHELXL [13b] whereas the other calculations were performed using the WINGX programme, Ver 1.80.05 [14]. All of the non-hydrogen atoms were calculated assuming ideal geometries of the atom

Table 1

Data collection and structure refinement parameters for the complexes [{(pmtpm) $Cu(Cl)_2 \mu$ -Cl](ClO₄) (**2**) and [{(pmtpm)Cu}_2(\mu-Cl)_2](ClO₄)₂ (**3**).

Complex	2	3
Chemical formula	$C_{26}H_{24}N_4S_2Cl_4O_4Cu_2$	$C_{26}H_{24}N_4S_2Cl_4O_8Cu_2$
Formula weight	789.5	853.49
Crystal system	triclinic	triclinic
Color	green	green
Space group	ΡĪ	ΡĪ
a (Å)	7.698(5)	8.284(4)
b (Å)	8.269(5)	9.421(4)
<i>c</i> (Å)	12.777(5)	11.442(5)
α (°)	83.349(5)	74.082(9)
β (°)	83.078(5)	70.352(10)
γ (°)	66.989(5)	72.987(10)
V (Å ³)	741.0(7)	788.7(6)
Ζ	1	1
$D_{\rm calc} ({ m g}{ m cm}^{-3})$	1.769	1.797
Absorption coefficient (mm ⁻¹)	1.978	1.875
Transmission factor (T_{\min}/T_{\max})	0.714/0.717	0.713/0.717
F(0 0 0)	398	430
Reflections/parameters	8592/212	6836/209
Unique reflections	2606	2767
Goodness-of-fit (GOF) on F^2	1.052	1.127
$R_1 \left[I > 2\sigma \right]^a$	0.0245	0.0375
$wR_2 [I > 2\sigma]^b$	0.0658	0.0976
R_1 (all data)	0.0257	0.0399
wR_2 (all data)	0.0666	0.0990
Highest peak	0.47	0.66
Deepest hole	-0.48	-0.85

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|.$

^b $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum w[(F_0^2)^2] \}^{1/2}.$

concerned and their positions and thermal parameters were not refined. The perchlorate anion of 2 was found to be disordered and was solved considering two positions for each of the oxygen atom with site occupancy factors of 0.5 so that the total multiplicity for each oxygen atom is unity. The perchlorate Cl atom (Cl3) resides on a center of inversion. The H atom on C6 is acidic and a very weak hydrogen bonding to the two oxygen atoms of the perchlorate anion is observed (average C6-O1, C6-O4 distance is 3.291 and C6-O2, C6-O3 distance is 3.506 Å, respectively). On the other hand no such disorder of the perchlorate anion is encountered for 3. For **3** the inversion center is in the middle of the Cu_2Cl_2 plane and symmetry operation will provide the full molecule view. Further crystallographic analysis and ORTEP generation were carried out using ORTEP programmes [15]. The crystallographic data such as data collection parameters and other crystallographic information for the complexes 2 and 3 are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of complexes

Complex **1** was first reported by Lindoy and Livingstone [8a] in 1968 and later it was structurally characterized by A. Mangia and coworkers [8b] in the year 1971. The better structure of **1** is reported (same cell parameters and space group but with much lower *R* value) again in 2006 by Palaniandavar and coworkers [8c] with it's detailed spectroscopic studies. Structural and spectral data of **1** has been considered from Ref. [8c] for comparing to that of the complexes **2** and **3** when necessary. Complex **2** has been prepared by reacting the ligand and anh CuCl₂ in a solvent mixture CH₂Cl₂/ MeOH (2:1 v/v) following the addition of NaClO₄ and kept for slow evaporation. Complex **2** can be synthesized separately from the solution of **1** and NaClO₄ in CH₂Cl₂/MeOH (2:1 v/v). Complex **1** is insoluble in MeOH and moderately soluble in CH₂Cl₂. Consequently, when a solution of **1** in CH₂Cl₂/MeOH store for prolong

Table 2

Selected bond lengths (Å) and angles (°) of 1, 2 and 3.

	Compound 1^{c}	Compound 2	Compound 3
Cu(1)-N(1)	2.0218(11)	2.0196(19)	2.020(3)
Cu(1) - N(2)	2.0084(11)	1.9943(19)	1.975(3)
Cu(1) - S(1)	2.3380(4)	2.3253(11)	2.3271(11)
$Cu(1)-Cl(1)^{a}$	2.2511(4)	2.2307(12)	2.2513(12)
$Cu(1)-Cl(2)^{b}$	2.4394(4)	2.5597(9)	-
$Cu(1)-Cl(1)^{i}$	-	-	2.7037(12)
$Cu(1)-Cu(1)^{i}$	-	5.119	3.416
C(6) - N(2)	1.2889(17)	1.286(4)	1.280(3)
N(1)-Cu(1)-N(2)	80.44(5)	80.89(8)	81.62(11)
N(1)-Cu(1)-S(1)	162.50(4)	160.64(5)	162.31(8)
N(1)-Cu(1)-Cl(1)	98.15(4)	97.47(7)	97.80(8)
N(2)-Cu(1)-S(1)	84.06(3)	84.14(6)	85.76(8)
N(2)-Cu(1)-Cl(1)	158.03(4)	159.93(5)	173.30(8)
S(1)-Cu(1)-Cl(1)	93.178(14)	92.39(4)	93.29(4)
Cl(2)-Cu(1)-N(1)	98.12(4)	101.06(5)	106.74(8)
Cl(2)-Cu(1)-N(2)	96.11(4)	98.94(5)	93.21(8)
Cl(2)-Cu(1)-S(1)	91.540(14)	93.31(4)	86.22(4)
Cl(2)-Cu(1)-Cl(1)	105.756(16)	101.00(3)	93.35(3)

^a Equatorial Cl(1) coordination.

^b Axial Cl(2) coordination (in case of compound **3**, Cl(1)ⁱ is axial).

^c Data from Ref. [8c].

time, the conversion of **1** to the cationic **2** with a Cl⁻ counter anion occurs that in presence of NaClO₄ produce **2** with an exchanged, preferred bigger size ClO_4^- counter ion. The halide displacement from **2** by reacting with AgClO₄ afforded **3** in high yield. Although **2** equivalent of AgClO₄ is used in boiling MeOH the displacement of one out of two terminal chloride ions from **2** has been observed. This fact indirectly proved that the labile chloride dissociation of **3** in polar solvent like MeOH will be less than **2**.

The IR spectrum of pmtpm display an intense stretch at 1622 cm⁻¹ and 693 cm⁻¹ correspond to $v_{C=N}$ [16] of imine and $v_{\text{C-S}}$, respectively. The $v_{\text{C=N}}$ of pmtpm for **1** (1592 cm⁻¹) [8c], **2** (1594 cm^{-1}) and **3** (1596 cm^{-1}) are red shifted than the $v_{C=N}$ of the free ligand (1622 cm⁻¹), indicating imine N coordination. Similar red shift of v_{C-S} from 693 cm⁻¹ (free pmtpm) to ~645 cm⁻¹ in complexes 1, 2 and 3 indicates the thioether S coordination to Cu(II) ion. The intense and broad stretches for the perchlorate counter anion have been found at $\sim 1100 \text{ cm}^{-1}$ and 623 cm⁻¹ for both **2** and **3**. The molar conductivity of **2** ($\Lambda_{\rm M}$ = 130 M⁻¹ cm⁻¹) and **3** ($\Lambda_{\rm M}$ = 245 M⁻¹ cm⁻¹) in MeCN are fairly consistent with a 1:1 and a 2:1 electrolyte, respectively [17]. The ESI positive mass spectra of the complexes 2 and 3 were recorded in MeCN solution that display the 100% molecular ion peaks at m/z, 325.81 and 325.83, respectively that corresponds to $[{(pmtpm)Cu}_2(\mu-Cl)_2]^{2+}$ for both the complexes. In case of 2 an additional less intense (~25%) peak at m/z 688.64 corresponds to [{(pmtpm)Cu(Cl)}₂ μ -Cl]⁺ was observed (supporting information, Figs. S1 and S2 for 2 and 3, respectively) which is absent in the spectrum of **3**. Based on the microanalytical data in addition to the above facts, we preliminarily proposed the formulation of these two new complexes as $[{(pmtpm)Cu(Cl)}_2\mu$ -Cl](ClO₄) (**2**) and $[{(pmtpm)Cu}_2$ $(\mu$ -Cl)₂](ClO₄)₂ (**3**), which were finally confirmed from their X-ray crystal structure determination.

3.2. Description of the structures of [{(pmtpm)Cu(Cl)}₂ μ -Cl](ClO₄) (**2**) and [{(pmtpm)Cu}₂(μ -Cl)₂](ClO₄)₂ (**3**)

Perspective views of the cationic part of the complexes **2** and **3** have been shown in Figs. 1 and 2, respectively along with atom labeling scheme. Selected bond distances and angles are tabulated in Table 2. For both the complexes the coordination geometry around the Cu(II) ions are distorted square pyramidal as are evidenced from the values of trigonality index, τ (τ for **1**, **2** and **3**



Fig. 1. ORTEP view of the cationic part of **2**. The thermal ellipsoids are at the 50% probability scale and the hydrogen atoms are omitted for clarity.

are 0.07, 0.01 and 0.18, respectively) defined as $\tau = [|\theta - \phi|/60]$, where θ and ϕ are the two largest coordination angles. The expected values of τ are 0 and 1 for perfect square-pyramidal (SP) and ideal trigonal-bipyramidal (TBP) coordination geometry, respectively [18]. The pmtpm ligand coordinate meridionally to the central Cu(II) ion like other reported complexes of this ligand [8c]. Three corners of the square plane are occupied by the pyridine nitrogen N(1), imine nitrogen N(2) and the thioether sulfur S(1) atoms. The remaining one corner of the square plane is occupied by a chloride ion, namely Cl(1) which is terminally coordinated in case of **2** while it is a bridging chloride ion in case of **3**. The bridging chloride ion Cl(2) in **2** and the symmetry generated Cl(1)ⁱ in **3** are situated at the apex of the square pyramidal structures. The equatorial Cu–Cl distances in both the complexes are

much shorter [for **2**: 2.2307(12) Å and for **3**: 2.2513(12) Å] than the axial Cu–Cl distances [for **2**: 2.5597(9) Å and for **3**: 2.7037(12) Å]. The Cu(II) ions are not perfectly situated in the square plane and it is 0.322 Å and 0.184 Å out of plane towards the axial Cl⁻ ion in **2** and **3**, respectively. X-ray structure of **2** and **3** clearly reveals that two square pyramids are fused together at the apex in **2** and at the base-to-apex edge in **3** (Scheme 2).

The equatorial and axial Cu–Cl distances of **2** are comparable to those of the similar type reported complexes [7,19], where square pyramidal coordination environment around Cu(II) has been observed with a tridentate supporting ligand along with terminal/bridging chloride ions. However, Cu–Cl–Cu angle of **2** (180°) differs noticeably than the reported complex $[Cu_2(bzpy)_2Cl_3]ClO_4 \cdot 0.5H_2O$ [19] where it is 136.9(1)°. For other two reported oligomeric complexes [7b] this angle ranges from 144.57(6)° to 144.69(6)°. Other one penta-coordinated mono-chloro bridged dicopper(II) complex, $[Cu_2(py2)_2Cl_3](PF_6)$ (where py2 is bis(2-(2-pyridyl)ethylamine) [20] with the Cu(II) ions at a distorted trigonal bipyramidal geometry is also known where the long Cu–Cl distance of 2.549 Å and a Cu–Cl–Cu bridging angle of 178.0(1)° is observed.

The Cu–Cl distances of 2.2513(12) Å and 2.7037(12) and the Cu–Cl–Cu angle of 93.35(3)° in **3** are fairly consistent with the corresponding Cu–Cl distances and the Cu–Cl–Cu angles of the similar bis- μ -chloro-bridged dicopper(II) complexes with a supporting bidentate [21] or tridentate ligand [22].

The Cu–N_{py}, Cu–N_{imine} [8c,21,22] and Cu–S_{thioether} [8c,23] distances for both **2** and **3** are within the ranges found for other reported complexes. The Cu–N_{imine} distances *trans* to the equatorial Cu–Cl bond follow a trend of shorter distances like **2** > **3** [for **2**: 1.9943(19) Å and for **3**: 1.975(3) Å]. Due to this trans effect the equatorial Cu–Cl distance of **3** (2.2513(12) Å) is 0.021 Å longer than that of **2** (2.2307(12) Å) is observed.

It is necessary to mention, that **1** and **3** are the two extreme structures so far the axial Cu–Cl elongation is concerned. The equatorial Cu–Cl distances for **1** [2.2511(4)Å] and **3** [2.2513(12)Å] are almost equal while all the donor atoms of pmtpm to Cu(II) distances are shorter in **3** than **1** (see Table 2). This situation gives



Fig. 2. ORTEP view of the cationic part of 3. The thermal ellipsoids are at the 50% probability scale and the hydrogen atoms are omitted for clarity.



Scheme 2. Arrangement of polyhedra (square pyramids) for 1, 2 and 3: for 2 apex [Cl2] sharing and for 3 apex-to-base edge [Cl1-Cl1i] sharing, atom labeling is according to the X-ray structures.



Fig. 3. Electronic absorption spectra of 2 and 3 in MeCN (the inset shows the solid state reflectance spectra of 2 and 3).

Table 3Absorption spectral data for the complexes 1–3.

Complex	λ_{max} (nm) ($\epsilon\!\!\!, M^{-1}cm^{-1})^a$ in MeCN solution	λ_{\max} (nm) in solid state
1 ^b	238(8385), 277(6255), 332(11340), 724(60)	746
2	227(32080), 275 (sh, 19860), 333(28000), 752(260)	738
3	229(37800), 275 (sh, 23900), 333(24500), 657(190)	678

 $^{a}~\epsilon\,(M^{-1}\,cm^{-1})$ values for $\boldsymbol{2}$ and $\boldsymbol{3}$ are per dimer.

^b Data from Ref. [8c].

us an opportunity to conclude that pmtpm acts as a stronger donor ligand in **3** than in **1**. The greater is the in plane ligand donor strength the longer will be the axial Cu–Cl bond. In fact, with no exception here, 0.264 Å longer Cu–Cl_{axial} bond is found in **3** (2.7037(12) Å) than in **1** (2.4394(4) Å).

3.3. Electronic spectra

The electronic spectra of **2** and **3** in MeCN solution and their solid state diffuse reflectance spectra were shown in Fig. 3. The spectral data have been tabulated in Table 3. Complexes **2** and **3** display a lower energy band at 752 nm and 657 nm, respectively with low extinction coefficient values that correspond to the d-d transition. This d-d transition band at 657 nm for **3** (longest Cu-Cl_{axial} bond

distance) is 95 nm and 67 nm blue shifted than that of the complexes **2** (752 nm) and **1** (724 nm) [8c], respectively. Similar trend in the solid state diffuse reflectance spectrum of **2** and **3** has been found that display the broad d-d band centered at 738 nm and 678 nm, respectively (shown in the inset of Fig. 3; for larger view see supporting information: Fig. S3). These broad bands are the envelop of the transitions from B₁ ($d_{x^2-y^2}$) ground state to the excited A₁ (d_z^2), B₂ (d_{xy}) and E (d_{xz} , d_{yz}) states in C4v symmetry. A weakening of the axial bond along *z*-axis is expected to shift the absorptions involving electronic *z*-components to higher energies. Thus



Fig. 4. X-band EPR spectra of (a) powder sample and (b) MeCN solution of 3 at 77 K.



Fig. 5. Cyclic voltammograms (scan rate 50 mV/s) of **3** in MeCN solution of 0.1 M TBAP, using platinum working electrode. Potentials are vs. non-aquous Ag/Ag^{+} .



Scheme 3. Structures of the complexes involved in the most plausible pathway of consecutive electron transfer reaction for 3 in MeCN.

Table 4Electrochemical data^a for the complexes 2 and 3.

1.1
0.95
-
1.1

^a Potentials are vs. non-aqueous Ag/Ag⁺ reference electrode. F_c/F_c^+ couple in MeCN, $E_{1/2} = 0.436$ V, scan rate 50 mV/s, supporting electrolyte: tetra-*N*-butylammonium perchlorate (0.1 M).

^b Data from Ref. [8c].

for the solid state reflectance spectra at high temperature (298 K), the energy-averaged d–d transitions at 746, 738 and 678 nm for **1**, **2** and **3** were observed which is the expected sequence. The electronic spectra of a Cu(II) complex namely, $[Cu(L^5)_2(H_2O)]$ 'H₂O (where HL⁵ is N-(2-*chloro*-6-*methylphenyl*)*pyridine*-2-*carboxamide* and H is the dissociable amide proton) in two different geometries such as trigonal bipyramidal (solid state) and square pyramidal (solution phase) has been reported by Mukherjee and coworkers [24].

The higher energy band at ~330 nm for all three complexes with high extinction coefficient values are due to the coordinated thioether, $S(\sigma) \rightarrow Cu(II)$ charge transfer (LMCT) transition. The other higher energy intense transitions at 275 nm and 227 nm are due to the intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ charge transfer transitions (ILCT).

3.4. EPR spectra

The EPR spectra of the complexes **2** and **3** in polycrystalline solid state and in MeCN solution at 77 K and 293 K have been measured. The solid sample of **2** display two peaks at g values 2.183 and 2.053 corresponds to g_{\parallel} and g_{\perp} , respectively, while in MeCN solution it display an isotropic signal at g = 2.087. Complex **3** display similar EPR spectra (77 K, solid state: $g_{\parallel} = 2.166$, $g_{\perp} = 2.057$; 77 K in MeCN: g = 2.079 isotropic signal) that have been shown in Fig. 4. The forbidden singlet-triplet transition (Δ Ms = ±2), often detected for a dimeric copper(II) sample is only observable with high instrumental gain. This spectral behavior of the complexes are attributed to an axial symmetry with $d_{x^2-y^2}$ ground state [25] having elongated octahedral, square pyramidal or square planar coordination geometry around the Cu(II) ion. For a trigonal-bipyramidal coordination geometry around Cu(II) ion the $g_{\perp} > g_{\parallel} \approx g_{\parallel}$

trend will be followed [7,25]. The g values for these complexes are comparable to other reported binuclear bis μ -chloro bridged Cu(II) complexes [21,22]. The $g_{||}$ and g_{\perp} values reported for the complex **1** measured in the polycrystalline form at 77 K are 2.202 and 2.041, respectively thus the solid state $g_{||}$ values decreases in the order **1**(2.202) > **2**(2.183) > **3**(2.166). Thus the larger axial Cu-Cl distance, smaller $g_{||}$ value and the blue shifted ligand field transition have been observed for the complexes **1**–**3**.

3.5. Redox chemistry

The cyclic voltammograms (CV) of the complexes 2 and 3 were recorded in MeCN solvent at room temperature. Three electrode cell set up such as platinum, Ag/Ag⁺ (non-aquous) and a platinum wire as a working, reference and auxiliary electrode, respectively have been used for measurements. The cyclic voltammograms of one representative complex **3** have been shown in Fig. 5 and the electrochemical data have been tabulated in Table 4. The complexes 2 and 3 exhibit a quasireversible reductive response at $E_{1/2}$ value \approx +0.24 V versus Ag/Ag⁺ (non-aquous) correspond to Cu(II) to Cu(I) reduction. The appearance of same potential tempted us to examine whether it originates from the ligand oxidation/reduction or not. The CV of a mixture of ZnCl₂ and ligand (1:1 ratio) in MeCN does not display any response¹ at 0.24 V indicating that this $E_{1/2} \approx 0.24$ V response is not due to the ligand centered oxidation or reduction. Small differences in the ΔE_p values (86 mV, 103 mV and 116 mV for 1, 2 and 3, respectively) have been observed that increases in the order 1 < 2 < 3. The more ΔE_p value indicates more structural reorganization upon reduction to Cu(I). Thus the lowest ΔE_p value for **1** is reasonable as it can adopt a tetrahedral structure (with a dangling donor atom like shown in Scheme 3) for Cu(I) state more easily with two terminal chloride ions in it's coordination zone (less restrain) unlike the cases observed for 2 and 3 which are mono and doubly chloro bridged, respectively thus more and more restrain imposed to attain the tetrahedral geometry for reduced Cu(I) state.

Other two irreversible reductive responses at $E_{\rm pc}$ values -0.296 V and -0.493 V for **3** have been observed correspond to B \rightarrow C and C \rightarrow D transformation according to the most possible Scheme 3 (the possibility of dangling pyridine N instead of thioether S might also be possible as both will prefer Cu(I) state almost equally) shown below. The reverse scan from -0.6 V towards +1.1 V shows the anodic stripping potential at -0.215 V for **3** which is due to metallic Cu(0) to Cu(I) re-oxidation.

 $^{^1}$ No increase of current has been observed in the range +0.8 V to -0.8 V. The Cl⁻/Cl₂ oxidation at 1.1 V has been observed indicates the Cl⁻ liberation from the ZnCl₂ and ligand reaction in MeCN medium. This Cl⁻ to Cl₂ oxidation has been confirmed from the CV measurement of LiCl in MeCN that display this Cl⁻/Cl₂ potential at 1.1 V.

According to the scheme the reduction potential from $A \rightarrow B$ and from $B \rightarrow C$ are expected to be almost same for 2 and 3 (+0.243 V and -0.291 V for 2 and +0.241 V and -0.296 V for 3) as the coordination environment and the electron density around the copper center(s) responsible for reduction is almost same or can be adopted to make it same through the Cl⁻ bridge that communicate two Cu(II) ions in 2 and 3. Instead of MeCN in structure B and C for 3, Cl⁻ is there for complex 2. Thus a more cathodic potential is expected for $C \rightarrow D$ reduction in case of **2** (E_{pc} value is -0.591 V) than **3** (E_{pc} value is -0.491 V). Cu(ClO₄)₂ in organic solvent display similar cyclic voltammograms [26]. The electrochemical data for the reported µ-chloro and bis-µ-chloro bridged dicopper(II) complexes [21,22] are not available.

4. Conclusions

Following are the summary and conclusion of the present work:

- Two new chloro bridged dicopper(II) complexes, namely $[\{(pmtpm)Cu(Cl)\}_2 \ \mu-Cl\}(ClO_4) \ (2) \ and \ [\{(pmtpm)Cu\}_2(\mu-Cl)_2\}$ $(ClO_4)_2$ (3) have been characterized by means of solid and solution phase spectroscopic studies including the X-ray structures.
- Axial Cu-Cl bond elongation firmly establishes its effect on the spectral properties. Axial Cu-Cl bond distances increases in the order **1** < **2** < **3** (2.4394(4) Å, 2.5597(9) Å, 2.7037(12) Å for **1**, **2**, 3, respectively), solid state diffuse reflectance spectra display the lowest energy d-d transition (λ_{max}) in the sequence **3** < **2** < **1** (678 nm, 738 nm, 746 nm for **3**, **2**, **1**, respectively), and the g_{\parallel} tensor components for the solid samples at 77 K increase in the sequence 1 < 2 < 3 (2.202, 2.183, 2.166).

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Appendix A. Supplementary material

CCDC 776513 and 776514 contain the supplementary crystallographic data for complexes 2 and 3, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.01.068.

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