

## Dicopper(II) complexes with sulphur bridge: Syntheses, spectral and electrochemical properties

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**Abstract.** A family of dithiocarbonate sulphur bridged dinuclear copper(II) complexes containing  $[\text{Cu}_2^{\text{II}}(\mu\text{-Rx})\mu\text{-OPh}]^{2+}$  (R = Me, Et, <sup>n</sup>Pr, <sup>i</sup>Pr, <sup>n</sup>Bu, Bz; x = OCS<sub>2</sub>) core with supporting weak imidazolidine bridge has been synthesized for the first time using a *μ-bis*(tetradentate) amine phenol ligand (H<sub>3</sub>L). The ligand reacts with CuCl<sub>2</sub>·2H<sub>2</sub>O and different KRx in aqueous acetone in air affording crystalline  $[\text{Cu}_2(\mu\text{-Rx})(\mu\text{-L})]\cdot 2\text{H}_2\text{O}$  in excellent yields. Both the Cu(II)–Cu(II) and Cu(II)–Zn(II) complexes have MN<sub>2</sub>O<sub>2</sub>S coordination spheres. Taking the help of one exogenous bridging ligand (Rx<sup>−</sup>) the triply bridged Cu<sup>II</sup>–Cu<sup>II</sup> intimate complex is formed in a Schiff-base ligating environment. The ligand provides one imine and one inbuilt imidazolidine nitrogen and two phenolic bridging and terminal oxygen donors forming five- and six- membered chelate rings around each metal centre. In the pentacoordinated complexes  $[\text{Cu}_2(\mu\text{-Rx})(\mu\text{-L})]\cdot 2\text{H}_2\text{O}$ , dithiocarbonate ligands are present as exogenous bridging ligands. The presence of large polarizable sulphur atoms around each copper(II) centre significantly modify the nature of the complexes to be electroactive as detected by cyclic voltammetry, compared to the analogous exogenous acetate bridging complexes. The copper-copper magnetic interaction is dependent on the nature of different R groups and presence of S donors. Both electron transfer behaviours and magnetic properties of copper(II)-copper(II) complexes are assessed with respect to a heterodinuclear copper(II)-zinc(II) complex in identical ligating environment.

**Keywords.** Dicopper; binucleating; sulphur; electrochemical; imidazolidine.

### 1. Introduction

Synthesis of binuclear copper(II) complexes in identical ligating environments has grown considerable interest in recent years to study the inorganic perspectives of these metal centres for small molecule activation and biological catalysis. Here cooperativity between adjacent metal ions is important for their functional behaviour such as in phosphate diester cleaving agents<sup>1</sup>. The purple Cu centres in Cu<sub>A</sub> of Cco(Cytochrome C oxidase) and NOR(N<sub>2</sub>O reductase) do not belong to types known so far<sup>2</sup> and have different spectroscopic properties than the Type III sites in Hc (Hemocyanine) and Ty (Tyrosinase) owing to the presence of at least one sulphur ligand. This recently detected binuclear purple copper centre in sulphur ligating environment offers definite advantage in electron transfer reactions required for the scission of oxygen-oxygen or nitrogen-oxygen bonds<sup>3</sup>. Thus synthesis and physicochemical characterization of

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sulphur bridged suitable low molecular weight pentacoordinated dicopper complexes are important to examine the role of sulphur atoms towards molecular structure and reactivity compared to oxygen bridging. The copper(II) thiolate complexes have intrinsic tendency to suffer autoreduction of metal centre by the coordinated thiolates with the concomitant formation of disulphides<sup>4</sup>. Investigation into the reactivity behaviour of this class of molecules may give some insight into biological functioning of various dicopper (II) centres. In model dicopper (II) complexes the presence of a three atom sulphur donor bridging ligand (dithiocarbonate) in addition to the monatomic (phenolate) and five-membered heterocycle bridging (imidazolidine) is expected to show different Cu–Cu interaction for electron transfer property and magnetic interaction. This work forms part of our ongoing programme on the use of simple binucleating butterfly-like acyclic ligands for stable triply bridged dicopper (II) complexes. The work demonstrates the first authentic example of dithiocarbonate bridged dicopper (II) complexes of the  $\text{CuN}_2\text{O}_2\text{S}$  chromophoric class. Herein we report the synthesis, spectroscopic, magnetic and electron transfer properties of a family of  $[\text{Cu}_2(\mu\text{-Rx})(\mu\text{-L})]\cdot 2\text{H}_2\text{O}$  complexes.

## 2. Experimental

### 2.1 Materials

$\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  was obtained from BDH, Mumbai, India.  $\text{ZnCl}_2\cdot 2\text{H}_2\text{O}$ , 1-butanol, benzyl alcohol, carbon disulphide, triethylenetetramine were purchased from SD Fine Chemicals, Mumbai, India and salicylaldehyde was purchased from SRL, Mumbai, India. 1-Propanol and 2-propanol were purchased from E Merck AG, Darmstad, Germany and Sarabhai Chemicals, Vadodara, India respectively. Commercial tetraethylammonium bromide was converted into pure tetraethylammonium perchlorate (TEAP) by an available procedure<sup>5</sup>. Dinitrogen gas for electrochemical work was purified by successive bubbling through alkaline dithionite and concentrated sulphuric acid.

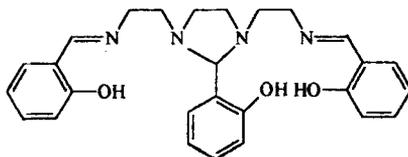
### 2.2 Physical measurements

Elemental analyses (C,H,N) were performed by the microanalytical laboratory of the Indian Association for the Cultivation of Science, Calcutta with a Perkin-Elmer model 240C elemental analyzer. Infrared spectra were obtained on a Perkin-Elmer 883 spectrophotometer ( $200\text{--}400\text{ cm}^{-1}$ ) with samples prepared as KBr pellets. Electronic spectra (DMF, 1 cm quartz cell) were recorded on Shimadzu UV/VIS/NIR 3100 ( $190\text{--}3200\text{ cm}$ ) spectrophotometer. Room temperature magnetic susceptibilities in the solid state were measured using a home built Gouy balance fitted with a Polytronic d.c. power supply and a PAR 155 vibrating sample magnetometer. The experimental magnetic susceptibilities were corrected for the diamagnetic response using Pascal's constants. Solution electrical conductivity was measured using a Unitech type U131C digital conductivity meter with a solute concentration of about  $10^{-3}\text{ M}$ . Electrochemical measurements were made using the PAR model 370–4 electrochemistry system incorporating the following components: 174 A polarographic analyzer, 175 universal programmer, RE 0074 X–Y recorder, 173 potentiostat and 377 cell system. All electrochemical experiments were performed under a pure dry nitrogen atmosphere. A planar Beckman 39273 platinum-inlay working electrode, a platinum-wire auxiliary

electrode and an aqueous calomel electrode (SCE) were used in a three-electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for the junction contributions.

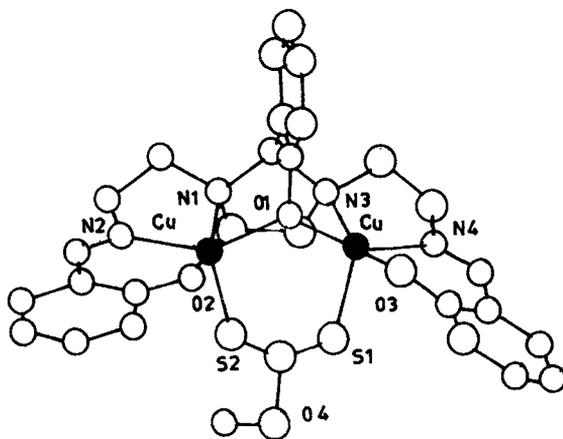
### 2.3 Synthesis of ligands and complexes

2.3a *Synthesis of H<sub>3</sub>L*: The ligand H<sub>3</sub>L (1) used in the present work has been prepared according to the published procedure<sup>6</sup> and the purity is checked by comparing melting points, IR and NMR spectra. Different O-alkyldithiocarbonates were prepared following a textbook procedure<sup>7</sup>.



**imidazolidine- $\mu$ -bis(salen), H<sub>3</sub>L (1)**

2.3b *Metal complexes*: A general procedure was followed for the preparation and isolation of all complexes of type [Cu<sub>2</sub>( $\mu$ -Rx)( $\mu$ -L)]·2H<sub>2</sub>O and [CuZn( $\mu$ -Rx)( $\mu$ -L)]·2H<sub>2</sub>O (2; R = Me).



Details are given below for representative cases. Sequential metalation procedures have been employed successfully in preparing mixed-metal complexes<sup>8</sup>, without isolating the mononuclear precursors. The present ligand H<sub>3</sub>L also forms hetero-bimetallic complexes directly.

2.3c ( $\mu$ -O-ethylthiocarbonato)(triethylenetetraminetrisalicylidiminato) dicopper(II) dihydrate. [Cu<sub>2</sub>( $\mu$ -EtS)( $\mu$ -L)]·2H<sub>2</sub>O: An aqueous solution (10 ml) of copper(II) chloride dihydrate (375 mg, 2.2 mmol) was dropwise added to a magnetically stirred acetone solution (20 ml) of H<sub>3</sub>L (500 mg, 1.09 mmol) during 15 min. After 10 min of stirring an aqueous solution (10 ml) of potassium O-ethylthiocarbonate (175 mg, 1.1 mmol) was slowly added to the previous solution. After complete addition a green

compound was seen separating in solution. The whole reaction mixture was further stirred magnetically for 1 h at room temperature. The resultant green solid was filtered through a G 4 frit and washed thoroughly with ice-water, acetone and hexane. The solid compound thus obtained was finally dried *in vacuo* over  $P_4O_{10}$ . Yield 563 mg (70%). Found: C, 48.60; H, 4.85; N, 7.45; Cu, 17.06. Calc. for  $C_{30}H_{36}N_4O_6S_2Cu_2$ : C, 48.71; H, 4.87, N, 7.57; Cu, 17.20%.

2.3d ( $\mu$ -O-ethylthiocarbonato)(triethylenetetraminetrisalicylidiminato) copper(II) zinc(II) dihydrate.  $[CuZn(\mu-Etx)(\mu-L)] \cdot 2H_2O$ : An aqueous solution (15 ml) of copper(II) chloride dihydrate (186 mg, 1.09 mmol) was dropwise added to a magnetically stirred acetone solution (20 ml) of  $H_3L$  (500 mg, 1.09 mmol) during 15 min followed by an aqueous solution of zinc(II) chloride dihydrate (150 mg, 1.09 mmol). After 10 min of stirring an aqueous solution (10 ml) of potassium O-ethylthiocarbonate (175 mg, 1.1 mmol) was slowly added to the previous solution. Immediately after complete addition a green compound was seen separating in solution. The whole reaction mixture was further stirred magnetically for 1 h at room temperature. The resultant green solid was filtered through a G 4 frit and washed thoroughly with ice-water, acetone and hexane. The solid compound thus obtained was finally dried *in vacuo* over  $P_4O_{10}$ . Yield 565 mg (70%). Found: C, 48.51; H, 4.82; N, 7.58; Cu, 8.52; Zn, 8.91%. Calc. for  $C_{30}H_{36}N_4O_6S_2CuZn$ : C, 48.59, H, 4.86; N, 7.56; Cu, 8.58; Zn, 8.83%.

### 3. Results and discussion

The electronic spectral data, magnetic moment values and cyclic voltammetric data are collected in tables 1 and 2 respectively.

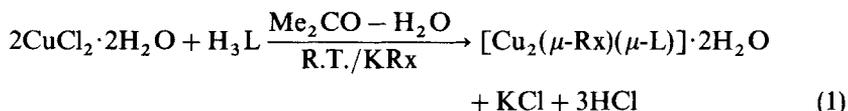
#### 3.1 Ligand design and synthesis

By introducing two bridging spacer groups in the form of an imidazolidine ring and a pendent phenolic group inside the saltrien ligand framework, the fused *bis*(salen) ligand (**1**) is obtained. The salen winged butterfly-type ligand (**1**) could take up one metal ion in each wing and fold further along the spacer line with the help of triatomic S,S exogenous bridging. The free ligand has a folded minimum energy conformation ( $-25.5 \text{ kJ mol}^{-1}$  as calculated using desktop molecular modeller program). The four donor atoms, coordinating to each copper(II) centre, have unequal basicities as two nitrogens and oxygens are either originating from different donor functions (imine, imidazolidine) or take part in bridging (phenol). The ligand architecture helps the exogenous bridging by facilitating a distortion from square planar geometry and apical coordination for fifth site.

The binucleating Schiff base ligand, trisalicylidetriethylenetetramine ( $H_3L$ , **1**) has been synthesized according to a published procedure<sup>6</sup>. The ligand can easily be prepared by a simple low temperature Schiff base condensation in alcohol medium at high dilution. Like other binucleating compartmental macrocyclic ligands, the present ligand design provides multiple bridging ability with endogenous imidazolidine nitrogen ring and phenolic oxygen donors, but unlike macrocyclic ligands, the present acyclic ligand is not restricted to only square planar geometry around metal ions.

### 3.2 Synthesis and characterization of dicopper(II) and copper(II)-zinc(II) complexes

The reaction of  $H_3L$  (1) with copper(II) acetate monohydrate in a 1:2 molar ratio in presence of different dithiocarbonates leads to the formation of dinuclear pentacoordinated neutral complexes. The formation of a  $[Cu_2^{\text{II}}(\mu-S_2COR)(\mu\text{-phenoxo})]^{2+}$  core from mononuclear  $CuCl_2 \cdot 2H_2O$  salt involves the introduction of two metal ions within the ligand cavity as shown in (1). The reaction of  $CuCl_2 \cdot H_2O$  with  $H_3L$  in presence of  $NEt_3$  and in absence



of  $KR_x$  gives the  $[Cu_2^{\text{II}}(\mu\text{-phenoxo})]^{3+}$  core quantitatively and exogenous bridging by  $Cl^-$  in case of  $[Cu_2(\mu-L)]Cl \cdot 2H_2O$  has not been observed<sup>9</sup>. Possibly this tetracoordinated dicopper(II) entity is formed first in the solution and then reacted with exogenous S, S bridging ligand. The compounds are moderately soluble in DMF or DMSO and are stable in presence of air and moisture. Solution electrical conductivity measurements show the electro-neutral character of these complexes. The complexes are amorphous in nature. So far we have not been successful in growing X-ray quality single crystals for molecular structure determination. Recently we have structurally characterized an analogous O, O bridged  $[CuZn(\mu-OAc)(\mu-L)] \cdot 2H_2O$  compound<sup>10</sup>, whose gross molecular geometry is expected to be similar to these complexes.

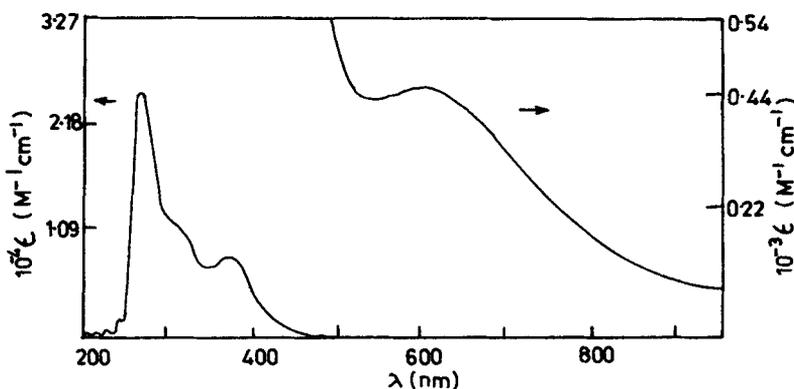
### 3.3 Infrared and electronic spectra

The IR spectra of the complexes show strong C=N stretching frequency of the terminal imine functions at  $\sim 1635\text{ cm}^{-1}$ . The C-O vibration for the free ligand occurs at  $\sim 1267\text{ cm}^{-1}$ . The complexes have characteristic  $\mu$ -bridging phenolic C-O stretching frequencies in the range of  $1530\text{--}1537\text{ cm}^{-1}$ <sup>11-13</sup>. In all the complexes a broad band around  $3400\text{ cm}^{-1}$  suggests the presence of lattice water. No broad band centered at  $\sim 3550\text{ cm}^{-1}$  is observed, indicating the absence of bound aqua ligand. In the region  $1200\text{--}1000\text{ cm}^{-1}$  the spectra of the new complexes are very similar and show three strong absorptions due to vibrations arising from the xanthate ligands. The bands for free xanthate anion are  $\approx 1190, 1112$  and  $1052\text{ cm}^{-1}$ . In complexes these are shifted to  $1204\text{--}1196, 1141\text{--}1125$  and  $1042\text{--}1035\text{ cm}^{-1}$ <sup>14-16</sup>.

The electronic spectral (UV/VIS) data are tabulated in table 1 and the spectrum of  $[Cu_2(\mu\text{-Etx})(\mu-L)] \cdot 2H_2O$  is shown in figure 1. The d-d absorption band of most copper(II) complexes with coordinated N, O donor ligands generally appears between 500 and 700 nm with  $\epsilon < 100\text{ M}^{-1}\text{ m}^{-1}$ . The corresponding band in the present family of complexes is red shifted in the range of 585–655 nm possibly due to a distorted square pyramidal geometry with smaller d-d splitting. The higher value of  $\epsilon$  is observed due to either the loss of centrosymmetry or the Laporte-forbidden d-d transitions which take some intensity from their mixing with LMCT states associated with sulphur  $\rightarrow$  Cu(II) transitions. All the complexes exhibit essentially identical spectral features with a broad d-d absorption band. In similarly constituted complexes the dithiocarboxylate bridging registers absorption in the slightly longer wavelength region compared to the acetato bridging. The peak in the 364–375 nm region may presumably be assigned to a phenolate  $\rightarrow$  Cu<sup>II</sup> charge transfer transition. Any  $Im^- \rightarrow$  Cu<sup>II</sup> charge transfer transition is absent in all the reported complexes.

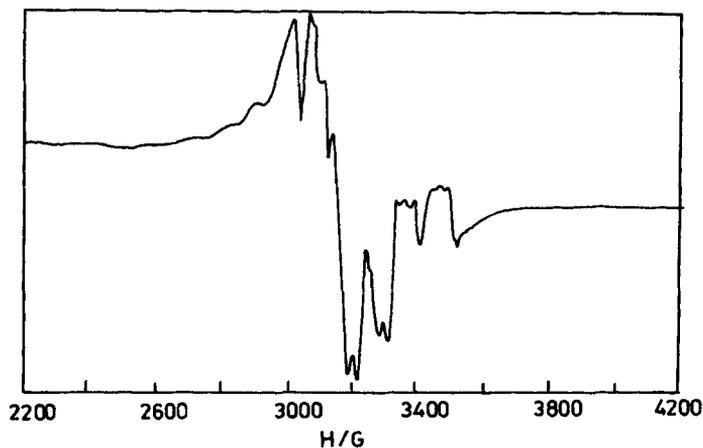
**Table 1.** Magnetic moments and electronic spectral data in dimethylformamide solution at 298 K.

Compounds	$\lambda_{\max}$ , nm ( $\epsilon$ , $M^{-1} \text{ cm}^{-1}$ ) <sup>a</sup>	$\frac{\mu_{\text{eff}}}{\mu_B/\text{Cu}}$
$[\text{Cu}_2(\mu\text{-Mex})(\mu\text{-L})] \cdot 2\text{H}_2\text{O}$	621(412), 372(9115), 307 (11885), 278(8470)	1.15
$[\text{Cu}_2(\mu\text{-Etx})(\mu\text{-L})] \cdot 2\text{H}_2\text{O}$	601(425), 373(8290), 319 (10930), 256(25310)	1.49
$[\text{Cu}_2(\mu\text{-}^n\text{Prx})(\mu\text{-L})] \cdot 2\text{H}_2\text{O}$	652(440), 375(10249), 311 (14422), 271(25432)	1.40
$[\text{Cu}_2(\mu\text{-}^i\text{Prx})(\mu\text{-L})] \cdot 2\text{H}_2\text{O}$	612(467), 372(9722), 314 (11112), 267(28292)	1.70
$[\text{Cu}_2(\mu\text{-}^n\text{Bux})(\mu\text{-L})] \cdot 2\text{H}_2\text{O}$	635(334), 372(8199), 318 (8672), 266(25178)	1.70
$[\text{Cu}_2(\mu\text{-Bzx})(\mu\text{-L})] \cdot 2\text{H}_2\text{O}$	649(489), 375(7932), 317 (9607), 265(21972)	1.17
$[\text{CuZn}(\mu\text{-Etx})(\mu\text{-L})] \cdot 2\text{H}_2\text{O}$	589(515), 364(6920), 325 (9501), 263(18265)	1.65

**Figure 1.** Electronic spectra of  $[\text{Cu}_2(\mu\text{-Etx})(\mu\text{-L})] \cdot 2\text{H}_2\text{O}$  in dimethylformamide solution at 298 K.

### 3.4 Magnetism and electron paramagnetic resonance spectra

The room temperature magnetic moments of this class of complexes shown in table 1 were determined with the help of a Gouy balance using powdered polycrystalline samples. The observed magnetic moments per copper at room temperature of pentacoordinated triply bridged dinuclear copper(II) complexes are less than the spin only value (1.73 BM). This suggests the operation of a magnetic spin exchange interaction, which is dependent on the presence, and nature of the third exogenous bridging group in the complex. Lower magnetic moment is observed in case of S, S bridging compared



**Figure 2.** X-band (9.12 GHz) EPR spectra of  $[\text{Cu}_2(\mu\text{-Etx})(\mu\text{-L})]\cdot 2\text{H}_2\text{O}$  in dimethylformamide glass at 77 K.

to O, O bridging from acetate<sup>9</sup> in the same molecule. The imidazolidine bridge is not expected to contribute to magnetic exchange in these compounds. The different coordination geometries around each copper centre are responsible for different magnetic behaviour. A strong magnetic interaction requires both suitable orientation of the magnetic orbitals and superexchange properties of the bridging atoms. The room temperature magnetic moment (table 1) of heterodinuclear Cu–Zn complex is typical of pentacoordinated mononuclear copper complex showing absence of any magnetic interaction between two metal centres<sup>17</sup>.

The polycrystalline X-band EPR spectrum of  $[\text{Cu}_2(\mu\text{-Etx})(\mu\text{-L})]\cdot 2\text{H}_2\text{O}$  is isotropic at 300 K with  $g_{\text{av}} = 2$ . The corresponding spectrum in DMF glass at 77 K is axial with  $g_{\parallel} = 2.383$  ( $A_{\parallel} = 115$  G) and  $g_{\perp} = 2.064$  (figure 2). A very weak “half field” signal in the  $g = 4$  region is also observed here similar to the acetato (O, O) bridged complex<sup>9</sup>, and is characteristic of a triplet state and  $\Delta M_s = 2$  transition. The nature of the spectrum and the  $g$  values are typical of a variety of bridged copper(II) dimers<sup>18</sup>. Both the  $g_{\parallel}$  and  $g_{\perp}$  resonances are split by the hyperfine coupling between the unpaired electron on copper(II) and  $I = 3/2$  nuclear spin of copper. The coordinated nitrogen ( $I = 1$ ) hyperfine structure due to one nitrogen in the  $g_{\perp}$  region with  $a_{\perp} = 30$  G further complicates the spectrum. Three well-resolved ligand hyperfine lines due to one coordinating nitrogen were only evident in the glass spectra. The observed coupling to the nitrogen atom indicates greater covalent nature of the Cu–N bond in presence of xanthato (S, S) bridging, because this type of superhyperfine splitting is absent in case of acetato (O, O) bridging. The copper hyperfine splitting constant values are small compared to a typical tetragonal spectrum and more or less identical to that of  $[\text{Cu}_2\text{F}_2(\text{bnpy})_2]^{2+}$ <sup>19</sup>. These results suggest that here the actual EPR active species is  $[\text{Cu}_2(\mu\text{-Etx})(\mu\text{-L})]\cdot 2\text{H}_2\text{O}$  dimer itself. No ligand (sulphur) centred spectrum is observed for a possible unpaired electron density transfer of type  $\text{Cu}^{\text{II}}\text{-SSCOR} \leftrightarrow \text{Cu}\text{-SSCOR}$  and subsequent disulphide bond formation. This information therefore indicates that the unpaired spin on the copper centres interact and magnetically couple across the imidazolidine, phenolate and xanthate bridges.

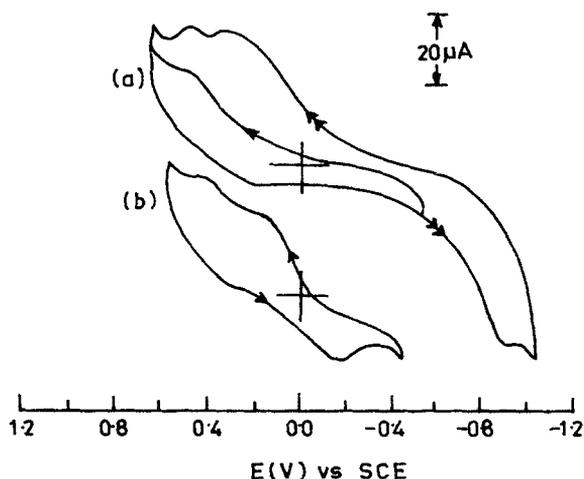
### 3.5 Molecular structure

In both the cases the metal is bonded in the distorted square pyramidal  $MN_2O_2S$  fashion with a typical NOS three-point bridging. The three-point bridging mode of binding of the present ligand system in presence of exogenous bridging has been authenticated for a heteronuclear Cu–Zn complex by single crystal X-ray structure determination<sup>10</sup>. Replacement of a Zn(II) ( $d^{10}$ , spherical) by a Cu(II) ( $d^9$ , Jahn–Teller distorted) in these  $Cu_2$  complexes might distort the overall structure. Each tetradentate half of the ligand incorporates metal ions in a distorted square planar geometry and the axial bridging from S, S donors completes the square pyramidal arrangement. The imine and imidazolidine nitrogen pair is coordinated *cis* to each other, so also the bridging and non-bridging phenolic oxygen pair. Of the four chelate rings around two metal ions two are six-membered and two are five-membered.

### 3.6 Electrochemistry

The electron-transfer behaviour of the complexes have been studied in dimethylformamide solution by cyclic voltammetry (CV) using a platinum working electrode at 298 K. Cyclic voltammograms were recorded in the potential range from +1.20 to –1.20 V vs saturated calomel electrode (SCE) in dimethylformamide (DMF). The scan rate was  $50 \text{ mVs}^{-1}$  in all cases. Tetraethylammonium perchlorate (TEAP) was used as supporting electrolyte. Representative voltammogram is shown in figure 3 and obtained peak potentials are summarized in table 2.

The cyclic voltammograms of all the studied xanthate bridged complexes reveal irreversible and ill defined cathodic reduction peaks in the range from +0.34 to –1.02 V vs SCE. In the cyclic voltammograms of Cu–Zn complex two oxidation and reduction peaks are observed. These peaks are assigned to the one-electron processes  $Cu^{II}(S^-)Zn^{II} \rightarrow Cu^{II}(S^{\cdot-})Zn^{II}$  and  $Cu^{II}(S^-)Zn^{II} \rightarrow Cu^I(S^-)Zn^{II}$ . For all other  $Cu_2$  complexes similar type of electron transfer behaviour is observed for oxidation to



**Figure 3.** Cyclic voltammograms (scan rate  $50 \text{ mVs}^{-1}$ ) of  $10^{-3}$  solutions. (a)  $[Cu_2(\mu\text{-Etx})(\mu\text{-L})] \cdot 2H_2O$  and (b)  $[CuZn(\mu\text{-Etx})(\mu\text{-L})] \cdot 2H_2O$  in dimethylformamide at a platinum electrode at 298 K.

**Table 2.** Cyclic voltammetric data in dimethylformamide solution

Complex	$E_{pc,1}/V$	$E_{pc,2}/V$	$E_{pa,1}/V$	$E_{pc,2}/V$
$[Cu_2(\mu-Mex)(\mu-L)] \cdot 2H_2O$	-0.1	-0.46	+0.69	+0.30
$[Cu_2(\mu-Etx)(\mu-L)] \cdot 2H_2O$	+0.2	-0.89	+0.49	+0.32
$[Cu_2(\mu^n-Prx)(\mu-L)] \cdot 2H_2O$	+0.13	-0.89	+0.46	+0.29
$[Cu_2(\mu^i-Prx)(\mu-L)] \cdot 2H_2O$	+0.16	-0.89	+0.45	+0.30
$[Cu_2(\mu^n-Bux)(\mu-L)] \cdot 2H_2O$	—	-1.02	+0.65	+0.37
$[Cu_2(\mu-Bzx)(\mu-L)] \cdot 2H_2O$	+0.19	-0.89	+0.39	+0.17
$[CuZn(\mu-Etx)(\mu-L)] \cdot 2H_2O$	+0.34	-0.11	+0.39	+0.16

$Cu^{II}(S^-)Cu^{II}$  and reduction to  $Cu^I Cu^{II}$  congeners, as against the formation of  $Cu^{II}(S^-)Cu^I$  and  $Cu^I(S^-)Cu^I$  species. In case of Cu–Zn complexes two step single electron reductions are not possible for metal center reductions. This therefore suggests that one step ligand based ( $S^-$ ) oxidation do occur at the same time. All the complexes exhibit nearly broad anodic peaks in the range from +0.16 to +0.69 V vs SCE.

These observations are typical of  $\mu$ -hydroxo bridged dicopper(II) complexes and have been found in electroanalytical studies of similar or analogous compounds<sup>20-22</sup>. Like  $HO^-$  and  $MeO^-$  bridges, the  $ROCS_2^-$  bridging in the present complexes have an inferior affinity to bind electrogenerated  $Cu^I$  centres and are expected to dissociate from the coordination sphere upon reduction. These type of electron transfers often show an irreversible nature. Irreversibility of redox processes in metal complexes in electrochemical experiments are attributed to changes in the coordination geometry or coordination number (eg. solvent coordination/dissociation) upon change of the oxidation state or even to the expulsion of metal ions from coordination sphere<sup>23</sup>. During electron transfer the structure of Cu coordination polyhedra changes considerably. After a complete cyclic scan, a re-association to the original xanthato bridged complex is most unlikely within the cyclic voltammetric time frame.

#### 4. Acknowledgements

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