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New dicopper(II/II) complexes with oxygen and sulfur bridges: synthesis, characterization and cyclic voltammetric studies[†]

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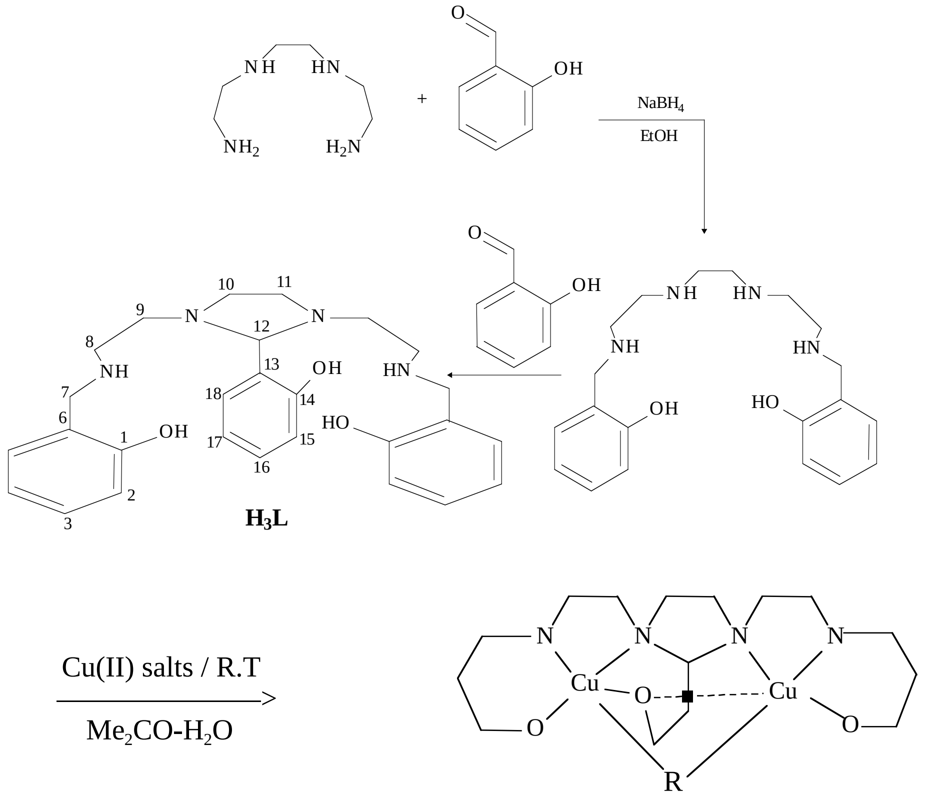
A new family of acetato oxygen and dithiocarbonato sulfur bridged dinuclear copper(II) complexes with weak imidazolidine bridge support is described for the first time; these complexes are studied for possible synthetic models of dicopper active sites.

Synthesis of binuclear copper(II/II) complexes in identical ligating environments has been increasingly used 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 understanding their functional behaviour such as in phosphate diester cleaving agents[1]. The purple Cu centres in Cu_A of Cco and N_2O reductase do not belong to types known so far[2] and have different spectroscopic properties than the Type 3 sites in Hc (hemocyanine) and Ty (tyrosinase) owing to the presence of at least one sulfur ligand. This recently detected binuclear purple copper centre in sulfur ligating environment offers a definite advantage in electron transfer reactions required for the scission of oxygen–oxygen or nitrogen–oxygen bonds[3]. Another Type 3 copper enzyme is catechol oxidase. The protein isolated from photogenic materials catalyses the oxidation of catechols to quinones without acting on tyrosine[4]. XAS investigations have revealed that the active site consists of a dinuclear copper(II/II) centre coordinated by N/O donor ligands[5].

The parent Schiff base ligand, H_2L' is obtained from an imine condensation of triethylenetetramine and salicylaldehyde as reported elsewhere[6]. The reduced compartmental ligand, H_3L was prepared following a two step synthetic protocol of reducing H_2L' with $NaBH_4$ and finally reacting with salicylaldehyde as shown in Scheme I. The ligand was characterized by mpt, IR, ^1H NMR and mass spectral analyses. The absence of >CH=N– hydrogen resonances at about 8 ppm and the presence of new benzylic CH_2 resonances at about 4 ppm in ^1H NMR indicate the reduction of the unsaturated Schiff base. The formation of the imidazolidine bridge from carbaldehyde group of salicylaldehyde is indicated by the characteristic proton at 3.78 ppm. In FAB mass spectrum the maximum molecular peak is observed at *m/z*, 459 which corresponds to the molecular ion $[C_{27}H_{34}N_4O_3]$, (calculated molecular weight = 462.58). The reactions of H_3L in acetone–water medium at room temperature with copper(II) acetate and chloride in a 1:2 molar ratio in absence and presence of different dithiocarbonates[7] lead to the formation of dinuclear pentacoordinated neutral $[Cu_2^{II/II}(\mu\text{-}L)(\mu\text{-}R)].2H_2O$ [R = $MeCO_2$, $MeOCS_2$, $EtOCS_2$, $^{n}PrOCS_2$] complexes. The compounds are moderately soluble in DMF or DMSO and stable in presence of air and moisture. Solution electrical



Scheme 1

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

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 $[CuZn(\mu\text{-}L^1)(\mu\text{-}OAc)].2H_2O$ compound[8], whose gross molecular geometry is expected to be similar to the present complexes.

The IR spectra of the complexes show strong C=N stretching frequency of the terminal imine functions at ~ 1635 cm^{-1}. The C–O vibration for the free ligand occurs at ~1267 cm^{-1}.[9] The complexes have characteristic μ-bridging phenolic C–O stretching frequencies in the range of 1530–1537 cm^{-1}. [10–12] In all the complexes a broad band around 3400 cm^{-1} suggests the presence of lattice water. The d–d absorption band of most copper(II) complexes with coordinated N,O donor ligands generally appears between 500 and 700 nm with $\varepsilon < 100$ lit mol^{-1} cm^{-1}. The corresponding band in the present family of complexes is redshifted in the range of 585–655 nm possibly due to a distorted square pyramidal geometry with smaller d–d splitting. The higher value of ε is observed due to either the loss of centrosymmetry or the Laporte-forbidden d–d transitions take some intensity from their mixing with LMCT states associated with sulfur → Cu(II) transitions. All the complexes exhibit essentially identical spectral features with a broad d–d absorption band. In similarly constituted complexes the dithiocarboxylato 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 $\rightarrow Cu^{II}$ charge transfer transition. Any imidazolate $\rightarrow Cu^{II}$ charge transfer transition is absent in all the reported complexes confirming further the presence of imidazolidine bridge.

The room temperature magnetic moments (μ_B) of this class of complexes per copper(II) were less than the spin only value (1.73 B.M.). 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. A lower magnetic moment is observed in case of S, S′ bridging compared to O, O′ bridging from acetate[13] in the same molecule.

The cyclic voltammograms of all the studied xanthato bridged complexes reveal irreversible cathodic reduction peaks in the range from + 0.26 to – 0.94 V vs SCE in dimethylformamide. (R = $MeOCS_2$, $EtOCS_2$, $^nPrOCS_2$; $E_{pc,1}$, $E_{pc,2}$: +0.26, –0.94; +0.23, –0.93; +0.19, –0.79 V) The cyclic voltammograms of Cu_2 complexes show two redox peaks for the one-electron processes $Cu^{II}(S^-)Cu^{II} \rightarrow Cu^{II}(S^{\cdot})Cu^{II}$ (oxidation) and $Cu^{II}(S^-)Cu^{II} \rightarrow Cu^{I}(S^-)Cu^{II}$ (reduction), as against to the formation of $Cu^{II}Cu^{I}$ and $Cu^{I}Cu^{I}$ species. Since two steps reductive only responses are not possible for an analogous Cu–Zn control complex one reduction is therefore considered for bridging ligand oxidation. All the complexes exhibit anodic peaks in the range from –0.05 to + 0.45 V vs SCE in dimethylformamide. (R = $MeOCS_2$, $EtOCS_2$, $^nPrOCS_2$; $E_{pa,1}$, $E_{pa,2}$: +0.44, +0.05; +0.45, -0.03; +0.32, –0.05 V) The nature of the voltammograms are typical for binuclear copper(II) complexes but are slightly broad compared to binuclear manganese(III) complexes of H_3L[14]. The corresponding acetato bridged complex is electrochemically silent in the above mentioned potential ranges. These observations are typical of μ-hydroxo bridged dicopper(II/II) complexes and have been found in electroanalytical studies of similar or analogous compounds[15–17]. Like HO^- and MeO^- bridges, the $ROCS_2^-$ bridging in the present complexes have an inferior affinity to bind electrogenerated Cu^I centres and expected to dissociate from the coordination sphere upon reduction. These types of electron transfers often show an irreversible nature. During electron transfer the structure of Cu coordination polyhedra changes considerably. After a complete cyclic scan, a reassociation to the original xanthato bridged complex is most unlikely within the cyclic voltammetric time frame (~20 s at a scan rate of 50 mVs^{-1}).

Experimental

Synthesis of 2-(2′-hydroxybenzyl)-2,3-bis[3′-aza-4′-(2″-hydroxyphenyl)prop-1′-yl]-1,3-imidazolidine, H_3L: To a hot solution of triethylenetetramine (1.372 g, 9.38 mmol) in ethanol (200 mL) was added a hot solution of salicylaldehyde (2.29 g, 18.75 mmol) in ethanol (100 mL). While the solution was still hot, $NaBH_4$ (0.726 g, 19.20 mmol) was added in small quantities over 10 min. The solution was heated (ca 50 ^{0}C) and stirred for an additional 2 h. and the solvent was removed under reduced pressure, leaving a white residue. NH_4OAc (1.5 g) in 50 mL water was added to the white residue. The aqueous mixture was then extracted with chloroform (3 × 75 ml). The organic fractions were combined, washed with distilled water (3 × 75 ml) and then dried over anhydrous $MgSO_4$. The solution was filtered and the chloroform removed on a rotary evaporator to give a yellow oil. The oil was dried *in vacuo* at 60 ^{0}C for 24 h. The oil was diluted again by adding metahnol (40 ml). Salicylaldehyde (1.15 g, 9.42 mmol) in methanol (15 ml) was dropwise added into the ice-cooled solution of the reduced oil. The mixture was stirred for an hour and then was allowed to warm to room temperature. The off white compound was separated out, filtered and washed with hexane and water, and dried *in vacuo* over P_4O_{10}. TLC of the white compound in $CHCl_3$ indicates the formation of H_3L as solid compound only from the second step of reaction. Yield 2.60 g (60 %). Melting point 150 ^{0}C.

A general procedure was followed for the preparation and isolation of all dicopper complexes.

$[Cu_2(\mu\text{-}L)(\mu\text{-}MeOCS_2)].2H_2O$: An aqueous solution (15 mL) of copper(II) chloride dihydrate (0.37 g, 2.17 mmol) was dopwise added to a magnetically stirred methanol solution (20 ml) of H_3L (0.5 g, 1.08 mmol) during 15 min. After 10 min of stirring an aqueous solution (10 ml) of potassium O-methyldithiocarbonate (0.16 g, 1.09 mmol) was slowly added to the previous solution and stirred magnetically for 1 h at room temperature. The green solid was filtered through a G4 frit and washed thoroughly with ice-water, methanol and hexane and dried *in vacuo* over P_4O_{10}. Yield 0.512 g (65 %). (Found: C, 47.55; H,5.37; N,7.25; Cu,17.55. $C_{29}H_{38}N_4O_6S_2Cu_2$ requires C, 47.72; H, 5.25; N, 7.68; Cu, 17.41 %)

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