Synthesis and characterisation of phenoxo bridged dinuclear complexes of copper(II)

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Abstract. A series of model complexes for the type III site, in oxidised hemocyanin, containing $Cu_2(\mu\text{-}OPh)^{3+}$ core have been synthesised using a heptadentate ligand (H_3L) formed from the Schiff base condensation of triethylenetetramine and salicylaldehyde. The ligand provides one imine and one inbuilt imidazole nitrogen and two phenolic oxygen donors with both five- and six-membered chelate rings to each metal centre. In the pentacoordinated complexes $[Cu_2(L)X] \cdot nH_2O$, a third exogenous bridging ligand is present. The TG curve indicates the loss of lattice water molecules between 70 and 125°C. The residue after decomposition is CuO above 550°C. The g values of the X-band EPR spectrum of $[Cu_2 L(\mu\text{-}OAc)] \cdot 2H_2O$ in methanol glass (77 K) are typical of a variety of bridged copper(II) dimers. The copper–copper magnetic interaction is dependent on the presence and nature of X in these complexes.

Keywords. Dicopper(II) complexes; phenoxo-bridging; EPR; magnetic properties.

1. Introduction

The synthesis and physicochemical characterisation of tetra and pentacoordinated dicopper complexes have made an impact on bioinorganic chemistry, since the spectral and magnetic features provided new insights into the structure of dioxygen binding in naturally occurring copper proteins. Both hemocyanin and tyrosinase contain a dicopper site which binds or activates dioxygen as peroxide in different coordination modes (Lerch 1981; Solomon *et al* 1992). The two copper ions are bivalent in the dioxygen binding state (so called oxyhemocyanin). The bridged dicopper(II) systems like antiferromagnetically coupled tetra-μ-carboxylato dicopper(II) complexes are well studied (Melnik 1982; Kato and Muto 1988). The symmetrically dibridged species like $[Cu_2^{II}(\mu\text{-}X)_2]^{2+}$ and asymmetrically dibridged species with a $[Cu_2^{II}(\mu\text{-}X)(\mu\text{-}Y)]^{2+}$ core are also well studied (Sorrell *et al* 1985; Davis and Lippard 1985; Wang *et al* 1992). In all these class of complexes the magnetostructural properties are of immense importance considering their relevance to the type III active centre, viz., oxyhemocyanin. In model dicopper(II) complexes the presence of a three-atom bridging ligand in addition to the monoatomic or tetraatomic one is expected to give a short Cu....Cu separation and a larger Cu-O-Cu angle suitable for promoting a strong antiferromagnetic interaction between the two copper(II) centres. This work forms part of our ongoing programme on the use of simple binucleating acyclic ligands for stable di- and tribridged binuclear complexes of copper(II).

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2. Experimental

All the chemicals and solvents used in syntheses were of reagent grade and used without further purification unless stated otherwise. Solution electrical conductivity and electronic spectra were obtained using a Unitech type U131C digital conductivity meter and a Shimadzu UV3100 UV/VIS/NIR spectrophotometer respectively. Magnetic susceptibilities in the solid state were measured with a Gouy balance fitted with a Polytronic d.c. power supply. The IR spectra in the solid state (KBr discs) and thermal data were recorded on a Perkin–Elmer 883 spectrophotometer and Shimadzu DT40 thermal analyzer respectively. X-band EPR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar flask for measurement at 77 K (liquid dinitrogen). The spectra were calibrated with diphenylpicrylhydrazyl (dpph) ($g = 2.0037$). Copper(II) was estimated volumetrically by sodium thiosulphate (Vogel 1969). The amount of water in all the complexes were determined from TG analysis. Elemental nitrogen was determined by Dumas method.

2.1 *Synthesis of* H_3L

The ligand H_3L (1) used in this work has been prepared according to the published procedure (Das Sarma and Bailer 1955) and the purity checked by comparing melting points.

1, H_3L

tbp

● Cu

2, $[Cu_2L(OAc)] \cdot 2H_2O$

● Cu^{sqp}

3, $[Cu_2L(OAc)] \cdot 2H_2O$
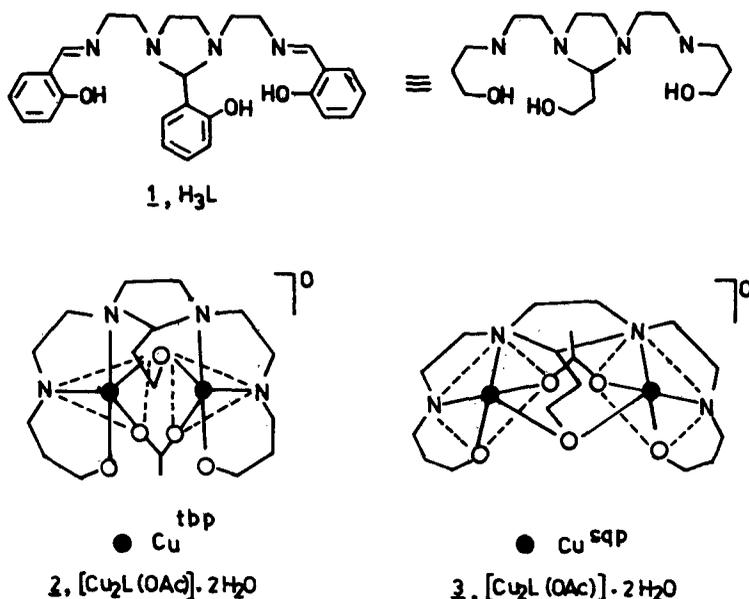
2.2 *Syntheses of complexes*

A general procedure was followed for the preparation and isolation of all $[Cu_2L]X$. nH_2O (X = ClO_4, Cl) and $[Cu_2L(X)] \cdot nH_2O$ (X = AcO, N_3, NO_3) complexes. Details are given below for representative examples of each class.

2.2a [$Cu_2 L$]$ClO_4 \cdot 2H_2O$: An aqueous methanolic solution of copper(II) perchlorate hexahydrate (800 mg, 2·16 mmol) was added to a methanolic (40 cm^3) solution of $H_3 L$ (460 mg, 1·0 mmol). The reaction mixture was stirred magnetically initially for 0·5 hours and after addition of 1 ml of NEt$_3$, the stirring was continued for another 0·5 hours. Upon subsequent concentration in air, a greenish-blue compound separated, which was washed with ice-water, diethyl ether and hexane. The solid compound thus obtained was finally dried *in vacuo* over $P_4 O_{10}$. Yield 70%. The [$Cu_2 L$]$Cl \cdot 2H_2O$ was prepared similarly from cupric chloride.

2.2b [$Cu_2 L(OAc)$]$\cdot 2H_2O$: An aqueous solution of copper(II) acetate monohydrate (300 mg, 2·1 mmol) was added to a methanolic (40 cm^3) solution of $H_3 L$ (460 mg, 1·0 mmol). The reaction mixture was stirred magnetically for 1 hour. On concentration in air a light green compound separated, which was washed thoroughly with water and methanol and finally dried *in vacuo* over $P_4 O_{10}$. Yield 80%. [$Cu_2 L(N_3)$]$\cdot H_2O$ and [$Cu_2 L(NO_3)$]$\cdot 2H_2O$ were prepared from [$Cu_2 L$]$ClO_4 \cdot 2H_2O$ by reacting with NaN$_3$ and from copper(II) nitrate trihydrate.

3. Results and discussion

The analytical results, molar conductivities and magnetic moments are given in table 1.

3.1 *Preparation of complexes*

The ligand reported in this paper belongs to a family of dinucleating Schiff base ligands and has easy synthetic accessibility. It can form chelates with relatively rigid five-membered and more flexible six-membered rings respectively, at each metal site. The reaction of $H_3 L$ with copper(II) perchlorate hexahydrate and copper(II) acetate monohydrate in a 1:2 molar ratio leads to the formation of dinuclear tetra and penta coordinated cationic and neutral complexes. In pentacoordinated complexes, like [$Cu_2 L(OAc)$]$\cdot 2H_2O$, the copper environments are either trigonal bipyramid (2) or square pyramid (3). The possible square–pyramidal molecular geometry is shown in figure 1.

Table 1. Analytical, molar conductivity[a] and magnetic moment[b] data.

Complex	Colour	Found (calc.)%		Λ_M (ohm^{-1} cm^2 mol^{-1})	μ_{eff} μ_B/Cu
		Cu	N		
[$Cu_2 L$]$ClO_4 \cdot 2H_2O$	Blue-green	17·70 (17·73)	7·65 (7·81)	98	1·63
[$Cu_2 L$]$Cl \cdot 2H_2O$	Blue-green	19·15 (19·44)	8·45 (8·57)	105	1·70
[$Cu_2 L(\mu\text{-}OAc)$]$\cdot 2H_2O$	Green	18·60 (18·76)	8·40 (8·27)	non-electrolyte	1·51
[$Cu_2 L(\mu\text{-}NO_3)$]$\cdot 2H_2O$	Light green	18·50 (18·68)	10·20 (10·29)	non-electrolyte	1·62
[$Cu_2 L(\mu\text{-}N_3)$]$\cdot H_2O$	Dark green	19·55 (19·79)	15·45 (15·26)	non-electrolyte	1·45

[a]In methanol solution, 1:1 electrolyte has Λ_M in the range 80–115 ohm^{-1} cm^2 mol^{-1}. [b]In the solid state at 298 K; $\mu_B \approx 9.27 \times 10^{24}$ JT^{-1}.
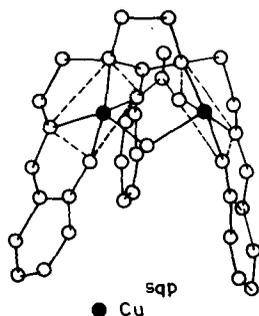
sqp
● Cu

Figure 1. The tentative ball and stick arrangement of the $[Cu_2L(\mu\text{-OAc})]\cdot 2H_2O$ molecule showing square–pyramidal geometry around each copper centre.

The formation of a $[Cu_2(\mu\text{-phenoxo})(\mu\text{-O}_2CMe)]^{2+}$ core from $[Cu_2(\mu\text{-O}_2CMe)_4 (H_2O)_2]$ involves an opening of the tetra-μ-acetato cage as below $[H_3L = \text{tri-salicylidene triethylenetetramine}]$.

$$[Cu_2(O_2CMe)_4(H_2O)_2] + H_3L \xrightarrow[\text{H}_2\text{O}]{\text{MeOH}} [Cu_2L(O_2CMe)]\cdot 2H_2O$$

$$+ 3MeCO_2H \qquad (1)$$
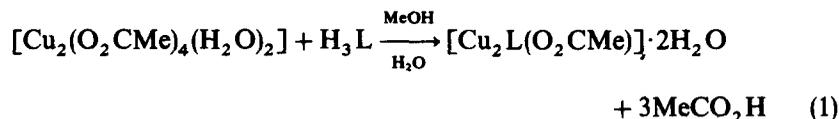
The reaction of $[Cu(H_2O)_6](ClO_4)_2$ with H_3L in presence of NEt_3 forms the $[Cu_2(\mu\text{-phenoxo})]^{3+}$ core quantitatively and exogenous bridging by Cl^- in case of $[Cu_2L]Cl\cdot 2H_2O$ has not been observed. The complexes are moderately soluble in methanol, acetonitrile, chloroform, DMF or DMSO, and are stable for several days in solution in the presence of air and moisture. Solution electrical conductivity measurements show the expected pattern. Because of the amorphous nature of the complexes, attempts to grow an X-ray quality single crystal have been unsuccessful so far.

3.2 *Infrared and visible spectra*

The IR spectra of the two types of complexes show strong C=N stretching vibration frequency of the terminal imine functions of Schiff base ligand at $\approx 1635\,\text{cm}^{-1}$. The C–O and aromatic C–C stretching vibrations occur ≈ 1265 and $\approx 1400\,\text{cm}^{-1}$ respectively. In $[Cu_2L]ClO_4\cdot 2H_2O$ the v_3 vibration of the uncoordinated perchlorate anion appears as a strong single unsplit band around $110\,\text{cm}^{-1}$ (Hathaway 1987). A broad band around $3400\,\text{cm}^{-1}$ suggests the presence of lattice water. No broad band centred at $\approx 3550\,\text{cm}^{-1}$ is observed indicating the absence of bound aqua ligand. For complex $[Cu_2L(OAc)]\cdot 2H_2O$, the CO_2^- stretch vibrations appear at $1530(v_{as})$ and $1395\,\text{cm}^{-1}(v_s)$. From the value of $\Delta v = v_{as} - v_s = 135\,\text{cm}^{-1}$, we can deduce that the acetate anion acts as a bidentate bridging anion, bridging the two metal ions (Nakamoto 1978; Deacon and Phillips 1980). The asymmetric azide stretching frequency of the $[Cu_2L(N_3)]\cdot H_2O$ complex appears at $2063\,\text{cm}^{-1}$ in KBr and is comparable to that at $2042\,\text{cm}^{-1}$ in metHc(N_3) (McKee *et al* 1984). The single IR active lower energy asymmetric stretching mode and lack of v_s indicates symmetrical μ-1,3-azide bridging, according to the expected trends (Karlin *et al* 1987; Casella *et al* 1993). This presumably occurs to maintain the complementary phenoxo bridge and to avoid the likely steric congestion of the alternative 1,1-bridging mode.

The electronic spectra of all the complexes were measured in methanol and DMF. All the complexes exhibit broad and featureless *d–d* bands in the 580–640 nm region. The moderately intense band observed in the near-UV region is due to the overlap of the transition of the azomethine with the charge transfer band from phenolic oxygen to the vacant *d*-orbital of the Cu^{II} (Okawa *et al* 1993).

3.3 *Thermal behaviour*

The thermal decomposition of $[Cu_2 L(\mu\text{-}OAc)] \cdot 2H_2O$ was studied using TG and DTA techniques. The elimination of the lattice water molecules is clearly observable. The TG curve shows a single step, first mass loss between 70 and 125°C, which corresponds exactly to the release of water content (found: 5·25; calc.:5·32%). The comparatively lower temperature of water loss shows that these are not coordinated to the copper atoms. A TG plateau is present from 130 to 190°C. The anhydrous complex decomposes in three steps between 190–265 and 450–550°C and in a slower process between 265 and 440°C. The absence of TG plateau during decomposition indicates that stable intermediates are not formed. The final, thermally stable residue is CuO (found 23·80, calc.:23·48%) above 550°C.

3.4 *Electron paramagnetic resonance*

The polycrystalline *X*-band EPR spectrum of $[Cu_2 L(\mu\text{-}OAc)] \cdot 2H_2O$ at 77 K shows an isotropic signal around $g = 2$ region. The g values of the X-band spectrum in a methanol glass are shown in figure 2. A very weak "half-field" signal in the $g = 4$ region, characteristic of triplet state and $\Delta M_g = 2$ transition, has also been observed. The nature of the spectrum and the g values are typical of a variety of bridged copper(II) dimers (Sanyal *et al* 1992). It may be noted that zero field splitting is not possible when the system has only one unpaired electron. Here in the strongly coordinating solvent, methanol, the bridged structure is retained. The hyperfine
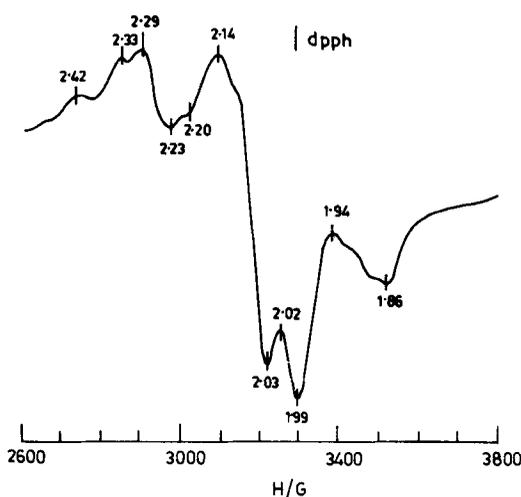

Figure 2. The *X*-band (9·095 GHz) EPR spectrum of $[Cu_2 L(\mu\text{-}OAc)] \cdot 2H_2O$ in methanol glass at 77 K.

splitting constant values are also small compared to the typical tetragonal spectrum. The spectrum is essentially identical with that of $[Cu_2 F_2(bnpy)_2]^{2+}$ (Lee and Holm 1993). These results suggest that the actual EPR-active species is $[Cu_2 L(\mu\text{-}OAc)] \cdot 2H_2O$ dimer itself.

3.5 *Magnetic behaviour*

The room temperature magnetic susceptibilities of the complexes were measured with a Gouy balance by using powdered samples. The observed magnetic moments of pentacoordinated triply-bridged complexes for each copper atom at room temperature are less than the spin-only values (1·73 B M). This suggests the operation of an antiferromagnetic spin-exchange interaction in these complexes. The variable-temperature magnetic susceptibility measurements for selected complexes are in progress, which would reveal quantatively the magnitudes of spin exchange interaction. The copper–copper magnetic interaction is dependent on the presence and nature of the third bridging group in the complexes. In all these complexes an inbuilt imidazole molecule, besides the phenolate group, bridges the metal centres. The imidazole bridge is not expected to contribute to magnetic exchange in these compounds (Hoffmann 1971; Hay *et al* 1975). The different coordination geometries around each copper centre are also responsible for different magnetic behaviour. The stereochemistry around the two copper centres may closely approximate either a trigonal-bipyramid ($d_{z^2}^1$ ground state) or a square-pyramid ($d_{x^2-y^2}^1$ ground state). A strong magnetic interaction requires both good orientation of the magnetic orbitals and good superexchange properties of the bridging atom(s). Phenolate bridging present in all these complexes is probably the best mediator of superexchange. The geometrical distortion of bridging oxygen from trigonal planar (sp^2) to pyramidal configuration (sp^3) leads to reduction of antiferromagnetic interaction (Mazurek *et al* 1985).

4. Conclusion

New asymmetrically tribridged dicopper(II) complexes using a simple acyclic Schiff base ligand with a pendant phenolate group have been prepared and characterised. Single crystal X-ray structural and variable temperature susceptibility results would be of significance for understanding the magnetostructural relationships in this new class of complexes of chemical and biological importance. We are presently extending the co-ordination chemistry of H_3L to mixed-metal species.

Acknowledgement

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