SHORT PAPER

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A novel doubly phenoxo-bridged Cu(II) trimer: synthesis, crystal structure and low-temperature magnetic behaviour

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A novel doubly phenoxo-bridged Cu(II) trimeric complex, [trinuclear diperchlorato {2,2´-[1,3-propanediylbis (nitriloethylidyne)]bisphenolato}-tricopper] has been synthesised with a tetradentate Schiff base ligand and characterised by IR, electronic spectra, X-ray structure and variable temperature magnetic moments. The Cu1 centre has square pyramidal geometry where as the Cu2 centre achieves square planar geometry. The dihedral angle between the two planes, Cu1 – O1 – O2 and Cu2 – O1 – O2 is 26.50°.

Keywords: tetradentate ligand, oxygen and nitrogen donor sites, copper(II) ion

The investigation of physical and physicochemical properties of transition metal complexes containing two or more metal centres in close proximity is a very important research area, which has led to the proposal of several models for some biochemical processes.[1,2] Many metalloenzymes contain two divalent transition metal ions in close proximity and in most cases the two metal centres cooperate with each other[3] and they have contributed to a better knowledge of oxygen transport as well as of some industrial catalytic processes.[4,5] Binuclear copper(II) complexes are of general interest as they are very useful model systems for biological studies and also for deriving magneto-structural correlations.[6-8] The known Cu(II)–phenolate complexes usually exhibit coordination numbers ranging from 4 to 6, as is typical for the coordination chemistry of Cu(II). The phenolates in most of these compounds usually are incorporated as part of multidentate ligand systems[9,10] and so complexes with simple, exogenous phenolate ligands are less common.[11] In this connection, recently some efforts to synthesise trinuclear copper complexes have been communicated.[12,13] The relationship between the peculiar spectroscopic properties of polynuclear complexes and their structural features is crucial to characterise protein models and can help in the understanding of reaction mechanisms or reaction details at the active site. Hightlighting this phenomenon, Bermejo and co-workers reported two interesting μ-phenoxo bridged Copper(II) trimeric complexes.[4,13] However, trinuclear doubly phenoxo-bridged metal complexes of transition metals are still very sparse in the literature.[14]

Herein, we describe the single crystal X-ray structure, spectroscopic study and low-temperature magnetic properties of a novel doubly phenoxo-bridged trinuclear copper(II) complex (**1**), with a tetradentate Schiff base ligand (H_2L) in which the central copper atom posses square planar and the two terminal copper atoms share square pyramidal geometry.

The ligand H_2L was synthesised by refluxing a 25 ml methanolic solution of 2-hydroxy acetophenone (2 mmol) and 1,3-diamino propane (1 mmol) for an hour. The resulting mixture gave a brown solution containing the liquid ligand which is used for the synthesis without further purification.

Table 1 Crystal data and structure refinement for **1**

Empirical formula	$C_{38}H_{40}Cl_2Cu_3N_4O_{12}$
Formula weight	1006.26
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Unit cell dimensions	a = 12.86(1) Å α = 90°
	b = 10.76(2) Å β = 99.67(1)°
	c = 14.32(3) Å γ = 90°
Volume	1955.6(6) Å^3
Z	2
Density (calculated)	1.709 mg/m^3
Absorptin coefficient	1.823 mm^{-1}
F(000)	1026
Crystal size	0.40 x 0.40 x 0.16 mm^3
Theta range for data collection	2.33 to 25.17°
Reflections collected	6085
Independent reflections	5853[R(int) = 0.0370]
Max. and min. transmission	0.7591 and 0.5292
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5853/0/270
Goodness-of-fit on F^2	1.020
Final R indices [I>2σ(I)]	$R1$ = 0.0571, $wR2$ = 0.1303
R indices (all data)	$R1$ = 0.1079, $wR2$ = 0.1548
Largest diff. Peak and hole	0.981 and –0.736 e.Å^{-3}

Table 2 Selected bond lengths [Å] and angles [°] for **1**

Cu(1)–O(2)	1.920(3)	Cu(1)–O(1)	1.937(3)
Cu(1)–N(2)	1.957(3)	Cu(1)-N(1)	1.965(3)
Cu(1)–O(3)	2.618(4)	Cu(1)–Cu(2)	2.946(6)
Cu(2)–O(1)	1.939(3)	Cu(2)–O(2)	1.969(3)
O(2)–Cu(1)–O(1)	78.16(12)	O(2)–Cu(1)–N(2)	91.63(14)
O(1)–Cu(1)–N(2)	169.54(15)	O(2)–Cu(1)–N(1)	166.10(13)
O(1)–Cu(1)–N(1)	88.79(13)	N(2)–Cu(1)–N(1)	101.19(15)

The ORTEP representation of the trinuclear unit for **1** is shown in Fig. 1 with important bond lengths and angles summarised in Table 2. Complex **1** crystallises in the monoclinic system with space group $P2(1)/n$. There are two types of geometrically different copper(II) centres, with a N_2O_3 donor set for Cu1 and an O_4 donor set for Cu2. In the trimeric unit, the copper atoms are held together by doubly μ_2-phenolate oxygen of the tetradentate Schiff base ligand. In this structure, the Cu1…Cu2 distance is 2.946(6) Å, and the

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

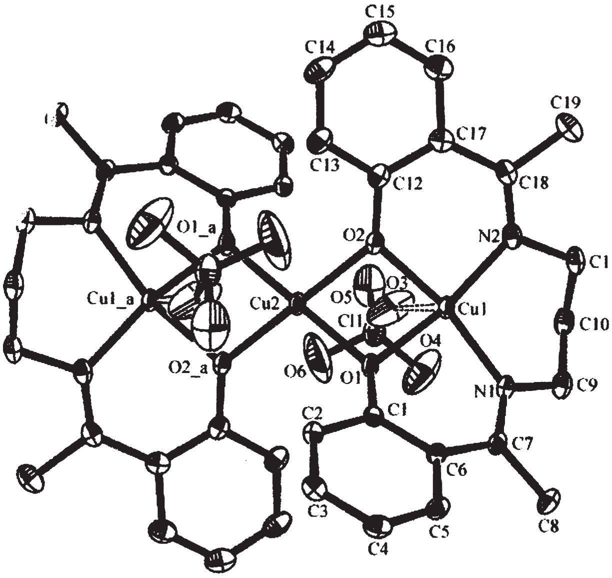

Fig. 1 An ORTEP plot of complex **1** drawn with 40% probability level.

Cu1–O1–Cu2 and Cu1–O2–Cu2 angles are 98.94(12) and 98.51(13)° taking Cu1–O1, Cu2–O1, Cu1–O2 and Cu2–O2 distances 1.937(3), 1.939(3), 1.920(3) and 1.969(3) Å, respectively.

In complex **1**, the Schiff base behaves as a N_2O_2 donor set and one perchlorate ion is joined to each of the terminal copper atoms with a monodentate orientation.

The geometry of the Cu1 centre is best described as a distorted (4+1) (NNOO + O) square based pyramid. The four atoms constituting the basal plane are the two nitrogen (N1 and N2) atoms and the two oxygen (O2 and O1) atoms of the Schiff base. The axial site is occupied by the O3 atom of the coordinated perchlorate ion. The Cu1 atom lies not in the basal plane but slightly out of it at a distance of 0.07 Å. In the basal plane, the average bond distances (Å) are Cu1–N1 = 1.965(3), Cu1–N2 = 1.957(3), Cu1–O1 = 1.937(3) and Cu1–O2 = 1.920(3). The axial distance is, Cu1–O3 = 2.618(4) Å, which is slightly longer than the basal bond lengths. The deviation from the square pyramidal geometry is also indicated by the bond angles involving the atoms in the *cis* positions which vary from 78.16(12) to 101.19(15)° as well as the angles involving the trans positions that vary to a large extent from 166.10(13) to 169.54(15)°.

The geometry around the Cu2 atom can be described as a (4O) (O+O+O+O) square planar. The Cu2 centre sites on a symmetry centre having the CuO_4 chromophore. The square plane is formed by the O1 and O2 atoms of one ligand and the symmetry equivalent O1_a and O2_a atoms of the other ligand. The basal bond distances are 1.939(3) and 1.969(3) Å for Cu2–O1 and Cu2–O2 respectively. The O1–Cu2–O1_a and O2–Cu2–O2_a angles are exactly 180.0°.

The infrared spectrum of **1** is consistent with the structural data presented in this paper. The band at 2936 cm^{-1} is due to imine stretching. The phenolic C=O stretching gives bands at 1274 and 1286 cm^{-1}. Bands in agreement with coordinated perchlorate anions could also be observed at, 1172, 1161–1086, 969, 650, 455 and 445 cm^{-1}. Ligand coordination to the copper centre is substantiated by two bands appearing at 465 (medium) and 355 (strong) cm^{-1}, attributable to ν(Cu–N) and ν(Cu–O), respectively.[15]

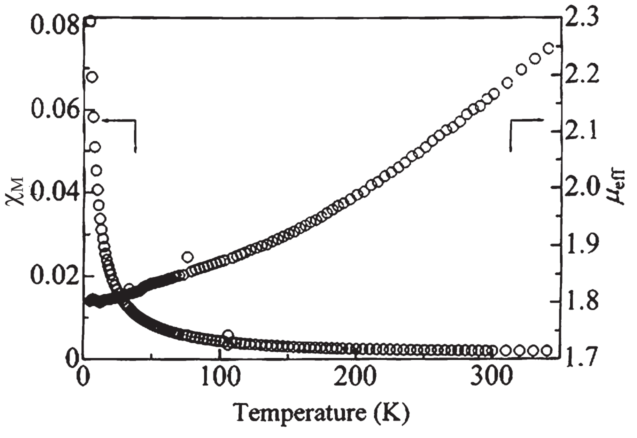

Fig. 2 Plot of temperature dependence of χ_M for complex **1**.

The electronic spectrum of **1** was recorded in methanol and displays two strong absorption bands at about 225 and 276 nm. These are clearly charge transfer in origin. The UV absorption band observed at 378 nm can be assigned to the charge transfer from the ligands to the Cu(II), transition. The band for an LMCT transition of the Cu–O–Cu skeleton is masked here by the other bands. The title complex shows absorption maxima in the range 610–620 nm. For the pentacoordinated Cu(II) complexes this spectral feature is typical for Cu(II) complexes with square-pyramidal or distorted square-pyramidal geometry, which generally exhibits a band in the range 550–660 nm range.

The solid-state ESR spectrum of **1** at room temperature exhibits only one broad signal at $g = 2.10$ and it does not vary on cooling. However, in acetonitrile solution of **1** four peaks are observed at room temperature, which are considered to be isotropic.

The room temperature magnetic moment $\mu_{eff} = 2.25\ \mu_B$ for complex **1** is considerably smaller than the expected value (3 μ_B) for three coupled Cu(II) ions, and it decreases considerably upon cooling of complex **1**. This is characteristics of significant antiferromagnetic interaction between Cu(II) ions within the trinuclear complex. The magnetic calculation is done with the susceptibility equation based on $H = -2J(S_1S_2+S_2S_1)$.

$$\chi_M = (Ng2\beta^2/4KT)\ [1+\exp(-2J/KT) + 10\exp(J/KT)]/[1+\exp(-2J/KT) + 2\exp(J/KT)] + N\alpha \quad (1)$$

Where χ_M denotes the susceptibility per trinuclear complex and Nα is the temperature independent paramagnetism. As shown in Fig. **2**, a strong antiferromagnetic spin-exchange interaction exists among the nearest Cu(II) centres within the molecule.

The study of magneto-structural correlation was carried out considering di-phenoxo-bridged Cu(II) complexes.[16] Recently, Thomson and coworkers derived the magneto-structural relationship for bis(phenoxide)-bridged binuclear Cu(II)complexes, $-J = 31.95\alpha - 2462$ cm^{-1} where α is the Cu1 – O1 (Phenol) – Cu2 angle.[17.] For the present complex, α is 98.9(1)° and the $-J$ value predicted by the equation should be 697.85. It is very much higher than the expected data. The dihedral angle between the two planes, Cu1 – O1 – O2 and Cu2 – O1 – O2 is 26.50°.

Di-phenoxo bridged complexes having a small α value (α less than 77°) could show a crossover from antiferromagnetism to ferromagnetism but it is still not known in the literature.[17]

Experimental

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of the material should be prepared and should be handled with care.

Synthesis of 1: To a methanolic solution of copper(II) perchlorate (2 mmol, 0.741 mg), 2 mmol of the ligand (HL) was added with stirring. Several days later good quality brown square-shaped crystals of **1** were separated out. They were filtered, washed with methanol–water mixture (1:1) and dried. Yield: 55%.

Analytical results of **1**: $C_{38}H_{40}Cl_2Cu_3N_4O_{12}$: C, 45.62; H, 4.09; N, 5.62; Cu, 18.97%. Found: C, 45.31; H, 4.00; N, 5.56; Cu, 18.93%.

Crystallographic data: $C_{38}H_{40}Cl_2Cu_3N_4O_{12}$, monoclinic, space group $P2(1)/n$, T = 293(2) K, a = 12.863(1), b = 10.767(2), c = 14.324(3) Å, α = 90, β = 99.67(1), γ = 90^o, V = 1955.6(6) Å^3, Z = 2, D_c = 1.709 mg/m^3, μ = 1.823 mm^{-1}, 5853 unique reflections, $2.33 \leq \theta \leq 25.17^o$, 270 parameters, $WR(F^2)$ = 0.1079 for all data, R = 0.0571 for 5853 data with $I > 2\sigma(I)$.

A single crystal was mounted on a CAD 4 diffractometer for data collection at 293 K and solved by direct methods using the SHELXTL PLUS[18] system and refined by a full-matrix least-squares methods based on F^2 using SHELXL93.[19]

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