

Crystal Structure of a Novel μ -Hydroxo Copper(II) Piperazine-Phenol Complex containing a Short Copper-Copper Distance and displaying Weak Exchange Coupling

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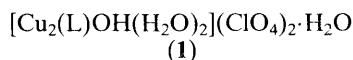
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The crystal structure of a binuclear Cu^{II} complex which contains both μ -phenoxo and μ -hydroxo bridging groups as well as two terminal piperazine N and one water O atoms on each Cu shows a very short Cu-Cu distance [2.872(2) Å] and an unusual pyramidal geometry around the phenoxo O atom; this complex is unusual in that no net antiferromagnetic coupling is evident and reasons are put forward to explain this reduced coupling.

A number of binuclear copper(II) complexes containing both binucleating ligands and single μ -hydroxo bridging ligands have recently been synthesized.^{1,2} One of the chief reasons for such studies is to prepare complexes capable of modelling the Type 3 Cu-Cu site in copper proteins and enzymes such as hemocyanin and tyrosinase. Spectroscopic and EXAFS studies on the oxidized 'met' form of these biomolecules

reveal active site geometries in which each Cu atom is four-co-ordinate with terminal *N*-histidine co-ordination, exogenous bridging ligands (*e.g.* halide, azide), and endogenous bridging ligands.³ The latter is probably an OR⁻ (*e.g.* tyrosine or serine) or an OH⁻ group. A Cu-Cu separation of *ca.* 3.5 Å and co-planar equatorial bridging geometry leads to the characteristic diamagnetism of these centres which results

from very strong antiferromagnetic coupling of the single electron on each Cu^{II} .⁴ The model μ -hydroxo complexes referred to above likewise generally display medium to strong antiferromagnetic coupling leading in some cases to overall diamagnetism. Many of the models also contain endogenous phenoxo or alkoxo bridges as part of the binucleating ligand, and it is difficult to apportion relative contributions to the exchange coupling from the two different super-exchange pathways.^{1,5}



In the present paper we describe a related complex $[\text{Cu}_2(\text{L})\text{OH}(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) in which LH is a 2,6-dipiperazine derived *p*-chlorophenol ligand (shown in Figure 1). This blue-green compound was obtained in a study of the co-ordination of Cu^{II} to a selective Cu-binding polymer, SIROREZ-Cu (see Figure 1),⁶ and to 'monomeric' fragments of the type LH.⁷ In contrast to other μ -hydroxo Cu^{II} complexes (see Table 1), compound (**1**) does not show any intramolecular antiferromagnetic coupling. The magnetic and spectral properties are: μ_{Cu} (295 K) = 1.94 μ_{B} ; λ_{max} (H_2O) 614 (ϵ 170 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 388 nm (ϵ 350); e.s.r. (dimethylformamide, 77 K) g_{\parallel} 2.25, g_{\perp} 2.06, A_{\parallel} $146 \times 10^{-4} \text{cm}^{-1}$. The first visible absorption band is of d-d character while the second is due to $\text{Cu} \leftarrow$ phenolate charge transfer.⁴ The e.s.r. parameters are fairly typical of tetragonally distorted Cu^{II} centres although the A value is smaller than expected for {N,O} co-ordination which may indicate some distortion from tetragonal symmetry.⁸ A broad, weak, ill-defined line observed at half-field is probably indicative of some dipolar coupling within Cu-Cu pairs.⁴ The magnetic moment remains independent of temperature in the range 300 to 80 K. A small increase in μ_{Cu} then occurs as the temperature decreases yielding a plateau between *ca.* 60 to 20 K followed by a more rapid decrease to 1.8 μ_{B} at 4.2 K. The corresponding χ_{Cu}^{-1} vs. T plot is Curie-like except for very gentle curvature in the middle temperature region. These magnetic data point to essentially uncoupled Cu^{II} ions with perhaps a small ferromagnetic contribution and very weak intermolecular antiferromagnetism or zero-field splitting below 20 K. As indicated above, this behaviour contrasts markedly with the reduced μ_{Cu} values and typical antiferromagnetic behaviour displayed by other single-hydroxo bridged systems (Table 1). The structure of the compound reveals some of the reasons for such differences.[†]

The asymmetric unit of this structure consists of two half molecules of $[\text{Cu}_2(\text{OH})(\text{C}_{18}\text{H}_{28}\text{ClN}_4\text{O})_2\text{H}_2\text{O}]^{2+}$, thus giving rise to two crystallographically distinct molecules. The counter ions are perchlorate ions. The unit cell also has four molecules of water of crystallization. Details of the molecular

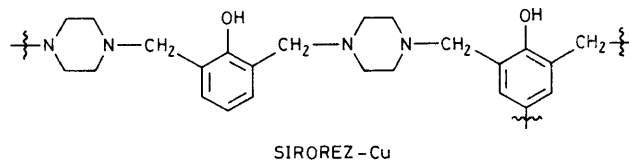
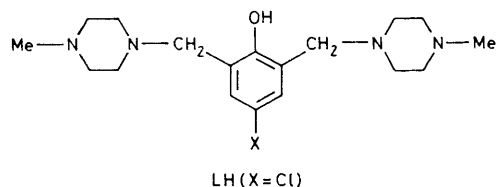


Figure 1

structure and labelling scheme are shown in Figure 2. Both molecules have the same gross stereochemistry but differ in minor detail. The pentadentate ligand, L, adopts a boat configuration in which the piperazine rings form the sides while the phenoxo ring forms the bottom of the boat. Consequently, when both nitrogen atoms of each piperazine co-ordinate to Cu, as is found, the $[\text{N}_2\text{Cu}(\text{OH})(\text{OPh})\text{N}_2]$ moiety lies at quite a steep angle (48.4° [42.7°]) (figures in square brackets relate to the second molecule) relative to the phenoxo plane. This contrasts with the more commonly observed geometry^{1,2,5} in which the bridging phenoxo (or alkoxo) O utilizes planar trigonal orbitals. In the present case the phenoxo O adopts a distorted pyramidal geometry with, presumably, a remaining lone-pair of electrons. Each Cu has square-pyramidal geometry, the fifth position being occupied by water molecules, the latter disposed *cis* to each other. The Cu-Cu distance is the shortest yet observed for binucleated species while the Cu-OH-Cu $\{96.5(4)^\circ$ [$96.4(5)^\circ$]} and Cu-OPh-Cu $\{91.7(4)^\circ$ [$91.4(4)^\circ$]} angles yield a flat almost square Cu_2O_2 moiety. The two piperazine nitrogen atoms are displaced 0.645(9) [0.722(9)] and 0.338(10) [0.718(9)] Å from the CuO_2N_2 best-plane.

In attempting to correlate structure with magnetism we note first that in the more common coplanar 'trigonal' phenoxo bridged complexes the antiferromagnetic coupling is much stronger than for (**1**), even though the Cu-Cu distance is significantly shorter in (**1**). This is also observed in dihydroxo bridged complexes where J has been found to correlate linearly with both the Cu-O-Cu angle and the Cu-Cu distance (smaller angle, smaller Cu-Cu distance, increased ferromagnetic contribution, and hence more positive J).^{9,10} The magnetic and structural data for (**1**) demonstrates that phenoxo bridged species also fit this pattern. What is evident, however, from the structures of (**1**) but not from the structural information on hydroxo bridged complexes is that the decreasing Cu-O-Cu angle is accompanied by an increasing dihedral angle between the C-O bond of the phenol and the Cu_2O_2 plane. In other words, the bonding to the oxygen atom is apparently shifting from trigonal planar (sp^2) to trigonal pyramidal (sp^3). This will presumably also be true for the hydroxide oxygen atom as the Cu-OH-Cu angle is narrow. Since the dominant pathway for super-exchange will involve σ -type overlap between the $d_{x^2-y^2}$ magnetic orbital on Cu and these ligand orbitals,¹⁰ it might be expected that the non-planarity of the orbitals on the bridging oxygen atom will produce a minor perturbation compared to the effects of the Cu-O-Cu angle and Cu-Cu distance unless the interaction of the remaining lone pair on O with out-of-plane Cu orbitals is

[†] Crystal data: $\text{C}_{18}\text{H}_{35}\text{Cl}_3\text{Cu}_2\text{N}_4\text{O}_{13}$, $M = 749.0$, orthorhombic, $Pmc2_1$ (from successful refinement), $a = 12.309(6)$, $b = 15.848(9)$, $c = 14.959(8)$ Å, $U = 2918.1$ Å³, $Z = 4$, $D_c = 1.70$, $D_m = 1.71(3)$ g cm^{-3} , $\mu(\text{Cu-K}\alpha) = 49.06 \text{cm}^{-1}$, $\lambda = 1.5418$ Å, crystal dimensions: $0.131(100, \bar{1}00) \times 0.075(001, 00\bar{1}) \times 0.025(010, 0\bar{1}0)$ mm, $R = 0.052$ and $R_w = 0.055$ for 1985 reflections with $I \geq 3\sigma(I)$ collected on a Philips PW1100 diffractometer.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table 1. Some representative mono μ -hydroxo Cu–Cu complexes containing binucleating ligands.^a

Complex	$r(\text{Cu–Cu})$ /Å	Cu–OH–Cu angle/°	Cu–OR–Cu angle/°	J/cm^{-1}	Ref.
$[\text{Cu}_2\text{L}(\text{OH})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (1)	2.87	96.5	91.7	0 ^b	This work
$[\text{Cu}_2\text{L}^{(2a)}(\text{OH})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	2.93	97.1	100.4	–142	1
$[\text{Cu}_2\text{L}^{(14)}(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$	3.14	110.3	—	–32 ^c	d
$[\text{Cu}_2\text{C A}(\text{OH})](\text{ClO}_4)_3$	3.64	141.6	—	–410	f
$[\text{Cu}_2(\text{macro})(\text{OH})](\text{BF}_4)_3$	3.38	132.2	—	–410	f
$[\text{Cu}_2(\text{N}_6\text{O})(\text{OH})](\text{BF}_4)_2$	3.05	103.6	101.9	–210	5

^a This is not an exhaustive list; abbreviations are those used in the relevant references. ^b Possible weak ferromagnetic contribution.

^c Only 90–300 K susceptibility data recorded. ^d Ref. 2, ch. by S. M. Nelson. ^e Ref. 2, ch. by S. J. Lippard. ^f Ref. 2, ch. by Y. L. Agnus.

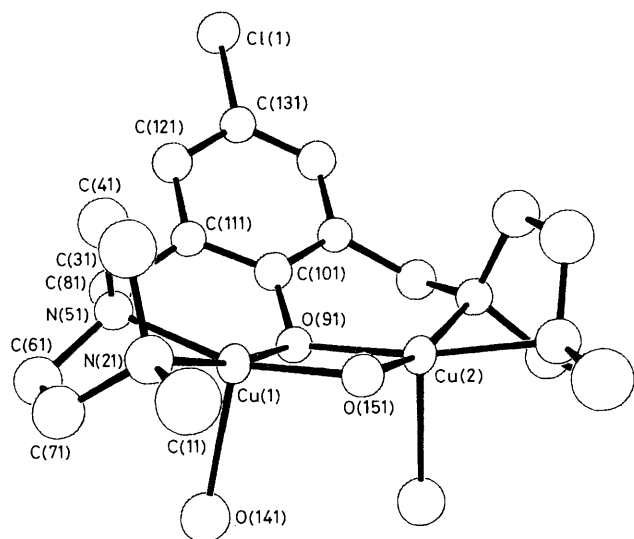


Figure 2. Important bond lengths (Å) and angles (°) for complex (1) (corresponding values for the second molecule are in square brackets): Cu(1)–Cu(2) 2.872(2) [2.857(3)], Cu(1)–O(91) 2.001(7) [1.996(7)], Cu(1)–O(151) 1.924(6) [1.916(7)], Cu(1)–N(21) 2.033(9) [2.039(10)], Cu(1)–N(51) 1.980(8) [1.992(9)], Cu(1)–O(141) 2.323(8) [2.268(8)]; Cu(1)–O(91)–Cu(2) 91.7(4) [91.4(4)], Cu(1)–O(151)–Cu(2) 96.5(4) [96.4(5)]; dihedral angle between C(101)–O(91) bond and Cu₂O₂ plane 48.4 [42.7].

significant (*i.e.* π -type overlap).¹¹ It is interesting to note that the latter contribution has recently been shown to be important in explaining variations in J values in related dihydroxo- and dialkoxo-bridged Cr^{III} dimers, some of which possess non-coplanar RO[–] and bridging moieties of the kind described here.^{12,13} An alternative explanation for the low net antiferromagnetic coupling in (1) is that the *cis* arrangement of the axial water ligands modifies the nature of the Cu magnetic orbitals in comparison to the situation in *trans*-co-ordinated compounds.^{2,5,14} This in turn would affect the degree of overlap of Cu–O–Cu orbitals. This would seem less likely than the explanation given above since the degree of overlap is determined primarily by the symmetry of the magnetic orbitals which should be the same irrespective of the disposition of the fifth ligand.^{9,10} However the relative phases of the orbitals would favour decreased antiferromagnetism in a *cis*-co-ordinated situation, as observed.

The present results may have some important consequences

with respect to postulates of Type 3 copper geometry. The Cu–Cu distance is considerably longer in oxidized hemocyanin and tyrosinase derivatives while the degree of net antiferromagnetism is very high in comparison to that of compound (1). If OH[–] is the ‘endogenous’ bridge in the proteins then a Cu–Cu distance of *ca.* 3.4 Å with concomitant bridging angle seems to be optimal for strong antiferromagnetic coupling.^{2,4} If a phenoxo group such as tyrosinate is the endogenous bridge responsible for transmitting strong coupling³ then the present results suggest that the aromatic ring would probably be coplanar with the Cu–Cu fragment rather than being in the present angular conformation.¹⁴

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