Magnetic Exchange in a Copper(II) Dimer with Oxime Bridging Groups

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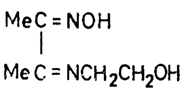
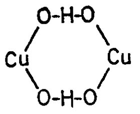
Summary An unusual dimeric structure with tetragonally co-ordinated copper(II) ions, bridged by oxime groups into six-membered rings, has been found for $CuLClO_4 \cdot H_2O$, where L represents the anion of 2-(2-hydroxyethyl)imine-3-oximatobutane; the low magnetic moment per copper atom (0·25 B.M.) results from superexchange coupling through the bridge.

Speculations on the mechanisms for magnetic superexchange through singly bridged (M–X–M) and four-membered cyclic bridged (M–X–M–X) units have caused considerable debate.[1] Arguments have been advanced to rationalize the observed ferromagnetic and antiferromagnetic effects *via* both σ- and π-interactions, in terms of the angle at M (X–M–X), the angle at X (M–X–M), and the overall structural features of the complex. We report the structure of a copper(II) dimer which contains a unique bridging arrangement and which exhibits almost complete spin pairing even at room temperature. The compound, the dimeric bis-{[2-(2-hydroxyethyl)imine-3-oximato-butane] copper(II) perchlorate monohydrate}, $Cu(C_6H_{11}N_2O_2)ClO_4$-H_2O, was prepared by the method of Ablov *et al.*[2] by adding the neutral ligand (I) to copper(II) perchlorate in methanol. *X*-Ray photographs of the black-green prismatic crystals indicate the space group to be $P2_1/c$ with cell parameters $a = 7{\cdot}868(2)$, $b = 14{\cdot}040(7)$, $c = 11{\cdot}401(5)$ Å, $\beta = 112{\cdot}73(4)°$, and $U = 1162{\cdot}3$ Å^3. The calculated (1·85 g cm^{-3}) and observed (1·83 g cm^{-3}) densities indicate two dimers per unit cell. The structure was solved by the heavy-atom method using 1602 diffractometric reflections with $I > 3\sigma$ and refined by least-squares methods with anisotropic thermal parameters for non-hydrogen atoms to the present residual, $R = 6{\cdot}8\%$. Further refinement with inclusion of hydrogen atoms and correction for absorption is in progress. A magnetic moment determination at 298 K by the Faraday method gave the value $\mu_{eff} = 0{\cdot}25$ B.M. per g atom Cu, assuming a diamagnetic correction of 128×10^{-6} c.g.s. per formula unit. The value reported previously is 0·41 B.M.[2]



$$\begin{array}{l} MeC=NOH \\ \quad | \\ MeC=NCH_2CH_2OH \end{array}$$

(I)



(II)

The molecular unit (Figure) consists of two formula units that are related by an inversion centre. Each copper is strongly co-ordinated to four donor groups, 2 nitrogens, and 2 oxygens, in a plane, and weakly co-ordinated to two axial groups, a water oxygen at 2·500(9) Å, and a perchlorate oxygen at 2·89(2) Å. The tridentate ligand occupies three of the planar positions and forms two five-membered chelate rings by co-ordinating through the oxime nitrogen, the imine nitrogen, and the alcohol oxygen. The fourth co-ordination position in the plane is occupied by the oxime oxygen of the adjacent unit so that N–O groups bridge the two copper atoms to form a six-membered ring which is planar to within 0·03 Å. The only other structure, to our knowledge, reporting a bridging oxime group is bis(dimethylglyoxime)copper(II)[3] in which the ring adopts a chair conformation with relatively long Cu–O bonds [2·301(3) Å]; at ambient temperature, that complex exhibits a normal magnetic moment, corresponding to one unpaired electron per copper atom in contrast to the very low moment observed for the compound described here. Oxime-bridging of the type found in this structure has been postulated previously to account for the low magnetic moment of another copper–oxime complex.[4]

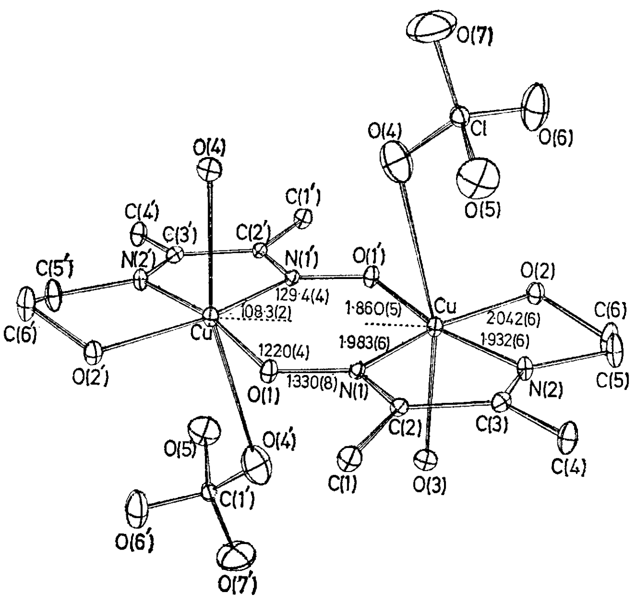


Figure. The molecular structure of $[Cu(C_6H_{11}(N_2O_2)H_2O)(ClO_4)]$

One of the two ionizable protons of the tridentate ligand remains bound in $[Cu(L)H_2O(ClO_4)]_2$. We surmise the oxime proton has been lost for the following reasons: (i) the oxime hydrogen is expected to be more acidic than the alcohol hydrogen, (ii) the anionic portion of the ligand might be expected in the bridging unit and the oxime does function in the bridge, and (iii) the region in the electron density map near the oxime groups is relatively flat whereas one of the strongest residual peaks appears at a reasonable distance and direction from the alcohol oxygen atom. The Cu–N and Cu–O distances and the remainder of the ligand geometry are in good agreement with previous determinations for di-imines and dioximes of butane-2,3-dione.[3,5]

The planarity of the $Cu_2N_2O_2$ ring and the strength of the magnetic coupling despite the magnitude of the Cu–Cu distance [3·580(3) Å] could indicate a delocalized ring sytem. However, the spin-coupling does not necessarily occur by a π-mechanism since a σ-pathway is also available and antiferromagnetic coupling through a σ-mechanism has been demonstrated. Antiferromagnetic coupling has been observed in a copper(II) dimer having the hydrogen-bridged structure (II).[6,7] In this structure appropriate π-pathways for superexchange do not exist.

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