Chloro-bridged Triplet Ground-state Copper(II) Dimer

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Summary Magnetic susceptibility measurements on the dimer di-μ-chloro-bis[chloro(dimethylglyoxime)copper(II)] indicate a triplet ground state with a singlet–triplet splitting of 6·3 cm^{-1}.

Although a limited number of hydroxo-bridged copper(II) dimers with triplet ground states has been characterized,[1] there has been, up to now, no report of a triplet ground-state chloro-bridged copper(II) molecular complex. The reason for this is the lack of adequate structural information, since there are few characterized chloro-bridged copper(II) dimers. We report here the results of low temperature magnetic measurements on the discrete dimer di-μ-chloro-bis[chloro(dimethylglyoxime)copper(II)], $[Cu(dmg)Cl_2]_2$, which indicate that the complex has a triplet ground state.

The structure[2] of $[Cu(dmg)Cl_2]_2$ is shown in Figure 1. The structure consists of chains of dimers held together by hydrogen bonds. The copper atom is five-co-ordinate in a square-based pyramidal arrangement consisting of a nearly square-planar arrangement of two nitrogen atoms and two tightly bound chlorine atoms with a chlorine atom from an adjacent unit in the apical position.

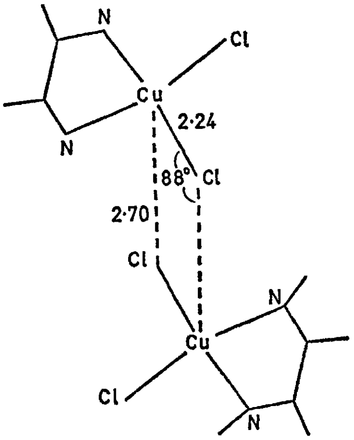

FIGURE 1. *Schematic structure of* $[Cu(dmg)Cl_2]_2$.

Magnetic susceptibility data were collected between 1·8 and 70 K using a Foner-type vibrating sample magnetometer which was calibrated with $HgCo(NCS)_4$.[3] Temperatures were measured with a calibrated-precision germanium resistance thermometer. The magnetic data can be described by the singlet–triplet equation (1), with $2J = 6{\cdot}3$ cm^{-1}, $g = 2{\cdot}06$, and $\theta = -1{\cdot}7°$. Additional evidence for

$$\chi_m = [Ng^2\beta^2/3k(T - \theta)][1 + (1/3)\exp(-2J/kT)]^{-1} \quad (1)$$

the triplet ground state is provided by the magnetization studies (see Figure 2). The magnetization curves for $S' = 1/2$ and $S' = 1$ were evaluated from the Brillouin function,[4] equation (2); where $X = (H/T)(S'g\beta/k)$ and S' is the

$$B(X) = \frac{2S' + 1}{2S'} \coth\left(\frac{2S' + 1}{2S'}\right)X - \frac{1}{2S'} \coth \frac{X}{2S'} \quad (2)$$

effective spin. To account for *inter*dimer interactions the field H was set equal to the external field plus a molecular field, H_m, where it was assumed that H_m was proportional to the magnetization. Thus, $H_m = N_W N\beta \langle\mu\rangle = gS'B(X)$ and $N_W = (3k\theta')/[Ng^2\beta^2S'(S' + 1)]$.[5] A best-fit (least-squares) of the experimental data was used to select a value of $-1{\cdot}2°$ for θ', thereby indicating an antiferromagnetic *inter*dimer interaction. The θ' term in the magnetization studies is very similar to the θ term in equation (1), but in view of the approximate nature of the theory, identical values for these interdimer interaction parameters are not expected.

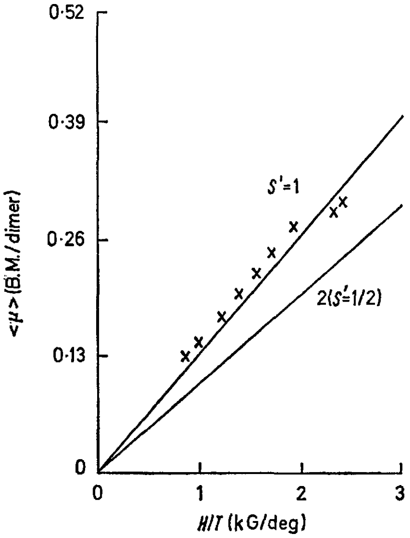

FIGURE 2. *Experimental data* (×) *and theoretical magnetization curves for* $[Cu(dmg)Cl_2]_2$.

The ferromagnetic interaction probably occurs by a superexchange mechanism. It is important to note that an increase in the bridging Cu–Cl–Cu′ angle from 88° in $[Cu(dmg)Cl_2]_2$ to 101·4° in $[Cu(\alpha\text{-picoline})_2Cl_2]_2$[6,7] accompanies a change in the exchange coupling constant from $+6{\cdot}3$ to $-7{\cdot}4$ cm^{-1}. This observation parallels the results for a series of di-μ-hydroxo-bridged copper(II) complexes and invites a search for additional chloro-bridged dimers so that the relationship between the angle at the bridging chlorine atom and the exchange coupling constant can be established.

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