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A MAGNETIZATION STUDY ON TETRAKIS(DIETHYLDITHIOCARBAMATO)DICOPPER(II)

Kenneth T. MCGREGOR, Richard P. ECKBERG, and William E. HATFIELD*
Department of Chemistry, University of North Carolina, Chapel Hill
North Carolina 27514, U.S.A.

A magnetization study on tetrakis(diethyldithiocarbamato)dicopper(II) has shown that the dimeric molecule has a triplet ground state resulting from a ferromagnetic intradimer interaction.

While spin-spin coupling leading to singlet ground states in bimetallic copper(II) complexes is readily apparent from temperature dependent magnetic susceptibility data, interactions which lead to triplet ground states are much more difficult to detect. Compounds thought to exhibit ferromagnetic intradimer interactions require extensive experimental documentation for the confirmation of the ground state. Since a triplet state has been detected in the dimeric molecule $[Cu(edtc)_2]_2$ (edtc is N,N-diethyldithiocarbamate) by electron spin resonance,1) and since low temperature magnetic susceptibility data are consistent with a triplet ground state and low-lying singlet state,2) it became important to determine the magnetization behavior of the compound in order to confirm the spin multiplicity. We wish to report here the results of the magnetization study which clearly indicate a ferromagnetic intradimer interaction and an antiferromagnetic interdimer interaction.

The preparation of the sample of $[Cu(edtc)_2]_2$ used for our magnetic measurements has been reported[2] previously. Anal. Calcd for $Cu(C_5H_{10}NS_2)_2$: C, 33.33; H, 5.60; N, 7.78. Found: C, 33.39; H, 5.74; N, 7.58.

The magnetic susceptibilities of a powdered sample of the complex were determined using a Foner-type vibrating sample magnetometer.3) The measurements were made at 1.7, 4.2 and 7.0°K with field strengths of 2.5, 5.0, 7.5, 10.0, 12.5, and 15.0 kG. The field was calibrated by nuclear resonance techniques. The temperatures were measured with a calibrated gallium-arsenide diode. Mercury tettrathiocyanatocobaltate(II) was used as a susceptibility standard.4) All susceptibilities were corrected for the diamagnetism of the substituent atoms using Pascal's constants and for the TIP of copper (estimated to be 60×10^{-6} cgsu/Cu).

A plot of the experimental magnetism versus H/T for $[Cu(edtc)_2]_2$ is shown in Figure 1. The solid lines in Figure 1 are computer plots of the calculated magnetization

$$\langle\mu\rangle = gS'B_{S'}(X)$$

where $B_{S'}(X)$ is the Brillouin function6)

$$B_{S'}(X) = [\frac{2S'+1}{2S'} \coth (\frac{2S'+1}{2S'}) X - \frac{1}{2S'} \coth (\frac{X}{2S'})]$$

Here $X = (H/T)(S'g\beta/k)$ where S' is the effective spin. From classical molecular field theory,[6)] the apparent field H is taken to be the sum of the applied external field and a molecular field, i.e., $H = H_{ext} + H_m$. The molecular field H_m is assumed to be proportional to the magnetization M as given by

$$H_m = N_w M = N_w N\beta\langle\mu\rangle$$

The value of H_m was estimated using the relation

$$N_w = \frac{3k\theta}{Ng^2\beta^2 S'(S'+1)}$$

where θ is determined from the temperature variation of the susceptibility.

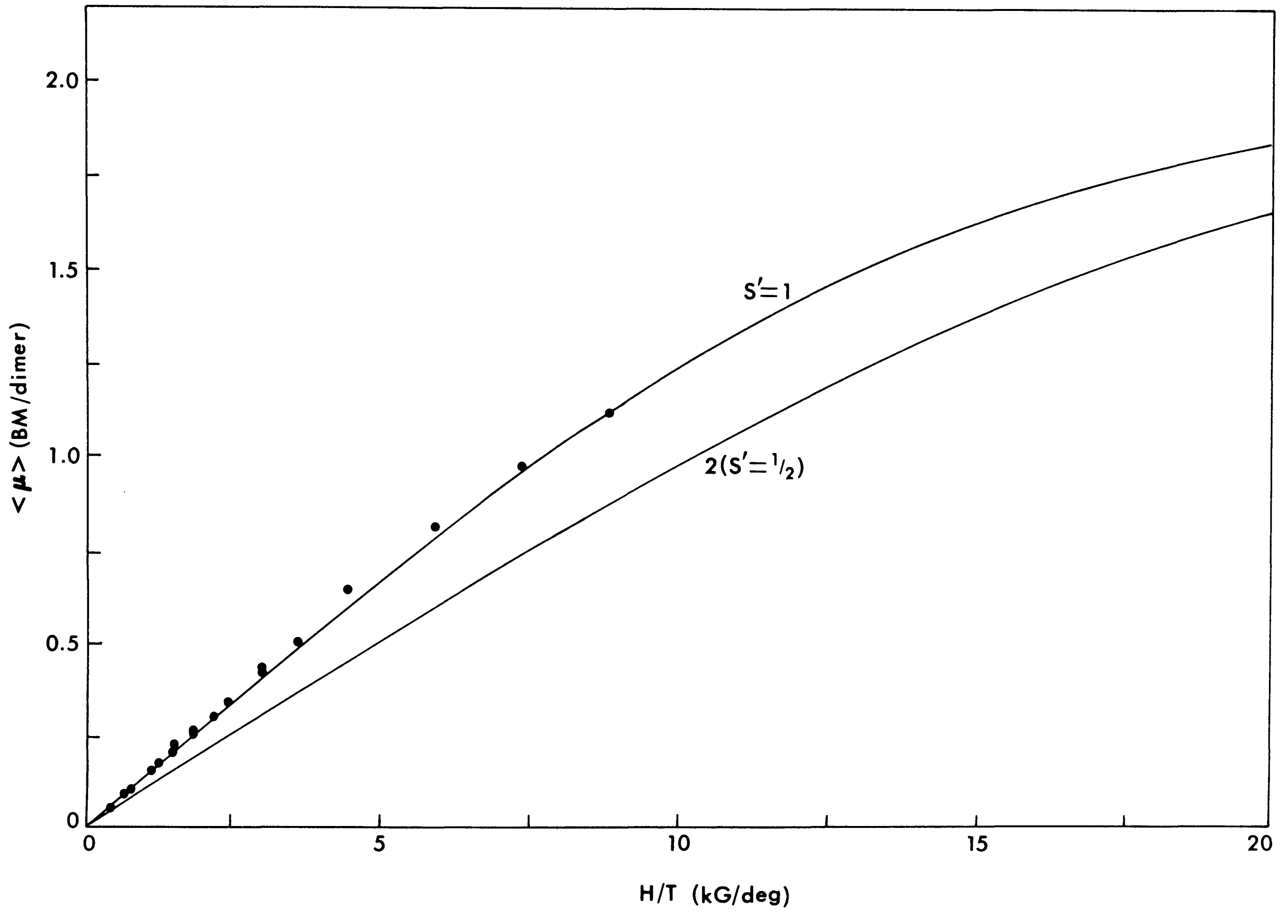

Figure 1. Magnetization data for $[Cu(edtc)_2]_2$. The full curves are the calculated properties for a triplet state and for two uncoupled doublet states.

The experimental data are compared with calculated curves for the triplet state and for two doublet states. The data are consistant with a triplet ground state for the dimer with a small interdimer antiferromagnetic interaction (*vide supra*). A θ-value of -1.15, accounting for the lattice interaction, and a g-value of 2.05 best fit the experimental data. This may be compared with a θ of -1.37 and a $\langle g \rangle$ of 2.05 which was determined from the temperature variation of the magnetic susceptibility reported[2)] previously for the complex. The singlet-triplet separation, 2J, was reported to be 24 cm^{-1}. Although the θ-values differ slightly, the results of both studies are suggestive of a small antiferromagnetic interaction between triplet ground state dimers.

The structure of $[Cu(edtc)_2]_2$ has been determined by Bonamico, et al.,[8)] and is shown in Figure 2. The copper atoms are in a distorted tetragonal pyramidal environment with four sulfur atoms comprising the basal plane. The apical sulfur atom, at 2.85 Å, is part of the basal plane of an adjacent copper(II) ion. The copper-copper separation is 3.59 Å. Although the copper environment appears to be basically pyramidal, a hydrogen atom belonging to an ethyl group of an adjacent dimer is found in the sixth octahedral position at 2.86 Å. This arrangement could provide a pathway for the small observed antiferromagnetic lattice interaction.

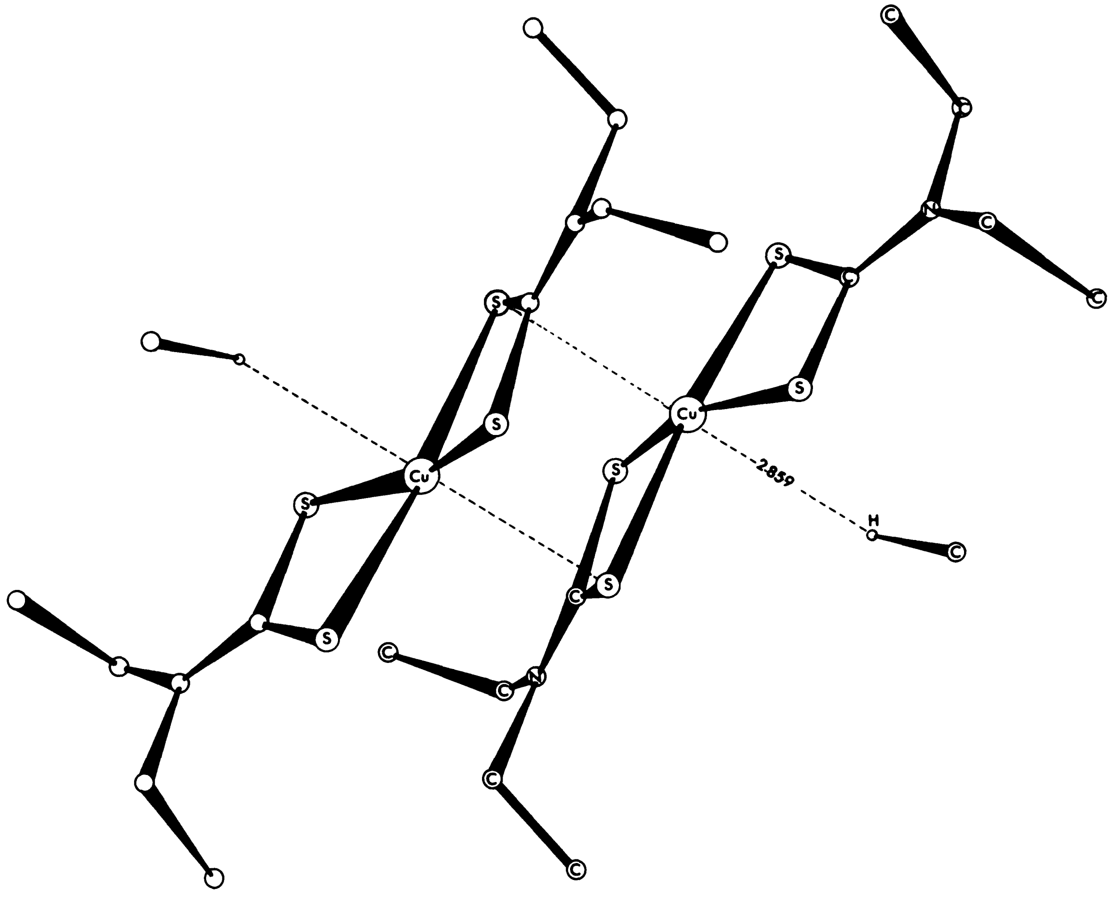

Figure 2. A view of the structure of $[Cu(edtc)_2]_2$, depicting both the dimeric nature of the complex and the interdimer contacts. Data from Ref. 8.

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   b) Our analysis of the data includes any population of the singlet state; the effects of the singlet state population was found to be very small at the experimental temperatures when $2J \simeq 20\ \text{cm}^{-1}$.
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