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Leonard W. Ter Haar [a] & William E. Hatfield [a]
[a] Department of Chemistry, University of North Carolina, Chapel Hill, N. C., 27514

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ONE-DIMENSIONAL FERROMAGNETIC EXCHANGE INTERACTIONS AND EPR LINEWIDTH ANOMALY IN THE BIS(μ-AQUO) CHAIN OF HYDROGEN COPPER(II) MALEATE TETRAHYDRATE

LEONARD W. ter HAAR and WILLIAM E. HATFIELD
Department of Chemistry, University of North Carolina, Chapel Hill, N. C. 27514.

Abstract Hydrogen copper(II) maleate tetrahydrate exhibits one-dimensional ferromagnetism with $J = 0.6\ cm^{-1}$. The EPR angular linewidth dependence shows a minimum along the chain axis, and has six minima/maxima points during a 180° rotation of the crystal about any axis normal to the chain axis.

INTRODUCTION

As part of our program dedicated towards characterizing ligand superexchange in low-dimensional magnetic systems, we have undertaken a study of the magnetic properties of hydrogen copper(II) maleate tetrahydrate (Cu-MTH). Cu-MTH is of extreme interest because of the unique bis(μ-aquo) bridges between copper(II) ions, and because of the unusual way in which the chains pack into layers which stack up to form the crystal lattice. Cu-MTH crystallizes[1] in the space group I2/m with cell parameters a = 3.594, b = 18.79, c = 9.69 Å and $\gamma = 93.25°$. The copper(II) ion is in a four-coordinate square plane formed by two trans terminal water molecules (W1) at 1.93 Å, and by two trans bridging water molecules (W2) at 1.96 Å. These units stack along the a-axis to form a $[Cu(H_2O)_4]_n^{n2+}$ cationic chain. The W2 molecules form long bonds (2.68 Å) to neighboring

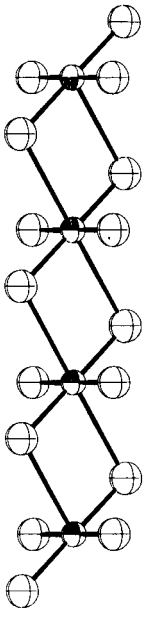

FIGURE 1. Planar bridged Cu-MTH chain, showing only the oxygens from the coordinated waters.

$Cu(H_2O)_4^{2+}$ units, resulting in a parallel planar bis(μ-aquo) bridged chain in which copper(II) ions are hexaquo coordinated (Figure 1). The W1 oxygens are non-bridging and form the shortest bonds to the copper(II) ion. The bridge angle of the W2 bridges between two copper(II) ions is 100.3°. The planar bridging unit lies in the ab-plane. The intrachain Cu-Cu distance is 3.60 Å. The maleate ions are not coordinated to copper(II) ions, but are able to hydrogen bond the chains into layers which are parallel to the ac-plane (Figure 2). The acidic proton has not been located, but it is important in the hydrogen bonding and it is probably disordered. The shortest interchain Cu-Cu

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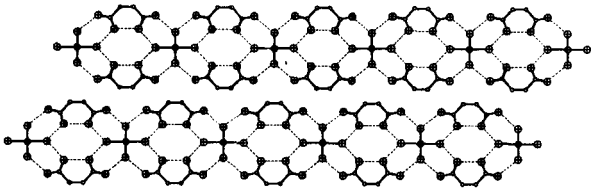

FIGURE 2. Edge view of two stacked layers, looking down the axes of several chains which are hydrogen bonded (---) to form the layers.

distance within this layer is about 9.70 Å. These layers stack in a canted manner and the shortest interchain Cu-Cu distance between chains in different layers is 10.6 Å.

EXPERIMENTAL

The material was prepared as previously described.[1] Magnetic susceptibility data were determined in the temperature range of 1.7 to 40 K using a vibrating sample magnetometer.[2] Magnetization was measured as function of the applied magnetic field at 1.7 K. EPR spectra were recorded using a Varian E-109 operating at X-band frequencies. Spectra for a single crystal were recorded as a function of crystal orientation with respect to the magnetic field in the temperature range of 80 to 295 K using commercially available equipment. Rotations were carried out in the orthogonal crystal coordinate system of the $\underline{a}$, $\underline{b}^*$, and $\underline{c}$ axes. The $\underline{a}$-axis is the chain axis, and both $\underline{b}^*$ and $\underline{c}$ are normal to it. The $\underline{b}^*$ axis is normal to

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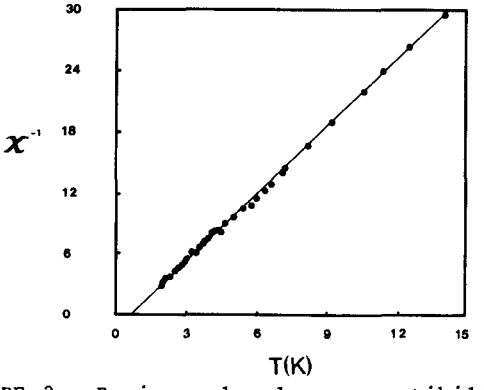

FIGURE 3. Reciprocal molar susceptibility of Cu-MTH.

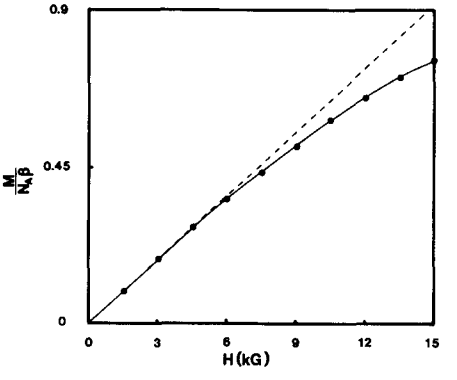

FIGURE 4. Magnetization data which shows low magnetic field saturation for S = 1/2 ion, g = 2.18.

the layer of chains, whereas the c axis lies in the layer.

RESULTS

The magnetic susceptibility data of a powdered sample of Cu-MTH are shown in Figure 3 as $1/\chi_m$ vs. T, where the positive θ value of 0.65 clearly indicates ferromagnetic exchange interactions in the Cu-MTH chain. An increase in the

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effective magnetic moment, μ_{eff}, from 1.95 B.M. at 40 K to nearly 2.3 B.M. at 1.7 K, also indicates ferromagnetic exchange interactions. The magnetic field dependence of the magnetization in Figure 4 also confirms the identification of ferromagnetic exchange interactions since saturation is approached near 1.5 to 2.0 T.

In view of the linear chain structure of Cu-MTH, it was expected that the magnetic properties could be explained by Heisenberg linear chain theory given by the Hamiltonian $H = -2J\Sigma\hat{S}_i \cdot \hat{S}_{i+1}$. Baker, et al.,[3] have developed a theoretical expression for a ferromagnetic S = 1/2 linear chain using the high temperature Padé expansion technique. The expression was modified for Cu-MTH, to account for the presence of magnetic interchain interactions, by the addition of a mean-field term to give the expression:

$$\chi_m = \chi_B/(1-2zJ'\chi_B/Ng^2\beta^2) \qquad (1)$$

In this equation, χ_B is the calculated magnetic susceptibility of the isolated chain given by the Baker expression, and χ_m is the molecular field corrected value of the molar susceptibility. The parameter zJ' is the product of z, the number of nearest neighbors, and J', the interchain magnetic exchange energy. The experimental data were fit to the expression using a nonlinear Simplex fitting routine. The best fit parameters of the magnetic data for Cu-MTH to the Baker model are J = 0.6 cm^{-1} and zJ' = -0.2 cm^{-1} when the EPR g_{av} value of 2.181 is used. The results of these analyses confirm one-dimensional ferromagnetic exchange interactions in Cu-MTH.

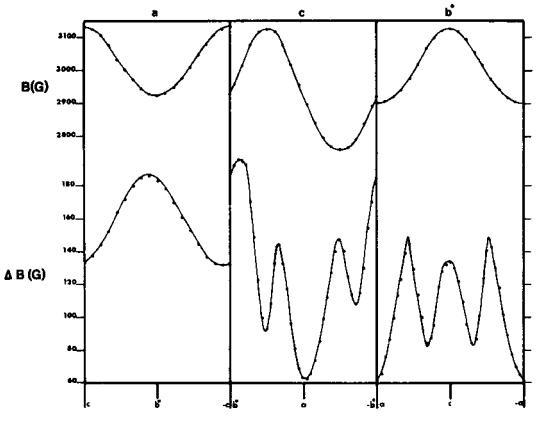

FIGURE 5. Angular EPR linewidth data for Cu-MTH.

The EPR spectrum of Cu-MTH consists of a single exchange narrowed line in all orientations of the crystal throughout the temperature range 80 K to 295 K. Analysis of rotational anisotropy data for the electronic g-factor, yields a g^2-tensor consistent with the structure, and independent of temperature. Principal molecular values are $g_x = 2.087$, $g_y = 2.091$, $g_z = 2.366$, and these lie approximately in the directions of the Cu-W1, Cu-W2(short), and Cu-W2(long) bonds, respectively.

The angular linewidth dependence of Cu-MTH is very unusual. The most prominent feature, which has never been observed before, is shown in Figure 5. Note the occurance of six minima/maxima points during the period of a 180° rotation of a single crystal about any axis (e.g. $\underline{b}^*$ or $\underline{c}$) which is perpendicular to the chain axis ($\underline{a}$-axis). The occurence of the minimum linewidth when H_o is parallel to

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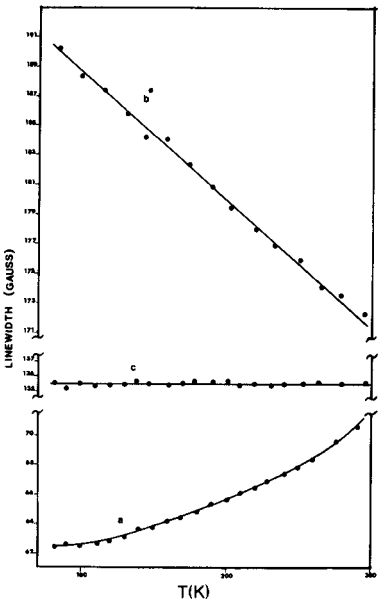

FIGURE 6. Temperature dependence of the EPR linewidth for the three important lattice directions.

the chain axis is also unusual compared to other chain systems. This observation is entirely unexpected in terms of low-dimensional EPR linewidth theory[4] which predicts that a maximum linewidth will occur for this orientation. Rotation of the crystal about the chain axis verifies that this direction is a major symmetry axis of spin diffusion since the linewidth varies inversely with the spin anisotropy as expected. Rotations about $\underline{b}^*$ and $\underline{c}$ indicate that the spin anisotropy contribution to the linewidth is comparable to the low dimensional spin diffusion effects,

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since the asymmetry in the linewidth data varies inversely with the spin anisotropy.

The temperature dependence of the EPR linewidth is also unusual (Figure 6). The linewidth, which is already unusually narrow when H_o is parallel to the chain axis, decreases even more when the temperature is decreased. When the field is perpendicular to the chain and the layer, the linewidth increases with decreasing temperature. Finally, when the temperature is varied and H_o is perpendicular to the chain but parallel to the layer, the linewidth remains unchanged. Remarkably, the linewidth along the a-axis changes nonlinearly with temperature, and the linewidth for the b^*-axis varies linearly with temperature.

DISCUSSION

From a stuctural viewpoint, Cu-MTH is a compound which should show interesting low-dimensional magnetic properties. Indeed, the magnetic susceptibility data and the EPR data verify that Cu-MTH is a low-dimensional magnetic system. Lattice dimensionality directly affects the nature of the magnetic dimensionality, and both of these dimensionalities determine a characteristic thermodynamic behavior which can be observed experimentally.[5] The Cu-MTH structure is clearly conducive to one-dimensional exchange interactions because of the cationic water bridged copper(II) linear chains. This conclusion is confirmed by the magnetic susceptibility data analysis, and by the linewidth dependence in the rotational spectra about the chain axis.

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The packing of the chains into layers, due to the hydrogen bonding provided by the maleate ions, decreases the pure one-dimensional behavior expected for isolated Cu-MTH chains. In typical quasi-one-dimensional lattice systems, the linear chains are subject to magnetic interchain exchange interactions which are generally operative in all directions normal to the chain axis, and long range 3-D magnetic order usually occurs at low temperatures. In Cu-MTH however, the hydrogen bonded layer of cationic chains forms a directionally anisotropic 2-D magnetic system which is magnetically insulated rather well from neighboring layers (Figure 2) by the maleate groups. The large zJ'/J value of 0.3 confirms the 2-D character of layers of chains.

The EPR data are also consistent with the idea of a low-dimensional system which is intermediate between a 1-D chain and a 2-D layer. The angular linewidth data not only show the magic angle of 54.7° with respect to the chain axis (two minima points), but also indicate the importance of additional interactions as reflected by two additional maxima in the linewidths. Qualitatively, these maxima are the result of the 2-D character of the crystal which is due to the highly anisotropic direction of the interchain exchange. Attempts to fit more quantitative spin diffusion terms to the linewidth data are in progress. Since the EPR frequency and the exchange interactions are similar, frequency-dependent EPR spectra are of interest and are presently being studied.

Magneto-structural correlations for magnetically exchange coupled, low-dimensional, transition metal complexes have been developed for a number of systems

through systematic research.[6] Although two other structurally and magnetically characterized water-bridged copper(II) chains are known,[7] the structures of the chains differ considerably, and it is not possible to propose any magneto-structural correlations at this time. This study on Cu-MTH indicates that water bridges provide effective superexchange pathways, and in addition, Cu-MTH has provided an opportunity to study mixed magnetic dimensionality and magnetic dimensionality crossover.

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