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Magnetic Exchange and Structure Relationships in Polymer Copper(II) Chloride-1,4-Dioxane (3:2)

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The magnetic susceptibility of the title compound has been measured over the temperature range 4-300 K. Several interesting structural-magnetic correlations have been extracted from the analysis of the data. The compound, whose structure consists of an unusual alternating bibridged copper chloride chain, is shown to behave magnetically as a linear chain of antiferromagnetically coupled ferromagnetic trimers. The intratrimer coupling, J, is large and positive: $J/k = 94$ K. The intertrimer coupling, J', is small and negative: $J'/k = -7.6$ K. The large $|J/J'|$ ratio allows the low-temperature susceptibility data to be treated on the basis of a $S = {}^3/_2$ Heisenberg antiferromagnetic chain. The results are shown to be consistent with predictions of superexchange arguments based on the observed geometry of the copper chloride chain.

Introduction

The experimental and theoretical aspects of the relationships between structure and magnetic coupling in copper(II) salts are becoming increasingly well understood. Hatfield, Hodgson, and co-workers[2] have shown, for example, that a linear relationship exists between the exchange energy, J (defined by $\mathcal{H} = -2JS_1 \cdot S_2$), and the metal-ligand-metal bridging angle, ϕ, in a wide series of planar bibridged copper(II) hydroxide complexes. The coupling energy, positive (ferromagnetic) at angles near 90°, becomes increasingly smaller (more antiferromagnetic) as the angle increases. Hay et al.[3] have shown that J can be expressed in a Hückel MO framework as

$$J = K_{\mathrm{ab}} - \frac{(\epsilon_{\mathrm{s}} - \epsilon_{\mathrm{a}})^2}{J_{\mathrm{aa}} - J_{\mathrm{ab}}}$$

where K_{ab} is inherently positive (ferromagnetic) and ϵ_{s} and ϵ_{a} are the one-electron energies of the symmetric and antisymmetric MO's formed from the magnetic orbitals of the individual copper ions. Their calculations, and similar angular overlap calculations by Bencini and Gatteschi[4] have shown that $|\epsilon_{\mathrm{s}} - \epsilon_{\mathrm{a}}|$ increases as ϕ deviates from 90°. Thus, as observed, the exchange interaction is predicted to become more antiferromagnetic as the angle ϕ increases.

Kahn and co-workers[5] have also examined hydroxide-bridged systems in which the dimer is not planar, but roof shaped. The structural parameter of interest here is the dihedral angle, δ, between the normals to the plane of the $\mathrm{CuL_4}$ moieties of the two halves of the dimer. They consider the case where ϕ is substantially greater than 90° so the antiferromagnetic contribution dominates, with $\epsilon_{\mathrm{a}} > \epsilon_{\mathrm{s}}$. When the dimer is folded in such a manner so as to keep the coordination geometry fixed, they showed that $|\epsilon_{\mathrm{a}} - \epsilon_{\mathrm{s}}|$ decreased. Since this method of folding the dimer also causes ϕ to decrease, the resulting decrease in the antiferromagnetic contribution to the exchange coupling is easily understood.

Our interest has centered on copper halide salts. There the systematics have not been as clearly delineated. However, the same principles are expected to apply. In particular, planar copper halide dimers have been encountered in only a few cases,[6,7] and no examples of roof-shaped dimers are known. The least ambiguous case occurs for $\mathrm{KCuCl_3}$, where $\phi = 96°$ and $2J/k = -55$ K.[8] From the behavior of the hydroxide-bridged series, it is strongly anticipated that increasing ϕ, or changing ϕ from 180°, should lead to an increasing antiferromagnetic contribution.

Additional information arises from a series of ferromagnetic, spin ${}^1/_2$ one-dimensional copper halide systems that has been synthesized and studied in this laboratory over the past several years.[9-12] These have all been characterized by the presence of one or more symmetrical Cu-X-Cu bridges between adjacent copper atoms in the linear chain with $\phi = 85-90°$. This geometry yields a strong ferromagnetic interaction, as would be expected from both the experimental and theoretical arguments given above. The most interesting systems in this series are (cyclohexylammonium)copper(II) trichloride (CHAC)[11] and (cyclopentylammonium)copper(II) trichloride (CPAC).[12] These contain symmetrically bibridged linear chains, with a square-pyramidal geometry around each copper ion. For CHAC, $\phi = 86.0°$ and $\delta = 155.8°$. Thus, the large (ferromagnetic) value of $J/k = 70$ K is not surprising.

In the search for other possible spin ${}^1/_2$ ferromagnetic linear chains, the structural determination of $\mathrm{3CuCl_2 \cdot 2dx}$, where dx = 1,4-dioxane, by Barnes and Weakley[13] was encountered. The structure consists of a symmetrically bibridged linear chain with an unusual repeat sequence of ϕ and δ values, as shown in Figure 1. Pairs of bridges with $\phi_2 = 85.5°$ and $\delta_2 = 130.6°$ are separated by bridges with $\phi_1 = 93.7°$ and $\delta_1 = 180°$. On the basis of the above structure-exchange correlations, the former interactions will clearly be ferromagnetic. The latter could be either antiferromagnetic or weakly ferromagnetic; sufficient structural data are not yet available to predict the sign of this exchange. Each adjacent pair of ϕ_2,δ_2 bridges defines a strong ferromagnetically coupled group of three copper ions. Thus, a linear chain of weakly coupled ferromagnetic trimers is anticipated, for which the sign of the weak intertrimer coupling will have to be determined by experiment. No close interchain contacts occur, so interchain coupling can

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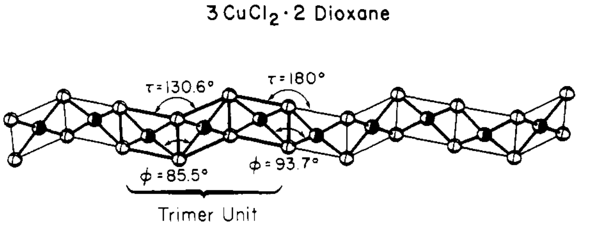

Figure 1. Illustration of the bibridged copper chloride chains in $3CuCl_2 \cdot 2dx$. The 1,4-dioxane rings have been omitted for clarity.

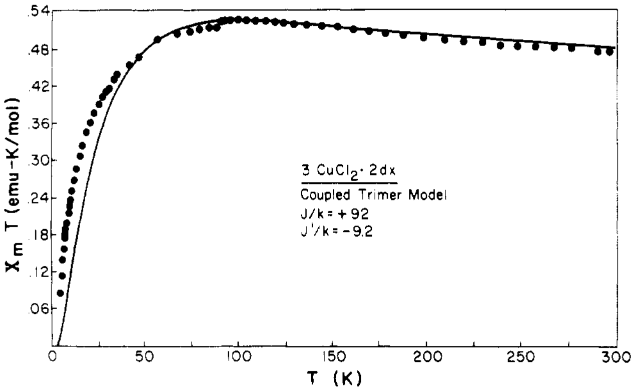

Figure 2. Plot of χT (per mole of Cu) vs. T for $3CuCl_2 \cdot 2dx$. The solid curve is the best fit of the data to a model of Ising coupled ferromagnetic trimers.

reasonably be neglected in the temperature range investigated.

Experimental Section

Compound Preparation. $3CuCl_2 \cdot 2dx$ was prepared by dissolving anhydrous cupric chloride in an excess of 1,4-dioxane. The resulting precipitate was then recrystallized from acetonitrile. A reddish brown solid was obtained, which consisted of fine, needlelike crystals.

Instrumentation. Powder susceptibility data were taken on a PAR vibrating-sample magnetometer, Model 155, with temperatures ranging from 4 to 300 K. For data collection at temperatures below 85 K, liquid helium was used as the refrigerant, and liquid nitrogen was used for temperatures above 80 K. All high-temperature data were taken with an applied field of 7250 G, while a field of 5202 G was used in the low-temperature region (an M vs. H curve was linear for $H < 6000$ Oe at $T = 4.2$ K). For low temperatures (<80 K), a germanium resistance thermometer was used; at higher temperatures, a thermocouple mounted on the heater block was used. Corrections were made on the thermocouple-measured temperatures to account for a temperature gradient between the heater block and the sample rod. (Temperatures at the heater block were typically found to be 1% higher than temperatures at the sample rod.) The diamagnetic correction term for the compound was found to be -272.32×10^{-6} cgsu/mol, and the temperature-independent paramagnetism was estimated to be 180×10^{-6} cgsu/mol.

Data Analysis

Examination of the susceptibility data for $3CuCl_2 \cdot 2dx$ gives experimental confirmation of theoretical relationships existing between structural and magnetic properties of this compound. An extrapolation of high-temperature data on the Curie–Weiss plot gives a Θ value of +32 K, indicative of strong ferromagnetic interactions. The slope of the plot at high temperatures is 0.815, corresponding to a Curie constant (C) of 1.227 for the compound. The C value per mole of copper is therefore 0.409, which is equivalent to a g value of 2.09. An average g value of 2.093 was independently measured by EPR of a powdered sample, with a line width of approximately 750 G at room temperature. The χT vs. T plot (Figure 2) confirms the existence of a ferromagnetic coupling dominating at high temperatures but clearly shows the existence of antiferromagnetic coupling for $T < 100$ K. A plot of χ vs. T (Figure 3) shows that the susceptibility turns over at ~7.4 K. The antiferromagnetic interactions that exist in the system are sufficiently strong that they must be associated with the intertrimer interactions, not interchain coupling. The χT data were fit to a theoretical model developed by Landee[14] for an Ising chain of Heisenberg trimers, $\chi_{I,H}(J,J')$, where J is the coupling energy within the trimer, and J' is the coupling energy between trimers. This model was derived from the susceptibility, $\chi_{I,I}(J,J')$, of a model for an Ising chain of Ising trimers, corrected as shown to account for Heisenberg interactions within the trimer:

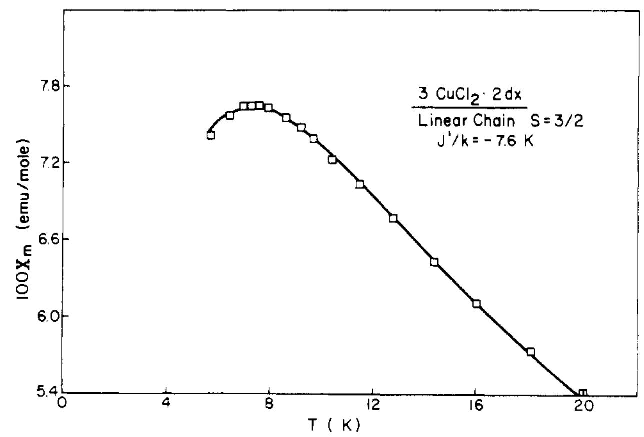

Figure 3. Plot of the low-temperature susceptibility of $3CuCl_2 \cdot 2dx$. The solid curve is the fit to Weng's calculation of the susceptibility of an $S = {}^3/_2$ antiferromagnetic Heisenberg chain.

$$\chi_{I,H}(J,J') = [\chi_{I,I}(J,J')][\chi_H(J)]/[\chi_I(J)]$$

where $\chi_H(J)$ and $\chi_I(J)$ correspond to the susceptibilities of independent Heisenberg or Ising trimers. This model fits the χT data to within 2.5% for the 40–300 K temperature range, with a J/k value of 94 K, and a J'/k value of −9.2 K (g fixed at 2.09). This value of J' will be only approximate, since it is clearly based on an Ising interaction, which gives incorrect low-temperature behavior.

A better estimate of J' can be obtained from the low-temperature data. The data (5–20 K) were fit to a model derived from Weng's[15] numerical calculations for a Heisenberg spin ${}^3/_2$ chain. The rationale behind this approximation is that at temperatures well below J/k (e.g., $T \leq 0.2J/k \approx 20$ K), essentially all of the trimers are in the spin ${}^3/_2$ ground state, as dictated by Boltzmann populations. Therefore, at low temperatures, the $3CuCl_2 \cdot 2dx$ system can be approximated by a spin ${}^3/_2$ chain with antiferromagnetic coupling. From the interpolated values of Weng for a spin ${}^3/_2$ chain, the susceptibility has a maximum at $kT/[J_{3/2}S(S+1)] = 1.24$.[16] Therefore

$$J'_{3/2}/k = \frac{T_{\max}}{[KT_{\max}/J'_{3/2}S(S+1)][S(S+1)]} = \frac{7.4\ \mathrm{K}}{1.24(15/4)} = -1.59\ \mathrm{K}$$

where $J'_{3/2}$ is the coupling between the ${}^3/_2$ ground states of adjacent trimers. However, the coupling of interest is that between adjacent spin ${}^1/_2$ copper ions, $J'_{1/2}$. By equating exchange energies of the spin ${}^1/_2$ and ${}^3/_2$ systems, one obtains

$$s(s+1)J'_s = S(S+1)J'_S$$

where $s = {}^1/_2$, $S = {}^3/_2$; it follows that

$$J'_{1/2}/k = 5J'_{3/2}/k = 8.0\ \mathrm{K}$$

Since this value is much less than the value determined for

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the trimer, it is valid to interpret the low-temperature data with the model based on Weng's calculations. A fit of experimental data from 5 to 20 K to the model gives excellent agreement (to within 0.7%) with $J'_{1/2}/k = -7.6$ K.

Discussion

From the experimental results, it is apparent that a great deal of information concerning magnetic properties can be deduced from structural parameters. The values of the bridging and dihedral angles within the trimeric units of $3CuCl_2{\cdot}2dx$ are 85.5 and 130.6°, respectively. This geometry is responsible for the strong ferromagnetic coupling (J/k = 94 K) in the trimer. Between the trimers, $\phi = 93.7°$ and $\delta = 180°$, and the coupling energy is found to be weakly antiferromagnetic ($J/k = -7.6$ K).

The intertrimer structure of $3CuCl_2{\cdot}2dx$ can be compared to the structure of $KCuCl_3$.[6] In these two cases, bridging angles greater than 90° are found; the dioxane complex has a bridging angle of 93.7°, and $KCuCl_3$ has a value of 95.9°. The trends in their respective coupling energies agree with the magnetostructural correlations observed for the planar hydroxide-bridged series. The between-trimer coupling for $3CuCl_2{\cdot}2dx$ is −7.6 K, and the coupling for $KCuCl_3$ (having a larger bridging angle) is −27.5 K. Assuming that a linear relationship holds between ϕ and J, as for the hydroxide-bridged salts,[2] we estimate $J/k \approx 9(\phi - 93)$ K. Thus, the crossover from ferro- to antiferromagnetic coupling occurs at ~93°, in contrast to 97.5° for the hydroxide-bridged salts. The rate of change of J with ϕ is, however, a factor of 6 smaller for the chloride bridges. This is in accord with the observation that decreasing the electron density at the bridging ligand leads to a decrease in the antiferromagnetic contribution to the exchange. That is, it reduces the premultiplier of the $(\epsilon_a - \epsilon_s)^2$ term.

We now focus our attention on the intratrimer interactions. The results obtained by Charlot et al. on the folding of the hydroxide-bridged dimers[5] lead one to predict a decreased antiferromagnetic contribution as the dimer is folded. Indeed, the interaction is found to be ferromagnetic in $3CuCl_2{\cdot}2dx$. Comparison of the dioxane trimer with CHAC substantiates this conclusion. The bridging angles (85.5° for $3CuCl_2{\cdot}2dx$, 86° for CHAC) are essentially equal. However, the dihedral angles are quite different for the two compounds. The value of δ for the dioxane complex is much less than that for CHAC, 130.6 vs. 155.8°. The coupling values of 94 K for $3CuCl_2{\cdot}2dx$ and 70 K for CHAC show that, indeed, the interactions do become more ferromagnetic as δ is decreased from 180°.

As pointed out in the Introduction, the method of folding the dimer utilized by Charlot et al.[5] involves a simultaneous change of δ and ϕ. For the purpose of making magnetostructural correlations, it is convenient to keep these two processes separated. We can do this, using as a guide calculations by Bencini and Gatteschi,[4] who have carried out calculations when a dimer is folded, keeping ϕ constant. They have shown that when $\epsilon_a > \epsilon_s$ (which is true for the antiferromagnetic regime in which $\phi > 90°$), the exchange interactions become increasingly antiferromagnetic as δ decreases from 180°. This is shown schematically in Figure 4. However the experimental results indicate that $\epsilon_a > \epsilon_s$ when $\phi = 85.5°$ as in $3CuCl_2{\cdot}2dx$. Then, as shown by the dashed line in Figure 4, the energy ϵ_a will be displaced downward so that $|\epsilon_a - \epsilon_s|$ will decrease as δ deviates from 180°. Thus we predict that the antiferromagnetic contribution to the exchange should decrease as δ deviates from 180° while ϕ is kept fixed. This is exactly the trend seen for CHAC and $3CuCl_2{\cdot}2dx$, as discussed above.

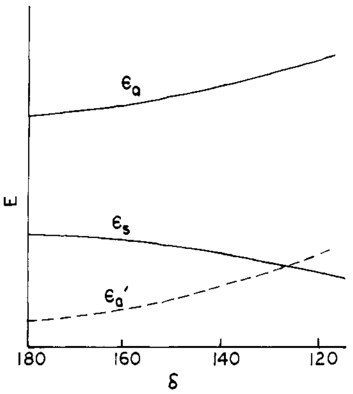

Figure 4. Qualitative plot of molecular orbital energies, ϵ_a and ϵ_s, vs. dihedral angle, δ. The solid lines correspond to $\phi > 90°$ with a net antiferromagnetic coupling at $\delta = 180°$. The dashed line labeled ϵ_a' corresponds to the energy of the antisymmetric magnetic orbital when ϕ is decreased to a value typical for a system with a net ferromagnetic coupling.

Conclusion

In summary, it has been seen that the experimentally determined properties of the three copper(II) complexes ($KCuCl_3$, CHAC, and $3CuCl_2{\cdot}2dx$) agree with the properties that would be expected from our knowledge of magnetostructural correlations. It follows that molecular structure is a powerful tool in predicting magnetic properties of compounds. It is planned to pursue C_p measurements to confirm the interpretation of the low-temperature magnetic behavior.

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Registry No. $3CuCl_2{\cdot}2dx$, 62444-80-8.