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Magnetic Investigation of Copper(II) Diethyldithiocarbamate

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The susceptibilities of $Cu(S_2CNEt_2)_2$ have been measured as a function of temperature, frequency, and applied field. The data are well described by a model based on weakly interacting dimers and result in a ferromagnetic intrapair-exchange constant of only about 0.9 K and an antiferromagnetic interpair interaction of −0.007 K.

Introduction

The compound bis(*N*,*N*-diethyldithiocarbamato)copper(II), $Cu(S_2CNEt_2)_2$ (hereafter, $Cu(dtc)_2$), has been investigated frequently.[1-3] The interest in the molecule lies with the fact that it has a binuclear structure and that several measurements[1,2] have been interpreted in terms of a strong ferromagnetic intradimer interaction. This analysis has depended upon susceptibility data taken above 4.2 K and the use of a modified Bleaney-Bowers equation[4] (eq 1) for 1 mol of in-

$$\chi_0 = [Ng^2\mu_B^2/3k_B(T-\Theta)][1 + \tfrac{1}{3}\exp(-2J/k_BT)]^{-1} \quad (1)$$

teracting $S = {}^1/_2$ ions. The parameters reported as fitting the data are $\langle g \rangle = 2.041$, $2J/k_B = 34.5$ K, and $\Theta = -1.37$ K. The negative Curie-Weiss constant was interpreted in terms of an antiferromagnetic interdimer interaction.

We questioned this interpretation in an earlier publication,[3] where susceptibility and relaxation data in the temperature range 1-20 K were presented. Further data, to lower temperatures, are presented here. If the large ferromagnetic interactions were important in $Cu(dtc)_2$, it should be apparent in our low-temperature susceptibility data. We find no such result. It is not simply a question of experimental accuracy; unpublished data between 1.7 and 7 K of Hatfield[5] furnished us do not match his previously reported results[1,2] but do agree with our susceptibility data. The different conclusions must therefore arise from the methods of data analysis presented in ref 1 and 2. By implication, the conclusion that strong ferromagnetic intradimer interaction occurs in all the molecules described in ref 1 and 2 must also be questioned.

Experimental Details

The compound $Cu(dtc)_2$ was prepared as reported.[1] No difference in magnetic properties was observed between the raw material and a sample recrystallized from chloroform. Proper composition was confirmed by both elemental analysis and by comparison of X-ray reflections with those reported in the literature.[6] Susceptibilities were measured by the mutual inductance technique in the usual fashion. Further details may be found in ref 7.

Results

The inverse zero-field ac susceptibility of $Cu(dtc)_2$ at low temperatures is displayed in Figure 1. Above 2 K, χ_0 obeys the Curie-Weiss law with $C = 0.397 \pm 0.008$ emu K mol^{-1} and $\Theta = 0.25 \pm 0.05$ K. Below 2 K, a deviation is observed, with χ_0^{-1} becoming larger.

The ac susceptibility as a function of applied field and frequency was also measured at 2 K. It was observed that the spin-lattice relaxation time τ increased from 10^{-5} to 4×10^{-5} s as H was varied from 1 to 30 kOe. Thus $\chi'(\omega)$ equals the isothermal susceptibility, χ_T, for frequencies of a few hundred hertz. The so-derived susceptibility, expressed as χ_T/χ_0, is illustrated in Figure 2.

The adiabatic susceptibility, χ_{ad}, was also measured at several temperatures. A measuring frequency of 480 kHz, which fulfills the condition[4] $\omega\tau >> 1$, was used. The usual relationship for the field-dependent behavior of χ_{ad} of paramagnets may be written as eq 2, where b/C is a measurement

$$\chi_0/\chi_{ad} = 1 + H^2/[(b/C)(1 - \Theta/T)^3] \quad (2)$$

of the internal field. This relationship was obeyed by $Cu(dtc_2)$ in fields less than 10 kOe, but deviations were observed at larger fields (Figure 3). The quantity $(b/C)(1 - \Theta/T)^3$ may be obtained from the linear part of the χ_0/χ_{ad} vs. H^2 relationship. Then, b/C could be determined from a plot of the third root of $(b/C)(1 - \Theta/T)^3$ vs. T^{-1}, as illustrated in Figure 4. This procedure leads to a fit with $b/C = 60 \pm 4$ kOe^2 and $\Theta = 0.4 \pm 0.1$ K. The deviations from this simple model, which occur at strong fields (Figure 3), will be discussed below.

Discussion

It was observed above that the Curie-Weiss law is not followed for temperatures below 2 K. A simple molecular field model for interdimer interactions,[7] too lengthy to reproduce here, leads to a modified Bleaney-Bowers relationship (eq 3).

$$\chi_0 = 4C(\tfrac{1}{2})/\{T[1 + \tfrac{1}{3}\exp(-2J/k_BT)] - 32J'/k_B\} \quad (3)$$

Here, $C({}^1/_2)$ is the Curie constant for a spin ${}^1/_2$ system, J/k_B is the intradimer-exchange constant, and J'/k_B is the interdimer-exchange constant. A positive exchange constant refers to ferromagnetic interaction, while antiferromagnetic interaction is characterized by a negative exchange constant. A least-squares fit (dashed line in Figure 1) of the data to eq 3 yielded $C({}^1/_2) = 0.389 \pm 0.004$ emu K mol^{-1} (corresponding to $g = 2.04 \pm 0.02$), $J/k_B = 0.96 \pm 0.1$ K, and $J'/k_B = -0.007 \pm 0.003$ K. The g value agrees well with that measured directly by EPR.[7]

The isothermal susceptibility for this system is readily calculated in terms of the local field $H_L = H + H_e$ where H is the applied field and H_e is the exchange field. The result[7] is

$$\frac{\chi_T(H)}{\chi_0} = \frac{\chi_T(H_L, J' = 0)}{\chi_0(J' = 0)} \frac{1 - \alpha\chi_0(J' = 0)}{1 - \alpha\chi_T(H_L, J' = 0)} \quad (4)$$

In this equation, $\alpha = 32J'/Ng^2\mu_B^2$ and the other expressions on the right-hand side refer to systems of isolated pairs. By choosing $g = 2.04$, one finds eq 4 is not sensitive to J' if both J and J' are used as parameters. For $J'/k_B = -0.007$ K, the

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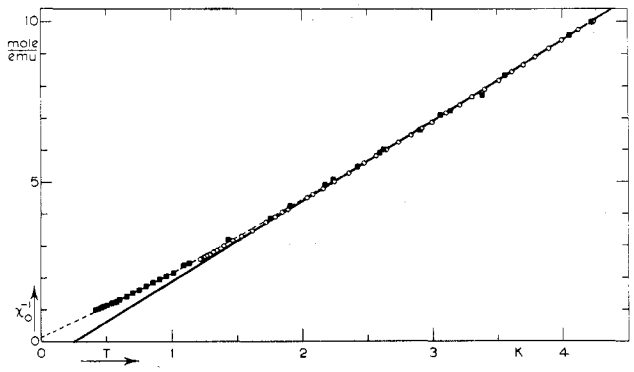

Figure 1. Inverse zero-field susceptibility of $Cu(S_2CNEt_2)_2$ as a function of the temperature. Measurements on the "raw material" are given as black squares, while the results of a sample consisting of powdered single crystals are shown as the open circles. The solid line represents the Curie–Weiss fit with $C = 0.397$ emu K mol^{-1} and $\Theta = 0.25$ K. The dashed curve is the theoretical fit as discussed in the text.

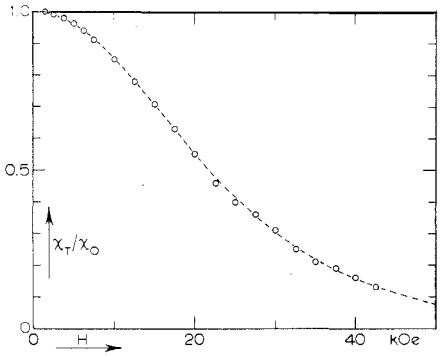

Figure 2. Normalized isothermal susceptibility of $Cu(S_2CNEt_2)_2$ (the "raw material") as a function of magnetic field, at $T = 2.00$ K. The dashed curve is the theoretical fit as discussed in the text.

value resulting from the χ_0 analysis, the best fit (dashed curve in Figure 2) corresponds to $J/k_B = 1.08$ K.

Turning now to the adiabatic susceptibility, a straightforward but again lengthy calculation within this model[7] shows that eq 2 should be modified to read as eq 5, where $1 + \epsilon \approx$

$$\frac{\chi_0}{\chi_0 - \chi_{ad}} = 1 + \epsilon + \left(\frac{b}{C}\right)\left(1 - \frac{\Theta}{T}\right)^3 / H^2 \qquad (5)$$

$1 - J/2k_BT$ and Θ is now defined as $J/2k_B + 8J'/k_B$. The experimental values of $\chi_0/(\chi_0 - \chi_{ad})$ were indeed found to follow a linear H^{-2} relationship up to the strongest fields (Figure 3). Again a value of $(b/C)^{1/3}(1 - \Theta/T)$ was obtained as a function of T^{-1}, which, in a similar way as mentioned above, yields $b/C = 58 \pm 4$ kOe^2. This result leads to $b = (23 \pm 2) \times 10^6$ ergs K mol^{-1}, by using the Curie constant as obtained from the χ_0 data. As in the high-temperature approximation $b = 3NJ^2/8k_B$,[7] this corresponds to an intradimer-exchange interaction $|J/k_B| = 0.86 \pm 0.05$ K, in nice agreement with the results from the low-frequency susceptibility data.

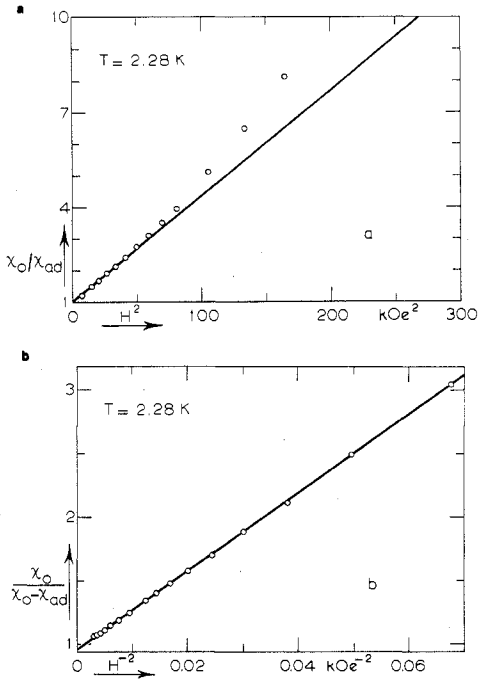

Figure 3. Example of the field dependence of the adiabatic susceptibility of $Cu(S_2CNEt_2)_2$ (the "raw material"): (a) plotted in the usual way to fit eq 2; (b) fit to eq 5.

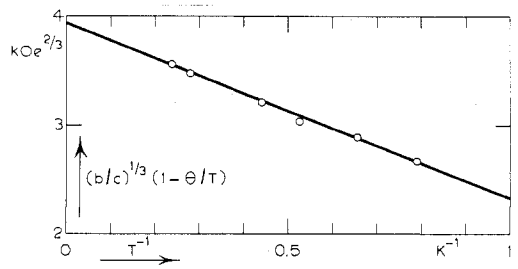

Figure 4. $(b/C)^{1/3}(1 - \Theta/T)$ as a function of the inverse temperature.

Conclusion

We have proposed a model of weakly interacting pairs of exchange-coupled copper ions which includes both the intrapair- and the interpair-exchange interactions in a quantitative way. This is in contrast to the earlier model,[2] which suggested a strong ferromagnetic intrapair interaction. The model gives a satisfactory description of the zero-field susceptibility as well as of the isothermal and adiabatic susceptibilities of $Cu(S_2CNEt_2)_2$, by using a J/k_B of about 0.9 K for the ferromagnetic intrapair-exchange interaction and $J'/k_B = -0.007$ K for the antiferromagnetic interaction between adjacent pairs. These results prove that the intrapair exchange is relatively weak, despite the close proximity of the metal ions to each other.

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Registry No. $Cu(dtc)_2$, 13681-87-3.