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Contribution from the Department of Chemistry,
University of Illinois at Chicago, Chicago, Illinois 60680,
and the Kamerlingh Onnes Laboratorium, University of Leiden,
Leiden, The Netherlands

Magnetic Reinvestigation of [$Cu(C_5H_5NO)_2(NO_3)_2$]: Lack of Evidence for a Triplet Ground State

Richard L. Carlin,* Ramon Burriel, R. M. Cornelisse,
and A. J. van Duyneveldt

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The report[1,2] of Hatfield and co-workers that certain structural dimers of copper(II) acted as ferromagnetic pairs has excited much interest. Susceptibility and magnetization measurements were interpreted in terms of an $S = 1$ ground state for $Cu(S_2CNEt_2)_2$, for example, with the $S = 0$ state lying some 34.5 K higher in energy. The compound [$Cu(C_5H_5NO)_2(NO_3)_2$] is supposed also to have such a ferromagnetic ground state, with the singlet lying 10 cm^{-1} (~14 K) higher in energy. The ligand C_5H_5NO is pyridine *N*-oxide.

We recently reinvestigated[3,4] $Cu(S_2CNEt_2)_2$ with a variety of magnetic measurements at low temperatures and showed that the molecule does not have the well-isolated $S = 1$ ground state that would be required by a pairwise ferromagnetic interaction of 34.5 K. This conclusion was confirmed by an independent group of investigators.[5] The low-temperature data[4] were interpreted in terms of a *weak* ($J/k = 0.9$ K) intramolecular coupling.

We were struck by the fact that three values of Θ, the Curie–Weiss constant, were reported[2] for [$Cu(C_5H_5NO)_2(NO_3)_2$], viz., 2, −2.7 and −0.50 K. Because of the ambiguity in sign and magnitude of this important parameter, we decided to reinvestigate this system as well. We show below that indeed there are no ferromagnetic dimers in [$Cu(C_5H_5NO)_2(NO_3)_2$].

Experimental Section

The sample of [$Cu(C_5H_5NO)_2(NO_3)_2$] was prepared according to published procedures.[6] Anal. Calcd: C, 31.80; H, 2.67; N, 14.83. Found: C, 31.95; H, 2.59; N, 14.68. Magnetic susceptibilities were measured by a standard ac mutual-inductance procedure in external fields up to 50 kOe; experimental details have been reported elsewhere.[7,8] Part of the susceptibility coil system was also used to determine the magnetization by integration of the induced voltage when the sample is moved.[9] The tabulated data are available from the authors.

Results

The susceptibility of [$Cu(C_5H_5NO)_2(NO_3)_2$] at zero static field, χ_0, is displayed in Figure 1 over the limited temperature interval between 1.2 and 10 K and in Figure 2 (as inverse susceptibility) between 1.2 and 80 K. These measurements were taken at a frequency of 117 Hz, and the ac field was about 1 Oe. For comparison, the data of Hatfield et al.[2] (as read from their published Curie–Weiss plot) are also displayed in Figure 2. It will be seen that the two data sets agree quite well at temperatures below 30 K but deviate at the higher temperatures. Our data were corrected for the diamagnetic contribution of the sample and sample holder to χ as well as for the temperature-independent susceptibilities in a way similar to that in ref 2, but these corrections are small compared to the observed differences. Therefore, the Curie–Weiss

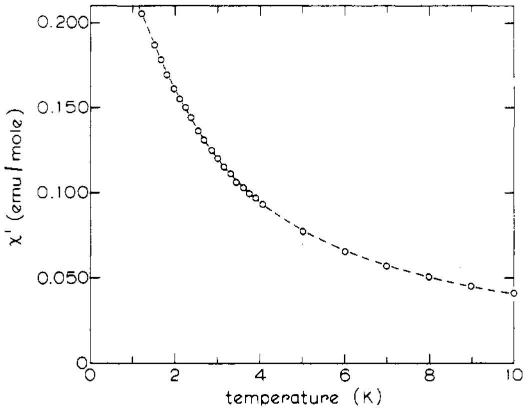

Figure 1. Zero-field susceptibility of powdered [$Cu(C_5H_5NO)_2(NO_3)_2$].

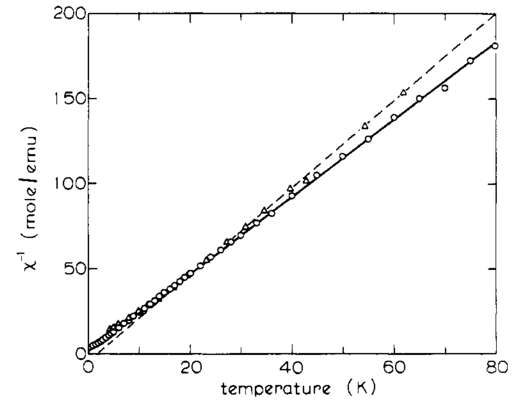

Figure 2. Curie–Weiss plot of the data in this paper (○) and of the earlier data of Hatfield (△).

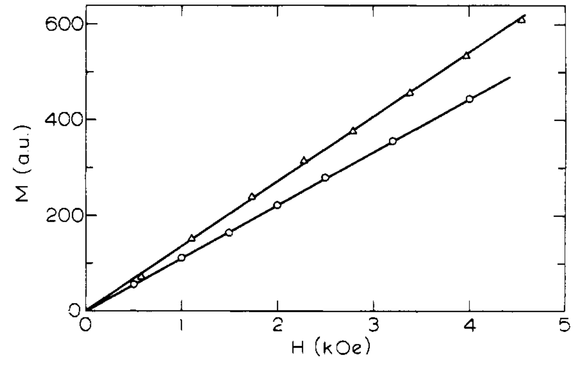

Figure 3. Magnetizations (relative) of manganese Tutton salt (△) and of [$Cu(C_5H_5NO)_2(NO_3)_2$] (○).

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* To whom correspondence should be addressed at the University of Illinois at Chicago.

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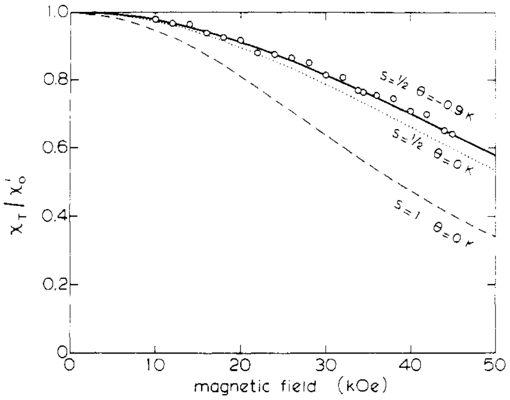

Figure 4. Isothermal susceptibility, χ_T/χ_0, at 4.2 K, of [Cu($C_5H_5NO)_2(NO_3)_2$]. The points are experimental; the solid curve is calculated (eq 2) for $S = {}^1/_2$, $g = 2.17$, and $\Theta = -0.9$ K. The dotted curve corresponds to $S = {}^1/_2$, $g = 2.17$, and $\Theta = 0$ K and the dashed curve to $S = 1$, $g = 2.17$, and $\Theta = 0$ K.

fits to the data differ appreciably. In the first case,[2] Curie–Weiss behavior was observed only above 11 K and the reported Weiss constant was +2 K. In the case of the new data that we report, Curie–Weiss behavior is observed over practically the whole measured temperature interval, with deviations only beginning to appear at the lowest temperatures. The fitted parameters are $C = 0.441$ emu K mol^{-1} and $\Theta = -0.8$ K, and thus $g = 2.17$ for $S = {}^1/_2$.

For an independent check of our absolute χ_0 results we determined the magnetization M of the pyridine N-oxide compound at several temperatures as a function of the static magnetic field. A typical example for $T = 4.21$ K is displayed in Figure 3 for a 474.5-mg sample, along with a similar measurement for 52.5 mg of manganese ammonium Tutton salt, $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The latter is known as one of the best examples of a Curie-law paramagnet, with $S = {}^5/_2$ and Curie constant $C = 4.38$ emu K/mol. The ratio of the slopes of the two curves in Figure 3 is 1.21 (1), which corresponds to a ratio of 11.4 (1) for the molar magnetization of the compounds. Consequently, for [Cu($C_5H_5NO)_2(NO_3)_2$], $\chi_{\text{static}} = M/H = 89.9\ (8) \times 10^{-3}$ emu/mol Cu at 4.21 K, in excellent agreement with the ac susceptibility result of $\chi_0 = 90.7\ (6) \times 10^{-3}$ emu/mol of Cu at 4.20 K.

Finally, in Figure 4, we present the normalized isothermal susceptibility of [Cu($C_5H_5NO)_2(NO_3)_2$] as a function of magnetic field at 4.20 K. The isothermal susceptibility, χ_T, is defined as

$$\chi_T(H,T) = (\partial M/\partial H)_T \qquad (1)$$

At $H = 0$, for a paramagnet, χ_T has the same value as χ_0. Thus $\chi_T/\chi_0 = 1$ at $H = 0$, but one can show that, as an external field is applied, the ratio χ_T/χ_0 becomes, in the molecular field approximation[10]

$$\chi_T/\chi_0 = (T - \Theta)(B'_s(x))/[T - \Theta(B'_s(x))] \qquad (2)$$

where Θ is once again the Weiss constant, $B_s(x)$ is the Brillouin function of $x = g\mu_B S(H + \Theta M)/kT$ and

$$B'_s(x) = \left(\frac{3S}{S+1}\right)\frac{\mathrm{d}(B_s(x))}{\mathrm{d}x} \qquad (3)$$

The symbol S stands for the spin of the system, and $\Theta M/C$ represents an effective field due to a small interaction.[10] The ratio χ_T/χ_0 at constant temperature is expected to decrease with increasing field.[10].

The circles in Figure 4 represent the measured isothermal susceptibility of [Cu($C_5H_5NO)_2(NO_3)_2$], up to quite strong external magnetic fields. The solid curve represents the calculation according to eq 2 with $S = {}^1/_2$, $g = 2.17$, and $\Theta = -0.9$ K. The dotted curve represents the same calculation with $S = {}^1/_2$ and $\Theta = 0$ K, while the dashed curve represents a calculation with $S = 1$ and $\Theta = 0$ K. A reasonable fit to the experimental data can of course also be obtained with the $S = 1$ curve, but then an unreasonably large value of Θ (~ -5 K) is needed.

Discussion

There can be no question about our conclusions: the data presented above require that the compound [Cu($C_5H_5NO)_2(NO_3)_2$] behave as an $S = {}^1/_2$ paramagnet down to liquid-helium temperatures. Any exchange interaction that may be present in the compound is only beginning to manifest itself at about 1.2 K.

If the compound were to consist of ferromagnetically aligned pairs, with an $S = 1$ ground state and with an $S = 0$ state at about 14 K, that would necessarily have been evident in our results. One may calculate, according to the Boltzmann factor, that the relative population of such a triplet state would be 96% at 4.2 K and 100% at 2 K. None of our data admit an analysis in terms of $S = 1$. Our χ_0 as well as $\chi_T(H)$ data can be described with one consistent set of parameters corresponding to $S = {}^1/_2$ and $g = 2.17$. Furthermore, the important exchange interaction is shown to be antiferromagnetic and leads to a Weiss constant of ~ -1 K only. Data at lower temperatures are required to distinguish whether this interaction is related to an intradimer or interdimer effect.

We admit surprise that the interactions are so weak in this compound, for the structural results[11] indeed show the existence of dimers. The bridge between the metal atoms is an oxygen atom from pyridine N-oxide, and the Cu–O–Cu angle is close to a right angle. So, either this geometry is unfavorable in general for the transmission of superexchange interaction or else pyridine N-oxide simply provides a very weak superexchange path in this compound. The latter is certainly true in a number of pyridine N-oxide complexes that have been studied recently,[12–16] but in those cases a M–O- - -O–M superexchange path is operative.

Nevertheless, one must now accept the fact that, when copper ions form structural dimers, the magnetic interaction between the ions is not necessarily very strong. The question of the existence of ferromagnetically aligned copper pairs remains an open one.[17,18]

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Registry No. [Cu($C_5H_5NO)_2(NO_3)_2$], 84028-38-6.

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(17) A reviewer points out to us that, from the structure of the molecule, the intramolecular coupling is expected to be extremely weak and antiferromagnetic in nature.

(18) Publication of this paper has been delayed at the request of the editor.