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The Low Temperature Magnetic Susceptibility of (4-Nitroquinoline N-oxide)copper(II) Chloride

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The magnetic susceptibility of Cu(4-nitroquinoline N-oxide)Cl_2 was measured in the temperature range 4.2-37.5°K in an attempt to ascertain the presence and nature of magnetic interactions, if any, in the compond. The data can be fitted to the Van Vleck equation for exchange coupled copper ions in a bimetallic complex with $<g>=2.2$ and $2J=135$ cm^{-1}, but the data do not unambiguously denote the nature of the magnetism. It is suggested that appropriate structural data be collected before definite conclusions concerning the magnetic state-of-affairs be put forth.

Introduction

As part of an investigation of substituted heterocyclic N-oxide complexes of copper(II), a series of complexes containing substituted quinoline N-oxides,[1] including a 1:1 adduct of $CuCl_2$ and 4-nitroquinoline N-oxide, were prepared and characterized. The 1:1 adduct had a magnetic moment of 2.08-2.12 B.M. in the temperature range 299-77°K. This «normal» moment is unusual in that many complexes of copper halides and substituted heterocyclic N-oxides of this formulation usually exhibit antiferromagnetic coupling between the metal ions.[1]

The (4-nitroquinoline N-oxide) copper (II) chloride complex was assumed to contain oxygen bridged coppers as had been reported for many similar systems.[2] With this assumption, Muto and Jonassen explained the magnetic data in terms of the electronic withdrawing effect of the 4-nitro group on the bridging oxygens. But on the basis of infrared comparisons, Hatfield[1] and co-workers suggested that this complex contains chloride rather than oxygen bridges. Thus Cu(4–nitroquinoline N–oxide)Cl_2 is distinctly different from many other heterocyclic N-oxide adducts of the copper(II) halides.

Recently Sinn[3] has suggested that this compound may be described as having a « pair-wise ferromagnetic interaction. » Unfortunately the analysis published by Sinn is based on only a modicum of data; and in view of the present interest in positive exchange coupling constants, we felt it necessary to study the EPR and low temperature magnetic susceptibility in order to understand more fully this system.

Experimental Section

A sample of the copper complex, (4–NO_2–quin N–O)Cl_2, was available from a previous preparation.[1] It was reanalyzed to ensure that it had not decomposed. (*Anal.* Calcd: C, 33.30; H, 1.86; N. 8.63. Found: C, 33.43; H, 1.93; N, 8.49).

In order to allow us to study the EPR of the copper complex as a magnetically dilute powder as well as the pure compound, we prepared a 20% solid solution of the copper adduct in the diamagnetic zinc analog.

The ligand, 4-nitroquinoline N-oxide, was prepared using the method of Ochiai.[4] Concentrated nitric acid (4.5 g, 3.5 ml) was added over a period of twenty minutes to 7.5 g quinoline N-oxide dissolved in 13 ml concentrated sulfuric acid. The reaction mixture was held at ~70°C for two hours, after which it was slowly cooled to room temperature and then poured over ice. The yellow precipitate was collected, washed with water, dilute sodium carbonate, water, and a small portion of absolute ethanol. The product recrystallized from acetone to yield 3.5 g of a yellow solid. (Reported m.p.: 153-54°C. Found: 153-54°C).

The solid solution of 20% Cu/Zn (4–NO_2–quin N–O)Cl_2 was prepared using the general method reported by Whyman, Copley, and Hatfield.[1] The ligand (.01 mole, 1.90 g) was dissolved in 10 ml hot butanol to give a yellow solution. A ten-fold excess of the mixed metal chlorides (.08 mole, 10.90 g $ZnCl_2$; .02 mole, 3.41 g $CuCl_2 . 2H_2O$) was dissolved in 200 ml hot butanol. The two hot solutions were mixed with stirring and then cooled slowly. The product was collected as yellow-green plates from the green-yellow mother liquor. The precipitate was washed with two portions of butanol and dried under nitrogen to yield 2.4 g product. (*Anal.* Calcd: C, 33.12; H, 1.84; N, 8.58; Cl, 21.71. Found: C, 33.40; H, 2.07; N, 8.42; Cl, 21.31). X-ray diffraction patterns were taken on powdered samples of both the pure copper complex and the solid solution. The two patterns were identical.

Magnetic susceptibility measurements below 70°K were made using a Foner-type[5] vibrating sample magnetometer manufactured by Princeton Applied Research, Inc. The magnetometer was operated at a field strength of 10,000 gauss. Data were corrected for the magnetism of the sample holder assembly, for

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[1] R. Whyman, D.B Copley, and W.E. Hatfield, *J. Amer. Chem. Soc.*, *89*, 3135 (1967).
[2] Y. Muto and H.B. Jonassen, *Bull. Chem. Soc. Japan*, *39*, 58 (1966).
[3] E. Sinn, *Inorg. Nucl. Chem. Letters*, *5*, 193 (1969).
[4] E. Ochiai, *J. Org. Chem.*, *18*, 568 (1953).
[5] S. Foner, *Rev. Sci. Instr.*, *30*, 548 (1959).

Table I. Hight Temperature Magnetic Data for Cu(4-NO_2-quin N-O)Cl_2

Temperature(°K)	χ_M^{corr} measured (c.g.s.u./Cu)	χ_M^{corr} calc. [a] (c.g.s.u./Cu)	$\mu_{meas.}$ [b] (B.M.)	$\mu_{calc.}$ [a, b] (B.M.)
299	.001809	.001810	2.08	2.08
196	.002756	.002845	2.08	2.11
77	.007298	.007369	2.12	2.13

[a] Calculated using $J_{12}=200cm^{-1}$ and $g=2.13$ as suggested in Reference 3. [b] $\mu_{eff}=2.828(\chi_M^{corr}\cdot T)^{1/2}$.

Table II. The Low Temperature Magnetic Data for Cu(4-nitroquinoline N-oxide)Cl_2.

Temperature, °K	$\chi_M^{corr.}$, cgs units	μ_{eff}, B.M.
37.5	.01540	2.15
28.6	.02153	2.22
22.6	.02903	2.29
16.9	.03631	2.22
14.4	.04242	2.21
11.2	.05375	2.19
8.1	.07243	2.17
6.4	.08739	2.12
5.1	.1044	2.06
4.2	.1169	1.98

the diamagnetism of the constituent atoms using Pascal's constants[6] (130×10^{-6} c.g.s.u./g atom copper), and for TIP (60×10^{-6} c.g.s.u./g atom copper).

EPR measurements were made on powdered samples in quartz tubes using a Varian E-3 spectrometer. Data were measured using X band (9.185 GHz) radiation.

Results

Table I shows the high temperature magnetic data for this complex corrected for diamagnetism and TIP. Also shown are values calculated from equation using the magnetic parameters reported by Sinn, that is, $J_{12}=200$ cm^{-1} and $<g>=2.13$. The actual values are different from those in Reference 3 because we have used the more accurate constant value of 2.828 instead of 2.84 to calculate μ_{eff}

$$\mu_{eff}=g[(1+\frac{1}{3\ \exp\ 2J_{12}/kT})^{-1}]^{1/2} \qquad (1)$$

Though magnetic parameters obtained by Sinn give calculated values that agree well with the experimental data, the approach is limited since only three temperature points were used. In short the data were designed not to be the basis of a precise calculation but only to distinguish this complex from several similar systems with distinctly subnormal moments at lower temperatures.

Inspection of equation (2) will show that as $2J_{12}/kT$ becomes large, $1/(3\ \exp\ 2J_{12}/kT)$ approaches zero so that for a given value of J there is a temperature below which μ_{eff} has $<g>$ as its maximum limit. If $J=200$ cm^{-1} and $<g>=2.13$, this temperature is 96°K. The magnetic data for Cu(4-nitroquinoline N-oxide)Cl_2 below 50°K listed in Table II clearly show that μ_{eff} did not reach a constant maximum at 96°K.

Detailed interpretation of the magnetic data is hampered by the absence of any structural data for this complex. Though it seems reasonable that the compound does involve bridging chloride ligands between copper ions, we have no information as to whether or not the system consists of distinct dimers, linear chains, or some more complex structure. Because of this uncertainty, we examined the magnetic data using the theoretical expressions for both dimeric and linear chain complexes.

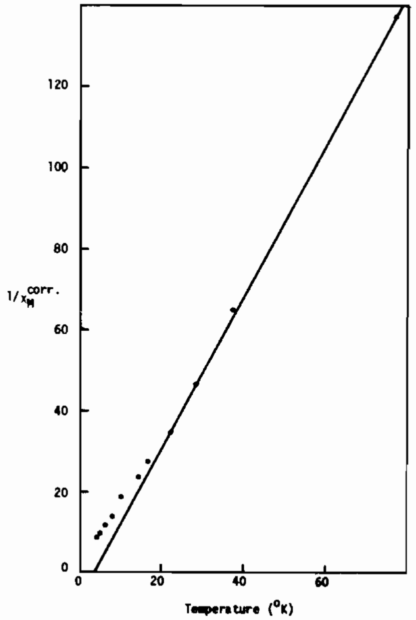

Figure 1. The inverse of the magnetic susceptibility *vs.* temperature curve for Cu(4-nitroquinoline N-oxide)Cl_2. The solid line is the best Curie-Weiss line for the data above 20°K.

The data were first fitted to the Van Vleck equation for magnetic coupling in a d^9–d^9 dimer as shown in (2).

$$\chi_M=\frac{g^2N\beta^2}{3kT}[1+(1/3)\exp(-2J/kT)]^{-1} \qquad (2)$$

The fitting process minimized the function

$$\sum_i\{\Delta\chi_i\cdot T_i\}^2$$

where $\Delta\chi$ is the difference in the experimental and calculated molar magnetic susceptibilities. The best fit was obtained for $<g>$ $=2.20$ and $2J=135$ cm^{-1}. For this fit, data for the three lowest temperatures

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(6) B.N. Figgis and J. Lewis in *Modern Coordination Chemistry*, J. Lewis and R. Wilkins, Editors, Interscience Publishers, Inc., New York, N. Y., 403 (1960).

were omitted from the calculation because of the possibility of field effects. Unfortunately this fitting process is not very sensitive to small changes in J. For example, while fitting eight of the mid-range temperature points of this system, it was observed that a change from $2J = 75$ cm^{-1}, the best fit for these data, to $2J = 100$ cm^{-1} produced a change of less than 1% in the sum of the squares of the deviations.

The Ising model[7] for linear chains of copper atoms was also used to fit the data measured above 8°K. The expression for χ_M for this model is shown below (3).

$$\chi_M = \frac{N\beta^2}{3kT}(3g^2/4)[\exp(2J/kT)] \qquad (3)$$

In this case, the best parameter values were $<g> = 2.22$ and $2J = 2.2$ cm^{-1}. The quality of this fit, as reflected in the sum of the squares of the deviations, is poorer by a factor of ten than the best fit using the dimer equation.

EPR spectra of dilute powders have been successfully used to characterize the triplet ground state of the bis(pyridine N-oxide)copper nitrate dimer,[8] a systems which exhibits magnetic behavior very similar to that reported here. In systems where we were unable to prepare magnetically dilute powders, such as $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$,[9] we have been able to observe the lines associated with the $\Delta M_s = \pm 2$ and high and low field parallel $\Delta M_s = \pm 1$ transitions in the EPR spectra of pure compounds.

In the present case, the EPR spectra of powdered samples of $Cu(4{-}NO_2{-}quin\ N{-}O)Cl_2$ and 20% $Cu/Zn(4{-}NO_2{-}quin\ N{-}O)Cl_2$ were recorded at both room temperature and 77°K. All of the spectra contained a single, very broad band centered at about 3160 gauss. No other features could be observed in the spectra. The spectra did exhibit an anomalous effect in that the band-width of the single line increased with the lowering of the temperature.

In spite of our inability to characterize this system in detail, the data do indicate that some magnetic coupling seems to be present and that J is positive. This conclusion is supported by the following reasoning: If $J = 0$, *i.e.* no magnetic coupling present, both equations (3) and (4) simplify to the same form, $\mu_{eff} = (\sqrt{3}/2)g \simeq 0.865$. Thus, if $J = 0$, g for this system becomes a function of temperature and varies between 2.4 and 2.6; these values for g are unacceptably large for this type of copper complex. If J were less than zero, g would have to be even larger than 2.6.

Information about the crystal structure of this complex is required before its magnetic properties can be fully understood.

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(7) L. Dubicki. C.M. Harris, E. Kokot, and R.L. Martin, *Inorg. Chem.*, *5*, 93 (1966).

(8) W.E. Hatfield, J.A. Barnes, D.Y. Jeter, R. Whyman, and E.R. Jones, *J. Amer. Chem. Soc.*, *92*, 4982 (1970).

(9) J.A Barnes, W.E. Hatfield, and D.J. Hodgson, *Chem. Phys. Letters*, *7*, 374 (1970).