Magnetism of the Quinoxaline Complex of Copper(II) Nitrate

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The magnetic susceptibility of the 1:1 complex of quinoxaline with copper(II) nitrate, $Cu(Q)(NO_3)_2$, has been measured from 1.7 to 300°K. The data show that an antiferromagnetic interaction is present with a susceptibility maximum at 8.3°K. The data are compared to structurally and magnetically related compounds and are discussed in terms of the Heisenberg and Ising models for one-dimensional linear chains. The room temperature epr spectrum of a powdered sample of $Cu(Q)(NO_3)_2$ is indicative of effective tetragonal geometry for the complex. Satisfactory simulation of the epr spectrum could be obtained using the parameters: $g_\parallel = 2.265$, $A_\parallel = 0.0124$ cm^{-1}, $LW(A_\parallel) = 58.5$, $g_\perp = 2.089$, $3A_\perp = 0.0144$ cm^{-1}, and $LW(A_\perp) = 70.0$ where LW is one-half of the peak-to-peak line width in gauss. The infrared spectrum of the compound is also discussed.

Introduction

Quinoxaline complexes of the type $QCuX_2$ (Q = quinoxaline, $X^- = Cl^-$, Br^-, NO_3^-, $C_2H_3O_2^-$) were first reported by Underhill. On the basis of infrared and reflectance spectra a structure consisting of chains of planar $Cu(NO_3)_2$ units bridged by the quinoxaline molecules was proposed for $QCu(NO_3)_2$ by Underhill.[2] Spectral results suggested that the nitrates were bound to the copper ions in the same manner as the 1:1 copper(II) nitrate complex with pyrazine whose structure has been determined.[3] The proposed structure of $QCu(NO_3)_2$ is illustrated in Figure 1.

Previous studies[4,5] of the magnetic properties of substituted quinoxaline–copper(II) halide complexes have revealed the presence of antiferromagnetic exchange interactions. Billing, et al.,[6] postulated that the exchange coupling occurred *via* the bidentate heterocyclic ligand even though the room temperature magnetic moment was normal. Such an exchange interaction was found in the analogous pyrazine complex[7] and probably also exists in the polymeric copper(II) halide complexes with pyridazine, phthalazine, and 3,4-benzocinnoline.[8]

The present work reports the magnetic susceptibility of $QCu(NO_3)_2$ from 1.7 to 300°K. The data have been analyzed in terms of the Heisenberg and Ising models[9,10] for chains of interacting ions. The infrared spectrum has been extended to 200 cm^{-1} and the epr spectrum of the powdered complex has been measured and simulated.

Experimental Section

Preparation of $QCu(NO_3)_2$. The complex was obtained by adding a 1 M solution of copper(II) nitrate trihydrate in absolute ethanol (which also contained sufficient 2,2-dimethoxypropane for the removal of water) dropwise with vigorous stirring to a 1 M solution of quinoxaline in absolute alcohol. The blue complex which precipitated was isolated by filtration, washed with ether, and air-dried. *Anal.* Calcd for $Cu(C_8H_6N_2)(NO_3)_2$: C, 30.2; H, 1.90; N, 17.6. Found: C, 30.4; H, 1.99; N, 17.5.

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The magnetic susceptibilities at 77, 195, and 298°K were measured using a Faraday balance.[11] Low-temperature measurements (1.7–68°K) were taken with a Foner-type vibrating sample magnetometer[12] operating at a field strength of 10,000 G which was calibrated with mercury(II) tetrathiocyanatocobaltate(II).[13,14] A value of 60×10^{-6} cgs unit was taken for the temperature-independent paramagnetism of the copper(II) ion. Electron paramagnetic resonance spectra were recorded on a Varian E-3 X-band spectrometer and a Magnion MVR-12X X-band spectrometer with accessories described previously.[15] The epr spectrum of $QCu(NO_3)_2$ was simulated using the computer program described by Venable[16] on an IBM 360-50 computer. Infrared spectra (4000–200 cm^{-1}) were measured with a Perkin-Elmer 621 recording spectrophotometer using Nujol mulls on cesium iodide plates.

Results

The infrared spectrum (4000–400 cm^{-1}) of $QCu(NO_3)_2$ was described by Underhill.[2] Since the metal–ligand stretching frequencies could be expected to occur at lower energies,[17] it was of interest to examine the infrared spectrum of the complex down to 200 cm^{-1}. In the region 800–200 cm^{-1} the complex shows absorptions at 795 (s), 740 (s), 650 (vw), 539 (w), 530 (w), 425 (s), 415 (s), 344 (m, br), and 290 cm^{-1} (m, br), whereas the ligand absorbs at 754 (s), 603 (m), 542 (w), 400 (s), and 392 cm^{-1} (w). In general, metal–oxygen stretching frequencies are larger than metal–nitrogen stretching frequencies. Therefore, we tentatively assign the 344-cm^{-1} band in $QCu(NO_3)_2$ to ν(Cu–O) and the 290-cm^{-1} band to ν(Cu–N). These assignments are in accord with those for a variety of complexes with oxygen[17,18] and nitrogen[17] donor ligands.

As shown in Figure 2 the magnetic susceptibility data obey the Curie-Weiss law, $\chi = C/(T + \Theta)$, in the temperature range 24–300°K with $C = 0.374$, a Weiss constant, $\Theta = 5°$, and $\mu_{eff} = 2.828\,C^{1/2} = 1.73$ BM. The Curie-Weiss law does not hold at lower temperatures. A minimum in the susceptibility curve is observed at approximately 8.3°K. This minimum (maximum χ) in the plot is characteristic of antiferromagnetic interactions.

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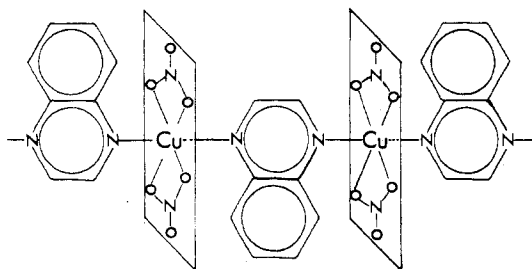(18) J. R. Wasson, C. I. Shyr, and C. Trapp, *Inorg. Chem.*, 7, 469 (1968).

Figure 1. A schematic representation of the structure of $QCu(NO_3)_2$.

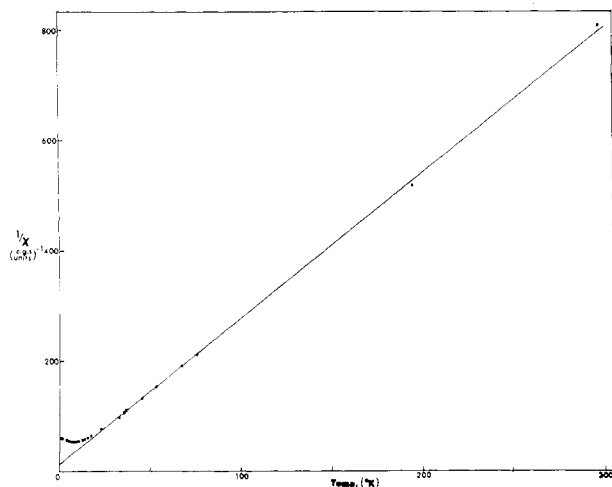**Figure 2.** Reciprocal molar susceptibility of $QCu(NO_3)_2$ plotted against temperature from 1.7 to 298°K.

The Hamiltonian for a linear chain of interacting spins is

$$\mathcal{H} = -J\sum_{i=1}^{N}[S_{iz}S_{(i+1)z} + \gamma(S_{ix}S_{(i+1)x} + S_{iy}S_{(i+1)y})]$$

where a negative J indicates antiferromagnetic interaction and γ may take values from 0 to 1. It is assumed that there is no further anisotropy to differentiate between the x and y directions. When $\gamma = 0$ the anisotropic Ising model obtains with the Hamiltonian $-JS_{iz}S_{jz}$ while $\gamma = 1$ defines the isotropic Heisenberg model.

Exact closed form expressions are not available[10] for the Heisenberg or intermediate γ spin Hamiltonians but approximations have been made for infinite chains where $kT_{max}/|J| \cong 1.282$ and $|J|\chi_{max}/g^2\beta^2N \cong 0.07346$ with $|J|$ as the exchange energy. Fisher[19] has also shown that the exact closed form expression for the anisotropic susceptibility of one-dimensional Ising chains of $S = {}^1/_2$ ions is

$$\chi_{\parallel} = [Ng^2\beta^2/4kT]\ \exp(2J/kT)$$

and

$$\chi_{\perp} = \frac{Ng^2\beta^2}{8|J|}[\tanh(J/kT) + (J/kT)\ \mathrm{sech}^2\ (J/kT)]$$

with the total susceptibility given as

$$\chi = {}^1/_3\chi_{\parallel} + {}^2/_3\chi_{\perp}$$

The values given by the best least-squares fit of the magnetic susceptibility data of $QCu(NO_3)_2$ with the Ising model and the values estimated using the Heisenberg approximations are listed in Table I along with the experimental g values.

The epr spectrum of powdered $QCu(NO_3)_2$ is given in Figure 3. The spectrum is one characteristic of a tetragonal copper(II) complex, the ground state probably being d_{xy} or
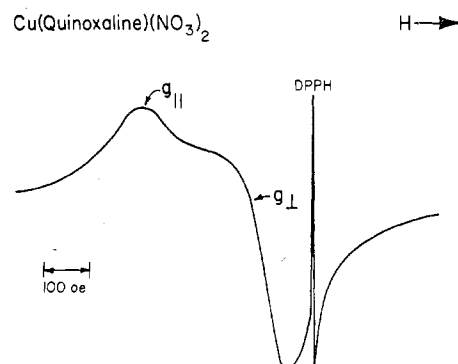
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$Cu(Quinoxaline)(NO_3)_2$ H →

Figure 3. The epr spectrum of a powdered sample of $QCu(NO_3)_2$.

Table I. Magnetic Parameters

		Heisenberg model		Ising model		
	g_{exp}	J, cm^{-1}	g_{calcd}	J, cm^{-1}	g_{calcd}	Ref
$QCu(NO_3)_2{}^a$	2.15	−4.5	2.14	−6.2	2.05	This work
$Cu(Paz)(NO_3)_2{}^b$		−3.6		−5.3		d
$Cu(DimeQ)Cl_2{}^c$		−33		−45		5

^{a} Q = quinoxaline. ^{b} Paz = pyrazine. ^{c} DimeQ = 2,3-dimethyl-quinoxaline. ^{d} Values based on recent single crystal measurements which are to be published elsewhere.

$d_{x^2-y^2}$. The epr spectrum of matrix isolated $Cu(NO_3)_2$ has been interpreted[20] in terms of effective D_{4h} symmetry with $g_{\parallel} = 2.2489 \pm 0.003$ and $g_{\perp} = 2.0522 \pm 0.0005$. The epr spectrum of $QCu(NO_3)_2$ could be simulated using Venable's program[16] with the parameters: $g_{\parallel} = 2.265, A_{\parallel} = 0.0124$ cm^{-1}, $LW(A_{\parallel}) = 58.5, g_{\perp} = 2.089, 3A_{\perp} = 0.0144$ cm^{-1}, and $LW(A_{\perp}) = 70.0$ where LW is one-half of the peak-to-peak line width in gauss.

Discussion

The quinoxaline complex probably has a structure (Figure 1) similar to the pyrazine copper(II) nitrate compound. In the latter compound the pyrazine bridge separates[3] the copper(II) ions by 6.7 Å and it is assumed that this is the approximate distance in the quinoxaline complex. If this assumption is correct, there is much interest in determining how the more complicated π system affects the exchange energy. The quinoxaline complex, having a greater degree of electron delocalization, may be expected to exhibit a larger exchange interaction than the pyrazine complex. This would arise if, as postulated, the σ^* unpaired electrons on the copper ions interact with the π electrons of the heterocyclic ligand bridge thus enabling the antiferromagnetic interaction to occur by a superexchange mechanism. However, if the exchange in the quinoxaline complex is not greater than that of the pyrazine complex, then it is likely that there is an increase in the canting of the heterocyclic amine groups. Structural data for the pyrazine complex[3] show that the pyrazine rings are canted with respect to the coordination plane (of two oxygen and two nitrogen atoms) of the copper ion. The increased steric requirements of the quinoxaline ligand may be sufficient to cause a greater cant thus affecting the 180° superexchange mechanism. The influence of these factors on the exchange energy cannot be adequately assessed until further structural data become available.

Comparison of the exchange coupling constants given in Table I for the pyrazine and quinoxaline complexes show that, in the Heisenberg model, the values are 20% higher for

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the quinoxaline complex. This, as mentioned above, is probably due to the greater electron delocalization of the ligand. It is noted that quinoxaline has a higher pK_a than pyrazine.

Another interesting compound for comparison with QCu-$(NO_3)_2$ is the 2,3-dimethylquinoxaline-copper(II) chloride complex[5] which is also thought to be bridged through the heterocyclic amines and not through the chlorides. The magnetic properties could be expected to be similar to those of the nitrato complex except for variations due to electronic and steric differences of the two anions. According to the Fisher–Ising model the interaction yields a J value of -45 cm^{-1} while the Heisenberg model gives a J of -33 cm^{-1}. It was because of this large interaction constant that the suggestion was made[5] that exchange occurred across the heterocyclic ligand and not through the chloride ions. Barraclough and Ng[21] noted that J values for chloride-bridged complexes of known structure appear to be small (<20 cm^{-1}) in most cases; however, this suggestion does not seem consistent since the quinoxaline molecule is almost definitely bridging in the QCu(NO_3)$_2$ complex and still the J values are very small. It does not seem reasonable, if the proposed structure for the substituted quinoxaline[6] complex is correct, that anion effects alone could account for the difference in the J values.

Studies by Griffiths,[22] Kadota, *et al.,*[23] Takeda, *et al.,*[24] Matsuura,[25] and Jeter and Hatfield[26] showed marked preference for the Heisenberg model. Bonner and Fisher[10] have evaluated a theoretical approximation relating magnetic susceptibility to temperature for a Heisenberg chain. This is illustrated in the lower curve of Figure 4. It is noted that the susceptibility passes through a rather broad maximum and then falls to 0.69 times its maximum value at absolute zero. For finite chains with an odd number of paramagnetic centers χ diverges to a value larger than for an infinite chain, and for finite chains with an even number of paramagnetic centers χ converges to a smaller value. For the anisotropic Ising model with $\gamma = 0$, $\chi_{\parallel}$ goes through a more narrow maximum and then converges to zero whereas $\chi_{\perp}$ reaches a finite value at 0°K. As γ is increased to 1 the maximum in $\chi_{\parallel}$ becomes much broader, and the value of χ at the maximum decreases. At $\gamma = 0$ and 1 the $kT/|J|$ values at the reduced χ_{max} are 1.00 and 1.28, respectively. Since the values of J are determined using these maxima, J will be somewhat smaller for the Heisenberg model.

In Figure 4 it is also noted that the experimental data conform to neither model in the lowest temperature region. Jeter and Hatfield[26] have shown [also on a polymeric copper-(II) complex] that this region varies from that expected theoretically with the Ising model. The J values are very small for the quinoxaline complex and it is likely that interchain interactions are playing a role in distorting the isolated one-dimensional chain and, thus, neither the Heisenberg nor the Ising model appears to be obeyed. Hyde, *et al.,*[27] have introduced a term in χ for monomeric impurities that might be present which could markedly influence low-temperature
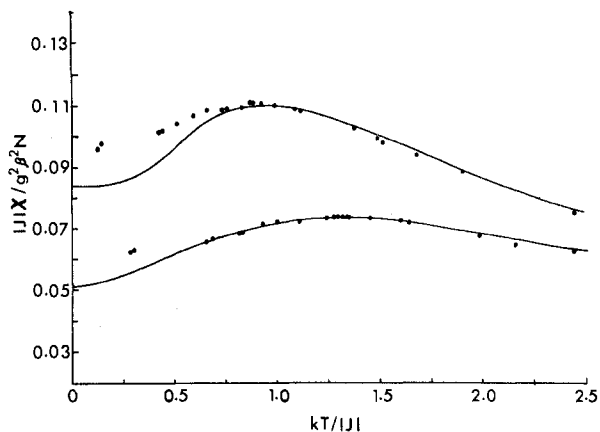

Figure 4. Proportionate susceptibility *vs.* temperature illustrating the Ising (upper line) and Heisenberg (lower line) models.

results. More recently, Reedjik, *et al.,*[28] have shown using epr techniques that paramagnetic impurities may be on the order of 2% for dimers. The epr data obtained in the present work do not indicate the presence of monomeric impurities. However, the observed epr spectrum is rather intense and this could mask signals arising from small amounts of impurities. It is noted that, if impurities are present, they have essentially the same g values and hyperfine coupling constants as QCu(NO_3)$_2$. If the Ising model is fit using $g = 2.14$, the fit is about six times worse than the theoretically calculated g value of 2.05 and J changes by about 12% to -7.0 cm^{-1}. The average g value ($g = {}^1\!/_3 g_{\parallel} + {}^2\!/_3 g_{\perp}$) determined using epr is 2.148 $\pm$ 0.005 which compared quite well with the $g = 2.14$ obtained using the Heisenberg model.

Following the line width arguments by Hyde, *et al.,*[29] and estimating D to be 5×10^{-2} cm^{-1} as an upper limit for anisotropic exchange, the γ in the Hamiltonian can be calculated from the expression

$$D/J_{exp} = (1 - \gamma)/\gamma$$

or

$$\gamma = J_{exp}/(J_{exp} + D)$$

Setting $J = 5$ cm^{-1} as a reasonable mean value for the two models gives $\gamma = (5$ cm$^{-1}/5.05$ cm$^{-1}) = 0.990$ which is very close to the Heisenberg approximation. Kokoszka, *et al.,*[30] have also examined a number of copper(II) ion "chains" with similar molecular geometry. They obtain isotropic exchange interaction values of about 600 cm^{-1} with anisotropic values of about 0.2 cm^{-1}. Apparently, epr and magnetic susceptibility data are consistent with isotropic exchange described by the Heisenberg model.

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