Magnetism of the Dinitrogen Tetraoxide Adduct of Copper(II) Nitrate

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The magnetic susceptibility of a powdered sample of $Cu(NO_3)_2{\cdot}N_2O_4$ has been determined in the temperature range of 1·7—298 K. The data may be described by a two-dimensional Heisenberg antiferromagnetic model yielding the exchange energy $|J|$ = 3·3 K and g = 2·20. The g value is in good agreement with the average g value determined from e.p.r. measurements.

DINITROGEN tetraoxide adducts of transition-metal nitrates comprise an interesting series of compounds. Some of these compounds are thermally stable and can be best formulated as nitrosonium salts of nitrato-complexes, *e.g.* $[NO][M(NO_3)_3]$.[1-3] Adducts of lower stability are thought to contain discrete N_2O_4 molecules.[4] The compound $Cu(NO_3)_2{\cdot}N_2O_4$ is known to be fairly stable,[5] and a preliminary crystal-structure report [6] has revealed that the nitrosonium formulation obtains for this compound. The copper-containing anions of $Cu(NO_3)_2{\cdot}N_2O_4$ form two-dimensional anionic polymeric sheets, with discrete nitrosonium cations completing the structure. Polymeric transition-metal complexes often possess unusual magnetic properties, and much research has been done on the magnetism of systems of this nature.[7] Recently, there has been considerable interest in the properties of two-dimensional polymeric complexes.[8] Therefore, in order to determine the extent and nature of any magnetic-exchange interactions in $Cu(NO_3)_2{\cdot}N_2O_4$ the magnetic susceptibility has been measured from 1·7 to 298 K at varying field strengths.

EXPERIMENTAL

The compound $Cu(NO_3)_2{\cdot}N_2O_4$ was prepared by a modification of the method of Addison and Hathaway.[5] Dinitrogen tetraoxide (*ca.* 4·6 g) (Matheson, commercial grade) was collected as a white solid in an Erlenmeyer flask (250 cm^3) cooled in a dry ice–acetone bath. The N_2O_4 was dissolved in nitromethane (50 cm^3) to make a solution of *ca.* 90 mol % nitromethane, the optimum concentration recommended by Addison and Hathaway.[5] The resulting solution was transferred to a dry-nitrogen atmosphere (anhydrous P_2O_5 was used as desiccant in a glove-bag). Copper turnings (*ca.* 5 g), filed to a bright finish, were then placed in the solution. Fine blue needle-like crystals of $Cu(NO_3)_2{\cdot}N_2O_4$ began to coat the metal surfaces after *ca.* 10 min; these crystals were periodically scraped off and new product allowed to form on the freshly exposed metal surfaces until the reaction appeared complete. The process required *ca.* 10 h. In a typical run, 1 g of product was obtained. The small light blue crystals were collected on a sintered glass filter and washed with liquid N_2O_4 and with nitromethane. Powdered samples were then immediately prepared in the glove-bag and stored in a desiccator under refrigeration until use (Found: Cu, 22·25; N, 19·95. Calc. for CuN_4O_{10}: Cu, 22·75; N, 20·05%). Microanalyses were carried out by Galbraith Laboratories, Knoxville, Tennessee.

Magnetic-susceptibility measurements were determined

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[4] C. C. Addison and D. Sutton, *J. Chem. Soc.*, 1964, 5553.

[5] C. C. Addison and B. J. Hathaway, *J. Chem. Soc.*, 1960, 1468.

[6] L. J. Blackwell, T. J. King, and A. Morris, *J.C.S. Chem. Comm.*, 1973, 644.

[7] See, for example, R. C. Slade, *Ann. Reports (A)*, 1972, **69**, 101 and refs. therein.

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in the temperature range 1·7—298 K using a P.A.R. Foner-type vibrating-sample magnetometer[9] calibrated with mercury(II) tetrathiocyanatocobaltate(II)[10] and with $[NH_4]_2Mn[SO_4]_2 \cdot 6H_2O$.[11] Temperatures were measured with a calibrated gallium arsenide diode, constant-current source, and digital voltmeter. Susceptibility data were corrected for the diamagnetism of constituent atoms using Pascal's constants[12] and for temperature-independent paramagnetism (t.i.p.)[13] (according to $N\Delta g\beta^2/\lambda = 60 \times 10^{-6}$ c.g.s. units). E.p.r. spectra were recorded at *X* band on a Varian model E-3 spectrometer using diphenylpicrylhydrazyl (dpph) as internal standard.

RESULTS AND DISCUSSION

The magnetic susceptibility of a powdered sample of $Cu(NO_3)_2 \cdot N_2O_4$ was determined in the temperature range 77—298 K at a field strength of 10 000 G. A second sample was prepared and its susceptibility was determined in the temperature range 1·7—77 K at field strengths of 100 and 500 G, since co-operative magnetic phenomena are sometimes masked by high measuring fields.[14] Field-dependence studies showed no significant field dependence nor hysteresis at 4·2 or 77 K. The e.p.r. spectrum of a powdered specimen of $Cu(NO_3)_2 \cdot N_2O_4$ was recorded at 77 K. The two *g*-value spectrum, which is typical of tetragonally distorted copper(II) systems,[15] was observed with resonances at $g_{\parallel} = 2{\cdot}33$ and $g_{\perp} = 2{\cdot}12$, yielding $\langle g \rangle = 2{\cdot}19$. No fine structure was observed.

The magnetic-susceptibility data for $Cu(NO_3)_2 \cdot N_2O_4$ obeyed the Curie–Weiss law (1) in the temperature range

$$\chi_m = C/(T - \theta) \qquad (1)$$

where

$$C = Ng^2\beta^2S(S+1)/3k \qquad (2)$$

25—300 K. The best fit of the experimental susceptibility to the Curie–Weiss expression (1) furnished the parameters $g = 2{\cdot}20$ and $\theta = -4{\cdot}7$ K and is depicted in Figure 1. For this fit, and the ones to be described below, a non-linear least-squares computer fitting program was used in which the quantity $\sum_i[\chi_i(\text{expt.}) - \chi_i(\text{calc.})]^2$ was minimized. The range of uncertainty in the experimental magnetic susceptibilities is estimated, from replicate measurements on the susceptibility standards, to be ±1%. Below 25 K the data deviated markedly from the Curie–Weiss expression, and there was a maximum in the χ_m against *T* plot at *ca.* 3·0 K. This behaviour is suggestive of an antiferromagnetic interaction between the copper(II) ions in the polymer.

The two-dimensional framework of anionic sheets in the adduct, as depicted by Blackwell *et al.*,[6] is displayed in Figure 2. The crystals belong to the space group $P2_1/m$, with $z = 2$, $a = 4{\cdot}69$, $b = 11{\cdot}10$, and $c = 7{\cdot}13$ Å (with $\beta = 102{\cdot}13°$), where the copper atoms lie on centres of symmetry at (0,0,0) and (0,1/2,0). Therefore the copper–copper separation along *a* is 4·69 Å, and along *b* is 5·55 Å, with the layers separated by *ca.* 7·1 Å. Chains of copper atoms along the crystallographic *a* axis are doubly bridged by nitrate ligands, while these chains are themselves connected by single nitrate groups along the *b* axis. Each copper atom is six-co-ordinate and is bonded to six oxygen atoms in a tetragonally distorted octahedral arrangement. Nitrosonium ions, not shown in Figure 2, occupy lattice sites at $y = 1/4$.

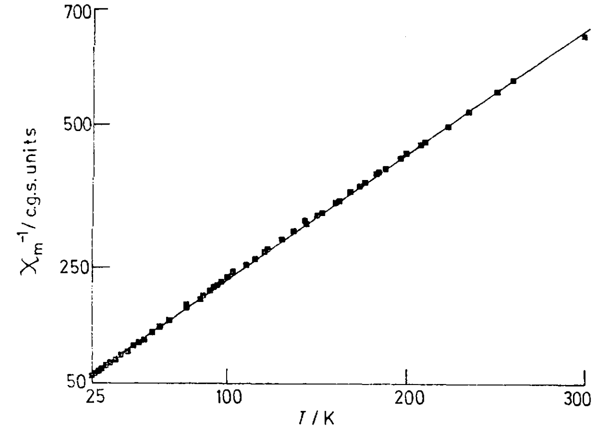

FIGURE 1 High-temperature dependence of the inverse molar susceptibility of $Cu(NO_3)_2 \cdot N_2O_4$: (■), experimental data; (——), best fit to the Curie–Weiss law

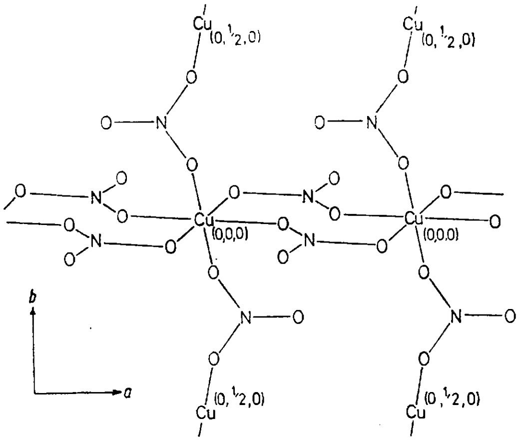

FIGURE 2 View of the two-dimensional polymeric framework of $Cu(NO_3)_2 \cdot N_2O_4$, after Blackwell *et al.*,[6] looking down the crystallographic *c* axis

The chain-like character of this structure, particularly

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along the crystallographic *a* axis, suggested that the observed antiferromagnetic interaction might be accounted for on the basis of a one-dimensional model. The spin Hamiltonian describing magnetic exchange in a chain of paramagnetic ions is (3),[16] where J is the

$$H = -J\sum_{i=1}^{n}[S_{iz}\cdot S_{(i+1)z} + \gamma(S_{ix}\cdot S_{(i+1)x} + S_{iy}\cdot S_{(i+1)y})] \quad (3)$$

exchange energy and γ can have values ranging from zero to one. For the limit $\gamma = 0$ the anisotropic Ising model results, while for $\gamma = 1$ the isotropic Heisenberg model obtains. The Heisenberg chain model was chosen to describe the experimental susceptibility results.[17] Although no closed-form expressions for the magnetic susceptibility of an isotropically coupled linear-chain antiferromagnet are available, the results of Bonner and Fisher[16] for infinite chains, where $\boldsymbol{k}T_{\text{max.}}/|J| \approx 1{\cdot}282$ and $|J|\chi_{\text{max.}}/g^2\beta^2N \approx 0{\cdot}0735$, may be used for graphical fitting. The best fit of the susceptibility of $Cu(NO_3)_2{\cdot}N_2O_4$ to the Heisenberg linear-chain model yielded the parameters $J = -1{\cdot}09$ K and $g = 2{\cdot}12$. Although the fit was good at high temperatures, the Heisenberg linear-chain model failed to adequately account for the observed magnetic behaviour at temperatures below the susceptibility maximum. Also, the calculated g value of 2·12 is not in good agreement with the experimentally determined g values obtained in the e.p.r. experiment; all of which implies that this linear-chain model of exchange is not an adequate description of the magnetic behaviour of $Cu(NO_3)_2{\cdot}N_2O_4$.

Copper(II) formate tetrahydrate, $Cu(O_2CH)_2{\cdot}4H_2O$, has a crystal structure very similar to that of $Cu(NO_3)_2{\cdot}N_2O_4$, with the copper ions arranged in sheets *ca.* 6·2 Å apart.[18] The magnetic behaviour of copper(II) formate tetrahydrate has been the subject of several studies[19-23] and is believed to provide a very good example of a two-dimensional antiferromagnetic lattice. In particular, a single-crystal susceptibility study[23] of the formate complex demonstrated the utility of the two-dimensional Heisenberg antiferromagnetic formalism for the description of magnetic properties of this general structure. Exact solutions for the magnetic susceptibilities of two-dimensional Heisenberg antiferromagnetic lattice structures are not available, but exact series expansions (in powers of reciprocal temperature) out to sixth-order terms for nearest-neighbour systems have been calculated by Rushbrooke and Wood.[24] Lines[25] has utilized these series expansions to generate an expression for the temperature dependence of the magnetic susceptibility of a quadratic-layer Heisenberg antiferromagnet (four nearest-neighbour interacting spins) from the exchange Hamiltonian (4) where the

$$H = \sum_{nn} JS_i{\cdot}S_j \quad (4)$$

summation includes all pairs of nearest-neighbour spins i and j. The most convenient series to employ is that for the reciprocal susceptibility χ^{-1}, for which equation (5)

$$Ng^2\beta^2/\chi J = 3\theta + \sum_{n=1}^{\infty} C_N/\theta^{n-1} \quad (5)$$

results. In equation (5), $\theta = \boldsymbol{k}T/JS(S+1)$ and C_N are the first six coefficients calculated from Rushbrooke and Wood's general formalism. For spin 1/2, $C_1 = 4{\cdot}0$, $C_2 = 2{\cdot}667$, $C_3 = 1{\cdot}185$, $C_4 = 0{\cdot}149$, $C_5 = -0{\cdot}191$, and $C_6 = 0{\cdot}001$. The exchange energy, J, in this expression is defined as positive for an antiferromagnetic interaction and is in units of K. Lines points out[25] that the series expansion (5) is only an approximation which ceases to be of much quantitative value below $\boldsymbol{k}T \sim 0{\cdot}9JS(S+1)$. Therefore, the lowest-temperature data (below 2·7 K) were not included in the fitting of experimental results to the above expression.

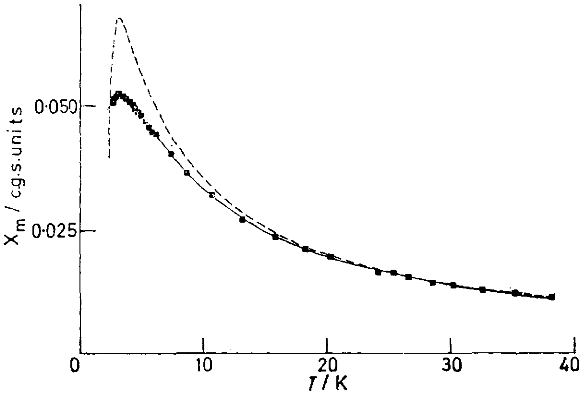

FIGURE 3 Low-temperature dependence of the molar susceptibility of $Cu(NO_3)_2{\cdot}N_2O_4$: (■), experimental data; (——), best-fit Heisenberg quadratic-layer antiferromagnetic expansion; (— — —), best-fit simple-cubic (three-dimensional) antiferromagnet expansion

The results of the best fit of the 100 G data to equation (5) are shown in Figure 3. The fit is extremely good in the whole experimental range $T = 2{\cdot}7$—300 K for the parameters $J = 3{\cdot}30$ K and $g = 2{\cdot}20$. The fact that experimental susceptibilities recorded below $T_{\text{max.}}$ match calculated values of χ_m may be coincidental. Although the experimental magnetic behaviour of $Cu(NO_3)_2{\cdot}N_2O_4$ appears to be well described by the Heisenberg two-dimensional antiferromagnetic model, it is difficult to justify predominantly two-dimensional magnetic character for the adduct solely on structural grounds.

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There does not appear to be a good insulator separating copper atoms along the *c* axis, and long-range exchange between copper ions along *c* is not ruled out on symmetry grounds. Therefore, a fit of the experimental data to the simple cubic-lattice antiferromagnetic approximation was made to determine the appropriateness of a three-dimensional model to this system.

Expression (6), where $\theta = \boldsymbol{k}T/JS(S+1)$, the reduced

$$\chi_0 J = (1/3\theta)\left[1 - (\sum_{i=1} B_i/\theta^i)\right] \qquad (6)$$

susceptibility $\chi_0 = \chi_m/Ng^2\beta^2$, and B_i are the coefficients (for $i \leqslant 9$) derived by Lines [25] for the series expansion (6), was utilized to generate the theoretical ' best fit ' curve depicted in Figure 3. With parameters $J =$ 1·90 K and $g = 2{\cdot}20$ the fit was good at high temperatures, but began to diverge from experimental data in the region $T < 20$ K finally becoming quite poor in the low-temperature region. Of course, the series expansion (6) is, like the two-dimensional expansion (5), of limited utility at very low temperatures. The two-dimensional model seems much more appropriate, however, because copper–copper separations in the *ab* plane are significantly smaller than the 7·1 Å separation along the crystallographic *c* axis, and because the bridging nitrato-groups in the *ab* plane can provide a ready exchange path between copper ions which is lacking in the *c* direction.

The powder susceptibility of $Cu(NO_3)_2{\cdot}2{\cdot}5H_2O$ has been found [26] to have a rounded maximum at 3·2 K; this behaviour is so similar to that found for $Cu(NO_3)_2{\cdot}N_2O_4$ that the possibility that our samples were in fact the former compound must be ruled out. $Cu(NO_3)_2{\cdot}N_2O_4$ Is thermally unstable; prolonged heat much above 30 °C will remove N_2O_4 and form anhydrous $Cu(NO_3)_2$.[5] Naturally, exposure to atmospheric moisture will then convert the material to the hydrated salt. Care was taken in the handling of $Cu(NO_3)_2{\cdot}N_2O_4$ to prevent exposure of the packaged samples to either excessive heat or moisture; the analytical results indicate that little, if any, decomposition of $Cu(NO_3)_2{\cdot}N_2O_4$ to $Cu(NO_3)_2{\cdot}2{\cdot}5H_2O$ had taken place, as copper and nitrogen in the hydrate are 27·3 and 12·05%, respectively. Freshly prepared specimens of $Cu(NO_3)_2{\cdot}N_2O_4$ were always surrounded by an aura of brown NO_2 gas at room temperature, which disappeared when the samples were cooled, in agreement with the reported behaviour of $Cu(NO_3)_2{\cdot}N_2O_4$.

The magnetism of the hydrated salt has been interpreted in terms of theoretical calculations for binary clusters.[26] Although the structure of $Cu(NO_3)_2{\cdot}N_2O_4$ does not suggest the likelihood of dimeric-type magnetic exchange between copper(II) ions, for the sake of completeness, an attempt was made to fit the experimental susceptibility data to the Bleaney–Bowers equation for exchange-coupled spin 1/2 ions.[27] The best fit to the dimer expression yielded the parameters $g = 2{\cdot}16$ and $2J = -3{\cdot}13$ K. Although the *g* value calculated is in reasonable agreement with experiment, the dimer expression (not unexpectedly) fails to provide a good account of the magnetism of $Cu(NO_3)_2{\cdot}N_2O_4$. In addition, the reported value of $\chi_{max.}$ at 3·2 K for $Cu(NO_3)_2{\cdot}2{\cdot}5H_2O$ is 0·065 c.g.s. units per mol,[26] which is considerably larger than the 0·052 c.g.s. units per mol found for $\chi_{max.}$ of $Cu(NO_3)_2{\cdot}N_2O_4$ at 3·0 K. Finally, the nature of the synthesis itself rules out as extremely unlikely the formation of substantial amounts of any other product save the desired $Cu(NO_3)_2{\cdot}N_2O_4$. Single-crystal susceptibility measurements of this species, to further characterize the ordered state, would certainly be desirable, should it be possible to synthesize crystals large enough for these measurements.

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