The Importance of Metal–Metal Bonding in the Antiferromagnetism of Copper(II) Acetate Monohydrate

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CUPRIC ACETATE MONOHYDRATE is antiferromagnetic, having a Néel temperature of 255° K. Although many have discussed the source of the antiferromagnetic coupling,[1-3] the most successful treatments are based on the work of Bleaney and Bowers,[2] who showed that the e.s.r. spectrum of this compound could be explained by a coupling, $-JS_1S_2$, between the spins of pairs of copper ions. By using the gyromagnetic ratio of 2·20 observed at low temperatures,[2] $-J$ must be *ca.* 300 cm.$^{-1}$ to fit the experimental data.

Bleaney and Bowers also showed that the temperature dependance of the magnetic moment is given by:

$$\mu_{\text{dimer}} = [\{6g^2/[3 + \exp(-J/kT)]\} + \alpha T]^{\frac{1}{2}}$$

where α allows for a contribution due to temperature-independant-paramagnetism.

Unfortunately, if the values of g and J obtained from the e.s.r. measurements are substituted into this relationship the calculated susceptibilities reach a maximum some 10° above the observed Néel temperature. Figgis and Martin,[1] by using the alternative procedure from the Néel temperature (with the approximate relationship, $-J/k = 1{\cdot}6T_N$) found $-J = 283$ cm.$^{-1}$, but to fit the experimental magnetic-moment data it was necessary to use a smaller g-value than that obtained from the e.s.r. measurements. A better experimental fit might be obtained by the assumption of temperature-dependant g-factors, exchange integrals, or both,[4] or by the assumption of a significant C_{2v} distortion at the individual copper ions.[5]

When two electrons (or, more appropriately in the present case, "holes") are allocated to two orbitals ϕ_1 and ϕ_2, six wavefunctions have to be considered. These are $\phi_1\phi_2$, $\overline{\phi_1\phi_2}$, $\phi_1,\overline{\phi_2}$, $\overline{\phi_1}\phi_2$, $\phi_1\overline{\phi_1}$, and $\phi_2\overline{\phi_2}$. Of these, only the first four are included in the Bleaney and Bowers treatment.[2] These authors worked prior to the publication of the crystal structure of the compound,[6] which showed the molecule to be dimeric, with a copper–copper distance of 2·64 Å. Evidently, in such a situation it is necessary to allow for the possible pairing of the electrons "originating" on adjacent copper atoms and, since this pairing is described by the last two of the set of six wavefunctions, these must be included *i.e.*, the metal–metal bonding must be explicitly included in the calculations. Figgis and Martin[1] were the first workers to suggest that the antiferromagnetism of cupric acetate monohydrate originates in metal–metal bonding, but in their own calculations they did not extend the basic set used by Bleaney and Bowers. Our calculations are based on the six functions listed. The salient differences between our results and those obtained by Bleaney and Bowers are contained in the Figure. Both approaches lead to a spin-singlet ground state with a triplet spin state some 300 cm.$^{-1}$ higher in energy. The two differ fundamentally, however, in the origin of these levels. We find that the ground state is derived from the functions not previously considered and that the spin-exchange between the copper atoms is *ferromagnetic*, although the overall energy level pattern is such that it leads to antiferromagnetic behaviour.

Our calculations involve two parameters, of which one is the spin–spin coupling constant J. The second is a covalency splitting parameter, which we denote as γ, and which is equal to one half the energy of separation of corresponding bonding and antibonding functions. One γ arises for each symmetry-allowed covalent interaction within the molecule and these we have inter-related by Forster and Ballhausens' method.[7] We have scaled our γ-values with respect to that corresponding to δ-bonding between the copper atoms because detailed consideration of the δ- and σ-bonded models shows that only the former is consistent with the g value observed in the e.s.r. measurements. (The departure of g from 2·00 depends upon the spin-orbit coupling constant, and this departure is approximately twice as much in the case of δ-bonding as for σ-bonding, where λ would have to exceed the free-ion value.)

We have assumed the symmetry of the dimeric unit to be D_{4h}, to which monopyridine copper(II) acetate conforms closely,[8] for our own refinement of the published data on the monohydrate was consistent with this assumption.

Our calculations lead to an expression for μ analogous to that found previously;[2] $\mu_{(\text{dimer})} = (6g^2/F + \alpha T)^{\frac{1}{2}}$, where $F = 3 + \exp(-J/kT) + 2\exp(-J/4kT) \times \cosh(2\gamma/kT)$.

Values of γ and J were obtained by substitution of the experimental value of g and the Néel point values of μ and T into this expression and computing the variation of J with γ. A value of 12×10^{-4} (°K)$^{-1}$ was calculated for α from the expression obtained for the temperature-independant-paramagnetism. A second relationship between J and γ was obtained by setting $\mathrm{d}X/\mathrm{d}T = 0$ at the Néel temperature. The variation of J with γ was again calculated numerically and the intersection between the two

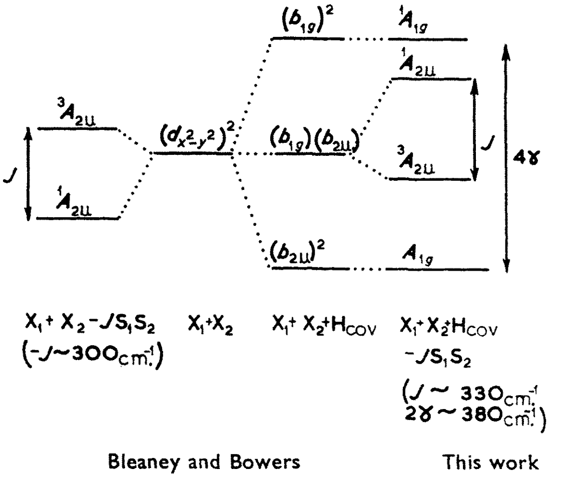

FIGURE. *The influence of metal-metal bonding and spin-exchange on the ground state of cupric acetate monohydrate* (D_{4h} *symmetry labels*).

plots of γ against J gave unique values to these two parameters. All the parameters in our calculation are therefore determined by experiment and not by "best fit" procedures.

For cupric acetate monohydrate we find $2\gamma = 381$ cm.$^{-1}$ and $-J = -327$ cm.$^{-1}$, as indicated in the Figure. With these values fit to within 1% is obtained between calculated and experimental magnetic moments over the whole range for which data[1] is available, 93·5 to 396·5° K. In particular, the fit is much better at low temperatures than that reported by Figgis and Martin.[1]

The values of "J" reported in the literature for copper carboxylate dimers are, in fact, approximately equal to our $2\gamma - \frac{1}{4}J$. In this may well lie the explanation of the apparently erratic behaviour amongst closely related species.[9]

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