

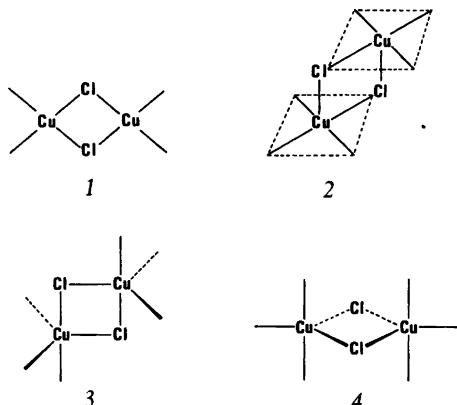
Magnetic Properties of the Dimeric Complex Di- μ -chloro-bis[bis-(benzotriazole)chlorocopper(II)] Monohydrate

DEREK J. HODGSON* and
ERIK PEDERSEN

Chemistry Department I, Inorganic Chemistry,
H. C. Ørsted Institute, University of Copenhagen,
Universitetsparken 5, DK-2100 Copenhagen Ø,
Denmark

The structural and magnetic properties of dimeric copper(II) complexes have been the subjects of intense recent research activity. For the case of planar complexes with two hydroxo bridges, $[\text{CuL}(\text{OH})_2]_2^{n+}$ where L is a bidentate ligand, a linear correlation between the isotropic magnetic exchange parameter, J , and the bridging Cu—O—Cu angle, ϕ , has been demonstrated,^{1,2} but distortions from square planar geometry³ or from bridge planarity⁴ give rise to complexes which do not follow this simple relationship between J and ϕ . A similar relationship apparently does obtain⁵ for the analogous, in-plane chloro-bridged dimers $[\text{CuL}(\text{Cl})_2]_2^{n+}$ (I), but this geometry is relatively uncommon for halogen-bridged copper(II) dimers which evidently prefer to form apical—basal bridges with either square pyramidal (2) or (less commonly) trigonal bipyramidal (3) geometry at copper.¹ We have been searching for a structural—magnetic correlation for complexes of types 2 and 3, but while we have made some progress in identifying the Cu—Cu' distance (R) and the Cu—Cl—Cu' angle (ϕ) as the principal structural parameters⁶ no entirely satisfying model has yet emerged.

We were, therefore, particularly interested to learn of the structure of the title complex, $[\text{Cu}(\text{BTAH})_2\text{Cl}_2]_2 \cdot \text{H}_2\text{O}$, (where $\text{BTAH} = \text{C}_6\text{H}_5\text{N}_3$) which was recently determined by Søtofte and Nielsen.⁷ This complex crystallizes with two independent dimeric units in the cell, both of which can be viewed as the hitherto unreported equatorial—equatorial trigonal bipyramidal dimer (4) or alternatively as highly distorted dimers of type 2. In the idealized case of 4, the magnetic orbital at each copper center is d_{z^2} and the axial systems at the two centers are parallel. The d_{z^2} orbitals transform as a_g



in either the idealized D_{2h} symmetry (where the axial ligands are assumed to be identical) or the observed⁷ C_i symmetry, and the overlap integral $\langle a_g | a_g \rangle$ between these magnetic orbitals is a function of the bridging angle ϕ . For most bridging angles, this overlap is expected to be very weak, and there will be some value of ϕ near 90° where it vanishes. Since we can write the magnetic exchange parameter J as the sum of ferromagnetic (J_F) and antiferromagnetic (J_{AF}) components⁸ where the antiferromagnetic contribution to J is a function of this overlap $\langle a_g | a_g \rangle$, and since ϕ is observed to be near 90° in both independent molecules,⁷ it is apparent that we expect $|J_{AF}|$ to be very small. The ferromagnetic term J_F is a function of the internuclear Cu—Cu' separation in the dimer and has been described⁹ as

$$J_F = K \langle \psi_A(1) \psi_B(2) | R^{-1} | \psi_A(2) \psi_B(1) \rangle$$

where A and B are the two metal centers. Since R here is⁷ approximately 3.5 Å rather than the value of approximately 3.0 Å observed² in the dihydroxo-bridged dimers, J_F is expected to be small also. Hence, on this qualitative basis, we anticipate that for the present dimer $|J|$ should be small and that J should be positive. In order to test these ideas, we have examined the magnetic susceptibility of the complex $[\text{Cu}(\text{BTAH})_2\text{Cl}_2]_2 \cdot \text{H}_2\text{O}$.

The magnetic susceptibility of a powdered sample (the generous gift of I. Søtofte) was measured by the Faraday method at a field strength of 12,000 Oe in the temperature range 4–240 K; a description of the instrumentation has been provided previously.^{10,11} Since it was apparent from the data that the isotropic exchange parameter, J , is small in magnitude and that consequently the application of the usual Bleaney-Bowers expression¹² is

* Permanent address: Department of Chemistry, University of North Carolina, Chapel Hill, NC 27514, U.S.A.

inappropriate since the necessary condition $|J| \gg g\mu_B H$ would not be satisfied, the data were fitted to the magnetization expression¹³ [eqn. (1)],

$$M = \frac{Ng\mu_B \sinh(g\mu_B H/kT)}{1 + \exp(-2J/kT) + 2 \cosh(g\mu_B H/kT)} \quad (1)$$

$$H_{\text{ex}} = -2J\vec{S}_1 \cdot \vec{S}_2 + g\mu_B H\vec{S} \quad (2)$$

where the exchange Hamiltonian is given by eqn. (2) and \vec{S} is the total spin (*i.e.* $\vec{S} = \vec{S}_1 + \vec{S}_2$). Inter-dimer interactions, which are not included in these expressions, can be estimated from a molecular field approximation, eqn. (3), where H_{eff} is the effective magnetic field. The susceptibility data were fitted to

$$H_{\text{eff}} = H + \gamma M \quad (3)$$

$$\chi = M/H \quad (4)$$

expression (1), where the magnetization M is defined by eqn. (4) with the parameters g and J as variables, using a non-linear least-squares procedure. This process resulted in the values $g = 2.055 \pm 0.006$ and $J = +0.90 \pm 0.09 \text{ cm}^{-1}$; the mean fractional deviation (MFD) for this fit was 0.026. It should be noted that with J defined as in expression (2) the single – triplet separation is $|2J|$ and positive values of J correspond to triplet ground states. Attempts to fit the data with non-zero values of γ [see expression (3)] were unsuccessful, presumably because for these data the parameters J and γ are more than 99% correlated.

An alternate model for the susceptibility of a dimer using a molecular field approach to inter-dimer interactions has recently been developed by van Santen, van Duyneveldt and Carlin [SDC],¹⁴ who derive an expression which can be written as eqn. (5), where J' represents the inter-dimer

$$\chi = Ng^2\mu_B^2/3k\{T[1 + 1/3 \exp(-2J/kT)] - 32 J'/k\} \quad (5)$$

exchange interaction and positive values of J and/or J' again imply ferromagnetic interactions. The use of this model is particularly appropriate when expressions involving only a single exchange parameter indicate large ferromagnetic interactions, and it was hoped that it would provide valuable insights in the present case also. The data fit reasonably well to expression (5) with J' fixed as zero and g and J as variables, which is equivalent to the Bleaney-Bowers expression,¹² and gave values of $g = 2.045 \pm 0.003$ and $J = +1.1 \pm 0.2 \text{ cm}^{-1}$. This fit, which has MFD=0.030, is not as good as that described above for expression (1), but it is encouraging to note that these values for g and J are not significantly different from those obtained above. Attempts at varying J' in addition to g and J

were unsuccessful, and the fit with a variety of fixed values of J' (both positive and negative) was far inferior to that obtained with $J'=0$. It may be that data at much lower temperatures would be required in the present case in order to abstract meaningful values of J' or, alternatively, of γ .

We can, however, conclude that the complex exhibits a weakly ferromagnetic interaction indicative of a triplet ground state lying $1.8 \pm 0.2 \text{ cm}^{-1}$ below the singlet excited state. This result, of course, is entirely consistent with our expectations based on the observed⁷ structure of the dimer.

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