The Magnetic Properties to 4·2K of the Complex Di-μ-hydroxybis(bipyridyl)dicopper(II) Sulphate Pentahydrate

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Summary The low-temperature magnetic susceptibility of the dimeric complex di-μ-hydroxybis(bipyridyl)dicopper(II) sulphate pentahydrate gives further support for the conclusion that the complex has a triplet ground state with a singlet excited state lying about 48 cm^{-1} above the ground state.

WE have been investigating the magnetic properties of oxygen-bridged, bimetallic copper complexes,[1] and have recently measured the magnetic susceptibility of di-μ-hydroxybis(bipyridyl)dicopper(II) sulphate pentahydrate, $[(bipy)Cu(OH)_2Cu(bipy)]SO_4,5H_2O$.

This dimer was first reported by Harris *et al.*[2] as one of a series of 2,2′-bipyridyl and 1,10-phenanthroline copper complexes. Recently the crystal structure of this complex and its magnetic susceptibility to 84K have been determined by Casey *et al.*[3] They have shown the dimer to contain two copper-centred, distorted square pyramids with a shared basal edge as is diagramatically shown in Figure 1. Their magnetic susceptibility data, some of which are included in Figure 2, showed an increase in the effective magnetic moment from 1·94 B.M. per copper atom at 298·5K to 2·04 B.M. at 84K. The reciprocal susceptibility followed

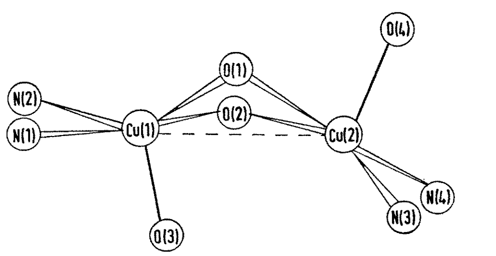

FIGURE 1. *The structure of* $[(bipy)Cu(OH)_2Cu(bipy)]SO_4,5H_2O$ *around the bridged copper atoms.* O-4 *is an oxygen atom from the sulphate anion.* O-3 *is the oxygen atom of one of the waters of hydration.* (*From ref.* 3).

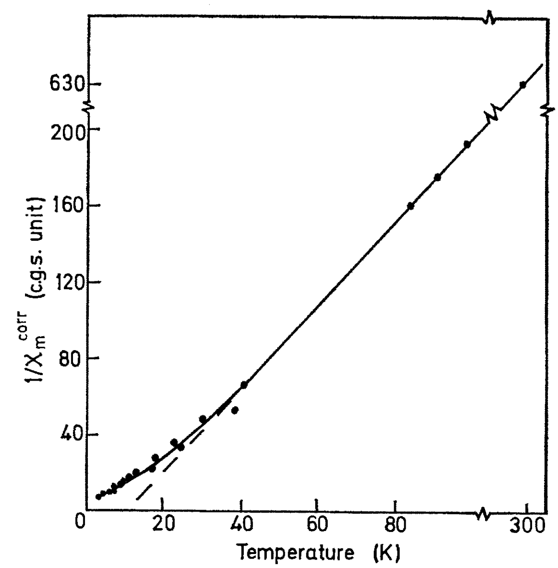

FIGURE 2. *The inverse of magnetic susceptibility per copper atom of* $[(bipy)Cu(OH)_2Cu(bipy)]SO_4,5H_2O$ *as a function of temperature. The solid line represents the values calculated from the Van Vleck equation, and the dashed line is the extrapolation of the Curie–Weiss law. Observed values are shown as black dots.* (*Data above* 80K *from ref.* 3).

the Curie–Weiss law with $\theta = -11$K. Casey *et al.* interpreted the increase in magnetic moment to indicate that this complex has a triplet ground state with the singlet state of the dimer being appreciably higher in energy. This report prompts us to communicate the results of our magnetic susceptibility measurements for [(bipy)(Cu(OH)$_2$-Cu(bipy)]SO_4,$5H_2O$ in the temperature range 4·2—41·2K; our observations tend to confirm the ground state assignment and yield an approximation of the singlet–triplet splitting.

The compound was prepared as reported previously.[2] Magnetic susceptibility measurements between 4·2 and 41·2K were made using a Foner-type vibrating-sample magnetometer[4] manufactured by Princeton Applied Research, Inc. Measurements were made at a field strength of 10,000 gauss. Temperatures were measured with a calibrated, precision germanium resistance thermometer. The data were corrected for the diamagnetism of the sample holder assembly, for the diamagnetism of the constituent atoms using Pascal's constants[5] (182×10^{-6} c.g.s.u. per Cu atom), and for temperature-independent paramagnetism (60×10^{-6} c.g.s.u. per Cu atom).

The temperature-dependent magnetic susceptibility data shown in Figure 2 clearly indicate a deviation at low temperature from the Curie–Weiss behaviour exhibited at higher temperatures. The measured magnetic susceptibility of the complex is lower than that predicted by the Curie–Weiss law at temperatures below about 35K. This behaviour is in agreement with the magnetic susceptibilities calculated from the Van Vleck equation for exchange-coupled copper ions with a positive J_{12} value corresponding to a triplet ground state. We have fitted the magnetic data to the Van Vleck equation using a least-squares fitting program. Unfortunately this equation is not very sensitive to variations in $2J_{12} > 0$, but the best fit of the susceptibility data to the theoretical equation gives values of $2J_{12} \simeq 48$ cm^{-1} (± 10 cm^{-1}) and $<g> \simeq 2{\cdot}2$ thus confirming the presence of a triplet ground state in this complex.

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