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Magnetic Properties of a Phosphate-Bridged Copper (II) Dimer

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Several ions such as PO_4^{3-}, ClO_4^-, or CrO_4^{2-} offer interesting pathways [1] to propagate magnetic exchange interactions between paramagnetic transition metal ions. Their tetrahedral geometries lead to a hybridization at the central atom that could result in a net ferromagnetic exchange interaction. For example, in valence bond terms the phosphorus atom in PO_4^{3-} employs sp^3 hybrid orbitals to bond to each oxygen. If a PO_4^{3-} ion bridges two copper(II) ions, interacting with each copper(II) ion with one oxygen atom, then the orthogonality of the two phosphorus hybrid orbitals would precipitate a net ferromagnetic interaction. There have been no studies of magnetic exchange interactions propagated by such tetrahedral ions and, as such, our interest was drawn to a very recent report of the crystal structure of a phosphate-bridged copper(II) dimer, $[Cu(5'\text{-UMP})(dpa)(H_2O)]_2 \cdot 5H_2O$, where 5′-UMP is uridine 5′-monophosphate and dpa is 2,2′-dipyridylamine [2].

The inner coordination sphere of the copper ions, including parts of the phosphate bridges, in $[Cu(5'\text{-UMP})(dpa)(H_2O)]_2 \cdot 5H_2O$ is illustrated in Figure 1. The dimer does not have a center of inversion (monoclinic space group $P2_1$), even though the separate halves of the molecule are identical in composition. Each copper(II) ion has square pyramidal coordination geometry. The two copper ions and the phosphate bridges form a puckered eight-membered ring where the Cu–Cu distance is 5.122(2) Å.

The variable-temperature (4.2–224 °K) magnetic susceptibility data for $[Cu\text{-}(5'\text{-UMP})(dpa)(H_2O)]_2 \cdot 5H_2O$, as illustrated in Figure 2, demonstrate the presence of an antiferromagnetic exchange interaction. The susceptibility shows a maximum at 9.1 °K and μ_{eff} runs from 1.81 μ_B at 224 °K to 0.55 μ_B at 4.2 °K. The data have been least-squares fit to the Bleaney–Bowers susceptibility equation [3] for a copper(II) dimer; the solid lines in Figure 2 represent this fit which can be seen to be very adequate.

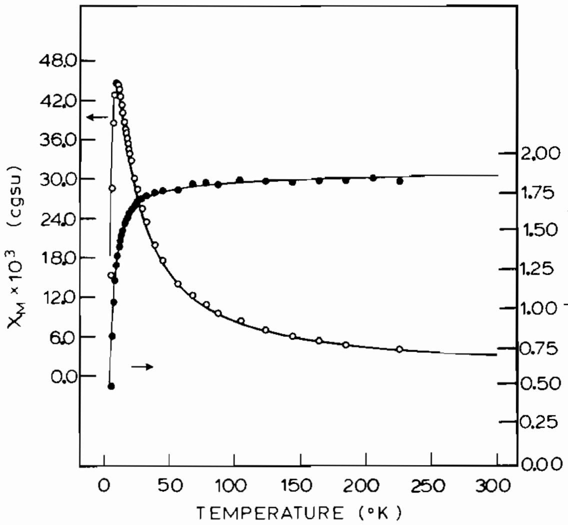

Figure 2. Corrected molar paramagnetism per binuclear complex, χ_M, and effective magnetic moment per copper(II) ion, μ_{eff}/Cu, plotted as a function of temperature for $[Cu\text{-}(5'\text{-UMP})(dpa)(H_2O)]_2 \cdot 5H_2O$. The solid lines result from least-square fitting the data to the Bleaney–Bowers equation.

The fitting parameters were found to be J = –5.4 cm^{-1} and g = 2.12 (spin Hamiltonian of $H = -2J\hat{S}_1 \cdot \hat{S}_2$). The fact that the data do fit well to the

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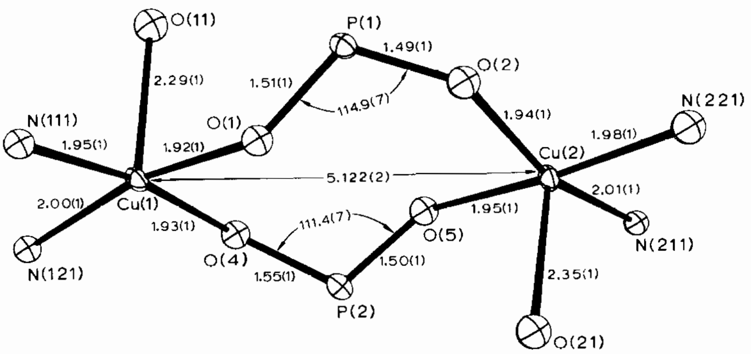

Figure 1. ORTEP plotting of the inner sphere copper(II) coordination geometry and phosphate bridges in $[Cu(5'\text{-UMP})(dpa)(H_2O)]_2 \cdot 5H_2O$.

equation for a dimer indicates that the exchange interaction is intramolecular. Further support for this was obtained from the EPR spectra for the compound. A powdered sample gave a Q-band spectrum with $g_{\parallel} = 2.178$, $g_{\perp} = 2.086$, and no hyperfine visible. Attempts to secure glass EPR spectra only gave signals characteristic of monomeric copper(II) complexes. The X-band EPR spectrum did show a $\Delta M_s = 2$ transition at 1536G; the presence of this feature indicates an exchange interaction in a dimeric copper(II) complex.

It is only possible to speculate as to why the two phosphate bridges in $[Cu(5'\text{-UMP})(dpa)(H_2O)]_2 \cdot 5H_2O$ support an antiferromagnetic exchange interaction instead of a ferromagnetic interaction. Examination of Figure 1 does show that the two bridgehead O–P–O angles deviate from a perfect 109.47° tetrahedral angle. Perhaps it is this small deviation, or admixture of other orbitals (phosphorus *d*-orbitals?) that lead to the net antiferromagnetic interaction. More examples of phosphate-bridged copper(II) dimers will have to be characterized.

Experimental

Compound Preparation

A sample of the compound was prepared as previously reported [2]. The compound was recrystallized by dissolving it in a minimum volume of boiling water, then an equal volume of acetonitrile was added and the solution placed in a freezer overnight. Well formed crystals resulted. *Anal.* Calcd for $[Cu(5'\text{-UMP})(dpa)(H_2O)]_2 \cdot 5H_2O$: C, 36.79; H, 4.39; N, 11.35; Cu, 10.24. Found (two independent samples examined): C, 36.87(36.59); H, 4.28(4.68); N, 11.14 (11.38); Cu, 10.37(10.39).

Physical measurements

The physical measurements and data analysis were carried out as indicated previously [4].

Acknowledgment

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