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Magnetic and Spectroscopic Properties of Poly-bis(μ-diphenylphosphinato)copper(II)

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As part of a general study of magneto-structural correlations in poly(metalphosphinates) [1–4], we prepared and studied the diphenylphosphinate of copper(II), $Cu[(C_6H_5)_2PO_2]_2$ [5]. This compound exhibits an electronic spectrum quite distinct from those of other copper(II) phosphinates and is ferromagnetic. The recent report of the structure of this compound [6] provides a clearer understanding of its properties and prompts this communication.

Experimental

Diphenylphosphinic acid (3.95 g) was dissolved in 700 ml aqueous ethanol (6:1, ethanol:water) and filtered after the pH was adjusted to 5.3 with aqueous sodium hydroxide. An aqueous solution of copper(II) sulfate pentahydrate (2.22 g in 135 ml) was added dropwise, over an hour to the stirring, heated (~60 °C) acid solution. A blue solid began precipitating after the addition of a few drops. When the addition was complete, the reaction mixture was warmed to facilitate evaporation of the ethanol and left stirring overnight, resulting in a reduction of the volume to ~200 ml. The solid was separated by filtration, washed with hot water, followed by hot ethanol, then dried under vacuum at 85 °C for 12 h. *Anal.* Calc. for $CuC_{24}H_{20}P_2O_4$: Cu, 12.76; C, 57.89; H, 4.05. Found: Cu, 12.80; C, 57.75; H, 4.05%.

Vibrational and electronic spectroscopy, differential scanning calorimetry and magnetic susceptibility studies were performed as described previously [2]. Magnetic susceptibilities were corrected for the diamagnetism of all atoms (-265×10^{-6} cm^3 mol^{-1}) and the temperature-independent paramagnetism of copper(II) (60×10^{-6} cm^{-3} mol^{-1}). Carbon and hydrogen microanalyses were obtained by P. Borda of this Department and copper was determined by EDTA titration.

Results and Discussion

We obtained $Cu[(C_6H_5)_2PO_2]_2$ from the reaction of sodium diphenylphosphinate with copper(II) sulfate pentahydrate in aqueous ethanol. The compound is insoluble in water, methanol, ethanol, acetone, dichloromethane, chloroform, carbon tetrachloride and benzene. Differential scanning calorimetry shows no phase transition or melting from room temperature to 320 °C where melting with decomposition begins.

The infrared spectrum of $Cu[(C_6H_5)_2PO_2]_2$ is relatively simple and shows PO_2 asymmetric and symmetric stretching vibrations at 1132 and 1051 cm^{-1} respectively. The band frequencies and separation are similar to those observed for the alkylphosphinates of copper(II) [1, 2, 4] and are consistent with the relatively symmetrical phosphinate bridging in these compounds and the similarities in their P–O bond lengths and O–P–O bond angles.

In view of the fact that $Cu[(C_6H_5)_2PO_2]_2$ has a square-planar CuO_4 chromophore while the dialkylphosphinate derivatives have flattened tetrahedral geometries [6], it is not too surprising that the electronic spectra differ. Whereas the latter group of compounds is characterized by broad absorption maxima in the $11.4–12.3 \times 10^3$ cm^{-1} region with shoulders around $13.2–14.4 \times 10^3$ cm^{-1} [4], the diphenylphosphinate exhibits three bands at 11.5, 14.9 and 16.4×10^3 cm^{-1} (Fig. 1). This spectrum may be assigned employing the crystal field model of Gerloch and Slade [7] as described previously [1]. Setting $\alpha = 90°$ for a square-planar geometry and the crystal field parameters *Dq* and *Cp* at 1500 and 1800 cm^{-1} respectively gives $^2B_2 \rightarrow {}^2A_1$, $\rightarrow {}^2B_1$, $\rightarrow {}^2E$ transition energies of 11.5, 15.0 and 16.1×10^3 cm^{-1}.

The magnetic properties of $Cu[(C_6H_5)_2PO_2]_2$ have been studied from 303 to 4.7 K. The effective magnetic moment increases on decreasing the temperature, rising particularly sharply below about 40 K: behaviour indicating ferromagnetic coupling. Employing, as before [2], the polynomial expression

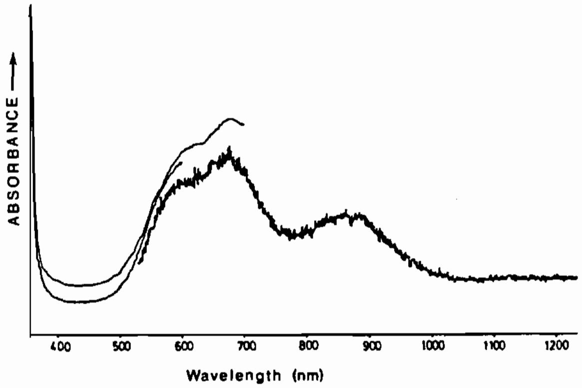

Fig. 1. Electronic spectrum of $Cu[(C_6H_5)_2PO_2]_2$ in Nujol mull.

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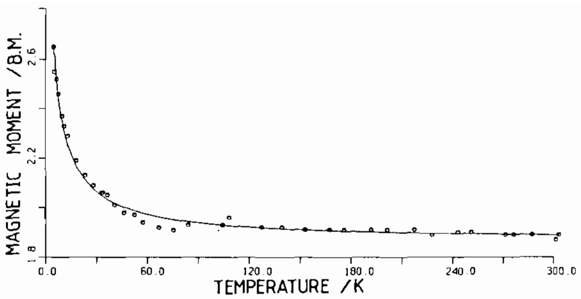

Fig. 2. Plot of magnetic moment *vs.* temperature for $Cu[(C_6H_5)_2PO_2]_2$. Points are experimental data. Line is calculated from theory for $g = 2.17$ and $J = 4.0$ cm^{-1}.

of Baker *et al.* [8, 9] for the isotropic Heisenberg model for ferromagnetically coupled chains, the best fit to the magnetic moment data over the entire temperature range studied gave a g value of 2.17 and a J value of +4.0 cm^{-1}. The data are plotted in Fig. 2 and the line is calculated using these g and J values. This is the highest J value we have observed for a ferromagnetic copper(II) phosphinate; the dialkylphosphinates studied to date exhibit J values between +1.8 and +2.6 cm^{-1} [2, 4].

We suggested earlier that in phosphinate chain polymers of copper(II) both ferromagnetic and antiferromagnetic pathways for superexchange may be available, with the former involving mainly σ-type and the latter π-type metal–ligand overlap [4]. In a square planar compound such as $Cu[(C_6H_5)_2PO_2]_2$ most of the unpaired electron density is in an e_g orbital which has zero overlap with ligand orbitals of π-symmetry. In this case the ferromagnetic pathway dominates, giving rise to the observed behaviour.

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