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Synthesis and Magnetic Susceptibility of Dimeric Copper(II) Acetate Adducts with Triphenylphosphine or Triphenylphosphine Oxide

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Synopsis. Two compounds of stoichiometry $Cu(CH_3COO)_2\cdot L$ (L=triphenylphosphine or triphenylphosphine oxide) were prepared. These compounds display the antiferromagnetic behavior typical of dimeric copper(II) carboxylates. The singlet-triplet splitting energy is 371 cm^{-1} for the phosphine adduct and 319 cm^{-1} for the phosphine oxide adduct.

A large number of dimeric copper(II) carboxylates have been studied because of their interesting magnetic and structural properties. However, the factors that determine the degree of antiferromagnetic interaction in these carboxylates still remain almost unsettled.[1] In this work, we prepared two copper(II) acetate adducts of stoichiometry $Cu(CH_3COO)_2\cdot L$, where L= triphenylphosphine (Ph_3P) or triphenylphosphine oxide (Ph_3PO), and measured their magnetic susceptibility as a function of temperature in order to study the effect of the additional ligand L on the magnetic interaction in these complexes.

Experimental

Synthesis. *$Cu(CH_3COO)_2\cdot Ph_3P$*: A solution of Ph_3P (5 mmol) in 30 ml of ether was added to a solution of $Cu(CH_3COO)_2\cdot H_2O$ (5 mmol) in 30 ml of ethanol with a few drops of glacial acetic acid. After the solution had been allowed to stand for several days at *ca.* 5 °C in a freezer, the separated green crystals were collected, washed twice with ethanol and once with ether, and dried *in vacuo.* Found: C, 59.36; H, 4.78; Cu, 14.40%. Calcd for $C_{22}H_{21}O_4PCu$: C, 59.52; H, 4.77; Cu, 14.31%.

$Cu(CH_3COO)_2\cdot Ph_3PO$: A solution of Ph_3PO (5 mmol) in 30 ml of ethanol was added to a solution of $Cu(CH_3COO)_2\cdot H_2O$ (5 mmol) in 30 ml of ethanol and 2 ml of 2,2-dimethoxypropane. After the mixed solution had been concentrated to one-half of its volume, it was allowed to stand overnight at *ca.* 5 °C in a freezer. The green crystals were collected, washed with ethanol, and dried at *ca.* 70 °C. Found: C, 57.38; H, 4.67; Cu, 13.84%. Calcd for $C_{22}H_{21}O_5PCu$: C, 57.45; H, 4.60; Cu, 13.82%.

Physical Measurement. Magnetic suceptibilities in the temperature range of 80—300 K were determined by the Gouy method. The correction for diamagnetic contributions was made by use of Pascal's constant.[2] Effective magnetic moments per copper ion at room temperature were calculated from the equation

$$\mu_{eff} = 2.83\sqrt{(\chi_A - N\alpha)\cdot T}, \qquad (1)$$

where χ_A is the corrected molar magnetic susceptibility and $N\alpha$ is the temperature-independent paramagnetism per gram-ion of copper(II); a value of $N\alpha = 60\times10^{-6}$ cgs emu mol^{-1}† was used.[3] The results are given in Table 1. The cryomagnetic susceptibility data are shown in Fig. 1 as plots of χ_A *vs.* *T*.

Table 1. Magnetic data

Complex	μ_{eff}/BM$^{a)}$	T/K	g	$-2J$/cm^{-1}
$Cu(CH_3COO)_2\cdot Ph_3P$	1.23	283	2.20	371
$Cu(CH_3COO)_2\cdot Ph_3PO$	1.39	293	2.24	319

a) 1 BM=9.27×10^{-24} A m^2.

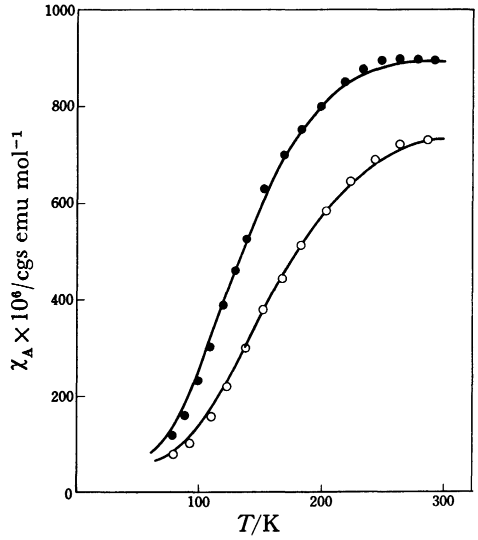

Fig. 1. Variation of magnetic suceptibilities with temperature. (○) $Cu(CH_3COO)_2\cdot Ph_3P$ and (●) $Cu(CH_3COO)_2\cdot Ph_3PO$. The solid curves were calculated by Eq. 2 with the parameters listed in Table 1 and $N\alpha$ of 60×10^{-6} cgs emu mol^{-1}.

Results and Discussion

The variable-temperature magnetic susceptibility data were analyzed by the Bleaney-Bowers equation for isotropic exchange in a copper(II) dimer:[4]

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + N\alpha, \qquad (2)$$

where g is the average g factor and J is the exchange integral. As can be seen in Fig. 1, the thermal magnetic data are well represented by Eq. 2. The best fit values for g and $-2J$ (a measure of the magnitude of magnetic interaction) are given in Table 1. On the basis of the magnetic behavior, a dimeric structure similar to that found in copper(II) acetate monohydrate can be proposed for the present acetate complexes.

The $-2J$ value of 371 cm^{-1} found for the Ph_3P adduct is considerably larger than that observed for any other dimeric copper(II) acetate adducts, indicating that the coordination of Ph_3P to dimeric copper(II) acetate units will cause a marked increase in antiferromagnetic interaction. On the other hand, the Ph_3PO adduct has a $-2J$ value (319 cm^{-1}) comparable to those found for well-characterized dimeric copper(II) acetate adducts (300—325 cm^{-1}).[5]

Edmonson and Lever[6] observed, in their study of dimeric copper(II) vinyl acetate and allyl acetate

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† 1 cgs emu mol^{-1}=$4\pi\times10^{-6}$ m^3 mol^{-1}.

complexes with pyrazine (pz), pyridine (py), and Ph_3P, that the effective magnetic moments (μ_{eff}) at room temperature decreased in the order of pz adducts> py adducts≫Ph_3P adducts; the decrease in μ_{eff} for the Ph_3P adducts was attributed to the polarizable nature of the phosphorous ligand. The corresponding acetate complexes show a similar trend: pz adduct7) ≈py adduct8) (≈1.35 BM)>Ph_3P adduct (1.23 BM). Ph_3P acts as a π-acceptor as well as a good σ-donor toward transition metals, while Ph_3PO functions simply as a σ-donor.9) A metal→ligand π-back-donation generally facilitates the ligand→metal σ-donation, leading to a strengthening of the bond through the synergic interaction. Thus, the Cu–P bond in $Cu(CH_3COO)_2 \cdot Ph_3P$ should be stronger than the Cu–O bond in $Cu(CH_3COO)_2 \cdot Ph_3PO$.

It has been noted that, in dimeric copper(II) carboxylate adducts, the variation of $-2J$ with properties of additional ligands is not a simple function of the base strength of the ligands or of any other readily evident parameters.10,11) However, the present magnetic data indicate that the bonding nature between Cu–L in $Cu(CH_3COO)_2 \cdot L$ is important in determining the magnitude of $-2J$.

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