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Magnetic Properties of Dimeric Copper(II) 2,2-Dimethylpropanoate Complexes

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Synopsis. Dimeric copper(II) 2,2-dimethylpropanoate complexes, $[Cu(Me_3CCOO)_2\cdot L]_2$, where L is pyridine, acridine, quinaldine, 2-picoline, 4-picoline, and 2,6-lutidine, have been prepared. Magnetic data show that the singlet–triplet separation ($-2J$) ranges from 319 to 397 cm^{-1}. Strong antiferromagnetic interaction observed for the acridine adduct ($-2J$=397 cm^{-1}) is discussed on the basis of weak Cu–N(acridine) bond. The magnetic behavior of the non-adduct compound $[Cu(Me_3CCOO)_2]_2$ ($-2J$=403 cm^{-1}) is explained with respect to its non-polymeric structure.

A large number of dimeric copper(II) carboxylate adducts, $[Cu(RCOO)_2\cdot L]_2$, have been studied to elucidate the factors affecting the magnetic properties of these compounds. In particular, effects of the carboxylate substituent R and of apical ligand L on the strength of antiferromagnetic interaction have been extensively investigated.[1,2] The X-ray diffraction and magnetic measurement by Kirillova et al.[3] on the dimeric copper(II) 2,2-dimethylpropanoate adduct with acridine, $[Cu(Me_3CCOO)_2(ac)]_2$, showed that the dimeric molecule has copper(II) acetate monohydrate structure. The singlet–triplet separation ($-2J$) of 340 cm^{-1}, which is considerably larger than those reported for the well-characterized dimeric copper(II) acetate adducts (284—325 cm^{-1}),[1] was attributed to electron-releasing properties of *t*-butyl substituents in the carboxylato bridges. A structural characteristic of the acridine adduct is the Cu–N distance of 2.371(5) Å, which is longer than those found for other dimeric copper(II) carboxylate adducts with pyridine analogues (2.10—2.20 Å).[1,2] The anomalies made us investigate the influence of apical ligand on magnetic interaction. We prepared purposely six copper(II) 2,2-dimethylpropanoate complexes, $Cu(Me_3CCOO)_2$ and $Cu(Me_3CCOO)_2\cdot L$, where L denotes pyridine (py), quinaldine (qu), 2-picoline (2-pic), 4-picoline (4-pic), and 2,6-lutidine (2,6-lu), to compare their magnetic properties with that of acridine adduct.

Rakitin et al.[4] reported magnetic properties of some of these complexes. They suggested that the molar magnetic susceptibility, χ_A, depends only weakly on the apical ligand.

Experimental

Syntheses. $Cu(Me_3CCOO)_2$: A solution of 2,2-dimethylpropanoic acid (12 mmol) in 0.25 M sodium hydroxide (100 ml (1 M=1 mol dm^{-3})) was filtered and neutralized with dilute nitric acid with phenolphthalein indicator. Addition of a solution of copper(II) nitrate (6 mmol) in water (25 ml) to the above solution with stirring gave green crystals. The crystals were recrystallized from acetone with a small amount of 2,2-dimethoxypropane.

$Cu(Me_3CCO)_2\cdot L$ (L=py, qu, ac, 2-pic, 4-pic, and 2,6-lu): Mixtures of $Cu(Me_3CCOO)_2$ (2 mmol) and L (3 mmol) in benzene (50 ml) were stirred for about 30 min at room temperature. The resultant solution was filtered and concentrated to one-third of the volume. When petroleum ether was added to the solution, green crystals precipitated, which were washed with petroleum ether and dried in vacuo at room temperature.

The results of the elemental analyses are given in Table 1.

Physical Measurements. Magnetic susceptibility in the temperature range of 80—300 K was determined by the Faraday method. The correction for diamagnetic contribution was made by use of Pascal's constants.[5] The cryomagnetic data were applied to the modified Bleaney–Bowers equation,

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1} \times (1-P) + \frac{Ng_i^2\beta^2}{4kT}\cdot P + N\alpha, \tag{1}$$

where P is the mole fraction of the noncoupled copper(II) impurity and g_i is the average g factor for the impurity. The values of g_i of 2.2 and $N\alpha$ of 60×10^{-6} cgs emu (1 cgs emu=$4\pi\times10^{-6}$ m^3) were used throughout the present study. The best-fit parameters of $-2J$, g, and P were obtained by a nonlinear least-squares fitting procedure. The quantity of fit was estimated by means of a discrepancy index,

$$\sigma_{dis} = \left[\frac{\Sigma(\chi_{obsd}-\chi_{calcd})^2}{\Sigma\chi_{obsd}^2}\right]^{1/2}. \tag{2}$$

Table 1. Analytical Data

Complex	Found(Calcd) (%)			
	C	H	N	Cu
$Cu(Me_3CCOO)_2$	44.83	6.93		23.91
	(45.19)	(6.83)		(23.91)
$Cu(Me_3CCOO)_2(py)$	52.20	6.69	4.04	18.53
	(52.24)	(6.72)	(4.06)	(18.42)
$Cu(Me_3CCOO)_2(ac)$	61.90	6.17	3.07	14.46
	(62.08)	(6.12)	(3.15)	(14.28)
$Cu(Me_3CCOO)_2(qu)$	58.86	6.76	3.42	15.53
	(58.73)	(6.65)	(3.42)	(15.54)
$Cu(Me_3CCOO)_2(2\text{-}pic)$	53.65	6.95	3.79	17.76
	(53.54)	(7.02)	(3.90)	(17.70)
$Cu(Me_3CCOO)_2(4\text{-}pic)$	53.59	7.03	3.91	17.61
	(53.54)	(7.02)	(3.90)	(17.70)
$Cu(Me_3CCOO)_2(2,6\text{-}lu)$	54.72	7.19	3.69	17.03
	(54.75)	(7.30)	(3.76)	(17.04)

Table 2. Magnetic Parameters and Magnetic Moments

Complex	$\frac{-2J}{\text{cm}^{-1}}$	g	$P\times 10^2$	$\sigma_{\text{dis}}\times 10^3$	$\frac{\mu_{\text{eff}}}{\text{B.M.}^{\text{a)}}}$	T/K
$Cu(Me_3CCOO)_2$	403	2.27	0.51	7.25	1.26	302
$Cu(Me_3CCOO)_2$(py)	366	2.29	0.50	5.05	1.34	299
$Cu(Me_3CCOO)_2$(ac)	397	2.30	1.51	9.11	1.28	295
$Cu(Me_3CCOO)_2$(qu)	393	2.29	0.40	7.70	1.29	301
$Cu(Me_3CCOO)_2$(2-pic)	371	2.29	0.49	4.15	1.32	293
$Cu(Me_3CCOO)_2$(4-pic)	319	2.23	1.40	4.87	1.38	289
$Cu(Me_3CCOO)_2$(2,6-lu)	379	2.29	0.29	6.37	1.29	289

a) 1 B.M. $=9.27\times 10^{-24}$ A m^2.

Effective magnetic moments at room temperature were calculated from the equation,

$$\mu_{\text{eff}} = 2.83\sqrt{(\chi_A - N\alpha)\cdot T}. \tag{3}$$

The values of $-2J$, g, P, σ_{dis}, and μ_{eff} are summarized in Table 2.

Polycrystalline powder EPR spectrum of $Cu(Me_3CCOO)_2$ in Fig. 1 was recorded by Jeolco JES-ME 2 spectrometer in the X-band range.

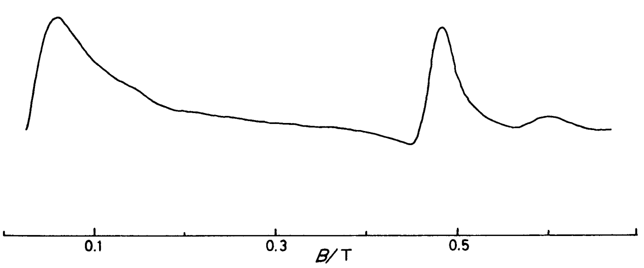

Fig. 1. Room-temperature polycrystalline powder EPR spectrum of $Cu(Me_3CCOO)_2$ at X-band frequency.

Results and Discussion

The magnetic susceptibility data of the complexes are well represented by Eq. 1, indicating that all complexes have a copper(II) acetate type dimeric structure. The $-2J$ value of 397 cm^{-1} observed for the acridine adduct prepared in the present study differs from the previously reported value of 340 cm^{-1};[3] this difference may partially be attributed to different fitting procedures of experimental χ_A values to those calculated from Eq. 1.

The $-2J$ value of acridine adduct is largest among values of adducts examined in the present study (cf. Table 2). Since the coordination bond between N of acridine and Cu seems to be weak as is indicated by long bond length (2.371 Å),[3] this result will be an evidence of the previous conclusion[6,7] that the antiferromagnetic interaction in dimeric copper(II) carboxylate adducts, $[Cu(RCOO)_2\cdot L]_2$, becomes stronger as the σ electron donation from L to copper becomes weaker. Weaker donation resulting in stronger Cu–O covalent bonds in CuO_4 basal planes enhances the spin–spin coupling between unpaired electrons of metal ions by superexchange interaction through bridging carboxylato ligands. This mechanism may be further supported by the following facts. First, the $-2J$ values of the adducts with quinaldine and 2,6-lutidine, both of which have substituents at 2- and 6-positions of pyridine ring, are larger than those of other adducts with apical ligands which have no or only one substituent at the ortho-position of pyridine ring (cf. Table 2). The apical ligation is hindered by the ortho-substituents as in the case of acridine in $[Cu(Me_3CCOO)_2(ac)]_2$[3] and, consequently, the N–Cu bonds in both the adducts must be weak. Secondly, as shown in Table 2, the $-2J$ value of 4-picoline adduct is much smaller than those of other adducts. Since 4-picoline has no substituent at ortho-position of the donor site and the basicity is higher than other pyridine bases examined in this study, except for 2,6-lutidine, the N–Cu bond in the 4-picoline adduct is considered to be much stronger than in other adducts. Thus, in contrast with the acridine adduct, the smallest $-2J$ value of 319 cm^{-1} found for 4-picoline adduct can be ascribed to strong Cu-N bond.

The $-2J$ value of 403 cm^{-1} found for the non-adduct compound, $Cu(Me_3CCOO)_2$, is larger than those of any other adducts in the present study. This fact differs from the general tendency that for many dimeric copper(II) carboxylates the $-2J$ values for non-adducts are smaller than those for the corresponding adducts.[8–10] In addition, the X-band EPR spectral pattern of $Cu(Me_3CCOO)_2$ is quite different from that of many non-adduct copper(II) carboxylates. In many cases, the EPR spectra of non-adduct copper(II) carboxylates show a single broad line in the 0.2—0.4 T region and this fact has been regarded as a sign of the existence of a polymeric chain structure consisting of dimeric molecules.[11–13] The EPR spectral feature of the present non-adduct compound shown in Fig. 1 is fundamentally the same as that usually observed for dimeric copper(II) carboxylates with axial ligands.[14] The obtained EPR parameters are: $g_\perp$ 2.139, $g_{/\!/}$ 2.415, g_{av} 2.235, and D 0.340 cm^{-1}. The relation commonly observed for dimeric copper(II) carboxylates is held; i.e., D (0.340 cm^{-1})$>H_0$ (0.316 cm^{-1}).[14,15] These facts suggest that the strong antiferromagnetic interaction in $Cu(Me_3CCOO)_2$ is due to absence of (or very weak) coordination at the apical positions.

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