

Magnetic & Spectroscopic Characterization of Some Dimeric Copper(II) Acetate Adducts

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Temperature-dependent magnetic susceptibilities and ESR spectra of the adducts of dimeric copper(II) acetate with methanol, acetic acid, N,N-dimethylformamide, 1,4-diazabicyclo[2.2.2]octane and urea are reported and discussed. The exchange interaction parameter ($-2J$) varies from 292 to 337 cm^{-1} .

Magnetic interaction between copper(II) ions in dimeric copper(II) carboxylates has been extensively studied¹⁻⁶. There have been attempts to correlate the magnitude of the exchange integral ($-2J$) with recognizable features of the constituents of the dimeric copper(II) carboxylates. For example, correlations of $|2J|$ values with the pK_a of the bridging and terminal ligands as well as with the bridge-lengths have been attempted^{3,4}. The present investigation deals with the magnetic and spectroscopic investigations on some adducts of dimeric copper(II) acetate, $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{L}$. The ligands(L) chosen are methanol, acetic acid, N,N-dimethylformamide (DMF), 1,4-diazabicyclo[2.2.2]octane (Dabco) and urea. The bridging ligand has been kept the same in order to avoid changes introduced by the variation in the electronic nature of the bridging system. The effect of varying base strength of the axial ligand on $|2J|$ values is discussed.

The methanol adduct was obtained by dehydrating powdered copper(II) acetate dihydrate initially to a

stoichiometric mass loss and then dissolving it in dry methanol containing a few ml of 2,2-dimethoxypropane. The concentrate was sealed in a conical flask and cooled to -10°C . Blue-green crystals of the adduct were formed after two days. The acetic acid adduct was similarly prepared using acetic acid-acetic anhydride (3:1) mixture. The other adducts were prepared by the reported procedures⁷⁻⁹.

Magnetic susceptibilities were measured on a Faraday balance standardized with $\text{Hg}[\text{Co}(\text{CNS})_4]$ at different temperatures down to liquid nitrogen temperature. The molar susceptibilities were corrected for diamagnetism using Pascal's constants¹⁰. While the Dabco adduct is stable, the other compounds decompose slowly in air. The latter compounds were, therefore, allowed to remain in the mother liquor (solvent) in the sample cup. The solvent was then carefully removed by evacuation and the measurements were made *in vacuo* ($\sim 10^{-4}$ mm).

The electron spin resonance (ESR) spectra for the adducts were recorded at X-band frequencies in solution and at ambient temperature on a Varian E109 spectrometer with diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) as the internal reference.

The room temperature magnetic moments are shown in Table 1. It was previously concluded^{1,9} that the ambient temperature magnetic moments for the DMF and Dabco adducts were typical of magnetically dilute copper(II) compounds. Such an inference is erroneous, since the magnetic moments reported⁸ were for the dimer and not for a single copper atom.

The molar susceptibilities of the adducts as a function of temperature (Fig. 1) exhibit a broad maximum near 265 K and fall off rapidly on further lowering of temperature. The susceptibilities may be

Table 1—Magnetic and ESR Data for $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{L}$

L†	Donor atom	Temp. (K)	Mag. moment (B.M.)	$-2J$ (cm^{-1})	g	Ref.
Acetic acid	O	295	1.37	337	2.16	This work
Methanol	O	297	1.44	309	2.17	This work
DMF	O	296	1.47	292	2.16	This work
Water	O	294	1.40	311	2.16	44
Urea	O	296	1.38	326	(2.16)	This work
Pyridine	N	290	1.35	324	2.17	15
Dabco	N	297	1.42	318	2.16	This work
Thiocyanate	N	292	1.44	315	2.19	16
Quinoline	N	—	—	329	2.17	3
2-Methylpyridine	N	—	—	312	2.16	3

†DMF = N,N-dimethylformamide, Dabco = 1,4-diazabicyclo[2.2.2]octane

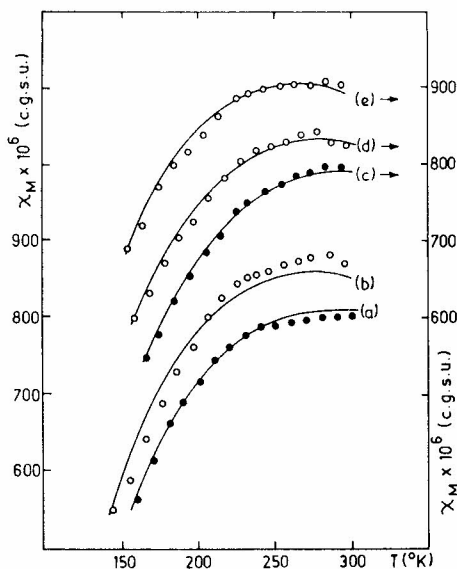


Fig. 1 -Corrected molar magnetic susceptibilities of $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{L}$ [L = Urea(a), methanol(b), acetic acid(c), Dabco(d) and DMF(e)]. Full lines are the calculated best fit to the Bleaney-Bowers equation]

described by the Bleaney-Bowers equation for exchange coupled dimers¹¹ (Eq. 1),

$$\chi_M = \frac{Ng^2\beta^2}{3kT} [1 + 1/3 \exp(-2J/kT)]^{-1} + N_x \quad \dots(1)$$

where χ_M is the experimental magnetic susceptibility corrected for diamagnetism and N , g , β , k , T and J have their usual meanings. The temperature-independent paramagnetism $N_x = 60 \times 10^{-6}$ c.g.s.u. was used as usual. There are differences in the methods proposed in literature for the determination of $2J$ values¹⁻³. In order to obtain the most meaningful values, $2J$ values have now been obtained by employing the ESR derived g -values as constants in the fitting process. Computations were made on a DEC 1090 computer system. The ESR spectra of the present samples in solution at 293 K show broad absorption bands of the dimeric species. The g -values obtained are similar to those usually found for the adducts of dimeric copper(II) acetate³. A g -value of 2.16 was assumed for the 2-methylpyridine adduct³. The uncertainty in the calculated $2J$ values is estimated to be $\pm 1.2 \text{ cm}^{-1}$. The exchange energy ($-2J$) for $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{CH}_3\text{COOH}$ is the highest in the series.

The susceptibilities for the methanol adduct could not be fitted into Eq. (1). Addition of a term for mononuclear impurities upto 2% did not improve the agreement with the experimental data. Such deviations have been noted by others also and different explanations have been put forth^{1,2}.

The spectroscopic and magnetic behaviours of the adducts support a binuclear structure of the type reported for copper(II) acetate monohydrate^{1,3}. Pairs of copper(II) atoms are bridged in these structural units by the acetate groups, while the molecules L, bonded through the oxygen or nitrogen atoms, are in the terminal positions.

An important trend noted for copper(II) carboxylates is the variation in $2J$ values with the variation in the terminal ligands^{3,4}, which is reflected in the present data also (Table I). The $2J$ values shown in Table I cover a range of 45 cm^{-1} . The axial ligands presently considered, containing both oxygen and nitrogen donors, are practically pure sigma donors. As already stated, there exists a general trend for $|2J|$ values to decrease as the axial ligand becomes a better donor. While this trend is more clearly discernible for the oxygen donors, the differences for the nitrogen donor ligands are too small to be useful. The deviation in the case of urea, amongst the oxygen donors, may be attributed to the presence of stronger mesomeric amide nitrogens resulting in the greater negative charge at the ureide oxygen. The value of $-2J$ for the copper(II) acetate adducts with oxygen donor ligands tends to increase in the order: acetic acid < urea < water ~ methanol < DMF, suggesting an increase in the sigma donor capacity of the ligands in this order.

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