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Spectral and Magnetic Properties of Copper(II) α,α′-Dichloropropionate and Its Dioxan Adduct

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Crystalline copper(II) α,α′-dichloropropionate and its dioxan adduct were prepared. The temperature variation of the magnetic susceptibilities of the compounds was determined between 90 and 300 K. In both cases the magnetic moments are subnormal and decrease with decreasing temperature.

The energy difference between the singlet and triplet states which arises from intramolecular exchange between pairs of contiguous copper atoms has been found to be 260 ± 8 cm^{-1}. The corresponding entropy and heat changes for the singlet-triplet equilibrium have also been calculated.

Absorption spectra of the compounds in the visible and near ultraviolet regions were measured. The structures of the title compounds are discussed.

A large number of copper(II) complexes which have subnormal magnetic moments at room temperature have been reported.

Very recently, low magnetic moments have been reported for copper(II) monohalogen-substituted propionates and copper(II) α,β-dibromopropionate as well as their dioxan adducts.[1–4]

The present work was undertaken to determine the influence of α,α′-dichlorosubstitution on the spectral and magnetic properties of the bridging binuclear structure of copper(II) propionate. For this purpose, copper(II) α,α′-dichloropropionate and its dioxan adduct were prepared.

EXPERIMENTAL

Preparation. Copper(II) α,α′-dichloropropionate was prepared by heating copper carbonate in a dilute water solution containing an excess of α,α′′-dichloropropionic acid at about 40°C. The fine blue-green microcrystals were isolated as in the case of copper(II) α-bromopropionate.[1] (Found: C 21.00; H 1.82; Cu 18.15. Calc. for $Cu(CH_3CCl_2COO)_2$: C 20.74; H 1.74; Cu 18.28.)

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Recrystallization of the $Cu(CH_3CCl_2COO)_2$ from hot dioxan gave an dioxan adduct similar in color to the anhydrous compound. (Found: C 24.42; H 2.68; Cu 16.05. Calc. for $Cu(CH_3CCl_2COO)_2 \cdot 0.5(C_4H_8O_2)$: C 24.54; H 2.57; Cu 16.23.)

Magnetic susceptibility determinations. Magnetic susceptibilities were measured at different temperatures by the Gouy method using an instrument manufactured by the Newport Instruments Ltd. Copper sulphate pentahydrate was used as standard [5] and diamagnetic corrections were estimated from Pascal's constants.[6] The effective magnetic moment, μ_{eff}, at each temperature was calculated from the expression $\mu_{eff} = 2.83 \sqrt{(\chi'_M - N\alpha)\,T}$, where $N\alpha$ represents the temperature-independent paramagnetism. In the present work, the value $N\alpha = 75 \times 10^6$ was used for the dioxan adduct and the value $N\alpha = 0$ for the anhydrous compound.

Spectral measurements. Absorption spectra in the visible and the near ultraviolet region were recorded on a Beckman DK 2A ratio recording spectrophotometer.

RESULTS AND DISCUSSION

The magnetic data are given in Table 1. From the values of susceptibilities we can see that, as the temperature increases, the paramagnetic triplet level becomes populated at the expense of the diamagnetic singlet level so that the

Table 1. Magnetic data.

$Cu(CH_3CCl_2COO)_2$ $(-\Delta \times 10^6 = 163)$

T K	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		μ_{eff} B. M.
		exptl.	calc.	
93	1.13	555	368	0.64
123	1.69	749	659	0.86
153	2.00	860	847	1.03
183	2.25	947	947	1.18
213	2.35	980	983	1.29
243	2.32	967	982	1.37
273	2.27	951	959	1.44
293	2.22	936	938	1.48
303	2.20	927	932	1.50

$Cu(CH_3CCl_2COO)_2 \cdot 0.5(C_4H_8O_2)$ $(-\Delta \times 10^6 = 185)$

T K	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		μ_{eff} B. M.
		exptl.	calc.	
93	0.64	436	364	0.46
123	1.18	648	629	0.75
153	1.57	805	821	0.95
183	1.89	925	930	1.12
213	2.03	980	981	1.24
243	2.05	990	990	1.33
273	1.98	962	979	1.39
293	1.91	932	964	1.42
303	1.90	929	959	1.44

susceptibility rapidly increases to a maximum value at 226 K in the case of copper(II) α,α′-dichloropropionate and at 240 K in the case of the dioxan adduct. Above these temperatures, the usual decrease in susceptibility with rising temperature is observed.

The splitting factor, g, the exchange coupling constant, $|2J|$, and the temperature-independent paramagnetic contribution, $N\alpha$, were calculated by means of the Bleaney-Bowers [7] expression:

$$\chi_M = \frac{g^2 N\beta^2}{3kT} \frac{1}{1+1/3 \exp 2J/kT} + N\alpha \quad (1)$$

The best values of g, $|2J|$, and $N\alpha$ selected by an Algol program written for the Elliott 803 B computer are given in Table 2.

Table 2. Values of T_N, g, $|2J|$, $N\alpha$, $\Delta H°$, and $\Delta S°$.

Compound	T_N K	g	$\|2J\|$ cm^{-1}	$N\alpha$	$\Delta H°$ cm^{-1}	$\Delta S°$ e.u.
$Cu(CH_3CCl_2COO)_2$	226	2.17	252	0	245	2.1
$Cu(CH_3CCl_2COO)_2 \cdot 0.5(C_4H_8O_2)$	240	2.16	267	75	264	2.0

The experimental susceptibility values are in reasonable agreement with those calculated from expression (1), although the experimental susceptibilities at low temperatures are higher than those predicted by theory. Such deviations could be due to the presence of a small amount of an impurity in the samples for which the magnetic interaction is weaker.

The deviation of the g values from the free-spin value, $g=2$, indicates spin-orbit coupling. The small increase of 15 cm^{-1} in $|2J|$ observed with the dioxan adduct, where the dioxan is probably in the terminal positions, slightly enhances the $3d_{x^2-y^2} - 3d_{x^2-y^2}$ exchange interaction.

Equilibrium constants for the singlet ⇌ triplet reaction were calculated from the magnetic data in the manner described by Hatfield *et al.*[8] The values of $\Delta H°$ and $\Delta S°$ are given in Table 2. The values of the heat change ($\Delta H°$) and entropy change ($\Delta S°$) are close to those expected for a singlet-triplet equilibrium.[8]

The absorption spectra of the compounds in "Nujol" exhibit a welldefined band at about 685 nm and a shoulder at about 375 nm, the latter a characteristic of binuclear copper(II) carboxylates.

The similarity of the spectral and magnetic properties of the title compounds with those of copper(II) acetate monohydrate suggests that copper(II) α,α′-dichloropropionate as well as its dioxan adduct have binuclear structures in which the copper(II) ions are held together by bridging acetate groups in a *syn-syn* arrangement.[9,10]

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