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Spectral and Magnetic Properties of Copper(II) α-Fluoropropionate and Its Dioxan Adduct

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Copper(II) α-fluoropropionate and its dioxan adduct were prepared and studied by spectral and magnetic methods. It is concluded from their spectral and magnetic properties that the compounds have a binuclear configuration.

Recently,[1,2] it was concluded from the spectral and magnetic properties of copper(II) α-chloro- and copper(II) α-bromopropionates and their dioxan adducts that these compounds have a binuclear configuration similar to that of copper(II) acetate monohydrate.[3,4]

In the present investigation, copper(II) α-fluoropropionate and its dioxan adduct were prepared and studied by spectral and magnetic methods.

EXPERIMENTAL

Copper(II) α-fluoropropionate and its dioxan adduct were prepared in the following way: Ethyl α-fluoropropionate was refluxed in an aqueous solution of sodium hydroxide (10 %) for several hours. After the reaction was over, the solution was mixed with an aqueous solution of copper sulfate, and concentrated under reduced pressure at about 50°C. The pale green microcrystals, that precipitated when the solution cooled, were isolated and recrystallized from hot dioxan. Fine dark green microcrystals of $Cu(CH_3CHFCOO)_2 \cdot 0.5(C_4H_8O_2)$ were collected and dried at room temperature. (Found: C 33.30; H 4.28; F 13.32; Cu 21.90. Calc. for $Cu(CH_3CHFOO)_2 \cdot 0.5(C_4H_8O_2)$: C 33.17; H 4.17; F 13.12; Cu 21.93.)

When the adduct was desolvated over phosphorus pentoxide in a vacuum at the temperature of boiling ethanol, green copper(II) α-fluoropropionate was recovered. (Found: C 29.56; H 3.32; F 15.82; Cu 25.72. Calc. for $Cu(CH_3CHFCOO)_2$: C 29.34; H 3.28; F 15.47; Cu 25.86.)

Spectral study. Electronic spectra were run on a Beckman DK 2A ratio recording spectrophotometer. EPR spectra were measured with a Varian Model E 4 spectrometer at room temperature. External magnetic fields of 2000 gauss and 5000 gauss were employed, and the scan range was ± 2000 gauss in both cases. The microwave frequency was 9520 MHz. The scan time was 8 min.

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Magnetic measurements. The magnetic susceptibilities of the compounds were measured over the temperature range 90 – 300°K by the Gouy method using an apparatus, manufactured by Newport Instruments Ltd. Copper sulfate pentahydrate was used for calibration.[5] Molar magnetic susceptibilities were corrected for the diamagnetism of the constituent atoms by means of Pascal's constants.[6]

RESULTS AND DISCUSSION

Copper(II) α-fluoropropionate and its dioxan adduct are both magnetically non-dilute. The magnetic data are given in Table 1. From the results it is seen that the magnetic susceptibility of copper(II) α-fluoropropionate increases

Table 1. Magnetic data.

$Cu(CH_3CHFCOO)_2$ $(-\Delta \times 10^6 = 101)$

T °K	$\chi_g \times 10^6$	$\chi_M' \times 10^6$			μ_{eff} B.M.
		Observed	Calculated		
93	5.04	1340	1205		1.0
123	5.65	1488	1458		1.21
153	5.716	1505	1506		1.358
183	5.556	1465	1465	1477[a]	1.466
213	5.259	1392	1392	1383[a]	1.54
243	4.926	1310	1309	1300[a]	1.597
273	4.595	1229	1229	1245[a]	1.64
293	4.377	1176	1178	1182[a]	1.66
303	4.23	1140	1140	1142[a]	1.664

[a] Values calculated from mean Weiss and Curie constants.

$Cu(CH_3CHFCOO)_2.0.5(C_4H_8O_2)$ $(-\Delta \times 10^6 = 123)$

T °K	$\chi_g \times 10^6$	$\chi_M' \times 10^6$	μ_{eff} B.M.
93	0.91	387	0.537
123	1.07	433	0.65
153	1.29	498	0.78
183	1.62	592	0.93
213	1.88	669	1.07
243	1.987	698	1.166
273	2.01	706	1.24
293	2.03	713	1.30

with decreasing temperature to a well-defined Néel temperature at T_n 150°K, and then decreases (Fig. 1). In the case of the dioxan adduct, the magnetic susceptibility decreases with decreasing temperature over the whole temperature range.

The Landé spectroscopic splitting factors and the theoretical molar magnetic susceptibilities were calculated by the theoretical expression [7]

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

where χ_M' is the molar magnetic susceptibility, g the Landé spectroscopic factor, N Avogadro's number, β the Bohr magneton, k Boltzmann's constant, and $N\alpha$ the temperature-independent paramagnetic contribution (60×10^{-6} for Cu(II)). The calculated values of T_n, $|2J|$, and g are given in Table 2.

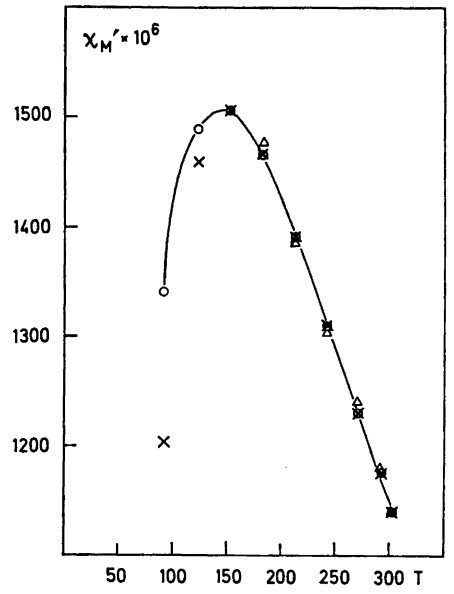

Fig. 1. Experimental and calculated molar magnetic susceptibilities of anhydrous copper(II) α-fluoropropionate: O, experimental; ×, calculated by expression (1); △, calculated from mean Weiss and Curie constants.

As can be seen in Fig. 1, the data for the anhydrous compound above 183°K obey the simple Curie-Weiss law of the form

$$\chi_M' = \frac{C}{T-\Theta} \qquad (2)$$

where C is the Curie constant, and Θ the Weiss constant.

The reciprocal susceptibilities vary linearly with temperature, the intercept with the temperature abscissa in the negative range being -258°K. The values of the Weiss constant, $\Theta = -258$°K, and the Curie constant, $C = 0.652$, indicate that there is a strong antiferromagnetic interaction.

EPR data for the compounds are given in Table 2. The EPR spectrum of the dioxan adduct showed absorption bands of the triplet state, as well as weak absorption bands of the doublet state. The EPR spectrum of the anhydrous compound was similar to the EPR spectra of copper(II) α-chloropropionate and copper(II) α-bromopropionate.[8] It seems that the molecules

Table 2.

Compound	T_n °K	$\|2J\|$ cm^{-1}	g	g_{av} (EPR)	$\Delta H°$ cm^{-1}	$\Delta S°$ e.u.	Θ°K	C
$Cu(CH_3CHFCOO)_2$	150	167	2.15	2.2	161	2.4	−258.2	0.652
$Cu(CH_3CHFCOO)_2 \cdot 0.5 (C_4H_8O_2)$[a]	345	384	[a]	2.21	290	1.6	–	–

[a] Other data obtained from EPR spectra: $g_{\|}=2.395$, $g_{\perp}=2.112$, $|D|=0.376$ cm^{-1}. Mononuclear impurity $g_{av}=2.125$.

in the triplet state form clusters which result in delocalization of the interacting unpaired electrons. The parameter data indicate the same axial symmetric type without hyperfine splitting as described previously.[8] The electronic spectra of the compounds in the solid state (in Nujol) show two absorption bands, one at about 675 nm and the other at about 375 nm in the spectrum of the dioxan adduct, and one at about 690 nm and the other at about 380 nm in the spectrum of the anhydrous compound.

Table 3. Absorption bands (λ_{max} in nm) of $Cu(CH_3CHFCOO)_2$ in solutions of

water	–	695
methanol	–	685
ethanol	375	685
acetone	375	675
dioxan	375	670

The solution spectra (Table 3) show that the binuclear structures persist in ethanol, acetone, and dioxan solutions, but not in aqueous or methanol solutions.

The mol fractions of the singlet and triplet states were calculated at various temperatures, using values of the effective magnetic moments, and values of the magnetic moments for the singlet (0.0 B.M.) and triplet states (3.04 B.M. for the anhydrous compound and 3.13 B.M. for the dioxan adduct).

The equilibrium constants of the singlet⇌triplet reaction were calculated from the mol fractions. The values of the heat of reaction ($\Delta H°$) and reaction entropy ($\Delta S°$) are listed in Table 2.

From the values of the singlet−triplet splitting energy and the heat of reaction, it is seen that the values are larger for the dioxan adduct than for the anhydrous compound. This means that the population of the lower energy level (singlet state) is relatively higher for the dioxan adduct than for the anhydrous compound. This agrees with the measured effective magnetic moments of the compounds.

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