Spectral and Magnetic Properties of Copper(II)

β-Iodopropionate and Its Dioxan Adduct

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Magnetic susceptibilities of copper(II) β-iodopropionate and its dioxan adduct over the temperature range 90 – 300 K are reported. The compounds exhibit magnetic behaviour typical of binuclear species. The values of the exchange integrals and the entropy and heat changes for the singlet-triplet equilibrium have been calculated.

The solid state spectra (in Nujol) and solution spectra of the compounds were measured. An absorption band is present near 380 nm in all the spectra.

Very recently, properties of several copper(II) salts of halogen-substituted propionic acids were reported.[1-3] From the spectral and magnetic properties, copper(II) chloro- and bromopropionates and their dioxan adducts were concluded to have a binuclear structure similar to that of copper(II) acetate monohydrate.[4,5]

In the present work, copper(II) β-iodopropionate and its dioxan adduct were prepared and their spectral and magnetic properties were measured. The structures of the compounds are discussed below.

EXPERIMENTAL

Copper(II) β-iodopropionate was prepared by adding copper carbonate in slight excess to a dilute aqueous solution of β-iodopropionic acid. After the reaction was over, the mixture was filtered. The filtrate was concentrated at about 50°C under reduced pressure and then left standing. The fine blue-green microcrystals that separated were washed with water and dried. (Found: C 15.59; H 1.78; Cu 13.75. Calc. for $Cu(ICH_2CH_2COO)_2$: C 15.62; H 1.75; Cu 13.77.)

Recrystallization of copper(II) β-iodopropionate from hot dioxan yielded a dark blue-green dioxan adduct. (Found: C 22.00; H 3.00; Cu 11.80. Calc. for $Cu(ICH_2CH_2COO)_2 \cdot C_4H_8O_2$: C 21.85; H 2.93; Cu 11.56.)

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Magnetic susceptibility determinations. The magnetic susceptibilities were measured over the temperature range 90 – 300 K by the Gouy method using apparatus from Newport Instruments Ltd. Copper sulphate pentahydrate was used as calibrant.[6] The molar magnetic susceptibilities were corrected for the diamagnetism of the constituent atoms by means of Pascal's constants.[7]

Electronic spectra. These were measured for the compounds in Nujol and in solution on a Beckman DK – 2A ratio recording spectrophotometer.

RESULTS

Data showing the temperature dependence of the magnetic susceptibilities are given in Table 1.

Table 1. Magnetic data.

$$Cu(ICH_2CH_2COO)_2 \qquad (-\varDelta \times 10^6 = 177.5)$$

T	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		μ_{eff} B.M.	
		exptl.	calc.	without $N\alpha$	with $N\alpha$
93	0.01	180	172	0.37	0.28
123	0.26	297	297	0.54	0.43
153	0.54	425	435	0.72	0.63
183	0.80	550	550	0.90	0.81
213	1.03	652	631	1.05	0.97
243	1.12	694	681	1.16	1.07
273	1.14	705	709	1.24	1.15
293	1.16	716	718	1.30	1.20
303	1.17	718	720	1.32	1.22

$$Cu(ICH_2CH_2COO)_2.C_4H_8O_2 \qquad (-\varDelta \times 10^6 = 221.5)$$

T	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		μ_{eff} B.M.	
		exptl.	calc.	without $N\alpha$	with $N\alpha$
93	− 0.15	136	131	0.32	0.27
123	0.06	257	262	0.50	0.45
153	0.33	404	414	0.70	0.65
183	0.59	547	547	0.89	0.84
213	0.78	653	644	1.05	1.00
243	0.88	707	707	1.17	1.12
273	0.93	735	743	1.26	1.21
293	0.97	755	756	1.33	1.27
303	0.98	760	760	1.36	1.30

The experimental molar susceptibilities calculated on the basis of a monomeric formula weight can be compared with the values predicted by the best fit of the theoretical expression (1) to the parameters g, $|2J|$ and $N\alpha$.

$$\chi_{\mathrm{M}} = \frac{g^2 N \beta^2}{3kT} \cdot \frac{1}{1 + \frac{1}{3}\,\exp(|2J|/kT)} + N\alpha \tag{1}$$

This equation describes the temperature dependence of the magnetic susceptibilities of an electronic system composed of singlet and triplet states separated by an energy difference $|2J|$, *i.e.*, when the energy of the singlet term is zero, the triplet term lies at $-2J$. In the equation χ_{M} is the molar magnetic susceptibility, g the Landé factor, N Avogadro's number, β the

Table 2. Values of T_{n}, $|2J|$, g, $N\alpha$, $\Delta H°$, and $\Delta S°$.

Compound	T_{n} (°K)	$|2J|$ (cm^{-1})	g	$N\alpha$ $\times 10^6$	$\Delta H°$ (cm^{-1})	$\Delta S°$ (e.u.)
$Cu(ICH_2CH_2COO)_2$	318	354	2.04	100	327	2.0
$Cu(ICH_2CH_2COO)_2 \cdot C_4H_8O_2$	328	365	2.21	62	338	2.0

Bohr magneton, k Boltzmann's constant ,and $N\alpha$ the temperature-independent paramagnetism. The best values of g, $|2J|$, and $N\alpha$ selected by an Algol program written for an Elliott 803 B computer are given in Table 2. Spectral data for the compounds in Nujol are shown in Fig. 1 and spectral data for the compounds in solution in Fig. 2.
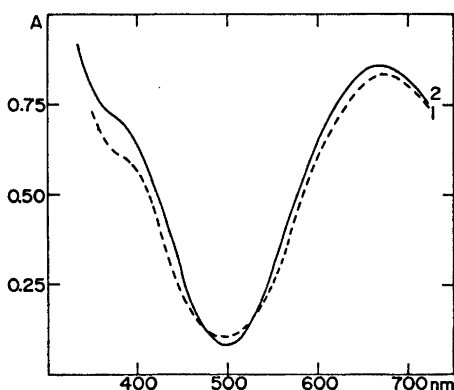

Fig. 1. Absorption spectra of $Cu(ICH_2CH_2COO)_2$ (1) and $Cu(ICH_2CH_2COO)_2 \cdot C_4H_8O_2$ (2) in the solid state (in Nujol).
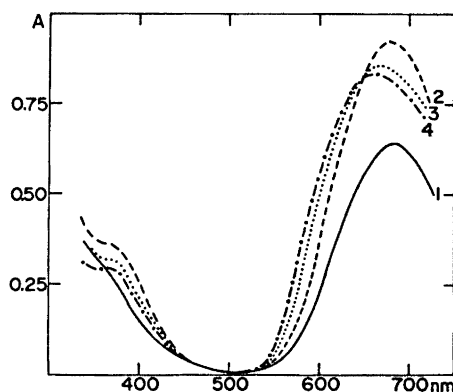

Fig. 2. Absorption spectra of $Cu(ICH_2CH_2COO)_2$ in methanol (1), ethanol (2), acetone (3), and dioxan (4).

DISCUSSION

The similarity of the spectral and magnetic properties of copper(II) β-iodopropionate and its dioxan adduct to those of copper(II) acetate monohydrate suggests that both compounds have a binuclear structure.

The spectra of the solid compounds in Nujol exhibit a well-defined band at about 675 nm and a shoulder at about 380 nm, the latter being a characteristic of binuclear species. The band at about 380 nm is very weak in the spectrum of copper(II) β-iodopropionate in methanol solution, but the spectra in ethanol, acetone, and dioxan exhibit a band at about 380 nm, which indicates that binuclear structures exist in these solutions. The long-wavelength band appears to change when the compound is dissolved. In dioxan solution, the long-wavelength band occurs at about 660 nm. In methanol the band is located at a longer wavelength, at about 690 nm. The $d-d$ band is shifted to the shortest wavelength in dioxan solution. This indicates that the magnetic interaction is stronger in dioxan than in acetone, ethanol, and methanol, in agreement with the results for copper(II) acetate.[8]

The temperature dependence of the magnetic susceptibilities is in accordance with a binuclear model. The singlet-triplet separation values are larger than for the other binuclear carboxylate salts. The magnetic moment of copper(II) iodopropionate is smaller than the moments of copper(II) chloro- and bromopropionates. It may be that differences in the nephelauxetic effects[9] of the halogen atoms produce such difference in magnetic moments. The greater cloud-expanding effect of the iodine atoms may produce a greater overlapping of the relevant orbitals of the ligand molecules and the metal ions. This would lead to bands of greater covalency and to smaller magnetic moments in the iodopropionates than in the chloro- and bromopropionates. Hatfield and Morrison[10] suggested that this phenomenon may be due to a difference in spin-orbit coupling and temperature-independent paramagnetism. The ligand fields of these iodopropionates are larger than those of the chloro or bromo propionates and contribute less to spin-orbit coupling. The equilibrium constants for the singlet $\rightleftharpoons$ triplet reaction at various temperatures have been calculated. The slopes of the plots of $-\ln K_{cg}$ vs. T and $RT \ln K_{cg}$ vs. T yielded for ΔH° and ΔS° the values which are given in Table 2. The values of ΔH° agree well with the values of the exchange coupling constants.

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