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Spectral and Magnetic Properties of Copper(II) Iodoacetate and Its Dioxan Adduct

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Copper(II) iodoacetate and its dioxan adduct were prepared. Magnetic and spectral properties of the compounds are reported. Copper(II) iodoacetate and its dioxan adduct display antiferromagnetic behaviour typical of binuclear compounds with copper(II) acetate-type structures. The electronic and infrared spectra of the compounds corraborate these conclusions.

Whereas copper(II) acetate and copper(II) chloroacetates have been studied extensively,[1] only the dissociation constant of copper(II) iodoacetate has been determined spectrophotometrically.[2] In the present paper, the preparation of copper(II) iodoacetate and its dioxan adduct is described, and electronic spectra, infrared spectra, and magnetic data for the compounds are presented.

EXPERIMENTAL

Preparations. Copper(II) iodoacetate was prepared by adding copper carbonate in slight excess to a dilute aqueous solution of mono-iodoacetic acid. After the reaction was over, the mixture was filtered and the filtrate was concentrated under reduced pressure at about 50°C and left to stand at room temperature. The fine green microcrystals which precipitated were filtered off, washed with cold water and dried at room temperature. (Found: C 11.15; H 1.09; Cu 14.61. Calc. for $Cu(ICH_2COO)_2$: C 11.08; H 0.93; Cu 14.66.)

When the copper(II) iodoacetate was recrystallized from hot dioxan, dark blue-green microcrystals of the composition $Cu(ICH_2COO)_2.0.5(C_4H_8O_2)$ separated. (Found: C 15.2; H 1.75; Cu 13.48. Calc. for $Cu(ICH_2COO)_2.0.5(C_4H_8O_2)$: C 15.09; H 1.69; Cu 13.31.)

Spectral studies. Electronic spectra were measured on a Beckman DK 2A ratio recording spectrophotometer. Infrared spectra in Nujol were run on a Perkin-Elmer Model 125 spectrophotometer.

Magnetic measurements. Magnetic properties of the compounds were measured over the temperature range 90 – 300 K by the Gouy method using apparatus manufactured by Newport Instruments Ltd. Copper sulphate pentahydrate was used for calibration.[3] The molar magnetic susceptibilities were corrected for the diamagnetism of the constituent atoms by means of Pascal's constants.[4]

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RESULTS AND DISCUSSION

The magnetic data are given in Table 1. From the values of the magnetic susceptibilities we can see that the susceptibility increases steeply with rising

Table 1. Magnetic data.

$Cu(ICH_2COO)_2$				$(-\Delta \times 10^6 = 154)$
T	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		μ_{eff} B.M.
		Exptl.	Calc.	
93	0.31	289	283	0.43
123	0.88	535	533	0.70
153	1.31	722	728	0.92
183	1.60	849	846	1.09
213	1.75	914	905	1.22
243	1.78	926	924	1.32
273	1.77	920	919	1.39
293	1.73	902	908	1.42
303	1.71	895	902	1.44

$Cu(ICH_2COO)_2.0.5(C_4H_8O_2)$				$(-\Delta \times 10^6 = 176)$
T	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		μ_{eff} B.M.
		Exptl.	Calc.	
93	0.50	413	405	0.43
123	1.00	654	656	0.70
153	1.41	850	852	0.92
183	1.66	970	971	1.08
213	1.83	1050	1030	1.23
243	1.83	1050	1050	1.32
273	1.82	1045	1045	1.39
293	1.78	1025	1034	1.42
303	1.76	1020	1026	1.44

temperature to a well-defined Néel point at 252 K, and then decreases with further increase in temperature. This magnetic behaviour is very similar to that observed for copper(II) acetate.[5] On the basis of this similarity, it seems reasonable to conclude that copper(II) iodoacetate and its dioxan adduct have structures similar to that of copper(II) acetate monohydrate [6,7] with a *syn-syn* arrangement of carboxylate groups in binuclear units.

The temperature dependence of the magnetic susceptibility of an electronic system composed of singlet and triplet states separated by an energy difference of $|2J|$, *i.e.* with the energy of the singlet term equal to zero and the triplet term located at $-2J$, is described by the theoretical equation:

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

In this equation χ_M' is the molar magnetic susceptibility, g the Landé spectroscopic splitting factor, N Avogadro's number, β the Bohr magneton, k the Boltzmann's constant, T the temperature (K), and $N\alpha$ the temperature independent paramagnetism. The best non-linear least squares values of g, $|2J|$ and $N\alpha$ calculated by an Algol program on an Elliott 803 B computer are shown in Table 2.

The equilibrium constants for the singlet-triplet reaction were calculated from the mole fractions at various temperatures. The values found for the reaction entropy are close to those expected for a singlet-triplet reaction. The values are listed 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})	$N\alpha$ $\times 10^6$	$\Delta H°$ (cm^{-1})	$\Delta S°$ (e.u.)
$Cu(ICH_2COO)_2$	252	2.18	280	36	275	2.1
$Cu(ICH_2COO)_2 \cdot 0.5(C_4H_8O_2)$	252	2.18	280	160	275	2.1

The electronic absorption spectra of copper(II) iodoacetate and its dioxan adduct were determined both in the solid state (in Nujol) and in solutions in different solvents.

The spectra of copper(II) iodoacetate and its dioxan adduct in Nujol (Fig. 1) exhibit two absorption bands, one at about 670 nm and the other at about 400 nm. The band at about 670 nm may be assigned to a spin-allowed $d-d$ transition and the band at about 400 nm may be due to a copper-to-copper linkage.

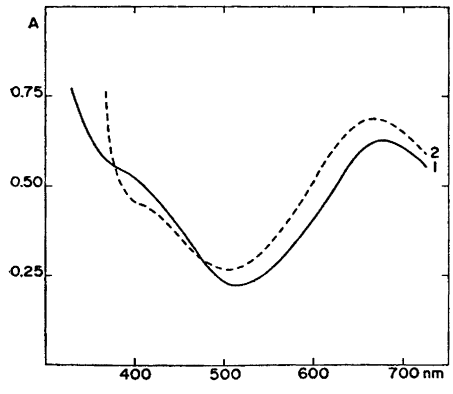

Fig. 1. Absorption spectra in the solid state (in Nujol) of $Cu(ICH_2COO)_2$ (1) and of $Cu(ICH_2COO)_2.0.5(C_4H_8O_2)$ (2).

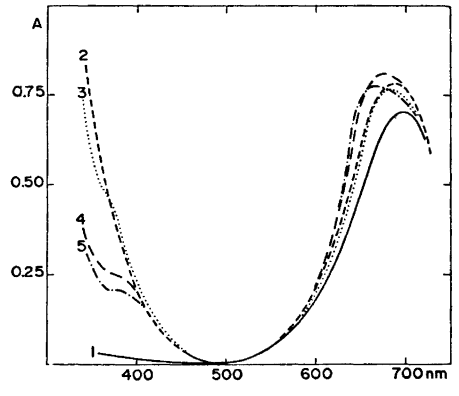

Fig. 2. Absorption spectra of $Cu(ICH_2COO)_2$ in water (1), methanol (2), ethanol (3), acetone (4) and dioxan (5).

As seen in Fig. 2, the electronic spectra of copper(II) iodoacetate in water and in methanol exhibit one ligand field band at about 700 nm, but no absorption band at about 375 nm which is usually characteristic of the binuclear structure. It seems that the binuclear structure does not persist in these solutions. On the other hand when the spectra were run on ethanol, acetone and dioxan solutions of the compound two absorption bands were recorded; these indicate that copper(II) iodoacetate has a binuclear structure in these solutions. We can also see that the $d-d$ transition band at 700 nm in aqueous solution is shifted to 660 nm in dioxan solution.

The infrared spectra of copper(II) acetate monohydrate which has a symmetrical bridge structure show that both the COO stretching bands are located at higher frequencies in dioxan.[8] In the infrared spectra of copper(II) iodoacetate and its dioxan adduct, the antisymmetric and symmetric stretching vibrations of the carboxyl groups have shifted in the same direction as in the spectra of copper(II) acetate monohydrate. The frequencies are given together with the frequencies in the spectrum of sodium iodoacetate [9] in Table 3.

Table 3. Antisymmetric, ν_a, and symmetric ν_s, COO stretching frequencies of copper(II) iodoacetates and sodium iodoacetate.

Compound	ν_a (cm^{-1})	ν_s (cm^{-1})	Separation
ICH_2COONa	1583	1394	189
$CU(ICH_2COO)_2$	1618	1405	213
$Cu(ICH_2COO)_2 \cdot 0.5(C_4H_8O_2)$	1620	1405	215

From the above results, it may be concluded that both copper(II) iodoacetate and its dioxan adduct have a structure similar to that of copper(II) acetate monohydrate.

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