

## Spectral and Magnetic Properties of Copper(II) $\alpha$ -Chloropropionate and Copper(II) $\beta$ -Chloropropionate

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Copper(II)  $\alpha$ -chloropropionate and copper(II)  $\beta$ -chloropropionate monohydrate were prepared and recrystallised from methanol, ethanol, acetone, and dioxan. The magnetic susceptibilities of the complexes were determined by means of a Gouy magnetic balance at room temperature. All complexes display subnormal magnetic moments and it is concluded that the structures are of the copper(II) acetate type. The electronic spectra of these complexes are in agreement with this conclusion.

It has been found recently<sup>1,2</sup> that copper(II) complexes of  $\alpha$ - and  $\beta$ -bromopropionate display magnetic and spectral properties similar to those of copper(II) acetate monohydrate, and the presence of analogous binuclear structural entities is indicated.<sup>3-8</sup>

For the study of analogous complexes the copper(II)  $\alpha$ -chloropropionate and copper(II)  $\beta$ -chloropropionate complexes have been prepared and recrystallised from several solvents for the purpose of studying the effect of solvents upon their magnetic and spectral properties.

### EXPERIMENTAL

*Preparations.* Copper(II)  $\alpha$ -chloropropionate was prepared by adding copper carbonate in slight excess to a dilute aqueous solution of  $\alpha$ -chloropropionic 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 dark green microcrystals which separated were washed with water and dried at room temperature.

Recrystallisation of the copper(II)  $\alpha$ -chloropropionate from hot methanol, ethanol, and acetone yielded in all cases anhydrous complexes which were similar in color to the salt which precipitated from aqueous solution.

Copper(II)  $\beta$ -chloropropionate monohydrate was prepared from copper carbonate and a dilute  $\beta$ -chloropropionic acid solution in the same manner as copper(II)  $\alpha$ -chloropropionate. The anhydrous complex was prepared from the monohydrate by dehydra-

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tion over phosphorus pentoxide in a vacuum drying pistol at 80°C. This complex was similar in color to the monohydrate and was stable in air.

Recrystallisation of the copper(II)  $\beta$ -chloropropionate monohydrate from hot acetone gave the monohydrate and recrystallisations from hot methanol and ethanol the hemihydrate, which were similar in color to the salt which crystallised from aqueous solution. Recrystallisation from hot dioxan yielded in both cases bluish green crystalline hemidioxan complexes.

A full list of complexes is given together with analytical data in Table 1.

Table 1. Analytical data for copper(II)  $\alpha$ -chloro- and  $\beta$ -chloropropionate complexes.

Complex	Calculated, %			Found, %			Precipitated from
	C	H	Cu	C	H	Cu	
Cu(CH <sub>2</sub> CHClCOO) <sub>2</sub>	25.87	2.89	22.81	26.01	3.00	22.82	water
Cu(CH <sub>2</sub> CHClCOO) <sub>2</sub>				25.92	2.91	22.90	methanol
Cu(CH <sub>2</sub> CHClCOO) <sub>2</sub>				25.98	2.88	22.75	ethanol
Cu(CH <sub>2</sub> CHClCOO) <sub>2</sub>				25.82	3.03	22.80	acetone
Cu(CH <sub>2</sub> CHClCOO) <sub>2</sub> ·0.5C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	29.78	3.75	19.69	30.00	3.88	19.84	dioxan
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·H <sub>2</sub> O <sup>a</sup>	24.29	3.39	21.42	24.60	3.21	21.39	water
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub>	25.87	2.89	22.81	26.00	2.95	22.87	
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·0.5H <sub>2</sub> O	25.05	3.15	22.09	24.92	3.10	22.06	methanol
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·0.5H <sub>2</sub> O				25.04	3.12	21.87	ethanol
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·H <sub>2</sub> O	24.29	3.39	21.42	24.47	3.24	21.22	acetone
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·0.5C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	29.78	3.75	19.69	30.30	3.79	19.78	dioxan

<sup>a</sup> Calculated H<sub>2</sub>O (%) = 6.07; found 6.01.

*Magnetic measurements.* The susceptibilities of powdered samples were measured by the Gouy method at room temperature using equipment and procedures which have been described previously.<sup>1</sup> The magnetic data are given in Table 2.

*Electronic spectra.* These were recorded on a Beckman DK 2A ratio recording spectrophotometer.

Table 2. Magnetic data for copper(II)  $\alpha$ - and  $\beta$ -chloropropionate complexes.

Complex	<i>T</i>	$\chi_g$ × 10 <sup>6</sup>	$\chi_M'$ × 10 <sup>6</sup>	$\mu_{eff}$ B.M.	Precipitated from
Cu(CH <sub>2</sub> CHClCOO) <sub>2</sub>	294.4	2.87	929	1.48	water
Cu(CH <sub>2</sub> CHClCOO) <sub>2</sub>	294.9	2.69	880	1.44	methanol
Cu(CH <sub>2</sub> CHClCOO) <sub>2</sub>	294	2.79	908	1.46	ethanol
Cu(CH <sub>2</sub> CHClCOO) <sub>2</sub>	294.4	2.79	906	1.46	acetone
Cu(CH <sub>2</sub> CHClCOO) <sub>2</sub> ·0.5C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	294.6	2.20	866	1.43	dioxan
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·H <sub>2</sub> O	296.2	2.43	862	1.43	water
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub>	295.2	2.60	854	1.42	
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·0.5H <sub>2</sub> O	294	2.42	833	1.40	methanol
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·0.5H <sub>2</sub> O	294	2.55	869	1.43	ethanol
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·H <sub>2</sub> O	294.6	2.57	905	1.46	acetone
Cu(ClCH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·0.5C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	295.9	1.96	780	1.36	dioxan

## RESULTS AND DISCUSSION

The similarity of the spectral and magnetic properties of the copper(II)  $\alpha$ -chloropropionate and copper(II)  $\beta$ -chloropropionate complexes to those of copper(II) acetate monohydrate suggests that the chloropropionates have binuclear structures.

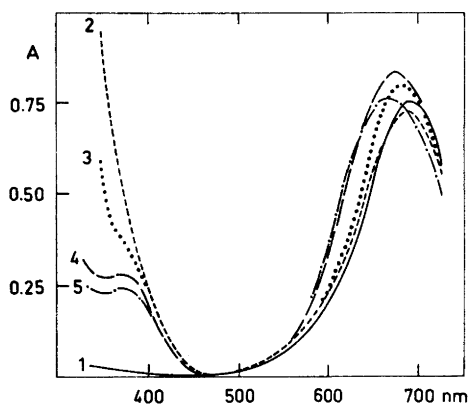


Fig. 1. Absorption spectra of  $\text{Cu}(\text{CH}_2\text{CHClCOO})_2$  in water (1), methanol (2), ethanol (3), acetone (4), and dioxan (5).

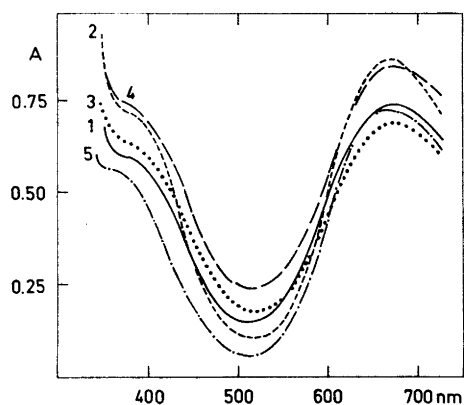


Fig. 2. Absorption spectra in the solid phase (Nujol) of  $\text{Cu}(\text{CH}_2\text{CHClCOO})_2$  precipitated from water (1), from methanol (2), from ethanol (3) and from acetone (4), and  $\text{Cu}(\text{CH}_2\text{CHClCOO})_2 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  (5).

The values of the magnetic moments of copper(II)  $\alpha$ -chloropropionate and copper(II)  $\beta$ -chloropropionate with coordinated dioxan are somewhat lower than the values for the corresponding species without coordinated dioxan. This leads to the conclusion that dioxan increases the magnetic interaction between copper ions in these cases.

The solid phase spectra (Nujol) (Figs. 2 and 4) of all of the complexes exhibit approximately the same well defined bands, one at about 690 nm and shoulder at about 375 nm, the latter being a characteristic of binuclear copper carboxylates. The spectra of the complexes in ethanol, acetone, and dioxan (Figs. 1 and 3) also show two bands, one at about 690 nm and the other at about 375 nm. It seems, that binuclear structures exist in these solutions. On the other hand, the spectra of solutions in water and methanol did not contain a band at about 375 nm. It seems, therefore, that the binuclear structures do not exist in water and methanol solutions. The tendency to form binuclear structures is seen to decrease with increasing dielectric constant of the solvent.

The  $\text{p}K_a$  values of propionic,  $\alpha$ -chloropropionic, and  $\beta$ -chloropropionic acids and the values of the magnetic moments of their copper(II) salts are summarized in Table 3. A distinct correlation seems to exist between these two quantities. The effective magnetic moment of the complex is seen to

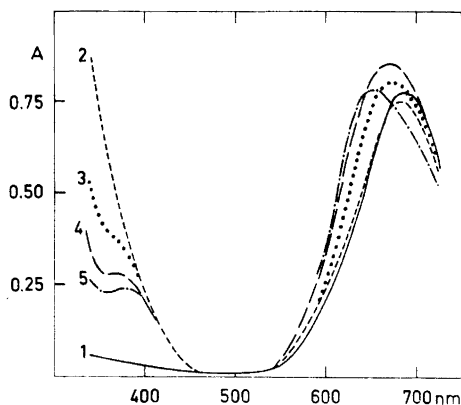


Fig. 3. Absorption spectra of  $\text{Cu}(\text{ClCH}_2\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$  in water (1), methanol (2), ethanol (3), acetone (4), and dioxan (5).

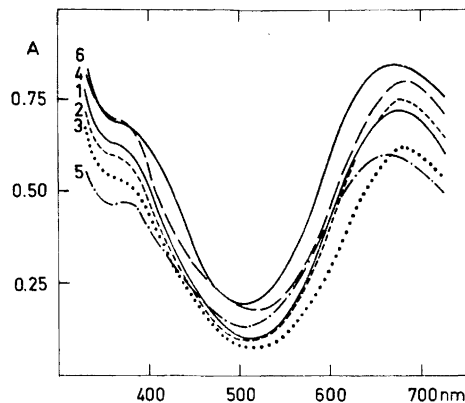


Fig. 4. Absorption spectra in the solid phase (Nujol) of  $\text{Cu}(\text{ClCH}_2\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$  precipitated from water (1),  $\text{Cu}(\text{ClCH}_2\text{CH}_2\text{COO})_2 \cdot 0.5\text{H}_2\text{O}$  from methanol (2) and from ethanol (3),  $\text{Cu}(\text{ClCH}_2\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$  from acetone (4),  $\text{Cu}(\text{ClCH}_2\text{CH}_2\text{COO})_2 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  (5), and  $\text{Cu}(\text{ClCH}_2\text{CH}_2\text{COO})_2$  (6).

increase with decreasing value of the  $\text{p}K_a$  of the corresponding acid. The  $\text{p}K_a$  value of an acid can be taken as a measure of the ability of the carboxylate ion to donate electrons to a copper ion. The same correlation has been found for the copper(II) propionate, copper(II)  $\alpha$ -bromopropionate, and copper(II)  $\beta$ -bromopropionate.<sup>2</sup>

Table 3.  $\text{p}K_a$  values of propionic,  $\alpha$ -chloropropionic, and  $\beta$ -chloropropionic acids and the magnetic moments of their copper(II) complexes.

Complex	$\text{p}K_a$	$\mu_{\text{eff}}$	$T$
$\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2$	4.89 <sup>a</sup>	1.40 <sup>a</sup>	289
$\text{Cu}(\text{ClCH}_2\text{CH}_2\text{COO})_2$	4.096 <sup>10</sup>	1.42	295.2
$\text{Cu}(\text{CH}_3\text{CHClCOO})_2$	2.879 <sup>10</sup>	1.48	294.4
$\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$		1.31 <sup>12</sup>	295
$\text{Cu}(\text{ClCH}_2\text{CH}_2\text{COO})_2 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$		1.36	295.9
$\text{Cu}(\text{CH}_3\text{CHClCOO})_2 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$		1.43	294.6

<sup>a</sup> This value was calculated from the results of Martin *et al.*<sup>11</sup> leaving out the temperature-independent paramagnetism,  $N\alpha$ , of a mole of copper atoms.

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