Spectrochemical Study of Microscopic Crystals. XXII.[1] *The Structure of Cupric Mono-, Di- and Trichloroacetate*[2]

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Previously the present authors[3,4] studied the structure of cupric *n*- and *iso*-alkanoates, anhydrous and hydrated, and showed mostly on the basis of the polarized absorption spectra that these carboxylates, in the crystalline state and in non-coordinating organic solvents, consist of binuclear molecules which are similar to that of cupric acetate and have a sort of copper-to-copper linkage within the molecules. In continuation of the former study, the structure of cupric mono-, di- and trichloroacetate has now been examined, and the effect of replacement by chlorine atoms discussed in relation to the dimer formation of the cupric carboxylates. A brief account of a part of this study was formerly presented as a short communication[5], the details of which are given below.

Experimental

Materials. — All the cupric chloroacetates were prepared according to the method of Bateman et al.[6,7] from cupric carbonate and the corresponding chloroacetic acid or from sodium carboxylate and cupric sulfate. All the compounds were identified by elemental analysis. Crystals of the anhydrous forms of the compounds were obtained by recrystallization using non-aqueous solvents after dehydrating the hydrated crystals. The absence of the water of crystallization was confirmed by infrared spectra and elemental analysis.

Anhydrous and hydrated cupric monochloroacetate were obtained in green crystals. The hydrated monochloroacetate corresponds to the formula, $Cu(ClCH_2COO)_2 \cdot 2.5H_2O$. Calcd.: Cu, 21.5; Cl, 30.6; C, 20.7; H, 2.61. Found: Cu, 21.5; Cl, 30.4; C, 20.4; H, 2.55%. A blue form has also been prepared besides the green form. Thus the blue crystals of the anhydrous monocloroacetate were obtained, when ethanol was added to an aqueous solution of the monochloroacetate.

Anhydrous cupric dichloroacetate was prepared in green crystals. Hydrated crystals, which are colored blue, were also obtained together with the anhydrous crystals, when recrystatallization was made from water. The result with the hydrated crystal is reported elsewhere.

Cupric trichloroacetate was obtained in blue crystals after recrystallization from water. The

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[1] Part XXI of this series, S. Yamada, H. Nishikawa and R. Tsuchida, This Bulletin, 33, 930 (1960).

[2] Presented in part at the Symposium on Co-ordination Copounds, Nagoya, November, 1958.

[3] R. Tsuchida and S. Yamada, *Nature*, 176, 1171 (1955). R. Tsuchida, S. Yamada and H. Nakamura, ibid., 178, 1192 (1956).

[4] S. Yamada, H. Nakamura and R. Tsuchida, This Bulletin, 30, 953 (1957); ibid., 31, 303 (1958).

[5] R. Tsuchida, S. Yamada and H. Nakamura, *Nature*, 181, 479 (1958).

[6] W. G. Bateman and A. B. Hoel, *J. Am. Chem. Soc.*, 36, 2517 (1914).

[7] W. G. Bateman and D. B. Conrad, ibid., 37, 2553 (1915).

elemental analysis by the present authors indicates that the blue crystals correspond to the formula, $Cu(Cl_3C\cdot COO)_2\cdot 3H_2O$, in agreement with the analysis by Bateman et al.[6]

Measurements.—Quantitative dichroism measurements in the visible and ultraviolet regions were carried out at room temperature by Tsuchida and Kobayashi's microscopic method[8].

Absorption spectra of the compounds in solution were determined by a Beckman DU spectrophotometer. It was confirmed in all the measurements that Beer's law was obeyed in the presence of the free carboxylic acid.

The notations in the present paper are the same as close used in the former papers of this series. Extinction coefficients, ε, are calculated on the basis of a formula-weight instead of a molecular weight.

Results and Discussion

Structure of Cupric Chloroacetates in the Crystalline State. — Previously the present authors[3-5] reported about the structure of cupric formate, acetate and higher carboxylates on the basis of their polarized absorption spectra. A similar treatment will be made in the present article concerning the structure of cupric chloroacetates. Since some of the results and the discussions in the former papers are used in the present work, it would be appropriate to give a brief account of the conclusions obtained formerly.

Cupric salts of acetic acid and higher fatty acids in the crystalline state and in non-coordinating organic solvents show in the visible and the near-ultraviolet region a band at about $80\times10^{13}\,\mathrm{sec}^{-1}$(band II) besides a band at about $43\times10^{13}\,\mathrm{sec}^{-1}$(band I), whereas most cupric compounds of an ordinary type show in this wavelength region only one band which may be considered as corresponding to the band at about $43\times10^{13}\,\mathrm{sec}^{-1}$ of cupric alkanoates. With the cupric carboxylates consisting of binuclear molecules, the following features characteristic of these compounds were observed in the dichroism. "For the band I, the electric vector is more strongly absorbed along the complex plane than along the Z-direction of the binuclear molecule, the Z-direction being the direction connecting the two copper ions in the binuclear molecule. For the band II, the electric vector is more strongly absorbed along the Z-direction. The polarization for the band II is thus seen to be the reverse of the polarization for the band I". These facts are considered to show that the compounds involve along the Z-direction a sort of copper-to-copper linkage characteristic of the binuclear molecules of the cupric alkanoates. On the contrary, cupric formate tetrahydrate[3,4], which is known from examination with X-rays[9] to have no copper-to-copper linkage[10], shows no absorption band at about $80\times10^{13}\,\mathrm{sec}^{-1}$. Thus the appearance of the band at about $80\times10^{13}\,\mathrm{sec}^{-1}$, combined with the polarization property of the band, may be regarded as showing the existence of the binuclear molecule similar to that of cupric acetate hydrate involving the copper-to-copper linkage.

The results of the present dichroism measurements are shown in Figs. 1 to 4. The components of the cupric compounds in the crystalline state may be under rather weak perturbation owing to the crystalline field, but the polarized absorption spectra as determined on a suitable plane are regarded as representing the main features of the dichroism of the component molecule. The exact arrangement of the molecules in the crystals is unknown for all the cupric compounds reported in the present work. It is easy, however, to find the principal characteristics of the dichroism of the molecules themselves by comparing their polarized absorption spectra with those of cupric acetate monohydrate, whose crystal structure was accurately determined, and also with those of cupric alkanoates, which were extensively studied on the basis of the comparison with cupric acetate.

The present measurement, as seen in Fig. 1, indicates that the green anhydrous cupric monochloroacetate in the crystalline state shows an absorption band at about $80\times10^{13}\,\mathrm{sec}^{-1}$, in

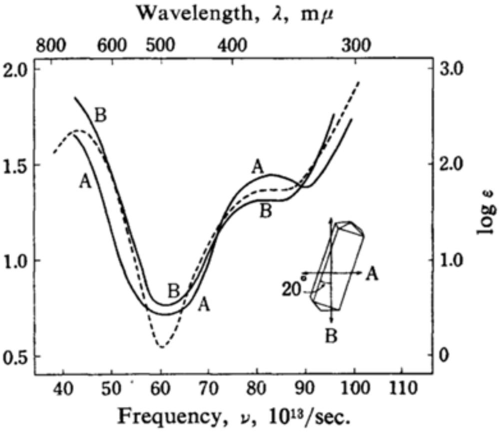

Fig. 1. Absorption spectra of anhydrous $Cu(Cl\cdot CH_2COO)_2$ in the crystalline state (——) and in dioxane (----).

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[8] R. Tsuchida and M. Kobayashi, "*The Color and the Structure of Metallic Compounds*", (*Kinzokukagōbutsu no Iro to Kōzō*), Zoshindo, Osaka, 1944, p. 180 (in Japanese).

[9] R. Kiriyama, H. Ibamoto and K. Matsuo, *Acta Cryst.*, 7, 482 (1954).

[10] Cupric formate in dioxan exists mostly as binuclear molecules of the acetate-type, and crystals of the formate consisting of the binuclear molecules were isolated. Cf. R. L. Martin and H. Waterman, *J. Chem. Soc.*, 1959, 1359.

addition to a band at about $40\times10^{13}\,\mathrm{sec}^{-1}$. Moreover, it is recognizable that the polarization for the former band is found to be the reverse of the polarization for the latter. This relationship, which closely resembles that encountered in the case of the acetate monohydrate and higher alkanoates[3,4], may suggest that the green anhydrous cupric monochloroacetate in the crystaline state consists of the binuclear molecules of the acetate-type, since the dichroism of the anhydrous monochloroacetate may be readily understandable when it is assumed that A- and B-absorption in Fig. 1 represent the main characteristics of the *Z*- and *X*, *Y*-absorption of the binuclear molecule, respectively.

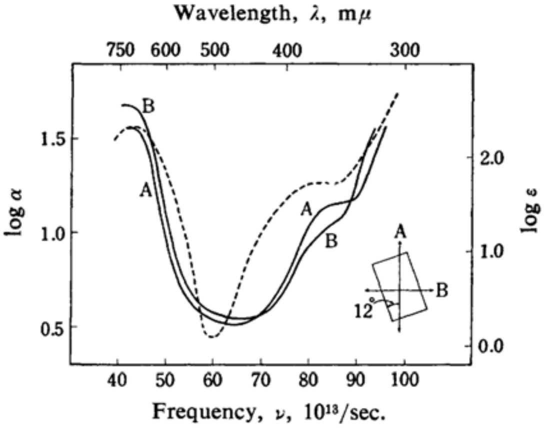

Fig. 2. Absorption spectra of $Cu(Cl\cdot CH_2COO)_2\cdot 2.5H_2O$ in the crystalline state (——) and in dioxane (----).

The present measurement also indicates that cupric monochloroacetate hydrate in the crystalline state shows dichroism with characteristics similar to those of cupric acetate, as is readily seen in Fig. 2. Thus the monochloroacetate hydrate shows an absorption band at about $80\times10^{13}\,\mathrm{sec}^{-1}$ in addition to a band at about $40\times10^{13}\,\mathrm{sec}^{-1}$. The main characteristics of the dichroism with the component molecule may be recognized, although the dichroism is not very remarkable. It is, therefore, concluded that cupric monochloroacetate hydrate consists of the binuclear molecule of the acetate-type. As comparison of the dichroism of the green anhydrous monochloroacetate with the dichroism of the green monochloroacetate hydrate shows, the presence of the water molecules of crystallization is expected to have a more or less remarkable effect upon the copper-to-copper linkage, but no marked difference was observed in the absorption maxima in the visible and the near-ultraviolet regions between the anhydrous and the hydrated form.

The blue form of anhydrous cupric monochloroacetate is also obtained when ethanol is added to an aqueous solution of the monochloroacetate. The blue crystal is found in the present work to show an absorption band in the near-infrared region, but no absorption band at about $80\times10^{13}\,\mathrm{sec}^{-1}$. It is, therefore, concluded that the blue form of the monochloroacetate contains no binuclear molecule.

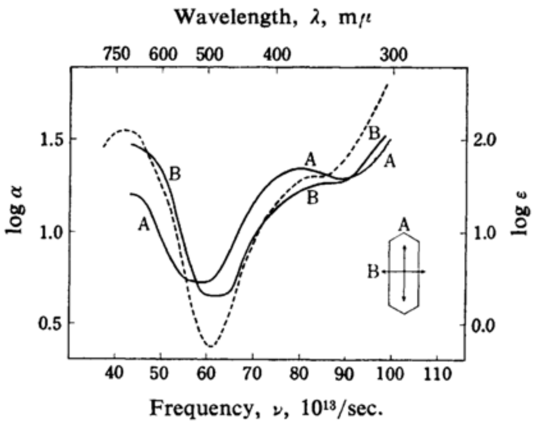

Fig. 3. Absorption spectra of anhydrous $Cu(Cl_2\cdot CHCOO)_2$ in the crystalline state (——) and in dioxane (----).

The present measurement, as seen in Fig. 3, indicates that the green crystal of anhydrous cupric dichloroacetate shows a band at about $80\times10^{13}\,\mathrm{sec}^{-1}$ besides a band at about $40\times10^{-13}\,\mathrm{sec}^{-1}$, the polarization of the former band being the reverse of the polarization of the latter. This relationship, which is similar to the relationship with cupric acetate hydrate, indicates that anhydorus cupric dichloroacetate in the crystalline state consists of binuclear molecules.

Cupric dichloroacetate is known to exist in a tetrahydrate as well. The dichroism of this form, which is colored blue, is not identical with that of the anhydrous form. The structure of the tetrahydrate will be discussed separately in a later communication.

Cupric trichloroacetate is obtained in the tetrahydrate, when recrystallized from water, ethanol-water, or dioxane-water. The trichloroacetate tetrahydrate shows the dichroism which is quite different from the dichroism of the green form of the mono- or the dichloroacetate. Thus the trichloroacetate tetrahydrate shows only one absorption band at about $40\times10^{13}\,\mathrm{sec}^{-1}$, but no absorption band in the neighborhood of the wavelength region around $80\times10^{13}\,\mathrm{sec}^{-1}$, as seen in Fig. 4. The absorption spectrum of the trichloroacetate, which is similar to the absorption spectra of ordinary cupric complexes such as cupric sulfate, indicates clearly that cupric trichloroacetate

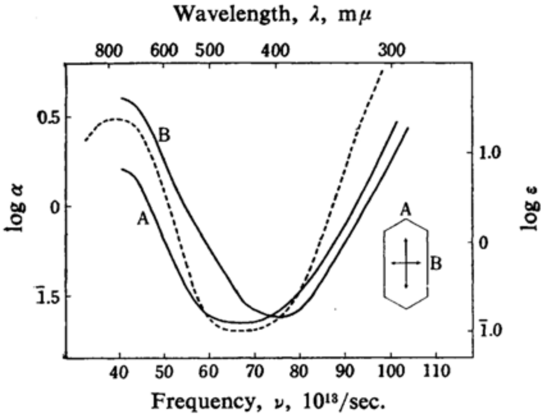

Fig. 4. Absorption spectra of $Cu(Cl_3C\cdot COO)_2\cdot 4H_2O$ in the crystalline state (——) and in dioxane (----).

tetrahydrate contains no binuclear molecule of the acetate-type in the crystalline state.

Anhydrous cupric trichloroacetate, which is obtained in green crystals when recrystallized from ethyl ether after dehydration of the tetrahydrate, may probably consist of the binuclear molecule of the acetate-type, but the dichroism measurement with the crystal has not been performed in the present work. As discussed in a later paragraph of the present article, the ultraviolet spectrum shows that the anhydrous trichloroacetate exists as the binuclear molecules in ethyl ether.

Magnetic susceptibility at room temperature was reported with cupric mono-, di- and trichloroacetates in the solid state¹¹⁾. The results seem to be compatible with the conclusions from the present study about the structure of these compounds.

Structure of Cupric Chloroacetates in Solution.—The binuclear cupric carboxylates in water are found to undergo dissociation most readily. Even cupric acetate exists in this solvent mostly as the monomer in equilibrium with the binuclear form in a smaller proportion, although the degree of dissociation depends upon the concentration of the solution. All the cupric monocarboxylates so far examined have been found to exist in water as their monomers to a considerable extent if they are soluble in water at all. This may evidently be due to the great tendency of water molecules to be co-ordinated with the cupric ion. On the contrary, dissociation into the monomeric complex-ion has been found to be quite small in non-co-ordinating organic solvents, such as ethanol, dioxane, ethyl ether and chloroform. Needless to say, cupric carboxylates in co-ordinating solvents such as pyridine undergo decomposition to form cupric complexes with the solvent molecules. In the present work, comparison of the absorption spectra is made with the cupric carboxylates in these solvents in almost the same concentration.

It was found in the former investigations that the cupric monocarboxylates having the binuclear molecules of the acetate-type show in non-co-ordinating organic solvents the characteristic absorption spectra with the following features⁴⁾.

(1) A band at about $40\times10^{13}\,sec^{-1}$ of the binuclear cupric carboxylate is much stronger than the corresponding band of the mononuclear cupric compounds. (2) Besides the absorption at about $40\times10^{13}\,sec^{-1}$ of the binuclear, cupric carboxylate shows another band at about $80\times10^{13}\,sec^{-1}$, which is about four times less in intensity than the band in the longer wave-length region of the same compound. As reported in the former papers³,⁴⁾, these features may be used as criteria in telling whether a cupric carboxylate exists mostly as binuclear molecules of the acetate-type or not.

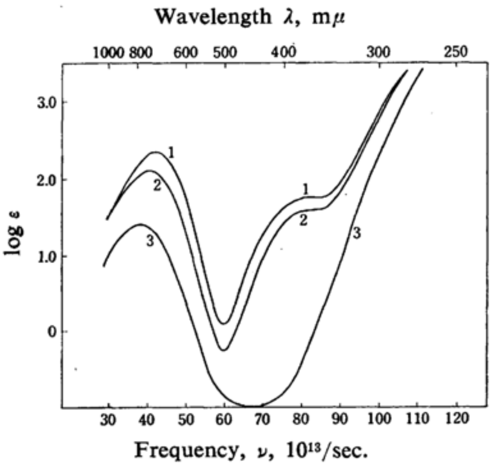

Fig. 5. Absorption spectra of $Cu(Cl_nH_{3-n}C\cdot COO)_2$ in dioxane: 1, $n=1$; 2, $n=2$; 3, $n=3$.

Absorption spectra of cupric chloroacetates in dioxane are shown in Fig. 5. The absorption spectra characteristic of the cupric carboxylates having binuclear structure of the acetate-type are observed with the mono- and the dichloroacetate. Thus the two chloroacetates in dioxan show an absorption band at about $80\times10^{13}\,sec^{-1}$, in addition to a band at about $40\times10^{13}\,sec^{-1}$ which has an extinction coefficient about nine times higher than the corresponding band of an ordinary type of cupric complex such as an aquated ion of copper. This fact indicates, on the basis of the criteria formerly obtained, that the mono- and the

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11) M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 1558 (1958).

dichloroacetate in dioxane exist, at least in most part, as binuclear molecules.

On the contrary, cupric trichloroacetate in dioxane shows an absorption band at about $40\times10^{13}\,\mathrm{sec}^{-1}$, but no absorption band at about $80\times10^{13}\,\mathrm{sec}^{-1}$. The spectrum shows the main features of the spectrum of ordinary cupric complexes without specific metal-to-metal linkage. It may be concluded, therefore, that cupric trichloroacetate does not contain the binuclear molecule of the acetate-type in dioxan. It is noteworthy that even anhydrous cupric trichloroacetate in dioxane shows no band at about $80\times10^{13}\,\mathrm{sec}^{-1}$, having no binuclear molecule in this solvent. It is most probable that two trichloroacetate ions are coordinated as bidentate ligands with a single cupric ion to form a planar complex-ion.

The present work shows that the maximum for the band I of the cupric carboxylate is displaced bathochromically, when the hydrogen atom is replaced by the chlorine atom in the series from the acetate to the trichloroacetate, as seen in Table I. The fact that this order seems to be parallel with the stability of the binuclear molecule may be readily understandable in terms of the ligand field theory, since the band I corresponds to the electronic transitions between the terms formed by splitting from the cupric ion under the ligand field, which is expected to be stronger, as the cupric carboxylates become more stable.

TABLE I. VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA OF CUPRIC MONOCARBOXYLATES WITH AN EMPIRICAL FORMULA OF $Cu(R\cdot COO)_2$

R	Solvent	Band I		Band II	
		ν	log ε	ν	log ε
CH_3	ethanol	42.8	2.25	82.0	1.65
	dioxane	45.2	2.25	81.1	1.81
$Cl\cdot CH_2$	ethanol	40.2	1.82	82	1.1
	dioxane	42.9	2.34	82	1.74
$Cl_2\cdot CH$	ethanol	38.5	1.58	83	0.5
	dioxane	41.1	2.12	83	1.60
$Cl_3\cdot C$	ethanol	38.0	1.47	none	
	dioxane	38.4	1.44	none	
	ethyl ether	38.3	2.18	ca. 84	1.50

ν: $10^{13}\,\mathrm{sec}^{-1}$.

From the above-mentioned observation with the cupric chloroacetates both in the crystalline state and in dioxane, it may be concluded that the tendency of the cupric carboxylates to form binuclear molecules of the acetate-type seems to decrease in the following order: $CH_3-{}>Cl\cdot CH_2-{}>Cl_2\cdot CH-{}>Cl_3\cdot C-$ for a series of compounds with an empirical formula of $Cu(R\cdot COO)_2$, R being the afore-mentioned radical. This trend may be understood as due primarily to the accumulation of the inductive effect of the chlorine. Thus, as the hydrogen atom in the CH_3- group is replaced by the chlorine atom, the electron-withdrawing power of group R becomes greater to the effect that the electron density on the oxygen atom of the carboxylate group becomes smaller and consequently the electron on the copper atom would be withdrawn more strongly toward the oxygen atom. If it is assumed that the increase in the electronic density on the copper atom means increase of the electronic charge available for the additional linkage between the two copper atoms, the copper-to-copper linkage might become weaker as the electronic charge on the copper decreases on going from the trichloroacetate to the acetate.

Dimer Formation of Cupric Chloroacetates in Different Solvents.—The tendency to the dimer formation of cupric carboxylates in solution is found to depend greatly upon the solvent used. In the present work, water, ethanol, dioxane and ethyl ether as a solvent were compared with one another in respect of the dimer formation of the cupric carboxylates. Examinations were made about the structure of the cupric chloroacetates in these solvents in almost equal concentration. Examinations were also made about the structure of the component molecules in the crystals obtained after recrystallization from these solvents.

Absorption spectra of cupric mono-, di- and trichloroacetates in ethanol are shown in Fig. 6. From the above-mentioned criteria, it may be readily concluded that cupric monochloroacetate in ethanol exists mostly as the binuclear molecules, since the compound shows an absorption band at about $80\times10^{13}\,\mathrm{sec}^{-1}$ in addition to a band at about $40\times10^{13}\,\mathrm{sec}^{-1}$, the intensity of these bands being characteristic of

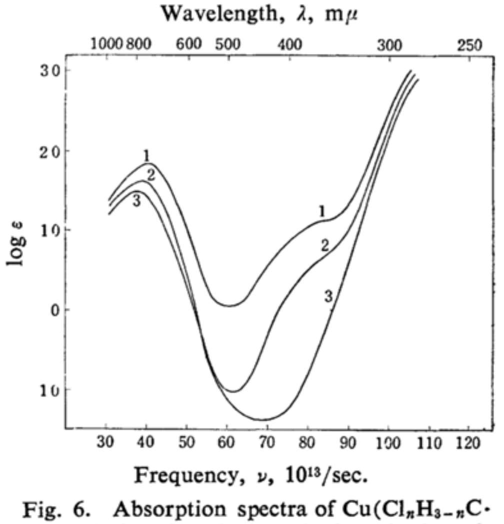

Fig. 6. Absorption spectra of $Cu(Cl_nH_{3-n}C\cdot COO)_2$ in ethanol: 1, $n=1$; 2, $n=2$; 3, $n=3$.

the binuclear cupric carboxylates. On the contrary, the dichloroacetate in ethanol shows only one band at about $40\times10^{13}\,\mathrm{sec}^{-1}$ which is much weaker than the corresponding band of cupric monochloroacetate. Moreover, the compound shows no band at about $80\times10^{13}\,\mathrm{sec}^{-1}$, although only a very small inflation was observed in this wavelength region. Judging from the criteria mentioned above, the dichloroacetate in ethanol exists mostly in the mononuclear form, although the binuclear molecule might be present in a very minor proportion. The trichloroacetate in ethanol is also seen to show an absorption spectrum, quite similar to the spectrum of the dichloroacetate in ethanol. It is, therefore, concluded that the trichloroacetate exists in the mononuclear form in this solvent. It is to be noted that the band at about $40\times10^{13}\,\mathrm{sec}^{-1}$ of the monochloroacetate in ethanol seems to be a little weaker than the corresponding band of the same compound in dioxane, where it exists as binuclear molecules. Therefore, even the monochloroacetate in ethanol contains mononuclear complexes in a very small amount, which is in equilibrium with the binuclear molecules in most part.

In a similar way, the ultraviolet spectra indicate that cupric mono- and dichloroacetate in ethyl ether exist mostly as their binuclear molecules. It is to be noted that anhydrous cupric trichloroacetate shows an absorption spectrum in ethyl ether which is quite different from its spectrum in dioxan, ethanol or water. The spectrum of anhydrous trichloroacetate in ethyl ether was determined in the present work and is shown in Fig. 7. It is seen from the figure that anhydrous cupric trichloroacetate in ethyl ether shows the two absorption bands at about 38 and $80\times10^{13}\,\mathrm{sec}^{-1}$, with the principal characteristics of the binuclear cupric carboxylates.

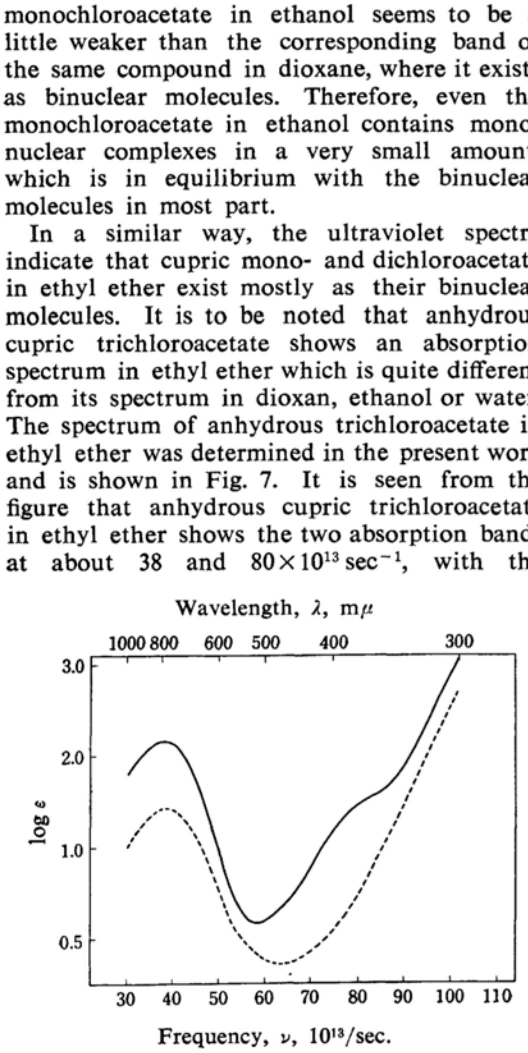

Fig. 7. Absorption spectra of anhydrous $Cu(Cl_3C\cdot COO)_2$ in ethyl ether (——) and in dioxane (----).

It is seen again that the band I of the cupric chloroacetates is displaced bathochromically, as the hydrogen atom is replaced by the chlorine atom in the series from the acetate to the trichloroacetate. This is in agreement with the relationship, which was derived in the case of dioxane as a solvent, and may be understood in a similar way. It is clearly seen that the cupric chloroacetates exist as binuclear molecules most readily in ethyl ether, of the solvents examined.

Thus the presentd work indicates that cupric trichloroacetate exists as mononuclear complexes in ethanol and in dioxane as well as in water, but that anhydrous cupric trichloroacetate exists in ethyl ether mostly as the binuclear molecules with the metal-to-metal linkage. Similarly it is found that cupric dichloroacetate exists as its binuclear form in dioxane and ether, but as the mononuclear form in ethanol and water. The monochloroacetate is found to exist mostly as binuclear molecules in ethyl ether, dioxane and ethanol, but as mononuclear molecules in water.

The dissociation of the dimer into the monomers takes place most readily in water. Even cupric acetate exists in this solvent mostly as monomeric complexes in equilibrium with the binuclear molecules in a small proportion, although the degree of dissociation depends upon the concentration of the solution. All the cupric monocarboxylates so far examined are found to exist in water as their monomers to a considerable extent if they are soluble in water at all.

Inspection of the data, which are summarized in Table II, reveals that the dimer formation of the cupric carboxylates in different solvents seems to become more difficult in the following order of the solvents: ethyl ether, dioxane, ethanol and water.

The order of the solvents, as presented above, is seen to agree with the increasing order of the electronic charge on the oxygen atom which also represents an increasing order of the co-ordinating capacity of the oxygen to

TABLE II. STRUCTURE OF CUPRIC CHLOROACETATES IN SOLUTION

	Water	Ethanol	Dioxane	Ethyl ether
Acetate	m	d	d	insoluble
Monochloro-〃	m	d	d	d
Dichloro- 〃	m	m	d	d
Trichloro- 〃	m	m	m	d

d: The compound exists mostly as binuclear molecules.
m: The compound exists mostly as mononuclear complexes.

the cupric ion. It is likely that the stronger co-ordination of the solvent molecules at the residual co-ordination position of the copper ion may break the binuclear molecules into the mononuclear complexes more easily. The present examinations also indicate that the mono- and the dichloroacetate give crystals consisting of the binuclear molecules, when recrystallized from water, ethanol or dioxane. On the contrary, the trichloroacetate gives from the same solvents no crystals of the binuclear molecules. The trichloroacetate, however, gives crystals of the binuclear molecules on recrystallization from ethyl ether after careful dehydration of the hydrated crystals. These observations, which are summarized in Table III, seem to be compatible with the above-mentioned order of the solvents concerning the dimer formation of the cupric monocarboxylates.

TABLE III. STRUCTURE OF THE COMPLEXES CONSTITUTING THE CRYSTALS OBTAINED BY RECRYSTALLIZATION OF CUPRIC CHLOROACETATES FROM VARIOUS SOLVENTS

	Water	Ethanol	Dioxane	Ethyl ether
Acetate	D	D	D	Insoluble
Monochloro-〃	D	D	D	D
Dichloro-〃	D	D	D	D
Trichloro-〃	M	M	M	D

D: Crystals consisting of dimeric molecules are obtained, aside from the question whether crystals of the monomeric complexes may be obtained or not.

M: Only crystals consisting of the monomeric complexes are obtained.

All these results are found to be in agreement with the conclusion that the trichloroacetate is the cupric chloroacetate which forms the binuclear molecule of the acetate-type with the greatest difficulty, the dichloroacetate being the next. Such a tendency may be understood as due primarily to the accumulation of the inductive effect of the chlorine, which seems to be in parallelism with the decrease in electronic density on the oxygen atom and with the decrease of dissociation constant of the free carboxylic acid. Among cupric carboxylates which are closely related with one another, the dissociation constant of the free carboxylic acid may be regarded as a measure of the formation of the binuclear molecule of the acetate-type.

Summary

In order to examine the structure of cupric chloroacetates, the dichroism in the visible and the ultraviolet region has been determined at room temperature by the microscopic method with mono-, di- and trichloroacetate. Visible and ultraviolet absorption spectra have also been determined with the above compounds in organic solvents.

The monochloroacetate consists of the binuclear molecules of the acetate-type in the crystalline state and in solution. It has been found that there is another form of the anhydrous monochloroacetate, which is colored blue and contains no binuclear molecule.

The dichloroacetate exists as binuclear molecules in ethyl ether and dioxane, but as mononuclear complexes in ethanol. The anhydrous dichloroacetate in the crystalline state consists of binuclear molecules of the acetate-type.

The trichloroacetate exists as mononuclear complexes in ethanol and in dioxane, and in the crystalline state. The compound exists as binuclear molecules in ethyl ether. Crystals of another form have also been obtained. These possibly consist of binuclear molecules.

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