Spectrochemical Study of Microscopic Crystals. XVII[1]. *The Structure of Cupric Salts with Monocarboxylic Fatty Acids*[2]

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In 1953 van Niekerk and Schoening[3] showed with X-ray that copper acetate monohydrate in the crystalline state consisted of dimeric molecules with a formula of $Cu_2(CH_3COO)_4\cdot 2H_2O$. It was concluded later from measurements of absorption spectra[1,4] that cupric propionate in organic solvents as well as in the crystalline state had dimeric molecules similar to those of cupric acetate monohydrate, involving a sort of interaction between the copper atoms. This was found to be in agreement with the conclusion derived from the unusual magnetic property of the compound in the crystalline state[5]. In these circumstances, it seemed to be of significance to examine whether cupric salts with higher homologues of monocarboxylic acids would involve the dimeric molecules, or not. About the structure of some of the cupric alkanoates, there have recently appeared a few reports[6,7], dealing mainly with magnetic properties. The present authors also have carried out

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[1] Part XVI of this series, S. Yamada, H. Nakamura and R. Tsuchida, This Bulletin, **30**, 953 (1957).

[2] R. Tsuchida, S. Yamada and H. Nakamura, Presented in part before the Symposium on Co-ordination Compounds, Tokyo, October, 1956.

[3] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

[4] R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1957).

[5] H. Abe, *Phys. Rev.*, **92**, 1572 (1953).

[6] R. C. Herron and R. C. Pink, *J. Chem. Soc.*, **1956**, 3948.

[7] R. L. Martin and H. Waterman, ibid., **1957**, 2545.

examinations about the structure of cupric butyrate, valerianate, capronate, caprylate, palmitate and stearate mostly on the basis of their polarized absorption spectra[2,8]. A brief report of this study was formerly presented as a communication[8], the detailed account of which is given below.

Experimental

Materials.—Cupric *n*-butyrate was prepared by the method of von Alth[9] from barium *n*-butyrate and cupric sulfate. Recrystallization of the product from water yielded the monohydrate in green crystals. Anhydrous cupric *n*-butyrate was obtained by repeated recrystallization from acetone or chloroform.

Cupric *iso*-butyrate was prepared in a similar way, and obtained in anhydrous crystals when recrystallized from water.

Cupric *n*-valerianate monohydrate was prepared by the same method as that for cupric butyrate[9]. Anhydrous cupric *n*-valerianate was obtained after dehydration of the monohydrate, followed by repeated recrystallization from chloroform.

Cupric *iso*-valerianate was prepared by the same method as in the case of the *n*-valerianate monohydrate. Recrystallization from water always yielded green crystals of the anhydrous *iso*-valerianate.

Cupric *n*-capronate was prepared according to the method of Freund[10] from cupric acetate and *n*-caproic acid. Recrystallization from ethanol gave green crystals of the anhydrous *n*-capronate.

Cupric *n*-caprylate was prepared according to the method of Zincke[11] from sodium *n*-caprylate and cupric sulfate. After recrystallization from ethanol, anhydrous *n*-caprylate was obtained in green crystals. The compound exists only in an anhydrous form.

The crystals of the above-described compounds all show a striking dichroism on their well-developed planes; that is, blue and green.

Cupric *n*-palmitate and *n*-stearate were prepared according to the method of Cady et al.[12] and Heintz[13]. Anhydrous forms of both the compounds were obtained in greenish-blue, powdery microcrystals. The crystals obtained were found to be too small for the dichroism measurement. Therefore, absorption spectra in the visible and the ultraviolet region of the compounds were determined only in solution.

Measurements.—Quantitative dichroism measurements in the visible and the ultraviolet region were carried out at room temperature by the same method as that in the previous papers of this series[14]. The measurements were made with respect to the directions of extinction on one of the well-developed planes which was shown in each figure. The notations refer to the directions shown in the figure.

Absorption spectra of the compounds in ethanol or carbon tetrachloride were determined at room temperature by a Beckman DU spectrophotometer. It was confirmed in every measurement that Beer's law was obeyed in the presence of the free aliphatic carboxylic acid in addition.

Infrared absorption spectra of the cupric compounds in Nujol mulls were determined in the rock salt region by a Hilger H-800 infrared spectrophotometer.

The notations in the present paper are the same as those used in the former papers of this series. Extinction coefficients, ε, are calculated, and referred to a formula weight instead of a molecular weight.

Results and Discussion

Polarized Absorption Spectra of the Cupric Alkanoates in the Crystalline State.—In the preceding paper[1], we have reported about the structure of cupric formate, acetate and propionate on the basis of their polarized absorption spectra. A similar treatment will be made here concerning the structure of cupric salts with higher homologues of monocarboxylic fatty acids. Since some of the results and discussions in the preceding paper are used in the present discussion, it would be appropriate to give a brief account of the conclusions obtained in the former paper.

Cupric acetate and propionate in the crystalline state and in organic solvents show in the visible and the near-ultraviolet region a band at about 80×10^{13}/sec. (band II) besides a band at about 43×10^{13}/sec. (band I), whereas most cupric compounds show in this wave-length region only one band which may be considered as corresponding to the band at 43×10^{13}/sec. For the band I, electric vector is more strongly absorbed along the complex plane than along the z-direction of the dimeric molecule. For the band II, electric vector is more strongly absorbed along the z-direction; the polarization for this band is the reverse of that for the band I. These facts were considered to show that the compounds involve along the z-direction a sort of copper-to-copper interaction characteristic of the dimeric molecule of the cupric carboxylates. The same result

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[8] R. Tsuchida, S. Yamada and H. Nakamura, *Nature*, **178**, 1192 (1956).

[9] T. von Alth, *Ann.*, **91**, 170 (1854).

[10] A. Freund, *J. prakt. Chem.*, (2) **3**, 233 (1871).

[11] T. Zincke, *Ann.*, **152**, 11 (1869).

[12] H. P. Cady and E. J. Baldwin, *J. Am. Chem. Soc.*, **43**, 648 (1921).

[13] W. Heintz, *Ann.*, **84**, 299 (1852).

[14] R. Tsuchida and M. Kobayashi, "The Colour and the Structure of Metallic Compounds," Zoshindo, Osaka, 1944, p. 180 (in Japanese).

was obtained with cupric propionate, hydrated or anhydrous. Thus the appearance of the band at about 80×10^{13}/sec., combined with the polarization property of the band, may be regarded as showing the existence of the dimeric molecule similar to that of cupric acetate or propionate involving the copper-to-copper interaction.

The results of the present measurements are shown in Figs. 1 to 8. As the components of the cupric compounds in the crystalline state may be under rather weak perturbation owing to the crystalline field, the polarized absorption spectra as determined on a suitable plane are regarded as representing the main features of the dichroism of the components. The exact arrangement of the components in the crystals is unknown for all the cupric compounds reported here. It is easy, however, to see the principal characteristics of the dichroism of the components themselves by comparing their absorption spectra with those of cupric acetate monohydrate whose crystal structure was accurately determined.

The present measurements indicate that cupric butyrate monohydrate in the crystalline state shows an absorption band at about 80×10^{13}/sec. in addition to a band at about 43×10^{13}/sec. Moreover, the polarization for the former band is found to be the reverse of the polarization for the latter (Fig. 1). This relationship, which closely resembles that encountered in the case of the acetate monohydrate, may suggest that cupric butyrate monohydrate in the crystalline state consists of the binuclear molecules resembling those of copper acetate monohydrate. The crystal structure was formerly examined by Iball[15], who noted an unusual number of the molecules involved in a unit cell of the compound. This may presumably be related to the dimeric structure of the compound. It is certain that the A- and the B-absorption in Fig. 1 may represent the characteristics of the absorption along and perpendicular to the complex-plane, respectively.

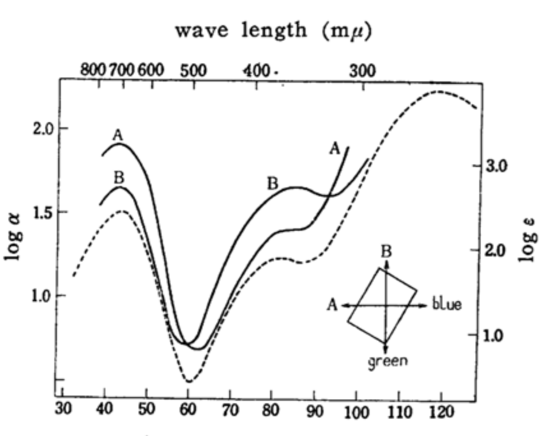

Fig. 1. Absorption spectra of $Cu(n\text{-}C_3H_7COO)_2\cdot H_2O$ in the crystalline state (——) and in ethanol (------).

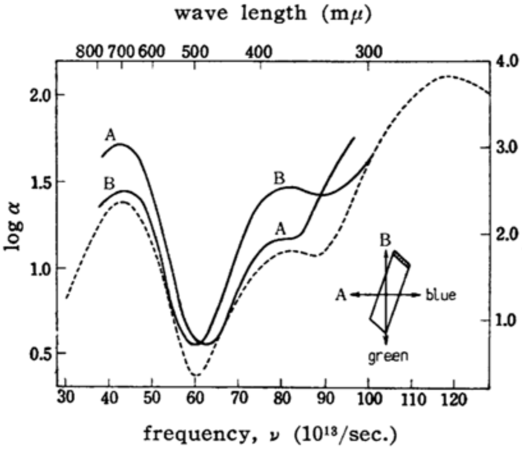

Fig. 2. Absorption spectra of $Cu(n\text{-}C_4H_9COO)_2\cdot H_2O$ in the crystalline state (——) and in ethanol (------).

Cupric valerianate monohydrate is found to show polarized absorption spectra, which are essentially similar to the acetate monohydrate[1)], as shown in Fig. 2. Thus the appearance of the band at 80×10^{13}/sec. and the polarization of the band unanimously show, on the basis of the criteria mentioned in the earlier part of this discussion, that the valerianate monohydrate also consists of dimeric molecules.

Cupric *n*-butyrate and *n*-valerianate exist in either a monohydrated or an anhydrous form. Polarized absorption spectra of the anhydrous *n*-butyrate have also been determined in the present work (Fig. 3). It is seen that the anhydrous butyrate exhibits absorption bands at about 43 and 80×10^{13}/sec., the polarization for the latter band being the reverse of the polarization for the former. This relationship bears a close resemblance to that with cupric butyrate, indicating that the anhydrous butyrate contains the dimeric molecule which is fundamentally similar to that of the monohydrate. It may, therefore, be

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[15] J. Iball, *Nature*, **159**, 95 (1947).

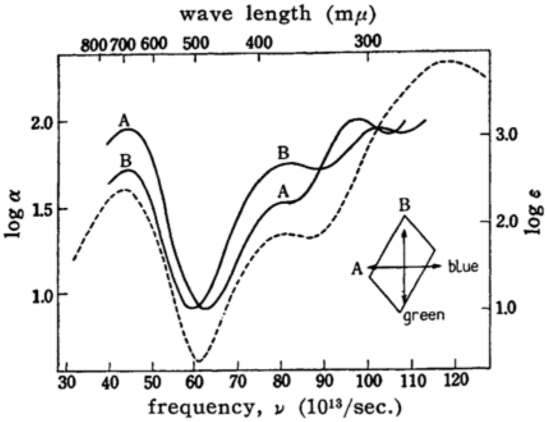

Fig. 3. Absorption spectra of $Cu(n\text{-}C_3H_7COO)_2$ in the crystalline state (——) and in ethanol (------).

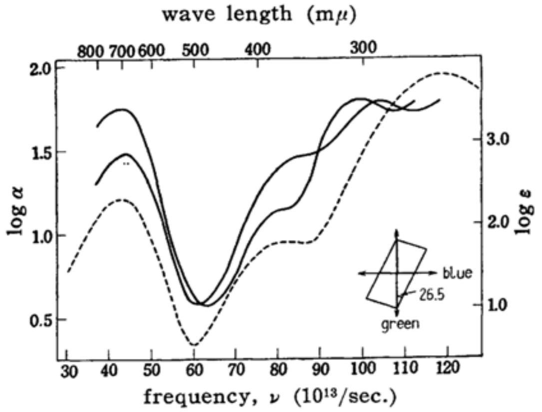

Fig. 4. Absorption spectra of $Cu(n\text{-}C_5H_{11}COO)_2$ in the crystalline state (——) and in ethanol (------).
(The angle 26.5 stands for 26.5°)

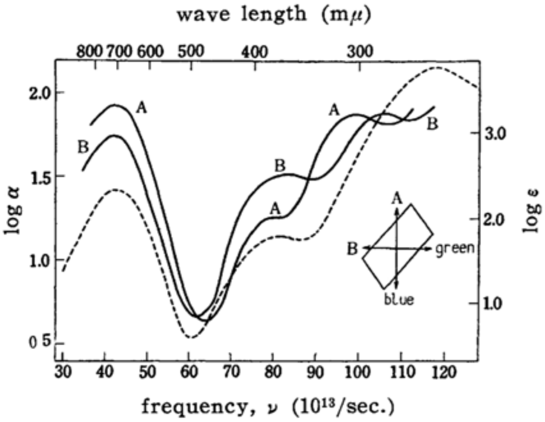

Fig. 5. Absorption spectra of $Cu(n\text{-}C_7H_{15}COO)_2$ in the crystalline state (——) and in ethanol (------).

concluded that both the monohydrated and the anhydrous form of cupric butyrate have the dimeric molecules with the possible interaction between the two copper atoms. Anhydrous cupric valerianate exhibits a similar color to that of the anhydrous butyrate. Although the dichroism has not been measured with the anhydrous valerianate, it may be certain that the anhydrous valerianate also shows polarized absorption spectra with the same characteristics as are observed with the butyrate, having the dimeric molecules of the same type. Note should be taken of the fact that the same relationships were obtained in the case of cupric propionate. It may be suggested that the linkage of the water molecule to the copper atom within the hydrated dimer is not strong.

Cupric capronate and caprylate exist only in an anhydrous form. Polarized absorption spectra of the two compounds have been determined in the crystalline state (Figs. 4 and 5). The crystal structure analysis has not been reported with either of them. It may be admitted, however, that the polarization property as well as the positions of the band maxima are the same as those of the compounds described above. It is most reasonable to assume that both the anhydrous compounds have the dimeric molecule with a general formula, $Cu_2(R\cdot COO)_4$.

In the above part, we have discussed about the cupric salts with normal carboxylic acids. Examination of the steric condition shows that the corresponding *iso*-alkanoates may be able to form the binuclear molecule, since the steric hindrance due to the branching alkyl-radical in the *iso*-series is not so great as to prohibit the formation of the binuclear molecules. Therefore, some of cupric

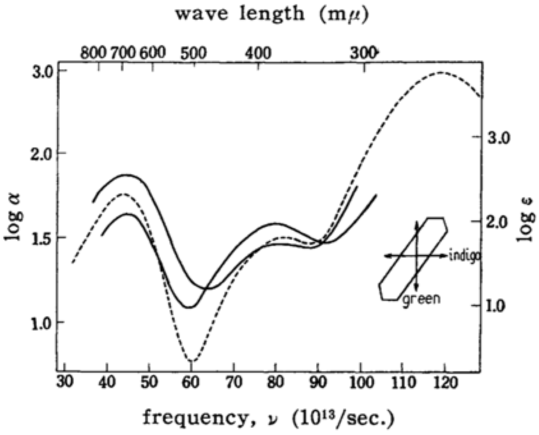

Fig. 6. Absorption spectra of $Cu(iso\text{-}C_3H_7COO)_2$ in the crystalline state (——) and in ethanol (------).

compounds with *iso*-carboxylic acids have been examined by the same method as that applied to the normal alkanoates. The polarized absorption spectra of anhydrous cupric *iso*-butyrate (Fig. 6) are found to be quite similar to those of cupric acetate monohydrate, showing the absorption band at about 80×10^{13}/sec. whose polarization is the reverse of that for the band at about 43×10^{13}/sec.

The same result has been obtained with cupric *iso*-valerianate (Fig. 7). These facts may readily be interpreted as showing, on the basis of the criteria as described above, that both cupric *iso*-butyrate and *iso*-valerianate have the dimeric molecules with a formula of Cu_2(*iso*-$R\cdot COO)_4$. It may safely be assumed that the cupric *iso*-alkanoates in general consist of the binuclear molecules similar to the corresponding normal alkanoates.

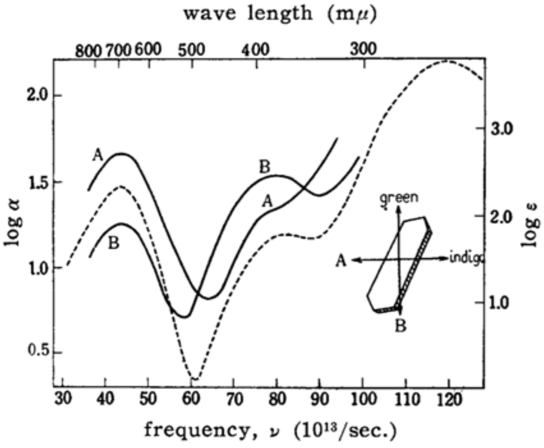

Fig. 7. Absorption spectra of $Cu(iso\text{-}C_4H_9COO)_2$ in the crystalline state (——) and in ethanol (------).

Absorption Spectra of the Cupric Alkanoates in Solution.—Some of the cupric compounds examined in the present and preceding papers are soluble in water to dissociate into component ions to a great extent. Thus the absorption spectra of the alkanoates in water show the main characteristics of the aquated cupric ion, indicating a considerably great degree of dissociation of the compounds. Absorption spectra, therefore, were measured in organic solvents. When ethanol is used as solvent, it is supposed to form some amount of the ethyl alkanoate with a part of the free ligand which is added in excess. In all the present measurements, however, it was confirmed that Beer's law was obeyed on addition of the free ligand throughout the whole concentration range examined. Without the addition of the free ligand, the cupric alkanoate in solution was found to show deviation from Beer's law in the shorter wave-length region when the solution was much diluted.

It is seen from the measurements (Fig. 8) that all the above compounds in solution show absorption spectra which are closely similar to one another in both the wave-length and the molar extinction coefficients at their absorption maxima. Thus they show absorption bands with maxima at about 43 and 82×10^{13}/sec., and a much more intense absorption band in the shorter wave-length region. It seems to be of significance that the compounds show an absorption band at 82×10^{13}/sec. even in solution. These facts indicate that the cupric alkanoates all have, in organic solvents, molecules of a similar type which may most probably be the binuclear molecule represented by a formula of $Cu_2(R\cdot COO)_4$. This molecule in solution may be solvated; then, this is represented by a molecular formula of $Cu_2(R\cdot COO)_4\cdot 2A$, A being a molecule of the solvent.

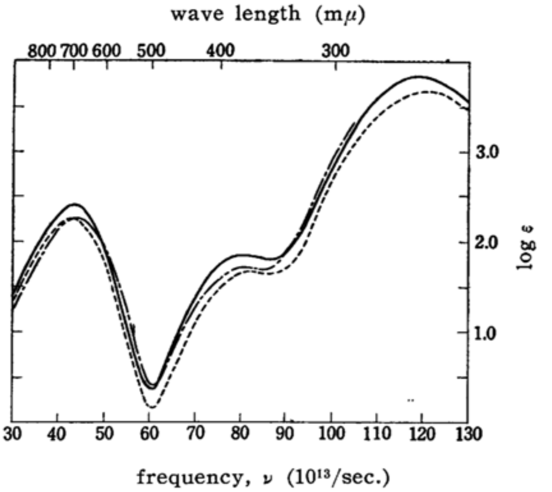

Fig. 8. Absorption spectra of cupric alkanoates: acetate (------) and butyrate (——) in ethyl alcohol, and palmitate (—·—·) in acetic anhydride.

Absorption spectra of cupric *n*-palmitate (C 16) and *n*-stearate (C 18) were determined in acetic anhydride, since their solubility in other solvents is not sufficiently high. The absorption curves (Fig. 8 and Table I) are quite similar to those of the other alkanoates in ethanol. It is reasonable to conclude that cupric

TABLE I

VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA OF CUPRIC MONOCARBOXYLATES WITH AN EMPIRICAL FORMULA OF $Cu(RCOO)_2$*

	band I		band II		band III	
R	ν (10^{13}/sec.)	log ε	ν (10^{13}/sec.)	log ε	ν (10^{13}/sec.)	log ε
CH_3	42.8	2.25	82.0	1.65	120.1	3.68
C_2H_5	43.0	2.27	82.0	1.75	118.9	3.71
n-C_3H_7	43.1	2.42	81.4	1.87	118.4	3.90
iso-C_3H_7	43.4	2.22	81.6	1.71	117.6	3.67
n-C_4H_9	43.1	2.37	82.4	1.82	118.2	3.85
iso-C_4H_9	43.2	2.32	81.7	1.76	118.0	3.75
n-C_5H_{11}	43.0	2.33	81.1	1.80	118.1	3.80
n-C_7H_{15}	43.0	2.33	81.1	1.78	117.7	3.80
n-$C_{15}H_{31}$**	44.2	2.27	82.0	1.71		
n-$C_{17}H_{35}$**	44.2	2.26	82.4	1.72		

* Unless otherwise indicated, the used solvent is ethanol.

** Data in acetic anhydride.

n-palmitate and *n*-stearate in acetic anhydride consist of the dimeric molecules similar to the above described.

Infrared Absorption Spectra.—It is known that the carboxylate ion in general exhibits anti-symmetrical vibrations in the region between 1550 and 1700 cm^{-1}. Anti-symmetrical vibrations due primarily to the carboxylate-group have been examined with the cupric carboxylates in pressed potassium bromide discs and in Nujol mulls. Sodium acetate, which contains carboxylate ions in an ionized form, shows a broad and strong band around 1560 cm^{-1}, and cupric formate, which involves carboxylate-groups coordinated to copper ions in such a way that the dimeric molecule of the cupric salt is not formed, shows a broad and strong band over the region between 1560 and 1600 cm^{-1}. On the other hand, cupric acetate, propionate, butyrate, valerianate, caprylate, capronate, palmitate and stearate show the absorption at about 1595 to 1600 cm^{-1}, which is rather sharp and well-defined. The infrared spectra indicate that the state of the carboxylate ion in the latter group of the cupric compounds differs from that in cupric formate or sodium acetate, being in agreement with the afore-mentioned conclusion that the cupric compounds examined in the present study may involve the binuclear molecules similar to those of cupric acetate or anhydrous cupric propionate. Although such an evidence alone is not to be regarded as decisive, this, combined with other materials, may be confirmatory enough for us to reach the above conclusion of the binuclear structure.

General Discussion

Visible and Ultraviolet Absorption Spectra of the Compounds.—It is seen from the measurements that the cupric alkanoates show in the visible and the ultra violet region absorption bands at about 43 (band I) and 80×10^{13}/sec. (band II) besides a strong absorption band in the region of the shorter wave length. It is most probable that the band I may correspond to the band in the long wave-length region of cupric complexes of an ordinary type, which is usually ascribed to the copper ion under perturbation of the surrounding ligands. On the other hand, the band II is assumed to be closely related with the copper-to-copper interaction. This is borne out by the solvent effect upon these absorption bands. Thus when a solvent is alternated with a more polar one, the band I undergoes red-shift, while the band II shows blue shift. The solvent effect upon the former band agrees with that upon the band at the longer wave length of the cupric ethylenediamine and acetylacetonate complexes, showing that the two bands may be originated from similar electronic transitions. On the contrary, the band II differs in the origin from the absorption bands of the above type. The detailed discussion on the solvent effect will be reported elsewhere.

Although the crystal structure analyses have not been reported with most of the compounds in the present paper, we may make the following generalization about the dichroism of the above compounds.

The band I is polarized along the $Cu(O)_4$-plane, while the band II is polarized along the z-axis of the dimeric molecule, along *which the copper-to-copper interaction is expected to exist.*

The relation for the band I is found to be the same as the dichroism for the absorption band at the longer wave length of cupric complexes, being in agreement with the assumption that these two bands correspond to each other.

Reviewing the absorption curves of the cupric alkanoates in organic solvents, we can obtain the following relationships which are valid for the cupric salts consisting of the dimeric molecules.

The compounds show absorption curves which are similar to one another. The wave length and the molar extinction coefficients at the corresponding band maxima are almost equal among the compounds. Moreover, the intensity ratio of the band I to the band II is equally three and a half for all the compounds examined in the present paper. This close similarity seems to be in agreement with the above conclusion that the compounds all have a similar structure, which involves the dimeric molecules.

The intensity of the band I is seen to be nearly ten times as great as that of the corresponding band exhibited by cupric complexes of an ordinary type with all the coordination positions occupied by oxygen atoms. This fact, which indicates a definite difference in the linkage between the present compounds and the compounds of an ordinary type, may be explained on the basis of the copper-to-copper linkage in the dimeric molecules of the cupric alkanoates.

Examination of the data (Table I) reveals that the intensity of the corresponding bands changes in the following order:

acet. < prop. < butyr. < valerian.
> capron. > capryl. (*n*-homologues).

Thus the intensity of the band increases as we go from the acetate to the valerianate, and then decreases as we go further down the series. Clear explanation for this tendency is not available at present.

Structure of the Cupric Alkanoates.— As described in the preceding part of the present paper, *cupric n- and iso-butyrate, n- and iso-valerianate, n-capronate, n-caprylate, n-palmitate and n-stearate, both in organic solvents and in the crystalline state, are considered to have the dimeric molecules with a kind of weak linkage between the two copper atoms.* Thus it is seen that the length or the shape of the alkyl-group causes no great effect upon the linkage of the carboxylate-group with the copper atom. It may be assumed further that cupric salts with higher homologues of *n*- or *iso*-carboxylic acids also contain the dimeric molecules, since increasing the length of the methylene chain or putting an alkyl-branch in the chain would give rise to no great change, sterically or electronically. This assumption is borne out by a recent study on the structure of cupric behenate (C 22) through magnetic measurements⁷⁾.

It is worth noting that cupric formate does not involve a dimeric molecule whereas the other cupric alkanoates consist of the dimeric molecules. This conspicuous difference may tentatively be explained from the standpoint of the electronic theory, when we take into account the effect caused upon the linkages around the copper atoms by increasing the number of the carbon atoms. As a radical neighboring the carboxylate-group is replaced by another, the electronic charge on the carbon atom in the carboxylate-group would change to a greater or lesser extent. Since the electronic theory of organic chemistry gives the following order with respect to the electron-attracting capacity: $H > CH_3 > C_2H_5 > C_3H_7 > \cdots\cdots$, the electronic charge on the carbon atom of the carboxylate-group may increase as we go from hydrogen down the series. The more the electronic density on the carbon atom of the carboxylate-group, the more negatively the oxygen atom would be charged, with the result that the electronic cloud on the copper atom would be withdrawn less strongly toward the oxygen atom. If we assume that the increase of 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 stronger as the electronic charge on the copper increases on going from the formate down the series of the homologous alkanoates. The above concept seems to be supported qualitatively by the decrease of acid strength on going from formic acid down the series of the homologous fatty acids.

Our measurements in the present and preceding papers show that a great difference in absorption maxima was not observed among the cupric alkanoates except cupric formate which involves components of an exceptional sort. This may be interpreted as indicating that the electron-attracting capacity of the alkyl-groups charges only very slightly from one alkyl-group to another. In contrast to the other cupric alkanoates, cupric formate was not found to have a dimeric molecule. The electronic charge of the copper atom in cupric formate is assumed to be withdrawn toward the oxygen atom to such an extent that the linkage could not be formed between the two copper atoms. Thus the striking difference in the structure between cupric formate and acetate may be understandable on the assumption that the line of demarcation with respect to the electronic charge on the oxygen atom could be drawn somewhere between the formate and the acetate.

As was mentioned in the preceding part, cupric *n*-capronate and higher *n*-alkanoates exist only in an anhydrous form, whereas the lower *n*-alkanoates of copper, such as the acetate, propionate, *n*-butyratë and *n*-valerianate, have the dimeric molecules with water molecules bonded to the copper atom[16]. Thus crystals of anhydrous cupric capronate are precipitated on addition of water to an ethanolic solution of the compound. This critical difference between cupric valerianate and capronate may also be understood on the above described assumption. According to the above mentioned concept, we may assume that the positive charge on the copper atom, which seems to be necessary for the combination of a water molecule with the copper atom, should be greater than a threshold value in order that the copper atom may bind a water molecule. Since the positive charge on the copper atom decreases slightly as we go from the formate down the series, the linkage of the water to the copper atom may become weaker in that order. Thus there is good reason for us to suppose that the line of demarcation may be drawn between the valerianate and the capronate, beyond which the copper atom in the dimeric cupric alkanoates may not be able to bind the water molecule with ease. The inductive effect of the alkyl-group, on the basis of which the above discussion has been made, may not be the only factor. However, the explanation, as given above, seems to be qualitatively correct.

The effect of the water molecule upon the copper in the hydrated dimer of the cupric alkanoates is found to be comparatively small, since no great difference between them was observed in the absorption spectra. It is most probable that the linkage of the water to the copper atom is highly ionic.

A definite difference, however, was reported in the exchange interaction, which was estimated from magnetic measurements[17]. Thus the exchange energy between the two copper atoms was found to be greater in cupric stearate than in cupric acetate monohydrate. In this case, two effects may be regarded as responsible for the observed difference. One is the effect of replacing acetate by stearate groups, and the other is the effect of the water molecules. The two effects would compensate each other to a certain extent, but the above result may be assumed to show that the former overshadows the latter in this case.

Nature of the Copper-to-copper Linkage.—It is shown in the preceding part of the present paper that cupric acetate and higher alkanoates may have the dimeric molecules with a sort of linkage between the two copper atoms in a molecule. Although the nature of the copper-to-copper linkage is not completely clarified, the following two models for the extraordinary linkage may be regarded as most probable. One involves the $d_\pi - d_\pi$ bonding. We assume in this model an extreme structure, in which the two copper atoms form octahedral d_2sp_3 hybridization orbitals. Two orbitals of them, each from one of the two copper atôms, over lap each other in the region above or below the complex-plane. It is interesting to note that the two copper atoms in this model have an electronic structure of a rare-gas type, the possible stability of which may be of some importance in this model.

In the second model, the overlap is assumed to take place between the two $3d_{x^2-y^2}$ orbitals, each from either of the two copper atoms in the molecule, since the copper atoms have non-bonding $3d_{x^2-y^2}$ orbitals which spread in the space above and below the complex-plane. This model was proposed by Martin et al.[7], who

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[16] We are here concerned with normal alkanoates only; cupric *iso*-butyrate and *iso*-valerianate are usually obtained as anhydrous compounds.

[17] K. Kido and T. Watanabe, Presented at the Symposium on Co-ordination Compounds, Nagoya, November, 1957.

considered, mostly on grounds of energy, this type of interaction as more probable than the $d_\pi-d_\pi$ interaction. The present authors, however, are inclined to consider that the decision between the two models could not be made for the present.

Summary

In order to examine the structure of cupric alkanoates, the dichroism in the visible and the ultra violet region has been determined by the microscopic method with normal butyrate, valerianate, capronate and caprylate of copper(II). Visible and ultra-violet absorption spectra in organic solvents and infrared absorption spectra in Nujol mulls have been determined with the above compounds, along with cupric palmitate and stearate. *Iso*-alkanoates have also been examined in a similar way.

All these compounds in the crystalline state and in organic solvents are found to show similar absorption spectra having the dichroism with characteristics fundamentally similar to those of cupric acetate and propionate which had earlier been reported. From these results, it has been concluded that all the above compounds consist of the dimeric molecules.

The anhydrous forms of the compounds have been shown to consist of the dimeric molecules resembling those of the hydrated form.

All the above compounds show absorption bands at about 43 and 80×10^{13}/sec. The former is polarized along the $Cu(O)_4$-plane and the latter along the direction binding the two copper atoms in a molecule.

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