Spectrochemical Study of Microscopic Crystals. XVI[1]. *Structure of Cupric Formate, Acetate and Propionate*[2]

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On the basis of magnetic measurements, Bleaney and Bowers[3] supposed that in the crystal of cupric acetate monohydrate there were isolated pairs of copper ions coupled by exchange forces, with each copper ion bonded by four oxygen atoms in a plane. Van Niekerk and Schoening[4] examined the crystal structure of cupric acetate monohydrate and found that the compound in the crystalline state consists of dimeric molecules having a molecular formula of $Cu_2(CH_3COO)_4 \cdot 2H_2O$, in which a sort of direct interaction might exist between the copper ions, judging from the comparatively short copper-to-copper distance. The nature of the possible copper-to-copper interaction, however, was not completely clarified by those studies. It seems significant to examine this point on the basis of other properties. In order to study the above problem in more detail and to find, if possible, some correlation between the light absorption and the possible metal-to-metal interaction, we have determined dichroism of cupric formate tetrahydrate, cupric acetate monohydrate, anhydrous cupric propionate and its monohydrate.

Experimental

Materials.—Cupric formate tetrahydrate was prepared from cupric carbonate and formic acid. Blue crystals belonging to the monoclinic system are usually obtained in rectangular plates with a well developed (001)-plane. The compound is soluble in water, but insoluble in organic solvents. The measurement of dichroism was made on the (001)-plane with polarized light having its electric vector along the *b*- and the *a*-axis[5]. The *b*- and the *a*-absorption represent the absorption with the electric vector along the *b*- and the *a*-axis, respectively.

Cupric acetate monohydrate of reagent grade was recrystallized from 50% ethanol. Bluish green crystals were usually obtained in monoclinic plates with the (001)- or the $(20\bar{1})$-plane well-developed[5]. The compound is soluble in water and ethanol, but insoluble in chloroform. The measurement of dichroism was made on the $(20\bar{1})$-plane with polarized light having its electric vector along and perpendicular to the *b*-axis. The *b*- and the *a*-absorption represent the absorption with the electric vector along and perpendicular to the *b*-axis.

Cupric propionate monohydrate was prepared from cupric hydroxide and propionic acid. Recrystallization from ethanol-water mixture yielded bluish green crystals having an empirical formula of $Cu(C_2H_5COO)_2 \cdot H_2O$. The measurement of dichroism was made on one of the well-developed planes[6].

Anhydrous cupric propionate was obtained in bluish green crystals by repeated recrystallization of the cupric propionate monohydrate from chloroform. The color of the anhydrous compound is similar to that of the monohydrate. The absence of water of crystallization was readily confirmed by its infra-red spectrum. The measurement of dichroism was carried out on a well-developed plane. Anhydrous cupric propionate is almost insoluble in water, but is soluble in organic solvents such as ethanol and chloroform.

Measurement. — Quantitative dichroism measurement in the visible and the ultra-violet region was made by Tsuchida-Kobayashi's microscopic method[7].

Absorption spectra of the compounds in ethanol or chloroform were determined with a Beckman DU spectrophotometer. When a solution is too dilute, Beer's law is not obeyed. Even in such a dilute solution, however, Beer's law holds in the presence of an excess of the free aliphatic carboxylic acid. When ethanol was used as a solvent, it was apt to form some amount of ethyl carboxylate with the free ligand which was added in excess. The measurement, therefore, was made as quickly as possible after the solution was prepared. In any case, the obedience of the solution to Beer's law was always confirmed in the presence of free ligand.

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[1] Part XV of this series, S. Yamada and R. Tsuchida, This Bulletin, **30**, 715 (1957).

[2] A brief summary of the present article was published as a letter to the editor: R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1955).

[3] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, **A214**, 451 (1952).

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

[5] We are indebted to Dr. R. Kiriyama of the Chemistry Department for the identification of the planes.

[6] P. Groth, "*Chemische Kristallographie*", part 3, Engelmann, Leipzig, 1910 p. 205.

[7] R. Tsuchida and M. Kobayashi, "*The Colour and the Structure of Metallic Compounds*", Zoshindo, Osaka, 1944, p. 180. See also previous papers of the present series.

Absorption spectra of cupric formate and acetate in aqueous solution were found to be essentially similar to that of the aquated cupric ion and, therefore, are not reported here.

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

Results and Discussion

Cupric Formate Tetrahydrate. — The results of the dichroism measurements are shown in Fig. 1. According to the crystal structure analysis[8], a copper ion is co-ordinated to four oxygen atoms in a plane of four formate ions, with two oxygen atoms of water molecules at a greater distance in the direction normal to the above plane. The crystal is found to show a band at about 38 to 39×10^{13}/sec. and a strong absorption band in the further ultra-violet region.

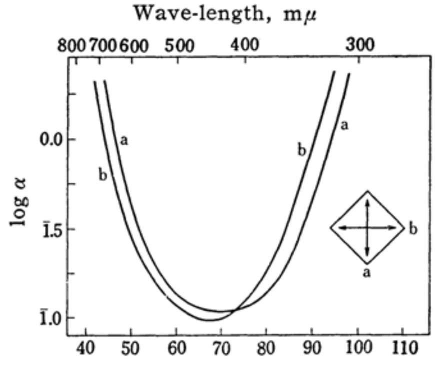

Fig. 1. Absorption spectra of cupric formate tetrahydrate.

Typical compounds of copper(II) are usually known to show only one absorption band of moderate intensity in the near infrared to the near ultra-violet and another absorption band of much greater intensity in the further ultra-violet region. This is found to be the case with the cupric formate. Hence, it is suggested that no extraordinary linkage may be involved in the crystal of cupric formate tetrahydrate.

Although we could not determine the maximum of the band, the slope in the long wave-length region suggests the following relationship. For the band of the cupric formate at the longer wave-length, which is supposed to be closely related with the linkage between a copper ion and ligands, absorption is much stronger along the complex plane than along the direction normal to the plane. This is in good agreement with the relationship on the dichroism of planar cupric complexes of an ordinary type[9,10].

Cupric Acetate Monohydrate.—The results of the measurements are shown in Fig. 2 and Table I. The crystal structure analysis of cupric acetate monohydrate was reported by van Niekerk and Schoening[4]. According to the structure analysis, the line joining the two copper ions within the dimeric molecule in the crystal makes an angle of 34.6° with the *ac*-plane and its projection onto the *ac*-plane an angle of 32.5° with the *c*-axis. Although the absorption spectra, which have been determined with the crystal, may represent the absorption spectra of the dimeric molecules under the crystalline field, we may approximately assume that the absorption spectra with the crystal represent the principal characteristics of the molecule itself. The intensity ratio of the Z-absorption to the X-absorption has been estimated from the present dichroism measurement and on the basis of the

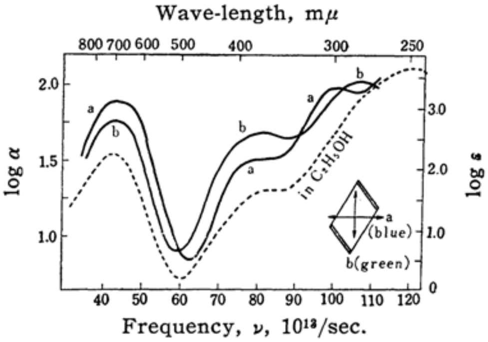

Fig. 2. Absorption spectra of cupric acetate monohydrate in the crystalline state (——), and in ethanol (----).

TABLE I

ABSORPTION MAXIMA OF CUPRIC ACETATE MONOHYDRATE IN THE CRYSTALLINE STATE

	band I		band II		band III	
	ν	log α	ν	log α	ν	log α
a-abs.	43	1.89	81	1.51	101	1.99
b-abs.		1.76		1.69	107	2.09

ν: 10^{13}/sec.

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

[9] S. Yamada and R. Tsuchida, This Bulletin, **29**, 694, 289 (1956).

[10] Idem, *Annual Rep. Scient. Works, Fac. Sci. Osaka Univ.*, **4**, 79 (1956).

structure analysis. For both the bands at 43 and 80×10^{13}/sec., the ratio has been found to be marked; *the ratio of* K_z *to* K_x *is nearly one tenth for the band at* 43×10^{13}/*sec., and about ten for the band at* 80×10^{13}/*sec.* The Z-absorption means the absorption with the electric vector along the line joining the two copper ions within a molecule, and the X-absorption, the absorption, with the electric vector along the plane which is normal to the *b*-axis (Fig. 3). It is assumed in the estimation that all the linkages between the copper and oxygen atoms are equivalent to one another.

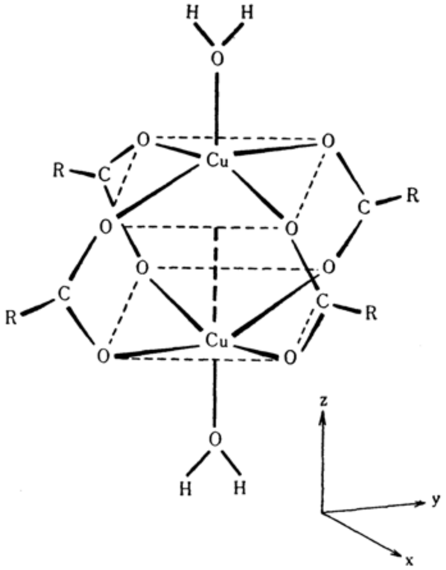

Fig. 3. Molecular structure of $Cu_2(R\cdot COO)_4\cdot 2H_2O$.

As was described in the preceding section, most cupric complexes of an ordinary type show only one band of moderate intensity in the region from the near infra red to the near ultra-violet. On the contrary, the present measurement indicates that cupric acetate monohydrate in the crystalline state shows two absorption bands at about 43 and 80×10^{13}/sec. (Fig. 2). The band at 43×10^{13}/sec. may apparently correspond to the so-called "copper band" which is characteristic of typical cupric complexes and which is supposed to be closely related with the linkages between the copper and the oxygen atoms. The band is usually considered as originating from the copper ion under the effect of the ligands. *For the band at* 43×10^{13}/*sec. absorption is found to be about ten times as strong with the electric vector along the complex plane as with the electric vector along the line joining the two copper ions within a molecule.* This is the same as the relationship found for the "copper band" of ordinary planar complexes of copper(II). These facts seem to support the above assignment of the absorption bands at about 43×10^{13}/sec. to the "copper band".

The absorption band at 80×10^{13}/sec. may be considered as an absorption band of a new kind for cupric complexes, judging from the wave-length and the intensity of the band. Therefore, the appearance of this band seems to suggest an extraordinary structure for this compound. This may be consistent with the hypothesis of the dimeric molecule with a formula of $Cu_2(CH_3COO)_4\cdot 2H_2O$.

Moreover, the polarization property with this new band at about 80×10^{13}/sec. is seen to be the reverse of the polarization with the band at 43×10^{13}/sec. *Thus for the band at about* 80×10^{13}/*sec. electric vector is absorbed much more strongly in the direction normal to the complex plane than along the plane.* The polarization with the band at 80×10^{13}/sec. may be understandable on the assumption of the copper-to-copper interaction, since the interaction may be expected in the direction normal to the complex plane. The band at about 80×10^{13}/sec. may be closely related with the copper-to-copper interaction.

The compound in the crystalline state shows an absorption band at about 100×10^{13}/sec. in addition to the two absorption bands. Although the origin of this band is not clear, we might assume the band to be due to the acetate groups in co-ordination. The band may well be called a kind of "specific absorption band" originating from the acetate ions in co-ordination. This band in solution is supposed to be hidden under a larger absorption band.

It is seen from Fig. 2 that cupric acetate in ethanol shows absorption bands at 43 and 80×10^{13}/sec., both with moderate intensity. French and Lowry[11] also reported absorption spectrum of cupric acetate in ethanol. The absorption curve, which they reported, agrees with ours in the longer wave-length, but differs from ours in the shorter wave-length. Thus they failed to find a band at about 80×10^{13}/sec. which has been clearly seen in our measurement. The appearance of the band at about 80×10^{13}/sec.,

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[11] H. S. French and T. M. Lowry, *Proc. Roy. Soc.*, **A 106**, 489 (1924).

as has been shown in the present measurement, may indicate that cupric acetate in ethanol involves similar components to those in the crystalline cupric acetate. It is supposed, therefore, that cupric acetate in alcohol consists of the dimeric molecules having a formula of $Cu_2(CH_3COO)_4\cdot X_2$, X being the solvent molecule.

Summarizing the above discussion, we may conclude that *cupric acetate in organic solvents as well as in the crystalline state consists of dimeric molecules, in which a direct type of interaction may exist between the two copper(II) ions.*

Cupric Propionate Monohydrate.—The results of the measurements are shown in Fig. 4 and Table II. It is seen that

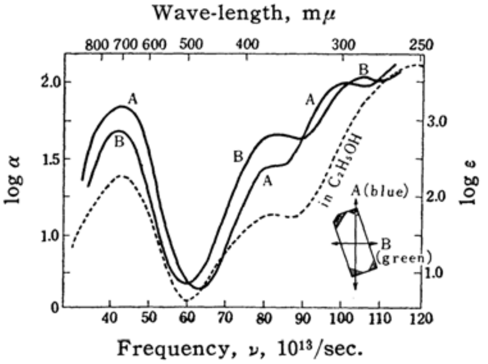

Fig. 4. Absorption spectra of cupric propionate monohydrate in the crystalline state (——), and in ethanol (----).

TABLE II
ABSORPTION MAXIMA OF CUPRIC PROPIONATE MONOHYDRATE IN THE CRYSTALLINE STATE

	band I		band II		band III	
	ν	log α	ν	log α	ν	log α
A-abs.	43	1.84	83	1.44	101	1.99
B-abs.		1.68		1.66	106	2.03

ν: 10^{13}/sec.

the absorption spectrum bears a close resemblance to the spectrum of cupric acetate. Thus cupric propionate in ethanol and chloroform and in the crystalline state exhibits two absorption bands at 43 and 80×10^{13}/sec. having almost the same intensity as the corresponding value of cupric acetate. As described in the above section, the appearance of the new absorption band at about 80×10^{13}/sec. may be regarded as showing the existence of the dimeric molecules.

Analysis of the crystal structure has not been done as yet. The present dichroism measurement, however, indicates that the polarization property with the band at about 80×10^{13}/sec. is the reverse of the polarization property with the band at about 43×10^{13}/sec. The reversal of the polarization property may readily be understood on the assumption of the presence of the dimeric molecule.

All the above facts seem to lead us to the conclusion that *cupric propionate monohydrate in organic solvents such as chloroform and ethanol and in the crystalline state may consist of the dimeric molecules with a formula of* $Cu_2(C_2H_5COO)_4\cdot X_2$, *where* X *represents* OH_2 *or a molecule of the organic solvent.* This conclusion seems to be in agreement with the anomalous paramagnetic resonance absorption of cupric propionate monohydrate[12].

Anhydrous Cupric Propionate. — The dichroism of the anhydrous cupric propionate is shown in Fig. 5 and in the data given in Table III. The crystal structure analysis of the anhydrous compound has not been reported as yet. But comparison of the dichroism of the anhydrous propionate with that of the monohydrate clearly indicates that the dichroisms for both compounds are essentially of an identical type, suggesting the existence of similar components in both the compounds. *Thus anhydrous cupric propionate in the crystalline*

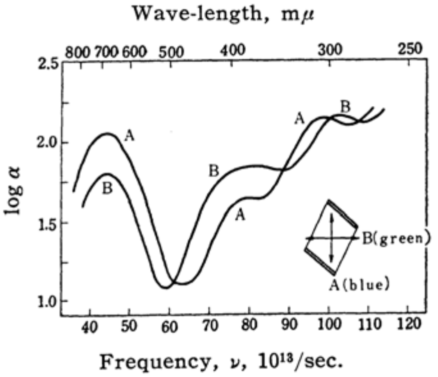

Fig. 5. Absorption spectra of anhydrous cupric propionate in the crystalline state.

TABLE III
ABSORPTION MAXIMA OF ANHYDROUS CUPRIC PROPIONATE IN THE CRYSTALLINE STATE

	band I		band II		band III	
	ν	log α	ν	log α	ν	log α
A-abs.	44	2.05	80	1.63	98	2.13
B-abs.		1.79		1.84	102	2.15

ν: 10^{13}/sec.

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12) H. Abe, *Phys. Rev.*, **92**, 1572 (1953).

state is supposed to consist of the dimeric molecules, in which a direct type of interaction may exist between the two copper ions.

It may also be concluded that *the water of crystallization has very little effect upon the dichroism*, and that *the linkage, if any, of the water molecules to the copper ion is not very strong in the crystal of cupric acetate monohydrate nor in cupric propionate monohydrate either.*

Direct Type of Interaction between the Copper Ions within a Molecule.—We have concluded in the preceding part of the present paper that cupric acetate and propionate in organic solvents and in the crystalline state consist of the dimeric molecules which involve a direct type of interaction between the two copper ions within the molecule. The absorption band at about 80×10^{13}/sec. may be related very closely with the direct interaction between the copper ions, although the nature of this band is not completely clear.

In previous papers we reported some examples in which a direct type of interaction might be expected between metallic ions[10,13]. In these compounds, there appeared, in the longer wave-length than the original absorption of their components, to exist a new type of absorption band polarized along the direction in which the metal-to-metal interaction was concluded. From this type of absorption bands the band at about 80×10^{13}/sec. of cupric acetate may differ, since the latter lies in the far shorter wave-length than the "copper band" which lies at 43×10^{13}/sec. We are inclined to suppose that the copper-tc-copper interaction in cupric acetate may be akin to a kind of ordinary linkage. This seems to be compatible with the significantly shorter distance of 2.64Å between the metallic ions in the molecule of cupric acetate than the corresponding distance in Magnus's green salt or bis-(dimethylglyoximato)-nickel(II), in which the metal-to-metal interaction may be assumed to be weaker. The metal-to-metal distances in the latter two compounds were found to be 3.16 and 3.25 Å, respectively[14,15].

It would be worth noting that the intensity of the absorption band at about 43×10^{13}/sec. of cupric acetate and propionate in solution is considerably great, as compared with the intensity of the ordinary "copper band" for typical complexes of copper (II). This fact might have some relation with the unusual structure of the present cupric compounds.

Summary

Dichroisms in the visible and the ultraviolet region have been determined by the microscopic method with cupric formate tetrahydrate, cupric acetate monohydrate, anhydrous cupric propionate and its monohydrate.

The cupric formate shows an absorption band at about 38—39×10^{13}/sec. which is considered to be due to the copper ion in combination with the ligands. For this band, electric vector is much more strongly absorbed along the plane of the complex than in the direction normal to the plane. The dichroism and the absorption spectrum of the cupric formate are of the same type as those of most cupric complexes involving no special effect upon the complexes.

Cupric acetate monohydrate, anhydrous cupric propionate and its monohydrate show an absorption band of a new kind at about 80×10^{13}/sec., in addition to a band at about 43×10^{13}/sec. which corresponds to the band at about 40×10^{13}/sec. of the cupric formate. The polarization for the band at 80×10^{13}/sec. is the reverse of the polarization for the band at 43×10^{13}/sec. From the appearance of the new band at 80×10^{13}/sec. and the reversal of the polarization property with this band, it has been concluded that the cupric compounds examined in this work, except the formate, consist of dimeric molecules having a structure similar to that of cupric acetate monohydrate.

It has also been shown that the water of crystallization has very little effect upon the linkages within the complex molecules. The cupric compounds, except the formate, show in organic solvents a band at 80×10^{13}/sec., involving the dimeric molecules in solution.

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13) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1579 (1951); This Bulletin, **24**, 125 (1951); S. Yamada and R. Tsuchida, ibid., **27**, 156 (1954).

14) E. G. Cox, *J. Chem. Soc.*, **1932**, 1905.

15) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).