Spectrochemical Study of Microscopic Crystals. XXIV.[1] *The Structure and Light Absorption of Copper(II) Complexes of Benzoic and Substituted Benzoic Acids*

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In previous reports about the molecular structure of copper(II) complexes of fatty acids[2] and halogenoacetic acids[3] in the crystalline state and in solution, it was found that the acid dissociation constant of the carboxylic acid seemed to be related in one way or another to the tendency of their copper(II) complexes to form binuclear complexes. It seemed that it would be interesting to examine, in more detail, the conditions for the formation of the binuclear cupric carboxylates of this type, in relation to the dissociation constant of the ligand carboxylic acids and to the copper-to-oxygen bond in their cupric complexes. In the present paper, copper(II) complexes of benzoic and substituted benzoic acids were examined, mostly on the basis of their electronic absorption spectra.

Experimental

Materials. — Cupric benzoate was prepared by conventional methods,[4] either from cupric carbonate or hydroxide and benzoic acid, or from cupric sulfate and sodium benzoate. Recrystallization of the product from hot water yielded pale-blue needle-like crystals of $Cu(benz)_2\cdot 3H_2O$, where " benz " denotes a benzoate ion. Recrystallization of the same product from ethanol yielded blue-green prismatic crystals of $Cu(benz)_2\cdot C_2H_5OH$, as reported by Inoue, Kishita and Kubo.[5] Recrystallization from methanol containing benzoic acid yielded blue-green crystals of $Cu(benz)_2(benzH)\cdot 0.5H_2O$.

Other cupric complexes of substituted benzoic acids were prepared in a way similar to that used for cupric benzoate and were purified by repeated recrystallization. The recrystallization was carried out using dioxan, dioxan-water, dioxan-methanol or dioxan-ethanol. The isolation of the crystals of all the possible forms with a substituted benzoic acid was not attempted in the present work, but one typical form of the cupric complex for each substituted benzoic acid was isolated as crystals by some of the normal procedures and was used for the spectral examination. The different forms of cupric benzoates and substituted benzoate were found to show identical electronic absorption spectra in dioxan. Some of them were also examined in the crystalline state.

The compounds in Table I were prepared according to the methods already reported, and their elemental analyses agreed with the formulae previously given. The main characteristics and elemental analyses of the other compounds are shown in Table II.

Measurements. — Dichroism was determined in the visible and near-ultraviolet regions by Tsuchida and Kobayashi's microscopic method[6] with crystals of cupric benzoate, *o*-methylbenzoate, *o*-chlorobenzoate, *o*-nitrobenzoate, *m*-hydroxybenzoate and *p*-hydroxybenzoate.

The electronic absorption spectra of the compounds in non-donor organic solvents, such as methanol, ethanol and dioxan, were determined with a Beckman DU spectrophotometer, insofar as the solubility allowed. Beer's law was generally obeyed in the concentration range between 10^{-2} and 10^{-5} F, but deviation from the law was sometimes observed in more dilute solutions.

The reflection spectra in the same frequency region were determined with a Hitachi EPU-2A spectrophotometer.

The notations are the same as those in the former papers of this series. Extinction coefficients are based on the monomeric formulae.

Results and Discussion

Cupric Benzoate in Solution and in the Crystalline State.—The electronic absorption spectra of cupric benzoate and substituted benzoates were determined in non-donor organic solvents. The solubility of these compounds in common solvents was generally low, except for dioxan. The results with dioxan as a solvent will be described extensively in the present paper.

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[1] Part XXIII of this series: S. Yamada and S. Miki, This Bulletin, 36, 680 (1963).

[2] R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1955); R. Tsuchida, S. Yamada and H. Nakamura, ibid., **178**, 1192 (1956); S. Yamada, H. Nakamura and R. Tsuchida, This Bulletin, **30**, 953 (1959); ibid., **31**, 303 (1958).

[3] R. Tsuchida and S. Yamada, *Nature*, **182**, 1230 (1958); Proceedings of the Symposium on the Chemistry of Coordination Compounds, Agra, India, Part II (1959), p. 35; S. Yamada, H. Nishikawa and R. Tsuchida, This Bulletin, **33**, 1278 (1960).

[4] F. Ephraim and A. Pfister, *Helv. Chim. Acta*, **8**, 369 (1925); F. Ephraim and E. Bolle, *Ber.*, **48**, 1770 (1915); etc.

[5] M. Inoue, M. Kishita and M. Kubo, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 759 (1963).

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

TABLE I. BENZOATE AND SUBSTITUTED BENZOATES OF COPPER(II) WHICH WERE PREPARED AS DESCRIBED PREVIOUSLY

Compound	Appearance	Method
$Cu(benz)_2 \cdot 3H_2O$	Blue crystals	Ref. 4
$Cu(benz)_2 \cdot C_2H_5OH$	Blue-green crystals	Ref. 5
$Cu(benz)_2(benzH) \cdot 0.5H_2O$	Blue-green crystals	Ref. 4
$Cu(o\text{-}NO_2\text{-}benz)_2$	Blue-green plates	a
$Cu(m\text{-}NO_2\text{-}benz)_2 \cdot H_2O$	Blue powder	b
$Cu(p\text{-}NO_2\text{-}benz)_2 \cdot H_2O$	Blue needles	a
$Cu(m\text{-}OH\text{-}benz)_2 \cdot H_2O$	Blue-green needles	c
$Cu(p\text{-}OH\text{-}benz)_2 \cdot 6H_2O$	Blue needles	Ref. 4

a) C. Schall, *Z. Electrochem.*, **19**, 830 (1913); H. J. S. King, *J. Chem. Soc.*, **1930**, 2307.
b) G. J. Mulder, *Lieb. Ann.*, **34**, 297 (1840).
c) H. Ley and O. Erler, *Z. anorg. Chem.*, **56**, 401 (1908).

TABLE II. MAIN CHARACTERISTICS AND ELEMENTAL ANALYSES OF SUBSTITUTED BENZOATES OF COPPER(II)

Compound	Appearance	Analyses			
		Found, %		Calcd., %	
		C	H	C	H
$Cu(o\text{-}CH_3\text{-}benz)_2$	Blue-green crystals	56.9	4.98	57.5	4.20
$Cu(m\text{-}CH_3\text{-}benz)_2$	Blue powder	56.8	5.02	57.5	4.20
$Cu(p\text{-}CH_3\text{-}benz)_2 \cdot H_2O$	Green-blue powder	54.7	5.02	54.6	5.11
$Cu(o\text{-}Cl\text{-}benz)_2 \cdot 2H_2O$	Blue-green crystals	40.2	3.34	40.9	2.95
$Cu(m\text{-}Cl\text{-}benz)_2$	Blue powder	45.2	2.35	44.9	2.15
$Cu(p\text{-}Cl\text{-}benz)_2$	Blue-green crystals	44.1	3.02	44.9	2.15
$Cu(o\text{-}OCH_3\text{-}benz)_2$	Blue-green crystals*	53.0	3.75	52.5	3.86
$Cu(p\text{-}OCH_3\text{-}benz)_2$	Blue-green crystals	51.8	4.31	52.5	3.86

* Analyzed after dehydration.

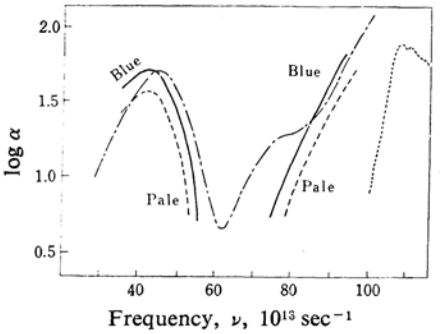

Fig. 1. Absorption spectra of $Cu(benz)_2 \cdot 3H_2O$ in dioxan containing benzoic acid in 1/50 F (—·—) and in the crystalline state (——). The notation "blue" and "pale" represent the absorption spectra along the blue polarization direction and along the pale-blue polarization direction, respectively. The absorption spectrum of benzoic acid in ether (----) is taken from H. Dannenberg, *Z. Naturforsch.*, **4b**, 327 (1949).

Cupric benzoate in dioxan shows an absorption band at about 80×10^{13} sec^{-1} (Band II) in addition to a band at about 44×10^{13} sec^{-1} (Band I), as may be seen in Fig. 1. It is found that Band I of cupric benzoate in dioxan is about ten times more intense than the intensity of the ligand field band of typical cupric complexes with no specific metal-to-metal bond, and that the intensity of Band II of cupric benzoate is considerably lower than the intensity of Band I of the same compound. These relations, which are quite similar to those of cupric alkanoates with the binuclear configuration,[2] seem to show that cupric benzoate in dioxan consists of binuclear molecules similar to those of cupric alkanoates with the copper-to-copper bond.

At least two types of crystals of cupric benzoate were obtained, one being green-blue crystals of $Cu(benz)_2 \cdot C_2H_5OH$ or $Cu(benz)_2 \cdot (benzH) \cdot 0 \cdot 5H_2O$ (Form A) and the other, pale-blue crystals of $Cu \cdot (benz)_2 \cdot 3H_2O$ (Form B). The absorption spectrum of the pale-blue crystal (Fig. 1) was determined on the (010) face with light polarized along the two extinction directions of the crystal. Cupric benzoate trihydrate in the crystalline state exhibits one ligand field band in the low frequency region (about 42×10^{13} sec^{-1}), but no absorption band at 80×10^{13} sec^{-1} until an intense absorption band, due mainly to the ligands, appears in the region of about $90\times10^{13}\,\text{sec}^{-1}$ to a higher frequency. The band at $42\times10^{13}\,\text{sec}^{-1}$ may be assigned to spin-allowed *d-d* transition. According to the crystal structure analysis,[7] the crystal consists of octahedra of $[\text{CuO}_6]$, which share two water molecules in such a way that a column extending along the c-axis is formed. The crystal structure analysis also indicates that the z-axis of one component of $[\text{CuO}_6]$ is inclined to the c-axis of the crystal at an angle of about 37° and to the a-axis at an angle of 53°. The estimate using the data of the crystal analysis shows that the ratio of K_{xy} to K_z is approximately 9 for the ligand field band at about $42\times10^{13}\,\text{sec}^{-1}$. The ratio derived above shows clearly that the xy-absorption is much more intense than the z-absorption, in agreement with the results of the former studies of cupric complexes of an ordinary kind with no specific copper-to-copper bond.[1,8] Thus the crystal spectrum of cupric benzoate trihydrate at room temperature is quite different from that expected for the binuclear complex with the copper-to-copper bond. It is concluded that, in the crystal of cupric benzoate trihydrate at room temperature, there is no copper-to-copper bond similar to the case of cupric acetate monohydrate, although the nearest copper-copper distance is comparatively short (3.15Å). This result is in agreement with the magnetic measurement.[5] This, however, does not completely exclude the possibility that the copper-to-copper bond formation may occur at a lower temperature.

On the contrary, the green-blue crystal of $\text{Cu(benz)}_2\cdot\text{C}_2\text{H}_5\text{OH}$ (Form A), which usually grows in the form of hexagonal prisms, exhibits absorption bands at about 79 and $44\times10^{13}\,\text{sec}^{-1}$, the polarization of the former band being the reverse of that latter. The absorption at about $79\times10^{13}\,\text{sec}^{-1}$ is far more intense along the needle-axis of the crystal than along the direction perpendicular to the needle-axis. The absorption at about $44\times10^{13}\,\text{sec}^{-1}$ is slightly (1/1.5 times) weaker along the needle-axis. This type of dichroism is quite similar to the dichroism reported for a number of cupric carboxylates with the copper-to-copper bond.[2,3] Although the crystal structure analysis of this form is not available, it may safely be concluded from the dichroism that the blue-green form of $\text{Cu(benz)}_2\cdot\text{C}_2\text{H}_5\text{OH}$ consists of binuclear molecules of the cupric-acetate type, with the copper-to-copper bond within the molecule. This result agrees with that of magnetic study.[5] An essentially similar relation was obtained for $\text{Cu(benz)}_2\cdot\text{(benzH)}\cdot0.5\text{H}_2\text{O}$ through the dichroism measurement.

The assignment of the absorption bands of the binuclear cupric complex with the metal-to-metal bond has not been finally settled, but it certainly is similar to cupric acetate and alkanoates.[9] A detailed discussion will be presented elsewhere.[10]

Forms A and B were found to give quite identical absorption curves in dioxan; it is therefore concluded that both of them consist of binuclear molecules of the acetate type in dioxan. It is also found, for substituted benzoates of copper(II), that different forms exhibit identical electronic absorption spectra in solution.

Cupric Complexes of Substituted Benzoic Acids.—As Fig. 2 shows, cupric complexes of *o*-, *m*- and *p*-methylbenzoic acids in dioxan all show an absorption band at about $43\sim45\times10^{13}\,\text{sec}^{-1}$ (Band I). In addition, the compounds show a band at about $80\times10^{13}\,\text{sec}^{-1}$ (Band II) the intensity of which is considerably lower than the intensity of band I. Another intense absorption band, which rises sharply from about $90\times10^{13}\,\text{sec}^{-1}$ towards a higher frequency, may be due to the charge-transfer-absorption system of the binuclear cupric complex, superposed over the absorption band due mainly to the methylbenzoate ion, since the methylbenzoate ions alone are found to show absorption bands in this frequency region. The intensity of Band I is several times higher than the ligand field band of cupric complexes of an ordinary type. On the same grounds as in the case of cupric

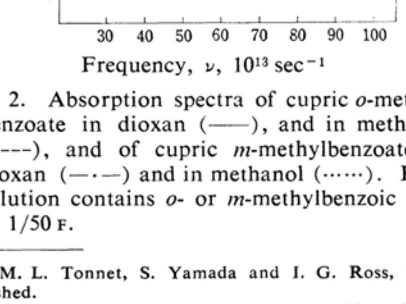

Fig. 2. Absorption spectra of cupric *o*-methylbenzoate in dioxan (——), and in methanol (----), and of cupric *m*-methylbenzoate in dioxan (—·—) and in methanol (······). Each solution contains *o*- or *m*-methylbenzoic acid in 1/50 F.

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[7] H. Koizumi, K. Osaki and T. Watanabe, *J. Phys. Soc. Japan*, **18**, 117 (1963).

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

[10] M. L. Tonnet, S. Yamada and I. G. Ross, to be published.

[9] L. S. Forster and C. J. Ballhausen, *Acta Chem. Scand.*, **16**, 1385 (1962); I. G. Ross, *Trans. Faraday Soc.*, **55**, 1058 (1959).

alkanoates, it has been concluded that *o*-, *m*- and *p*-methylbenzoates of copper(II) in dioxan consist of the binuclear molecules of the acetate type.

The *o*-, *m*- and *p*-chlorobenzoates of copper(II) in dioxan also show absorption spectra which are similar, in both the band maxima and the intensity relation, to one another and to the spectra of the methylbenzoates (Fig. 3).

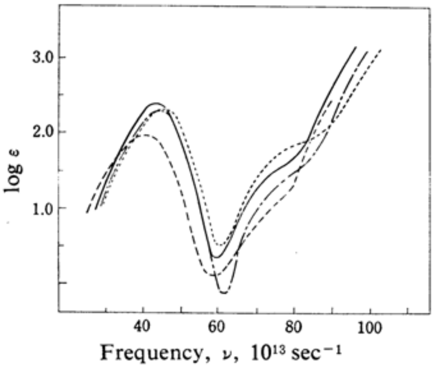

Fig. 3. Absorption spectra of cupric *o*-chlorobenzoate in dioxan (——) and in methanol (----), cupric *p*-chlorobenzoate (—·—), and cupric *p*-hydroxybenzoate (······) in dioxan. The solutions all contain the corresponding substituted benzoic acid in 1/50 F.

It has been similarly concluded that *o*-, *m*- and *p*-chlorobenzoates of copper(II) in dioxan consist of binuclear molecules of the acetate type with a direct type of linkage between the two copper ions.

The electronic absorption spectra of *o*- and *p*-methoxybenzoates of copper(II) have been determined in dioxan. Since the two complexes show quite similar spectra, only one of them is shown in Fig. 4. For the same reason, only cupric *o*-nitrobenzoate is shown in the figure. It has been concluded, in the same way as has been described above, that cupric complexes of *o*- and *p*-methoxybenzoates in dioxan consist of binuclear molecules of the acetate-type.

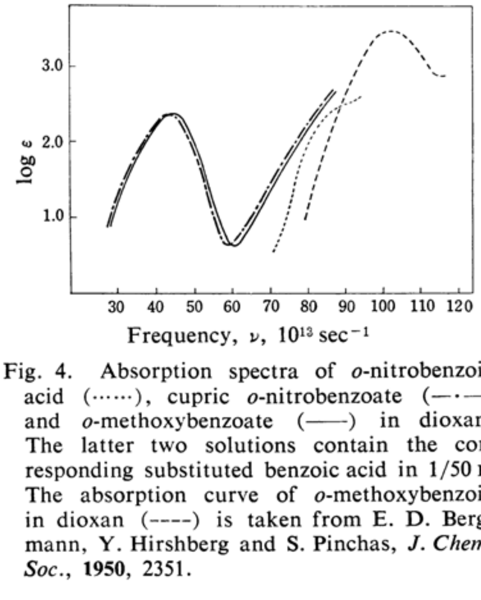

Fig. 4. Absorption spectra of *o*-nitrobenzoic acid (······), cupric *o*-nitrobenzoate (—·—) and *o*-methoxybenzoate (——) in dioxan. The latter two solutions contain the corresponding substituted benzoic acid in 1/50 F. The absorption curve of *o*-methoxybenzoic in dioxan (----) is taken from E. D. Bergmann, Y. Hirshberg and S. Pinchas, *J. Chem. Soc.*, **1950**, 2351.

The *m*- and *p*-hydroxybenzoate ions in the cupric complexes reported in this paper are considered to be co-ordinated with the cupric ion through their carboxylate group. The *o*-hydroxybenzoate is different from the *m*- and *p*-homologues in their way of co-ordination to the metallic ion, since it can be co-ordinated to the cupric ion through the oxygen atoms of both the phenolate and the carboxylate groups. The *o*-hydroxybenzoate of copper (II) is, therefore, omitted in the present paper.

Cupric *m*- and *p*-hydroxybenzoates show absorption bands at about 45×10^{13} sec^{-1}, but the band at about 80×10^{13} sec^{-1} is obscured to some extent by a much stronger specific absorption bands due mainly to the ligand ion (Fig. 3). A more precise inspection of the curves, however, clearly reveals the presence of the band at about 80×10^{13} sec^{-1}, which corresponds to Band II. It is concluded, therefore, that cupric *m*- and *p*-hydroxybenzoates consist of binuclear molecules similar to those of cupric alkanoates with copper-to-copper linkage within the molecules.

As may be seen in Fig. 4, cupric *o*-, *m*- and *p*-nitrobenzoates in dioxan all show their ligand field band at about 43 to 44×10^{13} sec^{-1}, in the frequency region slightly lower than that of cupric benzoate, but still in the region expected for the binuclear copper(II) carboxylates. Moreover, the intensity of Band I is several times higher than that of ligand field bands of ordinary cupric complexes. The quite high intensity of Band I and the frequency of the band maximum are in agreement with the assumption that the nitrobenzoates of copper(II) in dioxan consist of binuclear molecules similar to the molecules of cupric alkanoates. The band at about 80×10^{13} sec^{-1}, which is observed with the chloro- and methylbenzoates of copper(II), is not observed with cupric nitrobenzoates. This failure to be observed is, however, regarded as due to the much stronger absorption of the ligand, which is superposed over Band II. An analysis of the absorption curve, which involves the subtraction of the absorption expected for the ligand, reveals the presence of the band at about 80×10^{13} sec^{-1}, the intensity of the band being much lower than that of Band I. This agrees with the binuclear model for the cupric nitrobenzoates in dioxan.

The electronic absorption spectra of cupric chlorobenzoates and methylbenzoates were determined in methanol containing the corresponding substituted benzoic acids in 1/50 F (Figs. 2 and 3). The intensity of the absorption band at about $80\times10^{13}\,\mathrm{sec}^{-1}$ is greatly lowered, and Band I is displaced toward a lower frequency compared with the dioxan solution. This shows that the cupric carboxylates are more liable to form the binuclear complex of the acetate type in dioxan than in methanol, the dissociation of the binuclear complex most probably taking place to an appreciable extent in the latter solvent. This conclusion agrees with the findings about many other cupric carboxylates.3)

Crystal absorption spectra were examined with some of these cupric complexes (Table III). Since, however, the crystal structure of none of these complexes has been determined, a detailed analysis of the crystal spectra is not possible at the moment. The following points, however, have been definitely confirmed for the cupric *o*-methyl-, *o*-chloro-, *o*-nitro- and *m*-hydroxybenzoates. (1) The blue-green crystals of these complexes show absorption bands at about 43∼45 and $80\times10^{13}\,\mathrm{sec}^{-1}$, the former being several times more intense than the latter. (2) The polarization of the former band is the reverse of the latter. It has been safely concluded that these cupric carboxylates consist of binuclear molecules with the copper-to-copper bond.

TABLE III. ABSORPTION MAXIMA OF CUPRIC BENZOATE AND SUBSTITUTED BENZOATES IN THE SOLID STATE*

Cmpound	ν(Band I)	ν(Band II)
$Cu(benz)_2\cdot 3H_2O$	41.5	None
$Cu(benz)_2\cdot C_2H_5OH$	44.5	79.5
$Cu(benz)_2\cdot(benzH)\cdot 0.5H_2O$	44.3 43.8**	ca. 80 ca. 80**
Cu(*o*-CH_3-benz)$_2$	45.0	ca. 80
Cu(*o*-Cl-benz)$_2\cdot 2H_2O$	44.0	ca. 79
Cu(*m*-OH-benz)$_2\cdot H_2O$	45.0	ca. 79
Cu(*p*-OH-benz)$_2\cdot 6H_2O$	41.5	None
Cu(*m*-NO_2-benz)$_2\cdot H_2O$**	45.0	Covered
Cu(*o*-NO_2-benz)$_2$	44.5	Covered

ν: $10^{13}\,\mathrm{sec}^{-1}$

* Unless otherwise indicated, the value is based upon the crystal spectrum.

** Reflection spectrum of the powder.

On the contrary, Cu(*p*-OH-benz)$_2\cdot 6H_2O$ in the crystalline state shows an absorption band at about $41.5\times10^{13}\,\mathrm{sec}^{-1}$, but no band at about $80\times10^{13}\,\mathrm{sec}^{-1}$, so the crystal contains no binuclear complex of the acetate type.

General Discussion. — Regarding the same substituent, an inspection of Table IV reveals that the absorption maximum of Band I of cupric complexes is parallel with the acid dissociation constant of the substituted benzoic acids. Since the frequency of Band I is regarded as representing approximately the magnitude of the crystal field splitting of the copper(II) ion, the above relation may readily be understood if it is assumed that copper-to-ligand bond becomes stronger as the acid dissociation constant of the parent acid of the ligand decreases. This agrees qualitatively with the previous results about cupric complexes.11,12) It was also pointed out formerly3) that the larger acid dissociation constant of the ligand carboxylic acid does not favor the formation of the binuclear molecule with the copper-to-copper bond.

TABLE IV. ABSORPTION MAXIMA OF BAND I OF CUPRIC SUBSTITUTED BENZOATES AND DISSOCIATION CONSTANTS *K* OF THE SUBSTITUTED BENZOIC ACIDS*

R		*o*-	*m*-	*p*-
NO_2	ν	43.4	43.7	43.5
	log ε	2.37	2.34	2.22
	10^5K	671	32.1	37.6
Cl	ν	44.0	44.1	44.4
	log ε	2.40	2.38	2.40
	10^5K	114	14.8	10.5
CH_3	ν	44.6	44.6	44.7
	log ε	2.39	2.33	2.37
	10^5K	12.3	5.35	4.24
OH	ν	—	44.5	45.1
	log ε	—	2.25	2.33
	10^5K	—	8.3	2.9
OCH_3	ν	44.7	—	44.9
	log ε	2.38	—	2.38
	10^5K	8.06	—	3.38
H	ν(log ε)		44.7	(2.42)
	10^5K		6.27	

* The values of *K* are taken from A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York (1950), p. 65.

On closer examination of the data, however, deviation from the parallelism may be recognized in connection with the compounds of the *o*-series. Thus, it may be seen in Fig. 5 that, among *m*- and *p*-substituted benzoates of copper(II) with various substituents, there is a linear proportionality between the p*K* values of the carboxylic acids and the maxima

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11) B. R. James, M. Parris and R. J. P. Williams, *J. Chem. Soc.*, **1961**, 4630.

12) R. May and M. M. Jones, *J. Inorg. Nucl. Chem.*, **24**, 511 (1962).

of the ligand field bands (Band I) of their cupric compounds. The *o*-derivatives, however, show an appreciable deviation from the straight line of the *m*- and *p*-derivatives, although there seems to be a linear relation among the derivatives of the *o*-series alone. This behavior of the *o*-substituted benzoates seems to be related with the so-called "ortho-effect" which is often observed, for example, in the reactions of aromatic compounds, including the substituted benzoic acids.13) The apparent anomaly of the cupric complexes of *o*-substituted benzoates, as observed in the present work, seems to show that the ortho-effect may be operative in the case of cupric complexes, but in a different way from that of the substituted benzoic acids themselves. The ortho-effect in the dissociation constant of the substituted benzoic acids may be interpreted as mostly due to a twisting of the carboxyl-group from the benzene plane.13) If this mechanism is assumed to be correct, the observed deviation of the *o*-substituted complexes seems to indicate that the twisting of the carboxyl-group from the benzene plane may be different in the cupric complexes from the twisting in the nucomplexed ion of the substituted benzoates.

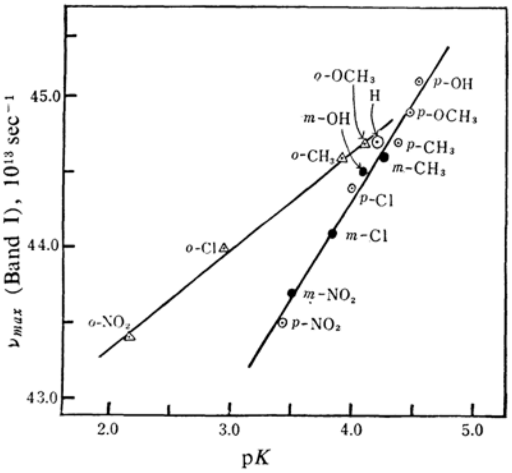

Fig. 5. Plots of absorption maxima (ν) of Band I of cupric substituted benzoates vs. p*K* ot the substituted benzoic acids.

On the other hand, Band II is obscured more or less significantly by much stronger absorption bands of other origins, so that it is difficult to determine the exact maximum for most complexes. No discussion similar to that above was, therefore, attempted on the basis of Band II.

Summary

Cupric complexes of benzoic and substituted benzoic acids have been prepared, and their configurations in the solid state and in dioxan examined. The substituents have included methyl, chloro, methoxy, nitro and hydroxy groups.

These cupric complexes in dioxan all consist of binuclear cupric complexes with the copper-to-copper bond. Crystal absorption spectra show that $Cu(benz)_2 \cdot C_2H_5OH$ and $Cu(benz)_2 \cdot (benzH) \cdot 0.5H_2O$ in the crystalline state consist of the binuclear complexes, whereas $Cu \cdot (benz)_2 \cdot 3H_2O$ has no such complexes with the copper-to-copper bond. The absorption spectra of several substituted benzoates of copper(II) in the solid state have also been determined, and the structure of the complexes discussed.

It has been found that the maxima of Band I of substituted benzoates of copper(II) in dioxan are linearly dependent upon the p*K* values of the substituted benzoic acids themselves.

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13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York (1953), p. 140, etc.