Spectrochemical Study of Microscopic Crystals. XII[1]. *Polarized Absorption Spectra of Cupric Complexes with Tropolone and Related Compounds*[2]

By Shoichiro YAMADA and Ryutaro TSUCHIDA

(Received April 10, 1956)

In the previous papers[3], the present authors studied the dichroism of planar quadri-co-ordinate complexes of platinum (II) and palladium (II), and induced the common rules on the dichroisms of these compounds. Besides those complexes of platinum and palladium, a number of cupric quadri-co-ordinate complexes are also known to possess planar configuration, for which a definite dichroism may be expected. In connection with the earlier studies on the planar complexes, it was supposed to be desirable to determine

---

[1] Part XI of this series, S. Yamada and R. Tsuchida, This Bulletin, **29**, 421 (1956).

[2] Presented in part at the sixth annual meeting of the Japan Chemical Society, Kyoto, April, 1953.

[3] S. Yamada, H. Yoneda and R. Tsuchida, *J. Chem. Soc. Japan*, **69**, 145 (1948) (in Japanese); S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 (1951); S. Yamada and R. Tsuchida, This Bulletin, **26**, 489 (1953).

the dichroism of planar complexes of copper (II). As ligands we have taken up tropolone4) and its derivative, which were kindly donated by Prof. T. Nozoe. In the study with compounds of tropolone and its derivative, it also seemed of great interest to make comparison of these metallic compounds with complexes of some β-diketones which bear resemblance to the former. In the present work, we have determined dichroisms of cupric complexes with tropolone, hinokitiol5), acetylacetone and salicylaldehyde6), all of these chelate groups co-ordinating to the metal through oxygen atoms, and the results have been discussed in relation to the above points.

Experimental

Materials.—Bis-(tropolonato)-copper(II).—The sample, which was kindly supplied by Professor T. Nozoe of Tohoku Univ., was recrystallized from alcohol. The green prismatic crystals belonging to the monoclinic system show an oblique extinction in the prism face. A marked dichroism was observed under the microscope. Measurement of the dichroism was made in the (110)-plane with polarized light vibrating along the directions of extinction the extinction angle being about 19.5° with reference to the *c*-axis.

Bis-(hinokitiolato)-copper (II).—The sample supplied by Prof. Nozoe was recrystallized from alcohol. The crystals obtained in green, monoclinic prisms show in the prism face a dichroism similar to that of the tropolonato-compound. Measurement of the dichroism was made in the prism face along the directions of extinction. The crystals exhibit an oblique extinction, the extinction angle being about 36° referred to the needle axis.

Bis-(acetylacetonato)-copper (II).—Was prepared from an aqueous solution of copper acetate and an alcoholic solution of acetylacetone7). Blue, monoclinic crystals of this compound, elongated along the *b*-axis, show a striking dichroism; they appear indigo with the electric vector along the *b*-axis, and greenish yellow with the electric vector perpendicular to the *b*-axis. The dichroism measurement was made with polarized light having its electric vector along the above two directions.

Bis-(*o*-formylphenolato)-copper (II).—Was prepared in green, monoclinic prisms according to the method of Tyson et al3). The crystals thus obtained exhibit a marked dichroism in the prism face; they appear yellow and brownish yellow, respectively, with the electric vector along and normal to the direction of elongation. The measurement was made with reference to the above two directions.

Measurements.—Quantitative dichroism measurements were made at room temperature in the region covering from 2400 to 7500 Å by Tsuchida-Kobayashi's microscopic method9). The symbol, α, represents absorption coefficient per mm. of a crystal.

Absorption spectrum in solution was determined with a Beckman DU quartz-spectrophotometer. ε represents extinction coefficient of the solution.

Results

Bis-(tropolonato)-copper (II).—The results of the measurements are shown in Fig. 1 and Table I. According to the X-ray analysis of the crystal structure by Robertson10), a copper atom and four oxygen atoms around it form a square, the whole molecule containing the tropolone-rings being planar. The normal to the planes of the complexes makes an angle of about 26.5° with the *c*-axis. The X-ray analysis indicated that the A-absorption involves more ||-absorption of the molecule11), and the B-absorption involves more ⊥-absorption (Fig. 1). The tropolonato-copper (II) complex in the crystalline state shows an absorption

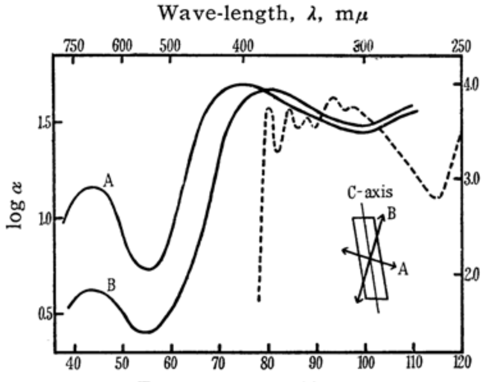

Fig. 1. Ultra-violet absorption spectra of bis-(tropolonato)-copper (II) and tropolone. The absorption spectrum of tropolone in hexane (dotted curve) is taken from J. W. Cook, A. R, Gibbs, R. A. Raphael and A. R. Somerville, *J. Chem. Soc.* 1951, 503.

TABLE I

ABSORPTION MAXIMA OF BIS-(TROPOLONATO)-COPPER (II)

	ν, 10^{13}/sec.	log α	ν, 10^{13}/sec.	log α
A-abs	43.8	1.16	76	1.88
B-abs	44	0.71	81	1.88

---

4) Tropolone represents cycloheptatriene-2, 4, 6-one-1-ol.

6) Salicylaldehyde may be regarded as *o*-formylphenol. The latter is preferred, when it is necessary to stress that this is one of the phenolic compounds.

7) W. C. Fernelius, "Inorganic Syntheses", Vol. 2 (1946), p. 14.

8) G. N. Tyson, Jr. and S. C. Adams, *J. Am. Chem. Soc.*, 62, 1228 (1940).

9) R. Tsuchida and M. Kobayashi, This Bulletin, 13, 388 (1938); "The Colour and the Structure of Metallic Compounds", *Zoshindo*, Osaka (1944), p. 180 (in Japanese).

10) J.M. Robertson, *J. Chem. Soc.*, 1951, 1223.

11) The ||- or ⊥-absorption represents absorption with polarized light having its electric vector along the plane of the complex or perpendicular to it, respectively.

band at about 44×10^{13}/sec. and another band at about 80×10^{13}/sec. and shorter wave-length. The former band (band A) may be considered as due to the copper atom in co-ordination with the ligand groups. The latter band may be due to the electronic transition in the ligand bound to the metal atom and should be designated as a specific band[12].

The following rules are obtained on the dichroism. (1) For the band A, the ||-absorption is remarkably hyperchromic to the ⊥-absorption, and (2) for the specific band, the ||-absorption is highly bathochromic to the ⊥-absorption.

Bis-(hinokitiolato)-copper (II).—The results of the measurements are shown in Fig. 2 and Table II. The compound shows a band at about 44×10^{13}/sec. and the other band at about 80×10^{13}/sec. and shorter wave-length region. The crystal structure has not yet been determined. The dichroism of the compound, however, may be understood in a way similar to the case of the tropolonato-compound, assuming that the A-absorption involves the characteristics of the ||-absorption and the B-absorption involves those of the ⊥-absorption. On the basis of the assumption, we are led to the rules, the same as those of the tropolonato-compound.

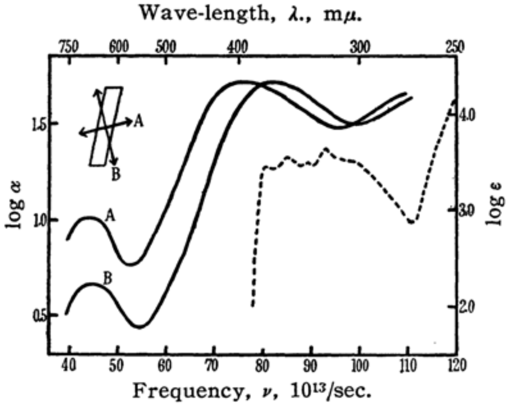

Fig. 2. Ultra-violet absorption spectra of bis-(hinokitiolato)-copper (II) and hinokitiol. The absorption spectrum, of hinokitiol in iso-octane (dotted curve) is taken from M. Tsuboi, This Bulletin, **25**, 369 (1952).

TABLE II
ABSORPTION MAXIMA OF BIS-(HINOKITIOLATO)-COPPER (II)

	ν, 10^{13}/sec.	log α	ν, 10^{13}/sec.	log α
A-abs.	44.2	1.0	76	1.70
B-abs.	44	0.62	80	1.72

Bis-(acetylacetonato)-copper (II).—The results of the measurements are shown in Fig. 3 and Table III. The analysis of the crystal structure was performed by Koyama et al.[13], indicating that the planes of the complex molecules inclined by about 53.5° to the *b*-plane. It is seen from the X-ray study that the *a*-absorption, absorption with the electric vector along the *a*-axis, involves more ⊥-absorption, and the *b*-absorption, absorption with the electric vector along the *b*-axis, involves more ||-absorption. The crystal shows two absorption bands, one at about 50 to 55×10^{13}/sec. and the other in the region shorter than 70×10^{13}/sec. The band at shorter wavelength apparently corresponds with the specific band which is due to the electronic transition of the π-electron system in combination with the copper atom. From the result of the measurement, we obtain the following rules on the dichroism of the planar complex. (1) For the band A, the ||-absorption is greatly hyperchromic to the ⊥-absorption, the former being slightly hypsochromic to the latter, and (2) for the specific band, the absorption with the electric vector along the π-electron system is bathochromic to the absorption with the electric vector normal to the π-electron system.

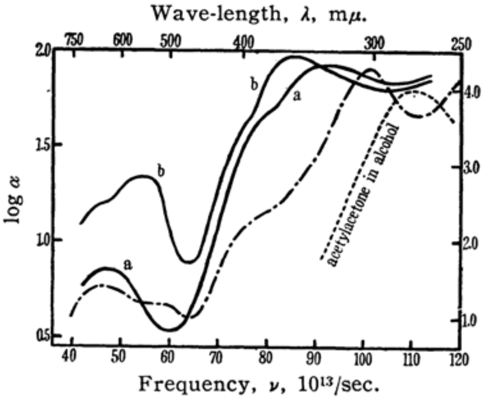

Fig. 3. Ultra-violet absorption spectra of bis-(acetylacetonato)-copper (II): ——— crystal; – – – – chloroform solution. The absorption spectrum of acetylacetone in alcohol (------) is taken from P. Grossmann, *Z. physik. Chem.*, **109**, 305 (1924).

TABLE III
ABSORPTION MAXIMA OF BIS-(ACETYLACETONATO)-COPPER (II)

	ν, 10^{13}/sec.	log α	ν, 10^{13}/sec.	log α
b-abs.	55.8	1.39	94	2.04
c-abs.	48	1.05	98	2.00

---

[12] About the specific band, see, for example, R. Tsuchida and M. Kobayashi, This Bulletin, 13, 476 (1938), etc.

[13] H. Koyama, Y. Saito and H. Kuroya, *J. Inst. Polytech. Osaka City Univ.*, Vol. 4, No. 4, Series C, p. 43 (1953).

Bis-(*o*-formylphenolato)-copper (II). — The results of the measurements are shown in Fig. 4 and Table IV. The crystal is found to show a band at about 50×10^{13}/sec. (band A) and another band at about 65×10^{13}/sec. and shorter wave-length. The latter band may be considered as due to the electronic transition in the *o*-formylphenolate ion co-ordinating to the copper atom, and should be designated as a specific band. The analysis of the crystal structure is not available as yet. Comparing the polarized absorption spectra of this compound with those of the other cupric complexs, however, we can readily assign the A- and B- absorption as representing the characteristics of the ||- and ⊥-absorption. Assuming the above assignment, the following relationships may be derived on the dichroism of the bis-(*o*-formylphenolato)-copper (II). (1) For the band A, the ||-absorption is greatly hyperchromic to the ⊥-absorption. (2) For the specific band, the ||-absorption is bathochromic to the ⊥-absorption.

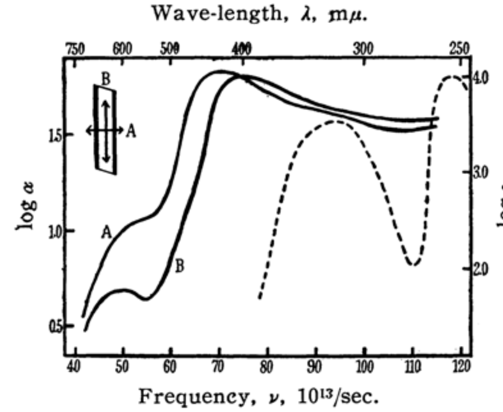

Fig. 4. Ultra-violet absorption spectra of bis-(*o*-formylphenolato)-copper (II). The absorption spectrum of *o*-formylphenol in hexane (dotted curve) is taken from R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, **1940**, 1347.

TABLE IV
ABSORPTION MAXIMA OF BIS-(*o*-FORMYL-PHENOLATO)-COPPER (II)

	ν, 10^{13}/sec.	log α	ν, 10^{13}/sec.	log α
A-abs.	51	1.01	69	1.82
B-abs.	51	0.70	73	1.84

Discussion of the Results

General Rules on the Polarized Absorption Spectra of the Cupric Complexes.—The planar complexes of copper (II) that have been examined in the present work are seen to show analogous absorption spectra and a quite similar type of dichroism. The four complexes exhibit two kinds of absorption bands, one in the visible region and the other in the ultra-violet.

The former (band A) may be considered as originating from the copper atom bound to the ligands. Reviewing the experimental data, the following rules which are common for the four cupric complexes may be derived for the band A. *The ||-absorption is much higher in intensity than the ⊥-absorption.* The same rule was also shown to hold for bis-(ethylenediamine)-copper (II) complexes[14] and bis-(dimethylglyoximato)-copper (II)[15]. In the previous papers[3], a similar relation on the dichroism was obtained with planar complexes of palladium (II) for the absorption band which was assumed to be due to the co-ordinate linkage between the metal and the ligands. The above rule on the dichroism implies that the electric moment responsible for the band in question is greater along the plane of the complex than that normal to the complex plane. This relationship seems to be readily understandable in a qualitative way. Thus, since the linkage lies in the plane of the complex, the electrons concerned with the linkage would be excited more readily with the electric vector along the plane of the complex than with the electric vector normal to the plane.

It is seen that with the four cupric complexes there are two types of dichroism for the band A. For the one, the ||- and ⊥-absorption show a band A at almost identical wave-lengths, and for the other, the ||- and ⊥-absorption show their band A at different wave-lengths. To the latter type, for example, belongs the acetylacetonato-complex. In the crystal of bis-(ethylenediamine)-copper (II) perchlorate also was observed a similar splitting of the band A, which was ascribed to the perturbations from the surrounding complex ions and anions[14]. According to the X-ray study, the closest distance between the copper atom and one CH group in the α-position of an adjacent molecule is 2.84 Å in the crystal of the acetylacetonato-complex, suggesting a kind of weak interaction between them. Therefore, the splitting of the band A in this compound might be ascribed mainly to the interaction between the *d*-electron of the copper atom in one molecule and the π-electron of the CH group in another in the crystalline state. Thus, the above interaction acting perpendicularly to the plane of the cupric complex is expected to give rise to the bathochromic shift with the ⊥-absorption.

---

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

[15] S. Yamada and R. Tsuchida, ibid., **27**, 156 (1954).

In connection with this, it also seems noteworthy that the absorption maximum for the band A of the acetylacetonato-copper (II) in the crystalline state is found at a wavelength considerably shorter than that in the solution. This fact suggests some bathochromic effect of the solvent molecules on the complex in solution. This effect may be due to close approach of the solvent molecules to the copper atom along the direction normal to the plane of the complex. The interaction between the complex molecules in the crystalline state might also be possible. The effect of the solvent molecules on the planar complexes, however, seems to be more probable, since the interaction between the complex molecules would be expected to cause bathochromic effect. This phenomenon would be similar to the bathochromic shift with the aqueous solution of bis-(ethylenediamine)-copper (II) complexes, where weak linkage of the solvent molecules to the copper atom was assumed in the direction along the normal to the plane of the complex[14].

The absorption band at the shorter wavelength may be considered as due to the characteristic absorption of the isolated ligands. It is seen that the characteristic absorption, which is exhibited by the isolated ligand in the ultra-violet region, is modified and displaced toward the longer wave-length when it is combined with the metal atom to form a complex molecule. As to the specific band of the ligand in the cupric complex, the present measurement shows (1) that *the absorption parallel to the π-electron system of the ligand is bathochromic to the absorption normal to the π-electron system*, and (2) that *the intensity is of almost equal magnitude for both the $\|$- and $\perp$-absorption.*

For the isolated molecules of the ligands that have been treated in the present work, we may expect a dichroism which is similar to that for the benzene ring, since all of them involve a conjugated π-electron system. It was formerly established for the isolated benzene derivatives that the absorption parallel to the benzene ring is highly hyperchromic and slightly bathochromic to the absorption normal to the ring[16]. The above rule (1) seems to be similar to the relation derived for the isolated benzene derivatives. The polarization property of the ligand is retained in this respect, when the ligand combines with the metal. The rule (2), however, is quite different from that with the benzene derivatives or from what would be expected for the isolated π-electron systems. Thus, the $\perp$-absorption which is forbidden in the isolated system of the ligand is seen to be allowed in forming the metallic complex. This change as to the polarization property of the specific band may be ascribed to the disturbance caused on the ligand when combining with the metal atom.

Absorption Spectra and Electronic Structure.—Comparison of the frequency at the maximum of the band A among the cupric complexes with different ligand ions gives the following hypsochromic order of the ligands: acetylacetone>salicylaldehyde>tropolone, hinokitiol. This order may be taken as one measure for the effect of the ligand on the electronic state about the copper. Thus, it is supposed that the effect of the ligand ion on the copper atom decreases in the above order.

The oxygen atoms directly attached to the metal atom would be greatly influenced by the neighbouring carbon atoms in the same ligand. According to Calvin et al.[17], who extensively studied stability constants of cupric complexes with a number of β-diketones, the most profound change within a ligand on its complex formation may be in the nature of the double bond between the two carbon atoms of the three-carbon systems forming the conjugated chain between the two oxygen atoms. They found a straightforward correlation between the stability constant of the cupric complexes and the nature of the double bond in the three-carbon systems of the conjugated chain. In those compounds which are treated in the present paper, the linkage between the oxygen and copper atom might involve, besides the ordinary σ-bond, some amount of additional π-binding which would be due to an overlap of atomic orbitals of the oxygen and copper atom. Thus, the chelate-ring system comprising the metal atom in the above type of compounds may be supposed to involve the conjugation of more or less unsaturated linkages, which would be somewhat analogous to that in the aromatic ring[17]. Going further on this assumption, the greater conjugation the many-carbon system between the two oxygen atoms would involve, the greater would be the contribution of the π-bond between the copper and oxygen atom, resulting in the stronger linkage between the metal and the ligand, which would yield

---

[16] R. Tsuchida, M. Kobayashi and K. Nakamoto, *J. Chem. Soc. Japan*, **70**, 12 and 14 (1949) (in Japanese); K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 390 (1952), etc.; G. Scheibe, S. Hartwig and H. Müller, *Z. Elektrochem.*, **49**, 372 (1943).

[17] M. Calvin and K.W. Wilson, *J. Am. Chem Soc.*, **67**, 2003 (1945).

the more hypsochromic shift of the absorption band A[18].

Following the hypothesis[19] that tropolone is a vinylog of an enolized β-diketone, with the linkage of a small bond order between the carbon atoms 1 and 2 (Fig. 5), the seven-carbon system of tropolone might be assumed to have a structure similar to that of acetylacetone, involving considerable conjugation between the two oxygen atoms. The present measurement, however, indicates that with respect to the absorption band A, which is supposed to be closely connected with the linkage between the copper and the ligand, the tropolonato-copper complex is highly bathochromic to the acetylacetonato-copper. The wave-length difference between them seems to be so marked that it would be reasonable to suppose that the linkages around the copper atom in the tropolonato-complex are considerably different from those in the acetylacetonato-complex. That is, besides the contribution of the vinylog structure, we can not overlook the contribution in tropolone of a structure which involves linkage between carbon atoms 1 and 2 having a bond order considerably larger than a single bond. This assumption appears to be in agreement with the hypothesis that the tropolone ring involves some amount of aromaticity[20].

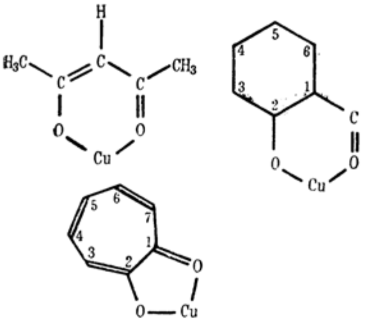

Fig. 5.

On the other hand, the present measurement also indicates that the cupric complex of salicylaldehyde shows its absorption band A at the shorter wave-length than the complex of tropolone, suggesting a stronger effect on the copper atom of salicylaldehyde than that of tropolone. Assuming for the compounds of the above type a similar criterion to that proposed by Calvin et al.[17], the stronger effect on the copper atom of salicylaldehyde seems to indicate a higher bond order of the carbon-to-carbon linkage (C_1—C_2) between the two oxygen atoms in salicylaldehyde than the corresponding C_1—C_2 linkage in tropolone (Fig. 5). This appears to be in agreement with the current concept on the structure of the tropolone ring.

When the ligand combines with a metal atom, the absorption of the ligand is seen to undergo some change or other according to the magnitude of the effect on the ligand. The magnitude of the change in the specific absorption band as compared with the original absorption of the isolated ligand may be taken roughly as one measure of the change in the electronic state of the ligand within the complex as compared with the free ligand. As the conjugation of the linkages would become greater within the chelate-ring involving the metal atom, the greater effect might be caused on the electronic state of the ligand and, in consequence, on its characteristic absorption. Thus, inspection of the previous data with the complexes in solution shows that the shift of the specific band of the metallic complex from the characteristic absorption of the free ligand molecule is smaller with the compound of tropolone than with the corresponding compound of acetylacetone and salicylaldehyde (Table V). This is parallel with the results described in the foregoing part of the present paper, leading to the same conclusion as that derived in the above.

TABLE V

WAVE-LENGTH SHIFT OF THE CHARACTERISTIC BAND OF THE LIGAND ON COMPLEX FORMATION WITH THE COPPER ATOM

Ligand	$\Delta\nu$, 10^{13}/sec.	ref.
Tropolone	1.2	(a), (b)
Salicylaldehyde	1.9	(c), (d)
Acetylacetone	8	(d), (e)

(a) J.W. Cook, A.R. Gibbs, R.A. Raphael and A.R. Somerville, *J. Chem. Soc.*, **1951**, 503.

(b) M. Tsuboi, This Bulletin. **25**, 369 (1952).

(c) R.A. Morton and A.L. Stubbs, *J. Chem. Soc.*, **1940**, 1347.

(d) K. Sone, *J. Am. Chem. Soc.*, **75**, 5207 (1953).

(e) P. Grossmann, *Z. physik. Chem.*, **109**, 305 (1924).

A similar frequency shift of the absorption band of the ligand may be expected in the infra-red spectra. Thus, the carbonyl stretching frequency of the free ligand molecule undergoes a shift to the lower frequency on its complex formation. As shown in Table VI, inspection of previous data seems to indicate that frequency shift is greatest for acetylacetone and smallest for tropolone. This is again coincident with the above hypsochromic order, giving another piece of

---

[18] Such arguement is not strictly valid in every case, but may be applicable to those compounds which have a structure closely related to each other.

[19] See, for example, W. von E. Doering and L.H. Knox, *J. Am. Chem. Soc.*, **74**, 5684 (1952), etc.

[20] See, for example, T. Nozoe, *Proc. Japan Acad.*, **26**, 30 (1950), etc.

TABLE VI

FREQUENCY SHIFT OF THE C=O STRETCHING ON COMPLEX FORMATION

Compound	Free, cm^{-1}	Cu(II)-compd., cm^{-1}	ref.
Acetylacetone	1639–1538	1550–1562	a
Salicylaldehyde	1661	1600	b
Tropolone	1615	1510, 1595	c

(a) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949); J. Le Comte, *Discuss. Faraday Soc.*, **9**, 125 (1950).

(b) I. M. Hunsberger, ibid, **72**, 5626 (1950).

(c) H. P. Koch, *J. Chem. Soc.*, **1951**, 512.

evidence for the conclusion on the electronic state of the ligands which has been reached in the former part of the present paper.

Summary

Polarized absorption spectra of cupric complexes with tropolone, hinokitiol, acetylacetone and salicylaldehyde have been determined in the visible and ultra-violet by Tsuchida-Kobayashi's microscopic method. The above compounds all exhibit two bands at about 40 to 55×10^{13}/sec. (band A) and at about 70×10^{13}/sec. or shorter wave-length (specific band). The following rules on the dichroism which are common for the above complexes, have been induced:

For the band A, the absorption parallel to the complex plane is highly hyperchromic to the absorption normal to the complex plane. For the specific band, the absorption parallel to the π-electron system is found considerably bathochromic to the absorption normal to the plane.

With different ligand ions, the wave-length of the band A of the cupric complexes have been compared, and the following hypsochromic order has been derived: acetylacetone> salicylaldehyde>tropolone, hinokitiol. The same order has been found for the wave-length shift of the specific band from the corresponding band of the free ligand.

The above results have been discussed in relation to the electronic state of the complexes and the ligands.

We thank Professor T. Nozoe and his collaborators for supplying us with the samples of the tropolonato- and hinokitiolato-complexes and drawing our attention to these compounds. We are also indebted to Professor M. Nakagawa for helpful discussions. The financial support of this work by the Education Ministry is gratefully aknowledged.

Department of Chemistry, Faculty of Science, Osaka University, Osaka