Spectrochemical Study of Microscopic Crystals. X.[1] *The Absorption Spectra and Configuration of Bis(ethylenediamine)-copper(II) Complexes*

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It is known that copper usually forms squareplanar complexes with ammonia and amines. Complexes of square-bipyramidal configuration, however, are also formed in some compounds involving water molecules of crystallization. For example, two molecules of water in the crystal of bis(ethylenediamine)-copper(II) nitrate dihydrate occupy positions comparatively close to the copper atom in the direction normal to the plane formed by one copper and four nitrogen atoms[2]. On the other hand, bis(ethylenediamine)-copper (II) perchlorate, which involves no water of crystallization, apparently has separate ions, $[Cu(en)_2]^{2+}$ [3], of planar configuration in the crystalline state. When molecules of ions approach the copper atom in the planar $[Cu(en)_2]$-group along the direction normal to the complex plane, the light absorption and its anisotropy usually undergo more or less distinct changes. Thus the measurement of the absorption spectra is expected to be of use to the elucidation of the problems on the configuration of the planar copper(II)-complexes. In the present paper polarized absorption spectra of bis(ethylenediamine)-copper(II) perchlorate, nitrate dihydrate, and tetrathiocyanato-mercurate have been determined in the crystalline state, and the above problems discussed using the results of the measurements.

Experimental

Materials.—Bis(ethylenediamine)-copper(II) perchlorate, $Cu(en)_2(ClO_4)_2$, was prepared in violet needles according to the method of Pfeiffer et al[4]. The crystal shows a striking dichroism on the prism face, that is, reddish purple and bluish purple. The measurement of polarized absorption spectra was made on the above face in the directions of extinction. The A- and B-absorption refer to the directions A and B as shown in the figure.

Bis(ethylenediamine)-copper(II) nitrate dihydrate, $Cu(en)_2(NO_3)_2 2H_2O$, was obtained in violet plates by the method of Grossmann et al[5]. The monoclinic crystals thus obtained show a marked dichroism on the well-developed (001)-face; it appears light purple with the electric vector along the b-axis and purplish blue with the electric vector along the a-axis. The dichroism measurement was made on the c-plane with polarized light vibrating along the a-axis and along the b-axis. The a- and b-absorption denote absorption with the electric vector along the a- and b-axis, respectively.

Bis(ethylenediamine)-copper(II) tetrathiocyanato-mercurate(II), $[Cu(en)_2][Hg(SCN)_4]$, was prepared in monoclinic plate-like crystals from aqueous solutions of $Cu(en)_2(NO_3)_2$ and of $K_2Hg(SCN)_4$. The crystals are deep purple, with the (010)-plane dominating. Dichroism is observed on the (010)[6]. The measurements of the absorption spectra were made on this plane with polarized light along α- and along β-direction of the crystal[7]. The a- and b-absorption refer to the absorption with the electric vector along the α- and β-direction, respectively.

Measurements.—Quantitative dichroism measurements of the crystals were made by Tsuchida-Kobayashi's microscopic method[8] with polarized light in the regions covering 7500 to 2400 Å. The notations used are the same as those in the previous papers of this series[1].

Results and Discussion

Dichroism of Bis(ethylenediamine)-copper (II) Perchlorate.—The results of the measurements are given in Fig. 1 and Table I. The crystal structure is unknown at present. But since the crystal has no water of crystallization, the perchlorate in the crystalline state involves the separate ions of $[Cu(en)_2]^{2+}$. Therefore, the absorption spectra obtained with this crystal are considered to represent the absorption of the separate planar complex ion, $[Cu(en)_2]^{2+}$, under rather small effect from external perchlorate ions. It is seen

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[1] Part IX of this series, S. Yamada and R. Tsuchida, This Bulletin, 28, 664 (1955).

[2] T. Watanabe and M. Atoji, *Kagaku*, 21, 301 (1951) (in Japanese); read before the meeting of the Chemical Society of Japan, Osaka, May, 1950.

[3] The notation, en, denotes a molecule of ethylenediamine.

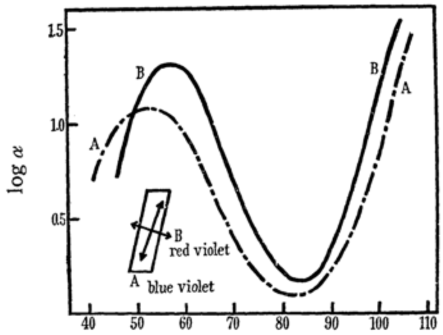
[4] P. Pfeiffer and H. Glaser, *J. Prakt. Chem.*, 151, 134 (1938).

[5] H. Grossmann and B. Schück, *Z. anorg. allgem. Chem.*, 50, 1 (1906).

[6] H. Scouloudi, *Nature*, 166, 357 (1950); *Acta Cryst.*, 6, 651 (1953).

[7] The notations, α, β and γ, represent conventional symbols for optic elasticity axes of the crystal. The γ-direction corresponds with the b-axis. See ref. (6).

[8] R. Tsuchida and M. Kobayashi, This Bulletin, 13, 619 (1938); "The Colours and the Structures of Metallic Compounds," Zoshindo, Osaka (1944), p. 180.



Frequency, ν, 10^{13}/sec.

Fig. 1. Absorption spectra of $[Cu(en)_2](ClO_4)_2$.

TABLE I

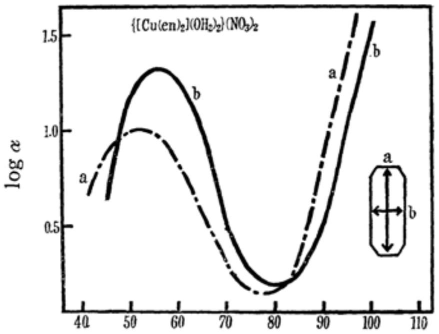
ABSORPTION MAXIMA OF BIS(ETHYLENEDIAMINE)-COPPER(II) PERCHLORATE IN THE CRYSTALLINE STATE

	ν, 10^{13}/sec.	log α	Half width
A-abs.	57.2	1.31	16.9
B-abs.	53.0	1.08	21.7

from the measurements that the crystal of the perchlorate shows absorption at about 50×10^{13}/sec. (band A) and at a wave-length shorter than 110×10^{13}/sec. (band B). The band at the longer wave-length is supposed to be due to the copper atom in combination with ligands. The absorption at the shorter wave-length may be considered as originating from the electron transfer between the copper atom and the ligand molecules, as will be discussed in the later part of this paper.

It was formerly established with planar complexes of copper(II)[9] that for the band A, absorption with the electric vector along the complex-plane, ∥-absorption, has a larger absorption coefficient than ⊥-absorption, absorption with the electric vector normal to the above. Therefore, it may be reasonable to suppose that the A- and B-absorption represent characteristics of the ∥-absorption and those of the ⊥-absorption, respectively. Thus the following relation on the dichroism may be derived. For the band A, the ∥-absorption shows its maximum at a shorter wave-length than the ⊥-absorption, and the absorption is much stronger with the ∥-absorption than with the ⊥-absorption. For the band B, the ∥-absorption is bathochromic to the ⊥-absorption.

Dichroism of Bis(ethylenediamine)-copper (II) Nitrate Dihydrate.—The results of the measurements are shown in Fig. 2 and Table II. According to the X-ray study of crystal structure, the copper atom is bound with four nitrogen atoms of ethylenediamine molecules in planar configuration, with the neighbouring oxygen atoms of water molecules at a slightly greater distance in the direction normal to the plane formed by the copper and four nitrogen atoms. The planes of the complexes are inclined to the bc-plane at a small angle. Referring to absorption with the electric vector along the a-axis as a-absorption and absorption with the electric vector along the b-axis as b-absorption, then the crystal analysis indicates that the a-absorption corresponds roughly with the ⊥-absorption of the planar complex ions and the b-absorption corresponds with the ∥-absorption[2].



Frequency, ν, 10^{13}/sec.

Fig. 2. Absorption spectra of $\{[Cu(en)_2](OH_2)_2\}(NO_3)_2$.

TABLE II

ABSORPTION MAXIMA OF BIS(ETHYLENEDIAMINE)-COPPER(II) NITRATE DIHYDRATE IN THE CRYSTALLINE STATE

	ν, 10^{13}/sec.	log α	Half width
b-abs.	56.0	1.33	16.5
a-abs.	52.2	1.00	21.5

The crystals of bis(ethylenediamine)-copper (II) nitrate dihydrate exhibit in the region of the present measurement two bands at 50–60×10^{13}/sec. (band A), and at the wave-length shorter than 110×10^{13}/sec. (band B), both bands corresponding to the absorption bands of the perchlorate.

The band A of this crystal is seen to be slightly displaced bathochromically as compared with the crystal of the perchlorate. This seems to indicate that the complexes, in the crystal of the nitrate dihydrate undergo an effect from the two water molecules in the direction normal to the complex-plane.

From the present measurement are obtained the following relations on the dichroism of the complex ion. *For the band A, the ∥-absorption has much greater intensity than the ⊥-absorption, and the former is hypsochromic*

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[9] R. Tsuchida and S. Yamada, Read before the sixth annual meeting of the Chemical Society of Japan, Kyoto, April, 1953.

to the latter. The above rule about the intensity is the same as that formerly derived with other planar complexes of copper(II) as well as with the perchlorate[9]. For the absorption bands of planar complexes of platinum(II) and palladium(II) which are considered as due mainly to co-ordinate linkages, the $\parallel$-absorption was found to have much greater oscillator strength than the $\perp$-absorption[10]. The above relation with the cupric complexes seems to be in good agreement with the general rule for planar complexes of palladium(II) and platinum(II).

The second rule that the $\parallel$-absorption is hypsochromic to the $\perp$-absorption seems to indicate that the band A consists of two components having opposite polarization properties. This may be discussed later with reference to the absorption of the complex ion, $[Cu(en)_2]^{2+}$, in solution.

The present measurement also shows that, *for the band B, the $\perp$-absorption is bathochromic to the $\parallel$-absorption.* The fact that the nitrate dihydrate shows with the band A polarization property essentially similar to the perchlorate seems to indicate that the effect of the two water molecules on the band A is small and, at the same time, that the energy level associated with the band A is disturbed very little. On the contrary, their marked effect is observed with the absorption at the shorter wave-length. Thus the polarization property for the band B of the nitrate dihydrate is found to be reversed, as compared with the perchlorate. This reversal, which is ascribed to the effect of the two water molecules close to the copper atom, will be discussed in the later part of this paper.

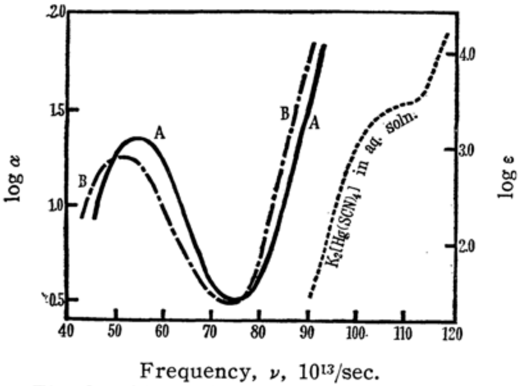

Fig. 3. Absorption spectra of $[Cu(en)_2][Hg(SCN)_4]$. The spectrum of the solution (dotted curve) is taken from ref. 1.

Bis(ethylenediamine)-copper(II) Tetrathiocyanato-mercurate(II).—The results of the present measurement are shown in Fig. 3 and Table III. According to the result of the crystal analysis[5], it is seen that the B-absorption involves more $\perp$-absorption of the $[Cu(en)_2]^{2+}$-ion than the $\parallel$-absorption, and that the A-absorption involves more $\parallel$-absorption. The crystal is found to show absorption bands at about 50×10^{13}/sec. and at a shorter wave-length than about 90×10^{13}/sec. The band at 50×10^{13}/sec. of the crystal clearly corresponds to the band A of the $[Cu(en)_2]^{2+}$-group, since the $[Hg(SCN)_4]^{2+}$-ion is expected to absorb at a much shorter wave-length region[1] (Fig. 3). For the $[Cu(en)_2]^{2+}$-ion in the crystal of $[Cu(en)_2][Hg(SCN)_4]$, the following relation is found on the dichroism. *For the band A, the $\parallel$-absorption is hypsochromic to the $\perp$-absorption the intensity being greater with the $\parallel$-absorption than with the $\perp$-absorption.* This relation is essentially similar to that with the crystal of $\{[Cu(en)_2](OH_2)_2\}(No_3)_2$.

TABLE III

ABSORPTION MAXIMA OF BIS(ETHYLENEDIAMINE)-COPPER(II) TETRATHIOCYANATO-MERCURATE(II) IN THE CRYSTALLINE STATE

	ν, 10^{13}/sec.	log α	Half width
A-abs.	54.8	1.18	15.0
B-abs.	51.5	1.05	17.3

The X-ray investigation showed that "two N atoms of the SCN-groups in the crystal of $[Cu(en)_2][Hg(SCN)_4]$ are co-ordinated to each copper atom at a distance of 2.58 Å in the direction perpendicular to the complex-plane, giving the copper atom a total of six-fold co-ordination"[5]. In the same report a value of 2.07 Å was obtained for the co-ordinate bond distance between the copper and nitrogen atoms in the plane formed from a copper and four nitrogen atoms of ethylenediamine molecules. The Cu-N distance of 2.58 Å seems to be too great for the ordinary co-ordinate linkage to be expected between the copper atom and the nitrogen atoms of the NCS-groups. The band A of $[Cu(en)_2][Hg(SCN)_4]$, however, is seen to be displaced slightly bathochromically, as compared with that of $[Cu(en)_2](ClO_4)_2$. This may be regarded as one effect by the interaction between copper and nirtogen atoms. The dichroism for the band A is the same as that with the perchlorate, as was found to be the case with the nitrate dihydrate.

Another absorption band in the ultra-violet may be considered as superposition of the

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

absorption bands of complex ions, $[Cu(en)_2]^{2+}$ and $[Hg(SCN)_4]^{2-}$. In any case, the absorption is seen to lie in the far longer wave-length regions than would be expected from the corresponding bands of either of the component complexes in solution. This bathochromic shift also may be taken as indicating that the complexes are subjected to the effect caused by the interaction between a copper and two nitrogen atoms of the NCS-groups. Judging from the absorption curves of the separate component complexes, the ascending curve at about $80-90\times10^{13}$/sec. may most probably be considered as due to the $[Cu(en)_2]^{2+}$-ion. *It is found for this band that the* $\parallel$*-absorption is hypsochromic to the* $\perp$*-absorption.* This dichroism, reverse to that of the $[Cu(en)_2](ClO_4)_2$, shows the effect of NCS^- ions on the $[Cu(en)_2]^{2+}$ group.

General Discussion

Inspecting the results presented above, we find the following rules about the effects on the absorption spectrum of the complex ion caused by the outer groups which come comparatively close to the copper atom. (1) *The band A is displaced bathochromically, its polarization property being unchanged.* (2) *The band B undergoes a large bathochromic shift, its polarization property being reversed.*

These changes, above all the reversal of the polarization property, are so definite that they may be used for determining whether or how close such molecules as water and ammonia in the crystalline state approach the copper atom in the direction normal to the square-planar complex.

The results stated above clearly indicate that water molecules in the nitrate dihydrate or thiocyanate ions in the tetrathiocyanatomercurate(II) have considerable effects on the copper atom. But judging from the distance between the copper atom and the approaching groups, as revealed by the X-ray analysis[2,6], the effect may be mostly electrostatic, and the linkage between them may be different from the linkage between the copper atom and ethylenediamine molecules in the complex-plane. Furthermore, the typical sexa-co-ordinate copper(II) complex of octahedral configuration would show its absorption in the much longer wave-length region, as may be readily realized from the absorption maximum at $40–45\times10^{13}$/sec. for the $[Cu(en)_3]^{2+}$ in aqueous solution against about $52–57\times10^{13}$/sec. for the $[Cu(en)_2]^{2+}$ in the crystalline state[11]. This also seems to support the above conclusion.

The magnitude of the bathochromic change for the band A and band B may be supposed to depend upon the strength of the effect of the approaching groups on the copper atom. Thus, inspecting the results, we obtain with both the bands the decreasing order of the effect on the copper atom: tetrathiocyanatomercurate(II) > nitrate dihydrate > perchlorate.

Formerly, one of the present authors (R. T.)[11] reported that the band A of planar quadri-co-ordinate complexes of copper(II) suffers large bathochromic change when taking up two more ligands to complete the sexa-co-ordination. This would indicate that the approach of the fifth or sixth group to the copper atom may cause bathochromic shift of the band. The general rule (1) seems to be in good agreement with it. This is also in qualitative agreement with the result obtained by Ballhausen[12] through quantum-theoretical treatment on the basis of the crystal field theory. It is to be noted that the polarization property for the band A is not changed on the approach of the fifth and sixth groups. This fact seems to show that the band A may originate from an electronic transition of the comparatively deeper part of the complex ion, favouring the interpretation that the absorption band A of copper (II)-complexes is due to transition of the *d*-electrons of the copper atom which is under the effect of the surrounding ligands.

The general rule (2) indicates that the effect of the approaching outer groups on the band B is seen to be quite large. One explanation for the general rule (2) may be that the same transition in the shorter wave-length that exist in the separate $[Cu(en)_2]^{2+}$-ion may have their polarization properties reversed due to the approach of the outer groups to the copper atom. But an alternative explanation may be that, as the groups come closer to the copper atom in a complex ion, a new transition polarized in the X-Cu-X direction, X being the approaching groups, is given rise to in the wave-length region slightly longer than the original transition. Assuming the latter interpretation, this new transition would most probably be due to the electron transfer from the copper atom to the ligands, as was assumed between the copper and ethylenediamine for the absorption band B of the separate complex ion without any specific effect from outside. Based on the electron transfer model on the supposed new band, we may consider that, when the outer groups come close enough to the copper atom, the electronic clouds on

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[11] R. Tsuchida and H. Ito, Read before the symposium on co-ordination compounds, Nagoya, November, 1953.

[12] C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, 29, No. 4 (1954).

the copper atom move to increase the electronic density toward the approaching groups, making the electron transfer easier with the electric vector along the L-Cu-L direction.

This mechanism of electron transfer provides the possibility of explaining the association band of planar complexes[13]. Thus when some anions in solution come very close to the metal atom in the centre of the planar complex ion, there would be electron transfer between the metal atom and the anions.

Now the absorption spectrum of $[Cu(en)_2]^{2+}$ in aqueous solution may be discussed using the above results. In aqueous solution, water molecules are considered to be located so close to the copper atom in the square-planar complex that the interaction of the above type may be expected between the copper atom and water molecules. In fact, the absorption maximum of $Cu(en)_2(NO_3)_2$ in aqueous solution lies at about 54×10^{13}/sec.[11], a much longer wave-length than the maximum of the perchlorate, and even longer than the nitrate dihydrate in the crystalline state. In consequence, the effect of water molecules on the $[Cu(en)_2]^{2+}$ ion may be greater in aqueous solution than in the crystals of the nitrate dihydrate. But, as is discussed in the preceding section of this paper, the approaching water molecules are not supposed to form strongly covalent bonds with the copper atom, since the supposed octahedral complex formed by strong bonds would show its absorption at a far longer wave-length.

It seems unusual that the absorption band A of the solution is quite symmetrical, since the simple superposition of the $\parallel$- and $\perp$-absorption, as obtained with the crystal, would yield unsymmetrical curve for the band A. It must be concluded, therefore, that the band A, which has only one component in the solution, is split in the crystalline state into two components having opposite polarization properties. The splitting of the band A in the crystal may be ascribed to the perturbation by the surrounding ions, and might be a kind of Davydov splitting[14].

A similar consideration applies to the absorption spectrum of $[Cu(en)_2]^{2+}$ in ammoniac solution, which exhibits the band A at about 48×10^{13}/sec.[15]. The bathochromic shift of the band A is seen to be much greater in ammoniac solution than in aqueous solution, and even than in the tetrathiocyanato-mercurate(II), suggesting that the effect of ammonia on the copper atom is greater than that of water molecules in the aqueous solution or that of thiocyanate ions in the latter. Judging from the remarkable, bathochromic shift, it may be reasonable to suppose that the linkage between ammonia molecules and the copper atom should have considerable covalent bond character.

Summary

Polarized absorption spectra of bis (ethylenediamine)-copper(II) perchlorate, nitrate dihydrate and tetrathiocyanato-mercurate(II) in the crystalline state have been determined by Tsuchida-Kobayashi's microscopic method in the region between 2400 and 7000Å. These compounds all show a band at about 50×10^{13}/sec. (band A) and another absorption at a wave-length shorter than 90×10^{13}/sec. (band B).

The band A of the latter two compounds suffers bathochromic effect, and the polarization property for the band B is reversed, as compared with the former. From these differences, it has been concluded that in the former two compounds, OH_2 or NCS^- causes a considerable effect upon the copper atom.

Using the results of the measurements, the nature of the absorption bands and absorption spectra of the complex ion in aqueous solution has been discussed.

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[13] H. Yoneda, to be published soon.

[14] A.S. Davydov, *Zhur. eksp. teor. Fiz.*, **18**, 210 (1948); *Akad. Nauk S.S.S.R., Pamyati S. I. Varilov*, **1952**, 197; *C.A.*, **43**, 4575 (1949).

[15] F. Rosenblatt, *Z. anorg. Chem.*, **204**, 351 (1932).