Spectrochemical Study of Microscopic Crystals. XX[1]*. The Dichroism of Tris(ethylenediamine)-cobalt(III) and -chromium(III)*[2]

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Knowledge about the electronic state of metallic complexes is important in understanding theoretically their optical activity, which is quite well-known in the history of the chemistry of coordination compounds. Since the dichroism is closely related to the electronic state of the metallic compounds, the experimental determination of the dichroism with tris(ethylenediamine)-cobalt(III) and -chromium(III) ions is thought to be useful for elucidating the optical rotatory dispersion as well as the electronic state of the metallic coordination compounds.

In this work, the authors have determined the dichroism with tris(ethylenediamine)-cobalt(III) and -chromium(III) halides in the crystalline state and discussed about the results of the measurements in relation to the above problems.

Experimental

Materials.—Crystals of d,l-[Co en$_3$]Cl$_3\cdot$3H$_2$O and d,l-[Co en$_3$]Br$_3\cdot$3H$_2$O were prepared according to the method of Grossman and Schück[3]. The hexagonal, prismatic crystals of the compound usually show the well-developed $(10\bar{1}0)$-plane[4]. The crystals show a discernible dichroism on the prism face; they are orange yellow with polarized light having its electric vector along the c-axis, and pale yellow with the electric vector perpendicular to the c-axis. The dichroism measurements were made on the well-developed prism face.

The optically active d-[Co en$_3$]Br$_3\cdot$2H$_2$O was prepared by resolution of the racemic d,l-[Co en$_3$]$\cdot$Cl$_3\cdot$3H$_2$O according to the method of Werner[5]. A slight but definite dichroism was observed under the microscope on the prism face (101), on which the dichroism measurement was carried out.

The racemic d,l-[Cr en$_3$]Cl$_3\cdot$3H$_2$O was prepared in yellow, hexagonal prismatic crystals by the method of Rollinson and Bailar[6]. The crystal of the compound appears to be isomorphous with that of d,l-[Co en$_3$]Cl$_3\cdot$3H$_2$O. It appears yellow with the polarized light having its electric vector along the c-axis, and very pale yellow with the electric vector perpendicular to the c-axis. The dichroism measurement was carried out on the well-developed prism face.

Measurements.—Quantitative dichroism measurements in the visible and ultraviolet regions have been carried out at room temperature by Tsuchida and Kobayashi's microscopic method[7].

The symbols used in the present paper are the same as those in the former papers of this series. Thus the molar absorption coefficient, K, was estimated from the following expression: $K=10M\alpha/\rho$.

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[1] Presented in part before the 4th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1951.

[2] Part XIX of this series: S. Yamada and R. Tsuchida, This Bulletin, **32**, 721 (1959).

[3] H. Grossman and B. Schück, *Ber.*, **39**, 1899 (1906).

[4] F. M. Jaeger, *Z. Krist.*, **39**, 551 (1904).

[5] A. Werner, *Ber.*, **45**, 121 (1912).

[6] L. Rollinson and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **65**, 250 (1943).

Results

Dichroism of the Tris(ethylenediamine)-cobalt(III) Ion.—The present dichroism measurements with d,l-[Co en$_3$] Cl$_3\cdot$3H$_2$O and d,l-[Co en$_3$] Br$_3\cdot$3H$_2$O are shown in Figs. 1 and 2, and Tables I and II. Formerly Kobayashi[7a] reported the absorption spectrum of tris(ethylenediamine)-cobalt(III) bromide trihydrate in the crystalline state using natural light. The absorption maxima determined in the present work agree with those formerly reported by Kobayashi, excepting for the region of the short wavelength. According to the crystal structure analysis[8], the c-axis in the crystal of d,l-[Co en$_3$] Cl$_3\cdot$3H$_2$O is found to be coincident with the threefold axis of the [Co en$_3$]$^{3+}$ ions. Although the crystal structure analysis of d,l-[Co en$_3$] Br$_3\cdot$3H$_2$O is not available at present, the bromide trihydrate presumably has the crystal structure of the same type as that of the chloride trihydrate. The c-absorption in Figs. 1 and 2, therefore, represents the z-absorption of the complex ion, that is, the absorption with the electric vector along the threefold axis of the complex ion.

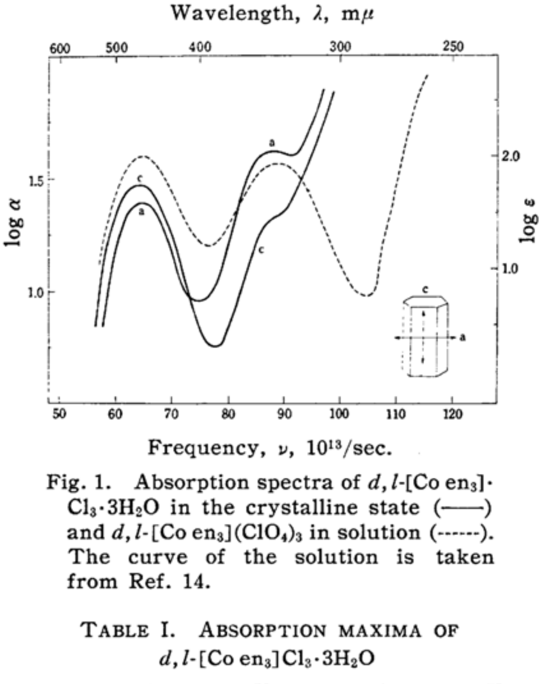

Fig. 1. Absorption spectra of d,l-[Co en$_3$]$\cdot$Cl$_3\cdot$3H$_2$O in the crystalline state (——) and d,l-[Co en$_3$](ClO$_4$)$_3$ in solution (------). The curve of the solution is taken from Ref. 14.

TABLE I. ABSORPTION MAXIMA OF d,l-[Co en$_3$]Cl$_3\cdot$3H$_2$O

	ν	log α	K	ν	log α	K
c-Abs.	63.8	1.49	9.55×10^4	(88)	1.22	5.13×10^4
a-Abs.	64.0	1.33	6.62×10^4	88.8	1.61	12.5×10^4
	ν	log ε	$10^3\,\varepsilon$	ν	log ε	$10^3\,\varepsilon$
Solution[a)]	64.4	1.99	9.96×10^4	88.5	1.94	9.73×10^4

a) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).
ν: 10^{13} sec^{-1}.

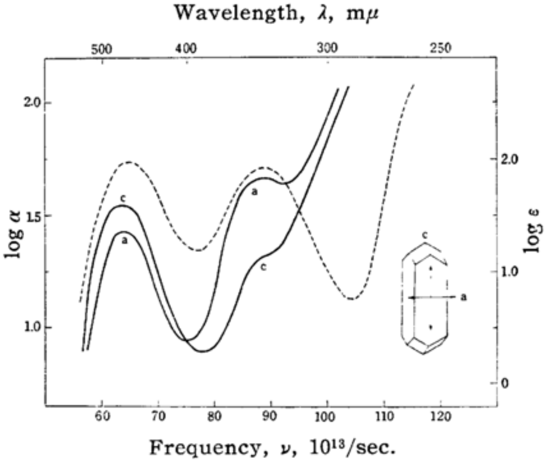

Fig. 2. Absorption spectra of d,l-[Co en$_3$]$\cdot$Br$_3\cdot$3H$_2$O in the crystalline state (——) and d,l-[Co en$_3$](ClO$_4$)$_3$ in solution (------).

TABLE II. ABSORPTION MAXIMA OF d,l-[Co en$_3$]Br$_3\cdot$3H$_2$O

	ν	log α	K	ν	log α	K
c-Abs.	64.4	1.48	8.72×10^4	88	(1.3)	5.14×10^4
a-Abs.	64.4	1.39	7.11×10^4	88	1.63	12.3×10^4

ν: 10^{13} sec^{-1}.

From the present measurement, the following relationships are obtained about the dichroism of the [Co en$_3$]$^{3+}$ ion.

(1) For the band at about 64×10^{13} sec^{-1} (469 mμ), the z-absorption of the complex ion is somewhat stronger than the x-absorption.

(2) For the band at about 88×10^{13} sec^{-1} (341 mμ), the x-absorption is about 2.5

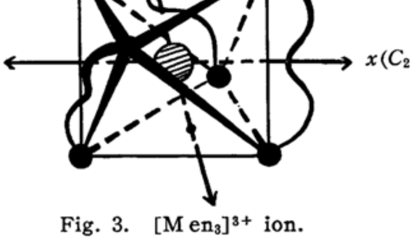

Fig. 3. [M en$_3$]$^{3+}$ ion.

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[7] (a) R. Tsuchida and M. Kobayashi, "The Color and the Structure of Metallic Compounds" (Kinzoku-kagobutsu no Iro to Kozo), Zoshindo, Osaka (1944), p. 180. (b) R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 619 (1938).

[8] K. Nakatsu, Y. Saito and H. Kuroya, This Bulletin, **29**, 428 (1956).

times stronger than the z-absorption. The z- and the x-absorption refer to the directions shown in Fig. 3.

The [Co en$_3$]$^{3+}$ ions in the crystal of d,l-[Co en$_3$] Cl$_3$·3H$_2$O are subjected to the field formed by the surrounding ions. However, the dichroism, as here determined, may be assumed in approximation to represent the dichroism of the isolated [Co en$_3$]$^{3+}$ ion itself.

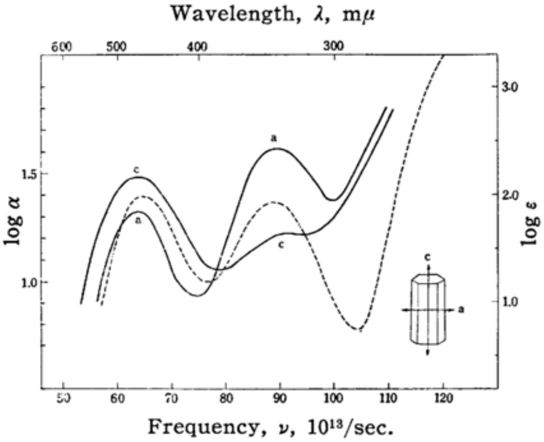

Fig. 4. Absorption spectra of d-[Co en$_3$]·Br$_2$·2H$_2$O in the crystalline state (——) and d,l-[Co en$_3$](ClO$_4$)$_3$ in solution (------).

TABLE III. ABSORPTION MAXIMA OF d-[Co en$_3$]Br$_3$·2H$_2$O

	ν	log α	K	ν	log α	K
c-Abs.	63.9	1.54	9.07×10^4	88	1.27	4.86×10^4
a-Abs.	64.1	1.43	7.03×10^4	88	1.67	12.2×10^4

ν: 10^{13} sec^{-1}.

The dichroism with a crystal of d-[Co en$_3$] Br$_3$·2H$_2$O is shown in Fig. 4 and Table III. The arrangement of the complex ions in the crystal of the optically active form is expected to be different from the arrangement in the crystal of its racemic compound, but the dichroism observed with d-[Co en$_3$] Br$_3$·2H$_2$O is regarded to represent the main features of the dichroism characteristic of the d-[Co en$_3$]$^{3+}$ ion. Comparison of the dichroism of d-[Co en$_3$] Br$_3$·2H$_2$O with the dichroism of d,l-[Co en$_3$] Br$_3$·3H$_2$O indicates unanimously that the c- and the a-absorption of the former crystal represent, respectively, the main characteristics of the z- and the x-absorption of the d-[Co en$_3$]$^{3+}$ ion.

From the dichroism with the three compounds above presented, the following relationships may be induced about the dichroism of the [Co en$_3$]$^{3+}$ ion.

(1) For the first absorption band, the z-absorption is somewhat stronger than the x-absorption.

(2) For the second absorption band, the x-absorption is a few times stronger than the z-absorption. The polarization is more marked for the second absorption band than for the first band.

(3) The optically active form of the [Co en$_3$]$^{3+}$ ion exhibits the same type of dichroism as the dichroism shown by its racemic complex compounds.

Dichroism of the Tris(ethylenediamine)-chromium(III) Ion.—The result of the dichroism measurements with d,l-[Cr en$_3$] Cl$_3$·3H$_2$O is shown in Fig. 5 and Table IV. The structure analysis of the crystal has not been reported as yet. The external form and optical property, however, are so closely similar to those of d,l-[Co en$_3$] Cl$_3$·3H$_2$O that the crystal of the chromium(III) complex is supposed to be isomorphous with the crystal of the corresponding cobalt(III) compound. Therefore, the c-absorption in Fig. 5, the absorption with the electric vector along the c-axis, may be regarded as corresponding with the z-absorption of the complex ion. Based

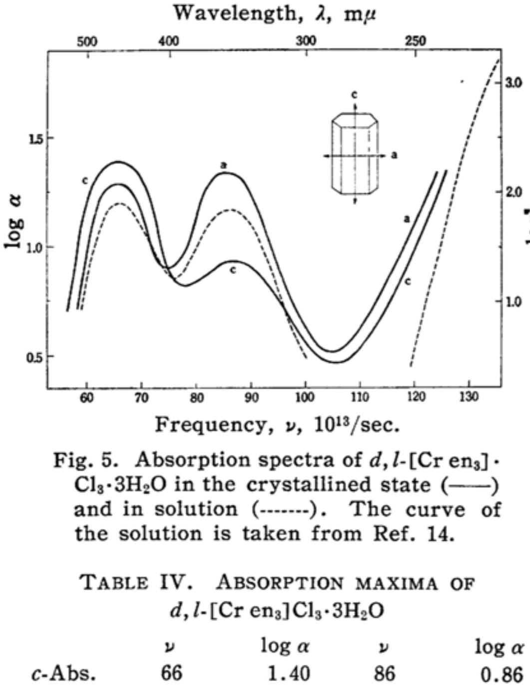

Fig. 5. Absorption spectra of d,l-[Cr en$_3$]·Cl$_3$·3H$_2$O in the crystallined state (——) and in solution (-------). The curve of the solution is taken from Ref. 14.

TABLE IV. ABSORPTION MAXIMA OF d,l-[Cr en$_3$]Cl$_3$·3H$_2$O

	ν	log α	ν	log α
c-Abs.	66	1.40	86	0.86
a-Abs.	66.3	1.25	85.6	1.24
	ν	log ε	ν	log ε
Solution[a]	65.6	1.90	85.5	1.84

a) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

ν: 10^{13} sec^{-1}.

on this assumption of the arragement of the complex ions in the crystal, the following relationships are derived about the dichroism of *d*, *l*-[Cr en$_3$] Cl$_3$·3H$_2$O.

(1) For the band at about 66×10^{13} sec^{-1} (454 mμ), the *z*-absorption is about 1.5 times stronger than the *x*-absorption.

(2) For the band at about 85.6×10^{13} sec^{-1} (350 mμ), the *x*-absorption is about 3 times stronger than the *z*-absorption.

These relationships are found to be of a similar type to those for the corresponding cobalt(III) complexes, as is expected from close similarity in absorption spectra between cobalt(III) and chromium(III) complexes in general. The similarity is also expected from consideration on the symmetry of the electronic state as well as the external form of the complex ions.

Discussion

Dichroism of the First and the Second Absorption Band.—The [Co en$_3$]$^{3+}$ ion has symmetry D$_3$, but its spectrum shows that the effective symmetry is much higher and approximates O$_h$. Thus, the absorption curve bears a close resemblance to those of the hexammine-cobalt(III) complexes with O$_h$ symmetry. The ligand field around the Co^{3+} in the [Co en$_3$]$^{3+}$ ion may be represented by the overall symmetry of O$_h$ with a trigonal field of D$_3$ symmetry as a small perturbation term. In the case of the hexammine-cobalt(III) ion, the absorption bands in the long wavelength region are forbidden owing to the $g \nleftrightarrow g$ selection rule, and become allowed in combination, with the vibrational motion of the complex. The [Co en$_2$]$^{3+}$ ion, however, has no center of symmetry, and the unsymmetrical field will allow the slight electric dipole transitions even in the absence of vibrational distortion.

The two absorption bands in the long wavelength region of the [Co en$_3$]$^{3+}$ ion correspond to those of the [Co(NH$_3$)$_6$]$^{3+}$ ion, which are due to the electronic transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. On grounds of energy⁹⁾ and from a consideration of the rotatory dispersion¹⁰⁾ of the [Co en$_3$]$^{3+}$ ion, the longer wavelength band around 4700 Å is ascribed to the transition $^1A_{1g} \rightarrow {}^1T_{1g}$ and the shorter wavelength band around 3400 Å to the transition $^1A_{1g} \rightarrow {}^1T_{2g}$, the complex ion being assumed to be approximately of O$_h$ symmetry. It is known that the chromium(III) complexes show absorption spectra quite similar to those of the corresponding cobaltic compounds. The first and the second absorption bands of the hexammine-chromium(III) ion are ascribed to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions, respectively. On the basis of Moffitt's theory, the assignment is found to be in agreement with the rotatory dispersion of the chromium(III) complex ion¹¹⁾.

In the D$_3$ group, species A$_{1g}$, A$_{2g}$ and E of the O$_h$ group go over into A$_1$, A$_2$ and E, respectively, whereas T$_{1g}$ splits itself into A$_2$+E and T$_{2g}$ into A$_1$+E. In practice, the degeneracies of the threefold T$_{1g}$ or T$_{2g}$ levels in the hexammines are not perceptibly resolved in their ethylenediamine analogues. The splitting due to the D$_3$ symmetry in these complexes is quite small, as is seen from the present dichroism measurements. Thus the splitting, if any, of the first absorption band under the field of D$_3$ symmetry is found to be very small. Nevertheless the dichroism of the [M en$_3$]$^{3+}$ ion is surely due to the effect of the field with the D$_3$ symmetry.

It might be interesting to point out that the dichroism of the [Co en$_3$]$^{3+}$ and the [Cr en$_3$]$^{3+}$ ion agree, on the basis of the above-mentioned assignment of the absorption bands, with the selection rule which was given by Moffitt¹⁰⁾ from discussion taking only the symmetry of the ground and the excited electronic state into consideration and discarding vibrational modes of the complex ion. This agreement, however, may be rather fortuitous. For complete analysis of the ultraviolet dichroism, account is to be taken of the vibrational modes of the complex ions.

Recently Sugano and Tanabe¹²⁾ experimentally determined optical anisotropy with the chromium ruby, in which the field around the Cr^{3+} ion is represented by C$_3$ symmetry and is quite similar to the field encountered in the [Cr en$_3$]$^{3+}$ ion. It was found from their measurements with the chromium ruby that for the first absorption band the *z*-absorption is stronger than the *x*-absorption, and that for the second band the *x*-absorption is stronger than the *z*-absorption, where the *z*- and the *x*-absorptions represent the absorption with polarized light having its electric vector along and perpendicular to the *c*-axis, respectively. This observation was shown to be in good agreement with

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9) L. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955) etc.

10) W. Moffitt, ibid., **25**, 1189 (1956).

11) J. P. Mathieu, *J. chim. phys.*, **33**, 78 (1936).

12) S. Sugano and Y. Tanabe, *J. Phys. Soc. Japan*, **13**, 880 (1958).

their theoretical interpretation, which also predicted the same type of dichroism for the $[Cr\,en_3]^{3+}$ and the $[Co\,en_3]^{3+}$ ion. This, however, is not the case with these complex ions. The present measurements indicate that the dichroism with the $[Cr\,en_3]^{3+}$ ion is reverse to the dichroism of thd chromium ruby. The difference in dichroism between the two types of the compounds show that the explanation for one case does not apply, at least in its original form, to the other. The dichroism with the $[Cr\,en_3]^{3+}$ ion may be understood, if this is assumed to belong, for some reason, to the case where the second term of F_{2u} type in the expansion of the hemihedral perturbation field, V_{trig}, is much greater than the first term of F_{1u} type in Sugano and Tanabe's treatment[13]. It is expected theoretically that the first term may be much larger than the second term in ordinary cases. The anomaly with the $[Cr\,en_3]^{3+}$ ion is not explained at present.

Dichroism and Optical Rotatory Dispersion of the Complex Ions.—The information about the dichroism of the complex ions is expected to be useful for the understanding of the rotatory dispersion[10]. The complex ions of the type here considered show two component absorptions corresponding to the "first absorption band", both of which may possibly be active, at least partly, in the optical rotation. In this case, superposition of the two inversive dispersions due to the component absorptions may be observed in the wavelength region of the first absorption band. In the tris(ethylenediamine)-cobalt(III) and -chromium(III), the splitting of the first absorption band is found from the present dichroism measurements to be quite small, so that the two sorts of Cotton effect due to the two components of the first band are not observed separately, but their superposition appears with only one maximum. On the other hand, the *d*-trioxalatochromate(III) ion shows in the wavelength region of the first absorption band a small, negative component of Cotton effect, in addition to a much larger component of a positive sign[11]. This may be explained qualitatively on the basis of the dichroism. The dichroism measurements, the details of which will be reported later, indicate that the $[Cr\,ox_3]^{3-}$ ion unambiguously shows two maxima at 51.0 and $51.8\times10^{13}\,sec^{-1}$, the splitting of the first band being much greater than in the tris-(ethylenediamine)-cobalt(III) or -chromium(III). The appearance of the small, negative component of Cotton effect may be understood, if it is assumed that the electronic transitions corresponding to the above two component absorptions give rise to Cotton effect of their own, the sign for one being reverse to the sign for the other.

Comparison of the Crystal Spectra with the Spectra of the Solution. — It is shown that difference is scarcely recognizable in maximum wavelength between the crystal and the solution. On the other hand, difference is observed in intensity of the first and the second absorption band, the difference being greater for the latter band than for the former. If the authors compare the average of K_z and K_x, as the value for the crystal, with $10^3\varepsilon$, which is regared as representing absorption coefficient by the compounds of one formula weight in solution, the present measurements show that intensity is greater for the solution than for the crystal, even when reflection from the surface of the crystal is taken into account. The difference seems to be definite, though it is generally small. This is readily understandable, since the perturbation due to the solvent molecules apparently contributes to absorption coefficient in solution, whereas this kind of contribution to the intensity is lacking in the crystal. The Schwarzschild-Villiger effect might be responsible partly for the difference, but is probably very small in the wavelength region under consideration.

Absorption Band due to Association of Ions. —Linhard[14] formerly found a new type of absorption bands in addition to the first and the second absorption band with the tris(ethylenediamine)-cobalt(III) and -chromium(III) complexes in solution. The new absorption band, which appears in the region of wave length slightly shorter than the second absorption band, is found to become stronger as the concentration of the halide ion increases, and is regarded by Linhard and others as due to association of the halide ions with the $[M\,en_3]^{3+}$ ion. The absorption band of this kind is evidently observed in the absorption curves of the complexes in the crystalline state, as reported in the present measurement with a single crystal. The present

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[13] See Ref. 12. The present authors are indebted to Dr. S. Sugano for the suggestion concerning the difference between the chromium ruby and the complex ions examined in the present work.

[14] M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

measurements indicate that the tris(ethylenediamine)-cobalt(III) complexes in the crystalline state show an absorption band in the region of longer wavelength than does $[\mathrm{Co\,en_3}](\mathrm{ClO_4})_3$ in solution. Thus *d,l*-$[\mathrm{Co\,en_3}]\mathrm{Br_3\cdot 3H_2O}$ shows the band at about $100\times10^{13}\,\mathrm{sec}^{-1}$, which is seen to superpose partly on the shorter wavelength side of the second absorption band. The X-ray study shows that in the crystals of the racemic tris(ethylenediamine)-cobalt(III) chloride trihydrate a complex ion is surrounded by nine chloride ions at about 3.2 Å from a nitrogen atom of the complex ions. A similar arrangement of ions is expected for the racemic bromide trihydrate in the crystalline state. The present measurements, therefore, may be regarded as evidence for the view that the new band is due to association of the complex ion with the surrounding halide ions. It is interesting to note here that the interaction takes place at such a distance, which seems to be comparatively great for the interaction. This type of the group composed of the complex ion and the halide ions surrounding it was formerly established to exist from the measurements of rotatory dispersion[15] and absorption spectra with the complex compounds in solution[14].

From the present dichroism measurements, the following relationships are derived about the absorption band due to the association of the ions.

(1) This kind of absorption band lies in the case of the bromide at longer wavelength than in the case of the chloride.

(2) The absorption is stronger with the electric vector along the trigonal axis of the complex than with the electric vector perpendicular to the axis.

(3) The first or the second absorption band undergoes very little effect even when the association band shifts to a longer wavelength region.

(4) The chromium(III) complex shows the association band in much shorter wavelength region than does the corresponding cobalt(III) complex.

The relationships 1, 3 and 4 are essentially the same as those obtained by Linhard[14] with the complexes in aqueous solution, and in agreement with Linhard's assumption that the association band be ascribed to the electronic transitions due primarily to the halide ions which are deformed under the field of the complex ion.

Since the halide ions without the specific field from the outside absorb in a shorter wavelength, it may be assumed that the absorption of the halide ions is displaced to a longer wavelength in the presence of the field by the complex ions as in the crystals of the compounds here examined. Rrelationship 4 shows that the $[\mathrm{Cr\,en_3}]^{3+}$ ion has smaller effect upon the halide ions than has the $[\mathrm{Co\,en_3}]^{3+}$ ion, being in agreement with Linhard's observation with the complexes in solution.

Summary

The dichroism in the visible and ultraviolet region has been quantitatively determined at room temperature by Tsuchida and Kobayashi's microscopic method with a single crystal of *d, l*-$[\mathrm{Co\,en_3}]\mathrm{Cl_3\cdot 3H_2O}$, *d, l*-$[\mathrm{Co\,en_3}]\mathrm{Br_3\cdot 3H_2O}$, *d*-$[\mathrm{Co\,en_3}]\mathrm{Br_3\cdot 2H_2O}$ and *d, l*-$[\mathrm{Cr\,en_3}]\mathrm{Cl_3\cdot 3H_2O}$.

It has been found that the $[\mathrm{Co\,en_3}]^{3+}$ and the $[\mathrm{Cr\,en_3}]^{3+}$ ion show a similar type of dichroism. For both the complex ions, the *z*-absorption is slightly stronger than the *x*-absorption in the wavelength region of the first absorption band and much weaker than the *x*-absorption in the region of the second absorption band.

The results of the measurements are discussed in relation to the electronic state and the optical rotatory dispersion of the complex ions.

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[15] R. Tsuchida, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*) 58, 621 (1937).