Spectrochemical Study of Microscopic Crystals. II. Dichroism of Cobalt (III)-Praseo Salts

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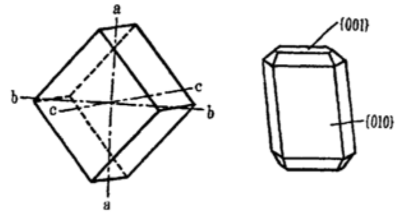
The crystal of the hydrochloride of the so-called "praseo-salts", 1, 6-dichloro-bis-(ethylenediamine)-Co(III) hydrochloride dihydrate, shows a striking dichroism, while that of the nitrate exhibits only a little dichroism compared with the former. This seems to be very interesting, being related to the fact that the hydrochloride easily effloresces in the air to lose its hydrogen chloride of crystallization and that the nitrate, stable in the air, is much less soluble than the hydrochloride. No research on these compounds, however, has been made in the crystalline state, nor has the analysis of the crystal structure or absorption spectrum of the crystal ever been reported. Previously, one of the present authors and M. Kobayashi, in the researches on pleochroism of the crystals of the metallic complex salts,(1) and the present authors, in the researches on dichroism of metallic planar complexes,(2), (3) showed that the measurement of pleochroism of the crystals was of great use to studies on the crystal structure and on the state of the complex ions in the crystals.

In this report, we can give the results of the measurement of dichroism with praseo-Co(III)-hydrochloride and nitrate, and discuss the orientations which the complex ions take in these crystals.

Experimental

Materials.—1, 6-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$(4) was prepared by the method of Werner.(5) The crystals obtained were green tablets on {001} bounded laterally by {110} (Fig. 1). These belong to the monoclinic system and exhibit extinction in the direction of the *b*- and the *a*-axis. The crystal shows marked dichroism in the above two directions, *i. e.*, blue by polarized light with electric vector parallel to the *a*-axis and yellow with a slight tint of green by that parallel to the *b*-axis. Analysis of the crystal structure has not been performed as yet. In this work dichroism measurement was made with microcrystals by light polarized in the above two directions.



(a) (b)

Fig. 1.—A modification of the crystal usually obtained: (a) praseo-hydrochloride dihydrate, (b) praseo-nitrate.

1, 6-$[Co(en)_2Cl_2]NO_3$ was prepared as green monoclinic crystals by adding concentrated nitric acid to the concentrated aqueous solution of the hydrochloride, acidified with hydrochloric acid. The crystals usually obtained are elongated in the *c*-direction, bounded by prism faces of {010} and {110} type. Very slight dichroism, as compared with the hydrochloride, can be observed in most faces, and the most distinct dichroism is found in {010}, *i. e.*, green by polarized light with electric vector parallel to the plane formed by the *a*- and the *b*-axis and greenish blue by that perpendicular to it. Dichroism measurement was made in that face by polarized light with electric vector in the above two directions. A little less distinct dichroism of a similar nature can be seen in {110}. Dichroism is discerned only slightly in {001} and {100}. The crystal structure has not been determined as yet.

Quantitative Dichroism Measurement.—The microscopic method(1), (6) was applied. The measurements were made with microcrystals of the respective salts by polarized light in the region covering about 7500 Å. to nearly 2000 Å. The crystals used in the measurements were several hundredths of mm. thick. The *b*- or *a*-absorption in Fig. 2 for the hydrochloride represents, respectively, absorption by polarized light with electric vector parallel to the *b*- or *a*-axis. ∥- or ⊥-absorption in Fig. 3 for the nitrate represents absorption by polarized light with electric vector parallel or perpendicular to the plane formed by the *a*-

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(1) R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds," Zoshindo, Osaka Japan (1944), (in Japanese).

(2) R. Tsuchida, S. Yamada and H. Yoneda, *J. Chem. Soc. Japan*, **69**, 145 (1948), (in Japanese).

(3) (a) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1579 (1951); (b) This Bulletin, **24**, 125 (1951).

(4) en represents ethylenediamine molecule.

(5) A. Werner, *Ber.*, **34**, 1733 (1901).

(6) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 (1951).

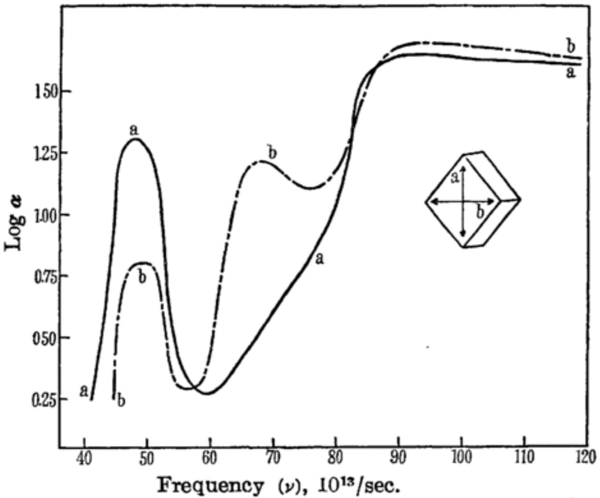

Fig. 2.—Dichroism of 1,6-$[Co(en)_2Cl_2]Cl\cdot HCl\cdot 2H_2O$.

and the *b*-axis. α denotes absorption coefficient per mm. of the crystal. Results of the measurements are shown in the figures 2 and 3, and summarized in Table 1.

Discussion

The Orientation of the Complex Ions in the Crystal of the Hydrochloride.—As is seen in Fig. 2, *b*- and *a*-absorption of the hydrochloride are quite different from each other. The difference between them is so large, as compared with that for planar complexes with four ligands, which was formerly determined,(6) that it may be inferred that all the complex ions take the same, at least almost the same, disposition in the crystal of this compound, since otherwise the crystal would not exhibit such a large difference between each of the absorptions. In the following, we shall discuss the orientations which the complex ions take in the crystal of the hydrochloride.

As to the first absorption band, a great difference in the extinction coefficient at the absorption maximum is observed between *a*- and *b*-abrorption, which we shall consider below. The transition probability in a certain direction for the first absorption band of a complex ion, which is considered as due to an electronic transition in an unsaturated transition shell,(7) can be, in general, supposed to be influenced most strongly by the ligands in that direction. On the basis of the above assumption the present authors found that there exists what we call "the hyperchromic series of ligands" which represents the decreasing order as to their effects on magnitude of molar extinction coefficient of a complex ion at an absorption maximum of its first absorption band.(8) In case of such a complex ion as 1,6-$[Co(en)_2Cl_2]^+$, it is reasonable to suppose that the effect of ligands on transition probability for the first band in the direction connecting the central Co atom with two Cl atoms is quite different from that in the direction perpendicular to the above, *i.e.*, in the plane containing one Co and four N atoms of two ethylenediamine molecules around the central Co atom. Since ethylenediamine stands much higher in the hyperchromic series than Cl^-, it is supposed that the extinction coefficient of the first band is much larger for the absorption by polarized light with electlic vector in the en-Co-en plane than for that by polarized light with electric vector in the direction of the straight line, Cl-Co-Cl.

Thus, it is presumed that *a*-absorption in Fig. 2 corresponds to the absorption by polarized light with electric vector parallel to the en-Co-en plane, that the *b*-absorption corresponds to that by polarized light with electric vector in the Cl-Co-Cl direction, and, therefore, that in the crystal of the hydrochloride the line connecting Co at the center of a complex ion with two Cl atoms is parallel to the *b*-axis and that the plane containing Co and four N atoms of ethylenediamine molecules around Co is perpendicular to the *b*-axis of the crystal.

As to the second absorption band, a great difference in intensity as well as in the wave length at absorption maximum can be found between *a*- and *b*-absorption. In the same way as for the first band, the effect of ligands on the second absorption band is expected to be different in the en-Co-en plane from that in the direction of the straight line binding one Co and two Cl atoms. As for the order in hypsochromic effects of ligands on the second absorption band of metallic complexes, there have been known "the spectrochemical series,"(7) in which Cl stands much lower than ethylenediamine, meaning that Cl, as a ligand, has much more bathochromic effect on the second band of a complex than en. Therefore, it is suggested that the second absorption band by polarized light with electric vector in the direction of the line, Cl-Co-Cl, lies in the region of a considerably longer wave length than that

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(7) R. Tsuchida, This Bulletin, **13**, 388, 436 (1938).

(8) The report dealing with the subject will be submitted later.

perpendicular to the above, and, in consequence that the former corresponds to *b*-absorption and that the latter corresponds to *a*-absorption in Fig. 2.

From the foregoing discussion on the first and the second absorption band, it is inferred that all the complex ions take the same or at least almost the same disposition to the crystal axes in the crystal of the hydrochloride, that the straight line connecting Co and two Cl atoms is parallel to the *b*-axis, and that the plane containing Co and four N atoms of the two ethylenediamine molecules coincides with the plane formed by the *a*- and the *c*-axis.

Thus it is found that the dichroism of the praseo-hydrochloride in Fig. 2 represents that for the single ion, 1, 6-$[Co(en)_2Cl_2]^+$ (Table 1). The dichroism of the single ion, as determined above, is in good accordance with the regularity as to the dichroism for the first and the second band of *trans*-disubstituted complex ions.(9) The fact that the nature of the dichroism for the first absorption band differs considerably from that for the second band suggests that the origins for those bands are different from each other. It was formerly stated(10) that extinction coefficients at absorption maxima of the first and the second band for complexes of some metals had almost equal magnitude, and it has been insisted that this is one of the principal grounds for the hypothesis that the first and the second band originate from similar transitions of electrons of the same kind. It is quite clear, however, that extinction coefficients at the absorption maxima of the first and the second band for the praseo-ion have remarkably different magnitudes in both the absorptions (Table 1) and that the two bands should be attributed to the electronic transitions of different kinds which are not related directly to each other.

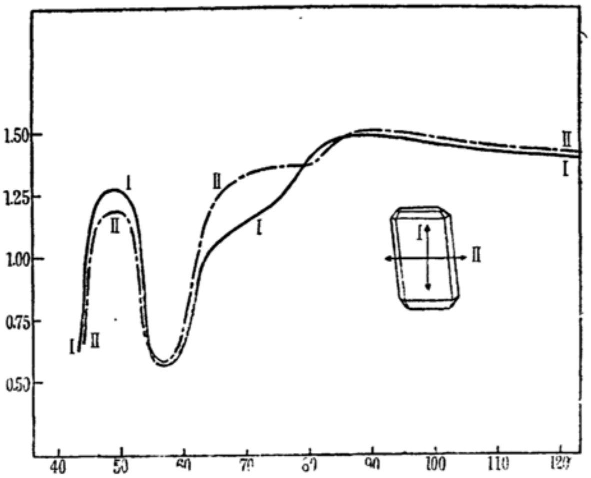

Fig. 3.—Dichroism of 1, 6-$[Co(en)_2Cl_2]NO_3$.

Arrangement of the Complex Ions in the Crystal of the Praseo-nitrate and its Comparison with that of the Hydrochloride.

—Since the dichroism for the crystal of the nitrate is found to be very slight as compared with that of the single praseo-complex ion, which has been determined from the dichroism measurement with the crystal of the hydrochloride, it must be presumed either that the complex ions in the crystal of the nitrate take considerably different orientations to one another, marked dichroism of single ions compensating for one another to such an extent that only a little dichroism is left in the crystal of the nitrate, or that the complex ions, all of which have the same orientations with refer-

Table 1

Absorption Maxima of Co(III)-Praseo-Ion

	1st Band		2nd Band		3rd Band	
Crystal	ν_{max}	log α_{max}	ν_{max}	log α_{max}	ν_{max}	log α_{max}
Cl-Co-Cl	48.7	0.80	68.0	1.21	flat	1.70
en-Co-en	48.0	1.30	(75)	—	flat	1.65
Solution(a)	ν_{max}	log ε_{max}	ν_{max}	log ε_{max}	ν_{max}	log ε_{max}
	48.0	1.54	66.7	1.41	119.0	4.31
			78.9	1.64		

(a) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950). This measurement was made with Methanol-H_2O solution of praseo-chloride.

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(9) Detailed report on the subject will be submitted later.

(10) K. Sone, *J. Chem. Soc. Japan*, **71**, 316 (1950), (in Japanese).

ence to the crystal axes, make considerably large angles to all of the three crystal axes so that absorption spectra in respective directions are not so distinctive as in the case of hydrochloride. In the same way as in the case of hydrochloride and on the basis of the results obtained in that case, the orientation of the complex ions in the nitrate can be inferred from observations as to the dichroism in some faces. Thus, by comparing the dichroism in {010} of the crystal of the nitrate with that of the single praseo-ion (Fig. 3), it is presumed that the en-Co-en plane of the praseo-complex ion in the crystal is, on the average, inclined at an angle considerably larger than 45° to the plane formed by the *a*- and the *b*-axis. Similarly, since the crystal does not exhibit distinct dichroism in {001}, showing only a little more greenish tone by polarized light with electric vector parallel to the *b*-axis than by polarized light perpendicular to it, it is supposed that the straight line, Cl-Co-Cl, in the complex ions makes to the *b*-axis an angle a little smaller than 45°, when viewed perpendicularly to the *ba*-plane. It is also suggested by comparing the nature of dichroism in {100} with that of the single complex ion that the straight line, Cl-Co-Cl, is, on the average, inclined to the *b*-axis at an angle only a little less than 45° when viewed perpendicularly to the *bc*-plane.

It seems that the complex ions are not usually arranged more disorderly in the crystal of the nitrate which contains planar nitrate ions than in the crystal of the hydrochloride with spherical chlorine ions instead of planar nitrate ions. Taking into consideration the fact that the crystal of the praseo-hydrochloride undergoes decomposition in the air at room temperature to give away one molecule of hydrogen chloride, it is suggested that the molecule of crystallization, HCl, plays an important part in holding the complex ions together so that all the complex ions take the same or at least almost the same orientation with their en-Co-en planes parallel to the *ac*-plane. This seems to be closely related to the fact that the violeo-salt in solution acidified with hydrochloric acid is readily changed into the praseo-salt and that the hydrochloride has not been found for the violeo-series whereas it is found for the praseo-series.

Summary

The dichroisms of 1, 6-$[Co(en)_2Cl_2]Cl\cdot HCl\cdot 2H_2O$ and of 1, 6-$[Co(en)_2Cl_2]NO_3$ have been measured by the microscopic method. From consideration of the results, it has been presumed that, in the crystal of the hydrochloride, the line connecting Co with two Cl atoms is almost parallel to the *b*-axis, that the plane containing one Co and four N atoms of two ethylenediamine molecules around Co is almost parallel to the plane formed by the *a*- and the *c*-axis. The nature of absorption bands of metallic complexes has been discussed on the basis of dichroism for the single praseo-ion, which has been determined from the above assumption. Arrangement of the complex ions in the nitrate has been inferred from observations as to the nature of dichroism in several faces. From comparison of the crystal structures of the two compounds and consideration of other properties, it has been suggested that the HCl molecule of crystallization in the crystal of the hydrochloride plays an important part in holding the complex ions together so that all the complex ions take the same orientation.

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