# *Spectrochemical Study of Microscopic Crystals. VII.*[1] *Absorption Spectra of Trans-dihalogeno-bis (ethylenediamine)-cobalt (III) Complexes*

By Shoichiro YAMADA, Akitsugu NAKAHARA, Yoichi SHIMURA and Ryutaro TSUCHIDA

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In the former paper of this series[2] the present authors reported on the dichroism of the crystal of *trans*-dichloro-bis-(ethylenediamine) cobalt (III) salts. One of the conclusions therein, concerning the way of arrangement of the complex cations in the crystal of the hydrochloride dihydrate was found to be in disagreement with the result of X-ray investigation performed subsequently by one of the present authors.[3] The interpretation on the absorption bands of the praseo-salts in the previous paper was found to be in a dequate. We have, therefore, repeated the dichroism measurement of the hydrochloride and further measured the

1) Part VI, S. Yamada and R. Tsuchida, This Bulletin, 27, 436 (1954).
2) S. Yamada and R. Tsuchida, ibid., 25, 127 (1952).
3) A. Nakahara, Y. Saito and H. Kuroya, ibid., 25, 331 (1952).

dichroism with crystals of *trans*-dichloro-bis (ethylenediamine)-cobalt (III) perchlorate and the hydrobromide of *trans*-dibromo-bis (ethylenediamine)-cobalt (III) bromide. In this paper we present the results of the above measurements and discuss the results on the basis of the revised interpretation about the absorption bands.

## Experimental

**Materials.—Trans-dichloro-bis (ethylenediamine)-cobalt (III) perchlorate.**—Green crystals were prepared according to the direction of Linhard et al.[4] These crystallize in rhombic plates belonging to the monoclinic system. The external form and dichroism are closely similar to those of *trans*-$[Co(en)_2Cl_2]$ $Cl\cdot HCl\cdot 2H_2O$.[2,3,5] In the dominant (001)-plane, the crystal exhibits a remarkable dichroism; it appears greenish yellow with the electric vector along the b-axis and blue with that perpendicular to the b-axis. Dichroism measurements were made along these two directions.

**Trans-dibromo-bis (ethylenediamine)-cobalt (III) bromide hydrobromide dihydrate, $[Co(en)_2Br_2]Br\cdot HBr\cdot 2H_2O$.**[6]—Green crystals were prepared by the method of Jörgensen.[7] This compound crystallizes in forms similar to those of the above praseo-salts, that is, in monoclinic crystals with well-developed (001)-planes. On the c-plane the crystal shows a striking dichroism; that is, it appears brownish yellow with the electric vector along the b-axis, and green with the electric vector perpendicular to the above. Dichroism measurements were made with respect to these directions.

**Trans-dichloro-bis (ethylenediamine) cobalt (III) chloride hydrochloride dihydrate, $[Co(en)_2Cl_2]$ $Cl\cdot HCl\cdot 2H_2O$.**—The preparation and properties were reported in the former paper.[2]

**Measurements.**—Quantitative dichroism measurements were performed with a microcrystal by Tsuchida-Kobayashi's microscopic method[8] in the region covering 2400 to 7500 Å. $\alpha$ denotes absorption coefficient per mm. of a crystal. Molecular absorption coefficients, K, were estimated from the relation, $K=10\,M\alpha/\rho$, where $M$ and $\rho$ represent the formula weight of the compound and the density of the crystal, respectively.

## Results and Discussion

**Dichroism of $[Co(en)_2Cl_2]$ $Cl\cdot HCl\cdot 2H_2O$ and $[Co(en)_2Cl_2]$ $ClO_4$.**—Redetermined absorption spectra of a crystal of the hydrochloride, which differ slightly from those in the former paper,[2] are shown in Fig. 1, and data given in Table I. Results with the praseo-perchlorate are given in Fig. 2 and Table II.

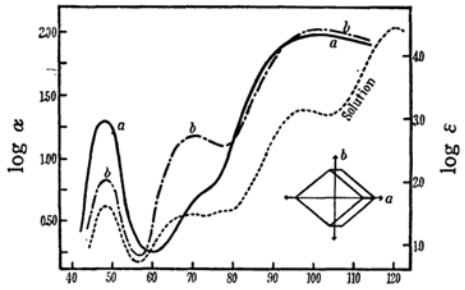


Fig. 1. Absorption spectra of $[Co(en)_2Cl_2]$ $Cl\cdot HCl\cdot 2H_2O$. The curve of the solution is taken from ref. 11.

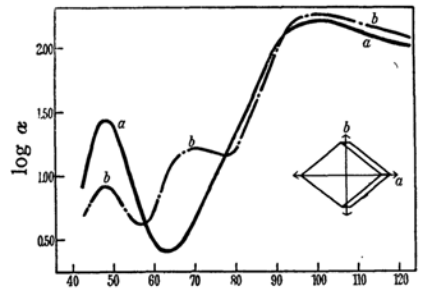


Fig. 2. Absorption spectra of $[Co(en)_2Cl_2]$ $ClO_4$.

TABLE I

ABSORPTION MAXIMA OF THE CRYSTALS OF $[Co(en)_2Cl_2]$ $Cl\cdot HCl\cdot 2H_2O$

| | $\nu$ $10^{13}$/sec. | log α | $\nu$ $10^{13}$/sec. | log α | $\nu$ $10^{13}$/sec. | log α |
|---|---|---|---|---|---|---|
| a-abs. | 48.2 | 1.29 | — | (0.65) | (100) | 1.97 |
| b-abs. | 48.3 | 0.82 | 70 | (1.18) | (102) | 2.02 |

TABLE II

ABSORPTION MAXIMA OF THE CRYSTALS OF $[Co(en)_2Cl_2]ClO_4$

| | $\nu$ $10^{13}$/sec. | log α | $\nu$ $10^{13}$/sec. | log α | $\nu$ $10^{13}$/sec. | log α |
|---|---|---|---|---|---|---|
| a-abs. | 48.0 | 1.44 | — | (0.7 ) | (100) | 2.20 |
| b-abs. | 48.1 | 0.91 | 70.8 | (1.22) | (102) | 2.25 |

In the former paper,[2] the authors presumed from the dichroism that the Cl-Co-Cl direction in the crystal of the hydrochloride should nearly conform with the b-axis.[9]

4) M. Linhard and G. Stirn, *Z. anorg. allg. Chem.*, 268, 105 (1952).

5) The notation, en, represents a molecule of ethylenediamine.

6) Two formulae have been proposed for this crystal, that is, one with two water molecules of crystallization and the other with one molecule of water. (Cf. "Gmelins Handb. anorg. Chem.", 8. Aufl., Teil 58 B, (1930) p. 252). In this paper we tentatively adopted the formula with two water molecules of crystallization, since the crystal shows a close similarity to that of $[Co(en)_2Cl_2]Cl\cdot HCl\cdot 2H_2O$.

7) S. M. Jörgensen, *J. prakt. Chem.*, (2) 41, 444 (1890).

8) R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds, (in Japanese)" Zoshindo, Osaka, Japan, (1944), p. 180. See also the previous papers of this series.

9) The a, b and c-axes adopted in the present paper and former paper (Ref. 2) correspond, respectively, to the c-, b- and a-axes in (Ref. 3).

This conclusion, however, was found to be incorrect. According to the X-ray crystal analysis with $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$,[3] the Cl-Co-Cl direction in this crystal nearly conforms with the a-axis,[9] more exactly, inclined by about 18° to the a-axis, and by 76° to the b-axis. Using the data of the X-ray analysis, the components of the molecular absorption coefficients for the praseo-complex cation in the crystal of the hydrochloride dihydrate were calculated from the data in Table I, and shown in Table III.[10] As can be seen in Table III, the absorption band at $48\times10^{13}$/sec. is polarized in the Cl-Co-Cl direction, and the absorption band at $70\times10^{13}$/sec. is polarized in the plane formed by a cobalt and four nitrogen atoms. $K_{Cl\text{-}Co\text{-}Cl}/K_{Co\text{-}en}$ is found to be 5.9 for the former band and 1/5.5 for the latter band.

Linhard et al.[11] extensively studied absorption spectra of *trans*-dihalogeno-tetrammine- and bis (ethylenediamine)-cobalt (III) complexes in solution, and showed from comparison of absorption spectra of many complexes that in the dihalogeno-complexes the "first band,"[12] which usually appears with one band maximum, splitts itself into two bands. Thus the bands at 48 and $70\times10^{13}$/sec. of the praseo-salts correspond to the first band. The band at $100\times10^{13}$/sec. may be considered as the "specific band."[13] Its second band may be covered under the large specific band.

The present measurement shows that the praseo-perchlorate in the crystalline state displays absorption bands at 48, 71 and $100\times10^{13}$/sec., which correspond with those of the hydrochloride. Corresponding bands are also observed in the absorption spectra of the solution.

It is also found that the crystal of the perchlorate shows a quite similar dichroism to that of the hydrochloride. Comparison of the dichroism and absorption spectra of both the crystals indicates that in the crystal of the perchlorate, just as in the case of the crystal of the chloride, the Cl-Co-Cl direction in the complex cation is nearly coincident with the a-axis. The angle which the Cl-Co-Cl direction makes with the a-axis in this crystal is estimated to be even a little smaller than in the crystal of the hydrochloride dihydrate.

TABLE III

DICHROISM OF THE COMPLEX-ION, *trans*-$[Co(en)_2Cl_2]^+$

| | $\nu$, $10^{13}$/sec. | $K_a$ | $K_b$ | $K_{Cl\text{-}Co\text{-}Cl}$ | $K_{Co\text{-}en}$ |
|---|---|---|---|---|---|
| Band Ia | 48 | $431\times10^3$ | $136\times10^3$ | $470\times10^3$ | $80\times10^3$ |
| Band Ib | 71 | $98.8\times10^3$ | $346\times10^3$ | $68\times10^3$ | $375\times10^3$ |

TABLE IV

ABSORPTION MAXIMA OF THE CRYSTALS OF $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$

| | $\nu$ | $\log\alpha$ | $\nu$ | $\log\alpha$ | $\nu$ | $\log\alpha$ | $\nu$ | $\log\alpha$ |
|---|---|---|---|---|---|---|---|---|
| a-abs. | 44.6 | 1.47 | —— | —— | 77 | 2.18 | 98.5 | 2.22 |
| b-abs. | 45.0 | 0.77 | 65 | 1.16 | 87 | 2.13 | 103 | 2.27 |
| | | $\log\varepsilon$ | | $\log\varepsilon$ | | $\log\varepsilon$ | | $\log\varepsilon$ |
| solution[a] | 45.6 | 1.73 | 65.0 | 1.49 | 84.3 | 3.35 | 103.8 | 4.34 |

a) These values are taken from ef. r12.

The band at $102\times10^{13}$/sec., which may be assigned to the "specific band,"[13] mainly due to the chlorine atoms in coordination, seems to be only slightly polarized. For this band, the Cl-Co-Cl absorption is found to be slightly bathochromic to the Co-en absorption.[14] It seems interesting enough that the hydrochloride and perchlorate crystallize in a closely similar form, in monoclinic plates with almost equal angles in the well-developed (001)-plane, showing also a quite similar dichroism, in spite of great difference in the size of the anions.

**Dichroism of the $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$.** —Results are shown in Fig. 3 and given in Table IV. The crystal shows absorption bands at 45, 65, 86 and $103\times10^{13}$/sec. These bands find corresponding bands in the absorption spectra of the solution at almost identical wave-lengths, although the intensity relation among bands is not same as that

10) Some of the values in Ref. 2 were corrected after repeated measurements. $K_{Cl\text{-}Co\text{-}Cl}$ and $K_{Co\text{-}en}$ are molecular absorption coefficients with the electric vector along the Cl-Co-Cl direction and along the plane constructed from one cobalt and four nitrogen atoms, respectively.

11) M. Linhard and M. Weigel, *Z. anorg. allg. Chem.*, **271**, 101 (1952).

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

13) R. Tsuchida, and M. Kobayashi, ibid., **13**, 471 (1938).

14) The X-Co-X-absorption, X being halogens, represents the absorption with the electric vector along the X-Co-X direction, and the Co-en-absorption the absorption with the electric vector along the plane formed by one cobalt and four nitrogen atoms.

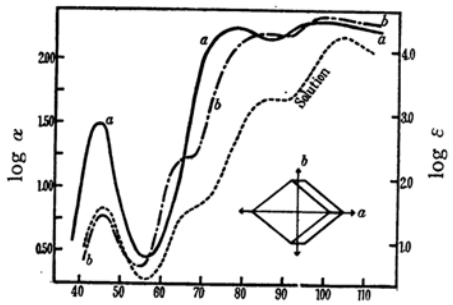


Fig. 3. Absorption spectra of $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$. The curve of the solution is taken from ref. 11.

for the solution. The first band of this compound, as in the case of the corresponding dichloro-compound, may be considered to split into two band maxima. Thus the bands at 45 and $65\times10^{13}$/sec. of $[Co(en)_2Br_2]^+$ correspond to the bands at 48 and $70\times10^{13}$/sec. of $[Co(en)_2Cl_2]^+$. It is readily seen that the cations, $[Co(en)_2Br_2]^+$ and $[Co(en)_2Cl_2]^+$, show quite similar dichroism. It may be supposed that the band at $45\times10^{13}$/sec. is almost completely polarized in the Br-Co-Br direction and that the band at $65\times10^{13}$/sec. is polarized in the plane formed by one cobalt and four nitrogen atoms. It is seen that the difference in the absorption coefficient for the band at $45\times10^{13}$/sec. between the b- and a- absorptions is even larger than that for the corresponding band with the hydrochloride of the praseo-salt. It is, therefore, most probable that the Br-Co-Br direction of the complex cations in the crystal corresponds almost exactly with the a-axis.

For the band at $70—90\times10^{13}$/sec., which may tentatively be assigned to the "specific band,"[13] mainly due to the bromine atoms in co-ordination, the Br-Co-Br-absorption[14] is bathochromic to the Co-en absorption. This relation agrees with that induced for the specific band of other ligands.[15] For the band at about $100\times10^{13}$/sec., which is assumed to be the "third band,"[12] the Br-Co-Br-absorption is slightly bathochromic to the Co-en-absorption. The relation is also found to be in good agreement with that for the corresponding band of $[Co(en)_2Cl_2]^+$.

Further, it is to be noted that $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$ appears to be isomorphous with $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$, both crystallizing in a closely similar form, monoclinic plates with nearly equal angles. Thus it is probable that in the crystals of the above two compounds the complex cations take an isomorphous arrangement, and, in consequence, that in the crystal of the latter compounds, like in the former,[16] there might exist a network of hydrogen bonds involving bromine atoms. This being the case, the compound would afford one of the few examples that would involve bromine atoms forming hydrogen bonds. The crystal structure investigation of the compound is expected to yield interesting results.

**Absorption Spectra of *Trans*-dihalogeno-bis(ethylenediamine)-compounds in the Crystalline State.**—As stated in the above paragraph, Linhard et al. showed clearly that in the solution of *trans*-dihalogeno-complexes the first band, which in most complexes appears with one band maximum, shows two separate maxima. Thus the bands at 48 and $70\times10^{13}$/sec. for $[Co(en)_2Cl_2]ClO_4$ and the bands at 45 and $65\times10^{13}$/sec. for $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$ are considered to correspond to the first band. For the first band of the *trans*-dihalogeno-complexes, the following relation can be induced. *The trans-dihalogeno-complexes show two separate absorption maxima corresponding to the first band. The absorption at the longer wave-length, polarized in the X-Co-X direction, takes place with the electric vector along the X-Co-X direction, and the absorption at the shorter wave-length occurs with the electric vector along the plane constructed from one cobalt and four nitrogen atoms.* The fact that the transition along the direction binding cobalt and halogen atoms requires much less energy much less than the transition in the plane formed by one cobalt and four nitrogen atoms may be understood qualitatively from the semi-empirical relation that halogen stands far behind ethylenediamine in the spectrochemical series;[12] the linkage between a metal and a nitrogen atom of an amine in a complex causes an electronic absorption in the shorter wave-length regions than the linkage between the metal and a halogen atom. Such a clear splitting of the first band as was observed in the above instances has not been found in many other complexes of a *trans*-configuration.[17] It may be assumed that, when two ligands in *trans*-positions stand much lower or higher in the spectrochemical series than the other four ligands, the complex would have its first band definitely split into two bands. In every *trans*-

15) To be submitted later.

16) In Ref. 3. on the crsytal structure of $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$, only the word "N-Cl bond" was used, and not any word, "hydrogen bond between N and Cl." But since the distance between N and Cl atoms is so short, 2.9 Å, that the bond is surely expected, it is reasonable to suppose that the H- atom originally attached to N of the ethylenediamine molecule should be directed toward Cl, and that the bond between the N and Cl should be a kind of hydrogen bonds.

17) To be submitted later.

disubstituted-tetrammine complex, more or less marked splitting of its first absorption band might be expected from symmetry consideration. But when the ligands in *trans*-positions stand rather close to en or $NH_3$ in the spectrochemical series, the splitting may be less distinct. Besides, the electrostatic effect of ligand ions could not be overlooked. Thus the strongly ionic character of the linkage between cobalt and chlorine atoms might be another cause for the above splitting of the band.

For both the third band and the specific band, the X-Co-X absorption is found to be slightly bathochromic to the Co-en-absorption. The relation that for the above two bands the electronic transition along the X-Co-X direction requires less energy than that along the Co-en plane may readily be understood qualitatively on the basis of the idea about the origins of the absorption bands,[12,13] proposed by one of the present authors, that the third absorption band is due to charge transfer between the central ion and a ligand anion which is especially facilitated in the case of the existence of two anions in *trans*-positions, and that the specific band is due to the ligand concerned in co-ordination.

**Absorption Spectra of the *Trans*-dihalogeno-tetrammine-complexes in Solution.**— Absorption spectra of the praseo-salts in solution may be understood in the light of the dichroism. Earlier, Mathieu[18] and one of the present authors[19] pointed out the possibility that absorption bands of sexa-co-ordinated complexes having lower symmetry might consist of a set of component absorptions, which would appear as separate maxima in some cases. Later, Ilse et al.[20] treated the absorption spectra of octahedral complexes of titanium (III) in terms of the group theory, and showed that the hexa-co-ordinated complexes of tetragonal symmetry involve more energy levels, and therefore give rise to more electronic transitions than those of octahedral symmetry. Linhard et al. showed experimentally that the *trans*-dihalogeno-complexes should have their first absorption bands split into two components and ascribed this phenomenon to the tetragonal symmetry of the complex-cations. The present dichroism measurements seem to afford an evidence for the above idea that the praseo-salts should exhibit two separate maxima corresponding to the components of their first band. Thus, of the two maxima for the first band, the one at the longer wave-length has been shown to be due principally to the transition along the Cl-Co-Cl direction, and the other at the shorter wave-length may be due to the transition along the plane formed by one cobalt and four nitrogen atoms. A small inflation at $75\times10^{13}$/sec. in the absorption spectrum of the solution of the dichloro-bis(ethylenediamine)-cobalt (III)-compound may be considered as due to the second absorption band.

Similar explanation may be applied to the absorption spectrum of the solution of dichloro-tetrammine-cobalt (III)-ion. Since the complex cation, *trans*-$[Co(NH_3)_4Cl_2]$, is unstable in solution, the conventional method is not applicable in determining the absorption spectrum of the complex. By making spectrographic analysis of the aquotization reaction, one of the present authors[21] determined the absorption spectrum of this complex cation (Table V). As in the case of the corresponding ethylenediaminecompounds, it seems reasonable to suppose that the maxima at 48 and $62\times10^{13}$/sec. correspond to the first band. Thus the band at $48\times10^{13}$/sec. may be due to the transition along the Cl-Co-Cl direction, and the one at $62\times10^{13}$/sec. may be due to the transition along the plane formed by one cobalt and four nitrogen atoms. The slight inflation at $75\times10^{13}$/sec. may be assigned as the second absorption band. The bands at 100 and $120\times10^{13}$/sec. should be assigned to the specific band and the third band, respectively.

On the basis of the foregoing discussion,

18) J. P. Mathieu, *Bull. soc. chim. France*, [5], 3, 463 (1936).
19) R. Tsuchida, *J. Chem. Soc. Japan*, 59, 586 (1938).
20) F. E. Ilse and H. Hartmann, *Z. physik. Chem.*, 197, 239 (1951).
21) R. Tsuchida, This Bulletin, 11, 721 (1936).

TABLE V

ABSORPTION MAXIMA OF *trans*-DIHALOGENO-COBALT (III) COMPLEXES IN SOLUTION

| | | 1st Band | | | | 2nd Band | | Specif. Band | | 3rd Band | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\nu$ | $\log\varepsilon$ | $\nu$ | $\log\varepsilon$ | $\nu$ | $\log\varepsilon$ | $\nu$ | $\log\varepsilon$ | $\nu$ | $\log\varepsilon$ |
| $[Co(NH_3)_4Cl_2]Cl$ | (a) | 50 | 1.21 | 62.3 | 1.41 | 77.0 | 1.40 | 100 | 3.16 | | |
| | (b) | 47.7 | 1.63 | 63.0 | 1.38 | 74.8 | 1.54 | 98.9 | 2.86 | 118.4 | 4.39 |
| $[Co(en)_2Cl_2]Cl$ | (b) | 48.4 | 1.61 | 67.5 | 1.46 | 77.8 | 1.49 | 97.5 | 3.12 | 120.8 | 4.43 |
| | (c) | 48.0 | 1.54 | 66.7 | 1.41 | 78.9 | 1.64 | — | — | 119.0 | 4.31 |
| $[CO(en)_2Br_2]Br$ | (b) | 45.6 | 1.73 | 65.1 | 1.49 | — | — | 84.3 | 3.35 | 103.8 | 4.34 |

(a) ref. 22. (b) ref. 11. (c) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

the absorption bands of the above *trans*-dihalogeno-complexes in solution may be designated as given in Table V.

The dichroism measurements should be expected to throw light upon the origins of the absorption bands of metallic complexes. Unfortunately, the second band has not been found as a separate maximum in the three compounds investigated. The investigation of the data obtained by Linhard et al.[11] indicates that the second band of the *trans*-dihalogeno-complexes appears to show no splitting, at least, none so distinct as the first band. On the other hand, the above measurements have shown that the first band splits itself into two bands. It seems, therefore, evident that the two bands, the first and second bands, should be ascribed to two transitions of different electrons. Although the decisive discussion on the origins of the first and second bands must be postponed until other materials are accumulated, the idea that the first band originates from *d*-electrons of a cobalt atom and the second band from co-ordination electrons seems to be one of the most probable.

**Summary**

Dichroism of the crystals of *trans*-$[Co(en)_2Cl_2]ClO_4$, $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ and $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$ have been quantitatively determined by Tsuchida-Kobayashi's microscopic method in the visible and ultraviolet regions.

As to the dichroism of the *trans*-dihalogeno-complexes, the following relations have been induced. The first band splits itself into two component absorptions. One at the longer wave-length is polarized in the X-Co-X direction, and the other at the shorter wave-length is polarized in the Co-en plane. For the third and specific bands, the X-Co-X-absorption is bathochromic to the Co-en-absorption.

On the basis of the above results, absorption spectra of several praseo-complexes in solution have been discussed.

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