Rotatory Dispersion of Metallic Co-ordination Compounds. I. Rotatory Dispersion in the First and the Second Absorption Bands of Cobaltic Compounds[1,2]

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In order to understand the nature of absorption bands, analyses of rotatory dispersion curves are considered to be of importance. In fact, there are a number of reports available concerning the rotatory dispersion of cobaltic complexes with ethylenediamine[3-7] but many of these studies are confined within a comparatively narrow wave-length region. Rotatory dispersion measurements over wider wave-length regions have been reported in some of the compounds, but only a very few of them have been precisely analyzed. In these circumstances, it was thought to be desirable to study more systematically the rotatory dispersion of metallic complexes on the basis of measurements in wider wave-length regions.

This paper presents rotatory dispersion measurements of optically active *cis*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride and *cis*-chloronitro-bis-(ethylenediamine)-cobalt(III) chloride in the visible and ultraviolet region, and discusses the results of the measurements in relation to their absorption spectra.

Experimental

Measurements.—A Rudolph photoelectric polarimeter 200S-80 was employed in the rotatory dispersion measurement.

The measurements were made at room temperature in the region from 666 mμ to 312 mμ using mainly the lines of the mercury spectrum: 58×10^{13}/sec. (577 mμ), 55×10^{13}/sec. (546 mμ), 68.8×10^{13}/sec. (436 mμ), 74×10^{13}/sec. (405 mμ), 82×10^{13}/sec. (365 mμ) and 89.8×10^{13}/sec. (334 mμ). A xenon-or a tungsten lamp was used occasionally.

The solvent employed was methyl alcohol for *cis*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride and 50% hydrochloric acid for *cis*-chloronitro-bis-(ethylenediamine)-cobalt(III) chloride.

In the measurements with *cis*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride, its solution was alternated with a new one at times. As *cis*-chloronitro-bis-(ethylenediamine)-cobalt (III) chloride is so unstable in solution that it is liable to undergo aquotization[8]. Therefore, its freshly prepared solution was used in each measurement. The measurements were made as rapidly as possible after preparation of the solution to keep the reactions of the complex with water at a minimum.

The concentrations for the measurements of *cis*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride were $1/3\times10^3$ F, $1/6\times10^3$ F and $1/8\times10^3$ F, and the cell lengths 20, 10 and 2 cm. For *cis*-chloronitro-bis-(ethylenediamine)-cobalt(III) chloride, the concentrations used were $1/3\times10^3$ F, $1/6\times10^3$ F and $1/8\times10^3$ F, and the cell lengths 20, 10 and 2 cm.

Material. — Racemic *cis*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride was prepared in violet crystals by the method of Werner[8] and resolved by the method of Bailar et al[9]. The preparation and the resolution of racemic *cis*-chloronitro-bis-(ethylenediamine)-cobalt(III) chloride were made according to the directions of Werner[10].

Both the optically active compounds, which were precipitated as more insoluble salts with *d*-α-bromocamphorsulphonic acid, gave positive values of optical rotation in sodium D line. According to Bailar, *cis*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride was a levo-salt and gave a negative value in sodium D line, but our and Douglas's experiments[11] have given a positive one. Thus the reagents employed in the present study may be regarded as *cis*-dextro-[Co $\mathrm{en_2Cl_2}$]Cl and *cis*-dextro-[Co $\mathrm{en_2ClNO_2}$]Cl.

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[1] R. Tsuchida, S. Yamada and J. Hidaka, Presented before the Symposium on Metallic Co-ordination Compounds, Nagoya, October, 1957.

[2] Abstracted in part from a thesis submitted by J. Hidaka to the Faculty of Science of Osaka University in partial fulfillment of the requirements for the degree of Master of Science, 1958.

[3] R. Tsuchida, *J. Chem. Soc. Japan*, (*Nippon Kwagaku Kwaisi*), **58**, 621 (1937); M. Kobayashi, ibid., **64**, 684 (1943).

[4] W. Kuhn and K. Bein, *Z. physik. Chem.*, **B24**, 355 (1934).

[5] J. P. Mathieu, *Bull. soc. chim. France*, (5) **6**, 873 (1939).

[6] J. P. Mathieu, ibid., (5) **3**, 476 (1936).

[7] J. P. Mathieu, *J. chim. phys.*, **83**, 78 (1936).

[8] A. Werner, *Ann.*, **386**, 48, 107 (1912).

[9] J. C. Bailar, Jr. and R. W. Auten, *J. Am. Chem. Soc.*, **56**, 774 (1934).

[10] A. Werner, *Ber.*, **44**, 3276 (1911); *Ann.*, **386**, 284 (1912).

[11] B. E. Douglas and W. C. Erdman, *J. Am. Chem. Soc.*, **79**, 3012 (1954).

Analyses

***Cis*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride.**—The rotatory dispersion of D-*cis*-[Co en_2Cl_2]Cl in the wave-length region from 450 mμ to 680 mμ, which has been reported by Mathieu[12], coincides with our result in this wave-length region. The first rotatory inversion in the longer wave-length side involves a positive value of the Cotton effect. Thus the molar rotations change from negative to positive values at about 636 mμ. On the other hand, the second inversion appears at about 520 mμ, and shows a negative Cotton effect.

The dispersion curve in the shorter wave-length side, as determined in the present work, was analyzed as follows. It is assumed that the observed curve is the superposition of partial rotations in the visible region and the tail of a large partial rotation which has its inversion centre in the far ultraviolet region. In the analysis of the curve, the method of trial and error was employed. The result of the analysis is shown in Fig. 1.

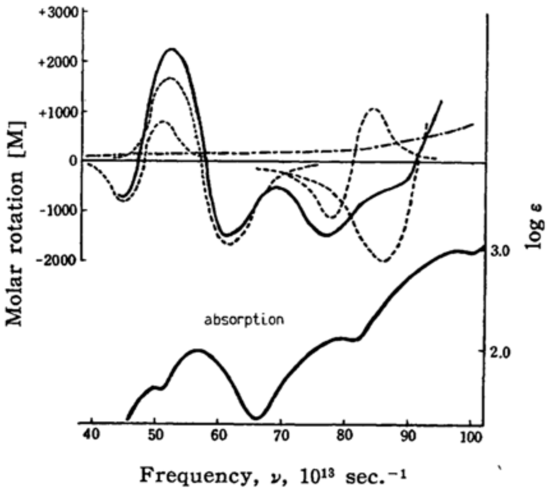

Fig. 1. Rotatory dispersion of D-*cis*-[Co en_2Cl_2]Cl in methanol: —— observed curve, ------ partial rotation obtained through analysis.

According to this result, the rotatory inversion with its centre at about 370 mμ shows a negative value of rotation in the longer wave-length side, its magnitude being almost equal to the rotatory inversion in the wave-length region of the "first absorption band". The rotatory inversion with its center at about 330 mμ is seen to give a negative value of rotation in the longer wave-length side.

***Cis*-chloronitro-bis-(ethylenediamine)-cobalt(III) chloride.**—In the wave-length region of the "first absorption band", the rotatory inversion with its center at about 544 mμ, which gives a positive value in the longer wave-length side, coincides with Mathieu's results[13] on the whole.

As the observed curve indicates, the maximal value of molar rotation in the region of the "first absorption band" is greater in the shorter wave-length side than in the longer wave-length side and the total dispersion curve is apparently displaced to the negative side. Therefore, it is assumed in the analysis of the curve that the observed curve is the superposition of the partial rotations under consideration in the visible region and the tail of a large partial rotation which has its inversion center in the far ultraviolet region. The curve was analyzed in the same way as in the former. The result of the analysis is shown in Fig. 2.

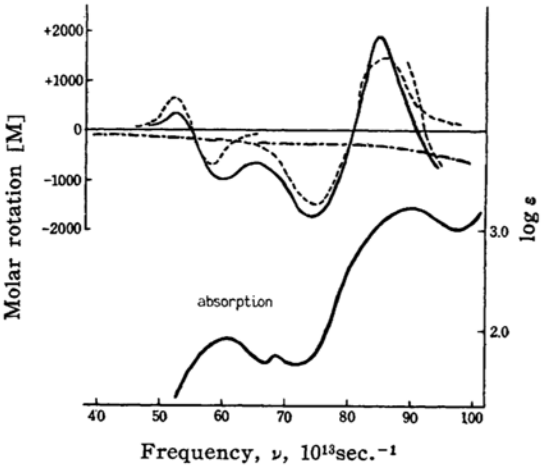

Fig. 2. Rotatory dispersion of D-*cis*-[Co en_2ClNO_2]Cl in 50% hydrochloric acid: —— observed curve, ------ partial rotation obtained through analysis.

Discussion

As described in the preceding part, the dextro-rotatory *cis*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride shows, in the wave-length region of the "first absorption band", two inversive rotatory dispersions. One of them has a positive value for the Cotton effect and the other

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[12] J. P. Mathieu, *Bull. soc. chim. France*, (5) **3**, 483 (1936).

[13] J. P. Mathieu, ibid., (5) **3**, 485 (1936).

a negative value. These may be regarded as corresponding to the two component absorptions resulting from the splitting of an original "first absorption band". In fact, the dichroism as determined in the crystalline state indicates that the violeo-salt shows two absorption bands at 51×10^{13}/sec. (588 mμ) and 57×10^{13}/sec. (527 mμ) which correspond to the component absorptions of the "first absorption band"[14]. This result is found to be in good agreement with the above described result of the present measurement.

In the wave-length region of the "first absorption band", dextro-rotatory *cis*-chloronitro-bis-(ethylenediamine)-cobalt (III) chloride shows a rotatory inversion with its center at about 55.5×10^{13}/sec. (541 mμ), a rotatory dispersion which is quite different from that of the violeo-salt. Judging from the symmetry of the complex ion, however, it is presumed that the chloronitro-salt shows separate absorption maxima corresponding to the components of the "first absorption band". In fact, the dichroism measurement indicates that the *cis*-chloronitro chloride in the crystalline state shows absorption bands at 54×10^{13}/sec. (551 mμ) and 58×10^{13}/sec. (517 mμ)[14], which may be regarded as corresponding to the first absorption band.

On the basis of the above consideration, the present observation that only one rotatory inversion appears in the wave-length region of the "first absorption band" might be understood in the following way. There would be actually two or more "rotatory inversions" which are superposed upon each other. The component absorptions are so close together that the superposition of the "rotatory inversions" gives the curve that has been experimentally determined.

A rotatory inversion at 81×10^{13}/sec. (370 mμ) for the violeo-salt and a similar sort of a rotatory inversion at about 81×10^{13}/sec. (370 mμ) for the chloronitro-salt may originate from the transitions closely related with the second absorption band. The magnitudes of both the inversive dispersions are found to be of an equal order. It is to be noted that such a type of rotatory inversion, as had previously been reported for the "first band", was observed for the "second band" as well.

Another inversive dispersion showing a Cotton effect with a negative sign is observed at about 91×10^{13}/sec. (330 mμ) for the violeo-salt. A rotatory inversion with a Cotton effect of a positive sign is also observed at an almost identical wave-length in the *cis*-chloronitro-complex. These inversions may be regarded as originating from the "specific absorption band" due to the chloride or nitro group in co-ordination with the metal.

Summarizing the results obtained in the present study, we may be able to derive the following conclusion (Table I and II.)

In the wave-length region of the "first absorption band", there appear two "inversive dispersions" due to the component absorptions, the sign of the Cotton effect for one being reverse to that for the other.

In the wave-length region of the "second absorption band", only one "inversive dispersion" is observed, its magnitude being of an identical order with that for the "first absorption band". An inversive rotatory dispersion is also observed in the wave-length region of the "specific absorption band", its magnitude being greater than that for the "first or the second absorption band".

General Discussion

As has been described in the preceding part of the present paper, optically active complex-ions such as *cis*-$[\mathrm{Co\ en_2X_2}]^+$ and *cis*-$[\mathrm{Co\ en_2XY}]^+$ show rotatory inversions corresponding to the component absorptions of the "first absorption band". Reexamining formerly reported data on the basis of the above result, complex ions may be divided into the following two groups from the nature of rotatory dispersion in the wave-length region of the "first absorption band". (1) In the first group, the sign of the Cotton effect for one component differs from that for the other, the examples of this type being *cis*-$[\mathrm{Co\ en_2Cl_2}]^+$ and *cis*-$[\mathrm{Co\ en_2ClNCS}]^+$. (2) In the second group, the sign of the Cotton effect is the same for the two components, the examples being *cis*-$[\mathrm{Co\ en_2NH_3OH_2}]^{3+}$, *cis*-$[\mathrm{Co\ en_2NH_3Br}]^{2+}$ and *cis*-$[\mathrm{Co\ en_2NH_3Cl}]^{2+}$.

Typical curves for the two types are shown in Fig. 3. The absolute configuration of optically active complexes has not been determined except for the tris-(ethylenediamine)-cobalt(III) ion[15].

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[14] S. Yamada and R. Tsuchida, to be published later.

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

TABLE I

ROTATORY DISPERSION AND UV ABSORPTION SPECTRA OF D-*cis*-[Co en_2Cl_2]Cl

		First band		Second band	Specific band
Absorption band ν_{max}	solution	49.5	57.5	79	98
	crystal	51	57		
Inverted dispersion	ν	48	57	81	91
	sign of Cotton effect	−	+	−	−
	$[M]_{max}$	750	1650	1150	

[M]: molar rotation, ν: frequency, 10^{13} sec.$^{-1}$

TABLE II

ROTATORY DISPERSION AND UV ABSORPTION SPECTRA OF D-*cis*-[Co en_2ClNO_2]Cl

		First band			Second band	Specific band
Absorption band ν_{max}	solution		60	68		89.5
	crystal	54.5	58	71		
Inverted dispersion	ν	55			81	91
	sign of Cotton effect	−			−	+
	$[M]_{max}$	600			1500	

[M]: molar rotation, ν: frequency, 10^{13} sec.$^{-1}$

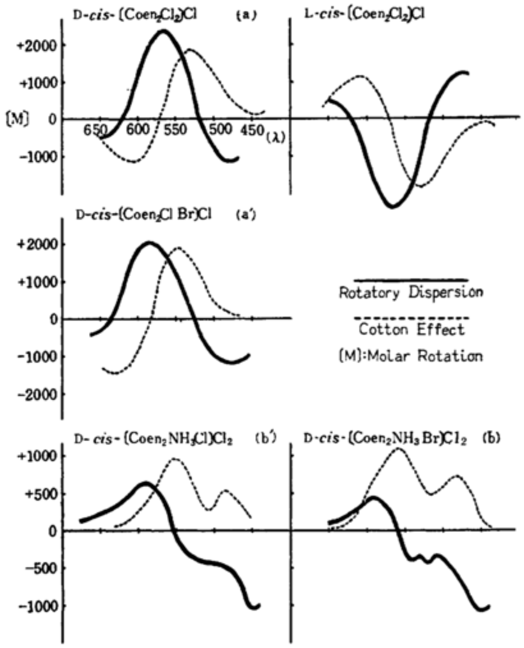

Fig. 3. Relationship between rotatory dispersion and Cotton effect. Data are taken from J. P. Mathieu, *Bull. soc. chim. France*, **3**, 476 (1936).

Making measurements of rotatory disperpersion in the longer wave-length range, Mathieu[16] suggested a possibility of determining the absolute configuration from the rotatory dispersion curves in the long wave-length range. This possibility, however, has not been fully examined up to the present. In the following, we will discuss this possibility by using the results obtained in the present study.

It has been shown in the present work that the "first absorption band" of *cis*-disubstituted-bis-(ethylenediamine)-complexes splits itself into components, each of which gives rise to a rotatory inversion of its own. If these components correspond to the same type of electronic transition in the optically active complex under consideration, the sign of the Cotton effect for these components should depend only upon the absolute configuration. Therefore, the Cotton effect may be used as a criterion for determining the absolute configuration of metallic complexes if precautions are taken.

In other words, if a comparison is made among compounds which are closely similar in the linkage involved, and consequently in the stability order of energy states of the metallic complex, we may assume that the compounds with the same type of absolute configuration would show the same sign of the Cotton effect and the same type of the rotatory inversion.

Now, if we choose complexes resembling each other in the linkage from the complexes in the group 1 or in the group 2, their absolute configuration may be determined on the basis of the sign of the Cotton effect. Thus, in the case of *cis*-[Co en_2Cl_2]$^+$ and *cis*-[Co en_2ClBr]$^+$, in which the above-mentioned requirements are satisfied, it seems possible to determine the absolute configuration.

It is seen in Fig. 3 that the diastereomer of *cis*-[Co en_2ClBr]$^+$, which forms a more

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[16] J. P. Mathieu, *J. chim. phys.*, **33**, 78 (1936).

insoluble compound with *d*-α-bromocamphorsulfonate than does the other diastereomer, shows a rotatory dispersion curve represented by the curve (a′) in Fig. 3. If we tentatively define a D-form of *cis*-$[\mathrm{Co\ en_2Cl_2}]^+$ to be the optically active form[17] related with the curve (a) in Fig. 3, it may be reasonable to assume that the former diastereomer of *cis*-$[\mathrm{Co\ en_2ClBr}]^+$ belongs to the D-series.

A similar consideration applies to the components classified as the group 2. Thus *cis*-$[\mathrm{Co\ en_2NH_3Br}]^{2+}$, *cis*-$[\mathrm{Co\ en_2NH_3Cl}]^{2+}$ and *cis*-$[\mathrm{Co\ en_2NH_3OH_2}]^{3+}$, all showing the rotatory dispersion of the type 2, closely resemble one another in the respect of the linkage involved.

It is seen in Fig. 3 that the diastereomer of *cis*-$[\mathrm{Co\ en_2NH_3Br}]^{2+}$, which forms with *d*-$\alpha$-bromocamphorsulfonate a more insoluble salt than does the corresponding salt of the other diastereomer, has the same sign for the Cotton effect as the sign possessed by the optically active form related with the curve b in Fig. 3.

If we tentatively assume that the curve b in Fig. 3 refers to the salt of the D-series, then the curve b′ may also be regarded as corresponding to the D-series.

So far, we have taken account of the rotatory behavior in the wave-length region of the "first absorption band" alone. The above discussion may be expected to become more reliable when due account is taken of the Cotton effect in the region covering the "second absorption band" as well. The discussion on this phase of the problem will be made in the succeeding papers of this series.

Summary

Rotatory dispersions in the visible and the ultraviolet region have been determined with *cis*-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl}$ and *cis*-$[\mathrm{Co\ en_2ClNO_2}]\mathrm{Cl}$, and dispersion curves have been analyzed by the method of successive approximation.

Both the complexes show two inversive dispersions in the wave-length region of the "first absorption band", and only one dispersion in the region of the "second absorption band".

The magnitude of those dispersions was found to be of the same order.

An inversive dispersion was also observed in the region of the "specific absorption band".

In the wave-length region of the "first absorption band", there appear two inversive dispersions due to the component absorptions, in accordance with the dichroism measurement. As for the inversive dispersions in the region of the "first absorption band", the sign of the Cotton effect for the one is reverse to that for the other in the violeo-salt, but in the *cis*-chloronitro-salt, the Cotton effect is the same for the two components.

A possibility of determining the absolute configuration was suggested from the rotatory dispersion curve in the wave-length region of the "first absorption band".

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[17] a diastereomer which forms with ammonium *d*-α-bromocamphorsulfonate a less easily soluble compound than does the other diastereomer of the complex salt.