

Rotatory Dispersion of Metallic Co-ordination Compounds. II. Absorption Spectra and Rotatory Dispersion of Cobalt(III) Complexes of EDTA

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It is well known that rotatory dispersion is closely related to the absorption band, and there are many reports¹⁾ concerning the rotatory dispersion of some metallic complex ions but very few on the relation between the partial "inversive dispersion" and the absorption band. In the former paper of this series²⁾, anomalous rotatory dispersion in the visible and ultraviolet region has been measured for the cobalt(III) ethylenediamine complexes, analyzed in partial "inversive dispersion" and discussed in relation to their absorption band. Furthermore, a possibility of determining the absolute configuration of the complex ion has been suggested from the viewpoint of the inversive dispersion curve in the wavelength region of the first absorption band.

In the present paper, the anomalous rotatory dispersion of $\text{D-Na}_2[\text{Co}(\text{edta})\text{NO}_2] \cdot 3\text{H}_2\text{O}$, $\text{D-K}[\text{Co}(\text{edta})] \cdot 3\text{H}_2\text{O}$ and $\text{D-K}_2[\text{Co}(\text{edta})\text{Cl}] \cdot 3\text{H}_2\text{O}$, which were recently resolved by Dwyer et al.^{3,4)}, and $\text{D-cis}[\text{Co}(\text{en}_2)(\text{NO}_2)_2]\text{I}$ will be studied in the visible and ultraviolet region in the same way as was done in the former paper²⁾.

Experimental

Measurements.—The rotatory dispersion measurements were carried out with a Rudolph photoelectric spectropolarimeter, Model 200S-80. The measurements were made in the region from 700 $\text{m}\mu$ ($42.8 \times 10^{13}/\text{sec.}$) to 365 $\text{m}\mu$ ($82 \times 10^{13}/\text{sec.}$) using mainly the lines of the mercury spectrum. A xenon or a tungsten lamp was also used when necessary. The measurements of $\text{D}[\text{Co}(\text{edta})\text{NO}_2]^{2-}$ and $\text{D}[\text{Co}(\text{edta})]^-$ were made in aqueous solutions of $1/5 \times 10^3 \text{ F}$, $1/10^3 \text{ F}$, $1/2 \times 10^3 \text{ F}$, and $1/4 \times 10^3 \text{ F}$. The solvent employed for $\text{D}[\text{Co}(\text{edta})\text{Cl}]^{2-}$ was hydrochloric acid (1:1) because this complex ion is not so stable in an aqueous solution that it undergoes aquotization rapidly. The concentration of the solu-

tion was $1/5 \times 10^2 \text{ F}$ or $1/10^3 \text{ F}$, and the measurements were made as rapidly as possible after preparation of the solution to reduce the reaction of the complex ion with water to the minimum. The concentration of $\text{D-cis}[\text{Co}(\text{en}_2)(\text{NO}_2)_2]^+$ was $1/10^3 \text{ F}$, $1/3 \times 10^3 \text{ F}$ and $1/6 \times 10^3 \text{ F}$ in aqueous solutions. The absorption measurements were made by a Beckman DU spectrophotometer. All measurements were made at room temperature.

Material.—Potassium-(ethylenediaminetetraacetato) cobalt(III) trihydrate, $\text{K}[\text{Co}(\text{edta})] \cdot 3\text{H}_2\text{O}$, was prepared in violet crystals and resolved by the method of Dwyer et al.³⁾. Optically active complex ions, $\text{D}[\text{Co}(\text{edta})]^-$, were precipitated as a more sparingly soluble salt with $\text{D}[\text{Co}(\text{en}_3)]^{3+,5)}$. The preparation and resolution of disodium nitro-(ethylenediaminetetraacetato) cobalt(III) trihydrate, $\text{Na}_2[\text{Co}(\text{edta})\text{NO}_2] \cdot 3\text{H}_2\text{O}$, and dipotassium chloro-(ethylenediaminetetraacetato) cobalt(III) trihydrate, $\text{K}_2[\text{Co}(\text{edta})\text{Cl}] \cdot 3\text{H}_2\text{O}$, were also made by the direction of Dwyer et al.⁴⁾ The D-isomer of both the complex ions was precipitated as a more sparingly soluble salt with L-cis-[$\text{Co}(\text{en}_2)(\text{NO}_2)_2$]⁺. cis-Dinitro-bis-(ethylenediamine) cobalt(III) iodide was prepared and resolved by the method of Werner⁶⁾. The D-isomer was precipitated as a more sparingly soluble salt with d-camphorsulphonic acid. These optically active complex ions gave positive value of optical rotation at green lines of a mercury spectrum, and were denoted as a D-isomer.

Results and Discussion

The rotatory dispersion and the absorption curve of $\text{D-Na}_2[\text{Co}(\text{edta})\text{NO}_2] \cdot 3\text{H}_2\text{O}$, $\text{D-K}[\text{Co}(\text{edta})] \cdot 3\text{H}_2\text{O}$, $\text{D-K}_2[\text{Co}(\text{edta})\text{Cl}] \cdot 3\text{H}_2\text{O}$ are shown in Figs. 1~3. The structures of these complex ions were well established by Dwyer⁴⁾ and other workers⁷⁾. The observed curves were analyzed on the basis of the following consideration. It is assumed that the observed curve is the superposition of the partial inversive dispersion⁸⁾ and the tail of a total dispersion which has its inversion center in the far ultraviolet

1) W. Kuhn and K. Bein, *Z. physik. Chem.*, **B24**, 355 (1943); W. Kuhn and K. Bein, *Z. anorg. allg. Chem.*, **216**, 321 (1934); J.-P. Mathieu, *J. chim. phys.*, **33**, 78 (1936); J.-P. Mathieu, *Bull. soc. chim. France*, [5] **3**, 476 (1936); R. Tsuchida, *J. Chem. Soc. Japan (Nippon Kagaku Zasshi)*, **58**, 621 (1937); M. Kobayashi, *ibid.*, **64**, 684 (1943).

2) J. Hidaka, S. Yamada and R. Tsuchida, *This Bulletin*, **31**, 921 (1958).

3) F. P. Dwyer, E. C. Gyrfas and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).

4) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1958).

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

6) A. Werner, *Ber.*, **44**, 2450 (1911).

7) D. H. Bush and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4576 (1953); G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949); M. L. Morris and D. H. Bush, *J. Am. Chem. Soc.*, **78**, 5178 (1956).

8) J.-P. Mathieu, *Compt. rend.*, **199**, 278 (1934); J.-P. Mathieu, *ibid.*, **201**, 1183 (1935); J.-P. Mathieu, *Bull. soc. chim. France*, [5] **3**, 476 (1936).

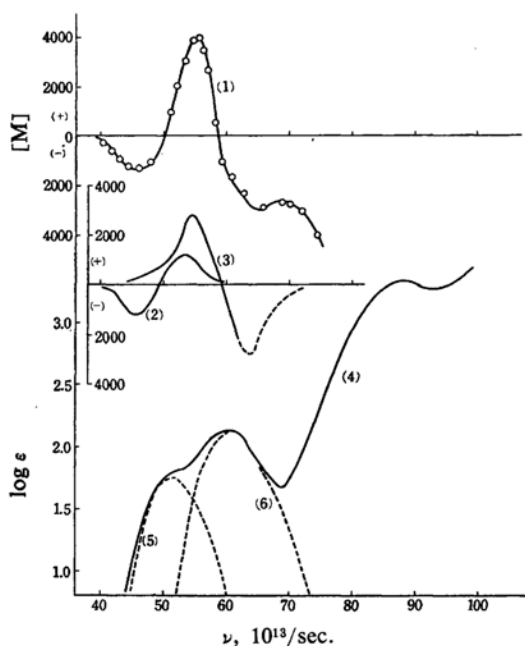


Fig. 1. Rotatory dispersion and absorption of $D\text{-Na}_2[\text{Co}(\text{edta})\text{NO}_2] \cdot 3\text{H}_2\text{O}$: 1, rotatory dispersion curve; 2—3, curve analyses of the rotatory dispersion curve; 4, absorption curve; 5—6, curve analyses of the first absorption band.

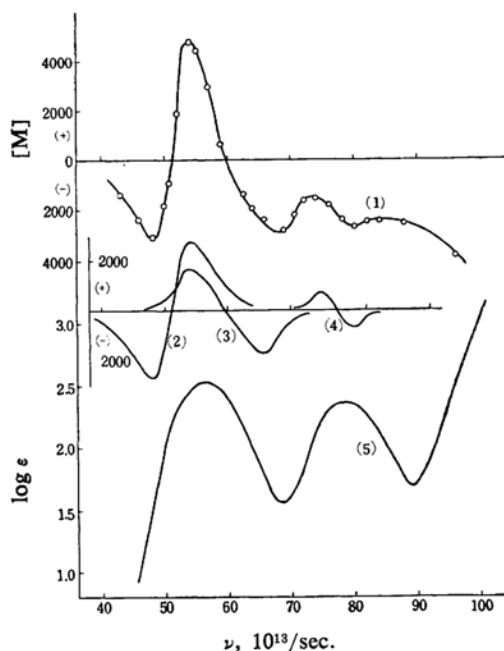


Fig. 2. Rotatory dispersion and absorption of $D\text{-K}[\text{Co}(\text{edta})] \cdot 3\text{H}_2\text{O}$: 1, rotatory dispersion curve; 2—4, curve analyses of the rotatory dispersion curve; 5, absorption curve.

region. For the analysis, the method of successive approximation was employed.

$D\text{-Na}_2[\text{Co}(\text{edta})\text{NO}_2] \cdot 3\text{H}_2\text{O}$. As is seen in Fig. 1, the observed curve indicates that total the dispersion curve is apparently displaced to the negative side on the whole. In the analysis of the curve, therefore it is assumed that the observed curve is the superposition of the partial dispersion in the visible region and the negative tail of a total dispersion concerned in the far ultraviolet region. The shape of the rotatory dispersion curve suggests that an overlapping of two inversive dispersions occurred in its first absorption band. As a result of tentative curve analysis, it was found that two inversive dispersions overlapped with each other in the visible region. The sign of the Cotton effect concerned in the first inversive dispersion is negative. Thus the molar rotation changes from negative (long wavelength side) to positive values (short wavelength side) at about $49 (\times 10^{13}/\text{sec.})$. On the other hand, the second inversive dispersion appears at about $59 (\times 10^{13}/\text{sec.})$ and shows a positive Cotton effect. The magnitudes of these two partial dispersions is found to be of the same order. The two inversive dispersions may be regarded as corresponding to the absorption band in these wavelength regions. As is shown in Fig. 1, the first absorption band of $[\text{Co}(\text{edta})\text{NO}_2]^{2-}$ distinctly splits into two components. The Ia-component is at $60.4 (\times 10^{13}/\text{sec.})$ in the shorter wavelength as compared with the first band of $[\text{Co}(\text{edta})]^{-}$, and the sub-component, Ib, is at $51.4 (\times 10^{13}/\text{sec.})$ in the long wavelength side of the first band of $[\text{Co}(\text{edta})]^{-}$. It has been reported that the center of the inversive rotatory dispersion was almost always in the longer wavelength region in comparison with the position of the absorption maximum¹⁰. In this respect, the result of the present measurements is in good agreement.

$D\text{-K}[\text{Co}(\text{edta})] \cdot 3\text{H}_2\text{O}$. The rotatory dispersion curve of $D\text{-}[\text{Co}(\text{edta})]^{-}$ is shown in Fig. 2. The total dispersion curve is apparently displaced to the negative side. This complex ion also shows two inversive dispersions in the region of the first absorption band. The one, with its center at about $51.5 (\times 10^{13}/\text{sec.})$, has a negative Cotton effect and the other, with its center at $61.0 (\times 10^{13}/\text{sec.})$, a positive Cotton effect. As is seen in Fig. 2, the first absorption band of this complex does not split. Judging from the symmetry of the complex ion, however, it is expected that its first absorption band splits into two component

9) Y. Shimura and R. Tsuchida, This Bulletin, 29, 643 (1956).

10) Y. Shimura, *ibid.*, 31, 315 (1957).

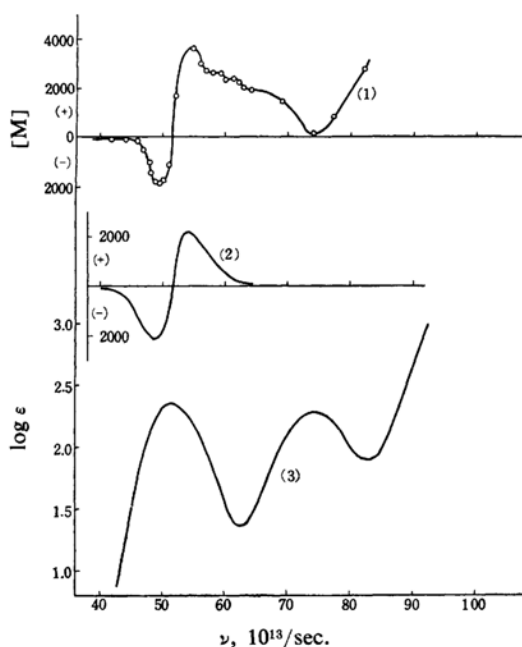


Fig. 3. Rotatory dispersion and absorption of $D\text{-K}_2[\text{Co}(\text{edta})\text{Cl}] \cdot 3\text{H}_2\text{O}$: 1, rotatory dispersion curve; 2, curve analyses of the rotatory dispersion curve; 3, absorption curve; first band, $\nu_{\text{max}} = \text{ca. } 52.0$ ($\log \epsilon_{\text{max}} = 2.35$); second band, $\text{ca. } 74.0$ (2.28).

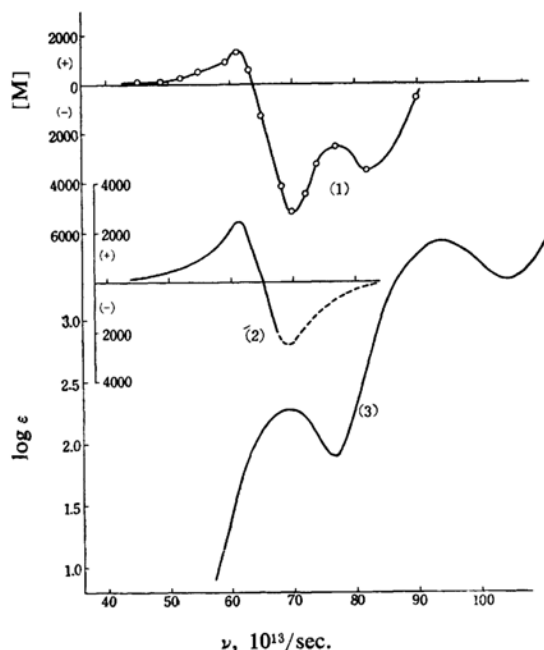


Fig. 4. Rotatory dispersion and absorption of $D\text{-cis-}[\text{Co en}_2(\text{NO}_2)_2]\text{I}$: 1, rotatory dispersion curve; 2, curve analyses of the rotatory dispersion curve; 3, absorption curve.

absorptions, Ia and Ib. It is considered, therefore, that the two inversive dispersions obtained above probably correspond to the two components of the first absorption band. The optical activity is due to the arrangement of the groups about the central cobalt atom, so the rotatory dispersion curve of complexes of similar configuration should have the same characteristic. Therefore, the similarity of the rotatory dispersion curve of $D\text{-}[\text{Co}(\text{edta})\text{-NO}_2]^{2-}$ and $D\text{-}[\text{Co}(\text{edta})]^-$ complexes, in the region of the first absorption band, shows that the two complex ions have a similar configuration. There is another small inversive dispersion with its center at about $77 (\times 10^{13}/\text{sec.})$, which probably belongs to the second absorption band.

$D\text{-K}_2[\text{Co}(\text{edta})\text{Cl}] \cdot 3\text{H}_2\text{O}$. Contrary to the preceding two complexes, the observed curve is apparently displaced to the positive side by the tail of total dispersion from the far ultraviolet side. The result of the measurement and the analysis is shown in Fig. 3. According to the analysis, the inversive dispersion of the first absorption band occurred at $51.8 (\times 10^{13}/\text{sec.})$, which has a negative Cotton effect. In the shorter wavelength side of the first absorption band at about $57\sim 63 (\times 10^{13}/\text{sec.})$, there is a small hump in the rotatory dispersion curve. This fact shows that the first absorption band has a sub-component in this region, although no evidence is observed in the absorption curve. Because this complex is not so stable toward aquotization in solutions, it was not possible to measure the rotation in the region of a wavelength shorter than $82.5 (\times 10^{13}/\text{sec.})$. However, as regards the behavior of the short wavelength end of the observed curve, it may be considered that an inversive dispersion which belongs to the second absorption band also contributes to the observed rotatory dispersion curve. From the results mentioned above for the cobalt(III) complexes of EDTA, it will easily be understood that the analysis of the rotatory dispersion curve is very useful for the study of the absorption bands, especially for the study of their splitting and overlapping.

$D\text{-cis-}[\text{Co en}_2(\text{NO}_2)_2]\text{I}$. In the region of the first absorption band, as is shown in Fig. 4, there is an inversive dispersion with its center at about $65.5 (\times 10^{13}/\text{sec.})$, which has a positive Cotton effect, and this result coincides with Methieu's¹¹. The behavior of the dispersion curve, that is that the observed curve has apparently one inversive dispersion in the region of the first band, resembles that of $D\text{-cis-}[\text{Co en}_2\text{Cl NO}_2]^+{}^{2+}$.

11) J.-P. Mathieu, *Bull. soc. chim. France*, [5] 3, 487 (1936).

This fact is considered as follows. The two components of the first absorption band, which have the positive sign of the Cotton effect, are so close together that a complete overlapping of two inversive dispersions occurred. In the shorter wavelength region, the observed value of the molar rotation is smaller. Judging from the position of the absorption maximum, it may be suggested that there begins in this region an inversive dispersion which belongs to the nitro-specific absorption band too. Similarly, on the observed curve of $D\text{-[Co(edta)NO}_2\text{]}^{2-}$, the increase of molar rotation for the negative side in the shorter wavelength end may be regarded as originating from the nitro-specific absorption band.

Summary

The rotatory dispersion measurements have been made for $D\text{-Na}_2\text{[Co(edta)NO}_2\text{]} \cdot 3\text{H}_2\text{O}$,

$D\text{-K[Co(edta)]} \cdot 3\text{H}_2\text{O}$, $D\text{-K}_2\text{[Co(edta)Cl]} \cdot 3\text{H}_2\text{O}$ and $D\text{-cis-[Co en}_2\text{(NO}_2\text{)}_2\text{]I}$. On the basis of these measurements, the relation of the splitting of the first absorption band with the so-called anomalous rotatory dispersion has been discussed. In the anomalous rotatory dispersion of $D\text{-[Co(edta)NO}_2\text{]}^{2-}$, there appear two inversive dispersions due to the component absorption, Ia and Ib, of the split first absorption band. Similarly considered, it has been shown that the first absorption band of [Co(edta)]^- or [Co(edta)Cl]^{2-} may have two component absorptions in accordance with the behavior of its rotatory dispersion curve.

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