Rotatory Dispersion of Metallic Co-ordination Compounds. III. Absorption Spectra and Rotatory Dispersion of Cobalt(III) Complexes of the $[CoN_2O_4]^-$ Type

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In a former paper of this series[1], the relation between the absorption band and the optical rotatory dispersion of D-[Co edta]$^-$ was discussed. In consequence of this study, the splitting of the first absorption band was considered to be of importance for analyses of the so-called "anomalous" rotatory dispersion curve. In order to study the above problem in more detail, the present paper deals with the absorption spectra and optical rotatory dispersion of the cobalt(III) complex ion which belongs to the general type [Co N_2O_4]$^-$, where N and O represent respectively a nitrogen and an oxygen atom of ligands attached directly to the central cobalt(III) ion.

There have been a few reports[2] concerning the preparations and the absorption spectra of the complexes of this type, besides some reports concerning Co(III)-EDTA complexes. The trend of splitting of the first absorption band of those complexes, however, has not completely been clarified up to the present. In the present paper, therefore, the absorption spectra of *cis*(N)-K [Co(ada)$_2$] $\cdot$2.5 H_2O, *trans*-(N)-K [Co(ada)$_2$] $\cdot$ 2H_2O and *cis*(N)-K [Co(ata)$\cdot$ gly] $\cdot$2 H_2O, which were newly synthesized, will be discussed, mainly in relation to the geometrical struture of the complex ions*.

Furthermore, the absorption spectra and the optical rotatory dispersion of Na [Co en ox$_2$] $\cdot$ H_2O and K [Co en malo$_2$] $\cdot$$H_2O$, which were recently resolved by Dwyer et al.[3], will be studies in the same way as was done in a former paper[1].

The absorption spectra of the complexes employed will also be considered for spin-forbidden transition bands, i. e., the so-called "A band" and "B band", in the near-infrared region.

Experimental

Preparation. — *cis(N)-K[Co(ada)$_2$]$\cdot$2.5 H_2O*. — In a solution of 7 g. adaH_2 in 40 ml. of water containing 5.5 g. of potassium hydroxide, 5 g. of cobalt chloride hexahydrate was dissolved. The mixture was cooled in an ice bath, and 15 ml. of 15% hydrogen peroxide was added drop by drop to the mixture. To complete the reaction the mixture was stirred and the desired complex gradually separated out. After being kept for several hours in a refrigerator, the reddish violet crystals deposited were separated by suction and recrystallized from a little water by the usual procedure. The crude product was contaminated by yellowish brown crystals, the solubility of which is comparatively smaller than that of the reddish violet crystals. Therefore, recrystallization was repeated to obtain the pure product.

After washing with a little ice water, ethanol and finally ether, the product was dried in the air.

Found: C, 26.40; H, 2.94; N, 7.74; H_2O, 11.15. Calcd. for $K[Co(C_4H_5O_4N)_2]\cdot 2.5\,H_2O$: C, 26.67: H, 2.79; N, 7.77; H_2O, 11.11%.

trans(N)-K[Co(ada)$_2$]$\cdot$2 H_2O.— In a solution of 3.5 g.of adaH_2 and 3 g. of potassium hydroxide in 40 ml. of water, 2 g. of cobalt chloride hexahydrate was completely dissolved. The mixture was warmed at about 80°C on a water bath and oxidized with 1 ml. of 30% hydrogen peroxide. A yellowish brown crystalline solid was then gradually deposited. The reaction mixture was cooled to room temperature and filtered by suction. An additional crude product was also obtained by boiling the filtrate on a water bath for half an hour. The yield, in total, was almost quantitative. The crude product was recrystallized from hot water and washed with ethanol and ether.

Found: C, 25.93; H, 2.83; N, 7.65; H_2O, 8.75. calcd. for $K[Co(C_4H_5O_4N)_2]\cdot 2\,H_2O$: C, 26.67; H, 2.79; N, 7.77; H_2O, 9.09%.

cis(N)-K[Co(ata)gly]$\cdot$2 H_2O. — Three grams of potassium acetate and 3 g. of glycine were dissolved in 30 ml. of warm water. To this solution 15 g. of β-K[Co(ata) (OH) (OH_2)] $\cdot$ 3 H_2O[4] was added. The solution was warmed for about 20 min. on a water bath. After removal of the insoluble substance by filtration, the reddish violet solution was allowed to cool. A large amount of ethanol was added to

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[1] J. Hidaka, Y. Shimura and R. Tsuchida, This Bulletin, **33**, 847 (1960).

[2] M. Mori, M. Shibata, E. Kyuno and T. Adachi, ibid., **29**, 883 (1956); **31**, 296 (1958).

* The sign ada represents a divalent ammoniadiacetate anion $NH(CH_2COO)_2^{2-}$ and ata, a trivalent ammoniatriacetate anion $N(CH_2COO)_3^{3-}$.

[3] F. P. Dwyer, I. K. Reid and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 1285 (1961).

[4] M. Mori, M. Shibata, E. Kyuno and Y. Okubo, This Bulletin, **31**, 940 (1958).

it, and the solution was kept overnight in a refrigerator.

The reddish violet crystals deposited were collected and recrystallized from the cooled solution by the addition of ethanol. The final product was washed with ethanol and ether.

Found: C, 26.66; H, 2.84; N, 7.77; H_2O, 9.09. Calcd. for $K[Co(C_6H_6O_6N)(C_2H_4O_2N)]\cdot 2H_2O$: C, 26.67; H, 2.79; N, 7.77; H_2O, 9.12%.

Sodium dioxalato-ethylenediamine-cobaltate(III) monohydrate, $Na[Co\ en\ ox_2]\cdot H_2O$, and potassium dimalonato-ethylenediamine-cobaltate(III) monohydrate, $K[Co\ en\ malo_2]\cdot H_2O$, were prepared in violet crystals and resolved by the method of Dwyer and his co-workers3). The optical active complex of the former was precipitated as a more sparingly soluble salt with D-$[Co\ en_2(NO_2)_2]^+$, and the latter, with L-$[Co\ en_2(NO_2)_2]^+$.

The optically active dinitro bis-ethylenediamine-cobalt(III) ion, which gives a positive value of optical rotation for green lines of mercury, has been denoted as a D-isomer. Potassium dicarbonato-diammine-cobaltate(III) monohydrate, $K[Co(NH_3)_2\cdot(CO_3)_2]\cdot H_2O$ was prepared by the method of Mori and his co-workers2).

Measurements.—The visible and ultraviolet absorption measurements were made by a Beckman DU spectrophotometer in aqueous solutions. The infrared spectra were obtained with a Parkin-Elmer model 21 (double beams) and a Hilger H-800 infrared spectrophotometer with sodium chloride prisms. The potassium bromide disk method was employed. The rotatory dispersion measurements were carried out in aqueous solutions with a Rudolph photoelectric spectropolarimeter, model 200 S-80. The concentration of the solution was 5.0×10^{-2} g. complex ion per liter.

All the measurements were made at room temperature.

Results and Discussion

Absorption Spectra.—The visible and ultraviolet absorption curves of the violet form and the brown form of bis-ammoniadiacetato-cobaltate(III) are shown in Fig. 1, in which the curve of Na[Co edta]5) is also plotted for comparison. The frequencies of the absorption maxima are summarized in Table I with other numerical data. As is seen in Fig. 1, the absorption curves of the violet form and of Na[Co edta] are similar on the whole. On the contrary, the absorption curve of the brown form differs distinctly; namely, the first absorption band I remarkably splits into two components Ia and Ib, and the second band II is shifted towards a shorter wavelength than those of the other two complexes. As will be seen in the figure, the main difference between the curves of the two isomers occurs in the region of the first band. In the absorption curve of the violet form, a component band which is smaller in intensity is recognized in the shorter wavelength side of the first band maximum, at about 58×10^{13}/sec.

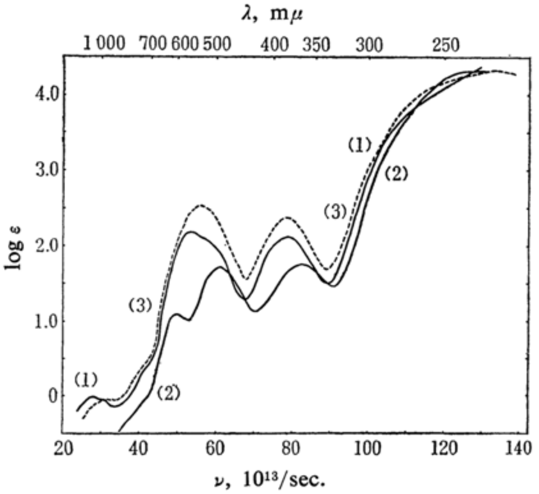

Fig. 1. Absorption spectra of:
1, *cis*(N)-$K[Co(ada)_2]\cdot 2H_2O$ (violet form)
2, *trans*(N)-$K[Co(ada)_2]\cdot 2H_2O$ (brown form)
3, $Na[Co\ edta]\cdot 4H_2O$ (dotted curve)

Judging from the symmetry of the complex ion, it can reasonably be considered that its first absorption band also splits into two components, Ia and Ib. This fact coincides with the conclusion of the analysis of the optical rotatory dispersion curve of D-K[Co edta]1) in the first absorption band. In the absorption curve of the brown form, the absorption component of the longer wavelength side is smaller in intensity than the component of the shorter wavelength side, and the difference is remarkable. From these trends in the splittings in the first absorption band, therefore, it is concluded that the violet form has one configuration in which the two nitrogen atoms occupy the cis-positions of a coordination octahedron, while the brown form has another configuration in which the two nitrogen atoms occupy trans-positions.

Some similar cases were reported by Linhard and Weigel6). Such assignments are also supported by Yamatera from semi-empirical molecular orbital calculations7).

Three geometrical isomers are possible for the complex ion, $[Co(ada)_2]^-$, as shown in Fig. 2. Two isomers of the trans(N)-form, II and III, are possible. Judging from the bond angles of a nitrogen atom of the ligand, the type suitable for the brown form may be assigned to the structure II.

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5) Y. Shimura, J. Fujita and R. Tsuchida, presented at the Symposium on Co-ordination Compounds, Fukuoka, October, 1959.

6) M. Linhard and M. Weigel, *Z anorg. Chem.*, **264**, 321 (1951).

7) H. Yamatera, This Bulletin, **31**, 95 (1958).

TABLE I. ABSORPTION DATA OF Co(III) COMPLEXES $[\mathrm{Co\,N_2O_4}]^-$ TYPE

Complex	A band $\nu_{\max}$ 10^{13}/sec. (log $\varepsilon_{\max}$)	B band $\nu_{\max}$ 10^{13}/sec. (log $\varepsilon_{\max}$)	I band* $\nu_{\max}$ 10^{13}/sec. (log $\varepsilon_{\max}$)	II band $\nu_{\max}$ 10^{13}/sec. (log $\varepsilon_{\max}$)	Spec. band $\nu_{\max}$ 10^{13}/sec. (log $\varepsilon_{\max}$)	Ref.
Na[Co edta]·4 H_2O	30.8($\bar{1}$.96)	ca. 43(0.4)	55.9(2.51)	78.1(2.36)	133(4.33)	5)
cis(N)-K[Co(ada)$_2$]·2.5 H_2O	28.4(0.00)*3	ca. 41(0.2)	53.4(2.18)	79.0(2.13)		
trans(N)-K[Co(ada)$_2$]·2 H_2O			Ia : 61.2(1.72) Ib : 50.0(1.06)	83.3(1.75)		
cis(N)-K[Co(ata)gly]·2 H_2O	27.3(0.07)	ca. 40(0.3)	53.0(2.35)	78.2(2.23)		
cis(N)-K[Co(NH_3)$_2$(CO_3)$_2$]·3 H_2O*2	27.3(0.64)	ca. 40(0.9)	52.2(2.24)	76.0(2.41)		
cis(N)-NH_4[Co(NH_3)$_2$ ox$_2$]·H_2O	31.2(0.02)	ca. 42(0.3)	54.0(2.04)	78.2(2.30)	128.8(4.26)	5)
Na[Co en ox$_2$]·H_2O	33.3($\bar{1}$.91)	ca. 44(0.2)	55.6(1.93)	77.9(2.12)	127.1(4.19)	
K[Co en malo$_2$]·H_2O	33.3(0.02)	ca. 43(0.2)	55.6(1.96)	77.9(2.08)		

*1 Expressed by the value of (Ia+Ib) except in the case of a trans(N)-form.

*2 Measured in saturated aq. soln. of ammonium carbonate.

*3 A sub-maximum was recognized in the shorter wavelength side : ca. 31($\bar{1}$.95).

TABLE II. ABSORPTION MAXIMUM AND INVERSIVE ROTATORY DISPERSION

Complex	ν_{abs} 10^{13}/sec. (log $\varepsilon_{\max}$)	ν_{rot} 10^{13}/sec.	Sign of Cotton effect	Degree of rotation*
Na[Co en ox$_2$]	55.6(1.93)	52	(−)	4500°
		60	(−)	1500°
K[Co en malo$_2$]	55.6(1.96)	50	(−)	4500°
		56	(+)	6000°

ν_{abs} : Absorption maximum

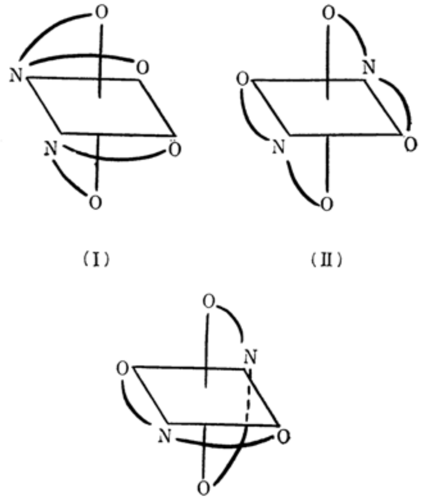
ν_{rot} : Center of inversive rotatory dispersion

* The difference between the maximum and the minimum value of the partial inversive rotatory dispersion was halved.

The absorption curves of ptassium glycinato-ammoniatriacetato-cobaltate(III) and potassium dicarbonato-diammine-cobaltate(III) are shown in Fig. 3.

As is seen in Figs. 1 and 3 and in Table I, the absorption spectra are quite similar in appearance to the absorption spectrum of the violet form of the bis-ammoniadiacetate-cobaltate(III) ion mentioned above and have a shoulder in the shorter wavelength side of the first band maximum. It is concluded, therefore, that probably these complexes also have a cis-structure involving the two nitrogen atoms of the ligands.

In Figs. 4 and 5, the absorption curves of sodium dioxalato-ethylenediamine-cobaltate(III) and potassium dimalonato-ethylenediamine-cobaltate(III) are shown with the optical rotatory dispersion curves of these complexes. The absorption curves of both the complexes are quite similar to that of Na[Co edta]. The oxalato complex involves two 5-membered chelate rings involving oxygen atoms of the ligands, while the malonato complex contains two 6-membered rings. This difference in structure was not reflected in the appearance of the absorption spectra. However, since the malonato complex is less stable than the oxalato complex in aqueous solution, no absorption spectra of the former were measured in the far ultraviolet region. As will be seen in Figs.



(I) (II) (III)

Fig. 2. The possible three geometrical isomers of $[\mathrm{Co(ada)_2}]^-$.

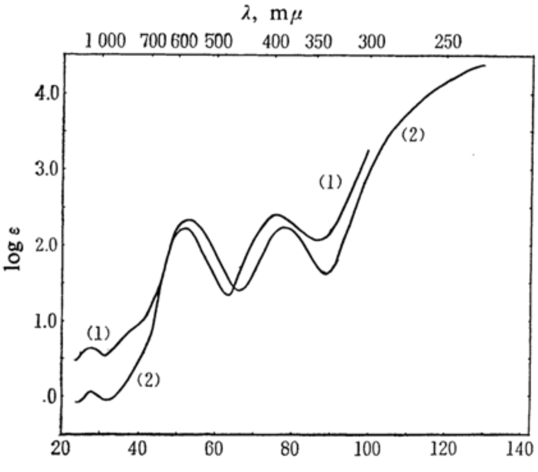


Fig. 3. Absorption spectra of:
1, *cis*(N)-$K[Co(NH_3)_2(CO_3)_2]\cdot 3\,H_2O$
2, *cis*(N)-$K[Co(ata)gly]\cdot 2\,H_2O$

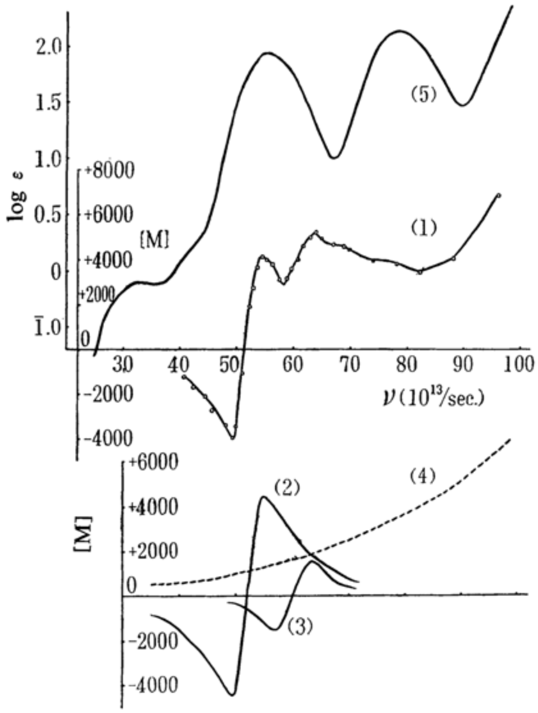


Fig. 4. Rotatory dispersion and absorption of $Na[Co\,en\,ox_2]$:
1, Rotatory dispersion curve; 2—4, Curve analyses of the rotatory dispersion curve; 5, Absorption curve.

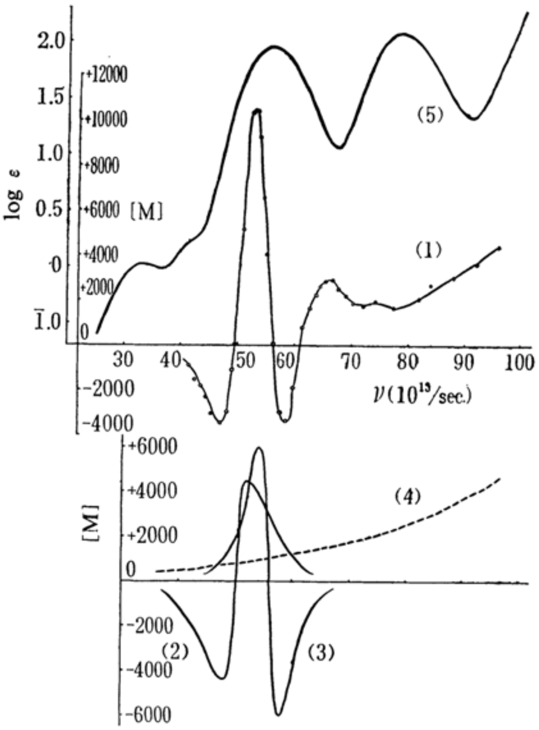


Fig. 5. Rotatory dispersion and absorption of $K[Co\,en\,malo_2]$:
1, Rotatory dispersion curve; 2—4, Curve analyses of the rotatory dispersion curve; 5, Absorption curve.

1, 3, 4 and 5 and in Table I in the present work, spin-forbidden transition bands are observed in the near-infrared region. After Linhard's notation[8], they can be described as follows: the band in the longer wavelength is the "A bond", and the one in the shorter wavelength, the "B band".

The intensity of the A or B band is found to be about hundredth as weak as that of the first band. The appearance and behavior of the A band are closely related to those of the first band[5]. Frequency differences between the first and the A bands show almost a constant value.

The shape of the A band may suggest that the band splits into some component bands, as does the first band.

The optical resolution of the potassium *cis*(N)-bis-ammoniadiacetato-cobaltate(III) complex was not studied in this work. Further studies will be carried out in the future.

Infrared Absorption Spectra. — Infrared absorption spectra of the three new complexes were measured to confirm that the carboxylate groups were coordinated. It is well known that the carboxylate group in general exhibits strong split bands in the region between 1550 and 1750 cm^{-1} for the free acids. All the spectra of the complexes studied show bands at 1625 and 1660 cm^{-1}.

It is obvious that these bands are due to

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[8] M. Linhard and M. Weigel, *Z. physik. Chem.*, *N F.*, **11**, 308 (1957).

coordinated carboxylate groups. Similar assignments have been established for some EDTA-complexes by Bush and Bailar[9].

Rotatory Dispersion.—The rotatory dispersion curves and the absorption curves of D-Na[Co en ox$_2$] and D-K[Co en malo$_2$] are shown in Figs. 4 and 5 and in Table II. The observed curves were analyzed on the basis of the following consideration: It is assumed that the observed curve is the superposition of several partial inversive dispersions[10] and a tail of normal dispersion which has its characteristic frequency in the ultraviolet region.

As is seen in the figures, both the observed curves are apparently displaced to the positive sign. Therefore, the positive tail of the normal dispersion has been presumed to be present. The rotatory dispersion behavior of D-[Co en ox$_2$]$^-$ in its first absorption band suggests that an overlapping of two inversive dispersions occurs. As a result of curve analyses, it has been shown that the observed curve I is reproduced by the overlap of curves 2, 3 and 4.

Thus, it is concluded that the first absorption band of this complex shows two inversive dispersions and that these two inversive dispersions have the negative signs of the Cotton effect equally. As was described in the preceding section, it is expected that the first absorption band of this complex splits into two components, Ia and Ib.

The two inversive dispersions above obtained, therefore, probably correspond to the two components. There is a small hump at about 75~84(10^{13}/sec.) in the rotatory dispersion.

This is similar to the hump in the second absorption band of an active trioxalato cobalt(III) complex ion which was reported by Kuhn and Bein[11]. It may be considered, therefore, that an inversive dispersion which belongs to the second absorption band also contributes to the observed rotatory dispersion.

The complex ion, D-[Co en malo$_2$]$^-$, also shows two inversive dispersions in the region of the first absorption band, as is seen in Fig. 5. In this case, however, two inversive dispersions which correspond to the two absorption components have different signs of the Cotton effect. The one in the longer wavelength has a negative sign, and the other in the shorter wavelength, a positive one, although the magnititude of these two partial dispersions has been found to be of the same order. The degree of rotation is greater in the malonato complex than in the oxalato complex.

The reason for this difference is unknown, but it may be due to the difference between the 5-membered chelate ring of a dioxalato complex ion and the 6-membered ring of a dimalonato complex ion, although no evidence for this is observed in the absorption curves. The behavior of the dispersion curve in the region of the second absorption band is similar to that of the dioxalato complex ion, and a small hump probably belongs to the second absorption band.

Summary

Three new complexes, *cis*(N)-K[Co(ada)$_2$]·2.5 H$_2$O, *trans*(N)-K[Co(ada)$_2$]·2 H$_2$O and *cis*(N)-K[Co(ata)gly]·H$_2$O, have been synthesized. The visible and the ultraviolet absorption spectra of these complexes have been measured and discussed in relation to the geometrical structures of the complex ions compared with other complexes of the [Co N$_2$O$_4$]$^-$ type. Rotatory dispersion measurements have also been made for D-Na[Co en ox$_2$] and D-K[Co en malo$_2$].

It has been shown that the so-called anomalous rotatory dispersions of these complexes are explicable by assuming the overlap of the two inversive dispersions in their first absorption bands. The slight inversive dispersions are also observed in their second absorption band.

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[9] D. H. Bush and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953); **78**, 716 (1956).

[10] 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).

[11] W. Kuhn and K. Bein, *Z. anorg. Chem.*, **216**, 321 (1934).