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Induced Circular Dichroism Spectra of Some Achiral and Racemic Cobalt(III)-Amine Complexes in Aqueous (*R*,*R*)-Tartrate and (*R*,*R*)-Tartratoantimonate(III) Solutions

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The induced circular dichroism (ICD) spectra were measured in the first d-d transition region for the following cobalt(III)–amine complexes in aqueous solutions of (*R*,*R*)-tartrate and (*R*,*R*)-tartratoantimonate(III) anions; $[Co(en)_n(NH_3)_{6-2n}]^{3+}$ (n=0—3) and *cis*-$[Co(en)_2(RNH_2)_2]^{3+}$ (R=methyl and ethyl). It was found that a single negative CD band was induced for all the complexes in (*R*,*R*)-tartrate solution, while a single positive one was induced for most of them in (*R*,*R*)-tartratoantimonate(III) solution; the ICD developed in it was composed of a single negative band for $[Co(en)_3]^{3+}$ and of two bands with opposite sign for *trans*-$[Co(en)_2(NH_3)_2]^{3+}$ and *cis*-$[Co(en)_2(EtNH_2)_2]^{3+}$. The ICD spectra obtained for racemic complexes were interpreted in terms of differential interactions of Λ- and Δ-enantiomers with (*R*,*R*)-tartrate or (*R*,*R*)-tartratoantimonate(III), and an attempt was made to correlate the sign of their ICD spectra with their chromatographic behavior on an SP-Sephadex ion-exchanger with these chiral anions as an eluent.

When a racemic or achiral metal complex is mixed with a chiral substance in solution, relatively weak circular dichroism (CD) is induced in the d-d transition region of the complex. If the racemic complex is optically labile, this phenomenon is referred to as the Pfeiffer effect and has been ascribed to a displacement of the chiral equilibrium between the enantiomers of the complex. On the other hand, CD is similarly induced even if the complex is optically stable or inherently achiral, and it is called induced circular dichroism (ICD).

Mason and Norman[1] were the first to report this phenomenon for a transition metal complex in aqueous diethyl (*R*,*R*)-tartrate. Since then, special attention has been paid to $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ to elucidate the mechanism leading to the ICD in achiral and racemic metal complexes.[2–4] In the present paper, an attempt is made to correlate the sign of the ICD spectra developed for a series of racemic cobalt(III)–amine complexes in aqueous (*R*,*R*)-tartrate and (*R*,*R*)-tartratoantimonate(III) solutions with their chromatographic behavior on an SP-Sephadex ion-exchanger with these chiral anions as an eluent.

Experimental

Preparation of the Complexes. *(1)* cis-*$[Co(en)_2(NH_3)_2]Br_3\cdot H_2O$ and* trans-*$[Co(en)_2(NH_3)_2](NO_3)_3$:* $[Co(CO_3)(en)_2]NO_3$[5] was added to concentrated nitric acid, which was then evaporated to dryness on a water bath. The resulting nitrato complex was dissolved in dimethylsulfoxide (DMSO), through which NH_3 gas was bubbled until the color of the DMSO solution changed to orange yellow. The precipitate formed by the addition of ethanol was dissolved in hot water. Less soluble *trans*-$[Co(en)_2(NH_3)_2](NO_3)_3$ was precipitated on cooling and was collected by filtration. The filtrate was loaded on an SP-Sephadex C-25 ion-exchanger and was eluted with sodium phosphate (0.05 M) to remove the *trans*-isomer completely. The addition of sodium bromide to the effluent led to the precipitation of the desired *cis*-isomer as bromide salt. Found: C; 12.05, H; 5.61, N; 32.13%. Calcd for *trans*-$[Co(en)_2(NH_3)_2](NO_3)_3$: C; 12.03, H; 5.51, N; 31.58%. Found: C; 10.32, H; 5.17, N; 17.54%. Calcd for *cis*-$[Co(en)_2(NH_3)_2]Br_3\cdot H_2O$: C; 10.20, H; 5.10, N; 17.83%. Optical resolution of the *cis*-isomer was performed after the method described in the literature.[6] The value of $\Delta\varepsilon$ at 492 nm was +0.575 and −0.561 for the Λ- and Δ-enantiomers, respectively (*cf.* 0.42 reported by McCaffery *et al.*[7]).

(2) cis-*$[Co(en)_2(RNH_2)_2](NO_3)_3$ ($R=CH_3$ and C_2H_5):* These were prepared from $[Co(CO_3)(en)_2]NO_3$ and the corresponding amines by the same method as described above. The yield of *trans*-isomers was so low that only *cis*-isomers were collected. *cis*-$[Co(en)_2(CH_3NH_2)_2]^{3+}$ was partially resolved *via* diastereomeric salt formation with *d*-α-nitrocamphoronate. Found: C, 16.78; H, 6.20; N, 29.82%. Calcd for *cis*-$[Co(en)_2(CH_3NH_2)_2](NO_3)_3$: C, 16.86; H, 6.09; N, 29.51%. Found: C, 20.25; H, 6.92; N, 26.75%. Calcd for *cis*-$[Co(en)_2(C_2H_5NH_2)_2](NO_3)_3\cdot H_2O$: C, 20.29; H, 6.77; N, 26.64%.

(3) $[Co(en)(NH_3)_4]I_3$: *trans(Cl),cis(N)*-$[Co(Cl)_2(en)(NH_3)_2]Cl$[8] was dissolved in DMSO, through which NH_3 gas was bubbled. The orange yellow crystal precipitated by the addition of ethanol was dissolved in a minimum amount of water. The iodide salt was obtained upon the addition of sodium iodide to the solution. Found: C, 4.50; H, 3.66; N, 14.84%. Calcd for $[Co(en)(NH_3)_4]I_3$: C, 4.23; H, 3.52; N, 14.79%.

(4) $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3\cdot 3H_2O$: These were prepared by well-established methods.

Chromatographic Resolution and Measurements. Chromatographic resolution of racemic complexes was carried out in the same manner as described by Kojima *et al.*[9] CD spectra were recorded on a JASCO J-40CS spectropolarimeter and ICD spectra were measured for aqueous sodium (*R*,*R*)-tartrate (0.1 M) or sodium (*R*,*R*)-tartratoantimonate(III) (0.1 M) solution containing 0.01 M of each complex. When the association constant was obtained by recording the CD intensities, the cell compartment was temperature-controlled at 25±0.2 °C.

Results and Discussion

In Figs. 1 and 2 are shown the ICD spectra obtained in the first d-d transition region for all the complexes examined in aqueous (*R*,*R*)-tartrate ((*R*,*R*)-$tart^{2-}$) and (*R*,*R*)-tartratoantimonate(III) (Sb_2(*R*,*R*)-$tart_2^{2-}$) solutions, respectively.

Achiral Complexes. The ICD spectra for achiral

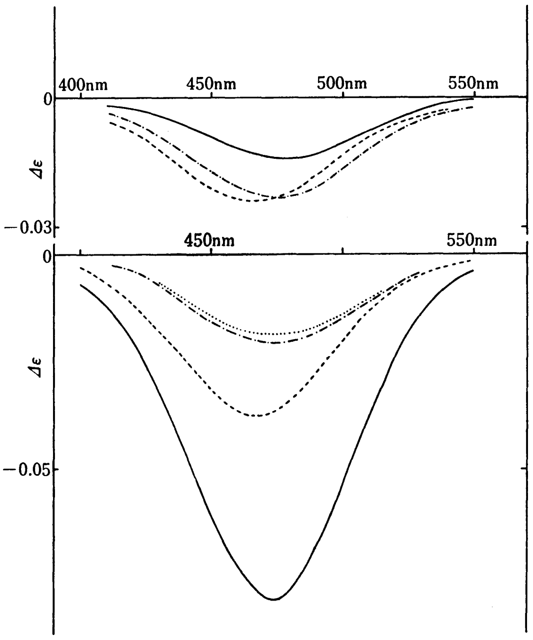

Fig. 1. ICD spectra in aqueous (*R*,*R*)-tart^{2-} solution. Upper curves; $[Co(NH_3)_6]^{3+}$(———), $[Co(en)(NH_3)_4]^{3+}$ (-·-·-), *trans*-$[Co(en)_2(NH_3)_2]^{3+}$(-----). Lower curves; *rac*-$[Co(en)_3]^{3+}$(———), *rac-cis*-$[Co(en)_2(NH_3)_2]^{3+}$(-----), *rac-cis*-$[Co(en)_2(MeNH_2)_2]^{3+}$ (-·-·-), *rac-cis*-$[Co(en)_2(EtNH_2)_2]^{3+}$ (······).

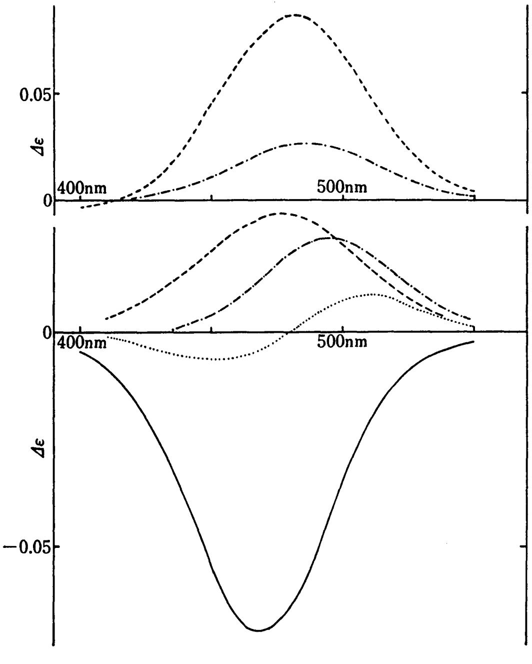

Fig. 2. ICD spectra in aqueous Sb_2(*R*,*R*)-tart$_2^{2-}$ solution. Upper curves; $[Co(en)(NH_3)_4]^{3+}$(-·-·-), *trans*-$[Co(en)_2(NH_3)_2]^{3+}$(-----). Lower curves; *rac*-$[Co(en)_3]^{3+}$(———), *rac-cis*-$[Co(en)_2(NH_3)_2]^{3+}$(-----), *rac-cis*-$[Co(en)_2(MeNH_2)_2]^{3+}$(-·-·-),*rac-cis*-$[Co(en)_2(EtNH_2)_2]^{3+}$ (······).

complexes are shown in the upper parts of Figs. 1 and 2. It is seen that, in (*R*,*R*)-tart^{2-} solution, a single negative CD band is induced, and its intensity decreases in the following order; *trans*-$[Co(en)_2(NH_3)_2]^{3+}$ $\gtrsim [Co(en)(NH_3)_4]^{3+} \gg [Co(NH_3)_6]^{3+}$. This order is tentatively ascribed to the difference in the degree of hydration of these complexes, because hydration of these amine complexes *via* their N–H groups are known to have a profound influence on their association behavior with various anions.[10] In contrast, Taniguchi *et al.*[11] reported the reversed order in acetone containing diethyl (*R*,*R*)-tartrate and interpreted it in terms of the number of N–H groups on the complexes available for hydrogen bonding with diethyl (*R*,*R*)-tartrate.

In Sb_2(*R*,*R*)-tart$_2^{2-}$ solution, on the other hand, $[Co(en)(NH_3)_4]^{3+}$ has a single positive ICD band, but *trans*-$[Co(en)_2(NH_3)_2]^{3+}$ has an additional small, negative band at the higher energy side of a dominant positive band. Since $[Co(NH_3)_6]^{3+}$ forms sparingly soluble precipitate with Sb_2(*R*,*R*)-tart$_2^{2-}$, the ICD measurement is impossible for this complex. A noteworthy fact is that the magnitude of the ICD is much greater for *trans*-$[Co(en)_2(NH_3)_2]^{3+}$ than for $[Co(en)(NH_3)_4]^{3+}$. This fact may be also interpreted in terms of the degree of hydration of these complexes and suggest some contribution to the ICD from a conformational change of en chelate rings caused by the association with Sb_2(*R*,*R*)-tart$_2^{2-}$, as Bonsnich pointed out.[12] However, it is difficult at this stage to offer precise explanation to the mechanism of the ICD developed in these achiral complexes.

Racemic Complexes. The ICD spectra for racemic complexes are shown in the lower parts of Figs. 1 and 2. In (*R*,*R*)-tart^{2-} solution, a single negative CD band is induced for all the racemic complexes just like for achiral complexes. On the other hand, different ICD patterns are developed in Sb_2(*R*,*R*)-tart$_2^{2-}$ solution; a single positive band is induced for *cis*-$[Co(en)_2(NH_3)_2]^{3+}$ and *cis*-$[Co(en)_2(MeNH_2)_2]^{3+}$, and two bands with opposite sign for *cis*-$[Co(en)_2(EtNH_2)_2]^{3+}$, but the ICD for $[Co(en)_3]^{3+}$ is composed of only a single negative band like in (*R*,*R*)-tart^{2-} solution.

It is now well known that the CD spectrum of $[Co(en)_3]^{3+}$ is appreciably affected by the addition of (*R*,*R*)-tart^{2-} [2,13] or Sb_2(*R*,*R*)-tart$_2^{2-}$;[14] the absolute intensity is decreased and increased for the E and A_2 components, respectively. Since Λ-$[Co(en)_3]^{3+}$ has positive E and negative A_2 components in the first d-d transition region, and the sign of the ICD for racemic $[Co(en)_3]^{3+}$ is negative in both (*R*,*R*)-tart^{2-} and Sb_2(*R*,*R*)-tart$_2^{2-}$ solutions, the CD change caused by the addition of these chiral anions must be greater for the Λ-enantiomer than for the Δ-enantiomer. This is easily confirmed experimentally.[14,15] If it is assumed that a greater CD change is brought about by the stronger association with (*R*,*R*)-tart^{2-} or Sb_2(*R*,*R*)-tart$_2^{2-}$, these anions are expected to have a greater affinity for Λ-$[Co(en)_3]^{3+}$. This has been actually verified by some workers.[2,14,16]

Recently a number of cationic metal complexes have been resolved on an SP-Sephadex ion-exchanger with (*R*,*R*)-tart^{2-} or Sb_2(*R*,*R*)-tart$_2^{2-}$ as an eluent. Present authors[14] and Searle[17] have explicitly evoked that the strength of ion association of metal complexes with the chiral eluent is the most important factor determining the elution order in ion exchange chromatography.

TABLE 1. ELUTION ORDER AND SIGN OF INDUCED CD

	Chromatography	Induced CD (affinity)
Na_2(*R*,*R*)-tart		
$[Co(en)_3]^{3+}$	Λ	negative (Λ)
cis-$[Co(en)_2(NH_3)_2]^{3+}$	(Λ)	negative (Λ)
cis-$[Co(en)_2(MeNH_2)_2]^{3+}$	(Λ)	negative (Λ)
cis-$[Co(en)_2(EtNH_2)_2]^{3+}$	(Λ)	negative (Λ)
Na_2Sb_2(*R*,*R*)-$tart_2$		
$[Co(en)_3]^{3+}$	Λ	negative (Λ)
cis-$[Co(en)_2(NH_3)_2]^{3+}$	Λ	positive (Δ)
cis-$[Co(en)_2(MeNH_2)_2]^{3+}$	(Δ)	positive (Δ)
cis-$[Co(en)_2(EtNH_2)_2]^{3+}$	(Δ)	positive (Δ)[a]

a) See the text.

Then, it is in principle possible to predict the elution order from the sign of the ICD spectra if the above-mentioned assumption is generally valid.

In Table 1 is summarized the sign of the ICD developed for a series of racemic complexes in (*R*,*R*)-$tart^{2-}$and Sb_2(*R*,*R*)-$tart_2^{2-}$ solutions. From the discussion presented above, negative and positive ICD corresponds to a greater affinity for the Λ- and Δ-enantiomer, respectively, as shown in the parentheses, since the Λ-enantiomers of these complexes have in common a dominant positive CD band (E component) at the longer wavelength region and its intensity is all diminished by the addition of (*R*,*R*)-$tart^{2-}$ or Sb_2(*R*,*R*)-$tart_2^{2-}$. Also listed under the heading of "chromatography" in Table 1 is the absolute configuration of the enantiomer eluted first by (*R*,*R*)-$tart^{2-}$ or Sb_2(*R*,*R*)-$tart_2^{2-}$ on an SP-Sephadex. The symbol Λ or Δ is parenthesized when the chromatographic resolution is incomplete under our experimental conditions. It is seen in Table 1 that, when (*R*,*R*)-$tart^{2-}$ is used, the resulting elution order is in complete agreement with the prediction from the sign of the ICD spectra for all the complexes.

When Sb_2(*R*,*R*)-$tart_2^{2-}$ is used, the Λ-enantiomer is eluted first for $[Co(en)_3]^{3+}$, in accord with the prediction from its ICD spectrum. Similarly the elution order for *cis*-$[Co(en)_2(MeNH_2)_2]^{3+}$ and *cis*-$[Co(en)_2(EtNH_2)_2]^{3+}$ is in agreement with the order expected from their ICD spectra, though the Δ-enantiomers are eluted first, as seen in Table 1. However, the ICD spectrum exceptionally fails to predict the elution order for *cis*-$[Co(en)_2(NH_3)_2]^{3+}$; its ICD is positive, suggesting a greater affinity of Sb_2(*R*,*R*)-$tart_2^{2-}$ for the Δ-enantiomer, but actually the Λ-enantiomer is eluted first. In order to solve this apparent discrepancy, the CD spectra of Λ- and Δ-*cis*-$[Co(en)_2(NH_3)_2]^{3+}$ were measured in water as well as in aqueous (*R*,*R*)-$tart^{2-}$ and Sb_2(*R*,*R*)-$tart_2^{2-}$ solutions, and they are shown in Figs. 3 and 4, where dotted curves correspond to the CD spectra in the presence of (*R*,*R*)-$tart^{2-}$ or Sb_2(*R*,*R*)-$tart_2^{2-}$. It is clearly seen that the CD change is greater for the Λ-enantiomer in (*R*,*R*)-$tart^{2-}$ solution, while it is greater for the Δ-enantiomer in Sb_2(*R*,*R*)-$tart_2^{2-}$ solution. Since the ICD spectrum is a simple sum of the two dotted curves, the ICD spectra of *cis*-$[Co(en)_2(NH_3)_2]^{3+}$ shown in Figs. 1 and 2 are completely reproduced here. That is to say, it is explicitly demonstrated in Figs. 3 and 4 that differential CD changes between the Λ- and Δ-enantiomers upon the addition of (*R*,*R*)-$tart^{2-}$ or Sb_2(*R*,*R*)-$tart_2^{2-}$ are responsible for the appearance of

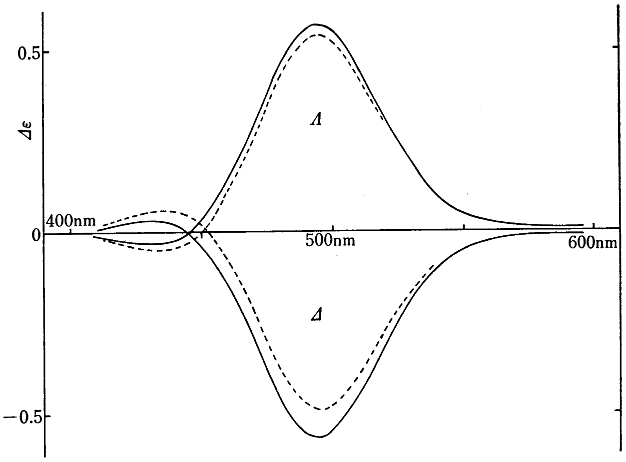

Fig. 4. CD spectra of Λ- and Δ-*cis*-$[Co(en)_2(NH_3)_2]^{3+}$ (4×10^{-3} M) in water (solid curves) and in 0.04 M aqueous Sb_2(*R*,*R*)-$tart_2^{2-}$ solution (dotted curves).

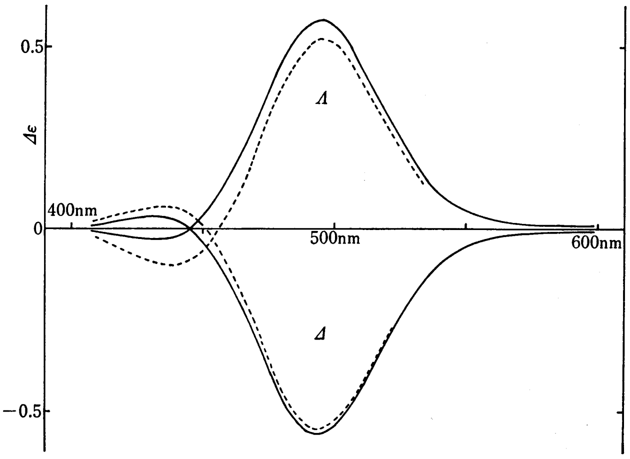

Fig. 3. CD spectra of Λ- and Δ-*cis*-$[Co(en)_2(NH_3)_2]^{3+}$(4×10^{-3} M) in water (solid curves) and in 0.04 M aqueous (*R*,*R*)-$tart^{2-}$ solution (dotted curves).

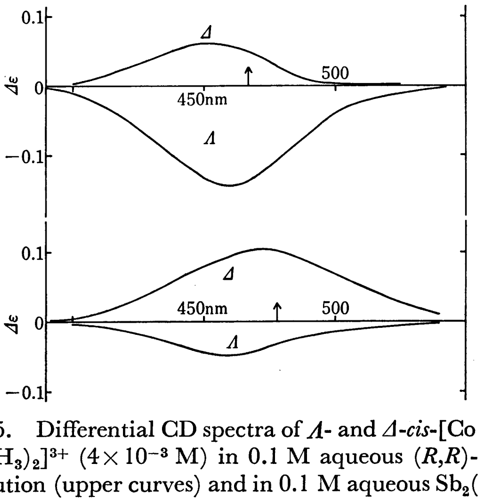

Fig. 5. Differential CD spectra of Λ- and Δ-*cis*-$[Co(en)_2(NH_3)_2]^{3+}$ (4×10^{-3} M) in 0.1 M aqueous (*R*,*R*)-$tart^{2-}$ solution (upper curves) and in 0.1 M aqueous Sb_2(*R*,*R*)-$tart_2^{2-}$ solution (lower curves).

the ICD for *cis*-$[Co(en)_2(NH_3)_2]^{3+}$. The same should hold for other racemic complexes.

This is more clearly confirmed in Fig. 5, where the difference CD spectra (the difference between the dotted and solid curves in Fig. 3 or 4) are depicted for *cis*-$[Co(en)_2(NH_3)_2]^{3+}$ both in (R,R)-$tart^{2-}$ and $Sb_2(R,R)$-$tart_2{}^{2-}$ solutions, and the position of a small arrow corresponds to the wavelength at which the ICD has a maximum intensity. It should be noted here that the difference CD spectrum of the Λ-enantiomer differs from that of the Δ-enantiomer not only in magnitude but also in pattern in both (R,R)-$tart^{2-}$ and $Sb_2(R,R)$-$tart_2{}^{2-}$ solutions. Therefore, it is concluded that both (R,R)-$tart^{2-}$ and $Sb_2(R,R)$-$tart_2{}^{2-}$ interact with one enantiomer of the complex in a different fashion from the other. The same is found true for $[Co(en)_3]^{3+}$. If the peak positions of difference CD spectra for Λ- and Δ-enantiomers differ greatly from each other, the resulting ICD spectrum is expected to have two components with opposite sign. This is probably the case with *cis*-$[Co(en)_2(EtNH_2)_2]^{3+}$ in $Sb_2(R,R)$-$tart_2{}^{2-}$ solution. Judging from the relative intensities of the two ICD components of this complex (Fig. 2), it is supposed the Δ-enantiomer is subject to a greater CD change in $Sb_2(R,R)$-$tart_2{}^{2-}$ solution, so that "positive (Δ)" is inserted in the last column of Table 1 for this complex.

Now, we have to solve one important problem why Λ-*cis*-$[Co(en)_2(NH_3)_2]^{3+}$ is eluted first by $Sb_2(R,R)$-$tart_2{}^{2-}$ on an SP-Sephadex, despite the fact that it gives rise to a greater CD change for the Δ-enantiomer, as shown in Fig. 5. For this purpose, the association constants of Λ- and Δ-*cis*-$[Co(en)_2(NH_3)_2]^{3+}$ with (R,R)-$tart^{2-}$ and $Sb_2(R,R)$-$tart_2{}^{2-}$ were obtained by measuring their CD intensities in aqueous solutions. Experimental details have been described earlier.[14] Since the CD change of *cis*-$[Co(en)_2(NH_3)_2]^{3+}$ was small as compared with that of $[Co(en)_3]^{3+}$, somewhat higher concentrations of Λ- or Δ-*cis*-$[Co(en)_2(NH_3)_2]Cl_3$ and $Na_2(R,R)$-tart or $K_2Sb_2(R,R)$-$tart_2$ had to be employed, so that sodium perchlorate was not added to adjust the ionic strength. Instead, the amounts of the complex and the chiral anion were appropriately varied to maintain a constant ionic strength. The final plots of $C_M(C_A-x)/(\Delta CD/2)$ *vs.* (C_A-x) obtained by a successive approximation[14] are shown in Fig. 6, and the derived association constant K_A and the value of molar CD change $(\Delta\varepsilon_{MA}-\Delta\varepsilon_M)$ are listed in Table 2. For comparison, the corresponding values for $[Co(en)_3]^{3+}$ obtained previously[14,16] are also given here.

It is seen in Table 2 that the association constant K_A of *cis*-$[Co(en)_2(NH_3)_2]^{3+}$ with (R,R)-$tart^{2-}$ is slightly greater for the Λ-enantiomer, in accord with the result of present chromatography that the Λ-enantiomer is eluted first by (R,R)-$tart^{2-}$, but only incomplete resolution is attained. On the other hand, the K_A value of the Λ-enantiomer with $Sb_2(R,R)$-$tart_2{}^{2-}$ is almost twice as great as that of the Δ-enantiomer. Then, it is natural that complete chromatographic resolution is effected with the Λ-enantiomer eluted first by $Sb_2(R,R)$-$tart_2{}^{2-}$. As a result, it follows that the Λ-enantiomer associates favorably with $Sb_2(R,R)$-$tart_2{}^{2-}$ in such a fashion that its CD spectrum is not appreciably affected in comparison with the Δ-enantiomer, as is indicated by the values of their molar CD change $(\Delta\varepsilon_{MA}-\Delta\varepsilon_M)$. In contrast, for $[Co(en)_3]^{3+}$, both the K_A and $(\Delta\varepsilon_{MA}-\Delta\varepsilon_M)$ values are greater for the Λ-enantiomer, so that the ICD spectra provide a correct prediction of the elution order

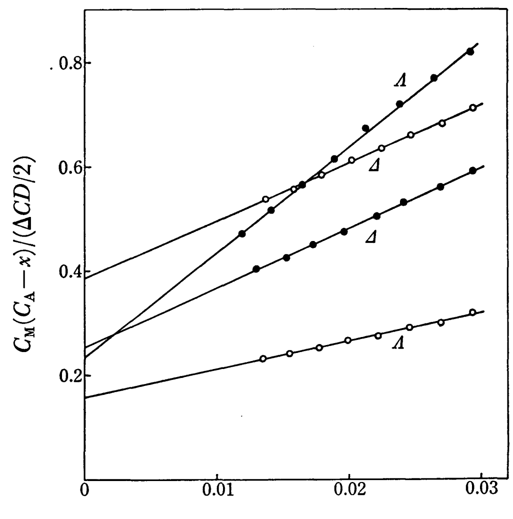

Fig. 6. Final plots of $C_M(C_A-x)/(\Delta CD/2)$ *vs.* (C_A-x) for *cis*-$[Co(en)_2(NH_3)_2]^{3+}$-(R,R)-$tart^{2-}$(○) and -Sb_2-(R,R)-$tart_2{}^{2-}$(●) system in water.

Table 2. Association constant K_A and molar CD change at 25 °C[a)]

	nm[b)]		K_A	$(\Delta\varepsilon_{MA}-\Delta\varepsilon_M)$
(R,R)-$tart^{2-}$				
cis-$[Co(en)_2(NH_3)_2]^{3+}$	446	Λ	32±1	0.192±0.005
		Δ	28±1	0.092±0.002
$[Co(en)_3]^{3+}$	430	Λ	13.0±0.1	0.85±0.01
		Δ	10.5±0.4	0.66±0.03
$Sb_2(R,R)$-$tart_2{}^{2-}$				
cis-$[Co(en)_2(NH_3)_2]^{3+}$	446	Λ	85±3	0.050±0.001
		Δ	45±1	0.088±0.001
$[Co(en)_3]^{3+}$	430	Λ	46.6±0.7	0.251±0.003
		Δ	25.6±0.9	0.197±0.006

a) Ionic strength is 0.1 adjusted by sodium perchlorate for $[Co(en)_3]^{3+}$ and is 0.08 without sodium perchlorate for *cis*-$[Co(en)_2(NH_3)_2]^{3+}$, so that the direct comparison of the two systems is almost meaningless. b) Wavelength at which CD changes were measured.

in both (R,R)-tart^{2-} and $Sb_2(R,R)$-tart$_2^{2-}$ solutions.

In this way, the ICD spectra are found useful to predict the elution order of several racemic complexes on an SP-Sephadex ion-exchanger with (R,R)-tart^{2-} or $Sb_2(R,R)$-tart$_2^{2-}$ as an eluent. Similar experiments on other metal complexes are now under way to extend the applicability of the ICD spectra to ion exchange chromatography.

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