Outer-sphere Assocation of Some Achiral Cobalt(III)-Amine Complexes as Measured by Their Induced Circular Dichroism Spectra in Aqueous (*R*,*R*)-Tartrate Solutions

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Outer-sphere association constants K_A of inherently achiral cobalt(III)–amine complexes, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(en)]^{3+}$, and *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ with (*R*,*R*)-tartrate anion (*d*-tart^{2-}) were determined by measuring their weak CD spectra induced when they were dissolved in aqueous *d*-tart^{2-} solutions at 25 °C. It was found that the K_A values are not so different among these three complexes, whereas their molar CD intensity $\Delta\varepsilon_{MX}$ gained by the association with *d*-tart^{2-} increases with increasing number of their chelate rings. This was tentatively interpreted to mean that the distortion of the Co(III)–N bonds brought about by outer-sphere association with chiral *d*-tart^{2-} is greater when bidentate ligands (en) are coordinated than when unidentate ones (NH_3) are, *i.e.*, when the complex has more chelate rings. Also it was found that the K_A value thus obtained for $[Co(NH_3)_6]^{3+}$ is much smaller than that determined by measuring the magnitude of its charge-transfer band which newly appears upon the addition of *d*-tart^{2-}. From the above finding and other experimental results, it was suggested that induced CD is well developed in these achiral amine complexes when the two hydroxyl oxygen atoms of *d*-tart^{2-} simultaneously form hydrogen-bonds with amine protons of the ligands.

It is well known that UV and CD spectra of metal complexes are subjected to a considerable change in shape and/or magnitude upon the addition of highly charged counterions in solution. The change is attributed to their outer-sphere association with added counterions, and has been utilized to investigate their outer-sphere interactions.[1)] In particular, tris(diamine)-cobalt(III) complexes have been widely studied by many workers.[1–5)] Among them, Ogino and Saito[6)] were the first to find that the association constant of $[Co(en)_3]^{3+}$ with (*R*,*R*)-tartrate anion (*d*-tart^{2-}) is different between its two enantiomers in aqueous solution, and their pioneering work initiated extensive studies[7–11)] on the discriminating interaction of chiral metal complexes with *d*-tart^{2-} in solution.

On the other hand, Mason and Norman[12)] found in 1965 that weak CD is induced for inherently achiral metal complexes like $[Co(NH_3)_6]^{3+}$ when they are dissolved in aqueous (*R*,*R*)-tartaric acid, sodium (*R*,*R*)-tartrate, or diethyl (*R*,*R*)-tartrate solution. Since then, several attempts[13–17)] have been made to elucidate the mechanisms leading to this phenomenon called induced CD (ICD) hereafter. Among several proposals made so far, outer-sphere association with the above chiral substances through hydrogen-bonding is the most plausible interpretation for the ICD of metal–amine complexes.[12–14,17,18)] If this interpretation is valid, the ICD is also applied to study the outer-sphere interaction of achiral metal–amine complexes with (*R*,*R*)-tartrate ion (*d*-tart^{2-}) in solution.

Recently, Jonas and Norden[14a)] estimated the molar ICD intensity of $[Co(NH_3)_6]^{3+}$ gained through the 1:1 association with *d*-tart^{2-} to be -1.57×10^{-2} in water at the wavelength of its maximum intensity (480 nm) by using its association constant determined by UV measurements.[10)] However, the steric requisite in the association with *d*-tart^{2-} is supposed to be severer for the induction of CD than for the development of a new charge-transfer band in achiral complexes like $[Co(NH_3)_6]^{3+}$, as already pointed out by Mason and Norman.[12)] In fact, it has been reported[10,19)] that CD measurements are apt to give somewhat smaller association constants than UV measurements, at least for the $[Co(en)_3]^{3+}$–*d*-tart^{2-} system.[20)] In the present study, the magnitude of the ICD for three achiral complexes, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(en)]^{3+}$, and *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ was measured in aqueous solutions as a function of *d*-tart^{2-} concentration, and their association constant K_A with *d*-tart^{2-} and accompanying molar ICD intensity $\Delta\varepsilon_{MX}$ were directly derived and compared with each other.

Experimental

Materials. All the complexes except $[Co(NH_3)_4(R\text{-}pn)]Cl_3$ and $[Co(NH_3)_4(tn)]Cl_3\cdot H_2O$ were prepared in the same manner as before[21)] and when necessary, they were converted to appropriate salts by ion-exchange techniques. The two tetraammine-complexes were prepared after the methods[22,23)] described in the literature. They were identified by their UV and/or CD spectra. Other chemicals used were of reagent grade.

Measurements. Induced CD spectra were recorded on a JASCO J-40CS spectropolarimeter for aqueous solutions of each complex (8.0×10^{-3} mol dm^{-3}) containing varying amounts of sodium (*R*,*R*)-tartrate (*d*-tart^{2-}), diethyl (*R*,*R*)-tartrate, or (*R*,*R*)-tartaric acid up to 3.0 mol dm^{-3}.

To obtain the association constant from the ICD spectra, the ICD magnitudes were measured at 25 °C for aqueous solutions containing sodium (*R*,*R*)-tartrate or sodium (*R*,*R*)-tartratoantimonate(III) (Sb_2d-tart$_2^{2-}$) ranging in concentration from 0.08 to 0.15 mol dm^{-3} or from 0.05 to 0.1 mol dm^{-3}, respectively. The concentration of each complex (chloride salt) was kept constant: 8.0×10^{-3} mol dm^{-3} in *d*-tart^{2-} and 7.0×10^{-3} mol dm^{-3} in Sb_2d-tart$_2^{2-}$ solutions. The ionic strength μ was adjusted with NaCl. The pH value of sample solutions thus prepared was around 7 for *d*-tart^{2-} and 4 to 5 for Sb_2d-tart$_2^{2-}$. For the determination of the association constant by UV measurements,[6,10,19)] the same experimental conditions as above were adopted except that $NaClO_4$ was added to adjust the ionic strength and perchlorate salts of respective complexes were used in place of the chloride salts.

Results and Discussion

Comparison of ICD Magnitudes. In Fig. 1 are shown the induced CD (ICD) spectra reported previously[21] in the first d-d transition region for $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(en)]^{3+}$, and *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ (0.01 mol dm^{-3} for each) in aqueous Na$_2$*d*-tart and Na$_2$Sb$_2$*d*-tart$_2$ solutions (0.1 mol dm^{-3}) together with that for $[Co(NH_3)_4(tn)]^{3+}$ in *d*-tart^{2-} solution. It is evident that the ICD magnitude increases in the following order in *d*-tart^{2-} solutions; $[Co(NH_3)_6]^{3+} \ll [Co(NH_3)_4(en)]^{3+} <$ *trans*-$[Co(NH_3)_2(en)_2]^{3+}$. In contrast, Taniguchi *et al.*[18] found the reversed order in acetone containing diethyl (*R*,*R*)-tartrate (*ca.* 5 mol dm^{-3}). However, direct comparison between their results and ours is meaningless, since the concentration of *d*-tart^{2-} employed in our experiments is much lower. Then, the ICD magnitude was measured as a function of the concentration of the two chiral substances, Na$_2$*d*-tart and diethyl (*R*,*R*)-tartrate up to 3 mol dm^{-3} in aqueous solutions. For comparison, the ICD magnitude was also measured in aqueous (*R*,*R*)-tartaric acid solutions.

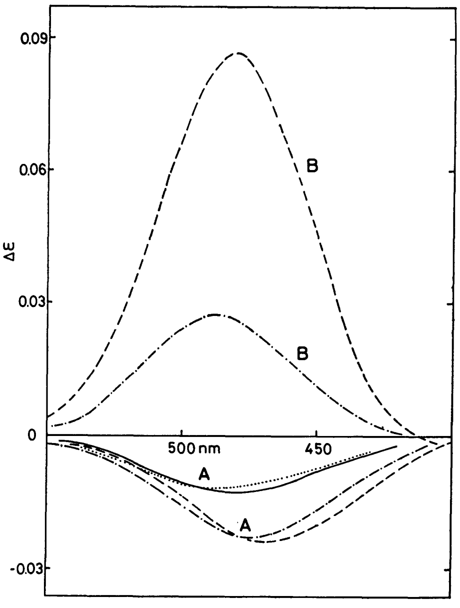

Fig. 1. Induced CD spectra for $[Co(NH_3)_6]^{3+}$(——), $[Co(NH_3)_4(en)]^{3+}$ (–·–·–), *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ (– – –), and $[Co(NH_3)_4(tn)]^{3+}$ (······) in aqueous *d*-tart^{2-} (A) and Sb$_2$*d*-tart$_2$$^{2-}$ (B) solutions.

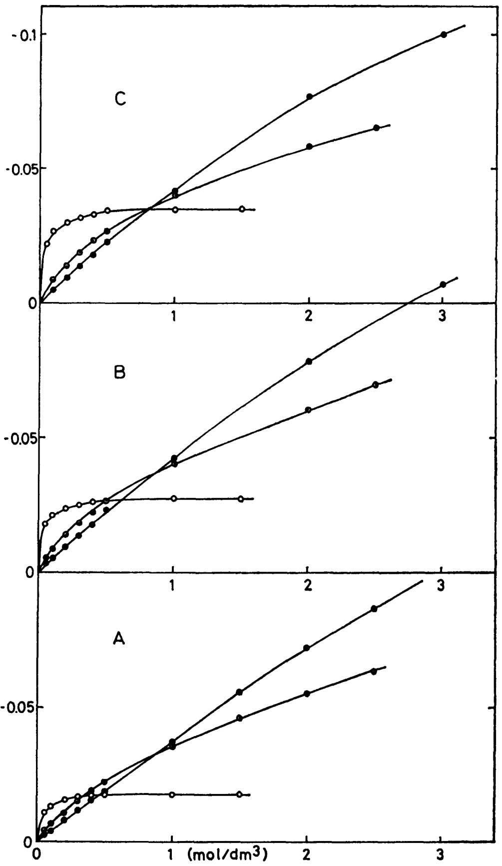

Fig. 2. Plots of the ICD magnitude for $[Co(NH_3)_6]^{3+}$ (A), $[Co(NH_3)_4(en)]^{3+}$(B), and *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ (C) at the wavelength of the maximum intensity against the concentration of sodium (*R*,*R*)-tartrate (○), diethyl (*R*,*R*)-tartrate (●), and (*R*,*R*)-tartaric acid (⊙) in aqueous solutions.

In Fig. 2 are plotted the ICD magnitudes obtained for $[Co(NH_3)_6]^{3+}$ (A), $[Co(NH_3)_4(en)]^{3+}$ (B), and *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ (C) (8×10^{-3} mol dm^{-3} for each) at the wavelength of their maximum intensity (478, 474, and 466 nm, respectively) against the concentration of Na$_2$*d*-tart, diethyl (*R*,*R*)-tartrate, and (*R*,*R*)-tartaric acid. When their concentration is low (below *ca.* 0.3 mol dm^{-3}), the ICD magnitude is greatest in *d*-tart^{2-} solutions for all the complexes and it increases in the following order $[Co(NH_3)_6]^{3+} < [Co(NH_3)_4(en)]^{3+} <$ *trans*-$[Co(NH_3)_2(en)_2]^{3+}$, irrespective of the kind of the chiral substances added. This order is in agreement with the increasing order of en chelate rings in the complexes. However, the ICD magnitude in *d*-tart^{2-} solutions gradually ceases to increase with *d*-tart^{2-} concentration and it finally becomes constant above *ca.* 0.5 mol dm^{-3}, the limiting ICD magnitude being -1.8×10^{-2}, -2.7×10^{-2}, and -3.5×10^{-2} for $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(en)]^{3+}$, and *trans*-$[Co(NH_3)_2(en)_2]^{3+}$, respectively. This indicates that no free complex (not associated with *d*-tart^{2-}) exists in such high *d*-tart^{2-} concentration ranges. On the contrary, the ICD magnitude gained in diethyl (*R*,*R*)-tartrate and (*R*,*R*)-tartaric acid solutions keeps increasing even at 3 mol dm^{-3}. These facts imply that the interaction of these cationic complexes with *d*-tart^{2-} anion is comparatively strong, probably due to the electrostatic attraction, while the interaction with diethyl (*R*,*R*)-tartrate or (*R*,*R*)-tartaric acid is very weak.[12] Furthermore, a close inspection of Fig. 2 reveals that the ICD magnitude gained in diethyl (*R*,*R*)-tartrate solution gradually becomes greater for $[Co(NH_3)_4(en)]^{3+}$ than for *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ as the diethyl (*R*,*R*)-tartrate concentration is increased. Therefore, we suppose that the increasing order of the ICD magnitude obtained at low concentration of diethyl (*R*,*R*)-tartrate will be eventually reversed and agree with the order found by Taniguchi *et al.* in more concentrated solutions.

Similar concentration dependence of the ICD magnitude could not be examined in Sb$_2$*d*-tart$_2^{2-}$ solutions owing to the solubility limitation. However, it is worthy of noting that the ICD for a particular complex is certainly greater in magnitude in Sb$_2$*d*-tart$_2^{2-}$ solutions than in *d*-tart$_2^{2-}$ solutions (Fig. 1). This will be discussed later.

Determination of Association Constants. If it is assumed that 1 : 1 association between the achiral complexes and *d*-tart^{2-} is completely attained in the concentration ranges where the curves for the ICD magnitude level off in Fig. 2 (*i.e.*, above *ca.* 0.5 mol dm^{-3}), the limiting ICD magnitude in *d*-tart^{2-} solutions should correspond to the molar ICD intensity of the achiral complexes gained by the association with one *d*-tart^{2-} ion. In fact, the limiting ICD magnitude of $[Co(NH_3)_6]^{3+}$ (-1.8×10^{-2}) is close to its molar ICD intensity estimated by Jonas and Norden (-1.57×10^{-2}).14a) However, this is quite an accidental coincidence, since the 1 : 2 association with *d*-tart^{2-} is expected to take place in such high concentration ranges, as shown later. Then, we attempted to determine directly the association constants K_A and accompanying ICD intensity $\Delta\varepsilon_{MX}$ by measuring the ICD spectra of the three achiral complexes in aqueous solutions containing varying amounts of *d*-tart^{2-} at 25 °C. When possible, the K_A and $\Delta\varepsilon_{MX}$ values were also determined in Sb$_2$*d*-tart$_2^{2-}$ solutions.

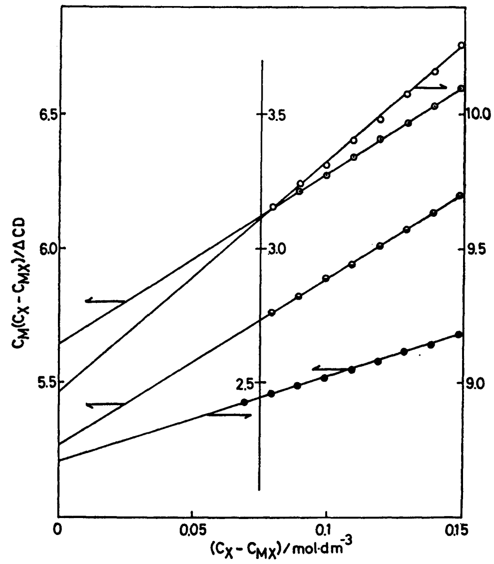

Fig. 3. Plots of Eq. 1 for $[Co(NH_3)_6]^{3+}$ (○), $[Co(NH_3)_4(en)]^{3+}$ (◎), *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ (◒), and *rac*-$[Co(en)_3]^{3+}$ (●) in aqueous *d*-tart^{2-} solutions.

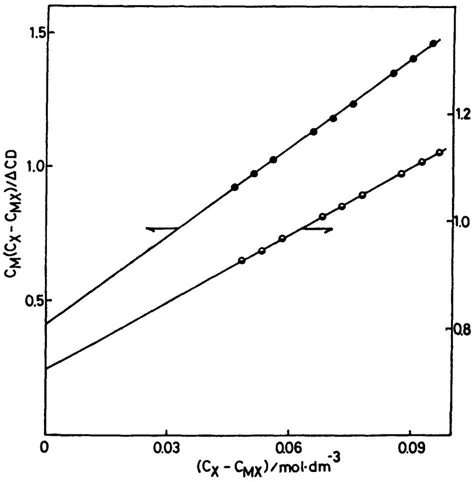

Fig. 4. Plots of Eq. 1 for *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ (◒) and *rac*-$[Co(en)_3]^{3+}$ (●) in aqueous Sb$_2$*d*-tart$_2^{2-}$ solutions.

All the data obtained were analyzed by using the following general equation11,19)

$$C_M(C_X-C_{MX})/\Delta CD = (C_X-C_{MX})/\Delta\varepsilon_{MX} + 1/K_A\Delta\varepsilon_{MX} \quad (1)$$

where C_M, C_X, and C_{MX} refer to the concentration of the complex (M), *d*-tart^{2-} or Sb$_2$*d*-tart$_2^{2-}$ (X), and their associated species (MX), and ΔCD and $\Delta\varepsilon_{MX}$ to the observed CD intensity and the molar ICD intensity of MX, respectively. The plots of the quantity on the left-hand side of Eq. 1 *vs.* $(C_X - C_{MX})$ gave fairly good straight lines (Figs. 3 and 4), indicating that only 1 : 1 association takes place for all the complexes under our present experimental conditions. The K_A and $\Delta\varepsilon_{MX}$ values obtained from these plots are listed in Table 1. For comparison, similar experiments were made on racemic $[Co(en)_3]^{3+}$ by using its ICD spectra arising from the differential CD change between its two enantiomers upon the addition of *d*-tart^{2-} or Sb$_2$*d*-tart$_2^{2-}$.21)

Two important facts should be noted in Table 1.

TABLE 1. ASSOCIATION CONSTANT K_A AND MOLAR ICD INTENSITY $\Delta\varepsilon_{MX}$ DETERMINED BY ICD MEASUREMENTS

	λ/nm a)	K_A	$\Delta\varepsilon_{MX}$	μ(NaCl)
(*R*,*R*)-tart^{2-}				
$[Co(NH_3)_6]^{3+}$	478	0.97±0.05	−0.116±0.005	0.49
$[Co(NH_3)_4(en)]^{3+}$	474	1.14±0.02	−0.156±0.003	0.49
trans-$[Co(NH_3)_2(en)_2]^{3+}$	466	1.19±0.02	−0.159±0.003	0.49
rac-$[Co(en)_3]^{3+}$	478	1.45±0.04	−0.314±0.009	0.49
Sb$_2$(*R*,*R*)-tart$_2^{2-}$				
trans-$[Co(NH_3)_2(en)_2]^{3+}$	484	5.8±1.0	0.239±0.003	0.33
rac-$[Co(en)_3]^{3+}$	461 b)	26.6±1.2	−0.091±0.002	0.32

a) Wavelength at which the ICD is measured and has its maximum intensity. b) *rac*-$[Co(en)_3]^{3+}$ has a maximum ICD intensity at 469 nm in Sb$_2$*d*-tart$_2^{2-}$ solution.

The first is that the K_A values with *d*-tart^{2-} are not appreciably different among three achiral complexes, while the $\Delta\varepsilon_{MX}$ value of $[Co(NH_3)_6]^{3+}$ is much smaller than those of the other two complexes. Therefore, a smaller $\Delta\varepsilon_{MX}$ value of $[Co(NH_3)_6]^{3+}$ is responsible for its weaker ICD developed in *d*-tart^{2-} solution (Fig. 1). On the other hand, both the K_A and $\Delta\varepsilon_{MX}$ values for *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ are slightly greater than the corresponding values for $[Co(NH_3)_4(en)]^{3+}$ in *d*-tart^{2-} solutions. Then, it is natural that the ICD similar in magnitude is developed for the two complexes as shown in Fig. 1.

Another noteworthy fact is that both the K_A and $\Delta\varepsilon_{MX}$ values for *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ are much greater in Sb_2*d*-tart$_2^{2-}$ solution than in *d*-tart^{2-} solution, though the ionic strength is somewhat lower in the former solution. As a result, it is this fact that is responsible for much stronger ICD developed for *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ in Sb_2*d*-tart$_2^{2-}$ than in *d*-tart^{2-} solutions. The same will probably hold for $[Co(NH_3)_4(en)]^{3+}$ whose association constant with Sb_2*d*-tart$_2^{2-}$ cannot be determined owing to the formation of a precipitate. Similarly, the K_A value obtained for *rac*-$[Co(en)_3]^{3+}$ is surprisingly greater with Sb_2*d*-tart$_2^{2-}$ than with *d*-tart^{2-}.[24] Therefore, we suppose that Sb_2*d*-tart$_2^{2-}$ interacts with these amine-complexes in quite a different fashion from *d*-tart^{2-}.[25] In fact, $[Co(NH_3)_4(en)]^{3+}$ and *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ show a positive ICD band in Sb_2*d*-tart$_2^{2-}$ solution, while the two complexes and $[Co(NH_3)_6]^{3+}$ show a negative ICD band in *d*-tart^{2-} solution. Furthermore, the wavelength at which the ICD of these complexes has a maximum intensity is considerably different between *d*-tart^{2-} and Sb_2*d*-tart$_2^{2-}$ solutions (Fig. 1 and Table 1).

For *rac*-$[Co(en)_3]^{3+}$, however, its apparent $\Delta\varepsilon_{MX}$ value is not directly compared with those of the achiral complexes, since the mechanism leading to the ICD in racemic complexes is essentially different from that in achiral complexes.[21]

In Table 2 are given the association constants K_A of $[Co(NH_3)_6]^{3+}$ and *rac*-$[Co(en)_3]^{3+}$ with *d*-tart^{2-} determined in the present study by UV measurements. Also given are the K_A values reported by other workers. Here the ionic strength μ is adjusted with $NaClO_4$. Again, two noticeable facts are found in Table 2. First, the K_A value obtained for $[Co(NH_3)_6]^{3+}$ is greater than that for $[Co(en)_3]^{3+}$. Nevertheless, when the ICD measurements are applied, the resulting K_A value is greater for *rac*-$[Co(en)_3]^{3+}$ than for $[Co(NH_3)_6]^{3+}$. Another fact to be noted is that the K_A value derived from ICD measurements is much smaller than that obtained by UV measurements both for $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$, as seen in Tables 1 and 2. These facts strongly suggest that the steric requisite in the association with *d*-tart^{2-} is much severer for the induction of CD in the first d-d transition region than for the development of a new charge transfer band in the UV region for achiral complexes.[12]

Table 2. Association constant K_A with (*R*,*R*)-tartrate determined by UV measurements

	λ/nm	K_A	($NaClO_4$)	Ref.
$[Co(NH_3)_6]^{3+}$	270	4.2±0.2	0.48	present study
	245	26.5±0.4	0.1	19)
	265	31 ±1	0.1	10)
rac-$[Co(en)_3]^{3+}$	277	4.2±0.1	0.48	present study
Λ-$[Co(en)_3]^{3+}$	265	22.5±0.4	0.1	19)
	265	23.4±1.0	0.1	6)[a]
	265	26 ±2	0.1	10)
Δ-$[Co(en)_3]^{3+}$	265	18.2±0.6	0.1	19)
	265	18.0±0.7	0.1	6)[a]
	265	22 ±2	0.1	10)

a) Recalcd in Ref. 6.

Mason and Norman[12] have already found that no detectable CD is induced[26] for $[Co(NH_3)_6]^{3+}$ when mixed with (*S*)-malic acid or sodium (*S*)-malate having only one OH group on the asymmetric carbon atom. However, the addition of (*S*)-malate^{2-} as well as *d*-tart^{2-} gives an appreciable change in the UV spectrum of the complex, suggesting that the interaction with the two $-COO^-$ groups gives rise to the change in the UV spectrum of the complex.[6] Therefore, we suppose that the ICD is well developed only when the two OH groups on the asymmetric carbon atoms simultaneously participate in the interaction with these achiral amine complexes. The most probable interaction imagined here is the hydrogen-bonding of the hydroxyl oxygen atoms with the amine protons of the ligands.[17] In fact, ICD is well developed for $[Co(NH_3)_6]^{3+}$ and other two achiral complexes when mixed with diethyl (*R*,*R*)-tartrate or (*R*,*R*)-tartaric acid having no $-COO^-$ group.[27]

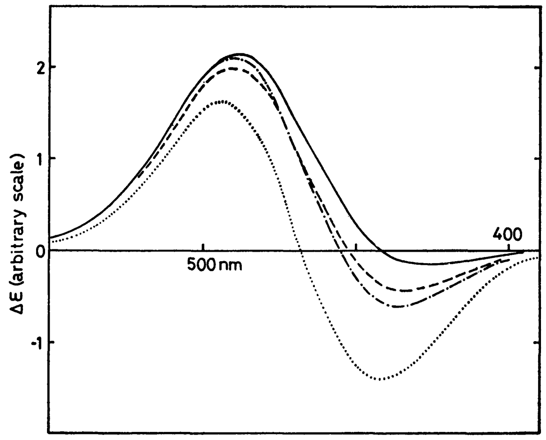

Fig. 5. CD spectra of Λ-$[Co(en)_3]^{3+}$ (2×10^{-3} mol dm^{-3}) in the absence (——) and presence of *d*-tart^{2-}; 0.0275 mol dm^{-3} (----) and 1.0 mol dm^{-3} (-·-·-), and calculated CD spectrum of Λ-$[Co(en)_3]^{3+}$ associated with *d*-tart^{2-} (······) in aqueous solutions.

Comparison of $\Delta\varepsilon_{MX}$ *Values with Limiting ICD Magnitudes.* Before the limiting ICD magnitudes attained in Fig. 2 are discussed and compared with the $\Delta\varepsilon_{MX}$ values listed in Table 1, the influence of added *d*-tart^{2-} on the natural CD spectrum of Λ-$[Co(en)_3]^{3+}$ is examined here. In Fig. 5 are shown the CD spectra of Λ-$[Co(en)_3]^{3+}$ (2×10^{-3} mol dm^{-3}) in water in the absence and presence of *d*-tart^{2-} (2.75×10^{-2} and 1.0 mol dm^{-3}).

The association constant of the complex with *d*-tart^{2-} has been estimated by CD measurements to be 13.0±1.0[11] at μ=0.1 ($NaClO_4$). By using this value, the hypothetical CD spectrum of Λ-$[Co(en)_3]^{3+}$ associated with *d*-tart^{2-} was calculated and is shown as a dotted line in Fig. 5. It is evident that the CD spectrum in the presence of a large amount of *d*-tart^{2-} (*e.g.*, 1.0 mol dm^{-3}) is entirely different from the calculated spectrum. This unambiguously means that successive association[4a] of the complex with *d*-tart^{2-} must be taken into account at such high *d*-tart^{2-} concentrations. The same is naturally expected for the three achiral complexes in question, since all of them bear 3+ charges like $[Co(en)_3]^{3+}$. However, the association higher than 1: 2 is improbable under our experimental conditions, as pointed out by Olsen and Bjerrum for the $[Co(en)_3]^{3+}$–$S_2O_3^{2-}$ system.[28] As a result, it follows that the 1: 2 association with *d*-tart^{2-} is completely attained in extremely high *d*-tart^{2-} concentration ranges (Fig. 2) and that the limiting ICD magnitudes thus correspond to the molar ICD intensities of the respective achiral complexes gained by interacting with two *d*-tart^{2-} ions at a time. On the other hand, the $\Delta\varepsilon_{MX}$ values correspond to the molar ICD intensities gained by the association with only one *d*-tart^{2-} ion.

Now we are ready to compare the limiting ICD magnitudes with the $\Delta\varepsilon_{MX}$ values. First of all, it should be noted that the limiting ICD magnitude is much smaller than the $\Delta\varepsilon_{MX}$ value for all the complexes examined. If the former indeed reflects the molar ICD intensity of the achiral complex associated with two *d*-tart^{2-} ions, we are obliged to conclude that the ICD magnitude gained in the 1: 1 association with *d*-tart^{2-} is greatly diminished (almost to one-fifth) in the 1: 2 association, probably due to restored high symmetry[4a] of the resulting outer-sphere complex with two *d*-tart^{2-} ions. It is also highly plausible that the strain imposed on the achiral complex in the 1: 1 association is relaxed in the 1: 2 association owing to the electrostatic repulsion between the two *d*-tart^{2-} anions, the overall ICD magnitude being thereby diminished greatly.

Finally, the most important problem remains unanswered why the $\Delta\varepsilon_{MX}$ value for *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ (−0.159) is only slightly greater than that for $[Co(NH_3)_4(en)]^{4+}$ (−0.156), while the limiting ICD magnitude is appreciably greater for the former complex (-3.5×10^{-2}) than for the latter (-2.7×10^{-2}). Though detailed mechanisms of the ICD developed in these achiral complexes are not known, some authors[13,18,29] favor the view that the ICD owes its origin to a fixed conformation (δ or λ) of the chelate rings of the complex in the presence of chiral substances. However, we are not inclined to adopt this view in the present system, since the ICD spectra obtained for *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ and $[Co(NH_3)_4(en)]^{3+}$ (Fig. 1) do not resemble the natural CD spectra of *trans*-$[Co(NH_3)_2$(*R*- or *S*-pn)$_2]^{3+}$ and $[Co(NH_3)_4$(*R*- or *S*-pn)$]^{3+}$,[22] respectively, and similar CD is induced also for $[Co(NH_3)_6]^{3+}$ having no chelate. In addition, $[Co(NH_3)_4$(*R*-pn)$]^{3+}$ in which a pn chelate ring is thought to be fixed to a λ-conformation suffers a considerable change in its CD spectrum when mixed with *d*-tart^{2-} or Sb_2*d*-tart$_2^{2-}$, as shown in Fig. 6.

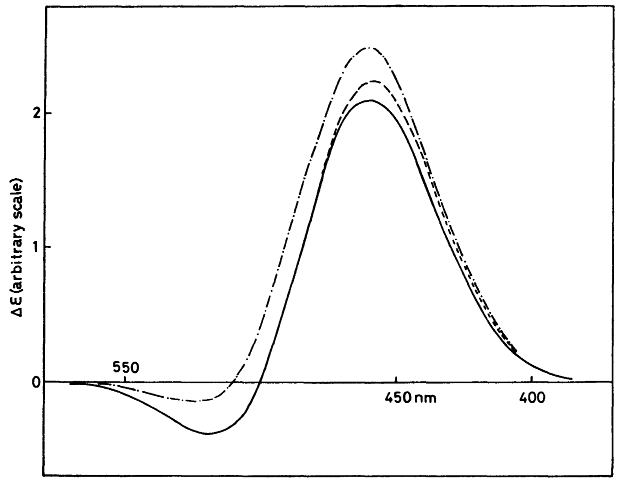

Fig. 6. CD spectra of $[Co(NH_3)_4$(*R*-pn)$]^{3+}$ in the absence (——) and presence of *d*-tart^{2-} (----) and of Sb_2*d*-tart$_2^{2-}$ (-·-·-) in aqueous solutions.

It is certain, however, that the ICD developed in *d*-tart^{2-} solution increases in magnitude with increasing number of en chelate rings in the complexes. This leads us to propose that the ICD magnitude depends on the degree of the distortion[13] of the Co(III)–N bonds brought about by the outer-sphere association with *d*-tart^{2-}, since a greater distortion is expected when the coordinated ligands are bidentate (en) than when they are unidentate (NH_3), *i.e.*, when the complex has more chelate rings. In accordance with this proposal, the ICD magnitude of $[Co(NH_3)_4(en)]^{3+}$ is greater than that of $[Co(NH_3)_4(tn)]^{3+}$, the strain exerted upon which is not effectively propagated to the central Co(III) ion owing to the flexibility of a tn chelate ring.

If our proposal that the strain exerted upon chelate rings is effective in inducing CD in achiral complexes is valid, a tentative answer can now be put forward to the problem mentioned above. In the 1: 1 association with *d*-tart^{2-}, both *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ and $[Co(NH_3)_4(en)]^{3+}$ having at least one en chelate ring are expected to suffer a similar distortion, since *d*-tart^{2-} cannot interact with *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ so as to exert a strain on the two en rings simultaneously. As a result, it is natural that CD similar in magnitude is induced for the two complexes. On the other hand, when the 1: 2 association takes place, *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ is differentiated from $[Co(NH_3)_4(en)]^{3+}$, since the former complex has another en chelate ring available for the further interaction with *d*-tart^{2-}, while the latter not. Therefore, relatively stronger CD is expected to be induced for the former complex in concentrated solution of *d*-tart^{2-}, though the overall ICD magnitude gained in the 1: 2 association is by far smaller than that in the 1: 1 association. In this way, an appreciably great difference in the limiting ICD magnitude between $[Co(NH_3)_4(en)]^{3+}$ and *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ is reasonably interpreted.

Though the solubility limitation does not allow us to obtain the limiting ICD magnitudes in Sb_2*d*-tart$_2^{2-}$ solution, the ICD magnitude for *trans*-$[Co(NH_3)_2(en)_2]^{3+}$

is considerably greater than that for $[Co(NH_3)_4(en)]^{3+}$ even when the concentration of Sb_2d-$tart_2^{2-}$ is relatively low (Fig. 1). This tacitly means that the arguments presented above are not applied to the interpretation of the ICD developed in Sb_2d-$tart_2^{2-}$ solutions.

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26) Weak positive CD is induced for $[Co(NH_3)_6]^{3+}$ as well as for $[Co(NH_3)_4(en)]^{3+}$ and *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ in aqueous solutions containing an extremely large excess of (*S*)-malic acid, suggesting that the two simultaneous hydrogen-bonds are not necessarily essential requirements for the induction of CD in these achiral complexes. See also Ref. 14.

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