Contribution from the Department of Chemistry,
Faculty of Science, Hiroshima University, Hiroshima 730, Japan

Circular Dichroism Study of the Chiral Interaction between Bis(μ-tartrato)diantimonate(III) Ions and Trigonal [Co(N)6]3+ Complexes in Solution[1]

USHIO SAKAGUCHI, AKIRA TSUGE, and HAYAMI YONEDA*

The effect of bis(μ-d-tartrato)- and bis(μ-l-tartrato)diantimonate(III) ions upon the circular dichroism spectra of six trigonal $[Co(N)_6]^{3+}$ complexes has been investigated. The association constants with bis(μ-l-tartrato)- and bis(μ-d-tartrato)diantimonate(III) ions, K_l and K_d, are as follows (K_l, K_d) (mol^{-1} dm^3 at 25 °C and $\mu = 0.1$ (NaClO$_4$)): (47.3 ± 0.6, 26.0 ± 0.5), (71.0 ± 7.5, 4.3 ± 0.3), (52.4 ± 1.3, 39.0 ± 2.9), (25.8 ● 0.5, 16.8 ± 0.4), (27.9 ± 0.2, 19.5 ± 0.3), and (21.3 ± 0.1, 14.0 ± 0.1) for Δ-[Co(en)$_3$]$^{3+}$, Δ-[Co(sen)]$^{3+}$, Δ-[Co(sep)]$^{3+}$, Δ-fac-lel_3- and Δ-mer-lel_3-[Co(l-pn)$_3$]$^{3+}$, and Δ-lel_3-[Co(l-chxn)$_3$]$^{3+}$, respectively, where en = ethylenediamine, sen = 1,1,1-tris(((2-aminoethyl)amino)methyl)ethane, sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane, l-pn = (−)-1,2-propanediamine, and l-chxn = (−)-$trans$-1,2-cyclohexanediamine. In Δ-[Co(sen)]$^{3+}$, 1:2 association with bis(μ-l-tartrato)diantimonate(III) also takes place with an association constant of 15.0 ± 3.0 mol^{-1} dm^3. From the degree of chiral discrimination and the direction of circular dichroism changes due to bis(μ-tartrato)diantimonate(III), the mode of chiral discrimination in these systems has been considered.

Introduction

The bis(μ-d-tartrato)diantimonate(III) ion, [Sb$_2$(d-tart)$_2$]$^{2-}$, seems to be the most versatile resolving agent for coordination compounds in that it can be used successfully to resolve many complexes with widely different structures and properties, e.g., *cis*-dianionobis(ethylenediamine)metal(III) ions[2] and tris-(1,10-phenanthroline)metal(II) ions.[3] This ion appears to be especially effective when it is employed as the eluent in chromatographic optical resolution.[4-8] Thus, the mode of chiral discrimination of this ion in solution attracted our keen interest.

Recently, we have studied the mode of chiral discrimination of *d*- and *l*-tartrate ions in aqueous solution.[9] The circular dichroism (CD) spectra have been shown to be quite useful in deducing the direction of access of tartrate ions toward complex cations. In this work, we have studied the effect of the [Sb$_2$(d-tart)$_2$]$^{2-}$ ion upon the CD spectra of some trigonal $[Co(N)_6]^{3+}$ complexes to infer the mode of chiral discrimination in solution. The complexes chosen for this study are Δ-[Co(en)$_3$]$^{3+}$, Δ-[Co(sen)]$^{3+}$, Δ-[Co(sep)]$^{3+}$, Δ-fac-lel_3- and Δ-mer-lel_3-[Co(l-pn)$_3$]$^{3+}$, Δ-lel_3-[Co(l-chxn)$_3$]$^{3+}$, and their mirror-image isomers (enantiomers), where en = ethylenediamine, sen = 1,1,1-tris(((2-aminoethyl)amino)methyl)-ethane, sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane, l-pn = (−)-1,2-propanediamine, l-chxn = (−)-*trans*-1,2-cyclohexanediamine, and *lel* means that the C–C bond of

the ethylenediamine moiety is approximately parallel to the C_3 axis. Since the Λ-[Co(N)$_6$]$^{3+}\cdots$[Sb$_2$(d-tart)$_2$]$^{2-}$ combination is equivalent to its mirror image, Δ-[Co(N)$_6$]$^{3+}\cdots$[Sb$_2$(l-tart)$_2$]$^{2-}$, the latter notation will be used throughout for the sake of convenience. Figure 1 illustrates schematically the structures of the Δ cations used in this work. The structures as well as the absolute configurations of all these complexes were determined previously by X-ray analyses.[10] The CD spectra of the Δ complexes in the first d–d region are given in Figure 2 as curves A. The CD peak of lowest energy is assigned to the E$_a$ transition and the higher energy one to the A$_2$ transition, except for Δ-[Co(sep)]$^{3+}$, for which the positive A$_2$ rotational strength, R(A$_2$), dominates the negative R(E$_a$).[11]

Experimental Section

Materials. The complexes used in this work were the perchlorate salts of Δ-[Co(en)$_3$]$^{3+}$ with $\Delta\epsilon = -1.87$ at 493 nm (lit.[12] −1.89), Λ-[Co(en)$_3$]$^{3+}$ with $\Delta\epsilon = +1.89$, Δ-[Co(sen)]$^{3+}$ with $\Delta\epsilon = +1.06$ at 449 nm (lit.[13] +1.05), Λ-[Co(sen)]$^{3+}$ with $\Delta\epsilon = -0.90$, Δ-[Co(sep)]$^{3+}$ with $\Delta\epsilon = +2.78$ at 465 nm (lit.[10d] +2.37), Λ-[Co(sep)]$^{3+}$ with $\Delta\epsilon = -2.76$, Δ-fac-lel_3-[Co(l-pn)$_3$]$^{3+}$ with $\Delta\epsilon = -2.27$ at 495 nm (lit.[14] −1.95), Λ-fac-lel_3-[Co(d-pn)$_3$]$^{3+}$ with $\Delta\epsilon = +1.69$, Δ-mer-lel_3-[Co-(l-pn)$_3$]$^{3+}$ with $\Delta\epsilon = -2.11$ at 494 nm (lit.[14] −1.95), Λ-mer-lel_3-[Co(d-pn)$_3$]$^{3+}$ with $\Delta\epsilon = +2.25$, Δ-lel_3-[Co(l-chxn)$_3$]$^{3+}$ with $\Delta\epsilon = -2.19$ at 500 nm (lit.[13] −2.15), and Λ-lel_3-[Co(d-chxn)$_3$]$^{3+}$ with $\Delta\epsilon = +2.27$. Disodium bis(μ-d-tartrato)diantimonate(III)–2.5-water was recrystallized twice from water. The other chemicals were used as supplied.

Measurements. Circular dichroism spectra were measured on a JASCO J-40CS recording spectropolarimeter, and the linearity of the recordings was better than 2%. The sample cell of 2-cm path length was kept at 25.0 ± 0.2 °C with a Haake circulator, Model FK. The difference CD (DCD) spectra, which are defined as the CD spectra with [Sb$_2$(tart)$_2$]$^{2-}$ minus the CD spectra without [Sb$_2$(tart)$_2$]$^{2-}$, were obtained by using the data processor compartment operating at 0.2 nm/step of processor resolution.

Except for the sen and *l*-chxn complexes, the concentration of the complex cation, c_M, was fixed at 6.0 × 10^{-4} mol dm^{-3} and that of the

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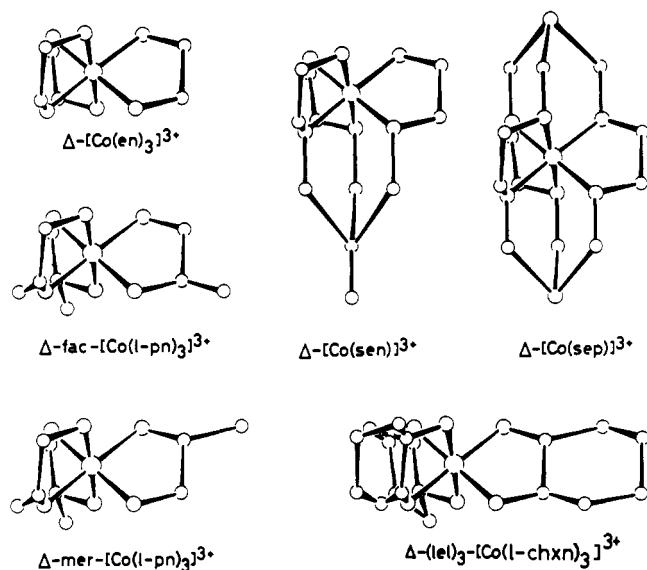(14) McCaffery, A. J.; Mason, S. F.; Ballard, R. E. *J. Chem. Soc.* **1965**, 2883.

Figure 1. Structures of the Δ complexes investigated in this work. Hydrogen atoms are omitted for clarity.

Table I. First-Step Association Constants, K_l and K_d (mol^{-1} dm^3), and $\Delta\epsilon_{MA}$ at 25 °C and $\mu = 0.1$ (NaClO$_4$)[a]

complex	λ, nm	K_l	K_d	$\Delta\epsilon_{MA}$	D[b]
Δ-[Co(en)₃]³⁺	450	47.3 (0.6)		+0.30	}29
	450		26.0 (0.3)	+0.14	
Δ-[Co(sen)]³⁺ c	485	73.0 (3.0)		÷0.09	
	460	65.0 (5.0)		+0.98	
	430	75.0 (3.0)		+0.72	}89
	465		4.5 (0.4)	-0.06	
	485		4.1 (0.1)	-0.59	
Δ-[Co(sep)]³⁺	480	52.4 (1.3)		÷0.83	}15
	480		39.0 (2.9)	+0.93	
Δ-fac-[Co(l-pn)₃]³⁺	460	25.8 (0.5)		÷0.67	}21
	460		16.8 (0.4)	+0.99	
Δ-mer-[Co(l-pn)₃]³⁺	460	27.9 (0.2)		+0.83	}18
	460		19.5 (0.3)	+1.00	
Δ-[Co(l-chxn)₃]³⁺	470	21.3 (0.1)		+1.80	}21
	470		14.0 (0.1)	+2.10	

[a] Estimated errors in parentheses. [b] $D = 100(K_l - K_d)/(K_l + K_d)$. [c] The second-step association constant with [Sb$_2$(l-tart)$_2$]²⁻ is $K_l = 15.0$ (3.0) mol^{-1} dm^3 and $\Delta\epsilon_{MA} = -0.045$ (485 nm), +0.83 (460 nm), and +0.68 (430 nm).

[Sb$_2$(tart)$_2$]²⁻ anion, c_A, was varied from 0 to 3.21 × 10^{-2} mol dm^{-3}. The perchlorate salt of the *l*-chxn complex was sparingly soluble in water, c_M of this complex was set to 6.0 × 10^{-5} mol dm^{-3} (c_A = 0 to 3.32 × 10^{-2} mol dm^{-3}), and a sample cell of 10-cm length was used. For the sen complex, two series of solutions containing c_M = 5.0 × 10^{-3} mol dm^{-3} (c_A = 0 to 2.33 × 10^{-2} mol dm^{-3}) and c_M = 1.0 × 10^{-3} mol dm^{-3} (c_A = 0 to 3.13 × 10^{-2} mol dm^{-3}) were used for reasons mentioned below. The ionic strength was adjusted to μ = 0.1 with sodium perchlorate.

Determination of Association Constants. All the systems except the Δ-[Co(sen)]³⁺···[Sb$_2$(l-tart)$_2$]²⁻ system exhibited the CD changes due to [Sb$_2$(tart)$_2$]²⁻, which are consistent with a 1:1 association. The DCD data for these systems were least-squares fitted to eq 1 to obtain

$$c_M/\text{DCD} = 1/(\Delta\epsilon_{MA} - \Delta\epsilon_M) + 1/K(\Delta\epsilon_{MA} - \Delta\epsilon_M)(c_A - x) \quad (1)$$

the association constant, K, and the CD of the ion pair, $\Delta\epsilon_{MA}$. In eq 1, $\Delta\epsilon_M$ is the CD of the complex cation in the absence of [Sb$_2$(tart)$_2$]²⁻ and x is the concentration of the ion-paired species.

For the Δ-[Co(sen)]³⁺···[Sb$_2$(l-tart)$_2$]²⁻ system, an apparent departure from linearity of the double-reciprocal plot of eq 1 (c_M/DCD vs. 1/($c_A - x$)) was observed at higher anion to complex ratios. In the region of the anion to complex ratio of up to about 2, the double-reciprocal plots could seemingly be approximated by eq 1, but the resulting K values differed considerably for different wavelengths at which the data were collected, indicating the effect of 1:2 association. The K values increased if the data points of higher anion to complex ratios are included in the analysis. Thus, the association constant for the first step was determined by eq 1 for solutions with c_M = 5.0 × 10^{-3} mol dm^{-3}, by using the data that were collected in the region of lower anion to complex ratios and yielded the same K value at three wavelengths.

To determine the association constant corresponding to the 1:2 association, data were collected at three wavelengths for two series of solutions (c_M = 1.0 × 10^{-3} and 5.0 × 10^{-3} mol dm^{-3}). A nonlinear least-squares program written in this laboratory[15] was used to minimize the sum of squared deviations between the calculated and observed DCD values. In this least-squares calculation, the first-step association constant and $\Delta\epsilon_{MA}$ value were kept fixed. The second-step association constants thuus obtained for three wavelengths were consistent.

All the measurements were repeated three times, and the quoted uncertainties in K values refer to the estimated range of reproducibilities.

Results and Discussion

Association Constants. For all the systems except Δ-[Co(sen)]³⁺···[Sb$_2$(l-tart)$_2$]²⁻, the 1/DCD vs. 1/($c_A - x$) plots, eq 1, were linear. An example of such plots is given in Figure

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3. The linearity of the plots is evidence for 1:1 association. Figure 4 shows examples of the double-reciprocal plots of the Δ-[Co(sen)]³⁺···[Sb$_2$(l-tart)$_2$]²⁻ system for two concentrations of the complex cation. The departure from linearity will be readily apparent at higher [Sb$_2$(l-tart)$_2$]²⁻ concentrations, and this behavior is more pronounced at lower complex concentrations or, equivalently, at higher anion to complex ratios. These behaviors of the Δ-[Co(sen)]³⁺···[Sb$_2$(l-tart)$_2$]²⁻ system are nicely reproduced by assuming the 1:2 association occurring simultaneously with the 1:1 association. The solid curves of Figure 4 are the calculated ones by assuming the first- and second-step association constants of 73.0 and 15.0 mol^{-1} dm^3, respectively, which are obtained by the curve-fitting procedures described in the Experimental Section. The association constants of all the complexes with [Sb$_2$(l-tart)$_2$]²⁻ and [Sb$_2$(d-tart)$_2$]²⁻, K_l and K_d, are summarized in Table I, along with the CD of the ion-paired species, $\Delta\epsilon_{MA}$. In Table I are also given the degrees of chiral discrimination as defined by $100(K_l - K_d)/(K_l + K_d)$.

The association constants of Δ-[Co(en)₃]³⁺ with [Sb$_2$(l-tart)$_2$]²⁻ and [Sb$_2$(d-tart)$_2$]²⁻ have been reported[6] previously as 47.0 ± 0.5 and 26.2 ± 0.8 mol^{-1} dm^3, respectively, at 25 °C and μ = 0.1 (NaClO$_4$). These values coincide very well with the corresponding values determined here, which lends credence to the present results.

Comparison of K values in Table I reveals several interesting features. The first point noted is that K_l is larger than K_d for all the complexes, indicating that these Δ complexes favor the association with [Sb$_2$(l-tart)$_2$]²⁻. This is consistent with the observation that in the chromatographic optical resolution of tris(diamine)cobalt(III) complexes with five- or six-membered chelate rings, Δ enantiomers are generally eluted faster by [Sb$_2$(l-tart)$_2$]²⁻ than their mirror-image isomers from cation-exchange resins.[8]

The second point noted is that K_l and K_d differ significantly in all the complexes including Δ-[Co(sep)]³⁺. This makes a sharp contrast to the case of the Δ-[Co(sep)]³⁺ system with *d*- and *l*-tartrate ions, where K_l was equal to K_d within experimental uncertainties.[9] Since the Δ-[Co(sep)]³⁺ ion has two covalent caps along the C_3 axis of the parent Δ-[Co(en)₃]³⁺ ion, the association of [Sb$_2$(tart)$_2$]²⁻ along the C_3 axis seems improbable. This inference has been substantiated previously for the *d*- and *l*-tartrate ions[9] and complex anions such as [Co(edta)]⁻, [Co(ox)$_2$(gly)]²⁻, and [Cr(mal)$_3$]³⁻ (edta = ethylenediaminetetraacetate, ox = oxalate, gly = glycinate, and mal = malonate)[16] and will be shown later to be supported

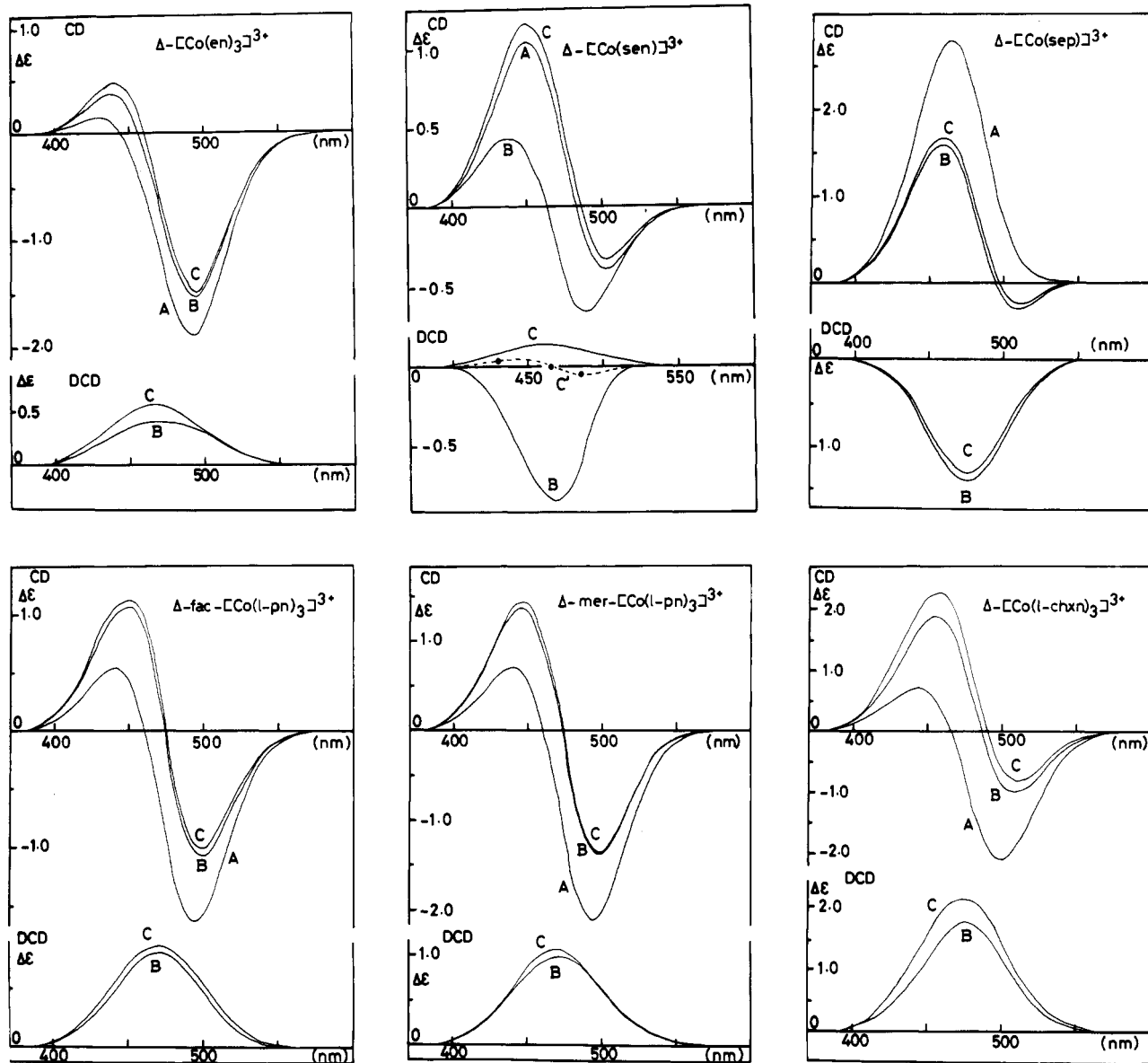**Figure 2.** Upper curves: CD spectra of the Δ complex (A) and of the ion pairs with [Sb$_2$(d-tart)$_2$]$^{2-}$ (B) and [Sb$_2$(l-tart)$_2$]$^{2-}$ (C). Lower curves: DCD spectra due to [Sb$_2$(d-tart)$_2$]$^{2-}$ (B) and [Sb$_2$(l-tart)$_2$]$^{2-}$ (C, C′). C′ refers to the ion triplet formed between Δ-[Co(sen)]$^{3+}$ and [Sb$_2$(l-tart)$_2$]$^{2-}$.
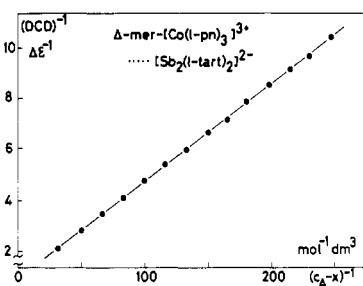
Figure 3. Plots of eq 1 for the system Δ-mer-lel_3-[Co(l-pn)$_3$]$^{3+}$··· [Sb$_2$(l-tart)$_2$]$^{2-}$ at 460 nm.

by the sign of the DCD spectra. Thus, the fact that the chirality of Δ-[Co(sep)]$^{3+}$ is discriminated by [Sb$_2$(tart)$_2$]$^{2-}$ suggests strongly that chiral discrimination for the en, l-pn, and l-chxn complexes is also effected along the C_2 axes of the complex cations. This assumption leads us to expect that the association constant and possibly the degree of chiral discrimination diminish along the series of the en, l-pn, and l-chxn

complexes, in this order, because the latter two complexes have substituent groups along the D_3 equatorial direction of Δ-[Co(en)$_3$]$^{3+}$. As seen from Table I, both K_l and K_d values decrease in the order Δ-[Co(en)$_3$]$^{3+}$ > Δ-mer-lel_3-[Co(l-pn)$_3$]$^{3+}$ > Δ-fac-lel_3-[Co(l-pn)$_3$]$^{3+}$ > Δ-lel_3-[Co(l-chxn)$_3$]$^{3+}$. The degree of chiral discrimination of the latter three complexes is smaller than that of Δ-[Co(en)$_3$]$^{3+}$ but almost the same within experimental uncertainties. The above order in K values parallels the order of decreasing bulkiness of the D_3 equatorial substituent groups; it will be seen from Figure 1 that Δ-mer-lel_3-[Co(l-pn)$_3$]$^{3+}$ possesses, along the C_2 direction, one unhindered inter-chelate-ring space, which is equal in unhinderedness to that of Δ-[Co(en)$_3$]$^{3+}$, while each of the three C_2 directions of the Δ-fac-lel_3 isomer is equally hindered, though not heavily, by one methyl group. These results seem to imply that the [Sb$_2$(tart)$_2$]$^{2-}$ anion approaches the en, l-pn, and l-chxn complexes along their C_2 axes in between the two blades of chelate rings.

The third point noted is the surprising difference in K_l and K_d values of Δ-[Co(sen)]$^{3+}$, resulting in the degree of chiral discrimination as high as about 90%. This value may be the highest degree of chiral discrimination in solution reported to date, and the free energy for discrimination, as defined by
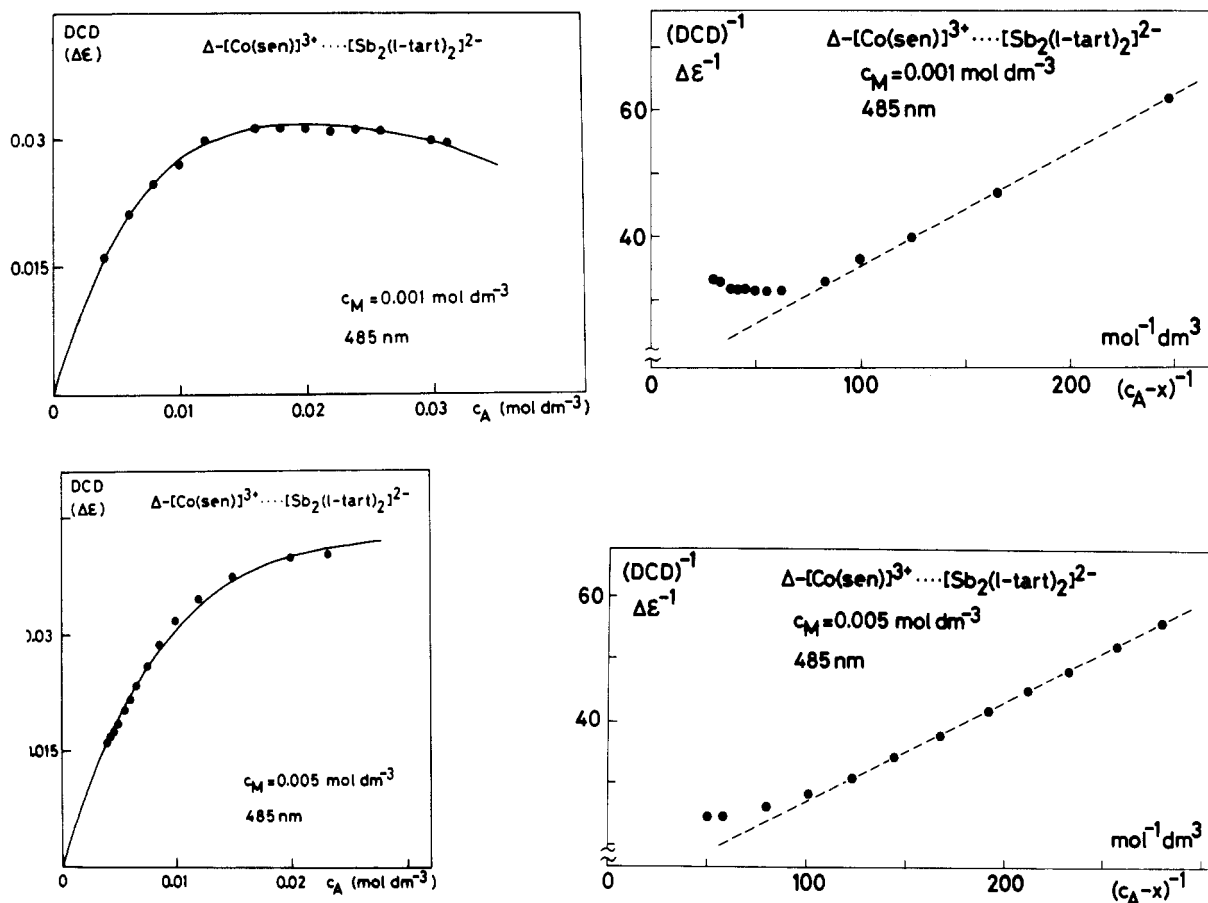
(16) Sakaguchi, U.; Yamamoto, I.; Izumoto, S.; Yoneda, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 153.

Figure 4. Left: Observed (●) and calculated (—) DCD intensities for Δ-[Co(sen)]$^{3+}$···[Sb$_2$(l-tart)$_2$]$^{2-}$, with both curves obtained by assuming first- and second-step association constants of 73.0 and 15.0 mol^{-1} dm^3, respectively. Right: Double-reciprocal plots of eq 1 of the system Δ-[Co(sen)]$^{3+}$···[Sb$_2$(l-tart)$_2$]$^{2-}$ for two complex concentrations.

$\delta\Delta G^{\ast} = RT \ln (K_l/K_d)$, amounts to 6.9 kJ mol^{-1} at 25 °C. This value should be compared with the $\delta\Delta G^{\ast}$ values of 0.73 and 1.5 kJ mol^{-1} (25 °C) for Δ-[Co(sep)]$^{3+}$ and Δ-[Co(en)$_3$]$^{3+}$, respectively. The sen complex ion possesses such a structure that one tris(methylene)ethane cap is added to the parent Δ-[Co(en)$_3$]$^{3+}$ alon its C_3 axis and the conformation of chelate rings is locked in the lel_3 form.[9,10b,13] By comparison of K values in Table I, it will be inferred that this astonishing discrimination is brought about by an anomalously small K_d value, rather than by the large K_l value. The reason for this minute K_d value is, however, not clear at present.

DCD Spectra. In Figure 2, the DCD spectra due to [Sb$_2$(d-tart)$_2$]$^{2-}$ (curves B) and [Sb$_2$(l-tart)$_2$]$^{2-}$ (curves C) are given. For complexes with two triangular facets composed of three axial NH hydrogens, i.e., Δ-[Co(en)$_3$]$^{3+}$, Δ-*fac-lel$_3$*-and Δ-*mer-lel$_3$*-[Co(l-pn)$_3$]$^{3+}$, and Δ-*lel$_3$*-[Co(l-chxn)$_3$]$^{3+}$, positive DCD's are observed, indicating that A$_2$ rotational strengths, $R(A_2)$, are enhanced upon association. Since perturbations along the D_3 axial and equatorial directions enhance generally $R(A_2)$ and $R(E_a)$, respectively,[9,17,18] these DCD's may be taken to indicate that [Sb$_2$(tart)$_2$]$^{2-}$ ions exert axial perturbations in the ion pairs. It should be noted that rather large DCD's of positive sign are observed only for those complexes that have two triangular NH facts but not for Δ-[Co(sen)]$^{3+}$ and Δ-[Co(sep)]$^{3+}$. This seems to suggest that the former cations utilize both triangular facets for the interaction with [Sb$_2$-(tart)$_2$]$^{2-}$ anions. Therefore, it is inferred with the axial perturbation results most probably from hydrogen bonding
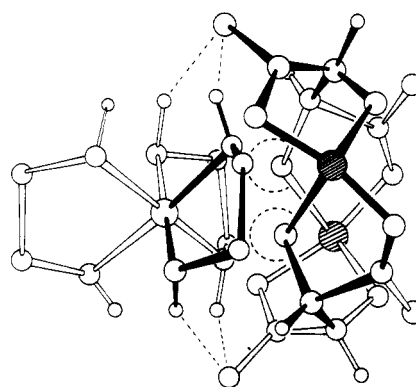

Figure 5. Proposed model for the favorable pair Δ-[Co(en)$_3$]$^{3+}$···[Sb$_2$(l-tart)$_2$]$^{2-}$. For clarity, only the relevant hydrogens are drawn for the cation. Solid bonds are situated in front.

between axial NH hydrogens on both trigonal faces of a complex cation and the oxygen atoms of [Sb$_2$(tart)$_2$]$^{2-}$. Consulation of X-ray structure data for these complexes[10] and the [Sb$_2$(d-tart)$_2$]$^{2-}$ anion[19] reveals that the distance between the axial NH hydrogens of two trigonal faces (about 4.0 Å) matches the distance between the two terminal carboxyl oxygen atoms (6.1–7.2 Å depending upon the crystal) for making

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the double hydrogen bonding suggested above. Thus, we may envisage the mode of ion pairing as illustrated in Figure 5. The figure is drawn for the favorable combination of Δ-[Co(en)₃]³⁺, namely the Δ-[Co(en)₃]³⁺···[Sb₂(*l*-tart)₂]²⁻ combination, as a representative for the en, *l*-pn, and *l*-chxn complexes. The anion approaches the cation along the cation's C_2 axis, as deduced above. This model seems to explain why the association constant decreases gradually with an increase in the steric bulk of the D_3 equatorial substituent. The substituents (methyl and cyclohexane ring) are known[10] to assume the equatorial position with respect to the "ethylenediamine" chelate ring and will not hinder so heavily as to suppress completely the depicted access of the anion. The two blades of the right-handed propeller of the Δ-[Co(en)₃]³⁺ chelate rings and the two alcoholic oxygen atoms of [Sb₂(*l*-tart)₂]²⁻ (encircled by broken circles in the figure) fit nicely. In the combination of Δ-[Co(en)₃]³⁺···[Sb₂(*d*-tart)₂]²⁻, which is diastereomeric to the illustrated one, a severe steric hindrance is clearly expected between the ethylenediamine chelate rings and the alcoholic oxygen atoms. Thus, in this model these two alcoholic oxygen atoms serve as chiral discriminators. The model seems to be compatible also with electrostatic considerations, because the anion is assumed to face the cation with anionic oxygen atoms in front. Of course, the model may not be taken too literally because the free energies of formation of these ion pairs are rather small[9] to assign a single fixed geometry, and the experimental results used to infer the model are not so concrete as to allow us to delineate detailed interactions.

In the depicted model, the upper and lower axial NH hydrogens take part simultaneously in hydrogen bonding with carboxyl oxygen atoms of the anion, and these hydrogen bonds anchor the complex cation. This double anchoring is not possible for Δ-[Co(sen)]³⁺ with one triangular NH facet replaced by the CH₃C(CH₂-)₃ group. Therefore, the fact that this capping rendered anomalous the association constants, the degree of chiral discrimination, and the DCD spectra (see below) of Δ-[Co(sen)]³⁺ seems to point to the relevance of the depicted double anchoring. The DCD intensity of the favorable pair Δ-[Co(sen)]³⁺···[Sb₂(*l*-tart)₂]²⁻ is considerably smaller than the DCD intensities observed for the en, *l*-pn, and *l*-chxn complexes. Though the origin of this minute DCD is not clear, one possible explanation may be that in this pair a D_3 equatorial perturbation operates at the expense of the D_3 axial one. Such a situation would be attained, for example, by replacing one axial hydrogen bond with an equatorial one. This line of reasoning points to an association model such that the [Sb₂(*l*-tart)₂]²⁻ anion anchors the Δ-[Co(sen)]³⁺ cation via axial and equatorial hydrogen bonds. Upon association of one more molecule of [Sb₂(*l*-tart)₂]²⁻, the DCD intensity (C′ of Figure 2) is still weakened. The DCD spectrum of the 1:2 ion aggregate is seen clearly to be composed of two opposing effects, axial and equatorial perturbations enhancing $R(A_2)$ and $E(E_a)$, respectively. The DCD spectra corresponding to the 1:1 and 1:2 association between Δ-[Co(sen)]³⁺ and [Sb₂(*l*-tart)₂]²⁻ seem, therefore, to be very interesting because they appear to point to an interpretation that the mutual

orientation of the cation and the anion in the 1:2 association is not necessarily the same as that in the 1:1 association. This appears to be very probable because the preexisting [Sb₂(*l*-tart)₂]²⁻ anion should reorient itself upon association of the second molecule, possibly to alleviate the mutual electrostatic repulsion between the anions. The very small magnitude and the plus–minus couplet of DCD spectra have been taken as a characteristic of weakly interacting systems.[20] Thus, an alternative explanation may be that in the 1:2 aggregate the interaction between the cation and the anion is considered to be weakened relative to that in the 1:1 pair.

Though it is clear that the [Sb₂(tart)₂]²⁻ anion approaches Δ-[Co(sep)]³⁺ along the cation's C_2 axis as inferred from the DCD spectra, we cannot visualize, at present, their mode of association.

Finally, we refer to the association model proposed previously[5] for the [Co(N)₆]³⁺···[Sb₂(tart)₂]²⁻ systems, where [Co(N)₆]³⁺ represents [Co(en)₃]³⁺, *cis-α-* and *cis-β-*[Co(trien)(en)]³⁺, *uns-fac-* and *s-fac-*[Co(dien)₂]³⁺ (trien = triethylenetetramine and dien = diethylenetriamine). The model was put forward to explain the results of chromatographic optical resolution and can be shown to be similar to the model of Figure 5 in the site of interaction of complex cations; the previous model utilizes two faces of an octahedron of a cation, while the present model uses four. Thus, it can be shown that the present model can explain equally well the results of the chromatographic experiments. The most significant difference between the two model lies in the orientation of the anion. In the previous model, the anion was assumed to face the complex cation with the tartrate backbone in front. It will be certain that this mode of access of the anion is not favored electrostatically over that of the present model. Also, an anomalous behavior of Δ-[Co(sen)]³⁺ as found here may not be expected from the previous model. In order to examine the validity of the present model, we are planning to make measurements by using bis(μ-*d*-dimethyltartrato)- and bis(μ-*l*-dimethyltartrato)diantimonate(III) ions,[21] in which each tartrate backbone now has two methyl substituents. For these anions, an almost zero degree of chiral discrimination is expected from the previous model, while the present model predicts that the degree of chiral discrimination may not be influenced greatly by the dimethyl substitution.

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