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CHROMATOGRAPHIC STUDY OF OPTICAL RESOLUTION

II*. SEPARATION OF OPTICALLY ACTIVE COBALT(III) COMPLEXES USING POTASSIUM ANTIMONY *d*-TARTRATE** AS ELUENT

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SUMMARY

Chromatographic separations of the optical isomers of cobalt(III) complexes, $[\text{Co}(\text{en})_3]^{3+}$, *cis-α*- $[\text{Co}(\text{trien})(\text{en})]^{3+}$, *cis-β*- $[\text{Co}(\text{trien})(\text{en})]^{3+}$, *u-fac*- $[\text{Co}(\text{dien})_2]^{3+}$, *s-fac*- $[\text{Co}(\text{dien})_2]^{3+}$ and *mer*- $[\text{Co}(\text{dien})_2]^{3+}$ (en = ethylenediamine, trien = triethylenetetramine and dien = diethylenetriamine; u = unsymmetrical; s = symmetrical) have been examined with potassium antimony *d*-tartrate as eluent, and adjusted retention volumes, separation factors and induced circular dichroism spectra have been determined. Based on these data, a key and lock type association model has been proposed for discrimination between *Δ* and *Λ* enantiomers.

INTRODUCTION

Ion-exchange chromatography has been used to separate geometrical isomers, and to resolve optical isomers of cobalt(III) complexes. The salts of *d*-tartrate (*d*-tart²⁻) and antimony *d*-tartrate, $[\text{Sb}_2(\textit{d-tart})_2]^{2-}$, are well known as effective eluents for the resolution of chiral metal complex cations. On the basis of X-ray analysis^{1,2} and the study of ion association in solution³, a stereoselective association model has been proposed to account for the discrimination effected by *d*-tart²⁻, in which four oxygen atoms of *d*-tart²⁻ approach a $[\text{Co}(\text{en})_3]^{3+}$ type complex along its three-fold axis and make a face-to-face close contact with the complex cation. However, for the other typical eluent, $[\text{Sb}_2(\textit{d-tart})_2]^{2-}$, no mechanism has been reported so far.

In our previous paper⁴ it was reported that the association constant of $[\text{Sb}_2(\textit{d-tart})_2]^{2-}$ with $[\text{Co}(\text{en})_3]^{3+}$ is greater than that of *d*-tart²⁻, and that K_{Δ}/K_{Λ} (the ratio of the association constant of a resolving agent with the *Δ* enantiomer to that with the *Λ* enantiomer of $[\text{Co}(\text{en})_3]^{3+}$) is considerably greater for $[\text{Sb}_2(\textit{d-tart})_2]^{2-}$ than for

* Part I: H. Yoneda and T. Yoshizawa, *Chem. Lett.*, (1976) 707.

** *d*-Tartrate refers to RR-tartrate.

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$d\text{-tart}^{2-}$. The separation factor* of $[\text{Co}(\text{en})_3]^{3+}$ obtained by ion-exchange chromatography (SP-Sephadex C-25) with 0.1 M $\text{K}_2[\text{Sb}_2(d\text{-tart})_2]$ is greater than that with 0.1 M $\text{Na}_2d\text{-tart}$: 1.42 for $\text{K}_2[\text{Sb}_2(d\text{-tart})_2]$ and 1.21 for $\text{Na}_2d\text{-tart}$ **⁵. From these data it is clear that $\text{K}_2[\text{Sb}_2(d\text{-tart})_2]$ is a better resolving agent than $\text{Na}_2d\text{-tart}$ for $[\text{Co}(\text{en})_3]^{3+}$, and this has generally been found to hold for other complexes; a salt of $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ has resolved more types of complexes than that of $d\text{-tart}^{2-}$. These facts seem to indicate that the mode of association of $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ is different from that of $d\text{-tart}^{2-}$.

In this paper we propose a stereoselective association model for $[\text{Sb}_2(d\text{-tart})_2]^{2-}$, and discuss it on the basis of retention volumes and separation factors for ion-exchange chromatography and induced circular dichroism (CD) spectra.

MODEL

Since the essence of the optical resolution of octahedral complexes lies in the discrimination of the configurational chiralities, Λ and Δ , it is preferable that the complexes have no side-chain in their chelate rings which might obscure the difference in configurational chiralities. In Table I are listed cobalt(III) complexes for which the chelate rings have no side-chain and for which optical resolution has been achieved by means of ion-exchange chromatography on SP-Sephadex using a salt of $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ as eluent.

First, trivalent metal complexes are examined for their structural similarities. Three complexes, $[\text{Co}(\text{tmd})_3]^{3+}$, $[\text{Co}(\text{tn})_2(\text{tmd})]^{3+}$ and $[\text{Co}(\text{tn})(\text{tmd})_2]^{3+}$, have flexible six- or seven-membered chelate rings and are only partially resolved, so that we do not refer to them further. For the other trivalent metal complexes except $[\text{Co}(\text{penten})]^{3+}$, it is found that the first enantiomers which are eluted, *i.e.*, the Λ -forms, have a special topography in common which is indicated by shading in Fig. 1. The characteristics of the special topography are an N-H proton at the apex which points vertically out of the plane of the paper, and only one chelate ring on the lower left side in Fig. 1. Such a special topography is not found in the enantiomers which are eluted second, *i.e.*, the Δ -forms.

Secondly, we considered the relation between the discrimination for complexes shown by $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ and the fact that the enantiomers eluted first have the special property shown in Fig. 1. The Λ - and Δ -configurations are characterized by the coordination of three ethylenediamine ligands in the case of $[\text{Co}(\text{en})_3]^{3+}$. The space between the three ethylenediamine ligands, *i.e.* the "channel", is determined by the Λ - and Δ -configurations. Fig. 2A shows Λ - $[\text{Co}(\text{en})_3]^{3+}$ and its "L-shaped channel". The special topography shown in Fig. 1 corresponds to the L-shaped channel. On the other hand, the three ethylenediamine ligands of Δ - $[\text{Co}(\text{en})_3]^{3+}$ form "J-shaped channels" as shown in Fig. 2B.

The structure of $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ was elucidated by X-ray analyses^{21,22}, and comprises two *d*-tartrate bridging groups with a four-coordination geometry as shown in Fig. 3A. Fig. 3B shows the hatched atoms in Fig. 3A, as viewed from the centre of

* The separation factor is the ratio of the adjusted retention volume of the second band to that of the first band, and is a measure of the degree of separation. The greater the separation factor the better two bands are separated, and no separation results when it is unity.

** Column, 1.2 × 90 cm; rate of elution, 0.33 ml/min.

TABLE I

COBALT(III) COMPLEXES AND ABSOLUTE CONFIGURATIONS OF FIRST ELUTED ENANTIOMERS USING A SALT OF $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ AS ELUENT

tmd = $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$; penten = $(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$; amb = $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}^-$; meta = $\text{NH}_2\text{CH}_2\text{CH}_2\text{O}^-$; cys = $\text{NH}_2\text{CH}_2\text{CH}_2\text{S}^-$; ida = $^- \text{O}_2\text{CCH}_2\text{-NHCH}_2\text{CO}_2^-$; aetp = $\text{NH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2^-$; tn = $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$.

Complex	Absolute configuration	Ref.
3+ cations		
$[\text{Co}(\text{en})_3]^{3+}$	Δ^{**}	4, 6
$[\text{Co}(\text{en})_2(\text{tn})]^{3+}$	Δ^*	7
$[\text{Co}(\text{en})(\text{tn})_2]^{3+}$	Δ^*	7
$[\text{Co}(\text{en})_2(\text{tmd})]^{3+}$	Δ^*	8
$[\text{Co}(\text{en})(\text{tmd})_2]^{3+}$	Δ^*	7
$[\text{Co}(\text{en})(\text{tn})(\text{tmd})]^{3+}$	Δ^*	7
<i>cis</i> - $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$	Δ^*	9
β - $[\text{Co}(\text{trien})(\text{en})]^{3+}$	Δ^*	10
<i>u-fac</i> - $[\text{Co}(\text{dien})_2]^{3+}$	Δ^{**}	11, 12
$[\text{Co}(\text{tmd})_3]^{3+}$	Δ^*	7
$[\text{Co}(\text{tn})_2(\text{tmd})]^{3+}$	Δ^*	7
$[\text{Co}(\text{tn})(\text{tmd})_2]^{3+}$	Δ^*	7
$[\text{Co}(\text{penten})]^{3+}$	Δ^{**}	13, 14, 15
<i>mer</i> - $[\text{Co}(\text{dien})_2]^{3+}$		11
2+ cations		
$[\text{Co}(\text{gly})(\text{en})_2]^{2+}$	Δ^*	16
$[\text{Co}(\beta\text{-ala})(\text{en})_2]^{2+}$	Δ^*	17
$[\text{Co}(\text{amb})(\text{en})_2]^{2+}$	Δ^*	17
$[\text{Co}(\text{meta})(\text{en})_2]^{2+}$	Δ^*	5
$[\text{Co}(\text{cys})(\text{en})_2]^{2+}$	Δ^*	5
$[\text{Co}(\text{gly})(\text{tn})]^{2+}$	Δ^*	16
1+ cations		
<i>cis</i> (O), <i>cis</i> (N)- $[\text{Co}(\text{gly})_2(\text{en})]^+$	Δ^*	16
<i>u-fac</i> - $[\text{Co}(\text{ida})(\text{dien})]^+$	Δ^*	18
<i>cis, cis, cis</i> - $[\text{Co}(\text{aetp})_2]^+$	Δ^*	19
<i>trans</i> (N)- $[\text{Co}(\text{aetp})_2]^+$	Δ^*	19
<i>trans</i> (S)- $[\text{Co}(\text{aetp})_2]^+$	Δ^*	19
$[\text{Co}(\text{N}_3)_2(\text{en})_2]^+$	Δ^*	16
α - $[\text{Co}(\text{N}_3)_2(\text{trien})]^+$	Δ^*	16
<i>cis</i> (O), <i>trans</i> (N), <i>cis</i> (NH ₃)- $[\text{Co}(\text{gly})_2(\text{NH}_3)_2]^+ \text{***}$	Unknown	20

* Speculation from CD spectra.

** Decided by X-ray analysis.

*** Dowex 50W-X8 was used.

this molecule. Two oxygen atoms of carbonyl groups and one hydrogen atom of a methylene group project below the paper. On examining molecular models, the projecting part of $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ shown in Fig. 3B fits the L-shaped channel of Δ - $[\text{Co}(\text{en})_3]^{3+}$ as shown in Fig. 4. One carbonyl oxygen of $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ is directed towards the N-H proton of the ethylenediamine ligand. The projecting part of $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ corresponds to a "key" and the channel of the complex to a "lock". On the other hand, $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ cannot be positioned so closely with Δ - $[\text{Co}(\text{en})_3]^{3+}$ because of its J-shaped channel. Therefore, if we suppose that the stereoselective

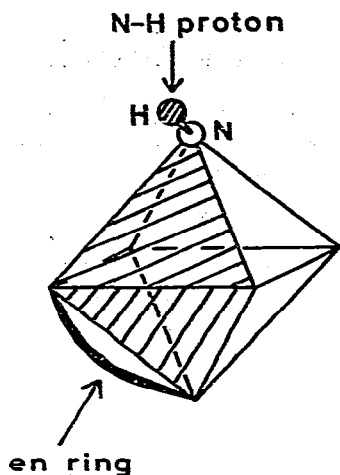


Fig. 1. A common special topography found in complexes resolved into enantiomers by $[\text{Sb}_2(d\text{-tart})_2]^{2-}$.

association of $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ with complexes is effected in this way, the resulting optical resolution is reasonably interpreted.

The enantiomer associated more closely with an eluent is generally eluted faster in ion-exchange chromatography. In order to demonstrate whether or not the "channel" plays a crucial role in optical resolution, the number of L-shaped channels in each complex was compared with the retention volume and the separation factor obtained by ion-exchange chromatography with $\text{K}_2[\text{Sb}_2(d\text{-tart})_2]$ as eluent. Supposing that $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ uses the L-shaped channel in resolving complexes, it is expected that the value of the retention volume of the first eluted enantiomer decreases and the separation factor increases as the number of L-shaped channels of the enantiomer

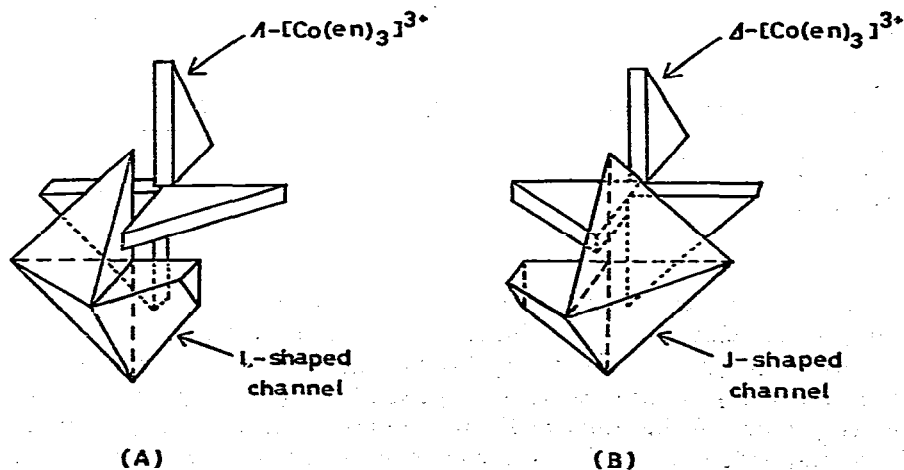
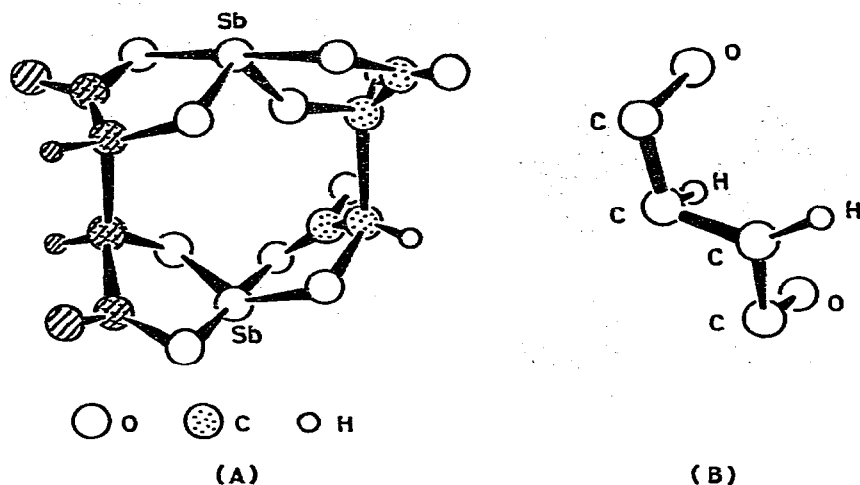
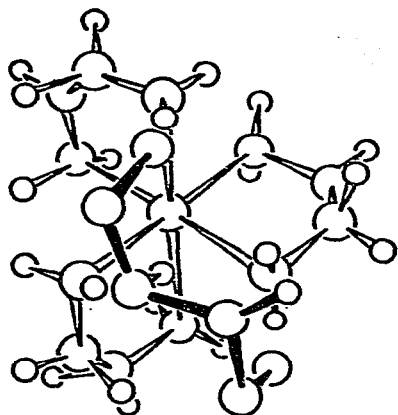


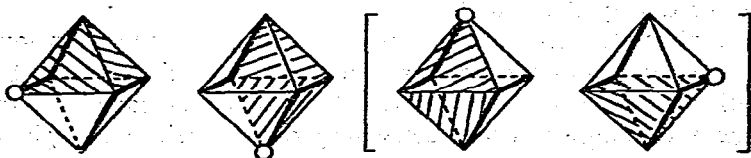
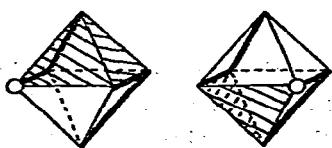
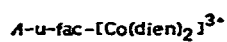
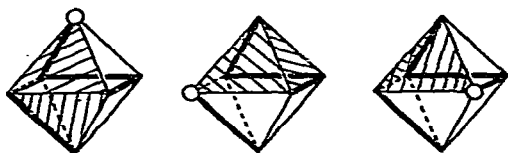
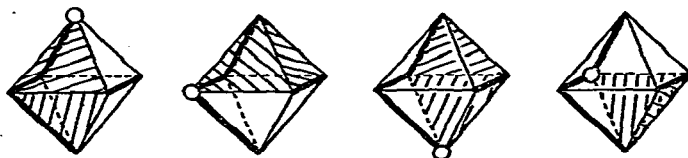
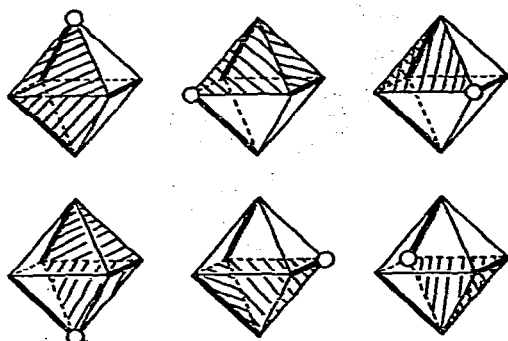
Fig. 2. Structure of $\Delta\text{-}[\text{Co}(\text{en})_3]^{3+}$ and L-shaped channel (A), and $\Delta\text{-}[\text{Co}(\text{en})_3]^{3+}$ and J-shaped channel (B).

Fig. 3. Structure of $[\text{Sb}_2(\text{d-tart})_2]^{2-}$.Fig. 4. Stereoselective association model of $[\text{Sb}_2(\text{d-tart})_2]^{2-}$ with one of the L-shaped channels of $\Delta\text{-}[\text{Co}(\text{en})_3]^{3+}$.

increases. The following complexes* were selected because they have the same charge (3+), do not possess any local charge, have the same number (four) of ethylenediamine bridges and yet have a different number of L-shaped channels: *cis-α*- $[\text{Co}(\text{trien})(\text{en})]^{3+}$, *cis-β*- $[\text{Co}(\text{trien})(\text{en})]^{3+}$, *u-fac*- $[\text{Co}(\text{dien})_2]^{3+}$, *s-fac*- $[\text{Co}(\text{dien})_2]^{3+}$ and *mer*- $[\text{Co}(\text{dien})_2]^{3+}$. The complex $[\text{Co}(\text{en})_3]^{3+}$ having three ethylenediamine bridges was also studied because it is the prototype of cobalt(III) complexes having enantiomers and has the largest number of L-shaped channels.

Fig. 5 shows the absolute configuration of the Δ -forms of the enantiomers which have L-shaped channels, and the positions of the L-shaped channels. Since *s-fac*- $[\text{Co}(\text{dien})_2]^{3+}$ with no optical isomers has two L- and two J-shaped channels, it is useful to examine this complex when discussing our model. Although *mer*-

* u = unsymmetrical and s = symmetrical; abbreviations for coordination modes of ligands.



J-shaped channel

Fig. 5. Absolute configurations of the first eluted enantiomers and the positions of the L-shaped channels.

$[\text{Co}(\text{dien})_2]^{3+}$ has no L-shaped channel, it possesses enantiomers because the configurations of two dien ligands are fixed owing to meridional coordination, and the secondary nitrogen atoms give rise to the dissymmetry.

EXPERIMENTAL

Preparation of complexes

(a) β - $[\text{Co}(\text{trien})(\text{en})]\text{Cl}_3$. This complex was prepared according to the method of Schaefer and Brubaker²³.

(b) α - $[\text{Co}(\text{trien})(\text{en})]\text{I}_3$. This complex was reported first by Schaefer and Brubaker²³, but the preparative method was found to lead to β - $[\text{Co}(\text{trien})(\text{en})]\text{Cl}_3$. Therefore we prepared and isolated it as follows. To α - $[\text{Co}(\text{trien})(\text{NO}_2)_2]\text{Cl}$ (ref. 24; 30 g, 0.09 M) in water (50 ml) was added concentrated HNO_3 (30 ml) dropwise with stirring at room temperature. Nitrogen dioxide gas was evolved and the colour of the solution changed to red. The solution was evaporated almost to dryness and a red sticky material, $[\text{Co}(\text{trien})(\text{NO}_3)_2]\text{NO}_3$, was left. This complex was dissolved in 100 ml of dimethyl sulphoxide (DMSO) and ethylenediamine (9 ml) was added to the cooled solution. After mechanical stirring for 0.5 h, ethanol (ca. 20 ml) was added. The tar formed was collected and dissolved in a small volume of water, to which a saturated solution of KI was then added. After cooling, α - $[\text{Co}(\text{trien})(\text{en})]\text{I}_3$ was precipitated, filtered off, washed with ethanol and recrystallized from hot water. Analysis: Calculated for $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_2\text{H}_8\text{N}_2)]\text{I}_3$: C, 14.87; H, 4.03; N, 13.01%. Found: C, 14.71; H, 4.13; N, 12.99%.

(c) *u-fac*-, *s-fac*- and *mer*- $[\text{Co}(\text{dien})_2]\text{I}_3$. $[\text{Co}(\text{dien})_2]\text{Br}_3$ was prepared according to the method of Keene and Searle²⁵. An aqueous solution of $[\text{Co}(\text{dien})_2]\text{Br}_3$ was applied to a column of SP-Sephadex C-25 cation-exchange resin and was eluted with 0.15 M Na_2SO_4 to separate the isomers in the order *s-fac* (eluted first), *u-fac*, *mer* (last)²⁶. Each fraction was applied again to a column of SP-Sephadex C-25 and eluted with 2 M LiCl to convert each isomer into the chloride form. Each effluent was concentrated to a small volume under reduced pressure and a saturated solution of KI was added. The iodide of each isomer was precipitated on cooling.

Measurements of retention volumes

SP-Sephadex C-25 was packed in a column (6.5 × 440 mm) and 0.1 M $\text{K}_2[\text{Sb}_2(d\text{-tart})_2]$ was used as eluent. Potassium chloride (0.4 M) was used as a reference. The void volume was determined by use of Blue Dextran 2000. A mixture of the appropriate amount of one complex and Blue Dextran was applied to the column of SP-Sephadex (which had already been equilibrated with the eluent) and was eluted with 0.1 M $\text{K}_2[\text{Sb}_2(d\text{-tart})_2]$ solution at a constant rate (0.7 ml/min). The effluent was led to a flow cell and detected by a spectrophotometer for measurement of the retention volumes of the first and second bands. The same procedure was applied to all the complexes.

Measurements of induced CD spectra

Induced CD spectra were obtained for solutions of complexes (0.01 M) containing $\text{K}_2[\text{Sb}_2(d\text{-tart})_2]$ (0.1 M) or $\text{Na}_2d\text{-tart}$ (0.1 M) on a JASCO J-40CS spectropolarimeter equipped with a 2-cm cell.

RESULTS AND DISCUSSION

The void volume was 4.8 ml. The adjusted retention volumes and separation factors are given in Table II. The experimental error of each adjusted retention volume was within ± 1.5 ml. The second column in Table II shows the number of L- and J-shaped channels in the first eluted enantiomer, *i.e.*, the Δ -form in these cases. Volume I and volume II are the adjusted retention volumes of the first and the second bands eluted with 0.1 M $K_2[Sb_2(d-tart)_2]$, and volume III is that of the band eluted with 0.4 M KCl. A slight difference among the values of volume III is noted, which presumably results from the differing extents of association of the complexes with Cl^- , or from differences in the affinities of the complexes for the resin. A slight difference in retention volumes arising from the same cause may also result when $K_2[Sb_2(d-tart)_2]$ is used as eluent. Therefore, in discussing the values of volume I and II, we should keep in mind the above inherent difference.

TABLE II

ADJUSTED RETENTION VOLUMES AND SEPARATION FACTORS

L, J = The number of L- and J-shaped channels in the first eluted enantiomer. Volume I = retention volume of the first band eluted with $K_2[Sb_2(d-tart)_2]$. Volume II = retention volume of the second band eluted with $K_2[Sb_2(d-tart)_2]$. Volume III = retention volume of the band eluted with KCl. Dif = volume II - volume I.

Complex	L, J	Volume I (ml)	Volume II (ml)	Volume III (ml)	Dif	Separation factor
1 $[Co(en)_3]^{3+}$	6, 0	200.1	289.3	113.9	89.2	1.45
2 α - $[Co(trien)(en)]^{3+}$	4, 0	199.1	272.6	104.3	73.5	1.37
3 β - $[Co(trien)(en)]^{3+}$	3, 0	214.5	275.0	106.7	60.5	1.28
4 <i>u-fac</i> - $[Co(dien)_2]^{3+}$	2, 0	236.4	283.7	110.4	47.3	1.20
5 <i>s-fac</i> - $[Co(dien)_2]^{3+}$	2, 2	238.9	—	104.8	—	—
6 <i>mer</i> - $[Co(dien)_2]^{3+}$	0, 0	265.2	(298.8)*	108.6	(33.6)	(1.13)

* Estimated, because of a partial resolution.

(i) Analysis of the separation factors

The separation factors of complexes 1, 2, 3 and 4 were 1.45, 1.37, 1.28 and 1.20, respectively, corresponding to a decrease in the number of L-shaped channels from 6 (Δ -form of complex 1) to 2 (Δ -form of complex 4). This regular change of the separation factors supports our idea that the L-shaped channel is used when $[Sb_2(d-tart)_2]^{2-}$ discriminates the enantiomers.

(ii) Analysis of volume II

According to our model, $[Sb_2(d-tart)_2]^{2-}$ fits the L-shaped channel of a complex but does not fit the J-shaped channel. Therefore, it is expected that the values of volume I depend on the type of complex listed in Table I, while those of volume II are expected to be constant because the Δ -form of each complex has no L-shaped channel. It was found from the experimental data that the values of volume II for complexes 1, 2, 3 and 4 are almost equal, providing we note that the variation of the values is about twice volume III.

(iii) *Analysis of volume I*

Since both complex 5 and the *A*-isomer of complex 4 have two L-shaped channels, their retention volumes are expected to be equal. According to our experimental data, the values for complex 4 and 5 are 236.4 and 238.9, respectively. This near equality further supports our proposal that $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ discriminates the enantiomers by use of the association with the L-shaped channel.

The chirality of complex 6 arises from the conformations of the ligands, and is different from the chirality of complexes 1–4 which arises from their configurations. Although both the enantiomers of complex 6 have neither L- nor J-shaped channels, complex 6 was resolved by $[\text{Sb}_2(d\text{-tart})_2]^{2-}$. This phenomenon would imply that complex 6 is resolved by another mechanism instead of that of our model. However, our mechanism based on the L- and the J-shaped channel would predominate in the resolution of complexes with $[\text{Sb}_2(d\text{-tart})_2]^{2-}$. It is for this reason that volume I of complex 6 is not as close to volume I of complex 4 as it is, to volume II of complex 4.

(iv) *Analysis of the difference between volume II and volume I*

The difference between volume II and volume I of complex 4 (described as Dif (4) below) is 47.3, Dif (3) = 60.5, Dif (2) = 73.5 and Dif (1) = 89.2. The difference between Dif (3) and Dif (4) [described as Dif (3) – Dif (4) below] is 13.2, Dif (2) – Dif (3) = 13.0 and Dif (1) – Dif (2) = 15.7. Dif (3) – Dif (4) represents the decrease in the adjusted retention volume caused by the decrease (by one) in the number of L-shaped channels, *i.e.*, the number of millilitres of an adjusted retention volume which corresponds to one L-shaped channel. Likewise, Dif (2) – Dif (3) can be taken as the decrease in the adjusted retention volume owing to one L-shaped channel. The fact that Dif (3) – Dif (4) and Dif (2) – Dif (3) are nearly equal suggests that the number of L-shaped channels plays an essential role in optical resolution. Dif (1) – Dif (2) should correspond to the decrease in the adjusted retention volume per two L-shaped channels, and this value, 15.7, might appear to be too small compared with the above volumes (2×13.0 or 2×13.2). The smaller value could be explained in terms of the different affinity of the complexes for the resin owing to the different number of ethylenediamine bridges; complex 1 has three, but the other complexes have four, such bridges.

(v) *Analysis of induced CD spectra*

The complexes selected in this work are suitable for the study of induced CD spectra, because they have many common properties; they are $[\text{Co}(\text{N})_6]^{3+}$ type complexes and their chelate rings consist of Co–N–C–C–N chains only. When a solution of $\text{Na}_2d\text{-tart}$ is used as a chiral medium, the complexes show similar CD spectra comprising a single negative band (dotted line in Fig. 6). On the other hand, in the presence of $\text{K}_2[\text{Sb}_2(d\text{-tart})_2]$, the complexes show a variety of CD bands (full lines in Fig. 6). These induced CD spectra imply that the association of $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ with the complexes is different from that of $d\text{-tart}^{2-}$. Although complex 5 has no enantiomer, its CD spectrum induced by $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ is similar to that of complex 4. Our model in which the L-shaped channel is mainly concerned with the stereoselective association would account for the similarity, since complexes 4 and 5 have two L-shaped channels.

Thus, for the complexes selected in the present experiment, on the basis of

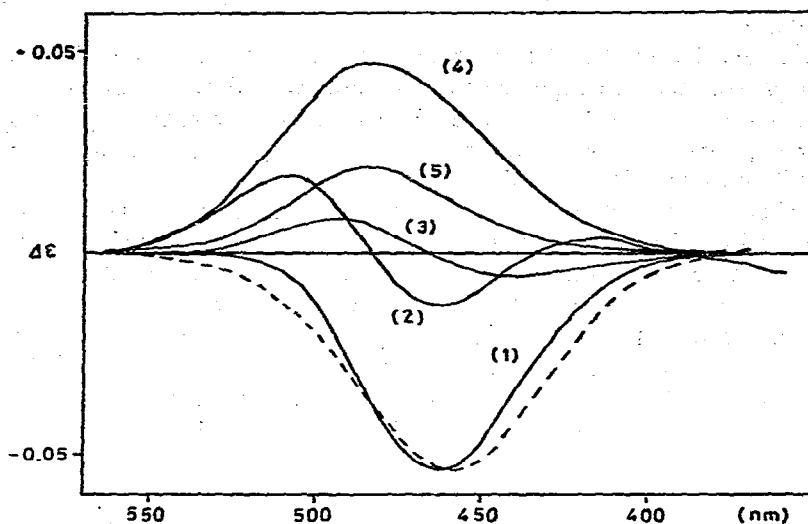


Fig. 6. Induced CD spectra in the presence of $d\text{-tart}^{2-}$ (---), and of $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ (—).

adjusted retention volumes, separation factors and induced CD spectra, it is concluded that the L-shaped channel plays an essential role in optical resolution using a salt of $[\text{Sb}(d\text{-tart})_2]^{2-}$ as eluent. *A*-enantiomers, having L-shaped channels, are eluted first not only for the selected trivalent cobalt complexes but also for univalent, bivalent and other trivalent complexes listed in Table I, which appears to lend credence to our model. We are now planning to undertake an X-ray analysis of one of diastereoisomers in order to support our model.

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