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Synthesis, Characterization, and Optical Resolution of Electrically Neutral Octahedral Cobalt(III) Complexes Containing the Tetradentate Ligand

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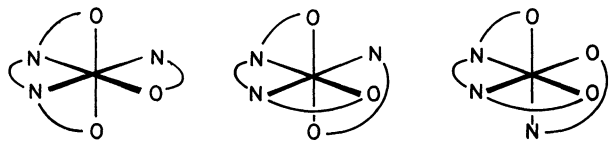
Three geometrical isomers of [Co(edda)(aa)] where edda=*N'*,*N*-ethylenediaminediacetato, aa=glycinato (gly), β-alaninato (β-ala), have been synthesized and characterized. They have been completely resolved into the enantiomers, except *unsym-cis-fac*-[Co(edda)(β-ala)], by the bis(μ-*d*-tartrato)diantimonate(III) anion, $[Sb_2(d\text{-tart})_2]^{2-}$, form of QAE-Sephadex resin with water as the eluent, and their absolute configurations have been determined based upon the circular dichroism spectra. It has been revealed that the *Δ* enantiomer is favored more by $[Sb_2(d\text{-tart})_2]^{2-}$ than the *Λ* enantiomer irrespective of the kind of the geometrical isomers. Consideration on the mechanism of the optical resolution has been presented.

The optical resolution of electrically neutral transition metal complexes is difficult, compared with that of cationic or anionic metal complexes, because they do not form diastereomers with an optically active resolving agent. Chromatographic technique is very effective to achieve the optical resolution of such neutral complexes.[1] Some neutral complexes have been reported to be partially resolved into the enantiomers; *cis*-[Co(dimethylglyoximato)$_2$(NH_3)Cl] by using a quartz powder column,[2] *mer*- and *fac*-[Co(gly)$_3$], and *s-cis-mer*-[Co(edda)(gly)] by using a potato starch column,[3] where gly and edda stand for glycinato and *N*,*N'*-ethylenediaminediacetato, respectively. The first complete resolution of neutral complexes was reported in 1976 by Yoneda for *fac*-[Co(β-ala)$_3$] (β-ala=β-alaninato) on the Na^+ form of CM-Sephadex cation exchanger with an ethanol-water solution of sodium *d*-tartrate, Na_2(d-tart), as the eluent.[4] Thereafter, the complete resolution of a series of enantiomeric pairs of *fac*-[Co(D/L-ser)$_{3-n}$(β-ala)$_n$] (*n*=0 to 3, ser=serinato) was achieved on Na^+ form of TSK-211 cation exchanger with sodium bis(μ-*d*-tartrato)diantimonate(III), Na_2-$[Sb_2(d\text{-tart})_2]$, aqueous solution as the eluent.[5] An anion-exchange column has also been indicated to be useful to resolve neutral complexes into enantiomers. Two series of enantiomeric pairs of *fac*-[Co(gly)$_{3-n}$(β-ala)$_n$] and *fac*-[Co(D/L-α-ala)$_{3-n}$(β-ala)$_n$] were completely resolved on the $[Sb_2(d\text{-tart})_2]^{2-}$ form of TSK-220 anion exchanger with water as the eluent.[6] Complete resolution of the meridional isomer of tris(amino acidato)-cobalt(III) complexes has also been achieved. After success of optical resolution of *mer*-[Co(β-ala)$_3$],[7] enantiomeric pairs of *mer*-[Co(gly)$_3$] and *mer*-[Co(D/L-α-ala)$_3$] were resolved on the $[Sb_2(d\text{-tart})_2]^{2-}$ form of QAE-Sephadex resin with water as the eluent.[8]

Neutral complexes, other than tris(amino acidato)-complexes, have also been tried to be resolved. Tris-(acetylacetonato)transition-metal complexes, [M-(acac)$_3$] (M=Cr, Co, Rh, Ru) were partially resolved by the use of a *d*-lactose column[9] or a quartz column[10] and [M(acac)$_3$] (M=Cr, Co, Ru) and [M(gly)$_{3-n}$(acac)$_n$] (*n*=3 to 1) were also partially resoluved on a *Δ*-[Ni(phen)$_3$]-montmorillonite column (phen=1,10-phenanthroline).[11] Recently, [Co(acac)$_3$] and [Cr-(acac)$_3$] were completely resoluved by HPLC on a (+)-poly(triphenylmethyl methacrylate) column.[12]

Neutral complexes completely resolved so far into enantiomers are limited only to tris-chelates. We report here the complete resolution of neutral complexes containing a tetradentate ligand by column chromatography. As such complexes, we chose [Co(edda)(gly)] and [Co(edda)(β-ala)]. For both complexes, there are three geometrical isomers shown in Scheme 1.



Scheme 1.

Experimental

General Remarks. *N*,*N'*-Ethylenediaminediacetic acid (H_2edda), glycine (Hgly), β-alanine (H-β-ala) were commercially available and were used without further purification. Na[Co(edda)(CO_3)]·1.5H_2O,[13] Co^{II}(edda),[14] and *s-cis-mer*-[Co(edda)(gly)][15] were prepared according to the literature methods. Absorption (AB) and circular dichroism (CD) spectra were recorded on a Shimadzu UV 200 and a JASCO J-40CS, respectively.

Synthesis and Separation of the Isomers of *u-cis-mer* and *u-cis-fac*-[Co(edda)(gly)]. To a solution of 4.00 g (0.012 mol) of Na[Co(edda)(CO_3)]·1.5H_2O in 30 cm^3 of water was added 0.90 g (0.012 mol) of glycine. The solution was heated to 50 °C, and 7.5 cm^3 of HCl aqueous solution containing 1.0 cm^3 of concentrated HCl was added dropwise. The heating was continued for 5 h. Then, the solution was filtered. The filtrate was placed on an anion-exchange column (Dowex 1-X8, Cl^- form) and eluted with water to remove any residual starting material or anionic products. The eluate was evaporated under an air stream to 10 cm^3 and again filtered to remove the s-cis-mer isomer. The filtrate was placed on a cation-exchange column (SP-Sephadex C-25, Na^+ form) and

washed through with water. The color materials separated into two bands, a blue-violet band and a slower moving red-violet band. The u-cis-mer isomer (1.2 g, 32%) and u-cis-fac isomer (1.0 g, 24%) were obtained from the first and the second eluted bands as crystals by concentration, respectively.

Found: C, 29.55; H, 5.09; N, 13.34%. Calcd for *u-cis-mer*-$[CoC_8H_{14}N_3O_6]\cdot 0.5H_2O$: C, 30.39; H, 4.78; N, 13.29%.

Found: C, 27.82; H, 5.07; N, 12.39%. Calcd for *u-cis-fac*-$[CoC_8H_{14}N_3O_6]\cdot 2H_2O$: C, 27.99; H, 5.29; N, 12.24%.

Synthesis of *s-cis-mer*-[Co(edda)(β-ala)]. The complex was prepared in the manner similar to that of the glycine analog. To 500 cm^3 of an aqueous solution containing 4.66 g (0.020 mol) of Co^{II}(edda) were added 2.00 g of activated charcoal and 1.78 g (0.020 mol) of β-alanine. A stream of air was passed through the suspended solution for ca. 8 h. Then, the solution was heated at 60 °C for 30 min. The charcoal was removed by filtration and washed with hot water several times. The filtrate and washings were combined, which were heated on a stream bath almost to dryness. Purple crystals were deposited as a crude product (2.3 g, 35%). The purple product (1.1 g, 17%) for elemantal analysis was obtained by recrystallization from hot water.

Found: C, 32.26; H, 5.16; N, 12.79%. Calcd for $[CoC_9H_{16}N_3O_6]\cdot 0.5H_2O$: C, 32.74; H, 5.19; N, 12.73%.

Synthesis and Separation of the Isomers of *u-cis-mer* and *u-cis-fac*-[Co(edda)(β-ala)]. The synthesis and separation were identical with that of the glycine analog except it was carried out using 1.13 g (0.013 mol) of β-alanine. Yield of the u-cis-mer isomer was 1.2 g (18%), and that of the u-cis-fac isomer was 1.0 g (15%).

Found: C, 32.56; H, 5.37; N, 12.57%. Calcd for *u-cis-mer*-$[CoC_9H_{16}N_3O_6]\cdot 0.5H_2O$: C, 32.74; H, 5.19; N, 12.73%.

Found: C, 32.20; H, 4.75; N, 12.48%. Calcd for *u-cis-fac*-$[CoC_9H_{16}N_3O_6]\cdot 0.5H_2O$: C, 32.74; H, 5.19; N, 12.73%.

Optical Resolution by Ion-Exchange Chromatography. A column of 1.0 cm inner diameter was filled with 82.5 cm length of QAE-Sephadex A-25 (anion exchanger) which had been treated with 0.1 mol aqueous solution of $K_2[Sb_2(d\text{-tart})_2]$. About 20 mg of each sample prepared in this paper was dissolved in ca. 2 cm^3 of water and the solution was loaded on the column. The elution was done with water at a flow rate 7.8×10^{-2} $cm^3\,min^{-1}$. The void volume was measured to be 30.9 cm^3 by using $[Fe(phen)_3]Cl_2$ (phen=1,10-phenanthroline) as a marker. An automatic fraction collector was connected to the end of the column to divide the eluate into fractions of 4 cm^3. The AB spectrum of each fraction was measured. Thus, the retention volumes were determined. Two fractions in which the concentration of the separated enantiomers was highest were passed through QAE-Sephadex A-25 (Cl^- form) with water as the eluent to remove $[Sb_2(d\text{-tart})_2]^{2-}$. The eluates obtained were subjected to AB and CD measurments.

Results and Discussion

Preparation and Assignment of Geometrical Isomers. *s-cis-mer*-[Co(edda)(gly)] complex was prepared from Co^{II}(edda), obtained from $CoCO_3$ and Ba(edda), and glycine according to the literature method.[15] The geometrical isomers of [Co(edda)(diamine)]$^+$ and [Co(edda)(L)] (L=gly, L-ala) prepared from Co^{II}(edda) were assigned exclusively to trans and s-cis-mer, respectively according to the absorption spectra and ^1H NMR spectra.[14,15] Therefore, [Co(edda)(β-ala)] prepared from Co^{II}(edda) and β-alanine can be thought to have s-cis-mer configuration. The similar absorption spectrum to that of *s-cis-mer*-[Co(edda)(gly)] also supports the s-cis-mer configuration. The purity was checked by elemental analysis and column chromatography.

The reaction of $Na[Co(edda)(CO_3)]$, prepared from $Na_3[Co(CO_3)_3]$ and H_2edda, with glycine produced the mixture of u-cis-mer and u-cis-fac isomers of [Co(edda)(gly)]. Although s-cis-mer isomer was also formed in this reaction as a minor product, it could be readily removed by filtration because of its low solubility in water. The two u-cis isomers were separated by pass-

Table 1. Absorption and Circular Dichroism Data of [Co(edda)(aa)]

Complex	Absorption Max./nm (ε)	Circular Dichroism Max./nm ($\Delta\varepsilon$)[a]
s-cis-mer-[Co(edda)(gly)]	542 (116) 470 sh 372 (133)	542 (−5.35) 465 (+2.17)
u-cis-mer-[Co(edda)(gly)]	525 (94) 370 (128)	543 (−2.48) 465 (+0.97)
u-cis-fac-[Co(edda)(gly)]	520 (223) 374 (167)	523 (−1.12)
s-cis-mer-[Co(edda)(β-ala)]	560 sh 505 (113) 374 (122)	550 (−3.67) 477 (+2.31)
u-cis-mer-[Co(edda)(β-ala)]	590 sh 505 (83) 373 (90)	553 (−1.58) 477 (+1.09)
u-cis-fac-[Co(edda)(β-ala)]	523 (252) 374 (147)	560 (−)[b] 500 (+)

a) For Δ-enantiomer. b) Partially resolved.

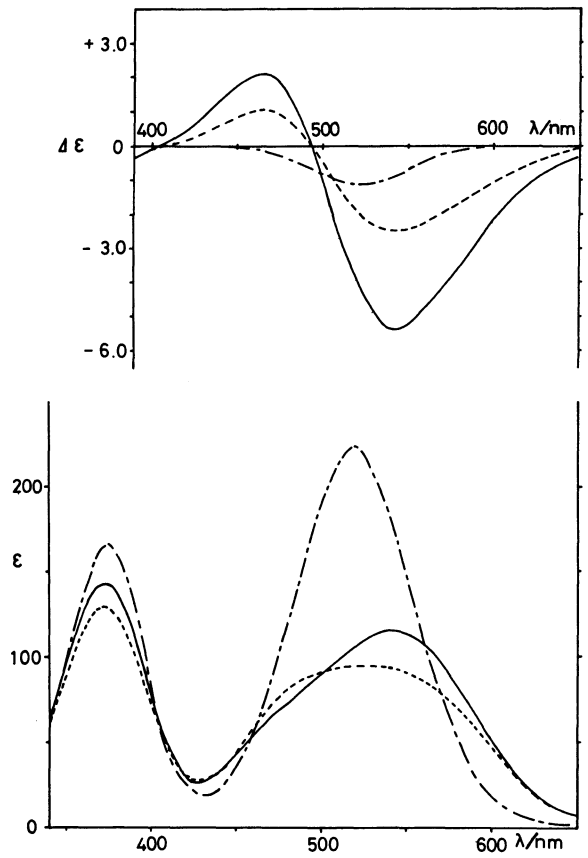


Fig. 1. Absorption spectra (below) and circular dichroism spectra (above) of *Δ*-[Co(edda)(gly)]; s-cis-mer (——), u-cis-mer (----), u-cis-fac (-·-·-).

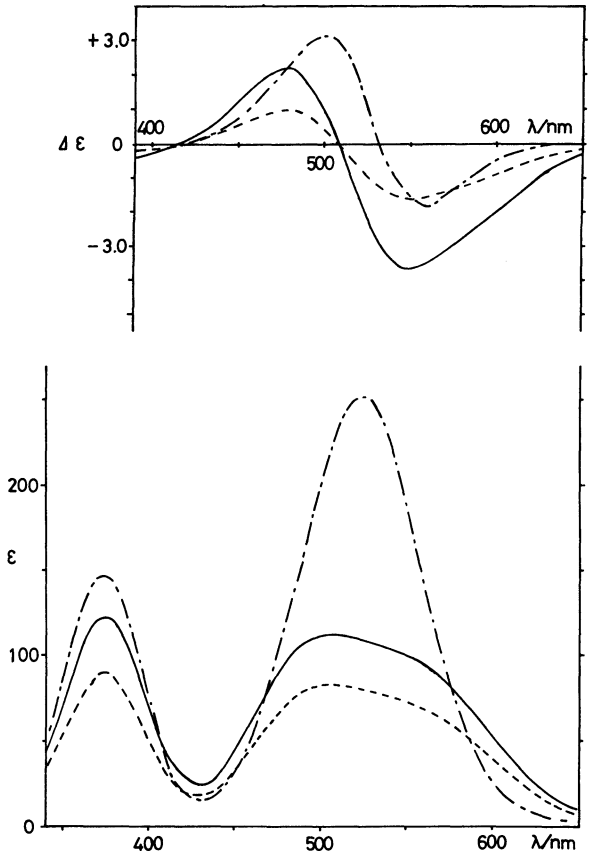


Fig. 2. Absorption spectra (below) and circular dichroism spectra (above) of *Δ*-[Co(edda)(β-ala)]; s-cis-mer (——), u-cis-mer (----), u-cis-fac(-·-·-). The scale is arbitrary for the u-cis-fac isomer due to the partial resolution.

ing through the SP-Sephadex C-25 column. The first eluted isomer was assigned to u-cis-mer and the second one to u-cis-fac, according to the reason mentioned below. The u-cis-mer and u-cis-fac isomers of [Co(edda)(β-ala)] were obtained in the manner identical with that of [Co(edda)(gly)].

The absorption (AB) and circular dichroism (CD) data of the neutral complexes prepared in this paper are given in Table 1. Figures 1 and 2 show the AB and CD spectra. The ligand field symmetry of the u-cis-fac isomer is higher than that of the u-cis-mer isomer. The decrease in symmetry from facial to meridional is expected to cause a splitting or at least a broadening of the lowest energy absorption band in the visible spectra. In [Co(edda)(gly)], broadening is obviously observed in the low-energy absorption band for the first eluted isomer. In [Co(edda)(β-ala)], a marginal shoulder is found for the first eluted isomers. In contrast, the second eluted isomers of [Co(edda)(gly)] and [Co(edda)-(β-ala)] exhibit a relatively sharp absorption band. Therefore, the first and the second eluted isomers for both [Co(edda)(gly)] and [Co(edda)(β-ala)] can be assigned to the u-cis-mer and u-cis-fac isomers, respectively. The similar assignment based upon the absorption spectra was done with respect to *u-cis-fac* and *u-cis-mer*-[Co(edda)(L-ala)] isomers.[13]

The assignment is consistent with the chromatographic behavior. Although both isomers are electrically neutral, the facial isomer has a greater dipole moment than the meridional isomer. Thus, the former is considered to interact more effectively with the functional group of SP-Sephadex C-25 cation exchanger than the later. Therefore, the facial isomer is expected to be eluted later than the meridional one. Such tendency has been actually observed (vide infra, see Table 2).

Circular Dichroism Spectra and Absolute Configurations. The partial optical resolution of *s-cis-mer*-[Co(edda)(gly)] has been attained and its absolute configuration has been established.[15] The CD spectrum of the *Δ* configuration consists of a dominant positive band at lower energy and a minor negative band at higher energy in the first d-d transition region. The sign of the dominant peak in the first d-d transition region of the CD spectrum can generally be related to the net chirality of the complex.[16,17] A *Δ* configuration of chelate rings is expected to produce a negative dominant peak in the d-d transition region while a *Λ* configuration would produce a positive dominant peak.[16] This argument has been applied to [Co(edda)(diamine)]$^{+}$[13] and *s-cis-mer*-[Co(edda)(aa)] (aa=gly, L-ala).[15] The CD spectra shown in Figs. 1 and 2 are

Table 2. Adjusted Retention Volumes and Separation Factors

Complex	Adjusted Retention Volume/cm³ First	Second	Separation Factor
s-cis-mer-[Co(edda)(gly)]	55.6 (*Λ*)[a]	63.6 (*Δ*)	1.14
u-cis-mer-[Co(edda)(gly)]	56.1 (*Λ*)	64.6 (*Δ*)	1.15
u-cis-fac-[Co(edda)(gly)]	197.1 (*Λ*)	221.1 (*Δ*)	1.12
s-cis-mer-[Co(edda)(*β*-ala)]	47.9 (*Λ*)	53.1 (*Δ*)	1.13
u-cis-mer-[Co(edda)(*β*-ala)]	45.1 (*Λ*)	53.1 (*Δ*)	1.17
u-cis-fac-[Co(edda)(*β*-ala)]	151.6[b]		—

a) Absolute configuration. b) Partial separation.

quite resemble to those of $[Co(edda)(diamine)]^+$ and *s-cis-mer*-[Co(edda)(aa)] (aa=gly, L-ala), although a minor positive band at higher energy is not observed in the case of *u-cis-fac*-[Co(edda)(gly)]. Therefore, the criterion to assign the absolute configuration from the sign of the CD spectra in the first d-d transition region should also be applicable to the u-cis-mer and u-cis-fac isomers of [Co(edda)(gly)] and [Co(edda)(*β*-ala)].

The CD spectra in Figs. 1 and 2 are for the second eluted enantiomers in the chromatographic separation. Since these CD spectra except that for *u-cis-fac*-[Co(edda)(*β*-ala)] comprise a dominant negative peak at lower energy and a minor positive peak at higher energy, the absolute configuration can be assigned to *Δ*. In the case of *u-cis-fac*-[Co(edda)(*β*-ala)], although the positive peak at higher energy is slightly greater than the negative peak at lower energy in intensity in its CD spectrum, it is highly likely that the absolute configuration is *Δ* from the quite similar CD pattern to those for the other complexes shown in Figs. 1 and 2.

Optical Resolution by Chromatography. The optical resolution was carried out by passing the neutral complexes through the $[Sb_2(d\text{-tart})_2]^{2-}$ form of QAE-Sephadex resin with water as the eluent. We chose $[Sb_2(d\text{-tart})_2]^{2-}$ as a resolving agent because $[Sb_2(d\text{-tart})_2]^{2-}$ is known to a very effective chiral selector not only for cationic transition metal complexes[1,18] but also for neutral complexes.[5-8] Water was used as the eluent in the present experiment. To obtain a good results, attention should be paid to the flow rate when neutral complexes are subjected to column chromatography in order to be resolved into enantiomers; the small flow rate seems to cause the better resolution. In the present experiment about 12 to 47 h, depending on complexes, were spent for each run. Two bands were clearly separated for every complex except for *u-cis-fac*-[Co(edda)(*β*-ala)]. The examination of the CD spectra of the eluates proved that the first eluted enantiomers have the *Λ* configurations (vide supra). In the case of *u-cis-fac*-[Co(edda)(*β*-ala)], though only one peak was obtained in the elution curve, the front and the rear fractions exhibited the enantiomeric CD spectra, indicating that the partial resolution was attained. The enantiomer in the front fraction had the *Λ* configuration. In the present chromatographic run, the chiral selector, $[Sb_2(d\text{-tart})_2]^{2-}$, was held in the stationary phase. Thus the second eluted enantiomer can be considered to have the greater affinity to $[Sb_2(d\text{-tart})_2]^{2-}$ than the first eluted enantiomer. For all neutral complexes examined in this paper, the *Δ* isomer is favored more by $[Sb_2(d\text{-tart})_2]^{2-}$ than the *Λ* isomer.

Before obtaining the adjusted retention volumes, the void volume of the column should be determined. Selection of a marker for determining the void volume is sometime difficult.[19] At first, we chose Blue Dextran 2000 as a marker since it is generally used for cation-exchange resin. However, it proved to be unsuitable because the band of Blue Dextran 2000 broadened considerably. Since QAE-Sephadex anion exchanger prevents to select anionic compounds as a marker, a cationic complex, $[Co(en)_3]Cl_3$, was used. This trial was, however, unsuccessful because it caused precipitation. The use of $[Cu(en)_2]Cl_2$ caused the greater retention volume than those of the neutral complexes. Finally, $[Fe(phen)_3]Cl_2$ proved to be a good marker to determine the retention volume of the QAE-Sephadex column. Since Sephadex contains many hydrophilic functional groups, $[Fe(phen)_3]^{2+}$ having hydrophobic ligands is presumed to have no significant interaction with the stationary phase. The resulting void volume, 30.9 cm³, may be a reasonable value, because the same void volume was obtained for SP-Sephadex-C25 cation-exchange column with the same diameter and length by using Blue Dextran as a marker, where QAE-Sephadex and SP-Sephadex resin used here have the same particle size.

The adjusted retention volumes and separation factors are listed in Table 2. For both the glycine and the *β*-alanine complexes, the retention volumes of the facial isomers are three to four times as large as those of the meridional isomers. This can be attributed to the greater dipole moment of the fac isomers. Between s-cis-mer and u-cis-mer isomers, there is no significant difference in the retention volumes. Comparison with the glycine and the *β*-alanine complexes in the same geometrical isomers reveals that the value for the glycine complex is greater than that for the *β*-alanine complex without exception. This tendency may be general because of the observation of the trend among tris(amino acidato)cobalt(III) complexes.[6,8] The

Table 3. Lists of Neutral Complexes Completely Resolved with $[Sb_2(d\text{-tart})_2]^{2-}$ Anion

Complex	Favorable enantiomer with $[Sb_2(d\text{-tart})_2]^{2-}$	Separation Factor	Reference[c]
fac-[Co(D/L-ser)$_3$]	Λ-D[a]	1.702	5
	Δ-D	1.510	5
fac-[Co(D/L-ser)$_2$(β-ala)]	Λ-D	1.349	5
	Δ-D	1.193	5
fac-[Co(D/L-ser)(β-ala)$_2$]	Λ-D	1.189	5
	Λ-L	1.060	5
fac-[Co(β-ala)$_3$]	Λ	1.060	5
fac-[Co(β-ala)$_3$]	Λ	1.152[b]	6
fac-[Co(β-ala)$_2$(gly)]	Λ	1.566[b]	6
fac-[Co(β-ala)(gly)$_2$]	Λ	1.456[b]	6
fac-[Co(gly)$_3$]	Λ	1.474[b]	6
fac-[Co(β-ala)$_2$(α-ala)]	Λ-D	1.293[b]	6
	Λ-L	1.323[b]	6
fac-[Co(β-ala)(α-ala)$_2$]	Λ-D	1.423[b]	6
fac-[Co(α-ala)$_3$]	Λ-D	1.993[b]	6
mer-[Co(gly)$_3$]	Δ	1.138	8
mer-[Co(β-ala)$_3$]	Δ	1.175	7, 8
mer-[Co(D/L-α-ala)$_3$]	Δ-L	1.512	8
	Δ-D	1.089	8
s-cis-mer-[Co(edda)(gly)]	Δ	1.14	This work
u-cis-mer-[Co(edda)(gly)]	Δ	1.15	This work
u-cis-fac-[Co(edda)(gly)]	Δ	1.12	This work
s-cis-mer-[Co(edda)(β-ala)]	Δ	1.13	This work
u-cis-mer-[Co(edda)(β-ala)]	Δ	1.17	This work

a) Λ and D stand for the configuration around Co(III) metal and of the amino acid ligand, respectively. This chromatographic separation was carried out for the enantiomeric pair of Λ-D and Δ-L. b) The values were calculated based upon the original data though these data are not shown in the literature. c) Brief chromatographic conditions: on Na^+ form of TSK-211 cation exchanger with $Na_2[Sb_2(d\text{-tart})_2]$ aqueous solution for Ref. 5; on $[Sb_2(d\text{-tart})_2]^{2-}$ form of TSK-220 anion exchanger with water for Ref 6; on $[Sb_2(d\text{-tart})_2]^{2-}$ form of QAE-Sephadex anion exchanger with water for Refs. 7, 8, and this work.

comparison among the separation factors in Table 2 reveals that there is no obvious defference (from 1.12 to 1.17).

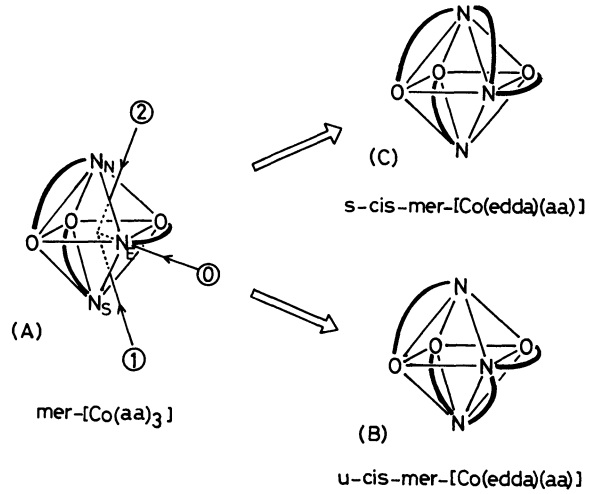
Mechanistic Consideration of Optical Resolution. Table 3 summarizes the neutral complexes completely resolved so far with $[Sb_2(d\text{-tart})_2]^{2-}$, together with the absolute configuration of the favorable enantiomer with the chiral anion, and the separation factors. As can be seen, with respect to the facial tris(amino acidato)-cobalt(III) complexes, the Λ enantiomers are favored unless two or more functional groups (hydroxyl groups) exist in the chelate rings, while the Δ enantiomers are favored in the case of the meridional complexes. This trend is kept for *mer*-[Co(edda)(aa)] complexes. However, it is not held for *fac*-[Co(edda)(aa)].

We have proposed the L-J model as a stereoselective ion-association model between a metal complex cation and $[Sb_2(d\text{-tart})_2]^{2-}$ anion.[1,20] The L-shaped channel was defined in the previous papers as the L-shaped opening between chelate rings, and the J-shaped channel as the mirror images of the L-shaped chennel. The optically active $[Sb_2(d\text{-tart})_2]^{2-}$ anion can associate intimately with that enantiomer of a metal complex cation that has the L-shaped channel, but cannot associate closely with the enantiomer that has only the J-shaped channel. In the case of *fac*-[Co(aa)$_3$], the Λ enantiomer has L-shaped channels in a position where $[Sb_2(d\text{-tart})_2]^{2-}$ anion is able to access electrostatically. Recently, the stereoselective ion-association model which is modefied and refined the L-J model has been proposed.[21] The model also suggests that the $[Sb_2(d\text{-tart})_2]^{2-}$ anion produces a favorable pair with the Λ enantiomer of the tris-chelate than with the Δ enantiomer. Thus, it is clear that the Λ enantiomer is favored by $[Sb_2(d\text{-tart})_2]^{2-}$ in homo and hetero facial tris(amino acidato)cobalt(III) neutral complexes. The chromatographic behaviour of *u-cis-fac*-[Co(edda)(aa)] that the Δ enantiomer makes an intimate pair with $[Sb_2(d\text{-tart})_2]^{2-}$ seems to be peculiar. However, the complex has neither L-shaped nor J-shaped channel. Although why the Δ enantiomer is favored more with the chiral anion and how the anion discriminates the enantiomers are not clear at present, we think this result is providing some clues about the chiral discrimination.

In meridional isomers, the Δ enantiomer is favored more by $[Sb_2(d\text{-tart})_2]^{2-}$ exclusively. Let us consider the reason. *mer*-[Co(aa)$_3$] is electrically neutral as a whole, but there is charge localization. It can be thought that the oxgen donor atom possesses a slightly negative charge and nitrogen donor atom does a slightly positive charge. From the pure electrostatic point of view, the most probable direction of the access

toward *mer*-[Co(aa)$_3$] for the [Sb$_2$(*d*-tart)$_2$]$^{2-}$ is considered to be the one indicated by arrow 0 in Scheme 2(A). However, the anion coming along this direction can not recognize the chirality of the complex because it touches the complex at only NH_2 group shown as N_E in Scheme 2(A). Next electrostatically favored access for the [Sb$_2$(*d*-tart)$_2$]$^{2-}$ is either one of the directions indicated by arrow 1 and 2. Although the two approaches are slightly different, they allow the anion to touch the complex at two NH_2 groups, N_E-N_S for arrow 1 and N_E-N_N for arrow 2. Then the anion can discriminate the absolute configuration of the complex. We consider that either one or both these two association modes 1 and 2, seem to play an important role in chiral discrimination.

u-cis-mer-[Co(edda)(aa)], Scheme 2(B), corresponds to the complex that N_E and N_S of the *mer*-[Co(aa)$_3$] are connected by a CH_2CH_2 bridge. The bridging of CH_2CH_2 group between N_E and N_N of complex (A) produces *s-cis-mer*-[Co(edda)(aa)], complex (C). The ethylene bridge between N_E and N_S precludes the access of [Sb$_2$(*d*-tart)$_2$]$^{2-}$ from the direction of arrow 1, and that between N_E and N_N prevents the access of the chiral selector from the direction of arrow 2. The two isomers, *u-cis-mer* and *s-cis-mer*-[Co(edda)(aa)], are presumed to accept the oncoming anion only through either one of the two association modes 1 and 2.



Scheme 2.

The retention volumes and the separation factors of the two isomers for both the glycine and β-alanine complexes exhibit no significant difference. Moreover, these separation factors are almost equal to those of *mer*-[Co(gly)$_3$] and *mer*-[Co(β-ala)$_3$]. Therefore, we can conclude that the two association models 1 and 2 are equally effecive on the chiral discrimination in *mer*-[Co(aa)$_3$] with using [Sb$_2$(*d*-tart)$_2$]$^{2-}$ as a resolving agent and only one mode is enough for complete resolution.

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