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The Mode of Stereoselective Association between Complex Cation and Complex Anion[1)]

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Ion-exchange chromatography on the IEX 220 anion-exchange resin has been used to measure the retention volumes of enantiomers of several complex anions when eluted by an aqueous solution of Δ-[Co(en)$_3$]$^{3+}$, Δ-[Co(sep)]$^{3+}$, or Δ-[Co{(−)-chxn}$_3$]$^{3+}$, where en=ethylenediamine, sep=1,3,6,8,10,13,16,19-octaazabicyclo-[6.6.6]eicosane, and chxn=*trans*-1,2-cyclohexanediamine. Comparison of these retention volumes suggests that chiral recognition in solution is effected along the C$_2$ axis of [Co(en)$_3$]$^{3+}$, [Co(mal)$_2$(en)]$^-$, and [Co(ox)$_2$(en)]$^-$, and along the C$_3$ (or pseudo C$_3$) axis of [Co(chxn)$_3$]$^{3+}$, [Co(edta)]$^-$, [Co(tdta)]$^-$, [Co(ox)$_2$(gly)]$^{2-}$, [Cr(mal)$_3$]$^{3-}$, and *fac*-[Co(β-ala)$_3$], where mal=malonate, ox=oxalate, edta=ethylenediaminetetraacetate, tdta=1,4-butanediaminetetraacetate, gly=glycinate, and ala=alaninate. The mode of stereoselective association of these complex ions has been proposed.

Optically active metal complexes have been used more and more frequently as the resolving agent for the optical resolution of complex compounds.[2)] It is now well recognized that an optically active complex cation can discriminate the absolute configuration of an enantiomer of a complex anion in solution. Recently, the mode of stereoselective interaction between optically active complexes in solution has been proposed by several workers.[3–6)] Among these, of particular relevance to the present work is the ion pair [Co(en)$_3$]$^{3+}\cdots$[Co(ox)$_2$(gly)]$^{2-}$,[7)] for which the anion is supposed to face the cation along the C$_3$ axis of the cation, with its three oxygen atoms of three different chelate rings, thereby forming a triple hydrogen bond with axial N–H hydrogens.[6)] In this work, we have used ion-exchange chromatography to infer the mode of stereoselective ion association between optically active complexes.

Experimental

Materials. The cationic complexes used in this work are the chloride or bromide salts of Δ-[Co(en)$_3$]$^{3+}$,[8)] Δ-[Co(sep)]$^{3+}$,[9)] and Δ-[Co{(−)-chxn}$_3$]$^{3+}$,[10)] which were prepared by the literature methods. The preparation and optical resolution of the following anionic complexes were accomplished according to the methods described in the literature; K$_2$[Co(ox)$_2$(gly)],[12)] K[Co(edta)],[13)] Na[Co(ox)$_2$(en)],[14)] and Na[Co(mal)$_2$(en)].[14)] The complexes K$_3$[Cr(mal)$_3$] and *fac*-[Co(β-ala)$_3$] were prepared after Chang[15)] and Celap *et al.*,[16)] respectively.

The preparation of K[Co(tdta)] was reported by Ogino *et al.*[17)] The optical resolution of this complex was effected by Λ-*cis*-[Co(en)$_2$(NO$_2$)$_2$]$^+$ obtained by the method of Dwyer and Garvan.[18)] The Δ enantiomer formed the less-soluble diastereoisomer and the potassium salt of the enantiomer was consistent with the formulation as the monohydrate. Found: C, 33.10; H, 4.25; N, 6.58. Calcd for KCoC$_{12}$H$_{18}$N$_2$O$_9$: C, 33.34; H, 4.20; N, 6.48. The circular dichroism spectrum in water had peaks at 623 ($\Delta\varepsilon=+2.98$), 553 (-4.20), 434 ($+0.752$), and 387 nm ($+1.19$).

The IEX 220 resin was the gift from Dr. S. Yamazaki, Toyo Soda Manufacturing Co., Ltd. (Tokyo).

Chromatographic Experiments. *Type (a) Experiment*: The SP-Sephadex C-25 resin (cation-exchanger) was packed in a column tube with an approximate size of 200 mm× 10 mm (i.d.) and loaded fully with an optically active cationic complex. The column was washed thoroughly with water and a racemic anionic complex was eluted with water. The eluent containing the partially resolved anionic complex was fractionally collected and the circular dichroism spectrum was measured immediately.

Type (b) Experiment: A home-built liquid chromatographic apparatus[19)] was used to measure the retention volume. A column (50 mm×4 mm) of the IEX 220 resin (anion-exchanger) was equilibrated by an eluent (aqueous solution of an optically active cationic complex). An aqueous solution containing one enantiomer of an anionic complex and bis(glycinato)copper(II), which was used as a marker for void volume measurement, was injected by a syringe on top of the column and eluted by the eluent at an elution rate of 0.3 cm^3/min. The adjusted retention volumes were obtained from the elution curves as in the previous studies.[19)] The concentration of the cationic complexes in eluents was varied from 4×10^{-3} to 60×10^{-3} mol dm^{-3}. The retention volumes were found to be reproducible to within 0.002 cm^3.

Results and Discussion

In type (a) experiment, an optically active complex cation (Δ cation) was adsorbed on the SP-Sephadex C-25 cation-exchanger and an anionic complex was eluted with water. Thus, the enantiomer that associates more favorably with the Δ cation is eluted later. In some complexes, the degree of optical resolution was very small and unambiguous assertion of later-eluted enantiomers could not be made. Further, it was found that the chirality of the resin matrix itself[20)] contributes to the optical resolution to some extent. Therefore, type (b) experiment was performed to obtain reliable and quantitative data by employing an achiral resin, IEX 220, which is based on the styrene-divinylbenzene-copolymer and carries the tetraalkylammonium functional group. The retention volumes obtained in type (b) experiment are given in Table 1. In type (b) experiment, one enantiomer of an anionic complex was adsorbed on the anion-exchange resin and eluted by an aqueous solution containing a Δ cation. Thus, the enantiomer that associates more favorably with the Δ cation shows a smaller retention volume than its enantiomorph. The results of both types of experiments were consistent with respect to favorable diastereoisomeric combina-

TABLE 1. THE ADJUSTED RETENTION VOLUMES (cm^3) OBTAINED IN TYPE (b) EXPERIMENT

		Δ-$[Co(en)_3]Cl_3$ 15×10^{-3} mol dm^{-3}	Δ-$[Co(sep)]Br_3$ 4×10^{-3} mol dm^{-3}	Δ-$[Co\{(-)\text{-chxn}\}_3]Cl_3$ 4×10^{-3} mol dm^{-3}
K[Co(edta)]	Δ	4.436	9.834	13.890
	Λ	4.380	9.675	14.660
K[Co(tdta)]	Δ	3.879	9.768	8.769
	Λ	3.625	9.711	10.240
$Na[Co(ox)_2(en)]$	Δ	3.213	3.115[a]	6.750[b]
	Λ	3.270	3.120[a]	6.330[b]
$Na[Co(mal)_2(en)]$	Δ	0.903	2.121	3.038
	Λ	0.922	2.143	3.014

a) The eluent concentration was 8.0×10^{-3} mol dm^{-3}. b) The eluent was the aqueous solution of Δ-$[Co\{(-)\text{-chxn}\}_3]Br_3$.

TABLE 2. THE ENANTIOMERS WHICH FORM FAVORABLE PAIRS WITH Δ CATIONS

	Δ cation		
	Δ-$[Co(en)_3]^{3+}$	Δ-$[Co(sep)]^{3+}$	Δ-$[Co\{(-)\text{-chxn}\}_3]^{3+}$
$[Co(edta)]^-$	Λ[a),b),c)]	Λ[a),b)]	Δ[a),b)]
$[Co(tdta)]^-$	Λ[b)]	Λ[b)]	Δ[b)]
$[Co(ox)_2(en)]^-$	Δ[b)]	Δ[b)]	Λ[b)]
$[Co(mal)_2(en)]^-$	Δ[b)]	Δ[b)]	Λ[b)]
$[Co(ox)_2(gly)]^{2-}$	Λ[a),c)]	Λ[a)]	Δ[a)]
$[Cr(mal)_3]^{3-}$	Λ[a),c)]	Λ[a)]	Δ[a)]
fac-$[Co(\beta\text{-ala})_3]$	Λ[a),c)]	Λ[a)]	Δ[a)]

a) From type (a) experiment. b) From type (b) experiment. c) Also reported by A. Tatehata *et al.*; A Tatehara, Y. Ejiri, and K. Kotsuji, Proc. 29th Symposium on Coordination Chemistry, Shizuoka, October 1979, Abstr. No. 1B01, p. 40.

tions. Therefore, both results are incorporated and Table 2 was made to facilitate the following discussion.

Structural Features of Complexes. The cationic complexes chosen for this study were Δ-$[Co(en)_3]^{3+}$, Δ-$[Co(sep)]^{3+}$, and Δ-$[Co\{(-)\text{-chxn}\}_3]^{3+}$. The chirality of these complexes can be specified by looking at the complexes either along the C_3 axis as P(C_3) or along the C_2 axis as M(C_2). These notations follow those of Mason *et al.*[21] and define the chirality by the handedness of mutual spatial disposition of three or two chelate rings. The chirality of the other complexes used in this work can be specified similarly; a Δ complex has P(C_3) and M(C_2) chiralities. Note here that if an anionic complex approaches a Δ cation from the cation's C_3 axis, the anion will experience the P(C_3) chirality (right-handed propellers), whereas in the case of the C_2 access (the access along the cation's C_2 axis from the side opposite to one ethylenediamine moiety), the anion will experience the reversed chirality, the M(C_2) chirality (left-handed propellers).

The direction of access of anionic complexes that can contribute to chiral discrimination is along either the C_3 or the C_2 axis for Δ-$[Co(en)_3]^{3+}$; in other words, Δ-$[Co(en)_3]^{3+}$ can "use" its C_3 or C_2 axis in discriminating the chirality of a complex anion. In Δ-$[Co(en)_3]^{3+}$, chiral discrimination through the C_3 access has been suggested for the (+)- and (−)-tartrate anions,[22] and that through the C_2 access was proposed for the (+)-tartratoantimonate(III) anion.[23] Therefore, both accesses may potentially contribute to the chiral discrimination by Δ-$[Co(en)_3]^{3+}$.

In Δ-$[Co(sep)]^{3+}$, chiral discrimination along its C_3 axis is unlikely owing to the presence of bulky covalent caps along this axis.[9b)] This is also supported by the equality of the association constants of Δ-$[Co(sep)]^{3+}$ with (+)- and (−)-tartrate ions ($K=40\pm2$ mol^{-1} dm^3 at 25 °C and $\mu=0.1$ with $NaClO_4$).[24] Thus, the chiral discrimination by this cation along the C_2 axis should be the only possibility, which constitutes the basis for the interpretation of our results.

In Δ-$[Co\{(-)\text{-chxn}\}_3]^{3+}$, though it appears that the C_3 access is preferred owing to the presence of bulky cyclohexane rings, the situation is not so clear and we leave both accesses as a possibility.

The reasoning similar to the above can be made for the anionic and electrically neutral complexes. Note here that these complexes contain negatively charged ligands, unlike the cationic complexes which have only electrically neutral ligands. Therefore, significant charge localization is expected for anionic and electrically neutral complexes. Previously, it has been shown[5,25] that in the ion association with complexes with significant charge localization, the site and/or the direction of ion association is dictated by localized electric charges. We here apply this criterion to the direction of ion association of anionic and neutral complexes. Thus, in the case of $[Co(ox)_2(en)]^-$ type of complexes, for example, an access of a cation along the C_2 axis and from the side opposite to the ethylenediamine ring is the only likelihood. In $[Co(edta)]^-$ type of complexes, an access of a cation along the anion's pseudo C_3 axis and from the side of three oxygen atoms is conceived. For $[Co(ox)_2(gly)]^{2-}$ and $[Cr(mal)_3]^{3-}$, we leave the pseudo C_3 and C_3 accesses as the possibility, respectively. Though other types of accesses can, in principle, lead to chiral discrimination, the above choices for the direction of access will be shown later to be consistent with the experimental results.

Stereoselective Association. The most noteworthy feature in Table 2 is that Δ-[Co(en)$_3$]$^{3+}$ and Δ-[Co(sep)]$^{3+}$ favor the association with the same enantiomer for all the anionic and electrically neutral complexes investigated here but the opposite enantiomer is preferred by Δ-[Co{(—)-chxn}$_3$]$^{3+}$. This result indicates clearly that (i) Δ-[Co(en)$_3$]$^{3+}$ uses its C_2 axis in discriminating the chirality of all the anionic and neutral complexes examined here, because Δ-[Co(en)$_3$]$^{3+}$ and Δ-[Co(sep)]$^{3+}$ prefer the same enantiomers and the C_2 access is the only effective discriminating interaction in Δ-[Co(sep)]$^{3+}$, (ii) Δ-[Co{(—)-chxn}$_3$]$^{3+}$ uses its C_3 axis in the chiral discrimination, because this cation has the P(C_3) propellers and prefers the opposite enantiomers to those favored by Δ-[Co(sep)]$^{3+}$ which uses the M(C_2) propellers.

Now that we have identified the directions of the cationic complexes which are used in chiral discrimination and such directions of anionic and neutral complexes are assumed in the above, we can now examine the mode of association between these complexes. Table 2 indicates that Δ-[Co(en)$_3$]$^{3+}$ favors Δ-[Co(ox)$_2$(en)]$^-$. Since both ions use their C_2 axes in chiral discrimination, the resulting ion pair should be as illustrated in Fig. 1. Figure 1 depicts schematically the mutual disposition of chelate rings in this Δ-Δ combination, as viewed along the collinear C_2 axes of both ions. The hydrogen atoms are omitted for clarity. As seen from this figure, the handedness of the chelate rings that overlap mutually in association is the same for this pair and this mode of pairing is sterically less hindered. A severe steric hindrance is clearly expected for the Δ-Λ combination, where the first chirality notation refers to the cation and the second one to the anion. The M(C_2)–M(C_2) pair depicted in Fig. 1 is also supported by electrostatic considerations; the cation will associate with the anion from the anionic side of the complex anion, namely along the C_2 axis of the anion and from the side opposite to the ethylenediamine chelate ring. Thus, the M(C_2)–M(C_2) combination is consistent with both steric and electrostatic considerations. The preference for the pairs Δ-[Co(en)$_3$]$^{3+}\cdots\Delta$-[Co(mal)$_2$(en)]$^-$, Δ-[Co(sep)]$^{3+}\cdots\Delta$-[Co(ox)$_2$(en)]$^-$, and Δ-[Co(sep)]$^{3+}\cdots\Delta$-[Co(mal)$_2$(en)]$^-$ can be understood similarly.

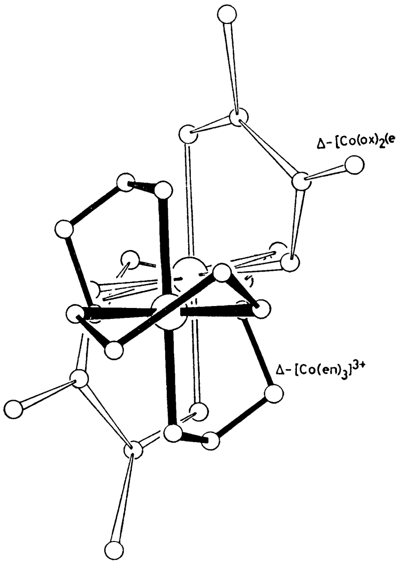

Fig. 1. Proposed structure for the preferred ion pair formed between Δ-[Co(en)$_3$]$^{3+}$ and Δ-[Co(ox)$_2$(en)]$^-$.

In the combination of [Co(ox)$_2$(en)]$^-$ and [Co(mal)$_2$(en)]$^-$ with Δ-[Co{(—)-chxn}$_3$]$^{3+}$, the Δ-Λ pair is seen from Table 2 to be preferred. Since the cation uses its C_3 axis and the anions use their C_2 axes in chiral discrimination, this Δ-Λ pair corresponds to the P(C_3)–P(C_2) pair. Namely, the propellers of both ions have the same handedness and the preference of this pair can be also understood in terms of a cozy fit of chelate rings of both ions.

Table 2 indicates that Λ-[Cr(mal)$_3$]$^{3-}$ forms the favorable ion pair with Δ-[Co(en)$_3$]$^{3+}$ and Δ-[Co(sep)]$^{3+}$. Since this anion uses its C_3 axis and the cations use their C_2 axes in chiral discrimination, these pairs are described as the M(C_2)–M(C_3) pairs. Here again we find that the handednesses of chelate rings of cation and anion, as viewed along the direction of the access, coincide. Thus, these Δ-Λ pairs are also explained by the notion that favorable ion pairs are formed between those ions that can fit spatially along the prescribed axes. The fact that the pair Δ-[Co{(—)-chxn}$_3$]$^{3+}\cdots\Delta$-[Cr(mal)$_3$]$^{3-}$ is preferred over the Δ-Λ pair is similarly understood by noting that this pair corresponds to the P(C_3)-P(C_3) combination. It will be evident from Table 2 that the results for *fac*-[Co(β-ala)$_3$] can be explained in the same way as for [Cr(mal)$_3$]$^{3-}$.

The Λ-enantiomers of [Co(edta)]$^-$ and [Co(tdta)]$^-$ preferentially associate with Δ-[Co(en)$_3$]$^{3+}$ and Δ-[Co(sep)]$^{3+}$ (see Table 2). Since these anions use the pseudo C_3 axes and the cations use their C_2 axes in chiral discrimination, the resulting pairs are the M(C_2)–M(pseudo C_3) combinations. The mode of ion pairing for the pair Λ-[Co(edta)]$^-\cdots\Delta$-[Co(en)$_3$]$^{3+}$ is shown schematically in Fig. 2. In Fig. 2, the Δ-[Co(en)$_3$]$^{3+}$ cation faces the Λ-[Co(edta)]$^-$ anion along the cation's

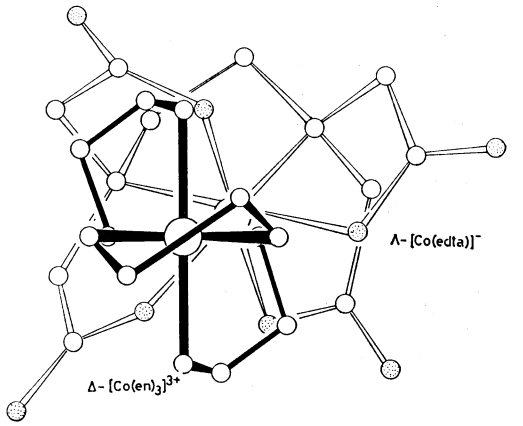

Fig. 2. Proposed structure for the favorable ion pair Δ-[Co(en)$_3$]$^{3+}\cdots\Lambda$-[Co(edta)]$^-$.

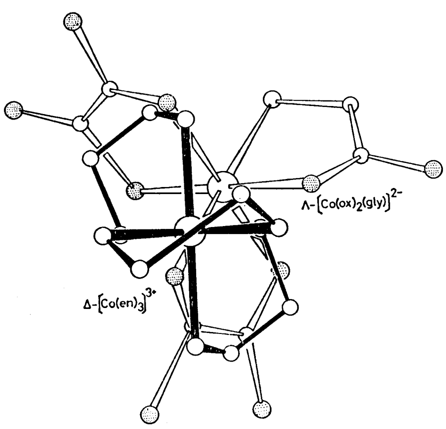

Fig. 3. Proposed mode of ion pairing between Δ-[Co(en)$_3$]$^{3+}$ and Λ-[Co(ox)$_2$(gly)]$^{2-}$.

C$_2$ axis and the anion faces the cation along the anion's pseudo C$_3$ axis with three anionic oxygen atoms. It can be seen from Fig. 2 that the chelate rings of both ions suffer less steric hindrance for the depicted Δ-Λ combination than for the Δ-Δ combination. Thus, the Δ-Λ combinations favored by these ions are again explained by a cozy fit of overlapping chelate rings. The formation of the favorable pair Δ-[Co{(−)-chxn}$_3$]$^{3+}$···Δ-[Co(edta)]$^-$ or Δ-[Co(tdta)]$^-$ can be explained in terms of the P(C$_3$)-P(pseudo C$_3$) pair; the propellers of both cation and anion have the same handedness when viewed along the C$_3$ or the pseudo C$_3$ axis.

The Λ-[Co(ox)$_2$(gly)]$^{2-}$ forms the favorable pairs with Δ-[Co(en)$_3$]$^{3+}$ and Δ-[Co(sep)]$^{3+}$ (see Table 2). By noting that [Co(ox)$_2$(gly)]$^{2-}$ uses its pseudo C$_3$ axis and the Δ-[Co(en)$_3$]$^{3+}$ cation uses its C$_2$ axis in chiral discrimination, the structure of the preferred ion pair formed between Δ-[Co(en)$_3$]$^{3+}$ and Λ-[Co(ox)$_2$(gly)]$^{2-}$ will be as illustrated in Fig. 3. The combination depicted in Fig. 3 is M(C$_2$)-M(pseudo C$_3$) and the handednesses of both ions, as viewed along the direction depicted, are the same. The preference of Λ-[Co(ox)$_2$(gly)]$^{2-}$ by Δ-[Co{(−)-chxn}$_3$]$^{3+}$ is explained in terms of the P(C$_3$)-P(psedo C$_3$) combination, namely by the same handedness of overlapping chelate rings.

In conclusion, all the elution orders in Table 2 are consistently explained, if we admit that (i) [Co(en)$_3$]$^{3+}$, [Co(sep)]$^{3+}$, [Co(ox)$_2$(en)]$^-$, and [Co(mal)$_2$(en)]$^-$ use their C$_2$ axes in chiral discrimination, (ii) [Co(chxn)$_3$]$^{3+}$, [Co(edta)]$^-$, [Co(tdta)]$^-$, [Co(ox)$_2$(gly)]$^{2-}$, and *fac*-[Co(β-ala)$_3$] use their C$_3$ or pseudo C$_3$ axes in chiral discrimination, and (iii) favorable pairs are formed between those ions that have the same handedness of chelate rings, when viewed along the above axes.

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7) Abbreviations; en=ethylenediamine, sep=1,3,6,8,10,13,16,19-octaaza-bicyclo[6.6.6]eicosane, chxn=*trans*-1,2-cyclohexanediamine, ox=oxalate, gly=glycinate, mal=malonate, edta=ethylenediaminetetraacetate, tdta=tetramethylenediaminetetraacetate, ala=alaninate, acac=2,4-pentanedionate, phen=1,10-phenanthroline.

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