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Chromatographic Optical Resolution Based on the Chiral Discrimination between Ions of the Same Sign, Anionic Cobalt(III) Complex Racemates and Anionic Selector $[Sb_2(d\text{-tart})_2]^{2-}$

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Column chromatographic optical resolutions of twenty-six typical univalent anionic cobalt(III) complexes, e.g., $[Co(edta)]^-$ and *fac*-$[Co(NO_2)_3(edma)]^-$, were carried out, using as a chiral eluent an aqueous solution of $[Sb_2(d\text{-tart})_2]^{2-}$ on a strongly basic anion exchanger, where edta=ethylenediamine-*N,N,N′,N′*-tetraacetate(4-), edma=ethylenediamine-*N*-acetate(1-), and *d*-tart=*d*-tartrate(4-). The racemates were resolved with separation factors comparable to those obtained in conventional resolutions by use of cationic selectors. From a comparison of elution orders of enantiomers and separation factors obtained for the racemates, a chiral discrimination mechanism without direct contact between the racemate and selector was proposed.

Chromatographic complete resolution of anionic metal complexes is difficult to achieve compared with that of cationic ones, although many attempts have been made from of old.[1—3] The first complete resolution of anionic complexes was achieved for $[Co(ox)_2(gly)]^{2-}$[4] by use of Λ-$[Co(en)_3]^{3+}$ as a selector (resolving agent) by Tatehata et al.[5] in 1981. Since then complete resolutions of several anionic cobalt(III) complexes have been attained by Tatehata et al.[6] and Yoneda et al.,[3,7—9] but the selectors used have been limited to cations, cationic metal complexes and alkaloid cations. In such systems, the resolution is governed by the chiral discrimination between ions of opposite signs. We have recently reported of a complete resolution based on the chiral discrimination between ions of the same sign: anionic racemates, *cis*(*N*)-$[Co(ida)_2]^-$ and $[Co(edta)]^-$, were resolved by an anionic selector $[Sb_2(d\text{-tart})_2]^{2-}$ on a strongly basic anion exchanger.[10] This resolution technique was first adopted on a DEAE-Sephadex (DEAE=2-(diethylamino)ethyl) column by Yoshikawa and Yamasaki[2] but resulted in unseparated elution curves with partial resolution. The efficiency of our resolutions is comparable to that obtained by the chiral discrimination between ions of opposite signs.[3,5—9] Such an unexpectedly high ability of discrimination is of interest for the stereoselective interaction in general between charged species, particularly in connection with weak chemical interactions important in biological systems.[11]

Chiral discrimination phenomena dependent on diastereomeric interactions have been recognized between ions of the same sign, in spite of the occurrence of interference with the mutual approach of ions by the inevitable electrostatic repulsion. Discriminatory interactions in cation–cation systems have been recognized as phenomena such as the Pfeiffer effect (the displacement of enantiomer equilibrium of a labile racemic complex caused by an optically active "environment substance")[9,12—14] and optical resolution.[15] On the other hand, phenomena in anion-anion systems have rarely been reported[16] except for the above observation.[2,10] Although the mechanism of chiral discrimination for the phenomena observed has been widely examined, its nature has not yet been clearly elucidated.[12—19] Furthermore, the phenomena have strangely been manifested only for systems containing racemic complexes with N-heterocyclic unsaturated ligands, such as 1,10-phenanthroline and 2,2′-bipyridine. Under these circumstances, further investigation on the present phenomenon, which occurs between anions having no unsaturated ligands, can be expected to provide important information regarding the origin of chiral discrimination.

The present work deals with chromatographic optical resolutions of a series of typical anionic cobalt(III) complexes by our method.[10] The mechanism of chiral discrimination will be discussed on the basis of the relation between the resolution behavior of enantiomers and the structure of complexes.

Experimental

Materials. The twenty-six racemic cobalt(III) complex anions (**1a**—**11**) used in this work are listed in Table 1, where the complexes are numbered with the same numeral for the same type of complexes. All these anions have been isolated as their sodium or potassium salts and their structures have been well characterized. Optical resolution has been achieved except for *unsym*-$[Co(ox)(aeida)]^-$ (**5a**). Absolute configurations have been determined on the basis of X-ray crystallographic, circular dichroism (CD) spectral, or stereochemical analysis, except for the aeida (**5a**[20] and **5b**[21]) and edma (**7**)[22] complexes: **1a**, **1b**, **1d**—**4**, and **6a** in a review by Radanović,[23] **1c**,[8] **6b**—**6e**,[24] **8a**, **9a**, **10a**,[25] **8b**, **9b**, **10b**,[26] and **11**.[27] Three (**1a**, **1b**, and **11**) of these complexes were determined X-ray crytallographically.

The optical resolution of the racemic *unsym*-$K[Co(ox)(aeida)]\cdot H_2O$ (**5a**)[20] was achieved by an up-scaled present type chromatography and the resolved complex was isolated as a potassium salt, $(+)^{CD}_{567}$-*unsym*-$K[Co(ox)(aeida)]\cdot 3H_2O$, from an eluate containing the early eluted enantiomer. Found: C, 23.33; H, 3.97; N, 6.66%. Calcd for $K[Co(ox)(aeida)]\cdot$

$3H_2O=KCoC_8H_{16}N_2O_{11}$: C, 23.20; H, 3.89; N, 6.76%. $[\alpha]_D = +300°$. $\Delta\varepsilon_{max}=+1.82$ (at 567 nm), −0.71 (497), and +0.23 (375).

The selector potassium bis(*d*-tartrato)diantimonate(III) trihydrate, $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$, was commercially available.

Chromatographic Resolution. The strongly basic anion-exchanger used was derived from Toyopearl (Fractogel TSK) HW50s gel (20—40 μm on swelling in water) in this laboratory.[10] The exchanger of form $[Sb_2(d\text{-tart})_2]^{2-}$ was packed in a glass column (1.0 cm×80 cm) and about 5 mg of a racemic cobalt(III) complex was loaded on the top of the column. The adsorbed band was eluted with 0.02 mol dm^{-3} aqueous solution of $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$. The elution rate was regulated to 0.25—0.27 cm^3 min^{-1} by a Pharmasia LKB 2132 type peristaltic pump. The elution curve was recorded at the wavelength of the first absorption maximum of the complex on a Shimadzu SPD-6AV spectrophotometric detector. The elution order of the enantiomers was determined by measuring CD spectra of fractional eluates.

Measurements. Elemental analysis was carried out at the Advanced Instrumentation Center for Chemical Analysis, Ehime University. The CD spectra were recorded on a JASCO J-20 spectropolarimeter using a 1.0 cm cell at room temperature.

Results and Discussion

Absolute Configuration of the Cobalt(III) Complexes. As described in the Experimental section, the absolute configurations of the three complexes, *unsym*-$[Co(ox)(aeida)]^-$ (**5a**), *unsym*-$[Co(NO_2)_2(aeida)]^-$ (**5b**), and *fac*-$[Co(NO_2)_3(edma)]^-$ (**7**), are unknown. The ring-pairing method cannot be applied to the absolute configurations of these complexes, because the complexes lack the net ring-pairing chirality.[28,29] Fortunately, the absolute configuration of *fac*-$[Co(edma)(NH_3)_3]^{2+}$, which has the same chromophore (CoN_5O) as *fac*-$[Co(NO_2)_3(edma)]^-$, has been determined: $(+)^{CD}_{512}$-*fac*-$[Co(edma)(NH_3)_3]^{2+}$ has an (*S*)-configuration with respect to the secondary nitrogen atom of the coordinated edma.[30] The CD curve of the early eluted enantiomer of *fac*-$[Co(NO_2)_3(edma)]^-$ ($\Delta\varepsilon_{max}=+1.095$ (at 485 nm) and −0.822 (at 427 nm))[22] shows the same general shape and sign pattern in the first absorption region as that of the (*S*)-isomer of *fac*-$[Co(edma)(NH_3)_3]^{2+}$ ($\Delta\varepsilon_{max}=+1.641$ (at 512 nm) and −0. 811 (at 444 nm)).[30] By comparison of the CD curves, thus, the absolute configuration of the early eluted enantiomer, $(+)^{CD}_{485}$-*fac*-

Table 1. Data of the Chromatographic Optical Resolution

No.	Racemic complex ion	Retention volume/cm^3 [a]	Separation factor (α)[b]	Early eluted enantiomer: Sign of CD extremum	Absolute configuration	Configuration of NNO-facet
1a	$[Co(edta)]^-$	115	1.08	$(-)_{582}$	Δ	LL
b	$[Co(trdta)]^-$	96	1.09	$(-)_{588}$	Δ	LL
c	$[Co(tdta)]^-$	86	1.06	$(-)_{623}$	Δ	LL
d	$[Co(pdta)]^-$ [c]	100	1.09	$(-)_{584}$	Δ	LL
e	$[Co(cydta)]^-$ [c]	95	s[d]	$(-)_{595}$	Δ	LL
2a	$[Co(NO_2)(ed3a)]^-$	137	1.10	$(+)_{582}$	—[e]	LL
b	$[Co(NO_2)(med3a)]^-$	114	1.06	$(-)_{575}$	—	LL
c	$[Co(NO_2)(hed3a)]^-$	118	1.07	$(-)_{578}$	—	LL
3a	*cis*-α-$[Co(ox)(edda)]^-$	97	1.16	$(+)_{560}$	Λ	LL
b	*cis*-α-$[Co(ox)(dmedda)]^-$	80	1.04	$(+)_{558}$	Λ	LL
4	*cis*-β-$[Co(ox)(edda)]^-$	95	1.04	$(+)_{544}$	Λ	R
5a	*unsym*-$[Co(ox)(aeida)]^-$	128	1.15	$(+)_{567}$	—	(L)[f]
b	*unsym*-$[Co(NO_2)_2(aeida)]^-$	271	1.08	$(+)_{502}$	—	(L)[f]
6a	*cis*(*N*)-$[Co(ida)_2]^-$	134	1.17	$(+)_{588}$	Λ[g]	RR
b	*cis*(*N*)-$[Co(ida)(mida)]^-$	110	1.13	$(-)_{592}$	Δ	LL
c	*cis*(*N*)-$[Co(mida)_2]^-$	86	1.07	$(-)_{613}$	Δ	LL
d	*cis*(*N*)-$[Co(ida)(eida)]^-$	95	1.04	$(-)_{592}$	Δ	LL
e	*cis*(*N*)-$[Co(eida)_2]^-$	77	1.05	$(-)_{620}$	Δ	LL
7	*fac*-$[Co(NO_2)_3(edma)]^-$	453	1.07	$(+)_{485}$	(*S*)[h]	L
8a	*trans*(*N*)-$[Co(ox)(gly)_2]^-$	78	s	$(-)_{530}$	Δ	—
b	*trans*(*N*)-$[Co(ox)(\beta\text{-ala})_2]^-$	59	s	$(-)_{637}$	Δ	—
9a	C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$	141	s	$(+)_{565}$	Λ	R
b	C_1-*cis*(*N*)-$[Co(ox)(\beta\text{-ala})_2]^-$	88	s	$(+)_{588}$	Λ	R
10a	C_2-*cis*(*N*)-$[Co(ox)(gly)_2]^-$	143	1.10	$(+)_{555}$	Λ	LL
b	C_2-*cis*(*N*)-$[Co(ox)(\beta\text{-ala})_2]^-$	87	1.10	$(+)_{607}$	Λ	LL
11	$[Co(ox)_2(en)]^-$	116	1.03	$(-)_{581}$	Δ	—

a) The mean value for the enantiomers. b) The void volume is not considered for the estimation of factor. c) Racemic $[Co(pdta)]^-$ and $[Co(cydta)]^-$ are an equimolar mixture of the enantiomers Δ-$[Co\{(R)\text{-pdta}\}]^-\cdots\Lambda$-$[Co\{(S)\text{-pdta}\}]^-$ and Δ-$[Co\{(R,R)\text{-cydta}\}]\cdots\Lambda$-$[Co\{(S,S)\text{-cydta}\}]^-$, respectively. d) Single elution curve. e) Not characterized by the IUPAC nomenclature concerned with the octahedral complexes (Ref. 29). f) Tentative assignment; see text. g) Erroneously determined in Ref. 10 and thus corrected here. h) Absolute configuration of the secondary nitrogen atom of coordinated edma.

$[Co(NO_2)_3(edma)]^-$, can be assigned to (*S*).

Chromatographic Resolution and Chiral Discrimination Mechanism. The representative elution curves in the present optical resolutions are shown in Fig. 1. The mean retention volumes and separation factors (α) are summarized in Table 1. The α value greater than about 1.07 corresponds to the virtual complete resolution in the present resolutions. Single elution curves were obtained for the five complexes (**1e**, **8a**—**9b**), but in every case partial resolution was confirmed by measuring CD spectra of fractional eluates. The α value is regarded approximately as the difference in free energy of distribution between for the enantiomers which results from the diastereomeric interaction of enantiomers with a selector in the ion-exchange process: $\Delta(\Delta G^\circ) = -RT\ln\,\alpha$.[31] In the present estimation of α values, the void volume of column used is not contained in the retention volumes, so that the true α values are larger than those shown in Table 1; for example, the value for *cis*(*N*)-$[Co(ida)_2]^-$ (**6a**) has been found to be 1.23 in a preliminary experiment. It is noted that the α values in the present resolutions are, on the whole, comparable to those obtained by use of cationic selectors, which are smaller than 1.28 except for two special examples[9] in many resolutions.[3,5–9]

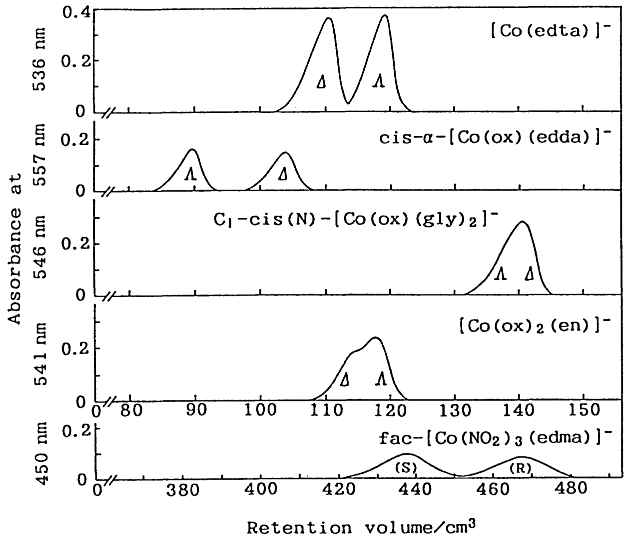

Fig. 1. Representative elution curves in the chromatographic resolution of the cobalt(III) complexes.

The signs of the CD extrema and absolute configurations of the early eluted enantiomers are shown in the forth and the fifth column, respectively, in Table 1. The absolute configurations of the ed3a type (**2a**—**2c**), aeida type (**5a** and **5b**), and edma (**7**) complexes cannot be characterized by the current IUPAC nomenclature concerned with octahedral complexes, because of the lack of net ring-pairing chirality.[29] The absolute configuration of the edma complex is designated with that of the secondary nitrogen atom. The structures of the enantiomers eluted early in each type are illustrated with chelate skeletons in Fig. 2. In each of the types with the plural complexes (**1**, **2**, **3**, **8**, **9**, and **10**), except for the bis(ida) type (**6**), the elution orders of the enantiomers are the same for all the complexes, as seen in Table 1. In the bis(ida) type, the elution order of *cis*(*N*)-$[Co(ida)_2]^-$ (**6a**) and that of the other complexes (**6b**—**6e**) are opposite; the structure in Fig. 2 is for the latter complexes. The absolute configurations of the aeida type complexes (**5a** and **5b**) are tentatively assigned in the present work (vide infra) and the structure for *unsym*-$[Co(ox)(aeida)]^-$ (**5a**) is illustrated in Fig. 2. As described above, the elution order of enantiomers can be correlated to the absolute configuration for the com-

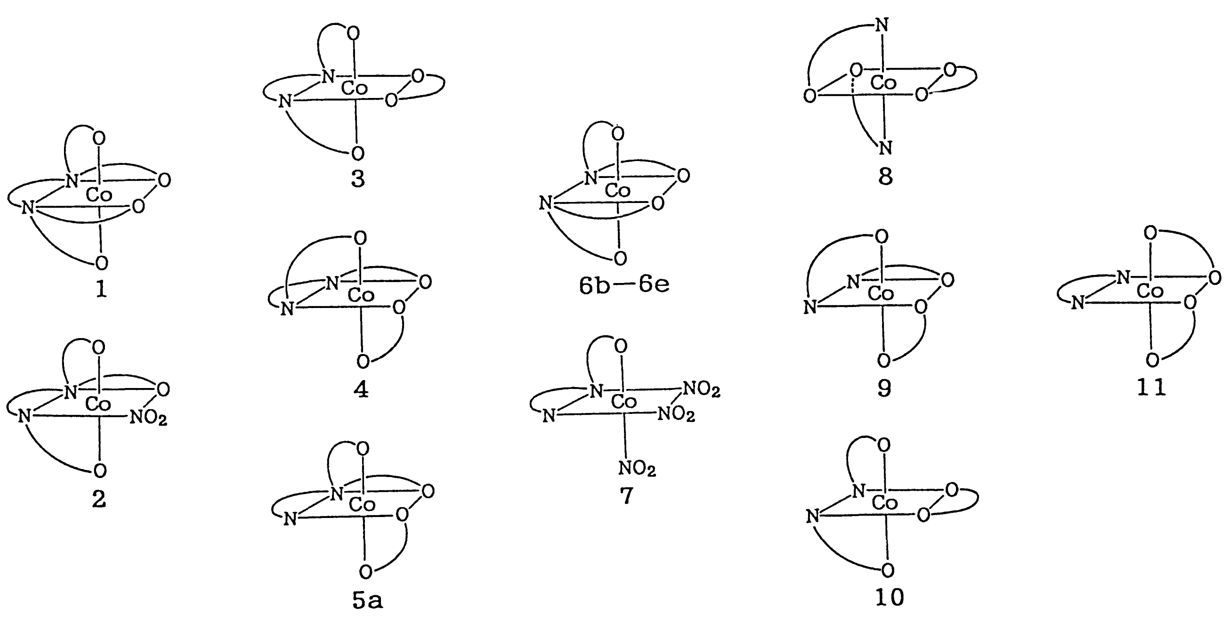

Fig. 2. Absolute configurations of the early eluted enantiomers.

plexes belonging to the same type, with the exception of *cis*(*N*)-$[Co(ida)_2]^-$ (**6a**). Such a correlation, however, is by no means recognized for the whole complexes used; namely, the *Δ*-isomers are early eluted for about half of the complexes and the *Λ*-isomers for the others. Accordingly, the chiral discrimination mechanism in the present systems is difficult to explain in relation with the absolute configuration, which is associated with the number of helical chelate pairs (*Δ* and *Λ*) in a complex.[29)]

All the univalent anionic complexes used are coordinated by the two neutral nitrogen atoms of the amino carboxylato ligand(s) and the four anionic groups, carboxyl and/or nitro ones. It is reasonable to consider that the moiety near the two nitrogen atoms of the amino carboxylato ligand(s), where a relatively positive charge is produced owing to charge localization in a complex, favorably interacts with the anionic selector. The complexes have one or two triangular "NNO-facets" in a complex as a common structural unit, except for *trans*(*N*)-$[Co(ox)(gly)_2]^-$ (**8a**), *trans*(*N*)-$[Co(ox)(\beta\text{-}ala)_2]^-$ (**8b**), and $[Co(ox)_2(en)]^-$ (**11**). The NNO-facet consists of the two nitrogen atoms of the amino carboxylato ligand(s) and the glycinato or *β*-alaninato chelate ring (N–O) toward the apical position from either of the two nitrogen atoms. The enantiomeric forms are possible for the NNO-facet and illustrated in Fig. 3. The configurations of NNO-facets are defined here as L (left) and R (right) to indicate the direction of the nitrogen atom contained in the N–O chelate ring, when the NNO-facet is viewed as in Fig. 3.

The configurations of the NNO-facets in the early eluted enantiomers are shown in the last column in Table 1. In the complexes having two NNO-facets in a complex, the NNO-facets share the moiety of two nitrogen atoms. In the complexes having the NNO-facet, except for the aeida complexes (**5a** and **5b**), the early eluted enantiomers for the seventeen complexes contain the NNO-facet of L- or LL-configuration, while those for the four complexes, *cis*-*β*-$[Co(ox)(edda)]^-$ (**4**), *cis*(*N*)-$[Co(ida)_2]^-$ (**6a**), C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$ (**9a**), and C_1-*cis*(*N*)-$[Co(ox)(\beta\text{-}ala)_2]^-$ (**9b**), contain the NNO-facet of R- or RR-configuration. Thus, it is reasonable to expect that the elution order of enantiomers can be correlated to the configuration of NNO-facet. On the other hand, all the complexes (**8a**, **8b**, and **11**) that have no NNO-facets give small *α* values (single—1.03). These facts suggest that the chirality of NNO-facet plays a dominant role in the chiral discrimination in the present resolution systems.

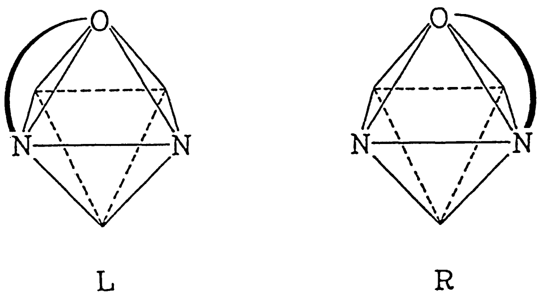

Fig. 3. L and R configurations of the NNO-facet.

It is to be noted as a simplified model for the chiral discrimination that *fac*-$[Co(NO_2)_3(edma)]^-$ (**7**) was completely resolved (Fig. 1), in spite of having no helical chelate arrangement (Fig. 2). This fact indicates that the helical chelate system is not essentially required for the chiral discrimination and that a significant unit in the discriminatory interactions exist in the facially coordinated edma moiety. The fact also is a strong support for the above suggestion concerning the role of NNO-facet for the discrimination, because the structure of edma is very close to that of the NNO-facet. It should also be noted for *cis*(*N*)-$[Co(ida)_2]^-$ (**6a**) that not only, the elution order is exceptional as described above but the *α* value is largest in the present resolutions (Table 1). This specific behavior in the bis(ida) type complexes (**6a**—**6e**) is particularly noteworthy, because it is caused only by the difference in *N*-substituent. This fact seems to hold a key to elucidate the chiral discrimination mechanism in the present resolutions. Although it cannot clearly be explained at present (vide infra), the fact at least adds support for the importance of NNO-facet for the chiral discrimination.

In most experimental studies on chiral discrimination phenomena between ions of the same sign, the direct contact mechanism has been proposed, where the racemic complex and environment substance (or selector) interact directly.[12—16)] On the other hand, a non-contact mechanism has also been postulated experimentally[17)] and theoretically.[18)] In all systems for which the direct contact mechanism was proposed, one or both of the racemic (e.g., $[Zn(phen)_3]^{2+}$ (1,10-phenanthroline)) and environment (*d*-cinchoninium) ions contain groups with aromaticity (N-heterocyclic unsaturated groups in most cases). The mechanism has been explained in terms of a sequence that the hydrogen bonding or the hydrophobic interactions in a wide sense lead to direct contact between ions of the same sign against their mutual electrostatic repulsion inevitably expected, and that this contact provides a main driving force for the chiral discrimination.

In the present resolution systems, in contrast, both the racemate and selector are hydrophilic. The selector has acceptor oxygen atoms but no donor hydrogen atoms. Accordingly, a probable attractive force is brought about by the hydrogen bonding between the donor hydrogen atom of racemate and the acceptor oxygen atom of selector. Nine of the present racemates, edta type (**1a**—**1e**), med3a (**2b**), dmedda (**3b**), bis(mida) (**6c**), and bis(eida) (**6e**), have no donor hydrogen atoms, indicating the absence of attractive force. Nevertheless, the *α* values for these complexes are fairly large on the average, although they are somewhat smaller than those for the other complexes having N-H bonds available for the hydrogen bonding (Table 1). By the way, it may be possible that direct contact is electrically allowed under special conditions at exchanging sites on the anion exchanger. Even if this is so, however, it appears to be difficult to explain the present results that the four edta type complexes (**1a**—**1d**) give α values (1.06—1.09) similar to one another; namely, it is difficult to construct such an interacting model as suggests the direct contact of the NNO-facet with the selector, because the N–N backbone chelates are distinctly different in their bulkiness.

The C_1- and C_2-cis(*N*) isomers of $[Co(ox)(gly\ or\ \beta\text{-}ala)_2]^-$ (**9a**—**10b**) have four N–H bonds in the NNO-facet. From X-ray structural studies, it has been found that the five-membered glycinato chelate is almost planar,[32] whereas the six-membered β-alaninato chelate exists in a puckered conformation with two kinds of N–H bonds, axial and equatorial.[33] In spite of such a clear difference of the N–H geometries in the NNO-facet, the glycinato and β-alaninato complexes show practically the same resolution behavior in the same geometrical isomer (Table 1). This fact is also difficult to explain in terms of direct and concrete interactions through hydrogen bonding to the selector, even if the N–H bonds participate in the chiral discrimination.

From these considerations, we conclude that the ability of the present discrimination has nothing to do with direct contact between the racemate and selector. Bosnich and Watts[17] have speculated such a noncontact mechanism, where the chiral discrimination is induced by the diastereomeric interaction between chiral solvent sheaths formed about enantiomers and selector. This mechanism can favorably explain the present discrimination phenomenon, because the presence of some waters intervening between ions of the same sign will effectively reduce the electrostatic repulsion between ions.

The alkyl substitution of the N–H proton of $[Co(NO_2)(ed3a)]^-$ (**2a**), forming $[Co(NO_2)(med3a)]^-$ (**2b**), significantly lowers the α value (from 1.10 to 1.06). Such is the case with the other pairs, *cis*-α-$[Co(ox)(edda)]^-$ (**3a**)$\cdots$*cis*-α-$[Co(ox)(dmedda)]^-$ (**3b**) (1.16 to 1.04) and *cis*(*N*)-$[Co(ida)(mida)]^-$ (**6b**)$\cdots$*cis*(*N*)-$[Co(mida)_2]^-$ (**6c**) (1.13 to 1.07), but the α values of *cis*(*N*)-$[Co(ida)(eida)]^-$ (**6d**) and *cis*(*N*)-$[Co(eida)_2]^-$ (**6e**) (1.04 to 1.05) are comparable to each other. This behavior is in contrast to the fact that the four edta type complexes (**1a**—**1d**) show similar α values (1.06—1.09) in spite of the variation in alkyl N–N backbone, as pointed out above. This fact, therefore, indicates a participation of the N–H proton in the chiral discrimination. According to our proposal, this may imply that the N–H proton(s) contribute to the formation of water sheaths about the racemate. It may first be considered that the number and direction of N–H bonds in an NNO-facet effectively affect the formation of water sheath. Molecular model considerations show that the two N–H bonds of cis(*N*)-$[Co(ida)_2]^-$ (**6a**) roughly face to each other. There are no complexes which have such a geometry of two N–H bonds in the present complexes, except for the four complexes (**9a**—**10b**), C_1- and C_2-*cis*(*N*)-$[Co(ox)(gly\ or\ \beta\text{-}ala)_2]^-$. The excluded complexes have two N–H bonds of a geometry similar to those of *cis*(*N*)-$[Co(ida)_2]^-$, but additionally two more N–H bonds. Thus, *cis*(*N*)-$[co(ida)_2]^-$ has the characteristic donor hydrogen atoms in the present complexes. This is a possible explanation for the exceptional behavior of *cis*(*N*)-$[Co(ida)_2]^-$ described above.

The α value for $[Co(cydta)]^-$ (**1e**) is markedly small compared with those for the other edta type complexes (**1a**—**1d**). This may be ascribed to the high hydrophobicity of the large-sized cyclohexane ring, by which the formation of water sheath about the complex is depressed. The *cis*-β-$[Co(ox)(edda)]^-$ (**4**), C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$ (**9a**), and C_1-*cis*(*N*)-$[Co(ox)(\beta\text{-}ala)_2]^-$ (**9b**) complexes show the exceptional behavior in elution order, as mentioned above. In addition to this fact, these complexes give small α values (single—1.04), out of proportion to the structure that the complexes have both the NNO-facet and some N–H bonds. The complexes have the same chelate skeleton, except for the presence or absence of the ethylene bridge spanned between two nitrogen atoms. Although it is presumed that the reason for the behavior observed is concealed in the common chelate structure in these complexes, its detail is not clear.

Under the situation described above, the elution order of enantiomers cannot confidently be correlated to the configuration of NNO-facet. The aeida complexes, *unsym*-$[Co(ox)(aeida)]^-$ (**5a**) and *unsym*-$[Co(NO_2)_2(aeida)]^-$ (**5b**), of which the absolute configurations are unknown, do not have such a structure as brings about the exceptional relation as described above. Accordingly, the regular relation may be applicable to these complexes; namely, their early eluted enantiomers are tentatively considered to have the NNO-facet of L-configuration and the absolute configuration which is self-evidently derived from it (Table 1 and Fig. 2). The *unsym*-$[Co(NO_2)_2(aeida)]^-$ (**5b**) complex is another example which has been completely resolved in spite of the lack of helical chelate arrangement.

In the present chromatographic resolution systems, the $[Sb_2(d\text{-}tart)_2]^{2-}$ selector participates in the chiral discrimination in both the stationary phase and the mobile phase. If it is assumed that the mode of diastereomeric interaction between the selector and racemate is the same in both phases, the selector exerts an opposite effect upon the elution order of the enantiomers, and the elution order depends on the relative concentrations of the selector in the phases. The concentration of the selector in the stationary phase ($0.24\ mmol\ cm^{-3}$ on the basis of the ion-exchange capacity of the exchanger used)[10] is more than ten times as high as that in the mobile one ($0.02\ mol\ dm^{-3}$). Thus, the elution order is governed by the selector in the stationary phase, that is, one of the enantiomers which interacts more favorably with the selector is late eluted than the other. A further study is now in progress.

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