Mechanism of Chiral Recognition of Octahedral Metal Complexes Effected by Bis(μ-*d*-tartrato)-diantimonate(III) Anion in Solution. I. Association Models and Their Application to Some $[Co(N)_6]^{3+}$-Type Complexes

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An association model has been proposed which accounts for how bis(μ-*d*-tartrato)-diantimonate(III) anion, $[Sb_2(d\text{-tart})_2]^{2-}$ ion recognizes the chirality of $[Co(en)_3]^{3+}$ (en=ethylenediamine) and some related cation complexes in solution. In this model, two oxygen atoms of the chiral anion, i.e., the carboxylic oxygen atom (coordinated to the Sb atom) of one *d*-tartrate moiety and the alcoholic oxygen atom (coordinated to the same Sb atom) of the other *d*-tartrate moiety, are hydrogen-bonded to the two amine protons in $[Co(en)_3]^{3+}$ which are directed along either the C_3 or C_2 axis. When these hydrogen bonds are formed along the C_3 axis (C_3 association), $[Sb_2(d\text{-tart})_2]^{2-}$ ion forms a more favorable ion pair with Λ-$[Co(en)_3]^{3+}$, whereas it does with Δ-$[Co(en)_3]^{3+}$ if the two amine protons directed along the C_2 axis are utilized for hydrogen bonding to it (C_2 association). This model is successfully applied to the interpretation of chromatographic behavior of some $[Co(N)_6]^{3+}$-type complexes as well as of their related complexes with amine or phosphine ligands.

It is well-known that bis(μ-*d*-tartrato)-diantimonate(III) anion, $[Sb_2(d\text{-tart})_2]^{2-}$ ion serves as an effective eluent in chromatographic resolution of various octahedral complex cations.[1–3] We have already proposed a so-called L–J model[4] which explains conceptually how the chiral anion recognizes the chirality of a series of $[Co(N)_6]^{3+}$-type complexes. However, this model does not tell us anything about the actual interaction prevailing between $[Sb_2(d\text{-tart})_2]^{2-}$ and $[Co(N)_6]^{3+}$ ions. In addition, several new experimental results have been accumulated which are not easily interpreted within the framework of the L–J model. In the present study, we propose a concrete association model in which $[Sb_2(d\text{-tart})_2]^{2-}$ ion interacts with $[Co(N)_6]^{3+}$-type complexes through intermolecular hydrogen bonding.

Association Models

Experimental Observations. We have at least two experimental results which are quite informative to construct an association model between $[Sb_2(d\text{-tart})_2]^{2-}$ and $[Co(N)_6]^{3+}$ ions. The first is concerned with the effect of added $[Sb_2(d\text{-tart})_2]^{2-}$ ion on the circular dichroism (CD) spectrum of $[Co(en)_3]^{3+}$ in solution; its A_2 component at the first ligand field band is enhanced upon the addition of the chiral anion.[5] Since the A_2 transition is polarized along the C_3 axis, this CD-spectral change implies that the chiral anion approaches the complex predominantly along its C_3 axis to perturb the rotational strength of the A_2 transition.[6] Another observation relevant to the present study is that $[Co(Me_2\text{-en})(en)_2]^{3+}$ (Me_2-en=*N,N′*-dimethylethylenediamine) having axial methyl groups almost parallel to the pseudo C_3 axis, i.e., a mixture of its Λ(RR) and Δ(SS) isomers, is eluted considerably slower than $[Co(en)_3]^{3+}$ on the SP-Sephadex column with $[Sb_2(d\text{-tart})_2]^{2-}$ ion employed as an eluent.[7] Furthermore, the degree of optical resolution attained is much lower for $[Co(Me_2\text{-en})(en)_2]^{3+}$. Similar difference in chromatographic behavior has been found between $[Co(sar)(en)_2]^{2+}$ (sar=sarcosinate anion) and its parent complex $[Co(gly)(en)_2]^{2+}$ (gly=glycinate anion).[8] These observations suggest that the axial NH protons directed along the (pseudo) C_3 axis are utilized in the hydrogen-bonding interaction with some oxygen atoms in $[Sb_2(d\text{-tart})_2]^{2-}$ anion.

C_3 Association Model. When the molecular structure of $[Sb_2(d\text{-tart})_2]^{2-}$ ion (shown in Fig. 1) is examined in detail, a pair of oxygen atoms are found whose lone-pair electrons are nicely disposed to interact with two of the three axial NH protons directed along the C_3 axis of $[Co(en)_3]^{3+}$. They are the alcoholic oxygen atom of one *d*-tartrate moiety which is coordinated to the Sb atom and the carboxylic oxygen atom of another *d*-tartrate moiety which is coordinated to the same Sb atom. $[Sb_2(d\text{-tart})_2]^{2-}$ ion

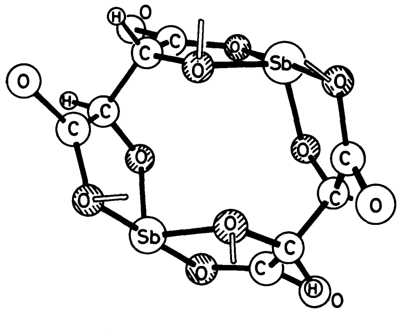


Fig. 1. Molecular structure of $[Sb_2(d\text{-tart})_2]^{2-}$ ion. Two shaded oxygen atoms coordinated to the same Sb atom are used for double hydrogen bonding.

has evidently four such pairs, which may be partly responsible for its high recognition efficiency as compared with *d*-tartrate ion.[9]

In Fig. 2 is depicted the C_3 association model which accomodates the above-mentioned experimental results, taking $[Co(en)_3]^{3+}$ as an example. In this model, the two oxygen atoms of $[Sb_2(d\text{-tart})_2]^{2-}$ ion participates in the double hydrogen bonding to two of the three axial NH protons directed along the C_3 axis, and the remaining part of the chiral anion is disposed opposite to the third NH group free from hydrogen bonding. If a bulky or negatively charged group is present in place of the third NH group, it will impose a steric or electrostatic repulsion on the carboxylic oxygen atom hydrogen-bonded to the complex. Since the double hydrogen bonds are formed along the C_3 axis, this model is called as the C_3 association model.

It is seen in Fig. 2 that the distal carboxylato group of $[Sb_2(d\text{-tart})_2]^{2-}$ ion is situated between the two en chelate rings in the C_3 association with Λ-$[Co(en)_3]^{3+}$ (left model) and a favorable ion pair is thus formed between the two ions, whereas the carboxylato group, particularly its C=O group experiences a steric hindrance from one en chelate ring in the C_3 association with Δ-$[Co(en)_3]^{3+}$ (right model), as indicated by an arrow. In this way, the C_3 association model predicts that $[Sb_2(d\text{-tart})_2]^{2-}$ ion associates more smoothly with the Λ complex than with the Δ complex, in accordance with the experimental result.[5] Since two axial NH protons are utilized in the C_3 association, it follows that six equivalent interaction sites are present in $[Co(en)_3]^{3+}$. Interaction sites are counted similarly for other $[Co(N)_6]^{3+}$-type complexes. Even if a complex is devoid of a true C_3 axis, it may have some C_3 interaction sites; if a set of three NH protons are present on a triangular facet[10] of a complex, they serve as interaction sites equivalent to true C_3 interaction sites. Furthermore, the C_3 interaction is possible even when only two NH protons are present on the triangular facet, provided that the third group is electrically neutral and/or is not bulky (see later).

Another C_3 association is conceivable in which all of the three axial NH protons of $[Co(en)_3]^{3+}$ are simultaneously hydrogen-bonded to three oxygen atoms of $[Sb_2(d\text{-tart})_2]^{2-}$ ion. The three oxygen atoms appropriately disposed in the chiral anion are two oxygen atoms of one carboxylato group in one *d*-tartrate moiety, and the alcoholic oxygen atom on the asymmetric carbon atom to which the other carboxylato group in the same *d*-tartrate moiety as above is directly attached; $[Sb_2(d\text{-tart})_2]^{2-}$ ion has apparently four sets of such three oxygen atoms, each *d*-tartrate moiety providing the two sets. A molecular model consideration reveals that the chiral recognition is similarly effected in this alternative C_3 association model through the steric repulsion imposed stereoselectively by the chelate ring of the Δ complex on the distal carboxylato group. However, this C_3 model is applicable only to those complexes which have three NH protons on the triangular facet. For example, complete chromatographic resolution of $[Co(phen)(en)_2]^{3+}$ and $[Co(acac)(en)_2]^{2+}$ (phen=1,10-phenanthroline and acac=acetylacetonate anion)[3] is not reasonably interpreted by this C_3 model in which triple hydrogen bonds are required. Consequently, we abandon this C_3 model and adopt the aforementioned C_3 model, to interpret the chromatographic behavior of various types of octahedral metal complexes throughout the present study.

C_2 Association Model. Since two NH protons in $[Co(en)_3]^{3+}$ are required for the interaction with $[Sb_2(d\text{-tart})_2]^{2-}$ ion, those NH protons which are directed along the C_2 axis can also be utilized for the double hydrogen bonding. This interaction is called as the C_2 association and its model is depicted in Fig. 3, taking *cis*-$[Co(X)_2(en)_2]^+$ (X=anion ligand) as an example. Here, $[Sb_2(d\text{-tart})_2]^{2-}$ ion approaches the complex along the C_2 axis from the side opposite to X so as to avoid an electrostatic repulsion from X, and

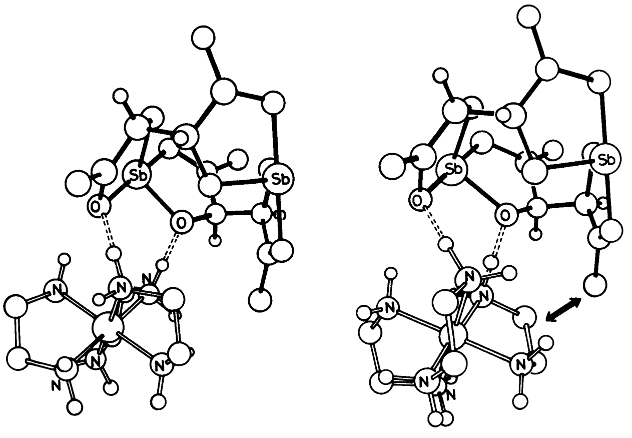


Fig. 2. C_3 Association models for Λ-$[Co(en)_3]^{3+}$-$[Sb_2(d\text{-tart})_2]^{2-}$ (left) and Δ-$[Co(en)_3]^{3+}$-$[Sb_2(d\text{-tart})_2]^{2-}$ (right).

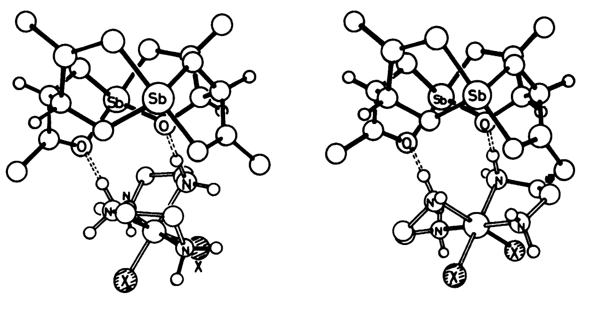


Fig. 3. C_2 Association models for Δ-*cis*-$[Co(X)_2(en)_2]^+$-$[Sb_2(d\text{-tart})_2]^{2-}$ (left) and Λ-*cis*-$[Co(X)_2(en)_2]^+$-$[Sb_2(d\text{-tart})_2]^{2-}$ (right).

the double hydrogen bonds are formed to the two NH protons directed along the C_2 axis. It is evident in Fig. 3 that the distal carboxylato group suffers a steric hindrance from one en chelate ring when the complex has a Λ configuration (right model). On the other hand, a smooth association is possible with Δ-*cis*-$[\mathrm{Co(X)_2(en)_2}]^+$ (left model),[11] since the distal carboxylato group is disposed between the two en chelate rings like in the C_3 association with Λ-$[\mathrm{Co(en)_3}]^{3+}$. Therefore, $[\mathrm{Sb_2}(d\text{-tart})_2]^{2-}$ ion forms a more favorable ion pair with the Δ complex in the C_2 association. In fact, $[\mathrm{Sb_2}(d\text{-tart})_2]^{2-}$ ion elutes the Δ isomer faster on an ion-exchange column for most of *cis*-$[\mathrm{Co(X)_2(en)_2}]^+$-type complexes[12] which adopt the C_2 association predominantly. It should be noted, however, that the C_2 association is possible also for $[\mathrm{Co(N)_6}]^{3+}$-type complexes. For example, $[\mathrm{Co(en)_3}]^{3+}$ has three C_2 interaction sites in addition to six C_3 interaction sites.

Comparison with Experimental Results

$[\mathrm{Co(N)_6}]^{3+}$-Type Complexes. Now, it is possible to count the C_3 and C_2 interaction sites for respective $[\mathrm{Co(N)_6}]^{3+}$-type complexes. For simplicity, those sites are neglected here in which the distal carboxylato group suffers a steric hindrance from the chelate ring, viz., no smooth association is possible. For example, Λ-$[\mathrm{Co(en)_3}]^{3+}$ has six favorable C_3 interaction sites but has no favorable C_2 site. By contrast, Δ-$[\mathrm{Co(en)_3}]^{3+}$ has no C_3 site but has three favorable C_2 sites. For $[\mathrm{Co(Me_2\text{-}en)(en)_2}]^{3+}$ and $[\mathrm{Co(Me\text{-}en)(en)_2}]^{3+}$ (Me-en=*N*-methylethylenediamine) having methyl group(s) almost parallel to the pseudo C_3 axis, interaction sites are counted on the assumption that the methyl group does not interfere with the C_3 interaction. Numbers of favorable interaction sites counted in this way agree perfectly with the numbers of L-shaped channels defined in the previous work for $[\mathrm{Co(N)_6}]^{3+}$-type complexes.[4] This means that the conceptual L–J model is automatically incorporated into the C_3 association model, but the C_2 association mode has been ignored in the L–J model. Numbers of C_3 and C_2 interaction sites N are given for respective $[\mathrm{Co(N)_6}]^{3+}$-type complexes in Table 1. It is naturally expected that a complex having a greater difference in N between its Λ and Δ enantiomers should be resolved more effectively by ion-exchange chromatography.

In Table 1 are also given the separation factors α, a measure of efficiency of optical resolution attained for respective complexes, when available. It is confirmed in Table 1 that the above expectation is actually fulfilled as far as the C_3 interaction mode is concerned. This suggests that the C_2 interaction mode which has not been taken into account in the L–J model, does not contribute appreciably to chiral recognition of $[\mathrm{Co(N)_6}]^{3+}$-type complexes.

Even for the complexes α values of which are not known, the elution order in chromatography is at least in good agreement with the prediction of our association models. The two complexes, *cis* α-$[\mathrm{Co(trien)(NH_3)_2}]^{3+}$ (trien=triethylenetetramine) and *fac,fac,mer*-$[\mathrm{Co(tetren)(NH_3)}]^{3+}$ (tetren=tetraethylenepentamine) need to examine somewhat in detail. The former complex has eight C_3 sites both for the Λ and Δ isomers; no practical resolution is expected. However, for the Λ isomer, a secondary amine proton is involved

Table 1. Number of Favorable Interaction Sites N, Separation Factor α, and Elution Order for $[\mathrm{Co(N)_6}]^{3+}$-Type Complexes

Complex	N				α	Enantiomer Eluted Faster		Ref.
	C_3		C_2					
	Λ	Δ	Λ	Δ		Obsd	Predic.	
$[\mathrm{Co(en)_3}]^{3+}$	6	0	0	3	1.45	Λ	Λ	4
$[\mathrm{Co(en)_2(Me\text{-}en)}]^{3+}(\Lambda R,\Delta S)$	4	0	0	3(1)		Λ	Λ	3
$[\mathrm{Co(en)_2(Me_2\text{-}en)}]^{3+}(\Lambda RR,\Delta SS)$	2	0	0	3(2)		(Λ)[a]	Λ	7
cis-$[\mathrm{Co(en)_2(NH_3)_2}]^{3+}$	10	8	0	1		Λ	Λ	3
$[\mathrm{Co(en)_2}(\mathrm{phen\ or\ bpy})]^{3+}$	2	0	0	1		Λ[b]	Λ	3
cis α-$[\mathrm{Co(trien)(en)}]^{3+}$	4(2)	0	0	2	1.37	Λ	Λ	4, 15
cis β-$[\mathrm{Co(trien)(en)}]^{3+}(\Lambda SS,\Delta RR)$	3	0	1(1)	2(1)	1.28	Λ	Λ	4, 15
cis β-$[\mathrm{Co(trien)(en)}]^{3+}(\Lambda SR,\Delta RS)$	3	0	1(1)	2(1)		Λ	Λ	15
cis α-$[\mathrm{Co(trien)(NH_3)_2}]^{3+}$	8(2)	8	0	0		Λ	Λ	14
cis β-$[\mathrm{Co(trien)(NH_3)_2}]^{3+}(\Lambda SS,\Delta RR)$	7(1)	6(1)	0	0		Λ	Λ	14
cis β-$[\mathrm{Co(trien)(NH_3)_2}]^{3+}(\Lambda SR,\Delta RS)$	7(1)	6(1)	0	0		Λ	Λ	14
unsym-fac-$[\mathrm{Co(dien)_2}]^{3+}$	4	2	1(1)	2(2)	1.20	Λ	Λ	4
unsym-fac-$[\mathrm{Co(dien)(en)(NH_3)}]^{3+}$	6(1)	4(1)	2	3(1)		Λ	Λ	15
fac,mer,fac-$[\mathrm{Co(tetren)(NH_3)}]^{3+}$	4(2)	2(2)	0	0		Λ	Λ	15
fac,fac,mer-$[\mathrm{Co(tetren)(NH_3)}]^{3+}(\Lambda S,\Delta R)$	3(1)	4	1	0		Λ	—	15

Numbers in parentheses denote numbers of interaction sites at which a secondary amine proton is involved in double hydrogen bonding (see the text). a) Partial resolution. b) Partial resolution for bpy complex.

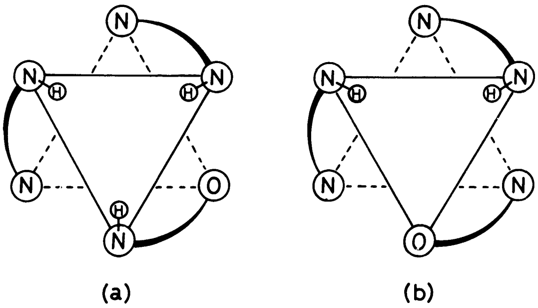
in the double hydrogen bonding at two of the eight C_3 sites. Since a secondary amine proton is generally more acidic than a primary one, a stronger hydrogen bond is formed with the former proton,[10,13] other conditions being equal. In short, interaction sites associated with a secondary amine proton contribute more to the interaction with $[Sb_2(d\text{-tart})_2]^{2-}$ ion than those with a primary amine proton. Since all of the interaction sites of the Δ isomer are associated with primary amines only, the Λ isomer is expected to interact with $[Sb_2(d\text{-tart})_2]^{2-}$ ion more strongly than the Δ isomer for *cis* α-$[Co(trien)(NH_3)_2]^{3+}$.[14]

For *fac,fac,mer*-$[Co(tetren)(NH_3)]^{3+}$, the Δ isomer has a greater N than the Λ isomer; the Δ isomer may be eluted faster. However, the Λ isomer has three C_3 interaction sites one of which is associated with a secondary amine, while only primary amines are involved in the double hydrogen bonding at all of the four C_3 interaction sites for the Δ isomer. Furthermore, one favorable C_2 site adds to the Λ isomer. In practice, $\Lambda(S)$-*fac,fac,mer*-$[Co(tetren)(NH_3)]^{3+}$ has been eluted faster.[15] This implies that a secondary amine proton contributes much more to the total hydrogen-bonding interaction with $[Sb_2(d\text{-tart})_2]^{2-}$ ion than a primary amine proton.[13] Then, the partial resolution of $[Co(Me_2\text{-en})(en)_2]^{3+}$ may be attributed to the fact that the Λ isomer has two usual C_3 sites only, but the Δ isomer has three C_2 sites two of which are associated with a secondary amine.

As is evident from the above discussions, the C_3 association model leads to a general prediction that Λ-$[Co(N)_6]^{3+}$-type complexes interact with $[Sb_2(d\text{-tart})_2]^{2-}$ ion more favorably than their antipodes. However, some complexes are known which behave oppositely to the above prediction. For example, Δ isomers are eluted faster in ion-exchange chromatography for a series of $[Co(en)_x(tn)_y(tmd)_z]^{3+}$ complexes when $x=0$[16] (tn=trimethylenediamine and tmd=tetramethylenediamine). In addition, Λ-*cis*-$[Co(tn)_2(NH_3)_2]^{3+}$ is eluted faster, but the elution order is reversed if tn ligands are replaced with tmd ligands.[17,18] These exceptional elution orders are not easily rationalized by our association models, but they may be attributed to conformational lability of these complexes. That is, since axial NH protons are not fixed in these higher-membered chelate complexes, the C_3 mode will not effectively contribute to chiral recognition for these flexible complexes. If the contribution of the C_3 mode is reduced to the extent that the C_2 mode predominates over the C_3 mode, Δ isomers should be eluted faster.

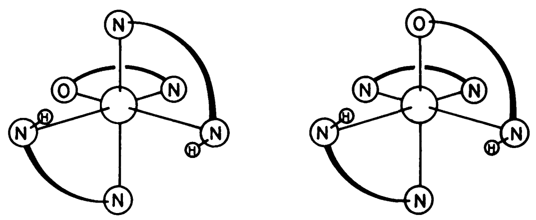
***cis*(*O*)-$[Co(O)_2(N)_4]^+$-Type Complexes.**[19] When negatively charged donor atom(s) are present in a complex, a care must be taken in counting the C_3 and C_2 interaction sites. For example, $[Co(gly)(en)_2]^{2+}$ has two triangular facets along the pseudo C_3 axis, one composed of three NH protons and the other of two NH protons and one oxygen atom of gly. They are shown schematically in Fig. 4. The former facet provides three normal C_3 sites for the Λ isomer (Fig. 4(a)), but the latter provides only one C_3 site which is expected to suffer an electrostatic repulsion from the negatively charged oxygen atom present nearby (Fig. 4(b)). Since this C_3 site is electrostatically handicapped, it contributes less than the normal C_3 site and is designated as the $C_3{}^*$ site to differentiate it from the normal one. Similar allowance has been made in the ranked L–J model,[19] and should be also made in counting the C_2 sites; Δ-$[Co(gly)(en)_2]^{2+}$ has two C_2 sites one of which ($C_2{}^*$) suffers an electrostatic repulsion from the oxygen atom of gly (Fig. 5). Numbers of interaction sites thus counted for *cis*(*O*)-$[Co(O)_2(N)_4]^+$-type and related complexes are given in Table 2, where starred numbers in parentheses denote the numbers of such handicapped sites out of all the possible C_3 or C_2 interaction sites.

Three points are mentioned in Table 2. The first is that our association models predict a correct elution order even for *cis*(*O*),*trans*(*N*),*cis*(*NH*$_3$)-$[Co(gly)_2(NH_3)_2]^+$ which is exceptional in that its Δ isomer is eluted faster.[19] The second point is that the elution order is not rationalized for C_2-$[Co(gly)_2(en)]^+$ if the $C_3{}^*$ site is neglected. Thus, the $C_3{}^*$ interaction should be taken into account, particularly when other rival interactions are not possible. Anyway, C_2-$[Co(gly)_2(en)]^+$ should not be resolved effectively.[19] Similarly,



(a) (b)

Fig. 4. Triangular facets providing C_3 (a) and $C_3{}^*$ (b) interaction sites in Λ-$[Co(gly)(en)_2]^{2+}$.



(a) (b)

Fig. 5. C_2 (a) and $C_2{}^*$ (b) interaction sites in Δ-[Co(gly)(en)$_2$]$^{2+}$.

no effective resolution is expected for *trans*(*O*)-$[Co(gly)_2(en)]^+$.

Finally, the last two complexes, *fac*(*NH*$_3$)-$[Co(X)(gly)(NH_3)_3]^+$ and $[Co(X)(gly)(tacn)]^+$ (X=anion ligand and tacn=1,4,7-triazacyclononane) have been prepared and resolved by ion-exchange chromatography.[20,21] These complexes have a chirality different from those defined by helical rearrangements of chelate rings. Schematic structures of their two enantiomers (a) and (b) are shown in Fig. 6. Shibata et al.[20,21] have found that the (a) enantiomer is eluted faster for the ammine complex, while the (b) enantiomer is for the tacn complex. Our association models predict a correct elution order straightforwardly for the former, while the elution order of the latter complex is not rationalized unless the C_3* mode predominates over the C_2* mode. This will happen since the C_3 mode generally predominates over the C_2 mode.

Complexes with Phosphine Chelates. Recently, Fujita and co-workers have prepared and resolved a number of octahedral Co(III) complexes with phosphine chelates. Since these complexes have invariably some substituents on the phosphorus donor atom(s), they provide us a chance to examine the steric effect of substituents on the C_3 and C_2 interactions.

When the C_3 and C_2 interaction sites are counted for phosphine complexes, an assumption is made that a methyl or phenyl group on the triangular facet prohibits the C_3 interaction involving the two NH protons on the same facet. For example, $[Co(en)_2(edmp\text{ or }edpp)]^{3+}$ (edmp=(2-aminoethyl)dimethylphosphine and edpp=(2-aminoethyl)diphenylphosphine) has two triangular facets, one of which has an axial methyl or phenyl group on the P atom, and thus the C_3 mode is sterically prohibited on this facet. As a result, the Λ isomer has three C_3 sites on the other facet, and the Δ isomer has two C_2 sites. Interaction sites are counted similarly for *fac*(*N*)-$[Co(en)(edmp)_2]^{3+}$ and *fac*(*N*)-$[Co(edmp)_3]^{3+}$. The results given in Table 3 predict correct elution orders for these complexes.[24]

For $[Co(en)_2(dmpe\text{ or }dppe)]^{3+}$ (dmpe=1,2-(dimethylphosphino)ethane and dppe=1,2-(diphenylphosphino)ethane), and *trans*(*P*,*P*)-$[Co(edmp)_2(dmpe)]^{3+}$, no C_3 interaction is possible. Instead, one C_2 site is present in the Δ isomers, which thus should be eluted faster.[25] On the other hand, $[Co(en)(dmpe\text{ or }dppe)_2]^{3+}$, *trans*(*P*,*N*)- and *trans*(*N*,*N*)-$[Co(edmp)_2(dmpe)]^{3+}$, and $[Co(dmpe\text{ or }dppe)_3]^{3+}$ have no NH protons available for the double hydrogen bonding to the chiral eluent anion, so that practical resolution is not attained for these complexes.[25] In this way, elution orders are correctly predicted for most of the phosphine complexes listed in Table 3 on the assumption that no C_3 interaction is possible on the triangular facet on which an axial methyl or phenyl group is attached to the P atom. In the preceding section, however, interaction sites are counted for *N*-methylated complexes by assuming that an axial methyl group on the N donor atom does not interfere with the C_3 interaction. If the methyl group also prohibits the C_3 interaction, our models fail to predict a correct elution order for $[Co(Me_2\text{-}en)(en)_2]^{3+}$. Thus, a methyl group should be regarded as a steric obstacle to the C_3 interaction only when it is attached to the P

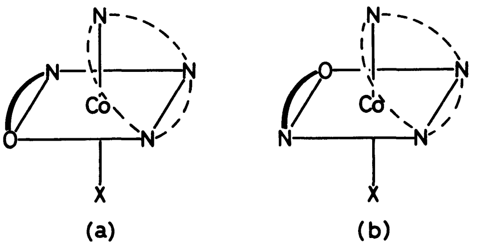


Fig. 6. Schematic structures of two possible enantiomers (a) and (b) for *fac*(*NH*$_3$)-$[Co(X)(gly)(NH_3)_3]^+$ and $[Co(X)(gly)(tacn)]^+$.

Table 2. Interaction Sites *N* and Elution Orders for *cis*(*O*)-$[Co(O)_2(N)_4]^+$-Type and Related Complexes

Complex	*N*				Enantiomer Eluted Faster		Ref.
	C_3		C_2				
	Λ	Δ	Λ	Δ	Obsd	Predic.	
$[Co(gly\text{ or }\beta\text{-ala})(en)_2]^{2+}$	4 (1*)	0	0	2 (1*)	Λ	Λ	22
cis(*O*),*cis*(*N*),*cis*(*NH*$_3$)-$[Co(gly)_2(NH_3)_2]^+$	6 (1*)	5 (1*)	0	0	(Λ)$^{\text{d)}}$	Λ	19
cis(*O*),*trans*(*N*),*cis*(*NH*$_3$)-$[Co(gly)_2(NH_3)_2]^+$	5 (1*)	7 (1*)	0	0	Δ	Δ	19
C_1-$[Co(gly)_2(en)]^+$	3	0	0	1 (1*)	Λ	Λ	19
C_2-$[Co(gly)_2(en)]^+$	2 (2*)	0	0	2 (2*)	(Λ)$^{\text{d)}}$	—	19
trans(*O*)-$[Co(gly)_2(en)]^+$	2 (2*)	0	0	1 (1*)	c)	—	—
fac-$[Co(amino\ acidato)_3]$	3	0	0	0	Λ	Λ	23
fac(NH$_3$)-$[Co(X)(gly)(NH_3)_3]^+$	8 (2*)$^{\text{a)}}$	7 (2*)$^{\text{b)}}$	0$^{\text{a)}}$	0$^{\text{b)}}$	a	a	20
$[Co(X)(gly)(tacn)]^+$	0$^{\text{a)}}$	1 (1*)$^{\text{b)}}$	1 (1*)$^{\text{a)}}$	0$^{\text{b)}}$	b	—	21

Starred numbers in parentheses denote the numbers of handicapped C_3* or C_2* interaction sites (see the text). a, b) a and b correspond to absolute configurations shown in Fig. 6(a) and 6(b) respectively. c) Not known. d) Partial resolution.

Table 3. Interaction Sites *N* and Elution Orders for Phosphine Complexes

Complex	*N*				Enantiomer Eluted Faster		Ref.
	C_3		C_2				
	Λ	Δ	Λ	Δ	Obsd	Predic.	
[Co(en)$_2$(edmp or edpp)]$^{3+}$	3	0	0	2	Λ	Λ	24
fac(*N*)-[Co(en)(edmp)$_2$]$^{3+}$	3	0	0	1	Λ	Λ	24
fac(*N*)-[Co(edmp)$_3$]$^{3+}$	3	0	0	0	Λ	Λ	24
[Co(en)$_2$(dmpe or dppe)]$^{3+}$	0	0	0	1	Δ	Δ	25
[Co(en)(dmpe or dppe)$_2$]$^{3+}$	0	0	0	0	(Δ)a,e)	—	25
trans(*P*,*P*)-[Co(edmp)$_2$(dmpe)]$^{3+}$	0	0	0	1	b)	Δ	27
trans(*P*,*N*)-[Co(edmp)$_2$(dmpe)]$^{3+}$	0	0	0	0	b)	—	27
trans(*N*,*N*)-[Co(edmp)$_2$(dmpe)]$^{3+}$	0	0	0	0	b)	—	27
[Co(dmpe or dppe)$_3$]$^{3+}$	0	0	0	0	—c,e)	—	25
[Co(acac)(en)$_2$]$^{2+}$	2*	0	0	1	Λ	Λ	12
[Co(ox)(en)$_2$]$^{+}$	0	0	0	1	(Δ)a)	Δ	12
fac(*N*)-[Co(acac)(en)(edmp or edpp)]$^{2+}$	1*	0	0	1	(Λ)a,d)	Λ	28
fac(*N*)-[Co(ox)(en)(edmp or edpp)]$^{+}$	0	0	0	1	b)	Δ	—
trans(*P*,*N*)-[Co(acac)(edmp or edpp)$_2$]$^{2+}$	1*	0	0	0	Λd)	Λ	29
trans(*P*,*N*)-[Co(ox)(edmp or edpp)$_2$]$^{+}$	0	0	0	0	(Λ)a,d)	—	29
trans(*P*,*P*)-[Co(acac)(edpp)$_2$]$^{2+}$	0	0	0	1	Λ	Δ	29
trans(*P*,*P*)-[Co(ox)(edpp)$_2$]$^{+}$	0	0	0	1	(Λ)a)	Δ	29
[Co(acac)(en)(dmpe or dppe)]$^{2+}$	0	0	0	0	(Λ)a)	—	25, 29
[Co(ox)(en)(dmpe or dppe)]$^{+}$	0	0	0	0	—c)	—	29
[Co(acac)(dmpe or dppe)$_2$]$^{2+}$	0	0	0	0	—c)	—	25
[Co(acac)$_2$(edmp or edpp)]$^{+}$	0	0	0	0	(Λ)a)	—	30
[Co(acac)$_2$(dmpe or dppe)]$^{+}$	0	0	0	0	(Λ)a)	—	25, 30

Starred numbers denote the numbers of handicapped interaction sites (see the text). a) Partial resolution. b) Not known. c) No resolution. d) Elution order for edpp complex. e) Elution order for dmpe complex.

donor atom. Since a P atom is much bigger in size than an N atom, the above claim seems reasonable. A phenyl group is, on the other hand, so bulky that it will always serve as an obstacle whether it is on the P atom or on the N atom, and will exert an additional influence on the C_2 interaction (see later).

Finally, our attention is focused on phosphine complexes with negatively charged ligand(s) such as acetylacetonate (acac) or oxalate (ox) anion. Before they are examined, interaction sites are counted for the two parent complexes, [Co(acac)(en)$_2$]$^{2+}$ and [Co(ox)(en)$_2$]$^{+}$. They have two triangular facets composed of two NH protons and one oxygen atom. If an electrostatic repulsion due to the negatively charged oxygen atom of acac or ox is taken into account, they have no C_3 site but have one C_2 site. As a result, the Δ isomer should be eluted faster. In fact, Δ-[Co(ox)(en)$_2$]$^{+}$ is eluted faster as expected, but Δ-[Co(acac)(en)$_2$]$^{2+}$ is eluted *later*.12) This means, according to our models, that the $C_3{}^*$ interaction is possible for [Co(acac)(en)$_2$]$^{2+}$. Since the oxygen atom of acac carries a formal charge of -0.5, its electrostatic field is not as strong26) as that of ox^{2-} or gly^{-} which bears a formal charge of -1.0 on the oxygen atom. In fact, we assumed before that such an electrostatically handicapped $C_3{}^*$ interaction comes into play even for [Co(gly)$_2$(en)]$^{+}$-type complexes, when other interaction modes do not contribute appreciably. Thus, interaction sites are counted in the following complexes on a fairly valid assumption that the triangular facet composed of two NH protons and one oxygen atom of acac provides one $C_3{}^*$ site, but that of two NH protons and one oxygen atom of ox (or gly) does not. However, the latter facet may contribute if other rival interaction sites are not present or do not contribute appreciably, like in C_2-[Co(gly)$_2$(en)]$^{+}$, *trans*(*O*)-[Co(gly)$_2$(en)]$^{+}$, and *trans*(*P*,*N*)-[Co(ox)(edmp or edpp)$_2$]$^{+}$ (see later). Detailed discussions on the $C_3{}^*$ interaction will be presented elsewhere in connection with the interpretation of chromatographic resolution of *cis*-[Co(X)$_2$(en)$_2$]$^{+}$-type complexes.

Now, it is confirmed in Table 3 that our association models afford a satisfactory prediction of the elution order for most of the phosphine complexes with an acac or ox ligand. For example, the Λ isomer should be eluted faster for *fac*(*N*)-[Co(acac)(en)(edmp or edpp)]$^{2+}$,28) since it has one $C_3{}^*$ site besides one C_2 site, whereas the elution order is reversed for the corresponding ox complex, since the $C_3{}^*$ interaction is prohibited but one C_2 site survives in the ox complex. For *trans*(*P*,*N*)-[Co(acac)(edmp or edpp)$_2$]$^{2+}$ which has one $C_3{}^*$ site, the Λ isomer should be eluted faster. By contrast, no effective resolution is expected for the corresponding ox complex, since it has neither the C_3

(or C_3*) nor the C_2 site.

For *trans(P,P)*-$[Co(acac)(edpp)_2]^{2+}$ and *trans(P,P)*-$[Co(ox)(edpp)_2]^+$, the Λ isomers are eluted unexpectedly faster, though both of the two *trans(P,P)* complexes have one C_2 site only. In order to rationalize these anomalous elution orders, the steric influence of a bulky phenyl group must be taken into account. It is true that two phenyl groups are situated in these complexes such that the distal carboxylato group experiences a steric repulsion from either of them in the C_2 interaction with the Δ isomer, while they do not impose any steric hindrance on the antipode. Then, if the steric repulsion due to the phenyl group in the C_2 interaction with the Δ isomer predominates over the usual repulsion due to the P–N chelate ring in the C_2 interaction with the Λ isomer, the Λ isomer should form a relatively stable ion pair with $[Sb_2(d\text{-tart})_2]^{2-}$ ion as compared with the Δ isomer. If the methyl group on the P atom is not bulky enough to serve as a steric obstacle to the C_2 interaction, the Δ isomer should be eluted faster, as our models predict, for the corresponding edmp complexes, *trans(P,P)*-$[Co(acac)(edmp)_2]^{2+}$ and -$[Co(ox)(edmp)_2]^+$. Similarly, the Δ isomer should be eluted faster for *trans(P,P)*-$[Co(edmp)_2(\text{dmpe or dppe})]^{3+}$, whereas the elution order should be reversed for the corresponding edpp complex, *trans(P,P)*-$[Co(edpp)_2(\text{dmpe or dppe})]^{3+}$. Anyway, experimental data are not enough to decide whether the methyl group on the P atom exerts a similar steric effect on the C_2 interaction.

Any of other complexes listed in Table 3 have neither the C_3 (or C_3*) nor the C_2 interaction site, so that no practical resolution is expected for them. However, for *trans(P,N)*-$[Co(ox)(\text{edmp or edpp})_2]^+$, one electrostatically handicapped C_3* interaction is conceivable which has been neglected and is shown in Fig. 4(b), and it will come into play because of complete absence of other interactions. Consequently, optical resolution, though it may be partial, is potentially possible with the Λ isomer eluted faster.[29]

The reason is not known why $[Co(en)(dmpe)_2]^{3+}$, $[Co(acac)(en)(\text{dmpe or dppe})]^{2+}$, $[Co(acac)_2(\text{dmpe or dppe})]^+$, and $[Co(acac)_2(edpp)]^+$ have been partially resolved by ion-exchange chromatography with $[Sb_2(d\text{-tart})_2]^{2-}$ ion employed as an eluent. Interaction modes other than the C_3 and C_2 hydrogen-bonding interactions must be invoked. Since the SP-Sephadex column is used for the resolution of these complexes, its chirality might be in part responsible.

Hydrophobic Complexes with Aromatic Ligands. It is note worthy that $[Sb_2(d\text{-tart})_2]^{2-}$ ion can recognize the chirality of some hydrophobic complexes with aromatic ligands such as phen or bpy (phen=1,10-phenanthroline and bpy=2,2′-bipyridine). For example, $[Cr(\text{phen or bpy})_2(bpdo)]^{3+}$ (bpdo=2,2′-bipyridine *N,N′*-dioxide),[31] $[Cr(acac)_2(bpdo)]^+$,[32] $[Cr(bpy)(phen)(\text{bpdo or mbdo})]^{3+}$ (mbdo=3,3′-dimethyl-2,2′-bipyridine *N,N′*-dioxide),[33] $[Co(acac)(en)(bpy)]^{2+}$, *mer(N)*-$[Co(acac)(\text{empp or edpp})(bpy)]^{2+}$ (empp=(2-aminoethyl)methylphenylphosphine),[28] and $[Ru(bpy)_n(Hpda)_{3-n}]^{2+}$ (Hpda=di-2-pyridylamine)[34] have been resolved by ion-exchange chromatography with $[Sb_2(d\text{-tart})_2]^{2-}$ ion employed as an eluent. Furthermore, complete chromatographic resolution has been attained for some Co(III) complexes with 2,2′-biimidazole[35] and its related ligands,[36] and the Pfeiffer effect has been detected for $[M(\text{phen or bpy})_3]^{2+}$ in the presence of $[Sb_2(d\text{-tart})_2]^{2-}$ ion.[37] Since the above complexes have no NH protons available for the double hydrogen bonding to the chiral anion, they associate with it through some interactions other than hydrogen bonding. Though a so-called hydrophobic interaction is one of the plausible interactions, its detailed nature is out of the scope of the present study.

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