A Fairly Effective Environment Substance $[Co(sep)]^{3+}$ Ion in the Pfeiffer Effect of Some Oxalato Complexes of Chromium(III)

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Synopsis. A chiral complex ion $[Co(sep)]^{3+}$ (sep=1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) was found to displace the chiral equilibrium between Δ and Λ enantiomers greatly for moderately optically labile metal complexes $[Cr(ox)_2(acac)]^{2-}$ and $[Cr(ox)_2(gly)]^{2-}$ in dioxane–water mixtures.

When an optically labile and racemic complex is mixed with a certain chiral compound (called an environment substance hereafter) in solution, new optical activity due to the initially racemic complex is sometimes induced. This phenomenon is referred to as the Pfeiffer effect,[1)] and has been ascribed to a shift in a chiral equilibrium between two enantiomers of the racemic complex. Several organic compounds have been so far reported to induce the equilibrium shift. Nordquist[2)] was probably the first to study the Pfeiffer effect in which a dissymmetric metal complex, *e.g.*, resolved $[Co(en)_3]^{3+}$(en=ethylenediamine), was used as an environment substance. Pollock *et al.*[3)] have also examined this complex as an environment substance to $[Ni(acac)_3]^-$ (acac=acetylacetonate ion) in water. However, the above two studies did not afford direct evidence that the chiral equilibrium was actually displaced by chiral $[Co(en)_3]^{3+}$ ion.[4a)] Subsequently, Yoneda and coworkers[4,5)] unambiguously demonstrated that one enantiomer of $[Cr(ox)_3]^{3-}$ (ox=oxalate dianion) was enriched at a rate comparable to its racemization rate in the presence of resolved *cis*-$[Co(X)(Y)(en)_2]^{n+}$-type complexes (X and/or Y=anionic unidentate ligand) as well as $[Co(phen)_3]^{3+}$ (phen=1,10-phenanthroline). The enantiomeric excess (ee) attained with these chiral complexes, however, amounts to only a few per cent, despite the expectation that these cationic complexes associate with $[Cr(ox)_3]^{3-}$ more strongly than do usual organic environment substances such as *d*-cinchoninium ion. We report herein that an optically active cation complex $[Co(sep)]^{3+}$ (sep=1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) derived from resolved $[Co(en)_3]^{3+}$ serves as a fairly effective environment substance to some oxalato complexes of Cr(III) in dioxane–water mixtures.

Experimental

Preparation of Complexes. Perchlorate salts of Λ-$[Co(en)_3]^{3+}$, Λ-$[Co(d\text{-}pn)_3]^{3+}$ (*d*-pn=(S)-propylenediamine), and Λ-$[Co(sep)]^{3+}$ employed as an environment substance were available from our previous works.[6)] Λ-$[Co(phen)_3]^{3+}$ was obtained as a chloride salt as before.[4a)] Racemic complexes $K_2[Cr(ox)_2(acac)]$ and $K_2[Cr(ox)_2(gly)]$ (gly=glycinate anion) were prepared as described in the literature,[7,8)] and their purity was checked by ion-exchange chromatography and/or their absorption spectra. They were resolved by the methods applied to the corresponding Co(III) complexes.[9,10)] The $\Delta\varepsilon$ values of $-3.40\ mol^{-1}\,dm^3\,cm^{-1}$ (at 545 nm) and $+1.23\ mol^{-1}\,dm^3\,cm^{-1}$ (at 533 nm) were obtained for Δ-$[Cr(ox)_2(acac)]^{2-}$ and Λ-$[Cr(ox)_2(gly)]^{2-}$, respectively. Since these complexes were moderately optically labile, their recrystallization did not lead to improved optical purity, and hence no further attempt was made to obtain correct $\Delta\varepsilon$ values. The correct $\Delta\varepsilon$ value for the gly complex must be much higher than was obtained above. Absolute configurations were assigned to these complexes on the criterion that the Λ enantiomers have a positive main CD component at the first d-d transition region.[11)]

Detection of the Pfeiffer Effect. The degree and direction of the equilibrium shift attained in the racemic Cr(III) complexes were determined in exactly the same manner as in the previous studies.[4a,12)] Sample solutions were prepared in volumetric flasks (10 cm³) to which 3 cm³ of dioxane had been added, so that they contained the racemic Cr(III) complex in $8\ mmol\,dm^{-3}$ and the chiral environment substance in $30\ mmol\,dm^{-3}$. CD spectra of these solutions were recorded as quickly as possible after the environment substance was removed by passing them through a cation-exchange column.

Results and Dicussion

Figure 1 shows the CD spectra recorded for initially racemic complexes $[Cr(ox)_2(acac)]^{2-}$ and $[Cr(ox)_2(gly)]^{2-}$ after they had been mixed with Λ-$[Co(sep)]^{3+}$ in dioxane–water mixtures. These spectra are the same in pattern as those of the respective complexes resolved separately. Thus, it is evident that the Δ enantiomer is enriched for both complexes in the presence of Λ-$[Co(sep)]^{3+}$. If the $\Delta\varepsilon$ of $-3.40\ mol^{-1}\,dm^3\,cm^{-1}$ at 545 nm is adopted for the pure Δ-$[Cr(ox)_2(acac)]^{2-}$, the ee is estimated to be 10.9%, which is fairly high. A high ee is probably attained for the gly complex also, though a correct CD intensity for its pure enantiomer is not known. On the other hand, when Λ-$[Co(en)_3]^{3+}$ from which Λ-$[Co(sep)]^{3+}$ is derived is employed as an environment substance, the Δ enantiomer is similarly enriched for both complexes,[13)] but the ee's are very low; an ee of 0.4% is estimated for the acac complex.

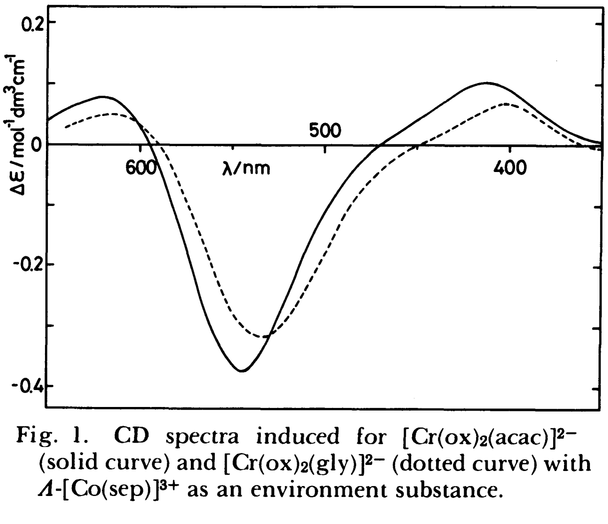

Fig. 1. CD spectra induced for $[Cr(ox)_2(acac)]^{2-}$ (solid curve) and $[Cr(ox)_2(gly)]^{2-}$ (dotted curve) with Λ-$[Co(sep)]^{3+}$ as an environment substance.

TABLE 1. ABSOLUTE CONFIGURATIONS OF ENANTIOMERS ENRICHED BY THE PFEIFFER EFFECT

Environment[a] Substance	Racemic Complex $[Cr(ox)_2(acac)]^{2-}$	$[Cr(ox)_2(gly)]^{2-}$
$[Co(sep)]^{3+}$	Δ	Δ
$[Co(en)_3]^{3+}$	Δ	Δ
$[Co(d\text{-}pn)_3]^{3+}$[b]	Λ	Λ
$[Co(phen)_3]^{3+}$	Λ	Λ

a) All have a Λ configuration. b) A mixture of *fac-lel*$_3$ and *mer-lel*$_3$ isomers.

Since the ee's attained with Λ-$[Co(d\text{-}pn)_3]^{3+}$ and Λ-$[Co(phen)_3]^{3+}$ were also low (at most 1.4%), only the direction of the equilibrium shift was determined. In Table 1 are listed absolute configurations of the enantiomers of the two Cr(III) complexes enriched by the Pfeiffer effect. Table 1 indicates that Λ-$[Co(en)_3]^{3+}$ and Λ-$[Co(sep)]^{3+}$ interact with the Δ enantiomer more favorably than with the Λ enantiomer for the two Cr(III) complexes. This is consistent with the earlier observation that the Δ enantiomers of $[Co(ox)_2(acac)]^{2-}$ and $[Co(ox)_2(gly)]^{2-}$ are eluted faster on usual ion-exchange chromatography with Λ-$[Co(en)_3]^{3+}$ or Λ-$[Co(sep)]^{3+}$ as an eluent.[14,15] On the other hand, the Λ enantiomers of the two Cr(III) complexes are favored by Λ-$[Co(d\text{-}pn)_3]^{3+}$ and Λ-$[Co(phen)_3]^{3+}$ (Table 1), suggesting that the mode of chiral discrimination is different at least between the former two environment substances and the latter two.

In our previous work,[14] it was proposed that both chiral $[Co(en)_3]^{3+}$ and $[Co(sep)]^{3+}$ ions discriminate between Λ and Δ enantiomers of a usual complex anion with the C_2 axis directed to the anion to form hydrogen bonds to the anion (C_2 access). If the Δ anion is favored by Λ-$[Co(en)_3]^{3+}$ or Λ-$[Co(sep)]^{3+}$ in the C_2 access, it is a reasonable observation that the Λ anion is favored by Λ-$[Co(d\text{-}pn)_3]^{3+}$ which "uses" the C_3 axis predominantly owing to the steric hindrance due to methyl groups.[16] The interaction mode of $[Co(phen)_3]^{3+}$ seems complicated,[17] since it has no hydrogen atom available for the interaction with the anion complex.[18]

Finally, it is noteworthy that the efficiency of chiral discrimination is surprisingly enhanced when the environment substance $[Co(en)_3]^{3+}$ is capped covalently with alkyl groups along its C_3 axis to form $[Co(sep)]^{3+}$. This may be partly attributed to the resulting conformational rigidity of the environment substance[19] and/or to a greater affinity of the anion complex for $[Co(sep)]^{3+}$ than for $[Co(en)_3]^{3+}$, as exemplified by their association constants with *d*-tartrate and bis(μ-*d*-tartrato)-diantimonate(III) anions in water.[6] However, it is more tempting to suppose that chiral $[Co(en)_3]^{3+}$ can also "use" the C_3 axis to favor the enantiomer opposite to that favored by it in the C_2 access, its discrimination efficiency being thereby extremely low. By contrast, since $[Co(sep)]^{3+}$ is forced to "use" the C_2 axis only, it serves not only as an effective environment substance in the Pfeiffer effect, but also as an effective eluent in the chromatographic resolution of several anion complexes.[20]

References

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13) It has been recently demonstrated that the Δ enantiomer is enriched for tris(2,6-pyridinedicarboxylato)terbium(III) in the presence of Λ-$[Cr(en)_3]^{3+}$ in dioxane–water mixtures; see, J. S. Madaras and H. G. Brittain, *Inorg. Chem.*, **19**, 3841 (1980); F. Yan, R. A. Copeland, and H. G. Brittain, *Inorg. Chem.*, **21**, 1180 (1982).

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16) In accord with this observation, Λ-$[Co(ox)_2(gly)]^{2-}$ is eluted faster on ion-exchange chromatography when the chiral eluent used is Λ-$[Co(d\text{-}chxn)_3]^{3+}$ (*d*-chxn=(1*S*,2*S*)-cyclohexanediamine) which "uses" the C_3 axis exclusively owing to the presence of cyclohexane rings; see Ref. 14.

17) Λ-$[Cr(ox)_3]^{3-}$ and Λ-$[Co(ox)_3]^{3-}$ are similarly enriched in the presence of Λ-$[Co(phen)_3]^{3+}$; see Ref. 4a.

18) A. Tatehata, K. Andoh, M. Fujita, and Y. Asaba, 33rd Symposium on Coordination Chemistry, Osaka, October, 1983, Abstr. No. 1PA13.

19) It is informative to note that all the racemic complexes for which the equilibrium shifts have been confirmed are with no exception composed of planar ligands such as ox^{2-}, gly^{-}, $acac^{-}$, phen, 2,2′-bipyridine, 8-hydroxy-5-quinolinesulfonate^{2-}, and 2,6-pyridinedicarboxylate^{2-}. The ligand rigidity might be a necessary condition for the development of the Pfeiffer effect.

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