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APPLICATION OF THE PFEIFFER EFFECT TO PARTIAL RESOLUTION OF TRIS(ACETYLACETONATO)COBALT(III)

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Partial resolution of neutral [Co(acac)$_3$] was performed by extracting into 1,2-dichloroethane the complex formed when racemic Li[Co(acac)$_3$] was mixed with Δ- or Λ-[Co(phen)$_3$]Cl$_3$ in water. This system is the first Pfeiffer-active system in which a dissymmetric metal complex serves as a chiral environment compound.

The Pfeiffer effect$^{1)}$ is a change in optical activity observed when a racemic mixture of a labile metal complex is added to a solution containing a chiral environment compound. This phenomenon is usually attributed to an enrichment of one of the enantiomers of the racemic complex. In fact, [Ni(phen)$_3$]$^{2+}$, [Co(phen)$_3$]$^{3+}$, [Co(ox)$_3$]$^{3-}$, [Cr(ox)$_3$]$^{3-}$, and related complexes (phen = 1,10-phenanthroline and ox = oxalate dianion) have been partially resolved by exploiting the Pfeiffer effect.$^{1-3)}$ However, since they are all ionic, they can be resolved via diastereomeric salt formation. On the other hand, this method is not applicable to the resolution of neutral metal complexes, and thus a variety of techniques has been devised, such as chromatography, solvent extraction, photochemical reaction,etc. Furthermore, no Pfeiffer-active system is known yet in which a dissymmetric metal complex serves as an environment compound. In this paper, we report our preliminary study on the application of the Pfeiffer effect to partial resolution of a neutral complex, [Co(acac)$_3$] (acac = acetylacetonate anion), wherein a dissymmetric environment compound is employed.

Experimental Racemic Li[Co(acac)$_3$] was prepared after a well-established method$^{4)}$ (ε = 26.7 at 490 nm in water). Δ- and Λ-[Co(phen)$_3$](ClO$_4$)$_3$ were prepared by a usual method$^{5)}$ and were converted to the chloride by treating with a Dowex 1X8 anion exchange resin in Cl$^-$ form. To an aqueous solution of Δ- or Λ-[Co(phen)$_3$]Cl$_3$ was added racemic Li[Co(acac)$_3$], and after the resulting yellow precipitate was filtered off, the green complex left in the filtrate was extracted into 1,2-dichloroethane, which was then washed twice with dilute HCl solutions to remove small amounts of yellow by-products and [Co(phen)$_3$]$^{3+}$. After the organic phase was separated and dehydrated with anhydrous Na$_2$SO$_4$, its absorption (AB) and circular dichroism (CD) spectra were recorded on a Shimadzu UV-200 and a Jasco J-40CS spectrometer, respectively. The AB spectrum was found to be almost identical with that of [Co(acac)$_3$] in 1,2-dichloroethane (ε = 129 at λ_{max}(595 nm)).

Results and Discussion Figure 1 shows the AB and CD spectra of the organic phase obtained when Λ-[Co(phen)$_3$]Cl$_3$ was used as a chiral environment compound.

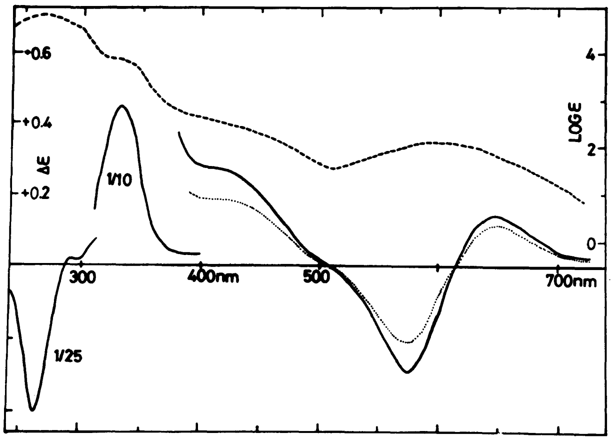

Fig.1. AB(--) and CD(—,...) spectra of partially resolved Δ-[Co(acac)$_3$].

TABLE 1

Λ-[Co(phen)$_3$]$^{3+}$	[Co(acac)$_3$]$^-$	$\Delta\varepsilon_{572nm}$ a)	% b)
5 ml c)	10 ml d)	-0.216	3.54
10 ml c)	5 ml d)	-0.275	4.50
15 ml c)	5 ml d)	-0.295	4.84

a) CD$_{max}$. b) Percentage resolution (Ref.7). c) 3.28x10^{-2}mole/l. d) 6.22x10^{-2}mole/l.

It is seen that optically-active [Co(acac)$_3$] is prepared in this Pfeiffer system, and that the enriched enantiomer has the absolute configuration of Δ.[6,7) When Δ-[Co(phen)$_3$]$^{3+}$ was employed, Λ-[Co(acac)$_3$] was enriched. These facts mean that the equilibrium between Δ- and Λ-[Co(acac)$_3$]$^-$ is certainly displaced under the influence of optically-active [Co(phen)$_3$]$^{3+}$, and that [Co(acac)$_3$]$^-$ is spontaneously oxidized to [Co(acac)$_3$], probably by giving one electron to [Co(phen)$_3$]$^{3+}$. All the data summarized in Table 1 indicate that optical purity of the resulting [Co(acac)$_3$] is enhanced as the amount of added [Co(phen)$_3$]$^{3+}$ is increased. However, low optical yield of the resulting complex suggests a lack of stereoselectivity in the electron-transfer process observed in this Pfeiffer system.8)

Δ- and Λ-[Ni(phen)$_3$]$^{2+}$ were examined as another dissymmetric environment compound. In this case, Λ- and Δ-enantiomers were enriched, respectively, after oxidation with H_2O_2 and extraction into 1,2-dichloroethane, but their CD spectra were slightly different at the d-d transition region from that reported in the literature.6,7) This may be due to a slight contamination of unknown by-products. On the other hand, when Δ- or Λ-[Co(en)$_3$]$^{3+}$ (en = ethylenediamine) was employed, a racemic complex was obtained.9)

The Pfeiffer system reported above is, we believe, only one example found so far in which a dissymmetric metal complex serves as a chiral environment compound.10)

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