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THE PFEIFFER EFFECT WITH A DISSYMMETRIC METAL COMPLEX AS AN ENVIRONMENT SUBSTANCE. II.[1] POSSIBILITY TO PREDICT THE ABSOLUTE CONFIGURATION OF METAL COMPLEXES

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The chiral equilibrium of $[Cr(ox)_3]^{3-}$ was found to be displaced in favor of its Δ-enantiomer when its racemate was mixed with the Λ-enantiomers of several complexes of the type cis-$[Co(en)_2(X)(Y)]^{n+}$ in dioxane-water mixtures. It was proposed that the Pfeiffer effect is useful to infer the absolute configuration of these Co(III) complexes.

When a chiral substance is mixed with a racemate of a labile metal complex in solution, new optical activity due to the complex is sometimes developed. This is known as the Pfeiffer effect[2] and is ascribed to an enrichment of one enantiomer of the complex under the influence of the chiral substance[3] (called an environment hereafter). A number of Pfeiffer-active systems have been reported[2] and the discriminating interaction in these systems has been discussed from both experimental[4,5] and theoretical[6] points of view. However, the chiral environments employed so far are all asymmetric organic compounds which have long been used as a resolving agent, e.g., d-cinchoninium ion and d-tartaric acid. In recent years, resolved dissymmetric metal complexes are often used successfully to resolve other metal complexes.[7] Consequently, these chiral complexes are expected to serve also as an environment in the Pfeiffer effect. Nevertheless, only two such systems are known to date.[1,3b] In this paper, it is reported that many chiral complexes of the type cis-$[Co(en)_2(X)(Y)]^{n+}$ serve well as an environment to $[Cr(ox)_3]^{3-}$ in dioxane-water mixtures.

All the metal complexes used were prepared and, if necessary, were resolved by well-known methods.[8] The Pfeiffer effect was detected in the same manner as before,[1] after the environment was removed with a cation-exchange resin. Absorption and CD spectra were recorded on a Shimadzu UV-200 and Jasco J-40CS spectrometer.

In Table 1 are summarized the experimental results obtained for the $[Cr(ox)_3]^{3-}$-Λ-$[Co(en)_2(gly)]^{2+}$ and $[Cr(ox)_3]^{3-}$-Λ-cis-$[Co(en)_2(NO_2)_2]^+$ systems. By comparing the CD intensities at 552 nm with that[9] of optically pure $[Cr(ox)_3]^{3-}$, the percentage resolution is estimated and listed in the last column of Table 1. It is seen that the percentage resolution is enhanced with the amount of the environment added. This tendency is usually observed in most of the Pfeiffer systems.[2] Also seen is the fact that divalent $[Co(en)_2(gly)]^{2+}$ is a more effective environment to $[Cr(ox)_3]^{3-}$ than monovalent cis-$[Co(en)_2(NO_2)_2]^+$. This suggests that electrostatic interaction plays an important role in the present Pfeiffer systems.

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TABLE 1. Pfeiffer Effect and Percentage Resolution Attained

Pfeiffer System	Volume Added[a)] Environment[b)]	Complex[c)]	Dioxane	$\Delta\varepsilon_{552nm}$	Resolution (%)
$[Cr(ox)_3]^{3-}$-Λ-$[Co(en)_2(gly)]^{2+}$	10 cm^3	5 cm^3	10 cm^3	-0.117	4.1
	7 cm^3	5 cm^3	10 cm^3	-0.101	3.6
$[Cr(ox)_3]^{3-}$-Λ-$[Co(en)_2(NO_2)_2]^+$	10 cm^3	5 cm^3	10 cm^3	-0.036	1.3
	7 cm^3	5 cm^3	10 cm^3	-0.030	1.1

a) Total volume = 25 cm^3. b) 0.06 M. c) 0.04 M.

TABLE 2. Absolute Configuration of the Enantiomer of $[Cr(ox)_3]^{3-}$ Enriched by the Pfeiffer Effect

Environment	Assigned[a)] by	Enriched[b)] Enantiomer
Λ-(+)-cis-$[Co(en)_2(NH_3)_2]^{3+}$	CD	ppt[c)]
Λ-(+)-cis-$[Co(en)_2(CH_3NH_2)_2]^{3+}$	CD	Δ
Λ-(+)-$[Co(en)_2(gly)]^{2+}$	CD	Δ
Λ-(+)-$[Co(en)_2(ox)]^+$	X-ray	-[d)]
Λ-(+)-cis-$[Co(en)_2(NO_2)_2]^+$	X-ray	Δ
Λ-(+)-cis-$[Co(en)_2(NO_2)(NCS)]^+$	CD	Δ
Λ-(+)-cis-$[Co(en)_2(NO_2)(N_3)]^+$	CD	Δ
Λ-(-)-cis-$[Co(en)_2(NCS)_2]^+$	CD	Δ
Λ-(-)-cis-$[Co(en)_2(N_3)_2]^+$	CD	Λ
Λ-(+)-cis-$[Co(tn)_2(NO_2)_2]^+$	CD	Δ
Λ-(+)-cis-α-$[Co(trien)(NO_2)_2]^+$	CD	Δ

a) Method by which the absolute configuration of the environment is assigned. b) Absolute configuration of enriched $[Cr(ox)_3]^{3-}$ (Ref.9). c) Precipitate formed. d) No Pfeiffer effect detected.

In Table 2 is listed the absolute configuration of $[Cr(ox)_3]^{3-}$ enriched by the Pfeiffer effect in which the Λ-enantiomers of cis-$[Co(en)_2(X)(Y)]^{n+}$ complexes are employed as a chiral environment. It is seen that the Δ-enantiomer is enriched by these chiral complexes except cis-$[Co(en)_2(N_3)_2]^+$. In other words, if it is assumed that the chiral equilibrium of $[Cr(ox)_3]^{3-}$ is always shifted toward its Δ-enantiomer in the presence of the Λ-enantiomers of these complexes, their absolute configuration is conversely predicted by the Pfeiffer effect. We suppose that the absolute configuration has been incorrectly assigned to cis-$[Co(en)_2(N_3)_2]^+$ from its CD spectrum.[8)] The same has been recently pointed out by Kindred and House,[10)] so that its X-ray analysis is now being undertaken in our laboratory.

Similar experiments are under way on other metal complexes including Cr(III) complexes to establish the Pfeiffer effect as a means of assigning the absolute configuration to dissymmetric metal complexes.

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