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THE PFEIFFER EFFECT, OUTER-SPHERE COMPLEXATION, AND THE ABSOLUTE CONFIGURATION OF DISSYMMETRIC COORDINATION COMPOUNDS

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Abstract — The Pfeiffer Effect is the change in optical rotation of a solution of one enantiomer an optically stable compound (called the "environment" substance) upon the addition of a racemic mixture of an optically labile complex compound. The nature of the Effect is described, along with evidence supporting the "equilibrium displacement" mechanism proposed for the Effect in tris bidentate complexes with carboxylic acid environment compounds. Further, the effect of Pfeiffer activity on the racemization and resolution of dissymmetric complexes is described, along with the application of the Pfeiffer Effect to the determination of absolute configuration of coordination compounds which are both optically active and optically labile. Still further, a proposal to describe the basic nature of the Effect at the molecular level is presented, which utilizes the concept of hydrogen bonding of the environment substance to pi-electron cloud systems of the ligands of the complex. With regard to dissymmetric, optically stable complexes, it has been shown that an interaction occurs between such complexes and environment substances when the latter are present in much higher concentrations than the former. A technique will be described which utilizes this phenomenon to predict the absolute configurations of dissymmetric, optically stable complexes, which is based upon a proposal of "outer-sphere" complexation through hydrogen bonding between the optically active environment substances and the ligands of the complexes.

INTRODUCTION

The Pfeiffer Effect (Ref. 3) is the change in rotation of an optically active solution (usually an optically inactive solvent containing one enantiomer of an optically active compound, called the "environment substance") upon addition of a racemic mixture of an optically labile coordination compound. There has been considerable work on this Effect (Refs. 4-10) and three different mechanisms have been proposed to explain the appearance of the Effect. In an excellent review, Schipper (Ref. 11) describes these proposals and discusses each in turn. At present the existing experimental evidence seems to favor the mechanism which proposes that a shift in the equilibrium between enantiomers of the complex occurs as a result of the presence of an optically active environment. However, Miyoshi and co-workers (Ref. 12) have published some information in support of a hydrophobic bonding mechanism (Ref. 10) in certain systems, as well as supporting evidence for the equilibrium shift mechanism (Ref. 13) in others.

The Effect is known in polar solvents such as water, dimethylformamide, and glacial acetic acid, and not in non-polar solvents such as benzene (Refs. 5, 6, 8). Further, the magnitude of the Effect is proportional to the concentrations of both the complex and the environment substance, making it possible to develop a series of equations for observed Pfeiffer rotation, specific Pfeiffer rotation, and molar Pfeiffer rotation which are analogous to those for observed optical rotation, specific rotation, and molar rotation, respectively (Refs. 5, 6, 8). They are:

Observed Pfeiffer Rotation: $P_{obs} = \alpha_{e+c} - \alpha_e$

Specific Pfeiffer Rotation: $[P]^t_\lambda = P_{obs}/(c)(e)(d)$

Molar Pfeiffer Rotation: $[P_M]^t_\lambda = P_{obs}/[c][e](d_m)$

where α_{e+c} is the observed rotation of the solution containing both the environment substance and the complex, α_e is the observed rotation of the solution containing only the environment substance, (c) is the complex concentration in g /ml, (e) is the environment substance concentration in g /ml, d is the path length in dm, [c] is the molar concentration of the environment substance, and (d_m) is the path length in meters, and [e] is the molar concentration of the environment substance. In this work the authors propose that when a racemic mixture of a given complex (e.g.D,L-$[Co(o\text{-phen})_3]^{2+}$, where o-phen = *ortho*-phenanthroline) is placed in a series of similar chiral environments (Ref. 14) (i.e. all of which have the "same" absolute configuration), the equilibrium between the enantiomers of the racemic complex will always shift in the same direction — in favor of the same enantiomer of the complex. This will produce an enrichment of that enantiomer, which is easily detectable polarimetrically. Therefore, a Pfeiffer Effect experiment was carried out with D,L-$[Co(o\text{-phen})_3]^{2+}$ with each of several carboxylic acids of known absolute configuration in order to test this proposal.

Further, the authors also propose that when racemic mixtures of a series of tris bidentate complexes are each placed in a solution containing an optically active environment substance of a given absolute configuration (e.g. $S(-)_D$ malic acid of $S(+)_D$ aspartic acid), the equilibrium between the enantiomers of the racemic complex will always shift in favor of an enantiomer of a given absolute configuration (e.g. Δ_{c3} $(-)_D$ $[Ni(o\text{-phen})_3]^{2+}$ or Δ_{c3} $(+)_D$ $[Fe(o\text{-phen})_3{}^{2+})$. This provides a relatively facile technique for the prediction of absolute configurations of chiral, optically labile tris bidentate complexes.

Still further, the authors propose that the phenomenon of "outer-sphere" complexation may be utilized to predict the absolute configurations of chiral, optically stable complexes (e.g. $[Co(en)_3]^{3+}$) which do not undergo the Pfeiffer Effect. In this instance, it is proposed that one enantiomer of a racemic mixture of a chiral, optically stable complex will interact more strongly with one enantiomer of a chiral compound (e.g. $S(-)_D$ malic acid) when this compound is present in a large excess relative to the concentration of the complex. It is proposed that the interaction occurs via hydrogen bonding of the chiral compound to the ligand atoms.

RESULTS AND DISCUSSION

Dwyer and co-workers (Ref. 4) and Kirschner and co-workers (Ref. 8) have proposed that there is an equilibrium between enantiomers of a racemic mixture of a dissymmetric complex in solution, and they have also proposed that it is possible for an environment substance (e.g. $S(-)_D$ malic acid) to cause the displacement of this equilibrium in favor of one of the enantiomers of the complex. An equation which can represent a typical equilibrium in a Pfeiffer Effect system is as follows:

$$\Lambda_{C3}(+)_D[Ni(o\text{-phen})_3)]^{2+} \rightleftarrows \Delta_{C3}\ (-)_D[Ni(o\text{-phen})_3]^{2+}$$

Several chiral carboxylic acids can be utilized as environment substances to displace the above equilibrium. Table 1 shows the results obtained with seven different carboxylic acids acting as environment substances on D,L-$[Co(o\text{-phen})_3{}^{2+}$. It should be noted that in each case the enantiomer of this complex which is enriched during the Pfeiffer Effect study is the negatively rotating one when the organic environment substance has an "S" absolute configuration (Ref. 14), and is the positive one when the organic environment substance has an "R" absolute configuration, which is supportive of the proposal given above. It should be noted, as expected, that there is no relationship between the sign of rotation of the environment substance and either its absolute configuration or the sign of rotation of the enantiomer of the complex enriched during the Pfeiffer Effect studies.

Therefore, the authors propose that the use of the Pfeiffer Effect to predict the absolute configurations of dissymmetric carboxylic acids is a relatively simple technique, no exceptions to which have yet been found. Work is continuing in order to determine whether the proposal can be extended to other types of environment substances, and the results will be reported in future communications. It should be emphasized that optically labile complexes (such as D,L-$[Co(o\text{-phen})_3]^{2+}$ and D,L-$[Ni(o\text{-phen})_3]^{2+}$) should be used for these studies. Rotational changes may be observed when optically stable complexes are used, but these are attributed to an "outer-sphere" interaction, which may not necessarily produce the same results as those obtained with the Pfeiffer Effect.

The pH dependence of the Pfeiffer Effect

During a study of the Pfeiffer Effect, it was decided to investigate the influence of the pH on the Pfeiffer Effect, and it was observed that, for the system involving the racemic nickel *ortho*-phenanthroline complex and levo-malic acid, the magnitude of the Pfeiffer Effect decreases markedly and the rate of appearance of the Effect increases markedly with increasing pH of the solution. The former was quite unexpected, because an increase in pH will result in the conversion of malic acid (a neutral species) to monohydrogen malate (or to malate) anion (negative ions), which might be expected to increase the interaction between complex (positive ions) and this environment compound. This, in turn, might be expected to enhance the magnitude of the Pfeiffer Effect (Ref. 8). However, it is now possible to explain the observation of the decrease in the magnitude of the Pfeiffer Effect with increasing

TABLE 1. The Pfeiffer Effect on D,L-[$Co(o\text{-phen})_3$] Cl_2 with various environment compounds*

Environment compound	$\alpha_e(°)$	$\alpha_{e+c}(°)$	$P\lambda$	$[P_M]^{24°}_D$	Absolute config. of environment	Sign of rotation of enriched enantiomer of complex
L-(+)-Alanine	+0.004	+0.002	-0.002	-25	S	LEVO
L-(+)-Aspartic acid	+0.028	-0.002	-0.030	-375	S	LEVO
L-(-)-Malic acid	-0.016	-0.186	-0.170	-2125	S	LEVO
L-(-)-Tartaric acid	-0.096	-0.423	-0.327	-4087	SS	LEVO
D-(+)-Malic acid	+0.011	+0.165	+0.154	+1925	R	DEXTRO
D-(-)-Mandelic acid	-0.915	-0.715	+0.200	+2500	R	DEXTRO
D-(+)-Tartaric acid	+0.098	+0.432	+0.334	+4165	RR	DEXTRO

* All rotations at the sodium D line at 24°C.

Concentration of environment compounds = 0.040 Molar = [e]

Concentration of complex = 0.020 Molar = [c]

Path length = 1 dm.; contact time = 1 hour

$[P_M]^{24°}_D = P\lambda/[c][e](d_m)$ where d_m = path length in meters.

pH on the basis of the molecular interaction between the environment substance and the complex, which is proposed to occur through hydrogen bonding between the environment substance and the π electron cloud of the ligand system of the complex (*vide infra*). Table 2 shows the change in the Pfeiffer Effect with increasing pH of the system.

The effect of absolute configuration of the environment substance on the equilibrium shift of complex enantiomers

Figure 1 shows the effect on the Pfeiffer circular dichroism (circular dichroism of a Pfeiffer Effect system) of D,L-[$Co(o\text{-phen})_3$]$^{2+}$ in the presence of three chiral environment substances. Initially it was not surprising that levo-malic acid and levo-tartaric acid resulted in the enrichment of the same enantiomer of the complex. However, the authors initially did not expect that dextro-cinchonine hydrochloride would produce an enrichment of the same enantiomer of the complex as do the malic and tartaric acids. They postulated, therefore, that the complex senses an "S" environment (absolute configuration) in the presence of each of the three environment substances, and the equilibrium shifts accordingly toward the Δc_3 enantiomer of the complex.

The authors undertook to do another Pfeiffer Effect experiment using $S(+)_D$ aspartic acid as the environment substance. This also produced an enrichment of the Δ_{c3} isomer of the complex, which led the authors to postulate that, in the presence of an environment composed of a chiral carboxylic acid of "S" absolute configuration, enrichment of the Δ_{c3} enantiomer of a tris bidentate, optically labile complex will occur. Therefore, this provides a mechanism for predicting absolute configurations of optically labile, tris-bidentate, dissymmetric complexes by the Pfeiffer Effect. Table 3 shows some examples of complexes with absolute configurations which have been predicted by the Pfeiffer Effect, and these predictions are in accord with X-ray structure determinations of the absolute configurations of these complexes.

The nature of the molecular interactions in the Pfeiffer Effect

In order for the Pfeiffer Effect to occur via the equilibrium displacement mechanism proposed for it, the complex and the environment substance must (a) attain close enough approach to each other to exert a steric influence on the equilibrium between the enantiomers of the complex, and (b) interact with each other with sufficient strength to inhibit the conversion of one enantiomer to the other. Further, it is proposed that this interaction occurs by hydrogen bonding between the hydroxyl groups of the chiral carboxylic acid and the π electron cloud systems (Refs. 15, 16) of the *ortho*-phenanthroline (Fig. 2). It should be noted that

TABLE 2. pH Dependence of the Pfeiffer Effect in the system D,L-[Ni(*o*-phen)$_3$] Cl$_2$ + 1 malic acid

pH	P^{a}_{obs}	$[P_M]_D$
1.0	0.134°	2680°
2.0	0.133	2660
2.4	0.135	2700
3.0	0.099	1980
4.0	0.041	820
5.0	0.019	380
6.0	0.016	320
7.0	0.017	340
8.0	0.004	80
9.0	0.006	120

[a][Ni(*o*-phen)$_3$]$^{2+}$	0.05 Molar
1-malic acid	0.05 Molar
Temperature	25° C.
Wavelength	589 nm.
Cell length	0.2 dm.

TABLE 3. Absolute configuration of metal complexes in Pfeiffer-active systems

Environment compound	Enriched complex enantiomer	Predicted absolute configuration	Observed absolute configuration
S$(-)_D$Malic acid	$(-)_D$[Ni(*o*-phen)$_3$]$^{2+}$	Δ_{c3}	Δ_{c3}
S$(-)_D$Malic acid	$(+)_D$[Fe(*o*-phen)$_3$]$^{2+}$	Δ_{c3}	Δ_{c3}
S$(-)_D$Malic acid	$(-)_D$[Co(*o*-phen)$_3$$^{2+}$	Δ_{c3}	*
S$(+)_D$Aspartic acid	$(-)_D$[Ni(*o*-phen)$_3$]$^{2+}$	Δ_{c3}	Δ_{c3}
S$(+)_D$Aspartic acid	$(-)_D$[Fe(*o*-phen)$_3$]$^{2+}$	Δ_{c3}	Δ_{c3}
S$(+)_D$Aspartic acid	$(-)_D$[Co(*o*-phen)$_3$]$^{2+}$	Δ_{c3}	*
RR-$(+)_D$Tartaric acid	$(+)_D$[Co(*o*-phen)$_3$]$^{2+}$	Δ_{c3}	*

o-phen = *ortho*-phenanthroline

*absolute configuration not yet determined

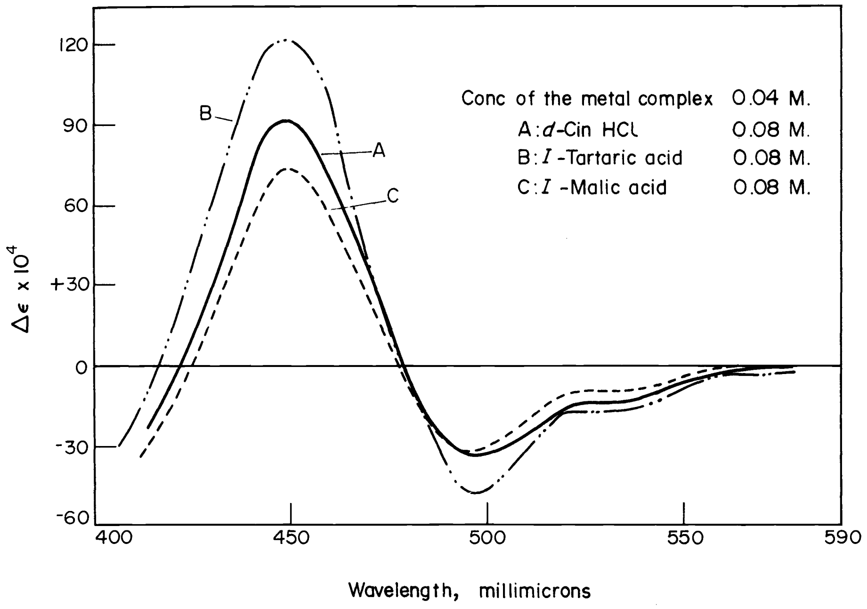

Fig. 1. CD spectra of $[Co(phen)_3]Cl_2$ in the presence of various optically active environment substances.

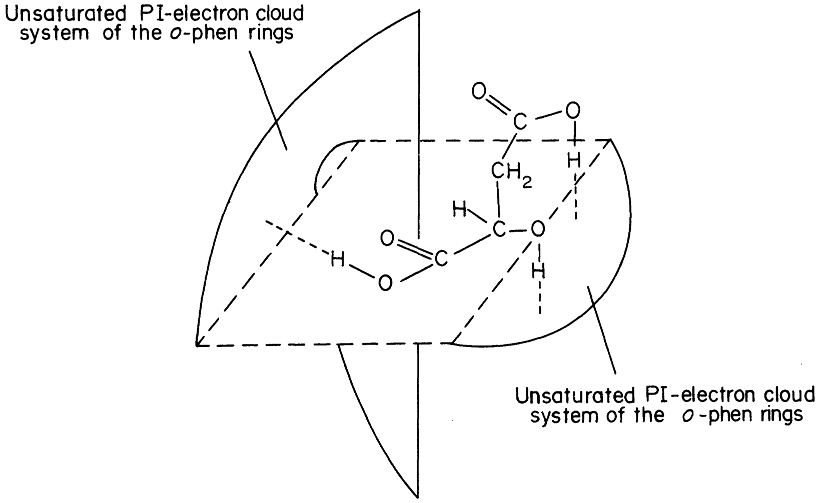

Fig. 2. Proposed mechanism of the Pfeiffer interaction. "Head-on" hydrogen bonding to π -electron cloud systems of the ligand rings $\Delta_{c3}(-)_D[Ni(o\text{-phen})_3]^{2+}$ with $S(-)_D$ malic acid.

this proposal explains two important phenomena which were unexpected when first observed: (a) the preferential inhibition of the conversion of the $(-)_D$ enantiomer of the complex to the $(+)_D$ isomer, thus permitting enrichment of the $(-)_D$ enantiomer (an explanation of the equilibrium shift mechanism), and, (b) diminution of the magnitude of the Pfeiffer Effect with increasing pH of the system. The preferential inhibition is proposed to occur because of the more facile hydrogen bond formation of the "S" enantiomer of malic acid to the Δ_{c3} enantiomer of the complex than to the Δ_{c3} enantiomer. Diminution of the magnitude of the Pfeiffer Effect with increasing pH is proposed to occur because loss of the carboxyl hydrogens with a pH rise would remove the protons necessary for hydrogen bond formation between the carboxyl oxygens and the $\underline{\pi}$-electron clouds of the ligands.

Outer-sphere complexation

In 1964 Bhatnagar and Kirschner (Ref. 17) described a method for utilizing optical rotatory dispersion (ORD) to predict the coordination and the degree of dentateness of optically active ligands to metal ions. In that paper they pointed out that the complex $[Co(NH_3)_6]_2(\underline{d}\text{-tartrate})_3$ exhibits a normal ORD curve without a Cotton Effect. In 1967 Norman and Mason (Ref. 18) showed that a Cotton Effect could be induced in the circular dichroism (CD) spectrum of this cobalt complex if diethyl-d-tartrate is present in a 400-fold excess.

In the present work a study has been undertaken of the interaction between $(+)_D$ tartaric acid (and $(-)_D$ malic acid) with both enantiomers of the $[Co(en)_3]^{3+}$ cation in an effort to determine whether differences in the degree of interaction between these enantiomers and the optically active organic compounds (in *ca.* 400-fold excess) could be utilized to predict the absolute configurations of the enantiomers of the complex. The authors found that the interaction between the Λ_{c3} enantiomer of the complex and the $RR(+)_D$ enantiomer of tartaric acid is significantly greater than the interaction between the Δ_{c3} complex and the same enantiomer of tartaric acid. Further, they found that the interaction between the Δ_{c3} enantiomer of the complex and $S(-)_D$ malic acid is significantly greater than the interaction between the Λ_{c3} enantiomer of the complex and the same enantiomer of malic acid. These interactions are easily detected by utilizing the CD spectra of the complexes in the presence of the optically active acids (Figs. 3 and 4).

Further, it was found that the observed CD spectrum of a mixture of the racemic complex and one enantiomer of the optically active acid is the exact, calculated resultant of the point-by-point difference between the CD spectrum of each enantiomer of the complex with the optically active acid, making it a relatively simple matter to determine which interaction is stronger (Figs. 5 and 6). Table 4 and Fig. 4 show clearly that the $\Lambda_{c3}(+)_D$ isomer of $[Co(en)_3]^{3+}$ interacts more strongly with the RR-tartaric acid than does the Δ_{c3} isomer of the complex, while the reverse is true if S-malic acid is used in place of RR-tartaric acid.

It is proposed, therefore, that for an optically stable, dissymmetric complex containing three bidentate ligands which can undergo hydrogen bonding (a form of outer-sphere complexation) to optically active organic acids, the enantiomer of the complex which interacts more strongly (as evidenced by the CD spectra) with the acid enantiomer of "S" absolute configuration is the Δ_{c3} isomer, and that which interacts more strongly with the acid enantiomer of "R" absolute configuration is the Λ_{c3} isomer. Table 5 gives a summary of the prediction of absolute configurations utilizing outer-sphere complexation techniques and circular dichroism measurements.

Nature of the interactions occuring during outer-sphere complexation

It is proposed that outer-sphere complexation occurs between an enantiomer of an optically stable complex (e.g. $[Co(en)_3]^{3+}$) and an enantiomer of an optically active organic acid (e.g. d-tartaric acid) which is present in a relatively high concentration, via hydrogen bonding between the organic acid's oxygens and the nitrogens of the ligands of the complex through the hydrogens on these nitrogens (Fig. 4A). This hydrogen bonding allows for a significant sterochemical interaction between the organic acids and the complex, although the interaction is not so strong as to influence the visible absorption spectrum of the complex. Further, the circular dichroism technique is sensitive enough to detect the fact that there is a stronger stereochemical interaction between one enantiomer of an optically stable complex and a given enantiomer of an organic acid than with the other enantiomer of the complex and that acid. Thus the technique can be utilized for the prediction of absolute configuration of optically stable complexes using organic compounds (when hydrogen bonding is possible). Such hydrogen bonding would not be expected to occur between the complex and malate or tartrate if the ligand were N,N,N',N' -tetraethylethylenediamine or some other ligand to which hydrogen bonding would not be possible. Experiments are under way to test this prediction. In such cases, outer-sphere complexation of the type described would not be expected to occur.

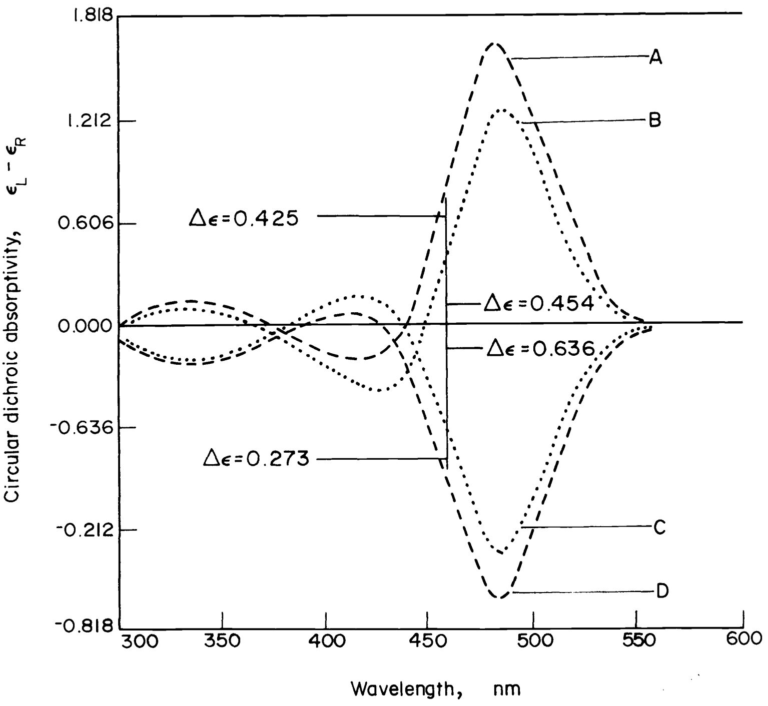

Fig. 3. The interaction of d̲-tartaric acid with Δ_{c3} and Δ_{c3} [Co(en)$_3$]I$_3$.

Circular dichroism spectra of:

A: $(+)_D$[Co(en)$_3$]I$_3$ in water solution.
B: $(+)_D$[Co(en)$_3$]I$_3$ in water solution (2M in d̲-tartaric acid).
C: $(-)_D$[Co(en)$_3$]I$_3$ in water solution (2M in d̲-tartaric acid).
D: $(-)_D$[Co(en)$_3$]I$_3$ in water solution.

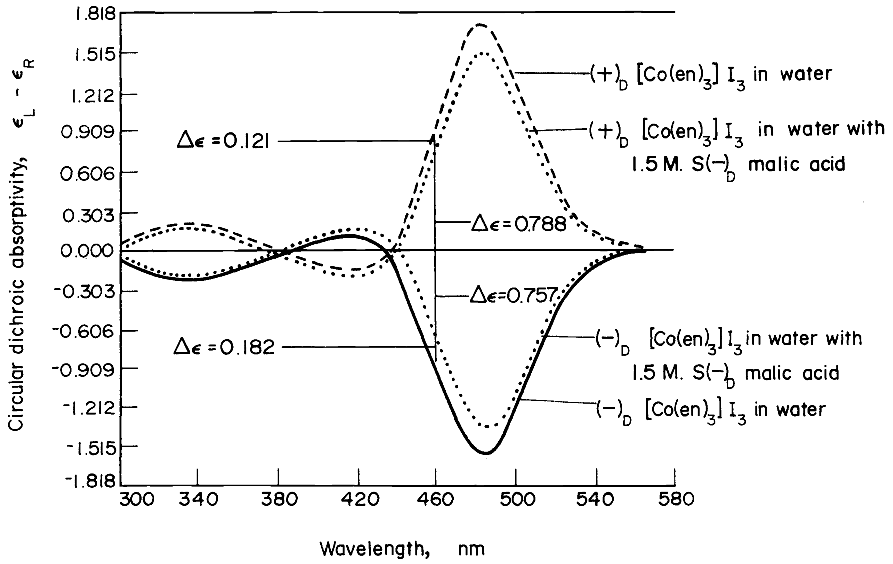

Fig. 4. The interaction of S$(-)_D$ malic acid with Δ_{c3} and Λ_{c3} [Co(en)$_3$]I$_3$.

TABLE 4. Outer-sphere complexation of optically active compounds to dissymmetric complexes

Compound	Optically active compound	λ	Δε complex alone	Δε Complex + compound	Δε difference
$\Lambda_{c3}(+)_D[Co(en)_3]^{3+}$	$R(+)_D$ - tartaric acid	460 nm	0.879	0.454	0.425
$\Delta_{c3}(-)_D[Co(en)_3]^{3+}$	$R(+)_D$ - tartaric acid	460 nm	0.909	0.636	0.273
$\Lambda_{c3}(+)_D[Co(en)_3]^{3+}$	$S(-)_D$-	460 nm	0.909	0.788	0.121
$\Delta_{c3}(-)_D[Co(en)_3]^{3+}$	$S(-)_D$- malic acid	460 nm	0.939	0.757	0.182

TABLE 5. Prediction of the absolute configurations of complexes by outer-sphere complexation

Environment substance	Enantiomer undergoing stronger outer-sphere interaction	Predicted absolute configuration	Found absolute configuration
$R(+)_D$ tartaric acid	$(+)_D[Co(en)_3]^{3+}$	Λ_{c3}	Λ_{c3}
$S(-)_D$ malic acid	$(-)_D[Co(en)_3]^{3+}$	Δ_{c3}	Δ_{c3}

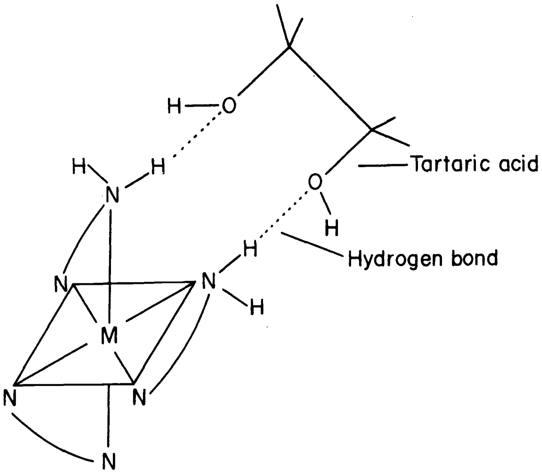

Fig. 4A. Proposed hydrogen bonding (outer-sphere complexation) between $[Co(en)_3]^{3+}$ and tartaric acid.

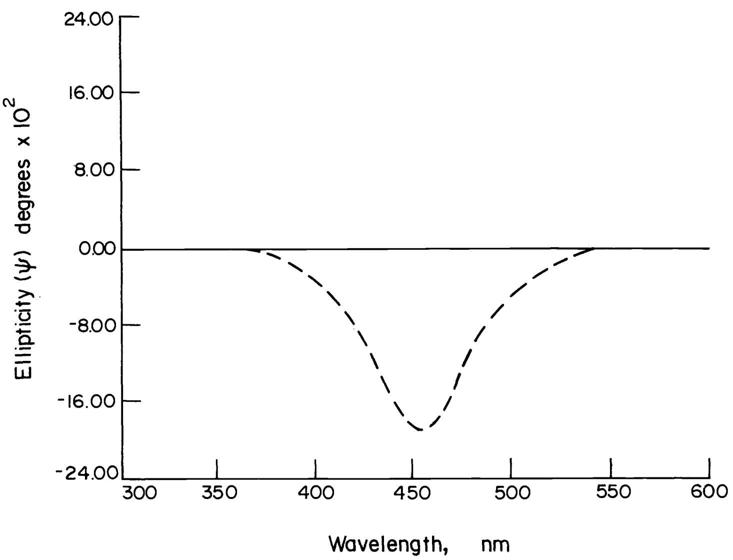

Fig. 5. Plotted resultant circular dichroism of $(-)_D[Co(en)_3]^{3+}$ and $(+)_D[Co(en)_3]^{3+}$. The experimental circular dichroism spectra of which were taken separately in the presence of a 400-fold excess of d-tartaric acid.

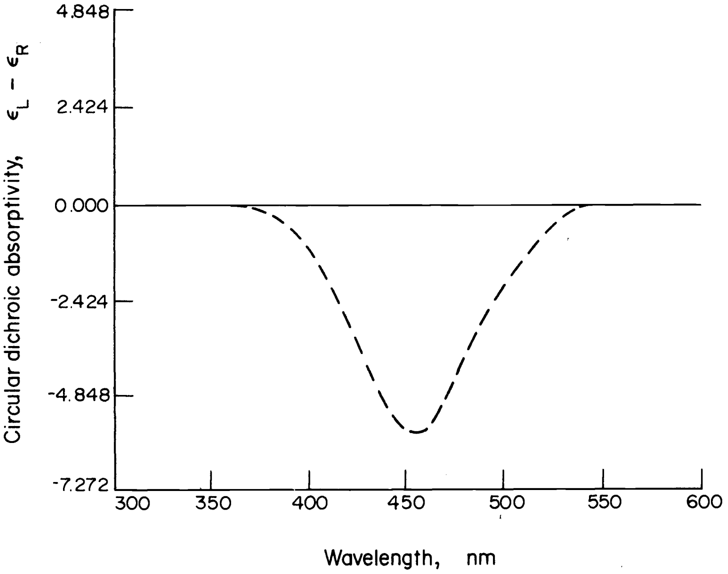

Fig. 6. Circular dichroise of D,L-$[Co(en)_3]I_3$ in the presence of a 400-fold excess of d-tartaric acid.

EXPERIMENTAL

The designations "R" and "S" refer to absolute configurations of organic compounds using the system developed by Cahn, Ingold, and Prelog (Refs. 19, 20). The absolute configurations of the organic compounds themselves are those reported in the literature (Refs. 21-24). These organic compounds were purchased in the purest available forms, and their rotations were checked against literature values. The complex D,L-[Co(*o*-phen)$_3$]$Cl_2 \cdot 6H_2O$ was prepared by dissolving 0.004 mole of $CoCl_2 \cdot 6H_2O$ in 15 ml of absolute methanol and adding a solution of 0.012 mole of 1, 10-phenanthroline dissolved in 10 ml of absolute methanol. The resulting mixture is placed under continuous vacuum until most of the methanol has evaporated (approximately five hours) and the crystals which form are filtered and air-dried.

The Pfeiffer Effect studies were carried out in aqueous solutions in which the concentrations of the complex were 0.02 molar and the concentrations of the organic environment substances were 0.04 molar. The contact time before polarimetric determination was 1 hour at room temperature (24° C) and the polarimeter cells were 1 dm. used at a wavelength of 589 nm. in a Perkin-Elmer 141 Photoelectric Polarimeter. The CD spectra were taken on a Cary-60 Spectropolarimeter with a CD attachment.

The observed Pfeiffer Rotation (P) is the difference between the observed rotation of the environment substance alone and the observed rotation of the solution containing both the environment substance and the complex. The sign of the Pfeiffer Rotation (P) is positive if the solution containing both the environment substances and the complex is more positive than that of the environment substance alone, and it is negative for the reverse case.

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