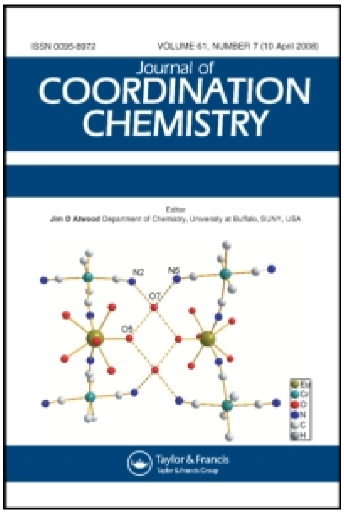

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FURTHER EVIDENCE ON THE ORIGINS OF THE PFEIFFER EFFECT USING CIRCULAR DICHROISM

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FURTHER EVIDENCE ON THE ORIGINS OF THE PFEIFFER EFFECT USING CIRCULAR DICHROISM

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The origins of the Pfeiffer Effect are characterized as zero and first order asymmetric transformations. Direct spectroscopic evidence using circular dichroism is presented for both types of transformations. Based on non-empirical criteria, the circular dichroism spectra obtained from the first order assymmetric transformations are used to characterize the absolute configuration of the enantiomer present in greater concentration.

INTRODUCTION

The apparent increased or decreased solution phase rotational strength of an optically active configurationally stable environment compound in the presence of a racemic enantiomeric complex ion is regarded as the Pfeiffer Effect. This effect, so named by Brasted and Dwyer in 1954,[2] has been subject to recurrent investigations since its disclosure in 1931 by Pfeiffer and Quehl.[3] Summaries of significant progress bearing on the origins and effects of variable parameters (e.g. environment compound, metal ion, ligand, concentration, time, *p*H, solvent medium, etc.) have been recently reported.[4,5,6]

Recent applications of the Pfeiffer Effect in predicting configurations of environment compounds[7] and facililtating photoresolution of complex ions[8] are based on definitive progress in the elucidation of the origins of the Pfeiffer Effect.

Origins of the Pfeiffer Effect

The first example of kinetic lability between enantiomers of a complex ion was reported by Werner in 1912.[9] Pfeiffer and Nakatsuka proposed this precedented behaviour as a plausible mechanism with which to explain the Pfeiffer Effect.[10] This phenomenon of equilibrium displacement of optically labile racemic species in the presence of an exogenous asymmetric environment was termed a "first order asymmetric transformation" by Kuhn,[11] and the driving force for this equilibrium displacement was termed "configurational activity" (activity in the thermodynamic sense) by Dwyer *et al.*[12] Previous work on Pfeiffer active systems by Kirschner and Ahmad lends conclusive support to the "first order asymmetric transformation" phenomenon.[5,13,14] A portion of the work presented herein is not only a further confirmation of the equilibrium displacement hypothesis, but is the first report of a Pfeiffer active system that specifies the absolute configuration of the enantiomeric excess by non-empirical criteria.

Contrary to Pfeiffer's original assumption, it was first suggested and has been subsequently verified by Brasted and co-workers that outer sphere interactions occur between complex ions and the environment species.[4,15,16] These outer sphere associations, regarded as the basic molecular interaction that produces the Pfeiffer Effect, are also presumed operative in producing previously reported Pfeiffer Effects that are not characteristic of a simple equilibrium displacement mechanism.[4,17,18]

This corollary type of Pfeiffer Effect shall be regarded as a "zero order asymmetric transformation". This extension of asymmetric transformation classes is formulated to encompass two similar but distinguishable situations: (i) a rotational strength modulation of existing optically active transitions due to diastereoisomeric associations, to be referred to as an asymmetric modulation, (ii) the induction of rotational strength in pre-existing but previously non-optically active transitions, referred to as asymmetric inductions.[19]

In Pfeiffer types of systems, the manifestations of "zero order asymmetric transformations" will be critically dependent on the dissymmetric discrimination of the environment compound relative to each enantiomorph, the inherent lack of lability of the racemate and the character and spectral location of electronic transitions within the system.

Asymmetric induction in symmetric complex ions has been reported by several investigators.[19-23] Kan and Brewer have reported an apparent asymmetric modulation of the environment compound in a Pfeiffer Effect system.[17] A portion of the work presented herein is the first disclosure of a zero order asymmetric transformation involving an asymmetric modulation of existing optically active coupled chromophores of the complex ion ligand system.

In this work circular dichroism spectra obtained in the region of $\pi \rightarrow \pi^*$ ligand transitions of racemic transition metal complex ions in the presence of selected environment compounds formed the bases for evaluating the type of asymmetric transformation involved. The environment compounds employed were non-circularly dichroic in the spectral regions examined.

EXPERIMENTAL

The circular dichroism spectra were obtained on a Cary 60 recording photoelectric spectropolarimeter employing a circular dichroism accessory. They are reported as a function of degrees ellipticity, θ, where $(\theta/lc) = 33.05\ (\epsilon_L - \epsilon_R)$. A positive θ corresponds to $\epsilon_L > \epsilon_R$; l = path length in cm and c = molar concentration.

The precision of measurement of circular dichroism bands in the region of ligand transitions was limited due to the inherently small rotational strength of Pfeiffer-active systems and the intrinsically high optical density of the system in the spectral regions examined. The high noise to signal ratio in the regions of high optical density could be accommodated only by utilizing dilute solutions and a short path length, $l = 0.0101$ cm. All scans were obtained using minimum scan rate and maximum pen damping. Instrumental specifications indicate an intrinsic uncertainty of 0.5 millidegree/θ_{obs}. (millidegree). Average pen position on the recorder could be estimated to the nearest 0.2 millidegree θ. For each spectrum reported, the inner interval of the error bars represents the average error obtained in several experiments. The outer interval represents two thirds of the maximum pen noise and can be interpreted as a ninety five percent confidence level interval. In each experiment the experimental trace was rescanned several times.

All studies were done in aqueous systems utilizing alkaline permanganate distilled water to insure no bio-organic residues. All systems were maintained at 27°C, the ambient operating temperature of the instrument. Stock solutions of the complexes and environment compounds were prepared by direct weighing of reagent grade materials into volumetric flasks. The complexes formed *in situ.* Pfeiffer systems were prepared by appropriate aliquoting, mixing and dilution of stock solutions.

RESULTS AND DISCUSSION

The racemic complexes employed in this study, e.g. $[M(o\text{-phen})_3]^{n+}$ and $[M(bipy)_3]^{n+}$ where o-phen = 1,10-phenanthroline, bipy = 2,2′-bipyridine and M = Cd^{2+} or Ni^{2+}, have been components of previously studied Pfeiffer-active systems.[3,5,13-16,24-27] L-(+)-glutamic acid is a new addition to the list of asymmetric compounds that have been shown to effect zero or first order asymmetric transformations.

Since it was previously established, by Drude equation analysis, that Pfeiffer activity originates from the ligand transitions for complexes of the above type,[4,16] the work presented here employed circular dichroism analysis of the wavelength region coincident with these ligand electronic transitions. Invariably, isotropic spectra of $[M(o\text{-phen})_3]^{n+}$ and $[M(bipy)_3]^{n+}$ complexes show, respectively, absorption maxima in the 255 nm to 285 nm and 285 nm to 315 nm regions.[28,29,32-36,40-42,45,46,50,51] For these complexes, which have D_3 symmetry, it is well known that the $\pi \rightarrow \pi^*$ ligand electronic transitions polarized parallel to the chelating nitrogens couple to yield two electronic transitions, $E \leftarrow A_1$ and $A_2 \leftarrow A_1$, each of which is a fully allowed electric and magnetic dipole transition. Considerations of dipole-dipole interactions, inter ligand bonding and metal ion-ligand π-bonding place the A_2 component at higher energy than the E component.[34,35,48] Theoretically these transitions have large, equal but opposite, rotational strengths.[28-44]. Experimentally, these transitions have somewhat diminished rotational strengths due to their opposing rotational strengths and close spectral proximity.[28–44] A survey of the reported circular dichroism spectra for resolved complexes of this type shows that these particular electronic transitions still have the most intense rotational strength of any electronic transition within the complex.[28-48] Although $[Cd(o\text{-}phen)_3]^{2+}$ complexes have never been resolved, the circular dichroism spectrum of the racemic complex in the presence of potassium antimonyl d-tartrate (Figure 1) is completely analogous in form and spectral location to the major bands in the circular dichroism spectra observed for resolved tris 1,10-phenanthroline complexes where the metal ion is Cr^{3+} [34,45], Ni^{2+} [34,45], Co^{3+} [32,34,45], Fe^{2+} [29,34,35], Ru^{2+} [28,34,35,40] and Os^{2+} [33-35]. Thus, the spectrum obtained is entirely consistent with an equilibrium displacement mechanism.

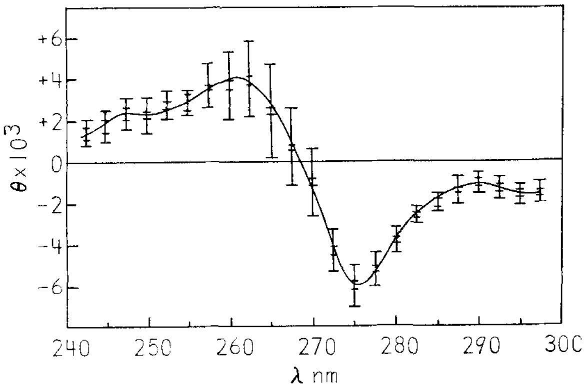

FIGURE 1 Circular dichroism spectrum of aqueous 2.5×10^{-3}M d,l-$[Cd(o\text{-}phen)_3]SO_4$ with 5.0×10^{-3}M potassium antimonyl d-tartrate.

Invoking the proposed IUPAC notation,[52] the absolute configuration of the enantiomeric excess is determined to be Δ as based on a non-empirical method to assign absolute configuration of tris complexes from the circular dichroism spectrum, first suggested by Mason and Ballard,[28] developed by Mason and co-workers,[28-37] Bosnich,[38-40] Hanazaki, Nagakura,[41,42] Ito *et al.*,[43,44] Saito,[54] and recently critically reviewed by Mason,[47] Gillard[48] and Hawkins *et al.*[45,46,49] Succinctly described, if, for a resolved complex ion, the circular dichroism spectrum associated with the $\pi \rightarrow \pi^*$ electronic transitions polarized parallel to the coordinating atoms exhibits a positive ($\epsilon_L > \epsilon_R$) and negative ($\epsilon_L < \epsilon_R$) band at lower and higher frequencies respectively, the absolute configuration is Λ; if the sign relationship is inverted, the absolute configuration is Δ.

The circular dichroism spectra of resolved d- and l-$[Ni(bipy)_3]^{2+}$ complexes have been previously reported.[34,45] The spectrum of racemic d,l-$[Ni(bipy)_3]^{2+}$ in the presence of potassium antimonyl d-tartrate obtained in the present work (Figure 2) is interpreted to be consistent with an equilibrium displacement mechanism also. Utilizing the non-empirical configuration determination method of Mason *et al.*, the absolute configuration of the enantiomeric excess is designated as Δ. Thus, utilizing the same environment resolved compound and different but similar racemic complexes, the absolute configuration of the enantiomeric excess was the same in both systems.

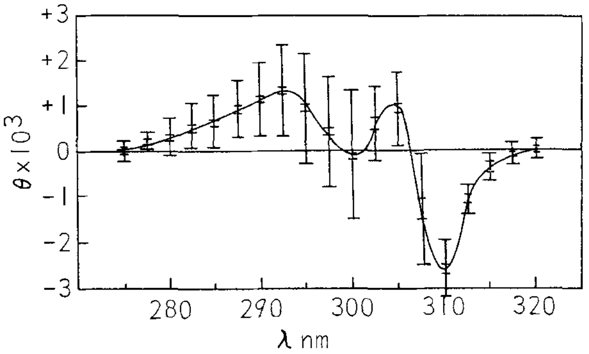

FIGURE 2 Circular dichroism spectrum of aqueous 5.0×10^{-3}M d,l-$[Ni(bipy)_3]SO_4$ with 1.0×10^{-2}M potassium antimonyl d-tartrate.

In Figure 2, the unusual cancellation observed in the 300 nm region, in contrast to spectra obtained for resolved complexes[34,35], is presumed related to non-equivalent conformational disposition of chelated bipyridine residues, a manifestation of the outer sphere association of the environment species.

Measurement of the circular dichroism spectrum of racemic d,l-$[Ni(o\text{-}phen)_3]^{2+}$ in the presence of L-(+)-glutamic acid (Figure 3) was initiated within three minutes after addition of the environment compound. The elapsed scan time did not exceed twenty five minutes. Since the reported racemization rate of the complex has a half life of fourteen hours[5] and is almost pH independent[53], no appreciable equilibrium displacement can have occurred during the course of the spectral examination under the conditions employed. The spectral peaks obtained in the present work, at 265 nm and

272 nm, are analogous in proximity but not characteristic of the opposing sign behaviour to those observed and reported for resolved $[Ni(o\text{-}phen)_3]^{2+}$ complexes.[34,45] This observation strongly suggests an asymmetric modulation mechanism.

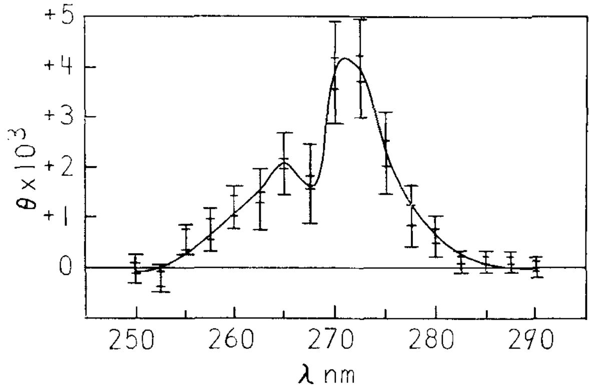

FIGURE 3 Circular dichroism spectrum of aqueous $2.5 \times 10^{-3}M$ d,l-$[Ni(o\text{-}phen)_3]SO_4$ with $2.0 \times 10^{-2}M$ L-(+)-glutamic acid; pH = 7.5 (adjusted with dilute $NH_3 \cdot H_2O$).

SUMMARY AND CONCLUSION

The origin of the Pfeiffer Effect appears to be multi-faceted. The mechanisms are embodied in the zero and first order asymmetric transformation concepts, these transformations resulting from diastereoisomeric interactions of the environment species with the racemic transition metal complexes.

Two more examples of first order asymmetric transformations were established via the observed circular dichroism spectral peaks associated with the $\pi \rightarrow \pi^*$ ligand electronic transitions of d,l-$[Cd(o\text{-}phen)_3]^{2+}$ and d,l-$[Ni(bipy)_3]^{2+}$ in the presence of potassium antimonyl d-tartrate. The absolute configurations of the enantiomeric excess were the same, and designated as Δ. It has also been shown recently by Gillard[48,51] that $[M(o\text{-}phen)_3]^{n+}$ and $[M(bipy)_3]^{n+}$ complexes of the same absolute configuration have comparable circular dichroism spectra in the $\pi \rightarrow \pi^*$ region, corresponding to the observations reported herein.

The first example of an asymmetric modulation (a class of zero order asymmetric transformations) is reported for the d,l-$[Ni(o\text{-}phen)_3]^{2+}$ plus L-(+)-glumatic acid system. This asymmetric modulation of optically active ligand $\pi \rightarrow \pi^*$ transitions is thought to correspond to the previously observed and reported instantaneous Pfeiffer Effect for d,l-$[Ni(o\text{-}phen)_3]^{2+}$ systems.[6,10,25] This instantaneous effect is a prelude to a subsequent and well documented time-dependent Pfeiffer Effect that parallels the racemization rate of a resolved enantiomer.[6]

The data reported herein for the first order asymmetric transformations, for reasons elaborated upon earlier, were insufficiently precise to ascertain any extent to which an asymmetric modulation might be superimposed on the equilibrium displacement. Further work is in progress to ascertain the relative and absolute contributions of zero versus first order asymmetric transformations to the Pfeiffer Effect in d,l-$[Ni(o\text{-}phen)_3]^{2+}$ systems.

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