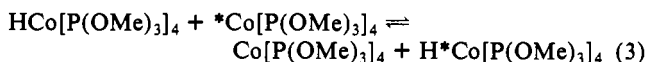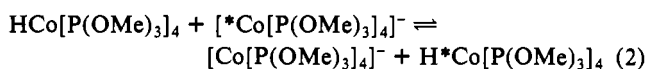erate transfers of other small particles in this system, e.g. protons (eq 2) and hydrogen atoms (eq 3). It will be interesting to see what parallels, if any, exist between these formally analogous reactions.

$$HCo[P(OMe)_3]_4 + [^*Co[P(OMe)_3]_4]^- \rightleftharpoons$$
$$[Co[P(OMe)_3]_4]^- + H^*Co[P(OMe)_3]_4 \quad (2)$$

$$HCo[P(OMe)_3]_4 + {}^*Co[P(OMe)_3]_4 \rightleftharpoons$$
$$Co[P(OMe)_3]_4 + H^*Co[P(OMe)_3]_4 \quad (3)$$

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Articles

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Quantitative Aspects of Pfeiffer Effect Optical Activity in Aqueous Dysprosium(III) Complexes with 2,6-Pyridinedicarboxylic Acid

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Under the assumptions that the addition of a chiral "environment compound" simply shifts the racemic equilibrium of labile enantiomers and does not preferentially quench enantiomeric excited states, it is demonstrated that the measurement of the circularly polarized luminescence (CPL) from racemic solutions using circularly polarized excitation, combined with the circular dichroism (CD) and CPL of the solution after the addition of the chiral adduct, can yield quantitative information concerning the equilibrium shift and the optical activity of the individual enantiomers. This is demonstrated for the equilibrium between Δ and Λ isomers of Dy(2,6-pyridinedicarboxylate = DPA)$_3$$^{3-}$ where the added chiral species is L-histidine. For this system we report the resultant enantiomeric excess and the dissymmetry ratios for selected electronic transitions of pure enantiomers, even though they cannot be resolved chemically.

Introduction

The "Pfeiffer effect" has as its origin the work of Pfeiffer and others on the enhancement in optical activity in solutions composed of a chiral "environment compound" and a racemic but kinetically labile metal complex.[1-3] This original work involved primarily transition-metal tris complexes with the bidentate ligands 2,2′-bipyridine and 1,10-phenanthroline, and the chiral environment compound was usually an alkaloid. In these early studies, and in most reports until very recently, the enhancement of optical activity was monitored through the measurement of optical rotation. It was later realized that the observed phenomenon was caused by a shift in the racemic equilibrium constant of the metal complex caused by the chiral environment compound, as evidenced by the appearance of circular dichroism (CD) in the spectral region corresponding to d–d absorptions.[4] The CD spectra obtained were in some cases identical with those of previously resolved enantiomers.[5]

In recent years, Brittain has demonstrated that, in racemic lanthanide tris complexes with 2,6-pyridinedicarboxylate (DPA), optical activity can be enhanced as measured by the circular polarization in the luminescence (CPL) from f–f emissive transitions.[6-11] This effect has been observed for a wide variety of

added chiral agents. Because these lanthanide complexes are generally more labile than the transition-metal complexes used in the original demonstration of Pfeiffer effect optical activity and because the coordination numbers of the lanthanide complexes are so variable, it is not clear that all of the reports of induced optical activity in these lanthanide complexes can be classified as simply a racemic equilibrium disturbance. In addition, because CPL is inherently an *excited-state* effect, one cannot rule out the possibility that the added chiral species is disturbing the emitting-state population instead of that of the ground state. At the present time, there exists no uniformly accepted classification as to what exactly constitutes a "Pfeiffer effect" for lanthanides.[12]

Recently, we have reported CPL spectra from racemic Ln-(DPA)$_3$$^{3-}$ solutions in which an optically active excited-state population was generated by employing a circularly polarized excitation beam.[13,14] This experiment is possible only if the emitting-state population is inert to racemization during the lifetime of the excited species. The fact that we observe CPL from the racemate without any added species allows us the opportunity to compare CPL spectra before and after the addition of chiral environment compounds. In those cases where the spectra are very similar, one can conclude that a simple equilibrium shift has

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occurred. If the spectra are very different, then, clearly, the added chiral compound has significantly perturbed the coordination geometry of the lanthanide ion.

In this work, we report that it is also possible to measure the CD spectra corresponding to certain f–f transitions in solutions of $Dy(DPA)_3^{3-}$ to which an optically active species has been added. In addition, we illustrate that, for these systems, the availabilities of CPL and CD spectra for the Pfeiffer systems and the CPL spectra for the racemic solutions yield not only quantitative information concerning the equilibrium shift but also values for absorption and emission dissymmetry ratios for "pure" enantiomers, even though they cannot be resolved. This is illustrated for the complex $Dy(DPA)_3^{3-}$ with L-histidine as the chiral environment compound.

Theory

The differential circularly polarized emission intensity at wavelength λ, $\Delta I(\lambda)$, is given by[15]

$$\Delta I(\lambda) \equiv I_{L(eft)} - I_{R(ight)} = N_n K(\lambda^3) (2R(g \leftarrow n)) f_{CPL}(\lambda) \quad (1)$$

where the g and n refer respectively to the ground and excited (emitting) states, N_n denotes the population of the emitting state, $f_{CPL}(\lambda)$ is a normalized line shape function, and $R(g \leftarrow n)$ is the rotatory strength for the emissive transition. In CPL spectroscopy one is most concerned with the so-called emission dissymmetry factor, g_{em}, which is defined as

$$g_{em} = \Delta I/(I/2) \quad (2)$$

where I is the total emission intensity.

In this study we are concerned with a solution containing N^Δ_n Δ isomers and N^Λ_n Λ isomers. For this mixture we rewrite eq 1 as

$$\Delta I = 2K(\lambda^3) [N^\Lambda_n R^\Lambda(g \leftarrow n) + N^\Delta_n R^\Delta(g \leftarrow n)] f_{CPL}(\lambda) \quad (3)$$

$$= 2K(\lambda^3) R^\Lambda(g \leftarrow n) [N^\Lambda_n - N^\Delta_n] f_{CPL}(\lambda) \quad (4)$$

where for the enantiomers Δ and Λ we have invoked the identity

$$R^\Lambda(g \leftarrow n) = -R^\Delta(g \leftarrow n) \quad (5)$$

The *total* emission intensity, I, for the mixture can be expressed similarly:

$$I = K(\lambda^3) D^\Lambda(g \leftarrow n) [N^\Lambda_n + N^\Delta_n] f_{TL}(\lambda) \quad (6)$$

where $D(g \leftarrow n)$ is the dipole strength and is the same for both isomers.

The *measured* dissymmetry ratio can be written as

$$g_{em} = [4R^\Lambda(g \leftarrow n) f_{CPL}(\lambda)]/[D^\Lambda(g \leftarrow n) f_{TL}(\lambda)]\eta_n \quad (7)$$

where η_n is the *enantiomeric excess* in the emitting state n:

$$\eta_n = [N^\Lambda_n - N^\Delta_n]/[N^\Lambda_n + N^\Delta_n] \quad (8)$$

Equation 7 may be expressed in terms of the emission dissymmetry ratio for the pure Λ enantiomer at frequency λ:

$$g_{em}(\lambda) = g^\Lambda_{em}(\lambda) \eta_n \quad (9)$$

A completely analogous expression can be developed for the differential *absorption* of circularly polarized light, i.e. circular dichroism (CD). In this case the measurement yields an absorption dissymmetry ratio at wavelength λ':

$$g_{abs}(\lambda') = g^\Lambda_{abs}(\lambda') \eta_g \quad (10)$$

where $g^\Lambda_{abs}(\lambda')$ is the absorption dissymmetry ratio for the Λ enantiomer and η_g is the enantiomeric excess in the ground state.

In our previous work[13,14] we have shown that for a *racemic* mixture (i.e. $N^\Lambda_g = N^\Delta_g$) it may be possible to generate a differential emitting-state population by using a circularly polarized exciting beam. In this case the measured g_{em} at wavelength λ following excitation at λ' is given by

$$g^{CP}_{em}(\lambda) = (1/2)g^\Lambda_{em}(\lambda) g^\Lambda_{abs}(\lambda') \quad (11)$$

In this expression, we have assumed that there is no racemization of enantiomers taking place during the lifetime of the excited state and that we can neglect any effects due to photoselection and orientational relaxation.

Although there has been one report of differential excited-state quenching by chiral species,[16] our experience is that, for the complexes studied here, this effect is negligible. In fact, the addition of the chiral Pfeiffer adduct L-histidine has little effect on the quantum yield of the transitions under study. Therefore, under *unpolarized* excitation

$$\eta_n = \eta_g \equiv \eta \quad (12)$$

Equations 9–11 serve as the basis for the analysis presented in this work. If we start with the assumption that the Pfeiffer agent is simply disturbing the racemic equilibrium, it is evident from these equations that the measurement of the CD and CPL of the solution with Pfeiffer agent added, combined with the measurement of the CPL following circularly polarized excitation in the absence of the Pfeiffer agent, will yield not only the enantiomeric excess but also the absorption and emission dissymmetry ratios for the "pure" enantiomeric species, even though they cannot be resolved.

Experimental Section

Dy_2O_3 (Aldrich) was dissolved in the minimum amount of dilute HCl with heating. The solution was then brought to pH 3.0 with concentrated NaOH. H_2DPA was added to the solution and the pH adjusted to 8 with NaOH. The final molar ratio [DPA:Dy(III)] was 3.3. L-Histidine (Sigma) was then added and the solution acidified with dilute HCl until a pH of 3.0 was obtained. The final concentrations were 0.015 M in $Dy(DPA)_3^{3-}$ and 0.075 M in L-histidine. CPL measurements were made on an instrument described previously, operating in a differential photon-counting mode.[15] The emission monochromator was a SPEX 1680B (0.22 m) double monochromator set at a 2-nm band-pass. The excitation source was a 150-W xenon arc lamp (Photon Technology) that was passed through a 20-cm monochromator (Instruments SA) with an 8-nm spectral band-pass and an excitation wavelength of 280 nm. CD measurements were performed on a JASCO 500A instrument using a band-pass of 0.5 nm and a 5-cm cell. Absorption spectra were recorded on a Cary 118C spectrophotometer. CPL spectra of racemic $Dy(DPA)_3^{3-}$ were performed with 457.9-nm laser excitation (Coherent Radiation CR-6) passed through a $^1/_4\lambda$ mica wave plate.

Results and Discussion

In Figure 1 we show the total luminescence and CPL from the solution of $Dy(DPA)_3^{3-}$ at pH 3.0. Complexes of lanthanides with 2,6-pyridinedicarboxylic acid in acid solutions are known to bind in a tris-terdendate fashion with approximate D_3 symmetry,[13] allowing for the existence of Δ and Λ optical isomers. As reported previously, this nine-coordinate complex is not labile on the emission time scale.[13] The CPL is generated by employing as the excitation source a circularly polarized Ar ion laser beam at 457.9 nm. This corresponds to the transition $^6H_{15/2} \rightarrow ^4I_{15/2}$. The emission shown is in the spectral region corresponding to the $^6H_{11/2} \leftarrow ^4F_{9/2}$ transition. One of the enantiomers absorbs the circularly polarized excitation to a larger extent than the other, and this excited-state population difference remains intact during the lifetime of the emitting state.

In Figure 2 we show total luminescence and CPL for a similarly prepared solution of $Dy(DPA)_3^{3-}$ after the addition of the chiral agent L-histidine. Comparison of the spectra in Figures 1 and 2 shows that they are very similar, leading to the conclusion that the major chiral emitting species in the two solutions is the same. It is important to note that, unlike the solution employed in Figure 1, the differential population generated by the addition of L-histidine must be in the ground state. Since the sign of the CPL spectra is the same in both figures, it follows that the L-histidine shifts the equilibrium toward the same isomer that preferentially absorbs the circularly polarized light. One can, in fact, select the other enantiomer either by exciting with circularly polarized light
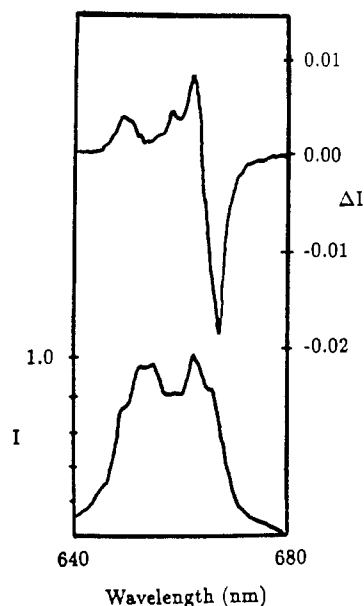
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Figure 1. Total luminescence (I) and circularly polarized luminescence (ΔI) for a solution of racemic $Dy(DPA)_3{}^{3-}$ at pH 3.0 excited with circularly polarized 457.9-nm excitation. The spectral region shown corresponds to the $^6H_{11/2} \leftarrow {}^4F_{9/2}$ transition.
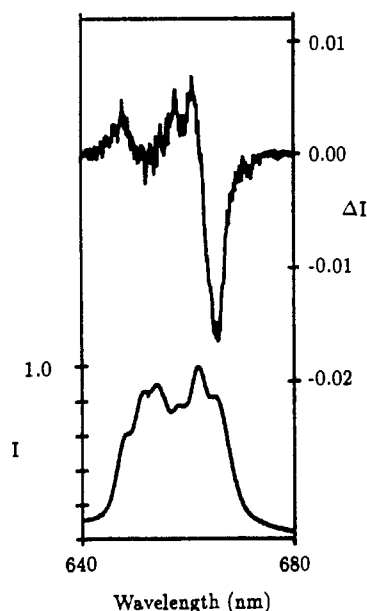

Figure 2. Total luminescence (I) and circularly polarized luminescence (ΔI) for a solution of $Dy(DPA)_3{}^{3-}$ at pH 3.0 after the addition of L-histidine excited with unpolarized radiation. [L-histidine]:[complex] = 5:1. The spectral region shown corresponds to the $^6H_{11/2} \leftarrow {}^4F_{9/2}$ transition.

of opposite polarization or by adding D-histidine. In both cases, a completely inverted CPL spectrum is obtained.

Figure 3 shows the absorption and CD spectra for the $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transition of Dy(III) in the same solution as that used for Figure 2. The arrow in this figure indicates the position of the exciting laser line used in the study of racemic $Dy(DPA)_3{}^{3-}$. This is to our knowledge the first report of Pfeiffer effect CD for lanthanides.

In Table I we list the appropriate measurements in regard to the analysis presented previously, namely, $g^{CP}_{em}(664.5$ nm), $g_{em}(664.5$ nm), and $g_{abs}(457.9$ nm). The absorption wavelength is fixed by the convenient Ar ion line; the emission wavelength chosen corresponds to the largest peak in the CPL spectra (see Figures 2 and 3). Using the equations derived previously, we can then determine values for $g^X_{abs}(457.9$ nm), $g^X_{em}(664.5$ nm), and η, where X = Δ or Λ and is undetermined as discussed below.
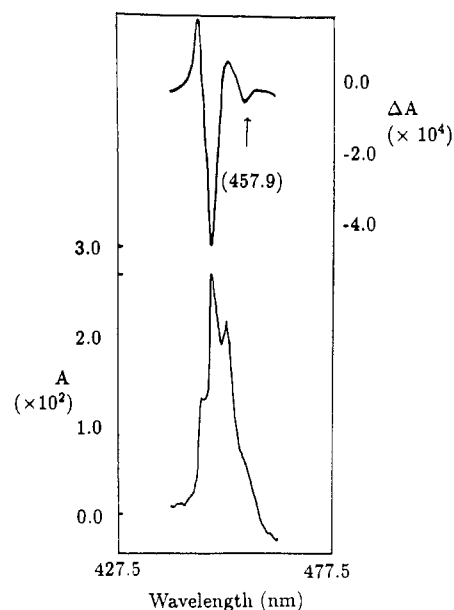

Figure 3. Absorption (A) and circular dichroism (ΔA) for a solution of $Dy(DPA)_3{}^{3-}$ at pH 3.0 after the addition of L-histidine. [L-histidine]: [complex] = 5:1. The spectral region shown corresponds to the $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transition. The arrow indicates the position of the wavelength used for laser excitation of the racemic solution.

Table I. Absorption and Emission Dissymmetry Ratios for Selected Transitions of $Dy(DPA)_3{}^{3-}$ at pH 3

$Dy(DPA)_3{}^{3-}$ (racemate)	transition
$g^{CP}_{em}(664.5$ nm) = -0.020	$^6H_{11/2} \leftarrow {}^4F_{9/2}$

$Dy(DPA)_3{}^{3-}$ + L-histidine	transition
$g_{abs}(457.9$ nm) = -0.0032	$^6H_{15/2} \rightarrow {}^1I_{15/2}$
$g_{em}(664.5$ nm) = -0.017	$^6H_{11/2} \leftarrow {}^4F_{9/2}$

$\Lambda(\Delta)$-$Dy(DPA)_3{}^{3-}$	transition
$g^X_{abs}(457.9$ nm) = -0.086	$^6H_{15/2} \rightarrow {}^4I_{15/2}$
$g^X_{abs}(450.0$ nm) = -0.413	$^6H_{15/2} \rightarrow {}^4I_{15/2}$
$g_{em}(664.5$ nm) = -0.459	$^6H_{11/2} \leftarrow {}^4F_{9/2}$
η = enantiomeric excess = 0.037	

These values are also listed in Table I. The determination of η yields g_{em} at other wavelengths through eq 9. The emission dissymmetry ratio for the most intense component of the $^6H_{11/12} \leftarrow {}^4F_{9/2}$ transition at 450.9 nm is also listed in this table.

Summary

Under the assumption that the addition of the chiral environment compound L-histidine simply perturbs the equilibrium between the two D_3 isomers of $Dy(DPA)_3{}^{3-}$, it has been shown that it is possible to determine the enantiomeric excess and the dissymmetry ratios for certain transitions of the pure enantiomers, even though they cannot be chemically resolved. The analysis also presumes that there is no differential excited-state quenching, so that the enantiomeric excess present in the ground state is identical with that in the emitting state. For this system, it has been shown that the addition of 5:1 L-histidine results in an enantiomeric excess of 3.7%.

The identification of precisely which enantiomer is favored, i.e. Δ or λ, depends ultimately on the availability of CPL measurements from optically active crystals or on accurate theoretical calculations of f–f optical activity or chiral discrimination. Unfortunately, crystallographic studies on several lanthanide–dipicolinate complexes with varying amounts of water using different lanthanides have yet to yield suitable crystals, i.e. uniaxial and enantiomorphic.[17-19] $Na_3Dy(DPA)_3\cdot15H_2O$, for example, has

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been shown to be triclinic (space group *P*1).[18]

The success of the experiments described above for Dy(III) is in large part due to the availability of suitable electronic transitions. The measurement of CPL from the racemic solution requires that *both* the absorption and emission transitions have large dissymmetry ratios, since, as illustrated in eq 11, the measurement of g^{CP}_{em} depends on their product. In normal operating conditions, the sensitivity of our experimental apparatus is such that dissymmetry ratios $>1 \times 10^{-4}$ can be measured easily. In the case of Dy(III), both the absorption and emission transitions used in this work have large dissymmetry ratios (see Table I). This result is consistent with the fact that these intraconfigurational f–f transitions satisfy magnetic dipole selection rules.[20]

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Photophysical, Photochemical, and Redox Behavior of a Series of Ligand-Bridged (OC)₅M–L–M'(CO)₅ (M, M' = Cr, Mo, W) Complexes

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Infrared spectra, electronic absorption data, redox potentials, and photophysical parameters are reported for a series of homonuclear and heteronuclear ligand-bridged (OC)₅M–L–M'(CO)₅ complexes, where M and M' = Cr, Mo, or W and L = pyrazine (pyz), 4,4'-bipyridine (bpy), *trans*-1,2-bis(4-pyridyl)ethylene (bpe), or 1,2-bis(4-pyridyl)ethane (bpa), and their corresponding mononuclear derivatives. Each complex exhibits low-lying ¹A₁ → ¹E ligand-field (LF) and M → π*(L) charge-transfer (MLCT) absorptions. The energy position of the MLCT transition is dependent on both the length and conjugation of the binucleating ligand; when L = pyz, bpy, and bpe, the MLCT states are at lowest energy, but when L = bpa, the LF states are lowest lying. Observed electronic absorption and electrochemical data illustrate that the ligand-bridged (OC)₅W–L–W(CO)₅ complexes vary considerably in the extent of ligand π*-orbital stabilization upon binucleation, being essentially unperturbed for L = bpa, weakly perturbed for L = bpe and bpy, and strongly perturbed for L = pyz. Calculated conproportionation constants, K_{con}, for these binuclear species are 2.5×10^4 (L = bpe), 2.9×10^8 (L = bpy), and 2.8×10^{18} (pyz), further illustrating the extent of electronic interaction. Each of the mononuclear and binuclear complexes, where L = bpy, bpe, and pyz, exhibits broad, relatively long-lived (18–770 ns) MLCT emission, centered at 550–720 nm, in deoxygenated solution at 283 K. Obtained photophysical parameters reflect strong electronic effects in the pyz-bridged complex. No emission was observed from the bpa complexes at 283 K, in accordance with the lowest lying LF assignment. On photoexcitation the mononuclear and binuclear complexes both undergo W–N bond cleavage. Effects of varying the ligand and excitation wavelength on the observed photochemical quantum yields are consistent with the model of a reactive ¹A₁ → ¹E LF state lying closely above an unreactive MLCT state.

Introduction

Since the first report on the now well-known mixed-valence Ru(II)–L–Ru(III) system,[1] there have been extensive studies on the electronic interaction between mononuclear components of ligand-bridged dimer complexes.[2] It has been demonstrated that upon light absorption by one of the chromophores these binuclear systems may undergo intramolecular energy transfer[3,4] or in-ner-sphere electron transfer[5,6] to the other chromophore. Photoreactions have also been documented following these intramolecular energy- and electron-transfer processes.[3,5]

In contrast, there has been relatively little attention paid to photoprocesses of zerovalent organometallic dimer complexes.[7] However, there is ample published spectroscopic and electrochemical evidence illustrating that the binucleating ligand π-system in a ligand-bridged binuclear metal carbonyl compound can be perturbed substantially from that of the corresponding mononuclear complexes.[7,8] Here we describe effects of varying the

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