Figure 7. Energy levels for the Pd and Pt complexes. ^{3}LC and ^{3}CT are the luminescent excited states. E_1 is likely a LC or MC level. E_2 is an upper limiting value for the energy of the ^{3}MC excited state. The relative energy positions of the E_2 levels are thought to reflect those of the corresponding ^{3}MC states. For more details, see text.

indicated in Figure 5(ii-2). This suggests that the upper excited level E_1 coming into play (Figures 6 and 7) is not strongly distorted compared to the luminescent level, typical for LC or CT levels. A similar situation of relatively closely spaced MLCT levels is common for Ru(II)–polypyridine complexes[38] and does not merit further discussion. We only wish to note that the lack of kinetic evidence for levels closely spaced from the lowest one for Pd(thpy)$_2$ and Rh(phpy)$_2$(bpy)$^+$ does not mean that such levels are not present. Simply, their appearance from the ln $(1/\tau)$ vs $1/T$ plots may be precluded because of one or more of the following conditions: (a) ΔE_1 is too small; (b) A_1 is too small; (c) ΔE_1 is too close to ΔE_2.

The strongly activated processes are characterized by high values of the preexponential factor A_2 (Table I). This suggests that the excited level E_2 coming into play (Figures 6 and 7) is either the crossing point between the ^{3}LC and ^{3}MC levels (case i, Figure 5) or an upper limiting value for the energy difference between the minima of the ^{3}LC and ^{3}MC surfaces (case ii-1, Figure 5). For Rh(thpy)$_2$(bpy)$^+$ and Rh(phpy)$_2$(bpy)$^+$ the obvious comparisons are with recently studied Rh(III) complexes of the polypyridine family. For Rh(bpy)$_3^{3+}$,[23] Rh(3,3'-dmbpy)$_3^{3+}$,[39] Rh(phen)$_3^{3+}$,[24,25,40] and Rh(4,7-dmphen)$_3^{3+}$ [25] (dm indicates dimethyl substituents) dual luminescence has been reported under

some experimental conditions, indicating that a ^{3}MC level lies at higher energy than the ^{3}LC level, which is responsible for the stronger (or unique) luminescence band at 77 K. For Rh(bpy)$_3^{3+}$, Rh(phen)$_3^{3+}$, and Rh(4,7-dmphen)$_3^{3+}$ a temperature dependence study has also been performed, leading to the following activation parameters: Rh(bpy)$_3^{3+}$, $A_2 \simeq 10^{12}$ s^{-1}, $\Delta E_2 = 2200$ cm^{-1} (in MeOH/EtOH, 1:4);[23] Rh(phen)$_3^{3+}$, $A_2 \simeq 10^{11}$ s^{-1}, $\Delta E_2 = 2100$ cm^{-1} (in acetonitrile);[25] Rh(4,7-dmphen)$_3^{3+}$, $A_2 \simeq 10^{11}$ s^{-1}, $\Delta E_2 = 2400$ cm^{-1} (in acetonitrile).[25] The behavior observed for Rh-(phpy)$_2$(bpy)$^+$ and Rh(thpy)$_2$(bpy)$^+$ (Table I, Figure 6) is consistent with that exhibited by the Rh(III)–polypyridine complexes. More specifically, the E_2 values obtained (Figure 6) suggest that the ligand field strength decreases in the order phpy$^-$ > bpy > thpy$^-$. While the higher ligand field strength of phpy$^-$ compared to that of bpy is clearly due to the higher σ-donor ability of C$^-$ compared to that of N, the lower ligand field strength of thpy$^-$ compared to that of bpy could be due to either σ or π factors.

Agreement between experimental results and ligand field expectations is also shown by the Pd and Pt complexes (Figure 7). The stronger ligand field of Pt(II) compared to that of Pd(II) is reflected in the relative energy position of the E_2 levels of Pt(thpy)$_2$ and Pd(thpy)$_2$. The much higher ligand field strength of Pt(IV) compared to those of Pd(II) and Pt(II) is reflected in the absence of accessible MC levels in Pt(thpy)$_2$(CHCl$_2$)Cl. On the basis of the experimental results, it can be estimated that, at room temperature (298 K), ΔE_2 for a process having $A_2 = 10^{13}$ s^{-1} should have been lower than 4600 cm^{-1} to make k_2 experimentally detectable for Pt(thpy)$_2$(CHCl$_2$)Cl (Figure 7).

Conclusion

From the study of the temperature dependence of the luminescence lifetimes of Pd(thpy)$_2$, Rh(thpy)$_2$(bpy)$^+$, Rh-(phpy)$_2$(bpy)$^+$, Pt(thpy)$_2$, and Pt(thpy)$_2$(CHCl$_2$)Cl between 77 and 310 K, it has been possible to obtain information on the factors that govern the decay of the luminescent ^{3}LC or ^{3}MLCT state via upper lying levels. We have also shown that for structurally similar complexes it is possible to infer the relative positions in the spectrochemical series of different cyclometalated ligands or of different metals in cyclometalated complexes.

Registry No. *cis*-Pd(thpy)$_2$, 115756-71-3; Rh(thpy)$_2$bpy$^+$, 107053-32-7; Rh(phpy)$_2$bpy$^+$, 106266-44-8; *cis*-Pt(thpy)$_2$, 100012-12-2; C,C,C-*fac*-Pt(thpy)$_2$(CHCl$_2$)Cl, 111822-52-7.

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Use of the Pfeiffer Effect To Probe the Optical Activity of Europium(III) Complexes with 2,6-Pyridinedicarboxylate

Nursen Coruh, Gary L. Hilmes, and James P. Riehl*

Circularly polarized luminescence (CPL) and circular dichroism (CD) results are presented for aqueous Eu(dipicolinate)$_3^{3-}$ upon addition of (+)-dimethyl-L-tartrate. The added chiral species has been shown to cause a shift in the racemic equilibrium of the approximately D_3 lanthanide complexes. Similar data for Dy(dipicolinate)$_3^{3-}$ are reported, and in combination with CPL measured from the racemic solution, these data yield quantitative information concerning the equilibrium shift and the chiroptical properties of the pure enantiomers. Comparison is made with published CD and CPL from crystalline Eu(oxydiacetate)$_3^{3-}$, and it is concluded that the addition of (+)-dimethyl-L-tartrate results in an excess of the Λ isomer.

Introduction

Aqueous lanthanide complexes with 2,6-pyridinedicarboxylate [dipicolinate = DPA] are known to be tris-terdentate complexes and possess D_3 symmetry over a wide range of pH.[1,2] These

relatively high-symmetry species have been studied fairly extensively, since they are easy to prepare in aqueous solution, are, in

(1) Grenthe, I.; Toblasson, I. *Acta Chem. Scand.* **1963**, *17*, 2101.

many cases, highly luminescent, and, thus, could serve as useful models for theoretical calculations or parametrizations of lanthanide electronic structure and f–f transition intensities.

Since these complexes exist in enantiomeric forms in solution, they have also been studied by chiroptical spectroscopic techniques, especially circularly polarized luminescence spectroscopy (CPL).[3] Until recently, since these complexes are not resolvable by classical methods, CPL has been possible only when the racemic equilibrium between the two enantiomers has been perturbed by an added chiral agent resulting in an excess of one enantiomer relative to the other.[4-9] This perturbation of a racemic equilibrium between labile chiral metal complexes has been named the "Pfeiffer effect" after the original work by Pfeiffer in the 1930s on the enhancement of optical rotation of optically active alkaloids in the presence of labile racemic transition-metal complexes.[10-12] The verification that this phenomenon is due to a shift in the equilibrium and not the formation of a new chiral absorbing complex was provided by measurement of circular dichroism (CD) on transition-metal complexes that could be resolved. The CD spectra for the resolved complex and the Pfeiffer-perturbed system were identical.[13]

Since, to date, no optically active D_3 lanthanide complexes have been chemically resolved, it has not been possible to verify that the added chiral species simply perturbs the racemic equilibrium in the same way that this was verified for transition-metal complexes. Furthermore, since CPL depends on the existence of a chiral emitting state, one can not rule out the possibility that the added Pfeiffer compound affects the emitting-state population, as opposed to inducing a ground-state equilibrium shift. Recently, we have shown, however, that is is possible to measure CPL from the racemic solution of several Ln–DPA complexes without any added chiral substance through the use of circularly polarized laser excitation.[14,15] CPL from $Ln(DPA)_3^{3-}$ (Ln = Tb, Eu, Sm, and Dy) have been reported. These experiments are successful because the two enantiomers absorb the circularly polarized excitation unequally, and this excited-state concentration difference is maintained during the emission lifetime. It is therefore possible to compare CPL from the racemic Ln–DPA complex with Pfeiffer agent added to that from the racemate, to determine if the emitting species is the same in these two systems.

Very recently we have shown that, for the case of $Dy(DPA)_3^{3-}$, the addition of L-histidine does, indeed, result in a simple equilibrium disturbance as evidenced by comparison of CPL spectra for the racemate with that for the racemate with L-histidine added to the solution.[16] Furthermore, it was demonstrated that, for this system, it was also possible to measure the CD at the laser line used for circularly polarized excitation of the racemate. These three measurements, namely, CPL from the racemate with circularly polarized excitation at λ_{ex}, CD at λ_{ex} for the L-histidine–$Dy(DPA)_3^{3-}$ solution, and CPL from the L-histidine–$Dy(DPA)_3^{3-}$ solution, provide enough information to determine the enantiomeric excess generated, as well as the absorption and emission dissymmetry factors for the pure enantiomers even though they can not be resolved chemically.

The most difficult measurement of the three listed above is the measurement of the CD at the laser frequency used for circularly polarized excitation. In order to generate the largest *differential* excited-state population, it is necessary to select the absorptive

transition with the largest discrimination between the two enantiomers. This corresponds to the transition with the largest magnitude for the absorption dissymmetry factor, $g_{abs} = \Delta\epsilon/\epsilon$. In general, one is restricted to transitions with very small values of ϵ, thereby requiring the use of high-intensity laser excitation. For the lanthanide ions that we have studied, the transition used for excitation of the racemic solutions have extinction values so low that they are barely detectable in absorption. One exception to this is the $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transition of $Dy(DPA)_3^{3-}$ which at 457.9 nm (corresponding to an Ar ion laser line) has an extinction coefficient of 0.125.

In this work we show that, under the assumption that, for a given concentration of added chiral compound, the equilibrium shift for different lanthanide–DPA complexes will be approximately the same, one can determine absorption and emission dissymmetry values for other $Ln(DPA)_3^{3-}$ complexes. This is accomplished by using the enantiomeric excess determined from the $Dy(DPA)_3^{3-}$ solution in which a chiral compound has been added, and measuring the CD and CPL from the other lanthanide species. This will be illustrated in this work for $Eu(DPA)_3^{3-}$ following the addition of (+)-dimethyl-L-tartrate.

Theory

The differential circularly polarized emission intensity at wavelength λ, $\Delta I(\lambda)$, is given by eq 1,[3] where the g and n refer,

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

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.

For a partially resolved solution containing N_n^Δ Δ isomers, and N_n^Λ Λ isomers, the *measured* dissymmetry ratio can be written as

$$g_{em}(\lambda) = g_{em}^\Delta(\lambda) \, \eta_n \quad (3)$$

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

$$\eta_n = [N_n^\Lambda - N_n^\Delta]/[N_n^\Lambda + N_n^\Delta] \quad (4)$$

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', $g_{abs}(\lambda')$

$$g_{abs}(\lambda') = g_{abs}^\Lambda(\lambda') \, \eta_g \quad (5)$$

where g_{abs}^Λ (λ') is the absorption dissymmetry ratio for the Λ enantiomer and η_g is the enantiomeric excess in the ground state.

We have shown previously that for a *racemic* mixture (i.e. $N_g^\Lambda = N_g^\Delta$) it may be possible to generate a differential emitting-state population by using a circularly polarized exciting beam.[17] In this case the measured g_{em} at wavelength λ following excitation at λ' is given by

$$g_{em}^{CP}(\lambda) = (1/2)g_{em}^\Lambda(\lambda) \, g_{abs}^\Lambda(\lambda') \quad (6)$$

In this expression, we have assumed that there is no racemization taking place during the lifetime of the emitting state.

For the complexes studied here, there does not appear to be any *differential* excited state quenching, thus

$$\eta_n = \eta_g \equiv \eta \quad (7)$$

The three equations, (3), (5), and (6), correspond to the three measurements described above, and allow one to calculate the three unknown quantities η, $g_{em}^\Lambda(\lambda)$, and $g_{abs}^\Lambda(\lambda')$. Absorption and emission dissymmetry values at wavelengths other than λ and λ' can be determined from (3) and (5), once the value of η is known.

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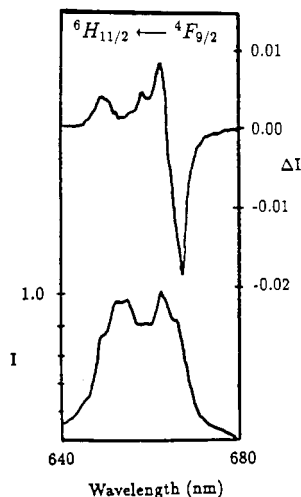
Figure 1. Circularly polarized luminescence (ΔI) and total luminescence (I) for *rac*-Dy(DPA)$_3^{3-}$ excited with circularly polarized 457.9-nm radiation. The spectral region displayed corresponds to the $^6H_{11/2} \leftarrow {}^4F_{9/2}$ transition.
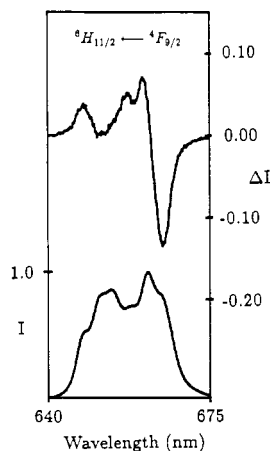
Figure 2. Circularly polarized luminescence (ΔI) and total luminescence (I) of Dy(DPA)$_3^{3-}$ after addition of 4.85 M (+)-dimethyl-L-tartrate. The spectral region displayed corresponds to the $^6H_{11/2} \leftarrow {}^4F_{9/2}$ transition.

Experimental Section

Dy$_2$O$_3$ and Eu$_2$O$_3$ (Aldrich) were dissolved in the minimum amount of dilute HCl with heating. The solutions were then brought to a pH of 3.0 with concentrated NaOH. DPA was added to the solutions and the pH adjusted to 8.0 with NaOH. The final molar ratio [DPA/lanthanide(III)] was 3.3. The pH was then lowered to 4.5. The final concentrations of the two solutions were 0.05 M. A 25-g sample of (+)-dimethyl-L-tartrate [=(+)-DMT] (Sigma) was then added to 10 mL of the solutions prepared above, which were then stirred until clear. The final volume was measured, and the concentration of lanthanide complex was determined to be 0.017 M and that of (+)-DMT to be 4.85 M. The optical properties of these solutions are known to be insensitive to pH changes between pH 3 and 6.

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 1-nm band-pass. The excitation source was a 150-W xenon arc lamp (Photon Technology), the light from which 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 waveplate.

Results

CPL and total luminescence (TL) spectra for racemic Dy-(DPA)$_3^{3-}$ are presented in Figure 1. This spectral region corresponds to the $^6H_{11/2} \leftarrow {}^4F_{9/2}$ transition. These spectra were obtained by circularly polarized excitation at 457.9 nm. In Figure

Table I. Dissymmetry Factors for Selected Transitions of Dy(DPA)$_3^{3-}$

transition	λ_{max}, nm	dissymmetry ratio
A. After Addition of 4.5 M (+)-Dimethyl-L-tartrate		
$^6H_{15/2} \rightarrow {}^4I_{15/2}$	457.9	-3.3×10^{-2}
$^6H_{11/2} \leftarrow {}^4F_{9/2}$	664.5	-1.7×10^{-1}
B. For the Racemic Solution Using Circularly Polarized Excitation		
$^6H_{11/2} \leftarrow {}^4F_{9/2}$	664.5	$+2.0 \times 10^{-2}$
C. For Pure Enantiomers Calculated from (3), (5), and (6)		
$^6H_{15/2} \rightarrow {}^4I_{15/2}$	457.9	-8.9×10^{-2}
		$(-8.6 \times 10^{-2})^a$
$^6H_{11/2} \leftarrow {}^4F_{9/2}$	664.5	-4.6×10^{-1}
		$(-4.6 \times 10^{-1})^a$

^{a} Value from ref 16.

Table II. Emission Dissymmetry Factors for Selected Transitions of Eu(DPA)$_3^{3-}$ upon Addition of 4.85 M (+)-Dimethyl-L-tartrate at pH 4.5

transition	λ_{max}, nm	g_{em}
$^7F_0 \leftarrow {}^5D_0$	580	0
$^7F_1 \leftarrow {}^5D_0$	590	$+5.5 \times 10^{-2}$
	594	$+1.0 \times 10^{-1}$
$^7F_2 \leftarrow {}^5D_0$	615	-2.6×10^{-2}
	619	$+2.7 \times 10^{-2}$
$^7F_3 \leftarrow {}^5D_0$	647	$+6.5 \times 10^{-2}$
	652	$+5.5 \times 10^{-2}$
$^7F_4 \leftarrow {}^5D_0$	694	-1.5×10^{-2}
	703	$+7.0 \times 10^{-2}$

Table III. Absorbance (A), Circular Dichroism (ΔA), and Absorption Dissymmetry Factors (g_{abs}) for Selected Transitions of Eu(DPA)$_3^{3-}$ in the Presence of 4.85 M (+)-Dimethyl-L-tartrate at pH 4.5

| transition	λ_{max}, nm	ΔA	A	g_{abs}
$^7F_0 \rightarrow {}^5D_2$	463.5	-1.97×10^{-3}	1.21×10^{-1}	-1.60×10^{-3}
$^7F_1 \rightarrow {}^5D_2$	472.0	$+6.1 \times 10^{-5}$	a	large
	473.5	-6.1×10^{-5}	a	large
$^7F_2 \rightarrow {}^5D_2$	(487)	a	a	
$^7F_0 \rightarrow {}^5D_1$	524.5	$+4.5 \times 10^{-4}$	5.0×10^{-3}	$+9.0 \times 10^{-2}$
$^7F_1 \rightarrow {}^5D_1$	532.5	$+2.4 \times 10^{-5}$	3.9×10^{-3}	$+6.2 \times 10^{-3}$
	537.5	$+3.0 \times 10^{-5}$	5.5×10^{-3}	$+5.4 \times 10^{-3}$
$^7F_2 \rightarrow {}^5D_1$	553.5	-3.0×10^{-5}	a	large
	556.2	$+3.0 \times 10^{-5}$	a	large
$^7F_1 \rightarrow {}^5D_0$	587.5	$+7.6 \times 10^{-5}$	1.0×10^{-3}	$+7.6 \times 10^{-2}$
	591.0	$+1.52 \times 10^{-4}$	1.55×10^{-5}	$+1.0 \times 10^{-1}$

^{a} Not detectable.

2 we show CPL and TL covering the same spectral region for a racemic solution of Dy(DPA)$_3^{3-}$ that also contains 4.85 M (+)-DMT. The similarity of these two spectra confirm the result that the emitting species is the same in both samples. In Figure 3, we plot the absorption and CD spectra for the $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transition. The exact position of the 457.9-nm excitation is marked on this figure. As described above and presented previously, these are sufficient data to determine the enantiomeric excess and values of the absorption and emission dissymmetry factors. These results are presented in Table I.

The huge excess of (+)-DMT results in a very large (0.37) enantiomeric excess. As shown in Table I, the values for the dissymmetry factors obtained here compare favorably with the values obtained in our previous work in which the chiral agent was L-histidine and the enantiomeric excess was 0.036.[16]

CPL and TL spectra for the Eu(DPA)$_3^{3-}$–(+)-DMT solution are presented in Figures 4–7. The spectral regions shown correspond to the emissions from the $^5D_0$ state to the $^7F_0$ and $^7F_1$ states (Figure 4), the $^7F_2$ state (Figure 5), the $^7F_3$ state (Figure 6), and the $^7F_4$ state (Figure 7). These spectra are all normalized to unit intensity at the peak maximum. The relative intensities of the various transitions are the same as that reported by Foster and Richardson.[18] g_{em} values at peak maxima are summarized in

(18) Foster, D. R.; Richardson, F. S. *Inorg. Chem.* **1983**, *22*, 3396.
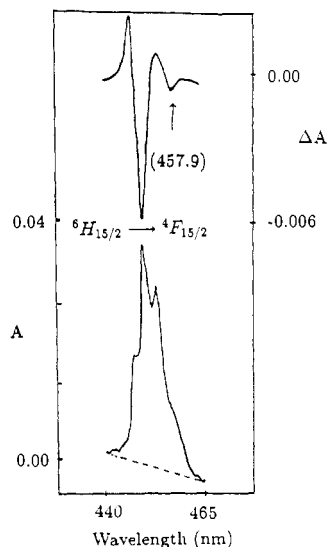
Figure 3. Circular dichroism (ΔA) and absorbance (A) of $Dy(DPA)_3^{3-}$ after addition of 4.85 M (+)-dimethyl-L-tartrate. The spectral region displayed corresponds to the $^6H_{15/2} \rightarrow {}^4F_{15/2}$ transition.
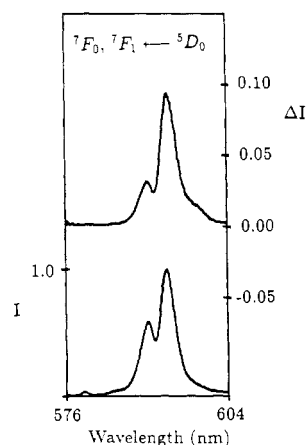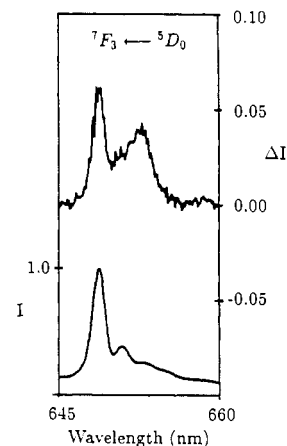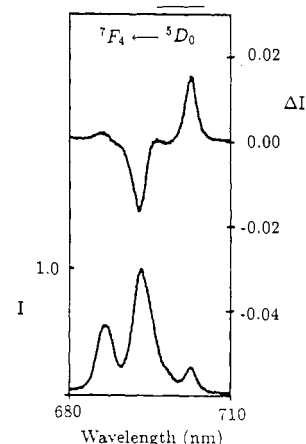

Figure 4. Circularly polarized luminescence (ΔI) and total luminescence (I) of $Eu(DPA)_3^{3-}$ after addition of 4.85 M (+)-dimethyl-L-tartrate. The spectral region displayed corresponds to the $^7F_0, {}^7F_1 \leftarrow {}^5D_0$ transitions.
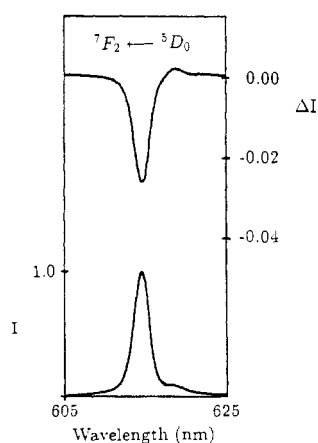
Figure 5. Circularly polarized luminescence (ΔI) and total luminescence (I) of $Eu(DPA)_3^{3-}$ after addition of 4.85 M (+)-dimethyl-L-tartrate. The spectral region displayed corresponds to the $^7F_2 \leftarrow {}^5D_0$ transition.

Table II. Smoothed absorbance and CD spectra for this solution from 460 to 600 nm are presented in Figures 8–10, and the data are summarized in Table III. In order to measure absorbances for the very weak $Eu(DPA)_3^{3-}$ transitions, 0.05 M solutions were prepared and an 8-cm cell was employed. Nevertheless, for some transitions the absorbance was so small that it could not be dis-

Figure 6. Circularly polarized luminescence (ΔI) and total luminescence (I) of $Eu(DPA)_3^{3-}$ after addition of 4.85 M (+)-dimethyl-L-tartrate. The spectral region displayed corresponds to the $^7F_3 \leftarrow {}^5D_0$ transition.

Figure 7. Circularly polarized luminescence (ΔI) and total luminescence (I) of $Eu(DPA)_3^{3-}$ after addition of 4.85 M (+)-dimethyl-L-tartrate. The spectral region displayed corresponds to the $^7F_4 \leftarrow {}^5D_0$ transition.
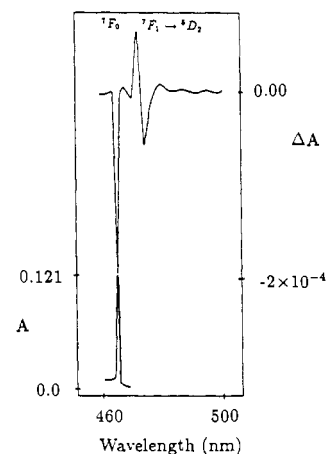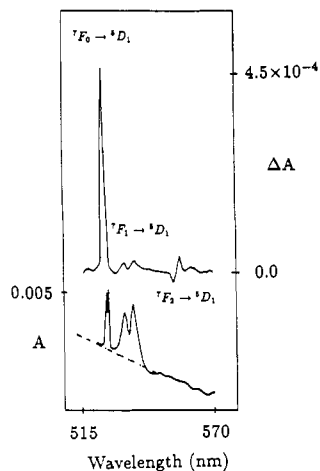

Figure 8. Circular dichroism (ΔA) and absorbance (A) of $Eu(DPA)_3^{3-}$ after addition of 4.85 M (+)-dimethyl-L-tartrate. The spectral region displayed corresponds to the $^7F_0, {}^7F_1 \rightarrow {}^5D_2$ transitions.

tinguished from the base line, even though the circular dichroism was easily measurable. As is evident in these figures, absorptions from the thermally populated $^7F_1$ and $^7F_2$ excited electronic states are observed. In Table IV, we list dissymmetry values for "pure" enantiomers calculated from (3) and (5) using the value of 0.37 for η.

Discussion

Under the assumption that the enantiomeric excess determined for the addition of (+)-DMT to $Dy(DPA)_3^{3-}$ is the same as that

Figure 9. Circular dichroism (ΔA) and absorbance (A) of $Eu(DPA)_3^{3-}$ after addition of 4.85 M (+)-dimethyl-L-tartrate. The spectral region displayed corresponds to the $^7F_0$, $^7F_1$, $^7F_2 \rightarrow {}^5D_1$ transitions.
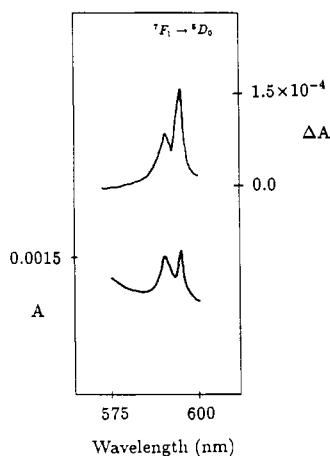
Figure 10. Circular dichroism (ΔA) and absorbance (A) of $Eu(DPA)_3^{3-}$ after addition of 4.85 M (+)-dimethyl-L-tartrate. The spectral region displayed corresponds to the $^7F_1 \rightarrow {}^5D_0$ transition.

Table IV. Emission and Absorption Dissymmetry Factors for Selected Transitions of $Eu(DPA)_3^{3-}$ Calculated from (3) and (5) by Using $\eta = 0.37$

absorption transition	λ_{max}, nm	g_{abs}
$^7F_0 \rightarrow {}^5D_2$	463.5	-4.3×10^{-3}
$^7F_0 \rightarrow {}^5D_1$	524.5	$+2.4 \times 10^{-1}$
$^7F_1 \rightarrow {}^5D_1$	532.5	$+1.7 \times 10^{-2}$
	537.5	$+1.4 \times 10^{-2}$
$^7F_1 \rightarrow {}^5D_0$	587.5	$+1.5 \times 10^{-1}$
	591.0	$+2.7 \times 10^{-1}$

emission transition	λ_{max}, nm	g_{em}
$^7F_1 \leftarrow {}^5D_0$	590	$+1.5 \times 10^{-1}$
	594	$+2.7 \times 10^{-1}$
$^7F_2 \leftarrow {}^5D_0$	615	-6.9×10^{-2}
	619	$+7.0 \times 10^{-2}$
$^7F_3 \leftarrow {}^5D_0$	647	$+1.7 \times 10^{-1}$
	652	$+1.5 \times 10^{-1}$
$^7F_4 \leftarrow {}^5D_0$	694	-4.0×10^{-2}
	703	$+1.9 \times 10^{-1}$

for $Eu(DPA)_3^{3-}$, we have been able to determine the dissymmetry ratios for a large number of absorption and emission transitions for $Eu(DPA)_3^{3-}$. These values should be important as one develops models for intensity and optical activity of these intraconfigurational f–f transitions. Eu(III) is a important species for this type of calculation since the ground state and the emitting state are

Table V. Emission and Absorption Dissymmetry Factors for Selected Transitions of $Na_3Eu(ODA)_3 \cdot 2NaClO_4 \cdot 6H_2O$

transition	$g_{em(abs)}$
Absorption[23]	
$^7F_0 \rightarrow {}^5D_0$	(not observed)
$^7F_0 \rightarrow {}^5D_1$	-4.6×10^{-1}
$^7F_0 \rightarrow {}^5D_2$	(a) -6.6×10^{-2}
	(b) -1×10^{-2}
$^7F_1 \rightarrow {}^5D_0$	-1.7×10^{-1}
$^7F_1 \rightarrow {}^5D_1$	(large negative)
$^7F_1 \rightarrow {}^5D_2$	(a) (large negative)
	(b) (large negative)
Emission[22]	
$^7F_0 \leftarrow {}^5D_0$	not observed
$^7F_1 \leftarrow {}^5D_0$	-1.44×10^{-1}
$^7F_2 \leftarrow {}^5D_0$	(a) -3.3×10^{-2}
	(b) no CPL detected
$^7F_3 \leftarrow {}^5D_0$	(a) -1.1×10^{-1}
	(b) -1.05×10^{-1}
$^7F_4 \leftarrow {}^5D_0$	(a) $+2.1 \times 10^{-2}$
	(b) $+1.5 \times 10^{-2}$

nondegenerate. The values presented in Table IV can also be used to determine the equilibrium shift (or equilibrium constant), for other Pfeiffer-systems through use of (3) and (5).

It should be mentioned that the results given here differ substantially from those of Yan et al. who determined "limiting" values for g_{em} for the $^7F_1 \leftarrow {}^5D_0$ and $^7F_2 \leftarrow {}^5D_2$ transitions. The values they report are +0.017, and $+5.2 \times 10^{-3}$, respectively.[7]

It is also important to note that since reliable calculations of f–f optical activity for these complexes have not been performed and since no optically active crystals are available,[19–21] it is not possible to unambiguously determine the absolute identity of the enantiomer (Λ or Δ) that is in excess. However, CPL and CD have been measured from optically active crystals of $Na_3Eu(ox-ydiacetato)_3 \cdot 2NaClO_4 \cdot 6H_2O$.[22,23] In Table V we list the absorption and emission dissymmetry values for a number of transitions of this D_3 complex at room temperature. Note that these values are not integrated over the band, but are simply calculated at the peak wavelength. Comparison of the data in Tables IV and V show that, for the transitions observed that satisfy magnetic dipole selection rules, i.e. $\Delta J = 0$, ± 1 except 0–0, that the dissymmetry ratios determined for $Eu(DPA)_3^{3-}$ in solution are opposite in sign to those measured for $Eu(ODA)_3^{3-}$ in the crystal. A similar relationship can be seen for the transition involving $\Delta J = 3$, but no such obvious conclusions can be drawn from the $\Delta J = \pm 2$ transitions.

Morley et al.[22] have shown that in CPL it is, in fact, the $^7F_2 \leftarrow {}^5D_0$ transition that is most sensitive to the nature of the ligand. This conclusion is consistent with the description of transitions of this type being classified as hypersensitive. We conclude, therefore, that since the data reported in Table V are for the Δ-isomer, the addition of (+)-DMT to the racemic solutions of $Ln(DPA)_3^{3-}$ results in a excess of the Λ-isomer and that the values reported in Table IV are for Λ-$Eu(DPA)_3^{3-}$. This identification of the excess enantiomer is in agreement with that of Yan and Brittain.[7]

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