

# Perturbation of the Racemic Equilibrium between $D_3$ Lanthanide Complexes through the Addition of Sugars

Ewa Huskowska<sup>†</sup> and James P. Riehl\*

Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931

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The perturbation of the racemic equilibrium of the  $D_3$  complexes of lanthanide (III) ions with 2,6-pyridinedicarboxylate by a number of sugars is studied by circularly polarized luminescence spectroscopy. Various spectroscopic probes show that the addition of the chiral sugar has no observable effect on the structure of the lanthanide complex. The dependence of the enantiomeric excess on the concentration of added sugar is shown to be linear for all of the sugars studied. This dependence is in agreement with an equilibrium model in which the optically-active lanthanide complex forms weakly bound diastereomeric outer-sphere associated species with the various sugars. No structural correlation is found between the configuration and conformation of the sugars studied and the sign of the enantiomeric excess.

## Introduction

The addition of a chiral "environment" compound to a kinetically labile racemic mixture of metal complexes may result in an equilibrium shift such that the concentrations of the two enantiomeric metal complexes are no longer equal. As first observed by Pfeiffer in the 1930's, this equilibrium shift may lead to a measurable optical rotation,<sup>1–3</sup> or, as demonstrated more recently, to the appearance of circular dichroism<sup>4</sup> (CD) or circularly polarized luminescence<sup>5</sup> (CPL). This phenomenon is often referred to as the "Pfeiffer Effect" although Pfeiffer attributed the observation to an increase in the optical rotation of the chiral "environment" compound by the metal complex. Until recently this phenomenon was observed only for the perturbation of the racemic equilibrium of transition metal complexes. The confirmation that the source of the increased optical activity was, in fact, due to an equilibrium perturbation of the metal complex equilibria was provided by comparison of the CD spectra of "Pfeiffer-active" systems involving transition metal complexes that could be prepared and resolved in pure or enriched forms.<sup>6</sup>

In recent years, Brittain and co-workers have shown that addition of a variety of chiral substances may cause a perturbation of the  $D_3$  equilibria between  $\Delta$ - and  $\Lambda$ -Tb(2,6-pyridinedicarboxylate = DPA)<sub>3</sub><sup>3-</sup> as evidenced by the measurement of CPL from the Tb(III) complex.<sup>5,7</sup> Unlike the situation for transition metal complexes, however, no comparison of the CPL spectra could be made to the pure or partially resolved system, because the Tb(DPA)<sub>3</sub><sup>3-</sup> complex racemizes too quickly for chemical resolution. Hilmes and Riehl, however, demonstrated that CPL could be measured from a *photoenriched* excited state of this complex if one uses circularly polarized excitation and if the lifetime of the excited state was shorter than the time

required for chemical racemization.<sup>8</sup> Comparison of the CPL spectra from the photoenriched sample and the "perturbed" system showed that the total emission and CPL line-shape were, in fact, identical, and that therefore this was truly an example of a Pfeiffer effect for a lanthanide complex. In our laboratory we have extended these types of measurements and observations to Eu(III) and Dy(III) complexes of DPA.<sup>9,10</sup> Of particular note is the measurement of the CD from an aqueous solution of Dy(DPA)<sub>3</sub><sup>3-</sup> into which L-histidine had been added.<sup>9</sup> This measurement, along with the measurement of the CPL from the perturbed and racemic solution, allowed for the determination of values for the chiroptical properties of the pure  $D_3$  enantiomers even though they could not be chemically resolved.

The identification of exactly which enantiomer ( $\Lambda$  or  $\Delta$ ) is produced in excess is a difficult issue, and we were able to make this determination only after comparison with previously published data on the CD and CPL of the related  $D_3$  compound Eu(oxydiacetate)<sub>3</sub><sup>3-</sup> which crystallizes as a pure enantiomer.<sup>10</sup> This comparison and eventual identification of which enantiomer has a negative CD or CPL at a particular wavelength hinges on the generally reliable assumption that the sign of the CPL for magnetic dipole allowed transitions of  $D_3$  Eu(III) complexes are independent of the ligand identity.

A theoretical description of the Pfeiffer effect based on the differential free energy of mixing has been presented by Schipper.<sup>11</sup> This author describes two possible models, namely an *associated* model, in which the chiral environment compound is directly associated with a metal complex, and a *dissociated* model, in which the chiral environment compounds are not assumed to be associated with any particular complex. Analysis of the concentration dependence of the several transition metal systems by Schipper led this author to conclude that these systems fit the dissociated model. Wu *et al.* have shown that the concentration dependence of the Pfeiffer effect on Tb(DPA)<sub>3</sub><sup>3-</sup> by L-histidine is also linear, and may therefore, also be described by the dissociated model of Schipper.<sup>12</sup> There have been some attempts at the potential use of the direction of the equilibrium

<sup>†</sup> Permanent Address, Institute of Chemistry, University of Wrocław, Wrocław, Poland.

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perturbation as an aid in the identification of the chirality of the environment compound.<sup>13,14</sup> However, these have met with limited success. Although there has been speculation on the nature of the intermolecular forces involved, to date, no detailed understanding of the molecular basis for an observed Pfeiffer effect in terms of specific *diastereomeric* interactions has appeared in the literature.

In this paper we report on observations of Pfeiffer-perturbed equilibria of racemic Tb(III) and Eu(III) complexes of DPA by a series of sugars. Comparison is made to the previous report of Brittain,<sup>13</sup> and on the potential use of this measurement as a structural probe.

### Experimental Section

Stock solutions of Ln(III) (Ln = Tb, Eu, Nd) were prepared from the lanthanide chlorides (Aldrich). 2,6-Pyridinedicarboxylic acid (DPA) was obtained from Aldrich and used without further purification. Aqueous stock solutions of the sugars (Aldrich) were prepared by dissolution in water, and waiting for at least 48 h before use in order to allow them to reach conformational equilibrium. Solutions for luminescence and absorption measurements were prepared by mixing stock solutions of LnCl<sub>3</sub> (pH ~ 3) and DPA (pH ~ 9) in a 1:3.5 ratio and adding sugar solution. The concentration of lanthanide complexes was in the range 0.005–0.03 M; the concentration of sugars used in this work was in the range 0.06–3.27 M. The final pH of solutions was approximately 8.0.

CPL and total luminescence spectra were recorded on an instrument constructed in our laboratory operating in a photon-counting mode.<sup>15</sup> This instrument measures the total luminescence (*I*) and circularly polarized luminescence ( $\Delta I$ ). In general, in CPL spectroscopy one reports results in terms of the so-called luminescence dissymmetry ratio  $g_{lum}$  which is defined as  $\Delta I/(I/2)$ , where  $\Delta I = I_{Left} - I_{Right}$ , and  $I = I_{Left} + I_{Right}$ . Direct excitation of Tb(III) was accomplished at 488 nm with a Coherent Innova-70 argon ion laser. An argon-laser CW pumped dye laser CR-599 (using rhodamine 110) was used as the excitation source for Eu(III). The excitation wavelength for Eu(III) was at 557.1 nm which corresponds to the <sup>7</sup>F<sub>2</sub> → <sup>5</sup>D<sub>1</sub> transition of Eu(III). The thermally excited <sup>7</sup>F<sub>2</sub> state is approximately 1% populated at room temperature. The emission was focussed on the entrance slits of a 0.22 m double monochromator (SPEX) using a resolution of 0.4 nm.

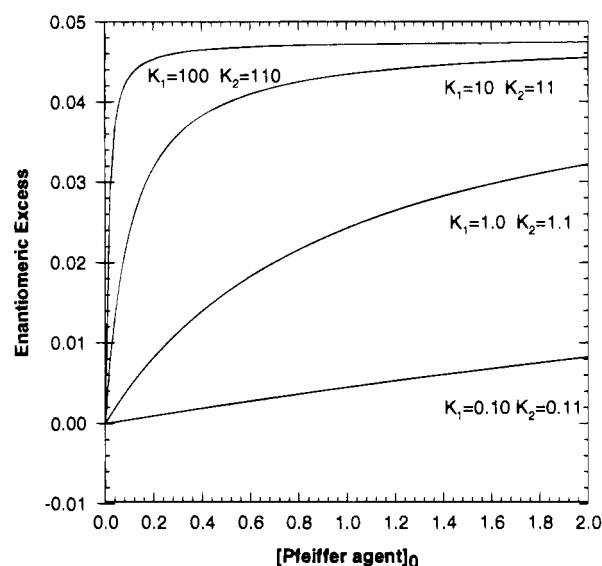
Absorption measurements for Nd(III) were made on a Cary 2200 spectrophotometer. Oscillator strengths for the electronic transitions were calculated by the graphical integration method using the expression  $P = 4.32 \times 10^{-9} \int \epsilon(\sigma) d\sigma$ , where  $\epsilon(\sigma)$  is the molar absorptivity at energy  $\sigma$  (cm<sup>-1</sup>).<sup>16</sup>

### Theory

In this work we choose to consider the effect of the added chiral substance to result in the preferential formation of one diastereomeric outer-sphere association complex over the other. The assumption of outer-sphere association is consistent with the requirement that the addition of the chiral environment compound does not significantly perturb the structure of the lanthanide complex. The three solution equilibria are illustrated in the following equations



where we have denoted the added chiral adduct as C\*, and the outer-sphere association complex by a colon (:). In this model



**Figure 1.** Enantiomeric excess versus concentration of chiral Pfeiffer compound for different values of the outer-sphere association constants ( $M^{-1}$ ).  $Ln_0 = 0.010$  M.

the concentrations of the unassociated lanthanide complex enantiomers are equal, *i.e.*  $[\Delta\text{-Ln}(\text{DPA})_3^{3-}] = [\Lambda\text{-Ln}(\text{DPA})_3^{3-}] \equiv Ln$ . Using the equilibria expressions and the mass balance relationships, one can derive the following expressions relating the concentrations of all species present in solution.

$$2Ln - \frac{Ln_0}{Ln} = (Ln_0 - C^*)(K_1 + K_2) \quad (4)$$

$$[C^*] = \frac{Ln_0 - 2Ln}{Ln(K_1 + K_2)} \quad (5)$$

$$\eta = \frac{\Delta Ln:C - \Lambda Ln:C}{Ln_0} = \frac{Ln[C^*](K_2 - K_1)}{Ln_0} \quad (6)$$

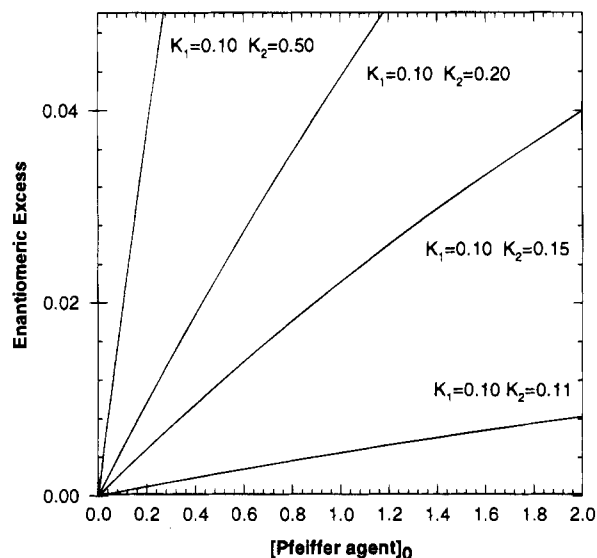
In these equations, the subscript 0 denotes the initial concentrations.  $\eta$  in eq. (6) is the resultant enantiomeric excess, and may be related to the measured luminescence dissymmetry factor as follows:

$$g_{lum}(\lambda) = \eta g_{lum}^{\Lambda}(\lambda) \quad (7)$$

In our experiments, we determine  $g_{lum}$  after the addition of fixed amounts of the chiral environment compound. As implied in eqs 4–6, the dependence of the enantiomeric excess on the initial concentration of C\* is quite complicated and depends, obviously, on the values of  $K_1$  and  $K_2$ . Although the magnitude of the association constants will vary considerably depending upon the nature of C\*, it is expected that the association constants for the two diastereomers will not be very different. In order to illustrate the kinds of results to be expected, we plot in Figure 1, the enantiomeric excess for a range of values in which  $K_1$  and  $K_2$  differ by 10%. For the calculations in this figure, it has been assumed that  $Ln_0 = 0.010$  M. As shown in this figure, for weak association, the dependence of the enantiomeric excess (and  $g_{lum}$ ) is approximately linear, however, for stronger association, a limiting value is obtained. In the

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**Figure 2.** Enantiomeric excess versus concentration of chiral Pfeiffer compound for different values for the outer-sphere association  $K_2$ .  $K_1 = 0.10 \text{ M}^{-1}$ ;  $L_{n0} = 0.010 \text{ M}$ .

limit of large concentrations of  $C^*$ , the concentration of free (*i.e.* unassociated) complex goes to zero. Substituting for  $[C^*]$  from eq 5 into eq 6, rearranging, and then taking the limit, we obtain the following result.

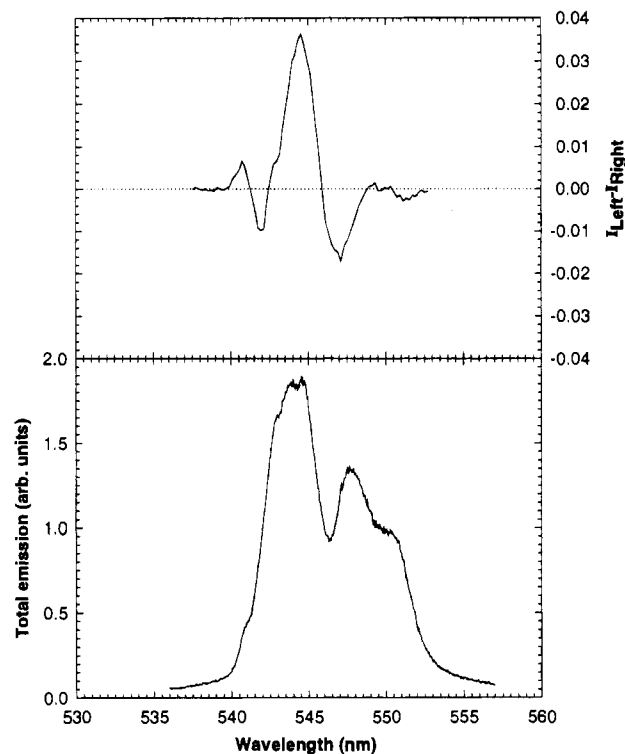
$$\eta = \frac{(L_{n0} - 2Ln)(K_2 - K_1)}{L_{n0}(K_2 + K_1)} = \frac{K_2 - K_1}{K_2 + K_1} \text{ (for } Ln \ll L_{n0}) \quad (8)$$

From this result, it is apparent that all of the plots in Figure 1 will approach the same limit (+0.0476) as the concentration of the chiral Pfeiffer compound is increased. In Figure 2 we show the dependence of the enantiomeric excess on the initial concentration of  $C^*$  for a range of  $K_2$  values assuming that  $K_1 = 0.1$ .

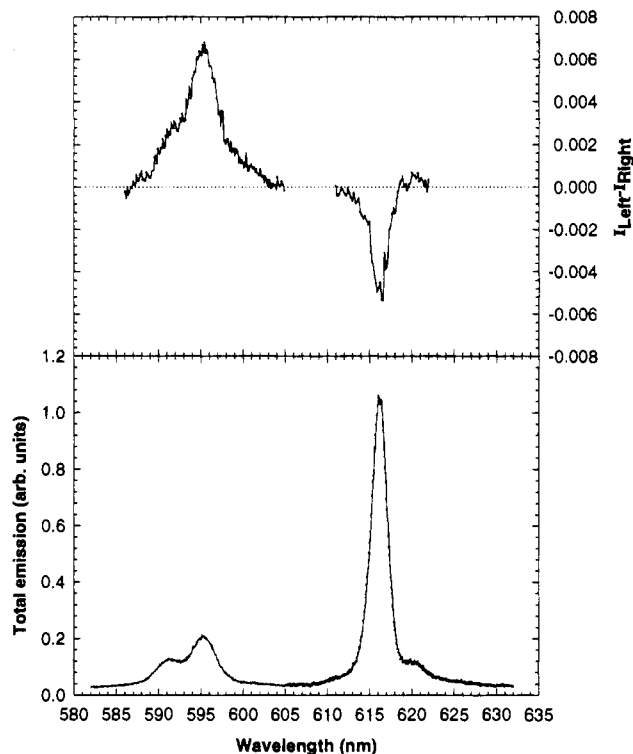
## Results and Discussion

Circularly polarized luminescence and total luminescence spectra for an aqueous solution of 0.01 M of  $\text{Tb}(\text{DPA})_3^{3-}$  and 1.90 M maltose is presented in Figure 3. The spectral region shown in this figure corresponds to the  $^5D_4 \rightarrow ^7F_5$  transition of Tb(III). This transition is known to be the most intense transition for this ion, and also, since it satisfies magnetic dipole selection rules, it is expected to be associated with large optical activity as measured by the dissymmetry ratio,  $g_{\text{lum}}$ .<sup>17</sup>  $\text{Tb}(\text{DPA})_3^{3-}$  has been shown to possess approximate  $D_3$  symmetry in the solid state; however, no circularly polarized luminescence is observed from a solution containing only  $\text{Tb}(\text{DPA})_3^{3-}$  under unpolarized or linearly polarized excitation due to the fact that the solution is racemic. CPL is observed under circularly polarized excitation because of differential absorption of the circularly polarized excitation beam by the  $\Delta$  and  $\Lambda$  enantiomers of this complex, generating a long-lived photoenriched excited state.<sup>18</sup> The CPL (and total luminescence) spectra shown in Figure 3 are identical in shape and relative magnitude to the spectra observed for the racemic solution of  $\text{Tb}(\text{DPA})_3^{3-}$ , indicating that the source of the optical activity in this case is due to a difference in concentration of the two enantiomers and not to the presence of a new species in solution.

In Figure 4 we show CPL and total luminescence spectra for



**Figure 3.** Circularly polarized luminescence ( $I_{\text{Left}} - I_{\text{Right}}$ ) and total luminescence spectra for a 0.010M solution of  $\text{Tb}(\text{DPA})_3^{3-}$  following the addition of 1.90 M maltose. The spectral region displayed corresponds to the  $^5D_4 \rightarrow ^7F_5$  transition of Tb(III).

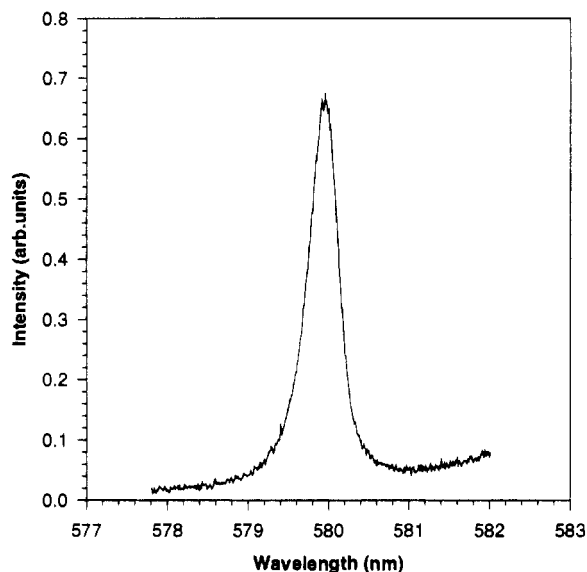


**Figure 4.** Circularly polarized luminescence ( $I_{\text{Left}} - I_{\text{Right}}$ ) and total luminescence spectra for a 0.010M solution of  $\text{Eu}(\text{DPA})_3^{3-}$  following the addition of 2.00 M maltose. The spectral region displayed corresponds to the  $^5D_0 \rightarrow ^7F_{1,2}$  transitions of Eu(III).

a solution of 2.00 M maltose and 0.01 M  $\text{Eu}(\text{DPA})_3^{3-}$ . The spectral region shown corresponds to the  $^5D_0 \rightarrow ^7F_1, ^7F_2$  transitions of Eu(III). These spectra are, again, identical to that obtained for solutions containing only  $\text{Eu}(\text{DPA})_3^{3-}$  excited by circularly polarized light as reported previously.<sup>18</sup> In general,

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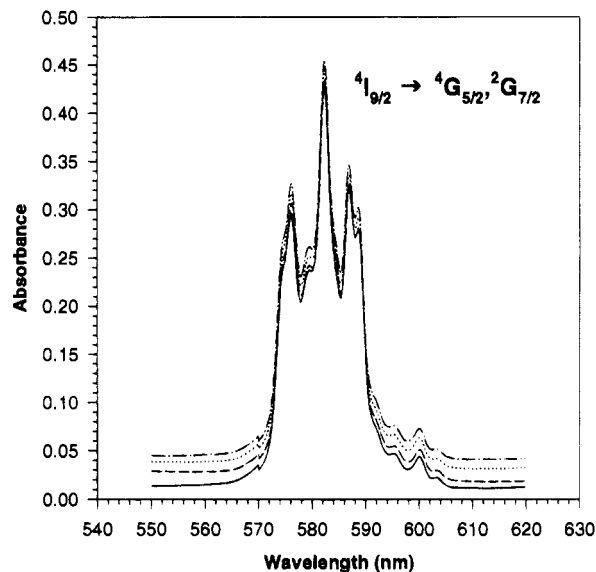
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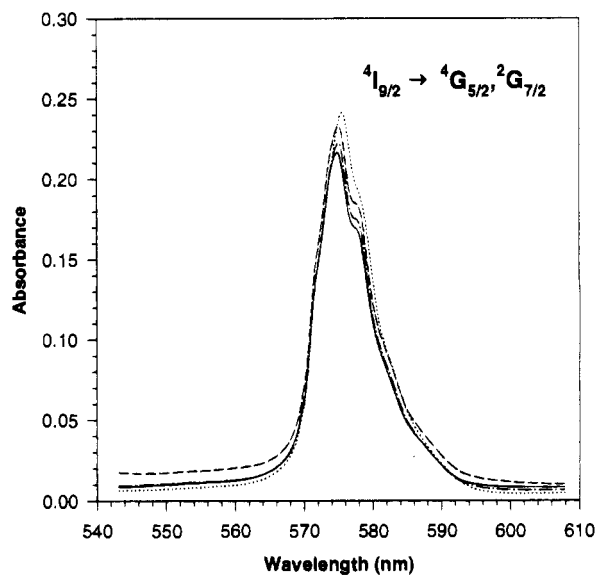
**Figure 5.** Wavelength selective excitation spectroscopy in the  ${}^7F_0 \rightarrow {}^5D_0$  region for a 0.010 M solution of  $\text{Eu}(\text{DPA})_3^{3-}$  following the addition of 2.00 M maltose. The total emission was monitored at 612 nm.

care must be taken in these types of experiments due to the lability of the ligands used and the fact that lanthanides have a variable coordination number. A particular concern is that the distribution of species in solution might be such that the strong total emission originates from one species, and the weak CPL is due to one or more minor species involving the added chiral compound. This has been observed previously<sup>19</sup> and makes the calculation of the dissymmetry ratio meaningless. Additional information concerning the nature of the emitting species may be obtained from wavelength selective excitation spectroscopy involving the  ${}^7F_0 \rightarrow {}^5D_0$  transition of Eu(III). In this experiment, the dye-laser excitation is scanned through the 578–582 nm region while monitoring the strong  ${}^5D_0 \rightarrow {}^7F_2$  emission at approximately 612 nm. In Figure 5 we show the results for such an experiment for a solution containing  $\text{Eu}(\text{DPA})_3^{3-}$  and maltose. Since both the ground and excited states are non-degenerate only one transition is expected for each species in solution. The observation of only one sharp peak in Figure 5 is consistent with the assumption that only one europium species is present in the solution.

Although the absorption coefficients of  $f \rightarrow f$  transitions are ordinarily very weak, it is possible to probe the coordination sphere of lanthanide ions through examination of electronic absorption spectra. It is commonly known, for example, that certain electronic transitions of lanthanide ions are especially sensitive to changes in the first coordination sphere. These so-called "hypersensitive transitions" are known to be associated with the selection rules  $\Delta J = \pm 2$  and  $\Delta S = 0$ .<sup>20</sup> In Figure 6 we plot the absorbance in the spectral region corresponding to the  ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$  transitions of Nd(III) for a solution containing only  $\text{Nd}(\text{DPA})_3^{3-}$  and for solutions into which sucrose, maltose, and fructose have been dissolved. Note that the spectra displayed have been offset so that they may be compared. When the spectra are superimposed they are virtually identical. Nd(III) ions has been selected for this experiment because the hypersensitive transitions for that ion have much higher extinction coefficients than that for the hypersensitive transition of Eu(III) ( ${}^7F_0 \rightarrow {}^5D_2$ ), thus reducing the error in the calculation of oscillator strengths. Figure 7 presents absorption spectra for the hypersensitive transition following the addition



**Figure 6.** Absorption spectra for the  ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$  transitions of Nd(III) for a 0.030 M solution of  $\text{Nd}(\text{DPA})_3^{3-}$  (—) and for solutions containing 1.706 M maltose (---), 2.818 M fructose (···), and 1.769 M sucrose (— · —). Note that the spectra have been offset for purposes of comparison.



**Figure 7.** Absorption spectra for the  ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$  transitions of Nd(III) for a 0.030 M solution of  $\text{NdCl}_3$  (—), and for solutions containing 1.730 M maltose (---), 3.271 M fructose (···), and 1.771 M sucrose (— · —).

of the three sugars to an aqueous solution of  $\text{NdCl}_3$ . In Table 1 we list the calculated oscillator strengths for these various samples. The  $P_{\text{exp}}$  values for solutions containing only  $\text{Nd}(\text{DPA})_3^{3-}$  and those in which the sugars were added are almost the same. These results support the conclusion that these sugars do not enter the first coordination sphere of lanthanide dipicolinate complex even when they are added in high concentrations. Some perturbations do take place when these sugars are added in high amounts into aqueous solution of  $\text{NdCl}_3$  as shown in the absorption spectra plotted in Figure 7, but even in this case they are not very large as can be seen from the tabulated oscillator strength values.

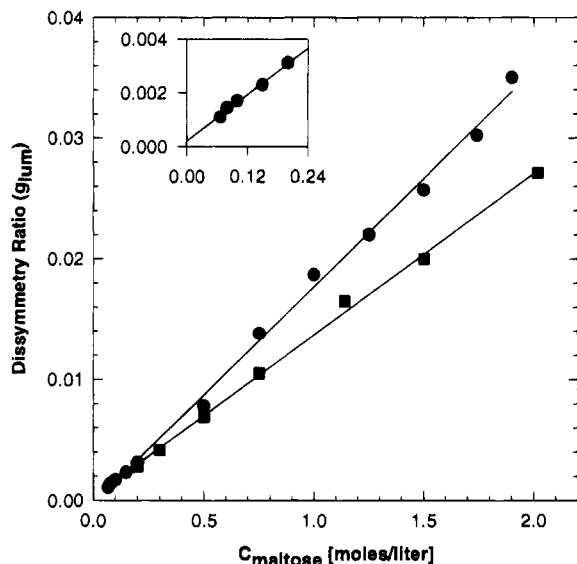
As described above, the different models for the Pfeiffer-effect predict a different concentration dependence for the equilibrium perturbation. For this reason, in Figure 8, we plot  $g_{\text{lum}}$  measured at 544.4 nm for  $\text{Tb}(\text{DPA})_3^{3-}$  and 595.3 nm for  $\text{Eu}(\text{DPA})_3^{3-}$  versus concentration of maltose. The results for

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**Table 1.** Oscillator Strength Values for <sup>4</sup>I<sub>9/2</sub> → <sup>4</sup>G<sub>5/2</sub>, <sup>2</sup>G<sub>7/2</sub> Transitions ([Nd(III)] = 0.03 M)

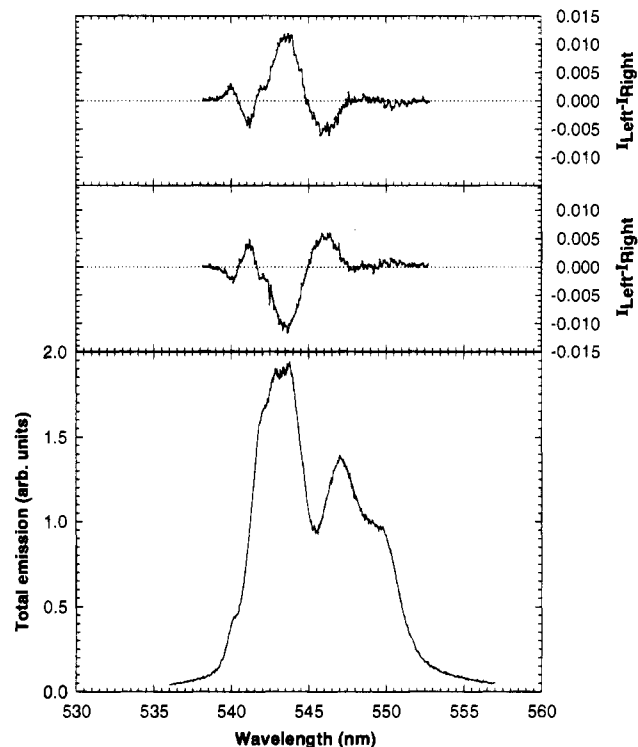
sugar	NdCl <sub>3</sub> + sugar				Nd(DPA) <sub>3</sub> <sup>3-</sup> + sugar			
	NdCl <sub>3</sub>	maltose	fructose	sucrose	Nd(DPA) <sub>3</sub> <sup>3-</sup>	maltose	fructose	sucrose
[sugar] (M)	0	1.730	3.271	1.771	0	1.706	2.818	1.769
<i>P</i> <sub>exp</sub> × 10 <sup>8</sup>	960.2	1020.1	1070.0	993.6	2516.7	2530.2	2483.3	2502.5

**Figure 8.** Plot of the luminescence dissymmetry ratio ( $g_{lum}$ ) at the peak wavelength of 544.4 nm for Tb(DPA)<sub>3</sub><sup>3-</sup> and 595.3 nm for Eu(DPA)<sub>3</sub><sup>3-</sup> as a function of added maltose. The insert corresponds to the low concentration results for Tb(DPA)<sub>3</sub><sup>3-</sup>.

low concentrations of maltose added to Tb(DPA)<sub>3</sub><sup>3-</sup> are enlarged in the insert in this figure. One must be careful in reporting  $g_{lum}$  values at a particular wavelength for these species, since changes in line-shape due to changes in the structure of the complex might be missed. In these studies complete CPL and total luminescence spectra were performed at regular intervals to ensure that no such changes were present. The solid lines in this figure are the results of a linear least-squares fit, and, as can be seen, the dependence is approximately linear throughout the entire concentration range. Obviously, for this system no limiting value for  $g_{lum}$  is obtained. As described above, this result is consistent with the assumption that the association of the sugars to the lanthanide complex is very weak.

In Figures 9–11 we show CPL results following the addition of several other sugars. Figures 9 and 10 are results for Tb(DPA)<sub>3</sub><sup>3-</sup>, and Figure 11 is for Eu(DPA)<sub>3</sub><sup>3-</sup>. A summary of the results for  $g_{lum}$  at the emission maximum for all solutions studied is presented in Table 2 for Tb(DPA)<sub>3</sub><sup>3-</sup> and in Table 3 for Eu(DPA)<sub>3</sub><sup>3-</sup>. In cases when the enantiomeric sugars were used the results were equal in magnitude, and opposite in sign. This is illustrated in Figure 9 for (+) and (–)-glucose added to Tb(DPA)<sub>3</sub><sup>3-</sup>. As can be seen in the tabulated data, for the same concentrations of sugars the magnitude of  $g_{lum}$  varies by a factor of 5. For each sugar in which the effect on the perturbation of the Tb(DPA)<sub>3</sub><sup>3-</sup> and Eu(DPA)<sub>3</sub><sup>3-</sup> equilibrium were examined, the sign of the measured dissymmetry ratios were identical.

Brittain has reported Pfeiffer-effect CPL results for Tb(DPA)<sub>3</sub><sup>3-</sup> for a fairly large number of sugars and related compounds with the goal of determining a structural correlation between some stereochemical aspect of the chiral sugars and the sign and magnitude of the CPL.<sup>13,14</sup> In one study it was reported that the sign of the CPL was correlated with the axial or equatorial position of the hydroxyl position at position 4 in a series of aldoses.<sup>13</sup> In this previous study the ratio of sugar to lanthanide complex was approximately 12:1.

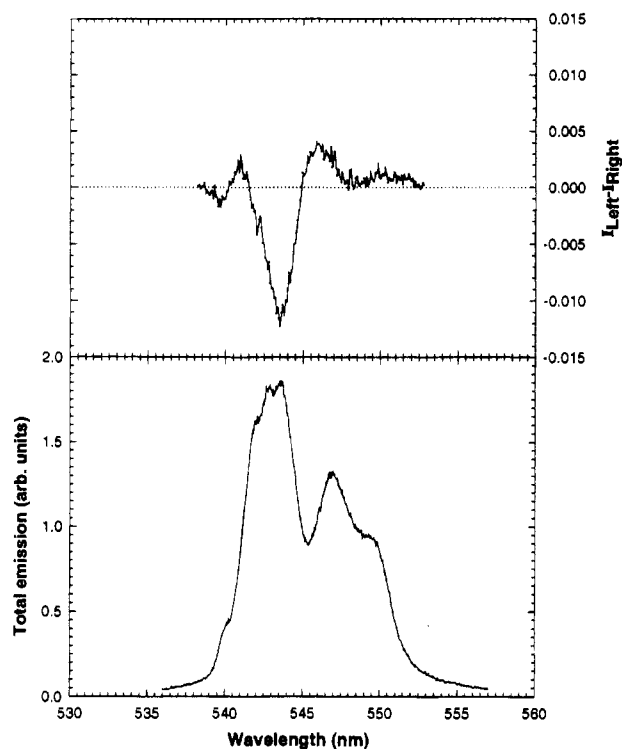
**Figure 9.** Circularly polarized luminescence ( $I_{Left} - I_{Right}$ ) and total luminescence spectra for a 0.010M solution of Tb(DPA)<sub>3</sub><sup>3-</sup> following the addition of 2.3 M D-glucose (upper plot) and L-glucose (middle plot).

In Table 4 we list the various sugars studied in this work and the sign of the measured luminescence dissymmetry factor. The completely digital instrument used to make the measurements reported here is significantly improved over the phase-sensitive detection systems used previously, especially for measurements of very small dissymmetry ratios for weakly luminescent systems.<sup>15</sup> For this reason, it is not completely unexpected that some of our results do not agree with those reported previously.<sup>13</sup> In particular, the sign of  $g_{lum}$  (and, as a result, the sign of  $\eta$ ) for addition of D-ribose and D-mannose to solutions of Tb(DPA)<sub>3</sub><sup>3-</sup> and Eu(DPA)<sub>3</sub><sup>3-</sup> is reversed. These changes affect the logic in the stereochemical correlation found in ref 13. Our examination of the sugar configurations and conformations and the direction of the equilibrium perturbation do not yield any stereochemical correlations for this system. It should be noted that, as expected, there is also no correlation between the sign of  $g_{lum}$  and the sign of the optical rotation.

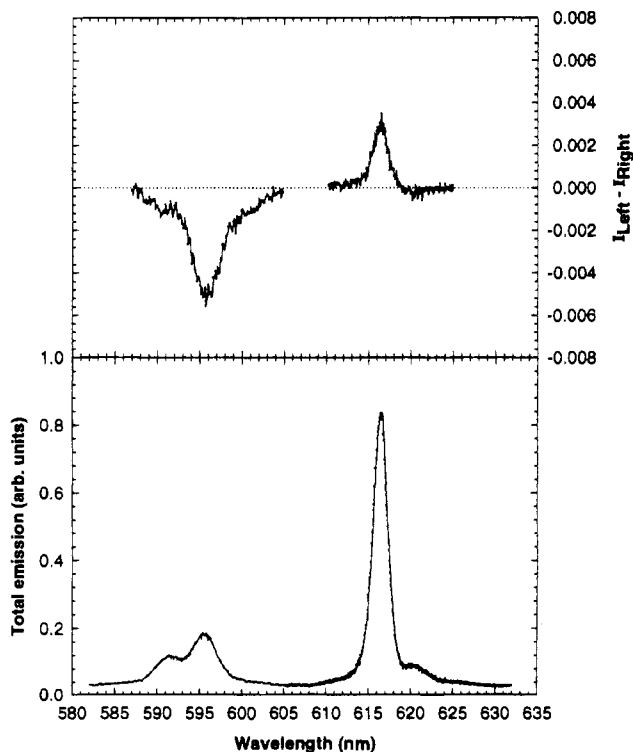
### Summary and Discussion

In addition to the equilibrium perturbation described here, and the generation of a nonracemic excited state by circularly polarized excitation, it is also possible in some cases to produce an enantiomeric excess by enantioselective quenching of an initially racemic excited state.<sup>21–24</sup> These experiments have been performed in both a steady-state and time resolved mode. In a

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**Figure 10.** Circularly polarized luminescence ( $I_{\text{Left}} - I_{\text{Right}}$ ) and total luminescence spectra for a 0.010M solution of  $\text{Tb}(\text{DPA})_3^{3-}$  following the addition of 2.00 M sucrose.



**Figure 11.** Circularly polarized luminescence ( $I_{\text{Left}} - I_{\text{Right}}$ ) and total luminescence spectra for a 0.010M solution of  $\text{Eu}(\text{DPA})_3^{3-}$  following the addition of 2.71 M fructose.

time-resolved enantioselective quenching experiment for  $\text{Tb}(\text{DPA})_3^{3-}$  using resolved  $\text{Ru}(1,10\text{-phenanthroline})_3^{2+}$  as the quencher, it has been possible to measure a limiting value  $g_{\text{lum}}$

**Table 2.** Luminescence Dissymmetry Factor,  $g_{\text{lum}}$  for  $\text{Tb}(\text{DPA})_3^{3-}$  (at 544.4 nm) as a Function of the Concentration of Various Sugars ( $[\text{Tb}(\text{III})] = 0.0010 \text{ M}$ )

[sugar] (M)	$g_{\text{lum}}(544.4 \text{ nm})$				
	maltose	fructose	galactose	sucrose	glucose
0.06	0.0011				
0.08	0.0014				
0.10	0.0017				
0.15	0.0024				
0.20	0.0031				
0.50	0.0075	-0.0027	-0.0017		
0.75	0.0138	-0.0064			
1.00	0.0187	-0.0083	-0.0061	-0.0041	0.0046
1.25	0.0220	-0.0103			
1.50	0.0257	-0.0126	-0.0100	-0.0076	0.0082
1.75	0.302	-0.0152		-0.0096	0.094
1.90	0.0361		-0.0121	-0.0118	0.0104
2.50		-0.0212	-0.0181		0.0133
2.90					0.0154
3.25					0.0171

**Table 3.** Luminescence Dissymmetry Factor,  $g_{\text{lum}}$  for  $\text{Eu}(\text{DPA})_3^{3-}$  (at 595.3 nm) as a Function of the Concentration of Various sugars ( $[\text{Eu}(\text{III})] = 0.01\text{M}$ )

[sugar] (M)	$g_{\text{lum}}(595.3 \text{ nm})$		
	maltose	fructose	sucrose
0.20	0.0028		
0.25		-0.0034	
0.30	0.0042		
0.50	0.0076	-0.0057	
0.75	0.0105		-0.0016
1.00		-0.0093	-0.0028
1.25	0.0181	-0.0117	-0.0040
1.50	0.0200	-0.0133	-0.0073
1.75		-0.0154	-0.0093
2.00	0.0271	-0.0168	-0.0107
2.50		-0.0211	
2.71		-0.0239	

**Table 4.** Sign of the Enantiomeric Excess for  $\text{Eu}(\text{DPA})_3^{3-}$  and  $\text{Tb}(\text{DPA})_3^{3-}$  following the Addition of Selected Sugars

sugar	specific rotation $[\alpha]_{\text{D}}^{20}$ (deg)	sign of $g_{\text{lum}}$
maltose	+136	+
lactose	+52.2	+
D-fructose	-92.3	-
D-galactose	+80.0	-
sucrose	+66.5	-
cellobiose	+35.0	-
D-glucose	+53.0	+
trehalose	+179.9	-
D-ribose	-21.5	-
D-xylose	+19.0	+
mellibiose	+129.5	-
L-sorbose	-43.1	+
D-arabinose	-105.0	+
D-mannose	+14.6	-

at the peak wavelength.<sup>21</sup> In this case the limiting value (-0.244) corresponds to the value for the pure  $\Delta$  enantiomer of  $\text{Tb}(\text{DPA})_3^{3-}$ . The identification of the precise enantiomer relies upon a series of measurements involving  $\text{Eu}(\text{DPA})_3^{3-}$  as described previously.<sup>10</sup> Using this result in eq 7 one can calculate the enantiomeric excess from the  $g_{\text{lum}}$  measurement. For example, from the data in Table 2, addition of 1.0 M maltose results in an enantiomeric excess of 7.7% of  $\Lambda$ - $\text{Tb}(\text{DPA})_3^{3-}$  whereas addition of 1.0 M sucrose yields a 1.7% excess of  $\Delta$ - $\text{Tb}(\text{DPA})_3^{3-}$ .

The equilibrium model we have used here to describe the concentration dependence of the enantiomeric excess is a simple one. Extension of the model to include multiple outer-sphere association may be performed, but such effects are not needed

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to explain the general results of this or earlier work. Such extensions, however, may be necessary for more quantitative comparisons. Furthermore, we have not analyzed the results reported here in terms of the models of Schipper in which the source of the equilibrium perturbation is attributed to a free energy of mixing.<sup>11</sup> In the dissociated model of Schipper a linear dependence of  $g_{lum}$  on the concentration of the Pfeiffer compound is also predicted; however, the underlying assumptions in this work concerning the nature of the solution structure do not appear to apply to our system.

As seen by Brittain in a number of related studies, and as predicted by eq 8, for medium to strong outer-sphere coordination, the enantiomeric excess approaches a limiting value as the concentration of Pfeiffer compound increases.<sup>7</sup> This author has used a limiting value of 0.022 in order to determine association constants for a number of different Pfeiffer-active compounds. As can be seen from eqs 6 and 7, for the model used here, the limiting  $g_{lum}$  value is not an intrinsic property of the lanthanide complex nor of the added chiral species, but rather reflects a limiting enantiomeric excess based upon the relative

difference in diastereomeric association constants. One expects, therefore, that different Pfeiffer-species will have different limiting values for  $g_{lum}$ , depending on the intimate details of the outer-sphere coordination. From the concentration dependence of  $g_{lum}$  and the limiting value, it should be possible to determine the individual diastereomeric association constants, although that is not possible in the case of the weakly associated sugars described here. Using the data plotted in Figure 8 and the value of 0.244 for  $g_{lum}$  for the pure  $\Delta$ -enantiomer, we can estimate an upper limit of approximately 0.2 for the value of the association constants for the range of sugars used in this work. Additional studies aimed at a more detailed understanding of the nature of the outer-sphere association complexes are underway.

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