

## Circularly Polarized Luminescence Studies of the Terbium(III) and Europium(III) Complexes with (*R*)-(-)-1,2-Propanediaminetetraacetic and (*R,R*)-*trans*-1,2-Cyclohexanediaminetetraacetic Acids

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Complex formation between lanthanide ions and chiral aminopolycarboxylate ligands was investigated by means of circularly polarized luminescence (CPL) spectroscopy. An examination of the pH dependence of the CPL spectra obtained for the Tb(III) and Eu(III) complexes revealed that a drastic configurational change of the ligand chelate system takes place between pH 10.5 and 11. The changes evident in the chiroptical spectra can be identified with the final deprotonation of the aminopolycarboxylate ligand and formation of hydroxide complexes within the LnY system. The optical activity of the (*R*)-(-)-1,2-propanediaminetetraacetic acid ((*R*)-(-)-PDTA) complex was significantly smaller than that of the (*R,R*)-(-)-*trans*-1,2-cyclohexanediaminetetraacetic acid ((*R,R*)-(-)-CDTA) complex, although the chirality did not appear to be additive. The CPL spectral line shapes within the f-f emission bands were similar for the two chelate systems (but not identical), thus indicating that the conformational properties of the chelate rings containing the dissymmetric atoms and the overall configurational chirality of the chelated metal ion are somewhat different in the two ligand systems.

### Introduction

While the optical activity associated with the d-d transitions of transition-metal complexes has received extensive study,<sup>2,3</sup> only recently have analogous studies of the optical activity within the f-f transitions of lanthanide compounds been carried out in comparable detail. The first report involving f-f optical activity involved measurement of the circular dichroism associated with lanthanide complexes of (*R*)-(-)-1,2-propanediaminetetraacetic acid (PDTA),<sup>4</sup> and since then a number of CD studies have been carried out on the lanthanide complexes of aminopolycarboxylate ligands.<sup>5-7</sup> Pearson et al. have described how the lanthanide ions may be titrated with (*R*)-(-)-PDTA<sup>8</sup> and (*R,R*)-(-)-*trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA),<sup>9</sup> with spectropolarimetry being used to detect the end point.

One of the problems associated with CD spectroscopy of lanthanide complexes is that, with the low absorptivity of f-f transitions, rather high concentrations of the compound are required to achieve reasonable signal/noise ratios. At these concentrations, it is not at all clear that the complexes are monomeric. Consequently, the trends found in the CD spectra may not necessarily be related to the stereochemistry of simple compounds but may instead reflect changes in the polynuclear association of the complexes.<sup>10</sup> However, one may obtain equally important chiroptical information from analysis of the luminescence of a chiral emitting system; thus, much lower concentrations of compound may be used. This new technique is termed circularly polarized luminescence (CPL) spectroscopy and involves measurement of the differential emission of left and right circularly polarized light by a chiral compound.<sup>11</sup>

In the present report, we detail the CPL spectra associated with the Tb(III) and Eu(III) complexes of (*R*)-(-)-PDTA and (*R,R*)-(-)-CDTA. The results represent the first determination of the excited-state optical activity associated with chiral lanthanide/aminopolycarboxylate complexes. However, due to the relatively nonbonding character of the f-f electron states, the results are expected to be directly comparable to those obtained from CD measurements of unexcited molecules. The pH dependence of the observed CPL spectra contains information regarding the conformation of the ligand existing in the varying types of protonated and hydroxylated complexes that exist at different pH values.

### Experimental Section

Tb(III) and Eu(III) stock solutions were prepared by dissolving weighed amounts of lanthanide oxide (Tb<sub>4</sub>O<sub>7</sub> or Eu<sub>2</sub>O<sub>3</sub>, 99.9% pure as obtained from Kerr-McGee) in the stoichiometric amount of HClO<sub>4</sub> with heating, neutralizing to pH 3 with NaOH, and then diluting to the desired volume. (*R*)-(-)-PDTA was prepared by a modified method of Dwyer and Garvan,<sup>12</sup> while (*R,R*)-(-)-CDTA was prepared according to Reinbold and Pearson.<sup>13</sup> The specific rotation of a 0.5% aqueous solution of (*R*)-(-)-PDTA was -47.0° at the sodium D line, while the specific rotation of an analogous solution of (*R,R*)-(-)-CDTA was found to be -53.4°; both values agree excellently with those reported in the literature.<sup>12-14</sup>

The lanthanide/aminopolycarboxylate complexes were prepared by mixing stock solutions of metal ion and ligand in a 1:1.25 mole ratio (the slight excess of ligand was used to insure full complexation of the lanthanide ions). The final Tb(III) concentration was 15 mM, while a concentration of 45 mM was required for the Eu(III) studies (this ion has a much lower quantum yield of emission). Sufficient NaClO<sub>4</sub> was added from a 0.5 M stock solution to ensure that the final ionic strength was 0.1. pH adjustment of the complex solutions was affected by adding microliter amounts of standard NaOH or HClO<sub>4</sub> directly to 3 mL of the sample solution in the fluorescence cuvette. The pH of the solutions was monitored on an Orion 701A pH meter (calibrated daily with phosphate buffers) by inserting a glass micro-combination electrode directly into the cuvette. For the observation of deprotonation behavior, all measurements were initiated at pH 1.5 and terminated near pH 12.75.

All CPL spectra were obtained on a high-resolution luminescence spectrometer.<sup>15</sup> The Tb(III) samples were excited by using a 200-W Hg-Xe arc lamp at 365 nm, while the Eu(III) complexes were excited at 301 nm. The UV excitation was selected by a 0.1-m grating

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monochromator and suitable glass filters. An excitation band-pass of 16 nm was used for all work, and an emission band-pass of 1 nm was sufficient to fully resolve all spectral features. All measurements were recorded in aqueous solution at room temperature.

### Results and Discussion

Excitation of Tb(III) and Eu(III) complexes in the near-UV region of the spectrum results in population of the luminescent  $^5D_4$  and  $^5D_0$  levels, respectively. The emission from these excited states consists of a sequence of transitions to the spin-orbit-split components of the  $^7F_J$  ground state. If we label the transitions by the appropriate  $J$  quantum numbers, the observed Tb(III) emission bands are the 4-6 (490 nm), 4-5 (545 nm), 4-4 (580 nm), and 4-3 (620 nm) bands. The Eu(III) luminescence bands studied are the 0-0 (580 nm), 0-1 (595 nm), 0-2 (615 nm), and 0-3 (650 nm) bands. For the Tb(III) complexes, the most intense transition is 4-5, while the 0-2 band is the most intense with the Eu(III) complexes. The identification of the various emission bands is quite straightforward, since covalency in the bonding is essentially nonexistent and the band positions are hardly shifted from the corresponding free-ion values.

The presence of a 0-0 luminescence band at 580 nm indicates that the metal ion site symmetry is significantly lower than octahedral. In  $O_h$ ,  $D_{3h}$ , or  $D_3$  symmetry, a transition from the excited  $^5D_0$  level to the ground-state  $^7F_0$  level is both electric and magnetic dipole forbidden. Lowering the symmetry still lower to either  $C_{3h}$  or  $C_{3v}$  relaxes the selection rules to such an extent that the transition can gain either magnetic ( $C_{3h}$ ) or electric ( $C_{3v}$ ) dipole allowedness. This allowedness arises from  $J$ - $J'$  mixing induced by the crystal field, and this mixing is promoted by axial terms in the crystal field Hamiltonian. Total removal of axial symmetry in the metal complex (obtained by placing the lanthanide ion in a site of very low symmetry) can lead to an increase in the intensity of the 0-0 band by adding more terms to the crystal field potential. The transition can actually become either magnetic or electric dipole allowed (depending on the point group) as a result of the descent in symmetry.

It was found that the total luminescence (TL) intensity of the aminopolycarboxylate complexes varied significantly with the pH of the solution. For a given metal ion, it was observed that all bands exhibited approximately the same variation in TL with pH, and it was also found that the trends exhibited by the Tb(III) and Eu(III) complexes were essentially the same. This dependence of TL on pH is illustrated in Figure 1 for the 4-5 transitions of the Tb/PDPA and Tb/CDTA complexes.

The trends shown in Figure 1 can be interpreted in terms of the known chemistry of the aminopolycarboxylate ligands. The first inflection observed is complete by pH 3, and examination of the acid dissociation constants of the ligands and formation constants of the lanthanide complexes<sup>16</sup> indicates that the formation of the  $LnHY$  complexes ( $Y$  = any aminopolycarboxylate ligand) is essentially complete even at these low pH values. It is known that lanthanide ions may be titrated at these low pH values and that the metal ion assists in the deprotonation of the ligand. The TL intensity remains quite constant until pH 10, even though formation of the  $LnY^-$  complex (after one more ligand deprotonation) is probably complete by pH 8.<sup>16</sup> This lack of a change in some experimental feature over this pH range has found a parallel in NMR studies of the acetate protons,<sup>17</sup> but spectra investigations of the  $4f \rightarrow 5d$  transitions of Ce(III) and Tb(III) complexes do exhibit features that indicate the presence of a change in the metal ion coordination sphere related to the deproton-

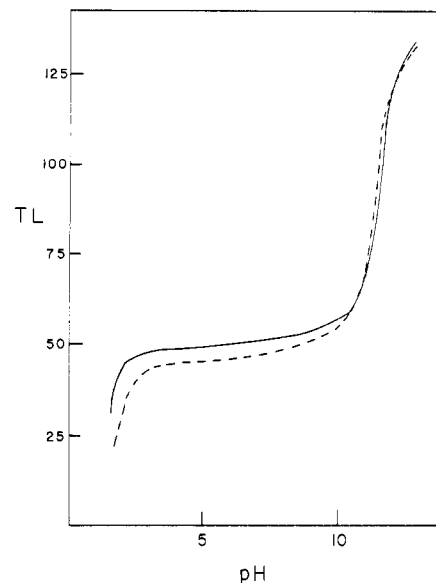


Figure 1. pH dependence of the total emission associated with the  $^5D_4 \rightarrow ^7F_5$  luminescence band systems of Tb/PDPA (solid line) and Tb/CDTA (dashed line). The intensity scale is in arbitrary units.

ation.<sup>18</sup> Proton magnetic resonance studies performed in this pH region have shown that the lifetime of the metal-oxygen bonds is short on the NMR time scale, while the lifetime of the metal-nitrogen bonds is long in the same time frame.<sup>19</sup>

The TL intensity increases rapidly at pH greater than 10 and appears to reach a limiting value at pH 13. In examinations of the kinetics of ligand-exchange reactions of (*R*)-(-)-PDPA and (*R,R*)-(-)-CDTA complexes, Pearson et al.<sup>13,20</sup> have found that at very high pH the existence of monohydroxy species must be taken into account. These monohydroxy complexes have been studied by other groups<sup>21</sup> and are formed by deprotonation of water molecules coordinated to the lanthanide ions in the  $LnY^-$  complexes. Therefore, the formation of the hydroxide species is apparently responsible for the sudden increase in TL intensity at high pH.

The sharp rise in luminescence quantum yield is probably due to increased protection of the metal ion from solvent quenching, which is the major cause of nonradiative deactivation of lanthanide excited states in solution. The efficiency of O-H oscillators as quenchers of lanthanide emission has been studied in detail.<sup>22</sup> Formation of a layer of ligand insulation and the possible ejection of one or more water molecules should accompany the formation of the  $LnY^-$  complexes and the consequent formation of two long-lived metal-nitrogen bonds. One might expect that formation of a hydroxy complex might actually lead to a decrease in emission intensity, but it is vital to remember that formation of the hydroxy complex actually is accompanied by a decrease in the number of OH oscillators in the vicinity of the Tb(III) or Eu(III) ions since these form via deprotonation of coordinated water molecules.

While the TL spectra associated with the 4-5 transition of the Tb(III) complexes mostly increased in intensity in the very high pH region (and did not display a great deal of variability in line shape), the TL associated with the 0-1 and 0-2 transitions of the Eu(III) complexes underwent a splitting at pH 10.4, which is in the pH region associated with large increases in TL intensity. At the same time, the 0-0 band diminished

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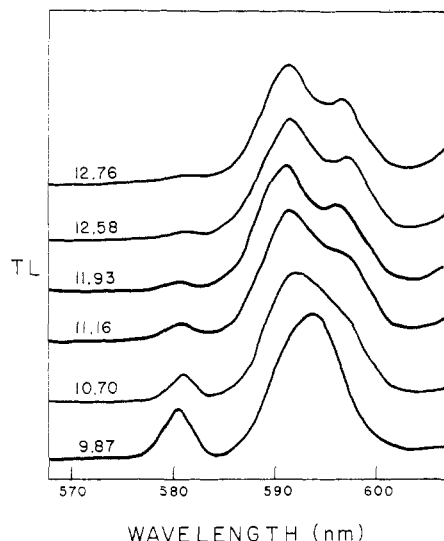
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**Figure 2.** Splitting of the  ${}^5D_0 \rightarrow {}^7F_1$  and disappearance of the  ${}^5D_0 \rightarrow {}^7F_0$  luminescence bands of Eu/PDTA at elevated pH values.

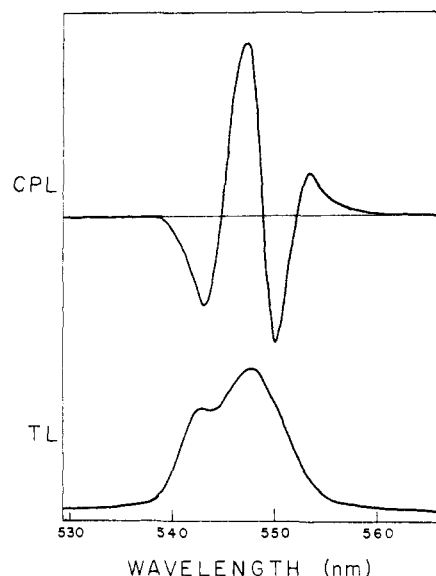
in intensity as the pH was increased, as has been illustrated in Figure 2 for the Eu/PDTA complex (line shape changes for the 0-0 and 0-1 band systems are shown). These trends indicate that formation of the hydroxy complexes is accompanied by significant changes in the complex configuration. The loss of intensity within the 0-0 transition indicates that the mechanism that permits this transition to be observed has essentially ceased to operate and would indicate a reversion to a reasonably symmetric (as far as the lanthanide ions are concerned) species. As shall be shown shortly, the chiroptical investigations also indicate the presence of configurational changes within this pH region, but the presence of optical activity signifies that the complex cannot contain any improper axes of rotation. Thus, when we speak of a highly symmetric lanthanide ion, we are referring only to the immediate coordination sphere of the metal and not to the overall symmetry of the complex.

A preliminary analysis of the intermolecular energy transfer between Tb(III) and Eu(III) complexes of ethylenediaminetetraacetic acid in this high-pH region indicates that polynuclear association of the complexes is negligible.<sup>23</sup> This result implies that the complexes remain monomeric even when the monohydroxy complexes form and that the spectral data apply to complexes whose geometry can be described with some degree of accuracy. The results also indicate that the spectral changes observed at high pH are not due to intermolecular processes but instead have their origin in intramolecular effects.

Optical activity is observed within the luminescence spectra of the Tb(III) and Eu(III) complexes within the entire pH region studied (1.5-13.0). The CPL spectra of the Eu(III) complexes proved much more difficult to study due to the relatively low emission quantum yields of these complexes, and as a result data were only obtainable in the 0-1 and 0-2 band systems. With the Tb(III) complexes, only the 4-5 band yielded useful signal/noise ratios over the entire pH region, but at very high pH values good spectra could be obtained for the 4-6, 4-4, and 4-3 bands.

Two phenomena are generated during the course of a CPL measurement, with the TL and CPL signals being obtained in proportional arbitrary units. The data can be placed on an absolute basis by taking the ratio of these quantities; this quotient is termed the luminescence dissymmetry factor

$$g_{\text{lum}} = \Delta I / (I/2) \quad (1)$$



**Figure 3.** TL (lower) and CPL (upper) spectra associated with the  ${}^5D_4 \rightarrow {}^7F_5$  transition of Tb/PDTA at pH 4.7.

and this factor may be related to the rotational strength of the optically active transition.<sup>11</sup> The TL intensity is defined as

$$I = I_L + I_R \quad (2)$$

while the CPL intensity is given by

$$\Delta I = I_L - I_R \quad (3)$$

In eq 2 and 3,  $I_L$  and  $I_R$  represent the emitted intensities for left and right circularly polarized light, respectively.

As Richardson has pointed out,<sup>24</sup> only the 4-5 transition of Tb(III) is well suited for the study of CPL, and only the 0-1 and 0-2 transitions of Eu(III) are equally useful. All the other possible luminescence bands of these two ions either possess too little intrinsic optical activity as a result of their orbital properties or do not display sufficient TL intensity as to yield reasonable signal/noise ratios. As a result, only data regarding the above-mentioned bands will be discussed hereafter. It may be seen that interpretation of the Eu(III) data is inherently much simpler than interpretation of analogous Tb(III) results, since the spectroscopy of the Eu(III) ion is far less complicated than the spectroscopy of the Tb(III) ion.

While the results obtained from TL measurements are useful, considerably more information is available in the CPL spectra. The pH dependence of the observed CPL line shapes followed the general trends established for the TL spectra: the optical activity increases rapidly up to pH 2.25, where a specific line shape and magnitude is held constant until pH 10. Above this pH, the CPL intensity (as measured by the luminescence dissymmetry factor) does not increase drastically (as did the TL) but instead undergoes sign inversions and peak splittings indicative of substantial conformational and configurational changes within the ligand ring system.

The low- and high-pH line shapes associated with the 4-5 transition of Tb/PDTA are shown in Figures 3 and 4, while analogous spectra for the 0-1 and 0-2 bands of Eu/PDTA may be seen in Figures 5 and 6. It may be observed that the Tb(III) spectra do not provide the dramatic evidence for the complex formation that is seen with the Eu(III) complexes; while the 547-nm peak of the 4-5 Tb(III) transition merely splits as a result of formation of the TbOHY complex, the CPL of the 0-1 band system undergoes a radical change. The weak CPL observed within the 591-nm Eu(III) band completely

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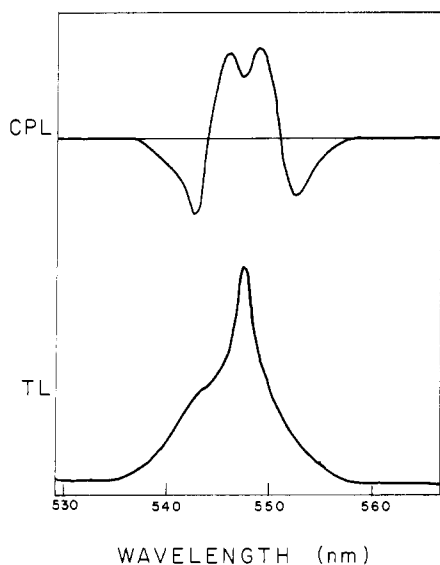


Figure 4. TL (lower) and CPL (upper) spectra associated with the  $^5D_4 \rightarrow ^7F_5$  transition of Tb/PDTA at pH 12.6.

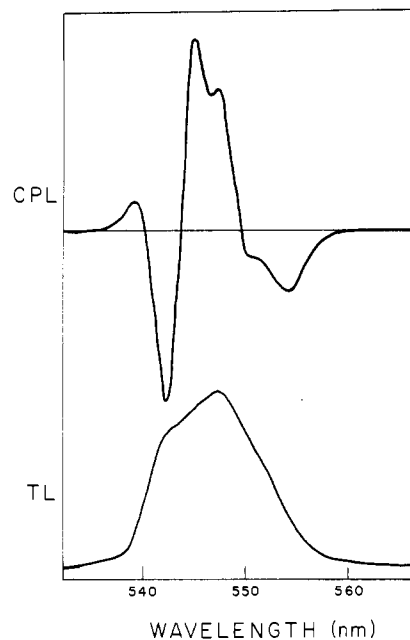


Figure 7. TL (lower) and CPL (upper) spectra associated with the  $^5D_4 \rightarrow ^7F_5$  transition of Tb/CDTA at pH 3.9.

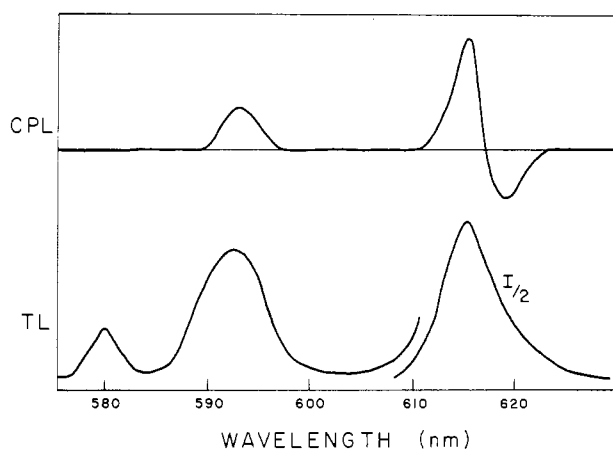


Figure 5. TL (lower) and CPL (upper) spectra associated with the  $^5D_0 \rightarrow ^7F_1$  and  $^5D_0 \rightarrow ^7F_2$  transitions of Eu/PDTA at pH 4.1.

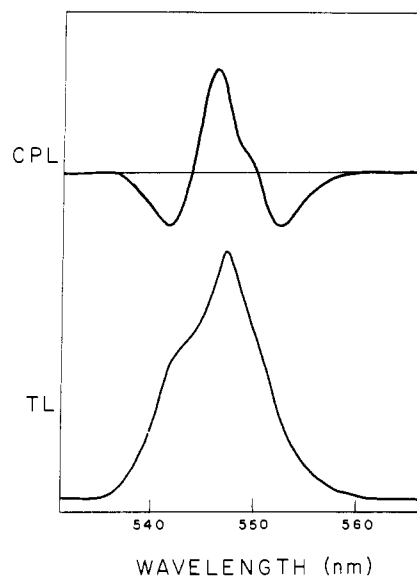


Figure 8. TL (lower) and CPL (upper) spectra associated with the  $^5D_4 \rightarrow ^7F_5$  transition of Tb/CDTA at pH 12.2.

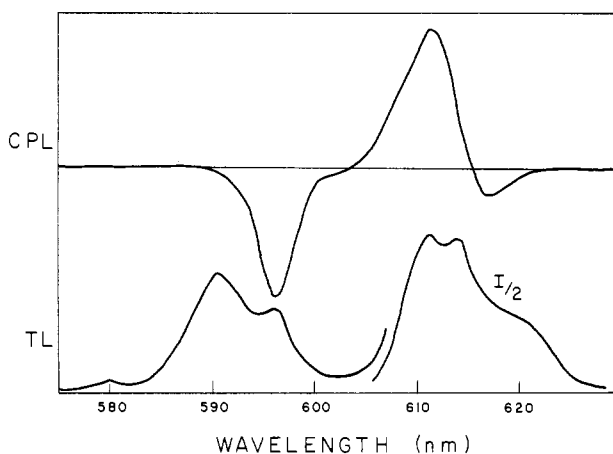


Figure 6. TL (lower) and CPL (upper) spectra associated with the  $^5D_0 \rightarrow ^7F_1$  and  $^5D_0 \rightarrow ^7F_2$  transitions of Eu/PDTA at pH 12.4.

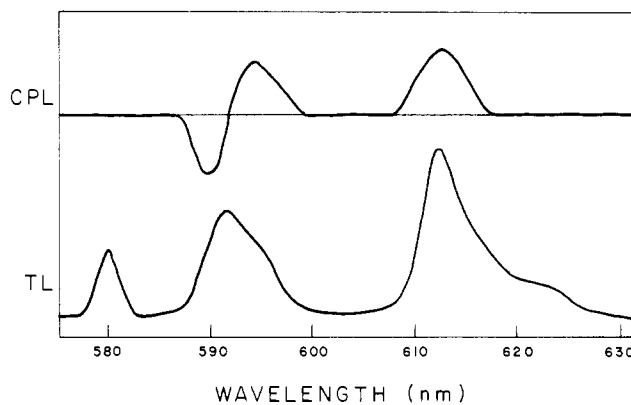
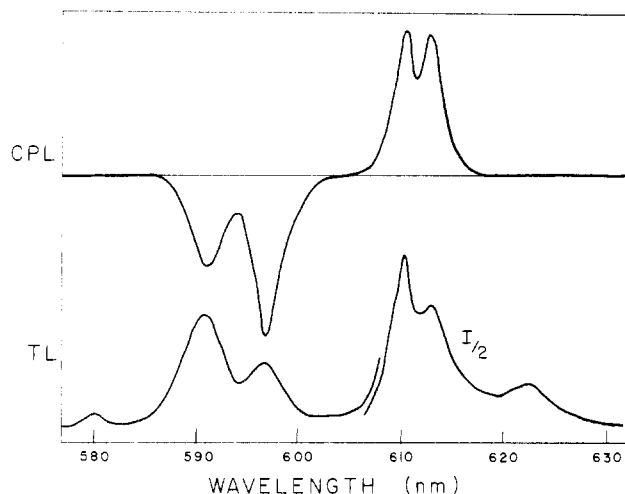


Figure 9. TL (lower) and CPL (upper) spectra associated with the  $^5D_0 \rightarrow ^7F_1$  and  $^5D_0 \rightarrow ^7F_2$  transitions of Eu/CDTA at pH 3.7.

vanishes above pH 11 and is replaced by CPL of the opposite sign, but the CPL is only observed within the new peak appearing at 597 nm.

A similar situation is noted with the CDTA complexes. Here, the degree of optical activity is much stronger than with the PDTA complexes, and this observation is undoubtedly due to the fact that the CDTA ligand has two centers of dissym-

metry. The CPL spectra observed at low and high pH for the Tb/CDTA complexes are shown in Figures 7 and 8; it may



**Figure 10.** TL (lower) and CPL (upper) spectra associated with the  $^5D_0 \rightarrow ^7F_1$  and  $^5D_0 \rightarrow ^7F_2$  transitions of Eu/CDTA at pH 12.1.

**Table I.** Luminescence Dissymmetry Factors within the  $^5D_4 \rightarrow ^7F_5$  Band System of the Tb(III) Complexes

wavelength, nm	$10^2 g_{lum}$		wavelength, nm	$10^2 g_{lum}$	
	low pH	high pH		low pH	high pH
(a) (R)-(-)-PDTA Complex					
543	-2.03	-2.08	549.5	-2.78	+1.58
546.5	<i>a</i>	+1.49	553	+2.91	-2.38
547.5	+2.72	<i>a</i>			
(b) (R,R)-(-)-CDTA Complex					
539.5	+3.44	<i>a</i>	547.5	+4.51	4.65
542.5	-7.20	-4.46	553	-1.30	-7.10
545.5	+6.53	<i>a</i>	554.5	-8.63	<i>a</i>

<sup>a</sup> No TL or CPL peak was observed at this wavelength.

be observed that while these do bear a superficial resemblance to the PDTA spectra, the different overall configuration of the aminopolycarboxylate ring does yield a differing line shape. The spectra obtained for Eu/CDTA are shown in Figures 9 and 10; these are seen to be significantly different from those obtained for the corresponding PDTA complex. At high pH, the same splitting in the 0-1 TL and CPL is observed (with the loss of the 0-0 emission), but now it is found that both TL components contain optical activity.

The chiroptical data provide strong evidence that essentially no conformational or configurational changes accompany deprotonation of the LnHY complex but do demonstrate that extensive changes in the metal ion coordination sphere accompany formation of the LnOHY complex. An examination of the pH dependence of the luminescence dissymmetry factors reveals that the degree of optical activity observed in all complexes is virtually constant from pH 2.5 to 9.5 and that the new CPL line shapes developed above pH 10.5 are constant in magnitude up to at least pH 12.75. The dissymmetry factors observed in these limiting situations have been collected in Table I for the Tb(III) complexes and Table II for the Eu(III) complexes.

The optical activity of a metal ion in a coordination complex is usually thought to arise from three main contributions: (a) the vicinal effect (chirality due to the presence of a dissymmetric atom in the ligand), (b) the conformational effect (chirality engendered by the presence of a dissymmetric atom in a chelate ring, thus rendering the ring dissymmetric on the whole if the ring is not planar), and (c) the configurational effect (chirality due to a dissymmetric placement of chelate rings about a metal ion). It is possible to observe optical activity in inert transition-metal complexes containing ethy-

**Table II.** Luminescence Dissymmetry Factors within the  $^5D_0 \rightarrow ^7F_1$  and  $^5D_0 \rightarrow ^7F_2$  Band Systems of the Eu(III) Complexes

wavelength, nm	band syst	$10^2 g_{lum}$	
		low pH	high pH
(a) (R)-(-)-PDTA Complex			
590.5	0-1	<i>a</i>	0.00 <sup>b</sup>
592.5	0-1	-1.84	<i>a</i>
596	0-1	<i>a</i>	-8.89
611	0-2	<i>a</i>	+2.49
614	0-2	<i>a</i>	0.00
615.5	0-2	+1.99	<i>a</i>
617.5	0-2	<i>a</i>	-0.833
619	0-2	-2.02	<i>a</i>
(R,R)-(-)-CDTA Complex			
590	0-1	-4.50	<i>a</i>
591.5	0-1	0.00	-6.79
594.5	0-1	+3.66	<i>a</i>
596.5	0-1	<i>a</i>	-21.18
610.5	0-2	<i>a</i>	+3.64
612.5	0-2	+2.11	+4.99

<sup>a</sup> No TL or CPL peak was observed at this wavelength.

<sup>b</sup>  $g_{lum} = 0.0$  implies that a TL peak was observed but that its CPL was zero.

lenediaminetetraacetate as a result of the configurational effect,<sup>3</sup> but the very labile nature of the lanthanide complexes effectively insures that any configurational effect be minor at most. Nevertheless, it is quite possible that even a small configurational effect could be equal in magnitude to a merged sum of vicinal and conformational effects and thus cannot be excluded without evidence indicating its absence.

It is significant to note that the dissymmetric atoms in the chelates are contained within the ring system which includes the metal-nitrogen bonds. Magnetic resonance studies have identified these bonds as being long-lived on the NMR time scale,<sup>19</sup> and for lanthanide complexes at the end of the series dissociation of the metal-nitrogen bond has been identified as the rate-determining step in ligand exchange between bound and free EDTA.<sup>25</sup> For the luminescent state of the aminopolycarboxylate complexes to be chiral, the chelate ring containing the dissymmetric atoms would have to exist during the lifetime of the excited state (about 200  $\mu$ s for the Eu(III) complex and 600  $\mu$ s for the Tb(III) complex).

The optical activity associated with the f-f transitions of the lanthanide complexes of (R)-(-)-PDTA and (R,R)-(-)-CDTA has been shown to be simpler to interpret with use of CPL spectroscopy, relative to the more conventional chiroptical methods (CD or ORD spectroscopies). Less overlap in the band systems and fewer peaks appearing in the luminescence spectra (and good signal/noise ratios) clearly permit CPL spectroscopy to be the technique most suited for the study of chiral lanthanide compounds. These features make it possible to correlate the observed spectral trends with plausible features of the solution-phase stereochemistry and ligand bonding. The luminescence studies have demonstrated the presence of significant configurational changes taking place at high pH values, and the CPL studies contain information regarding the stereochemical nature of these changes. The sign inversions observed within the 0-1 band system of the Eu(III) complexes provide strong evidence that the absolute configuration of the metal ion changes upon formation of the hydroxy complexes.

The sensitivity of CPL spectroscopy to conformational and configurational changes of bound chiral aminopolycarboxylate ligands is currently the focus of further studies, and the results of these will be reported in due course.

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