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Spectroscopic Studies of Lanthanide Ion Binding to Multidentate Ligands in Aqueous Solution. 3. Optically Active Tb(EHPG)$(L)_n$ and Tb$(DPA)_m(L)_n$ Complexes

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The optical activity induced by chiral ligands (L) coordinated to achiral terbium(III) complexes of *N,N'*-ethylenebis-(α-(*o*-hydroxyphenyl)glycine) (EHPG) and dipicolinic acid (DPA) in aqueous solution is studied by circularly polarized luminescence (CPL) spectroscopy. CPL/emission measurements are reported for experiments in which the following were varied: (1) solution pH, (2) chiral ligand type, and (3) molar ratios of Tb^{3+}, achiral ligand (EHPG or DPA), and chiral ligand (L). In all experiments terbium luminescence was excited via the following pathway: (1) near-ultraviolet excitation of the EHPG or DPA ligands followed by (2) nonradiative energy transfer to Tb^{3+}. CPL/emission spectra are reported that demonstrate the binding of a variety of chiral ligand types to Tb(EHPG) and Tb$(DPA)_m$ complexes under variable solution conditions. These spectra are interpreted in terms of the relative ligand chelation properties, the pH dependence of ligand binding, and the structural origins of ligand-induced terbium optical activity.

Introduction

Our previous studies on the spectroscopic properties of lanthanide complexes in aqueous solution have focused on two separate, but related, issues. On one hand we have been interested in elucidating the mechanisms whereby the lanthanide 4f-4f transitions acquire optical activity when the lanthanide ion is complexed to chiral ligands and in characterizing the chelate structural features responsible for generating this optical activity.[1-5] On the other hand, we have employed a variety of optical spectroscopic techniques to investigate the stepwise formation of lanthanide complexes as a function of solution pH and to determine the stoichiometries and total coordination numbers of these complexes.[6-8] The principal techniques used in these latter studies have been terbium (Tb^{3+}) and europium (Eu^{3+}) luminescence intensity and lifetime measurements (carried out in H_2O-D_2O solvent mixtures) and, when the complexes included one or more chiral ligands, circular polarization of luminescence (CPL) measurements.

In the present study we examine the optical activity generated by chiral ligands (L) in mixed-ligand complexes of the types Tb(EHPG)$(L)_n$ and Tb$(DPA)_m(L)_n$, where EHPG refers to *N,N'*-ethylenebis(α-(*o*-hydroxyphenyl)glycine) and DPA refers to dipicolinic acid. The structures of the EHPG and DPA ligands are shown in Figure 1, and the proper (IUPAC) names for these molecules are given in the caption to Figure 1. Among the chiral ligands (L) investigated in this study are camphorsulfonic acid, malic acid, tartaric acid, ascorbic acid, mandelic acid, aspartic acid, glutamic acid, (*p*-hydroxyphenyl)glycine, uridine, inosine, penicillin G, and a series of simple sugars and sugar acids. The EHPG ligand contains two chiral centers (asymmetric carbon atoms) in its structure, but in the present study only racemic EHPG was used.

The stepwise formation and structure of 1:1 Tb^{3+}-EHPG complexes in aqueous solution have recently been studied in this laboratory.[7] As solution pH is raised incrementally from 1.5 to ~8.0, the Tb^{3+} binds first the two ligand carboxylate groups, then the two ligand amino groups, and finally the two ligand phenolate groups. By pH 8.0, the EHPG ligand is bound hexadentately to the terbium ion, and the total coordination number of the fully formed 1:1 Tb(EHPG) complex was determined to be 8 (six coordination sites occupied by EHPG ligating groups and two occupied by bound water molecules). The characterization of the stepwise formation and structure of the 1:1 Tb(EHPG) complex was accomplished with use of potentiometric titration data, terbium emission lifetime and intensity measurements in H_2O-D_2O solutions of variable $[H_2O]$:$[D_2O]$ compositions, and near-ultraviolet excitation spectra of terbium luminescence.

The fully formed Tb(EHPG) complex is of special interest for a number of reasons. First, the nature of the ligating groups and the size and shape of the binding site are similar to what one might expect at the lanthanide ion binding site (pocket) of a protein molecule.[9] Second, the existence of an aromatic near-ultraviolet chromophore in the coordination sphere makes possible sensitization and enhancement of terbium luminescence via aromatic chromophore-to-Tb^{3+} radiationless energy-transfer processes when the complex is irradiated in the near-ultraviolet absorption region of the aromatic moiety. This latter excitation mode exploits the high absorptivity of the aromatic chromophore and eliminates the necessity of using extremely high excitation powers to excite the weakly absorbing Tb^{3+} directly. In the Tb(EHPG) complex, the phenolate groups act as very effective energy donors to the Tb^{3+} ion when excited around 290 nm.[7] Finally, the eight-coordinate nature of the Tb(EHPG)-aquo complexes suggests that two coordination sites are available for binding ligands that are strong enough to displace bound water molecules. It is possible, then, for a Tb(EHPG) complex to bind an optically active ligand in a bidentate chelation mode.

The stepwise formation and structural properties of Tb$(DPA)_m$ complexes in aqueous solution are less well characterized than are those of Tb(EHPG), although a series of recent studies by Brittain have shed considerable light on this problem.[10,11] Brittain prepared a series of Tb$(DPA)_m(L)_n$ systems (where L = malic acid or an amino acid) in aqueous solution by codissolving $Tb(ClO_4)_3$, DPA, and L in water and then varying the solution pH. In the case of L = alanine, he succeeded in precipitating a series of solids (at different solution pH values), which elemental analysis showed to have the formula structures Tb(DPA)·$6H_2O$, Tb$(DPA)_2$(Ala), and Tb$(DPA)_3$(Ala). Brittain then used circular polarization of luminescence (CPL) measurements in the $^5D_4 \rightarrow {}^7F_5$ terbium

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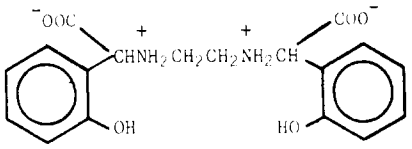
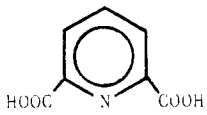


EHPG



DPA

Figure 1. Structures of the EHPG and DPA ligand molecules. EHPG = *N,N'*-ethylenebis(α-(*o*-hydroxyphenyl)glycine) *or* *N,N'*-bis(2-hydroxyphenyl)ethylenedinitrilo-*N,N'*-diacetate. DPA = dipicolinic acid *or* pyridine-2,6-dicarboxylic acid.

emission region to probe the structures of the $Tb(DPA)_m(L)_n$ systems in aqueous solution as a function of pH.

The DPA ligand, like EHPG, also contains a strongly absorbing near-ultraviolet chromophore, which, when DPA is bound to Tb^{3+}, acts as an efficient energy donor in a DPA-to-Tb^{3+} radiationless energy-transfer process. Bound DPA ligands, then, both sensitize and enhance the terbium luminescence.

The principal focus of the present study is on lanthanide optical activity as measured by terbium circular polarization of luminescence (CPL). Our previous studies[1-4] of terbium CPL in aqueous solution were carried out on systems in which only Tb^{3+} and the chiral ligands were present (in varying concentration ratios and at various solution pH values). Although the pH dependence of the CPL spectra obtained for these systems yielded clues regarding unidentate, bidentate, and (in a few cases) terdentate binding of ligands, little information could be deduced regarding the relative importance of mono-, bis-, or trischelation modes. For this reason, little could be said about what structural aspects of the ligand environment are most responsible for the observed CPL spectral features. Unlike transition-metal optical activity studies where structural contributions to the observed chiroptical properties can often be attributed to separately discernible chelate *configurational*, ligand *conformational*, or asymmetric site *vicinal* effects,[12] studies of lanthanide optical activity have produced few definitive spectra–structure relationships. The $Tb(EHPG)(L)_n$ complexes afford the opportunity to study the optical activity generated by just one chiral ligand (bound bidentately) or two chiral ligands (each bound unidentately) in a complex whose structural features are relatively well characterized. The $Tb(DPA)_m(L)_n$ complexes afford a similar opportunity, but in this case the structural features of the nonchiral parts of the complexes are less well characterized. In both $Tb(EHPG)(L)_n$ and $Tb(DPA)_m(L)_n$ advantage may be taken of ligand sensitization and enhancement of terbium luminescence, allowing lower complex concentrations to be used with near-ultraviolet excitation of the CPL/emission spectra.

Circular polarization of luminescence (CPL) spectroscopy is the emission analogue of circular dichroism (CD) and is dependent upon the same aspects of molecular structure in emitting states as CD is of molecular sturcture in ground states.[13] Structural differences between the ground and 4f-electron excited states of lanthanide complexes are negligible, so that for these systems CPL and CD provide identical structural information. CD measurements on lanthanide 4f–4f transitions are made difficult by the extremely low absorptivities exhibited by these transitions. On the other hand, terbium complexes luminesce rather strongly in aqueous solution so that CPL measurements are readily carried out. The major disadvantage of CPL vs. CD measurements is that the CPL-observable $\Delta I = I_L - I_R$ (where I_L and I_R represent the intensities of the left and right circularly polarized components of the luminescence, respectively) cannot be used to obtain absolute values of theoretical rotatory strengths unless both I_L and I_R are determined in terms of *absolute* intensity units. In the present study, ΔI values are given only in relative intensity units.

Experimental Section

$TbCl_3 \cdot 6H_2O$ and $Tb(NO_3)_3 \cdot 6H_2O$ were purchased from Alfa Inorganics. The sugars and sugar acids as well as uridine, inosine, and dipicolinic acid (DPA) were purchased from Sigma Chemical Co. Camphorsulfonic acid, malic acid, tartaric acid, and ascorbic acid were purchased from Aldrich. The amino acids and penicillin G were purchased from Calbiochem, mandelic acid was obtained from Norse Laboratories, and *N,N'*-ethylenebis(α-(o-hydroxyphenyl)glycine) (EHPG) was purchased from K & K Laboratories. Due to its sensitivity to air oxidation, the EHPG reagent had to be purified periodically by using procedures reported previously.[7]

All experiments were carried out at room temperature in aqueous solution, and pH adjustments were made with use of NaOH, HCl, or HNO_3. Absorption measurements were carried out with use of a Cary Model 14 spectrophotometer, and all CPL/emission experiments were carried out with use of an emission spectrophotometer constructed in this laboratory.[13] In all of the CPL/emission experiments, broad-band near-ultraviolet excitation was used. The excitation source was a 1000-W Xe–Hg arc lamp. CPL intensities are reported in terms of $\Delta I = I_L - I_R$, where I_L and I_R denote respectively the intensities of the left and right circularly polarized components of the luminescence. Total emission intensities are expressed as $I = I_L + I_R$. Both ΔI and I are expressed in arbitrary intensity units. Where luminescence dissymmetry factors, defined as $g_{lum} = 2\Delta I/I$, are reported, the ΔI and I quantities are referred to identical scales and the g_{lum} values are, therefore, given in absolute units.

Results and Discussion

$Tb(EHPG)(L)_n$ Complexes. All CPL/emission experiments on the $Tb(EHPG)(L)_n$ systems were carried out with $[Tb^{3+}] = 1.25$ mM, and with near-ultraviolet excitation centered at 290 nm. This excitation wavelength corresponds to an absorption maximum ($\epsilon \sim 4000$) in the near-ultraviolet spectrum of 1:1 Tb(EHPG), which is assigned to an electronic transition localized on the EHPG phenolate moieties. CPL/emission measurements were carried out as a function of solution pH (from pH 5 to 11) and as a function of $[Tb^{3+}]:[EHPG]:[L] = 1:1:n$, with n being varied from 0.25 to 4. Terbium was introduced into solution in the form $TbCl_3$.

Among all of the chiral ligands (L) included in this study only two were found to generate significant CPL when bound to 1:1 Tb(EHPG). These two were the structurally similar dicarboxylic acids malic acid and tartaric acid. CPL was also induced by aspartic acid and glutamic acid, but in these cases the signals were too weak to deal with quantitatively.

For $Tb(EHPG)(d\text{-malic acid})_n$ at pH >5, weak CPL appeared at $n = 0.5$ and the CPL intensity increased steadily with increasing n until leveling off at $n \simeq 1.5$. The pH dependence of the CPL (ΔI) observed in the $^5D_4 \rightarrow {}^7F_5$ transition region of Tb^{3+} in $Tb(EHPG)(d\text{-malic acid})_3$ is illustrated by the spectra shown in Figure 2. In our previous study[7] of 1:1 Tb(EHPG) in aqueous solution, we found that Tb^{3+}–phenolate binding begins at pH ~4.5 but is not complete until pH ~8. This progressive binding of phenolate groups as the solution

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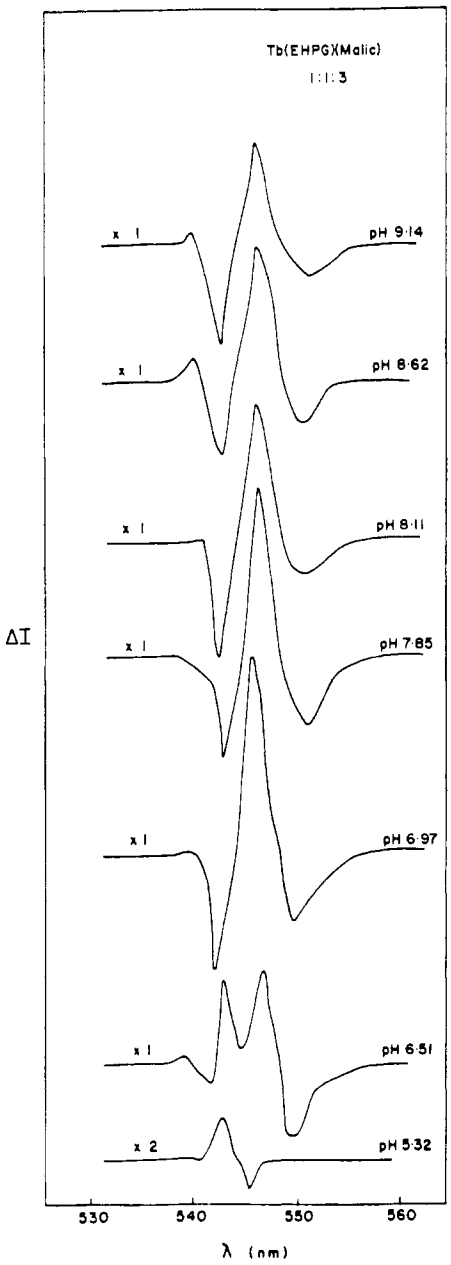

Figure 2. CPL spectra for 1:1:3 Tb(EHPG)(*d*-malic acid) systems in the $^5D_4 \rightarrow {}^7F_5$ terbium transition region. $[Tb^{3+}] = 1.25$ mM and $\lambda_{ex} = 290$ nm.

pH is raised leads to (1) an enhancement of terbium luminescence intensity (due to an increased phenolate-to-Tb^{3+} energy-transfer efficiency) and (2) changes in the emission band splittings (due to alterations in the crystal field about the terbium ion). Changes in the CPL intensities and band structure (including both splittings and sign patterns) as a function of pH may also be attributed to Tb^{3+}–phenolate binding. The most dramatic changes in the CPL spectra occur between pH 5 and pH 7 (see Figure 2) for the Tb(EHPG)-(*d*-malic acid)$_3$ system. Evidence that 1:1 Tb(EHPG) complexes are fully formed by pH 8 even in the presence of excess malic acid is provided by the observation that terbium emission enhancements in the presence and absence of malic acid are identical. The malic acid does not interfere with hexadentate Tb(EHPG) chelate formation.

For Tb(EHPG)(*d*-malic acid)$_3$ at pH 8, the largest values of $|g_{lum}|$ observed within the $^5D_4 \rightarrow {}^7F_5$ emission region are of the order of 10^{-3}. These values are only slightly smaller than those observed for 1:3 = $[Tb^{3+}]$:[*d*-malic acid] in aqueous solution at pH 8. Moreover, the sign patterns observed in the CPL spectra for Tb(EHPG)(*d*-malic acid)$_3$ and Tb(*d*-malic acid)$_3$ at pH 8 are identical.

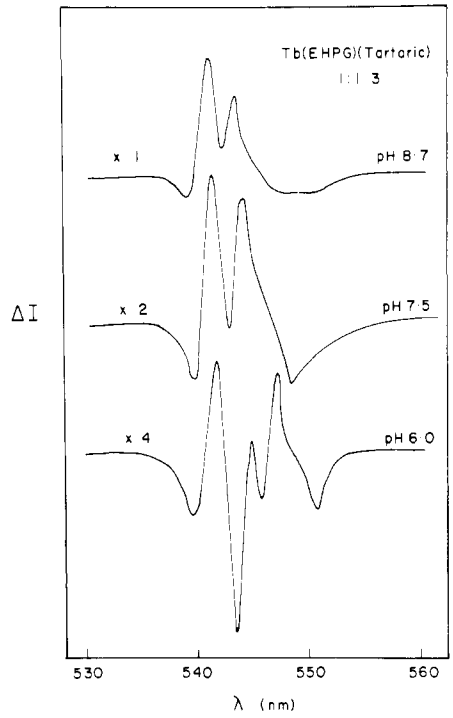

Figure 3. CPL spectra for 1:1:3 Tb(EHPG)(*l*-tartaric acid) systems in the $^5D_4 \rightarrow {}^7F_5$ terbium transition region. $[Tb^{3+}] = 1.25$ mM and $\lambda_{ex} = 290$ nm.

Holding the solution pH fixed at 8 but varying n from 0.5 to 1.5 for the 1:1:n = $[Tb^{3+}]$:[EHPG]:[*d*-malic acid] system results in a 1 order of magnitude increase in the values of $|g_{lum}|$ at both $\lambda = 543$ nm and $\lambda = 545.5$ nm. The sign variations in g_{lum} across the $^5D_4 \rightarrow {}^7F_5$ emission region do not change with changes in n. These results suggest that the essential elements of chirality in the ligand environment do not change upon varying n from 0.5 to 1.5 but that increasing n leads to greater binding of the *d*-malic acid to the Tb(EHPG) complex.

For Tb(EHPG)(*l*-tartaric acid)$_n$ at pH >6, weak CPL appeared at $n = 1$ and the CPL intensity increased steadily with increasing n until leveling off at $n \simeq 2$. The pH dependence of the CPL (ΔI) observed in the $^5D_4 \rightarrow {}^7F_5$ transition region is illustrated in Figure 3 for the Tb(EHPG)(*l*-tartaric acid)$_3$ system. Comparisons of the terbium emission enhancements observed for 1:1 Tb(EHPG) and for 1:1:n Tb(EHPG)(*l*-tartaric acid) as a function of solution pH showed that excess tartaric acid does not interfere with hexadentate Tb(EHPG) chelate formation between pH 5 and pH 8. We can assume, therefore, that by pH 8 fully formed Tb(EHPG) complexes exist in solution and that the tartaric acid ligands bind to these complexes to induce optical activity (CPL). The most dramatic changes in CPL intensities and in $|g_{lum}|$ values occur between pH 5 and pH 8, reflecting major alterations in the crystal field about the Tb^{3+} ion as Tb(EHPG) chelation is completed via Tb^{3+}–phenolate coordination.

Varying n from 1 to 3 in the Tb(EHPG)(*l*-tartaric acid)$_n$ systems at pH 8 produces no *qualitative* changes in either the ΔI or the g_{lum} spectra within the $^5D_4 \rightarrow {}^7F_5$ emission region. Both ΔI and g_{lum} increase in magnitude with increasing n (up to $n = 2$), reflecting greater *l*-tartaric acid binding. The maximum $|g_{lum}|$ values observed for the Tb(EHPG)(*l*-tartaric acid)$_n$ systems are comparable in magnitude to those observed for the Tb(EHPG)(*d*-malic acid)$_n$ systems. The CPL signatures exhibited by these two types of systems are, however, qualitatively different.

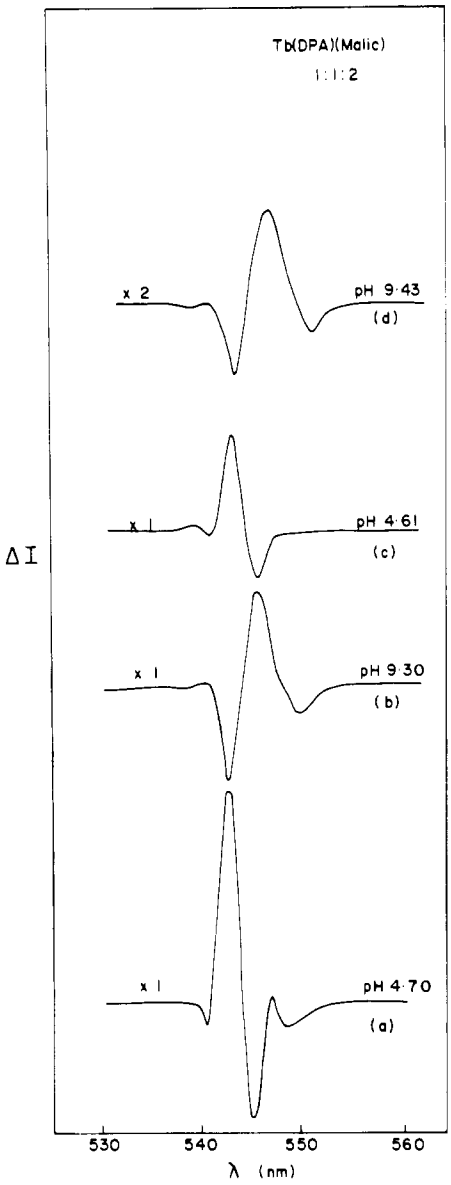

Figure 4. CPL spectra for 1:1:2 Tb(DPA)(*d*-malic acid) systems in the $^5D_4 \rightarrow {}^7F_5$ terbium transition region. For spectra a and b [$TbCl_3$] = 12.5 mM, and for spectra c and d [$Tb(NO_3)_3$] = 12.5 mM. λ_{ex} = 290 nm.

$Tb(DPA)_m(L)_n$ Complexes. All CPL/emission experiments on the $Tb(DPA)_m(L)_n$ systems were carried out with [Tb^{3+}] = 12.5 mM and with near-ultraviolet excitation centered at 290 nm. This excitation is directed to the dipicolinate (DPA^{2-}) ligand chromophore, and the terbium emission is sensitized via a dipicolinate-to-Tb^{3+} nonradiative energy-transfer process. The *m* and *n* subscripts in the $Tb(DPA)_m(L)_n$ formula refer to *relative* molar concentrations of the DPA and L ligands in solution with Tb^{3+}, and *do not* imply *known* stoichiometries for the complex species present in solution. That is, $Tb(DPA)_m(L)_n$ means a 1:*m*:*n* [Tb^{3+}]:[DPA]:[L] molar concentration ratio.

A series of terbium emission enhancement measurements were carried out for $Tb(DPA)_m$ (*m* = 1, 2, or 3) systems as a function of solution pH over the pH range 2–12. For *m* = 1, precipitation began to occur at pH 6.5. For *m* = 2 or 3, no precipitation was observed until the pH was raised to ~12. For each of the $Tb(DPA)_m$ systems (*m* = 1, 2, or 3), terbium emission enhancement reached a maximum value by pH 3 and this value remained constant with increasing pH until the onset of complex precipitation. Associating terbium emission enhancement with Tb^{3+}–DPA binding, these results suggest that in each case Tb^{3+}–DPA coordination is complete by pH 3. The relative emission enhancements found for the *m* = 1, 2, and 3 systems were in the ratio of 1:2:3, indicating that *m* is a good stoichiometric coefficient in the formula $Tb(DPA)_m$ and that each bound DPA ligand acts as an *independent* energy donor to the Tb^{3+} ion.

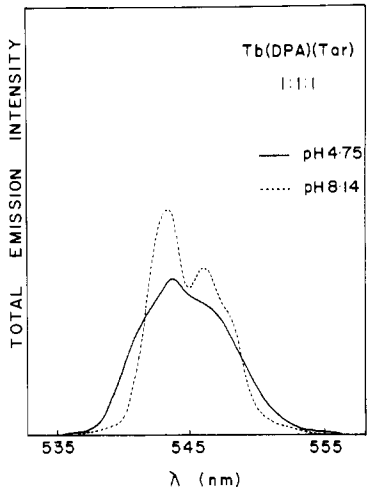

Figure 5. Total luminescence spectra for 1:1:1 Tb(DPA)(*l*-tartaric acid) in the $^5D_4 \rightarrow {}^7F_5$ emission region. [Tb^{3+}] = 12.5 mM and λ_{ex} = 290 nm.

Among all of the chiral ligands (L) included in this study only the following were found to generate significant CPL in the $Tb(DPA)_m$ (*m* = 1 or 2) systems: malic acid, tartaric acid, mandelic acid, aspartic acid, glutamic acid, *N*-acetylneuraminic acid, galacturonic acid, glucuronic acid, and ribose. The strongest CPL was induced by malic acid, tartaric acid, and *N*-acetylneuraminic acid. At pH > 3, no CPL was observed in any of the $Tb(DPA)_3(L)_n$ systems, suggesting that under these conditions the inner coordination sphere of the Tb^{3+} is completely filled by ligating groups of the achiral DPA ligands and that if the chiral ligands do indeed bind via outer-sphere coordination, they are ineffective in promoting f–f optical activity. Terbium emission enhancements observed for the $Tb(DPA)_m$ and $Tb(DPA)_m(L)_n$ systems are identical, providing further evidence that Tb^{3+}–DPA binding takes precedence over Tb^{3+}–L binding at pH >3.

Brittain has previously reported[10,11] the CPL spectra for the malic acid, aspartic acid, and glutamic acid complexes of $Tb(DPA)_m$, and our results are very similar to those reported by him. We present here only two sets of our CPL results on the Tb(DPA)(*d*-malic acid)$_2$ system (see Figure 4). Spectra a and b shown in Figure 4 were obtained on solutions prepared from $TbCl_3$ while spectra c and d of Figure 4 were obtained on solutions prepared from $Tb(NO_3)_3$. At a given pH, the differences between these two sets of CPL spectra are quantitative rather than qualitative. In both cases, however, going from pH ~4.65 to ~9.55 leads to a dramatic *qualitative* change in the CPL signatures. At the lower pH it is likely that two malic acid ligands are bound to Tb(DPA), each via a bidentate chelation mode, with the remaining inner-sphere coordination sites being filled by neutral water molecules. Raising the pH to 9 will lead to deprotonation of these bound water molecules (to OH^- ligands), causing a large change in the crystal field potential at the Tb^{3+} ion. At pH >9 it is also possible that the malic acid ligands can coordinate via a terdentate chelation mode involving their two carboxylate groups plus their hydroxyl moiety.[6] The maximum $|g_{lum}|$ values observed for the Tb(DPA)(*d*-malic acid)$_2$ systems at pH >9 are 5–10 times larger than those observed for Tb(EHPG)(*d*-malic acid)$_2$ at pH >8. In the latter systems it is likely that only

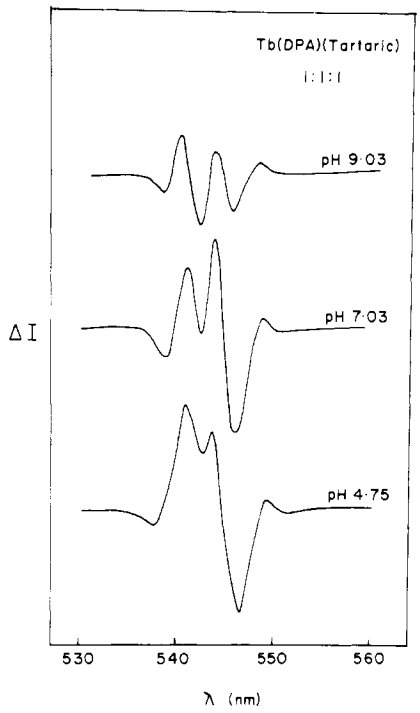

Figure 6. CPL spectra for 1:1:1 Tb(DPA)(*l*-tartaric acid) in the $^5D_4 \rightarrow {}^7F_5$ emission region. $[Tb^{3+}]$ = 12.5 mM and λ_{ex} = 290 nm.

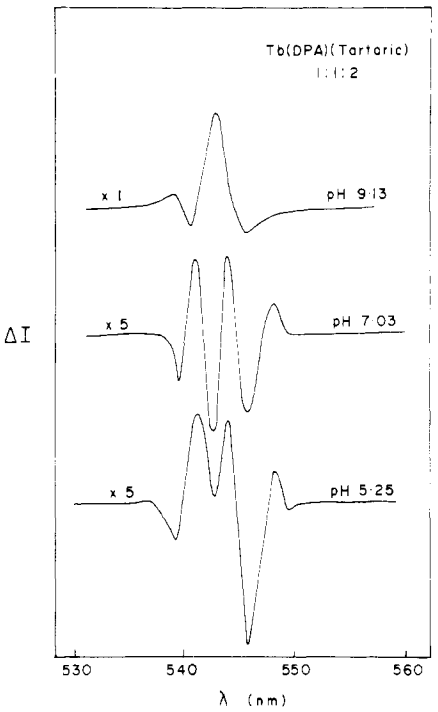

Figure 7. CPL spectra for 1:1:2 Tb(DPA)(*l*-tartaric acid) in the $^5D_4 \rightarrow {}^7F_5$ emission region. $[Tb^{3+}]$ = 12.5 mM and λ_{ex} = 290 nm.

one malic acid is bound to the Tb(EHPG) complex whereas in the former two malic acid ligands are bound to Tb(DPA).

Total emission spectra are shown in Figure 5 for the 1:1:1 Tb(DPA)(*l*-tartaric acid) system, and CPL spectra are displayed in Figures 6–9 for a variety of 1:*m*:*n* Tb(DPA)(*l*-tartaric acid) systems. Strong CPL was observed for the 1:1:1, 1:1:2, 1:1:3, 1:2:1, and 1:2:2 systems, with the 1:2:1 and 1:2:2 systems exhibiting almost identical CPL spectra. The 1:3:*n* systems (with *n* = 1, 2, or 3) exhibited no CPL at pH >3. The results on the 1:1:*n* systems suggest that three tartaric acid ligands may be accommodated within the inner coordination

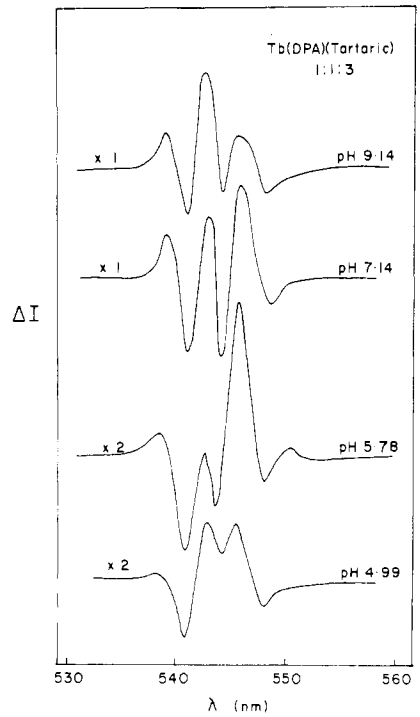

Figure 8. CPL spectra for 1:1:3 Tb(DPA)(*l*-tartaric acid) in the $^5D_4 \rightarrow {}^7F_5$ emission region. $[Tb^{3+}]$ = 12.5 mM and λ_{ex} = 290 nm.

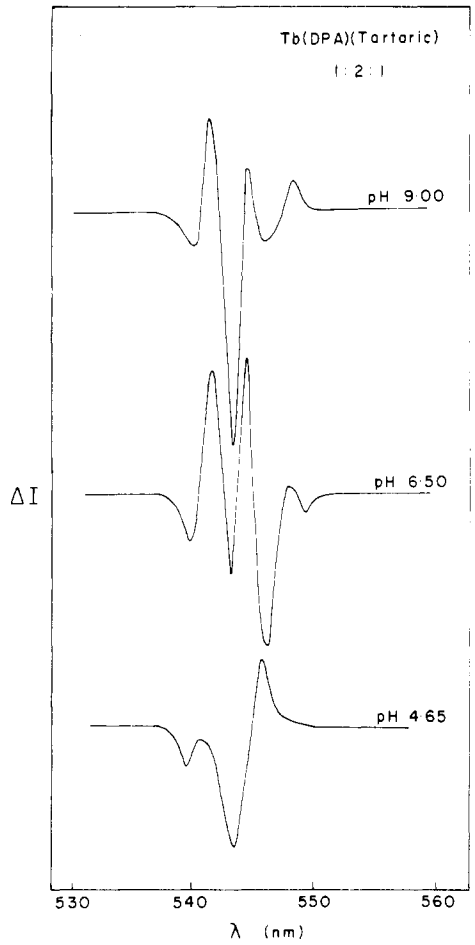

Figure 9. CPL spectra for 1:2:1 Tb(DPA)(*l*-tartaric acid) in the $^5D_4 \rightarrow {}^7F_5$ emission region. $[Tb^{3+}]$ = 12.5 mM and λ_{ex} = 290 nm.

sphere of a Tb(DPA) complex. The results on the 1:2:*n* systems suggest that $Tb(DPA)_2$ can bind only one tartaric acid ligand. For the 1:3:*n* systems, all of the inner-sphere coor-

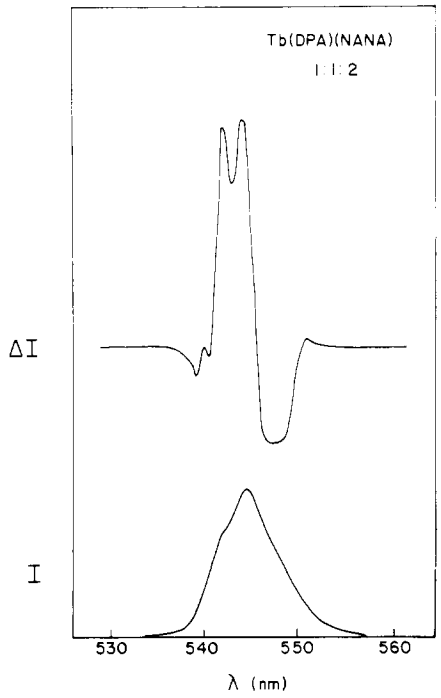

Figure 10. Total luminescence (I) and CPL (ΔI) spectra for 1:1:2 Tb(DPA)(*N*-acetylneuraminic acid) in the $^5D_4 \rightarrow {}^7F_5$ emission region. $[Tb^{3+}]$ = 2 mM, pH = 7.2, and λ_{ex} = 290 nm.

dination sites are apparently filled by DPA ligating groups. The pH dependence exhibited by the $Tb(DPA)_m$(*l*-tartaric acid)$_n$ CPL spectra indicates significant alterations in the crystal field potential occur as solution pH is changed. In general, the 1:1:*n* systems exhibited $|g_{lum}|$ values that were about 5 times larger than those observed for the 1:2:*n* systems. All $Tb(DPA)_m$(*l*-tartaric acid)$_n$ solutions were prepared with use of $TbCl_3$.

Two simple sugar acids, glucuronic acid and galacturonic acid, and one sugar acid derivative, *N*-acetylneuraminic acid (or sialic acid), were included among the chiral ligands (L) examined in this study. While none of these potential ligands were found to induce CPL in the 1:1 Tb(EHPG) system, each was effective in inducing observable CPL in the 1:1 and 1:2 Tb(DPA) systems at neutral pH. Terbium emission enhancements observed for these $Tb(DPA)_m(L)_n$ systems were identical with those observed for the corresponding $Tb(DPA)_m$ systems (in which $n = 0$), indicating that the L ligands have little influence on Tb^{3+}–DPA binding. The CPL spectra observed for the $Tb(DPA)(L)_n$ and $Tb(DPA)_2(L)_n$ systems were *qualitatively* identical for a given L species. Furthermore, the general characteristics of these CPL spectra were very similar to those observed in the CPL spectra of $[Tb^{3+}]$:[L] = 1:5 aqueous solutions of these sugar acids at neutral pH.[14] The maximum $|g_{lum}|$ values observed in the CPL/emission spectra of the $Tb(DPA)_m$(*N*-acetylneuraminic acid)$_n$ systems were of the same magnitude as those observed for the corresponding malic acid and tartaric acid complexes of $Tb(DPA)_m$ (m = 1 or 2). The maximum $|g_{lum}|$ values observed for the glucuronic acid and galacturonic acid complexes of $Tb(DPA)_m$ (m = 1 or 2) were 1 order of magnitude smaller ($<10^{-4}$). In previous CPL/emission studies of the $[Tb^{3+}]$:[L] = 1:5 systems in aqueous solution,[14] it was found that *N*-acetylneuraminic acid induced considerably greater lanthanide optical activity than did the glucuronic acid and galacturonic acid ligands.

Examples of CPL/emission spectra obtained for several *N*-acetylneuraminic acid, glucuronic acid, and galacturonic acid complexes of $Tb(DPA)_m$ are shown in Figures 10 and 11.

(14) Morley, J. P. Ph.D. Dissertation, University of Virginia, 1980.

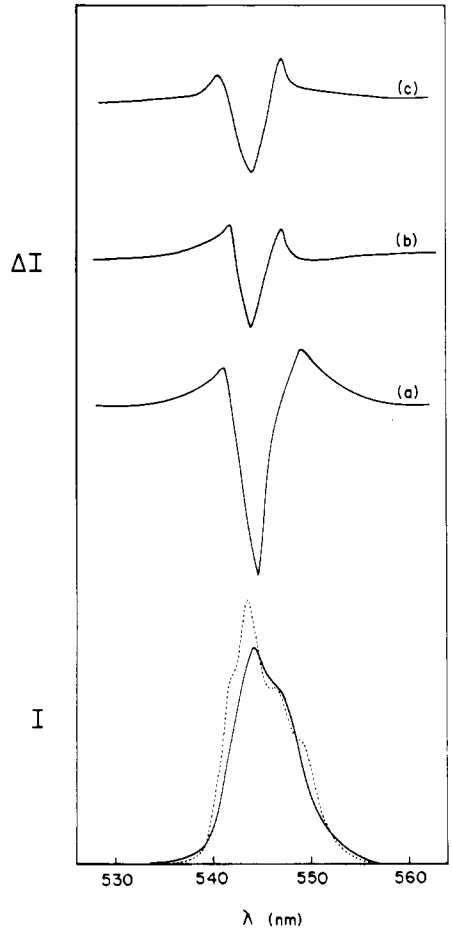

Figure 11. Total luminescence (I) spectra for 1:1:2 (solid curve) and 1:2:1 (dashed curve) Tb(DPA)(galacturonic acid) complexes in the $^5D_4 \rightarrow {}^7F_5$ emission region and CPL (ΔI) spectra for (a) 1:1:2 Tb(DPA)(galacturonic acid), (b) 1:2:1 Tb(DPA)(galacturonic acid), and (c) 1:1:2 Tb(DPA)(glucuronic acid) complexes. For the 1:1:2 systems, $[Tb^{3+}]$ = 16.6 mM. For the 1:2:1 system, $[Tb^{3+}]$ = 8.3 mM. In all cases pH = 7.1 and λ_{ex} = 290 nm.

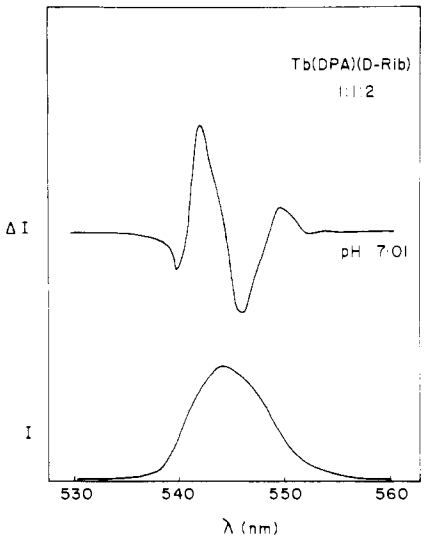

Figure 12. Total luminescence (I) and CPL (ΔI) spectra for 1:1:2 Tb(DPA)(D-ribose) in the $^5D_4 \rightarrow {}^7F_5$ emission region. $[Tb^{3+}]$ = 12.5 mM and λ_{ex} = 290 nm.

In each of these cases the sample solutions were prepared with use of $TbCl_3$.

The only $Tb(DPA)_m$(simple sugar)$_n$ system found to exhibit significant CPL was the $Tb(DPA)$(D-ribose)$_2$ system. The

CPL and total luminescence spectra for this system in the $^5D_4 \rightarrow {}^7F_5$ emission region are shown in Figure 12. The maximum $|g_{lum}|$ value in this case was $\sim 10^{-4}$, and the CPL signature matches very closely that found for $[Tb^{3+}]$:[D-ribose] = 1:5 in aqueous solution at pH 7.

Parallel sets of CPL/emission experiments were carried out on *l*:*m*:*n* Tb(DPA)(L) complexes (m = 1 or 2, and n = 1, 2, or 3) in which the L ligands were either mandelic acid or phenylglycine. The potential binding moieties in mandelic acid are its carboxylate group and its α-hydroxyl group. The potential binding moieties of phenylglycine are its carboxylate group and its α-amino group. The CPL induced by optically active phenylglycine was extremely weak and could not be quantitatively analyzed. On the other hand, optically active mandelic acid was found to induce very strong CPL in the $Tb(DPA)_m$ (m = 1 or 2) systems. The CPL intensities and g_{lum} values observed for the 1:1:1, 1:1:2, 1:2:1, and 1:2:2 Tb(DPA)(*d*-mandelic acid) systems were similar to (or slightly greater than) those observed for the corresponding $Tb(DPA)_m$(*d*-malic acid)$_n$ systems. These results suggest that the mandelic acid is capable of bidentate chelation to the Tb(DPA)$_m$ (m = 1 or 2) complexes via its carboxylate and α-hydroxyl groups. Amino groups are known to be relatively weak ligators to lanthanide ions. This apparently militates against bidentate chelation by the phenylglycine ligands. The CPL/emission spectra obtained for the various $Tb(DPA)_m$(*d*-mandelic acid)$_n$ systems were found to be qualitatively similar (exhibiting identical sign patterns).

Conclusions

Detailed spectra–structure relationships are beyond the capability of current lanthanide optical activity theory,[5] and empirical studies have produced only rather general correlations between spectral detail and structural features. The results obtained in the present study generally support most previous speculations regarding spectra–structure correlations.

The absence of observable CPL in the $Tb(DPA)_3(L)_n$ systems at pH >3 demonstrates that in order for chiral ligands to induce f–f optical activity, they must be bound in the inner coordination sphere of the Tb^{3+} ion. Our CPL results on the $Tb(EHPG)(L)_n$ and $Tb(DPA)_m(L)_n$ systems for different chiral ligand types L show that only those ligands that are capable of multidentate chelation will induce significant f–f optical activity. These *favorable* ligand types are characterized in the present study as those having two or more carboxylate or hydroxyl groups favorably disposed for ligation to Tb^{3+}. For example, malic acid, tartaric acid, mandelic acid, and the sugar acids each satisfy this criterion for strong multidentate chelation, and each was found to induce relatively strong CPL in the Tb(EHPG) and $Tb(DPA)_m$ systems.

The $Tb(DPA)_m(L)_n$ (m = 1 or 2) systems generally exhibited greater CPL intensities and larger $|g_{lum}|$ values than did the corresponding $Tb(EHPG)(L)_n$ systems. This observation can be accounted for in terms of a greater "inner coordination sphere accessibility" in the Tb(DPA) and Tb(DPA)$_2$ complexes vs. the Tb(EHPG) complex. By pH 8, the hexadentate Tb(EHPG) complex is fully formed and it presents only two available coordination sites to a chiral ligand L.[7] The available coordination sites on the Tb(DPA) and Tb(DPA)$_2$ complexes are both more numerous and less crowded than in the Tb(EHPG) complex at pH 8. The pH dependence of the CPL/emission results obtained for Tb(EHPG)(*d*-malic acid)$_3$ and Tb(EHPG)(*l*-tartaric acid)$_3$ (see Figures 2 and 3) demonstrates the importance of coordination-site availability in the Tb(EHPG) system. At the lower pH values it is likely that two optically active ligands are bound (each bidentate), while at pH >7 only one is bound. The CPL signatures are dramatically different at the high and low pH values for both L = *d*-malic acid and L = *l*-tartaric acid. Furthermore, although the CPL intensities (ΔI) are higher at the high pH values than at the lower pH values, the luminescence dissymmetry factors $|g_{lum}|$ are 3 times larger at the low pH values. The larger $|g_{lum}|$ values observed at pH <7 is compatible with the binding of two, rather than one, chiral ligands at the lower pH values. The lesser CPL intensity seen at pH <7 is attributable entirely to the fact that the phenolate energy donor groups of the EHPG ligand are only partially bound in this pH region, thus reducing the sensitization of the terbium total luminescence (I) and CPL (ΔI).[7] The magnitude of $g_{lum} = 2(\Delta I)/I$ is, of course, invariant to the efficiency of this sensitization process and depends only upon the degree of ligand chirality sensed by the Tb^{3+} ion.

The $|g_{lum}|$ values obtained for the 1:1:2 Tb(DPA)(L) systems were generally found to be about twice as large as those observed for the 1:1:1 Tb(DPA)(L) systems. These results suggest that for Tb(DPA) the chiral ligands make simple *additive* contributions to the terbium optical activity and that *configurational* contributions due to chiral distributions of chelate rings about the metal ion are negligible. On the other hand, the $|g_{lum}|$ values observed for the 1:1:2 Tb(DPA)(L) systems were generally found to be 5–10 times greater than those observed for the 1:2:1 and 1:2:2 Tb(DPA)(L) systems. These latter results reflect *nonadditivity* in the L ligand contributions to the terbium optical activity and show that the observed optical activity is quite sensitive to that part of the crystal field created by the achiral DPA ligand. At pH >9, the 1:1:2 and 1:2:1 Tb(DPA)(*l*-tartaric acid) systems give oppositely signed CPL signatures. It is possible that these results can be explained in terms of ligand-induced configurational dissymmetry in the $Tb(DPA)_2$ complexes, but it is also possible that these results simply reflect crystal field differences in the Tb(DPA) vs. $Tb(DPA)_2$ complexes, which have no implications regarding configurational dissymmetry. Our solution results cannot provide any definitive conclusions in this regard.

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Registry No. Tb, 7440-27-9; EHPG, 1170-02-1; DPA, 499-83-2; *d*-malic acid, 636-61-3; *l*-tartaric acid, 147-71-7; NANA, 131-48-6; galacturonic acid, 9046-40-6; glucuronic acid, 576-37-4; D-ribose, 50-69-1.