iron(II) toward both H_2O_2 and TiO_2^{2+} probably reflects the greater reducing strength of titanium(III).

The greater reactivity of H_2O_2 relative to TiO_2^{2+} persists even when allowance is made for the role of the hydrogen ion. Electrostatic effects could account for some of the difference. If the TiO_2^{2+} reactions are inner sphere, as the H_2O_2 reactions almost certainly are, then the reduced "nucleophilic" character of the peroxide moiety in TiO_2^{2+} may be important. Inner-sphere reductions of H_2O_2 by transition-metal ions are in general much more rapid than their outer-sphere counterparts.[1] Unfortunately, our results do not allow us to make a distinction between inner-sphere and outer-sphere mechanisms for the reduction of TiO_2^{2+} by either iron(II) or titanium(III).

In none of the three systems reported here is there a kinetic advantage imparted when the peroxide moiety is complexed to titanium(IV). That this is probably due to the nature of the reductants rather than a general effect may be inferred by consideration of the results obtained in other studies of d^0 metal ion peroxo complexes. Several of these metal ions, including titanium(IV), are effective catalysts in promoting the epoxidation of olefins by peroxides.[4] While the detailed mechanisms of these important reactions are debatable, there is a concensus[4] that the role of the metal ion is to organize the olefin and peroxide for reaction by coordination of both. A similar mechanism has been proposed for the reduction of peroxo complexes of vanadium(V) by iodide ion.[3a] Nucleophilic attack at the titanium(IV) center is unlikely for any of the reductants we have examined.

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Registry No. TiO_2^{2+}, 12179-34-9; SO_2, 7446-09-5; H_2O_2, 7722-84-1; Fe^{2+}, 15438-31-0; Ti^{3+}, 22541-75-9.

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Circularly Polarized Luminescence Studies of the Ternary Complexes Formed by Terbium(III) with Chiral Amino Polycarboxylates and Achiral Substrate Ligands

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Circularly polarized luminescence (CPL) spectroscopy has been used to study the ternary complexes formed by Tb(III) with chiral amino polycarboxylate (APC) and achiral carboxylate ligands. It was observed that when the steric requirements of the achiral carboxylate ligand were minor (e.g., small ligand bite), the Tb(III) chirality was essentially unchanged relative to that of the parent Tb(APC) complex. However, with certain bulky bidentate and tridentate ligands, the CPL spectra revealed that formation of the ternary complexes could perturb the amino polycarboxylate conformation. Above pH 10, the parent Tb(APC) compounds are known to exist as polynuclear species. The self-association process was found to take place in the ternary complexes when the substrate ligand bound too weakly to interfere with the process. When the substrate bound strongly with the Tb(APC) complex, the compounds remained monomeric at all pH values.

Introduction

Mixed-ligand lanthanide complexes containing an amino polycarboxylate (APC) ligand and other chelating species have recently been investigated since the Ln(APC) complexes appear to be useful as aqueous NMR shift reagents.[1-4] Peters and Kieboom have recently summarized the utility of lanthanide-induced shifts for study of molecular complexation in aqueous solutions.[5] Perhaps the greatest use of Ln(APC) complexes as aqueous shift reagents has been in the study of nucleotide conformation in aqueous solution.[6-8] The Eu(III) derivative of (*R*)-(−)-1,2-propanediaminetetraacetic acid ((*R*)-(−)-PDTA) has recently been shown to be an effective chiral shift reagent for the study of hydroxy, amino, and carboxylic acids in aqueous solutions.[9]

Studies of lanthanide ion chirality can be used to obtain useful information on these complexation processes. We have used circularly polarized luminescence (CPL) spectroscopy to study the complexation phenomena between Tb(APC) compounds and (*S*)-aspartic acid,[10] (*S*)-α-hydroxy carboxylic acids,[11] and (*R*,*R*)-tartaric acid.[12] At the onset, it was assumed that the nature of the achiral APC ligand would not affect the interaction of the Tb(III) ion and the chiral carboxylates. This assumption was not always found to be true;[12] hence, it has become clear that steric interactions may exist between the APC ligand and the additional carboxylate ligand.

These interactions among the ligands in the ternary complexes would be functions of the steric requirements of the various ligands. In the present work, the results of CPL investigations designed to study the steric interactions between APC and carboxylate ligands in Tb(III) complexes are reported. We have chosen to work with two chiral amino polycarboxylate ligands upon which CPL results have already been obtained for the simple binary complexes.[13] The amino polycarboxylate ligands used were (*R*)-(−)-PDTA and (*R*,*R*)-(−)-*trans*-1,2-cyclohexanediaminetetraacetic acid ((*R*,*R*)-(−)-CDTA). The mixed-ligand complexes of Tb((*R*)-(−)-PDTA), Tb(PDTA), and Tb((*R*,*R*)-(−)-CDTA), Tb(CDTA), were formed with a wide variety of achiral carboxylic acids, and the interaction phenomena were studied primarily by means of CPL spectroscopy.

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Experimental Section

(*R*)-(−)-PDTA was prepared by a modified method of Dwyer and Garvan,[14] while (*R*,*R*)-(−)-CDTA was prepared according to Reinbold and Pearson.[15] The specific rotations of 0.5% aqueous solutions of these ligands agreed excellently with the reported literature values.[14-16] All achiral ligands were obtained as reagent grade materials from either Aldrich or Eastman and were used as received. Stock solutions of Tb(III) were prepared by dissolving the 99.9% oxides (Research Chemicals) in a stoichiometric amount of 70% $HClO_4$, neutralizing to pH 3.5 with NaOH, and then diluting to the desired volume.

Stock solutions of Tb(APC) were prepared by mixing equimolar amounts of Tb(III) and either (*R*)-(−)-PDTA or (*R*,*R*)-(−)-CDTA. Various ratios of Tb(APC) to achiral ligand were examined, with the achiral ligands being added by additions from concentrated stock solutions. The Tb(APC) concentration was usually 15 mM and the Tb(APC):ligand ratios varied between 1:1 and 1:10, so as to fully form the Tb(APC)(ligand) complexes. The pH of these solutions varied between 3.0 and 11.5.

All CPL measurements were obtained on apparatus constructed at Seton Hall University. In most cases, the 350-nm output of an Ar ion laser was used as the excitation source, and CPL measurements were obtained within all Tb(III) band systems. In the CPL experiment, two observable quantities are produced. These are the total luminescence (TL) intensity, given as

$$I = I_L + I_R \tag{1}$$

and the circularly polarized luminescence (CPL) intensity, given as

$$\Delta I = I_L - I_R \tag{2}$$

Most luminescence work concentrated on the $^5D_4 \rightarrow {}^7F_5$ transition at 545 nm, since it has been established that this particular transition exhibits the highest degree of both total and circularly polarized emission.[17] The emission was analyzed by a 0.5-m grating monochromator at 0.8-nm resolution; it was determined that further increases in resolving power did not yield a significant improvement in the spectral features.

Emission lifetimes were obtained on a separate apparatus. Samples were excited by the 337-nm output of a pulsed nitrogen laser (PRS Associates, Model LN-1000). The transient currents developed upon pulsed excitation of the sample were converted into voltages by using a 220K load resistor, and these voltage pulses were captured for viewing on a storage oscilloscope. At the same time, the data were digitized at 4-μs intervals via a homebuilt analog/digital converter, and the digitized data were fed directly into a Commodore PET 4032 microcomputer. The details of the transient digitizer have been described.[18] Our program calculates the base line from data points taken before the laser pulse and subtracts the base line from the decay data. The corrected decay curves were then analyzed by using a linear regression analysis of the ln *I* vs. time data points. Plots of ln *I* vs. time were normally found to be linear and thus indicate the presence of only one predominant emitting species.

Variation of the solution pH within the solutions was effected by the addition of microliter amounts of standard $HClO_4$ or NaOH directly to the fluorescence cuvette. The pH was monitored on an Orion 701A pH meter using a glass microcombination electrode that could be inserted directly into the cuvette. The system was calibrated daily with phosphate buffers.

Results and Discussion

UV excitation of a Tb(III) complex usually results in efficient population of the $^5D_4$ excited state and in the observation of emissive transitions to the $^7F_6$ (490 nm), $^7F_5$ (545 nm), $^7F_4$ (585 nm), and $^7F_3$ (625 nm) states of the ground manifold. Since it is only the *J* quantum number of a given state that is defined for a Tb(III) ion, the spectroscopic transitions may be labeled merely by the *J* quantum numbers of the initial and final states. The intensities and lifetimes of these bands are normally found to be dependent both on solution pH and on the metal:ligand ratio. In most cases, adequate study of complexation phenomena could be performed merely through observation of the trends associated with the 4–5 Tb(III) emission band (545 nm), but in several instances referral to the other Tb(III) emission band systems was necessary.

A. Tb(CDTA) and Tb(PDTA) Parent Compounds. The addition of equimolar amounts of Tb(III) and either PDTA or CDTA (generalized as APC) results in the formation of 1:1 complexes:

$$Tb^{3+} + APC^{4-} \rightarrow Tb(APC)^- \tag{3}$$

The fully formed $Tb(APC)^-$ complexes actually contain three waters of hydration when APC = PDTA or CDTA.[12] These coordinated waters are labile and may be replaced by a variety of carboxylate ligands:

$$Tb(APC)(H_2O)_3^- + L^- \rightarrow Tb(APC)(L)(H_2O)_x^{3-} + (3 - x)H_2O \tag{4}$$

The expulsion of coordinated water molecules invariably led to changes in the Tb(III) emission lifetimes. Systematic variation in the concentration of the achiral substrate ligands resulted in lifetime data that were dependent on the concentrations of that ligand. At sufficiently high concentrations of substrate, the limiting Tb(III) lifetime could be obtained. Knowledge of that limiting value and the concentration of all reactants permits the computation of the complex association constant governing the addition of L to the Tb(aPC) complexes. The mole fraction of uncomplexed (Tb(APC), X_i, is given by

$$X_i = \frac{\tau_F - \tau_i}{\tau_i} \tag{5}$$

where τ_F is the limiting Tb(III) lifetime and τ_i is the lifetime at a given substrate concentration. If $[Tb]_a$ and $[L]_a$ represent the initial concentrations of the Tb(APC) complex and substrate, respectively, then

$$[Tb(APC)] = [Tb]_a X_i \tag{6}$$

$$[Tb(APC)(L)] = [Tb]_a - [Tb(APC)] \tag{7}$$

$$[L] = [L]_a - [Tb(APC)(L)] \tag{8}$$

The ternary formation constant is given by

$$K_1 = \frac{[Tb(APC)(L)]}{[Tb(APC)][L]} \tag{9}$$

At pH values exceeding 10 the coordinated waters of the parent compounds may be deprotonated:

$$Tb(APC)(H_2O)_3^- + yOH^- \rightarrow Tb(APC)(H_2O)_{3-y}(OH)_y^{(y+1)^-} + yH_2O \tag{10}$$

The Tb(PDTA) and Tb(CDTA) hydroxy complexes have been shown to undergo extensive self-association,[19] with these processes being most pronounced at pH 11.

In previous work, the CPL spectra associated with these simple Tb(III) and Eu(III) complexes of (*R*)-(−)-PDTA and (*R*,*R*)-(−)-CDTA have been reported.[13] The spectra were found to remain essentially unchanged between pH 3 and 10 and underwent large changes above pH 10. The CPL spectra demonstrate that formation of the hydroxo complexes drastically alters the stereochemistry of the APC ligand. These results are in accord with the results of the energy-transfer experiments,[19] since formation of polynuclear species would greatly alter the ligand conformations and these would produce large changes in the CPL spectra.

Therefore, the solution-phase coordination chemistry of the Tb(APC) complexes may be divided into two regions: (1) pH 3.0–9.5, where the compounds exist as simple Tb(APC) monomers; (2) pH 10.0–12.0, where the compounds exist as $[Tb(APC)]_x$ oligomers. In the ternary Tb(APC)(L) complexes, the achiral substrate ligand could conceivably perturb either (or both) Tb(APC) compound type. Over the low-pH region, appreciable steric interactions between the coordinated ligands would yield CPL

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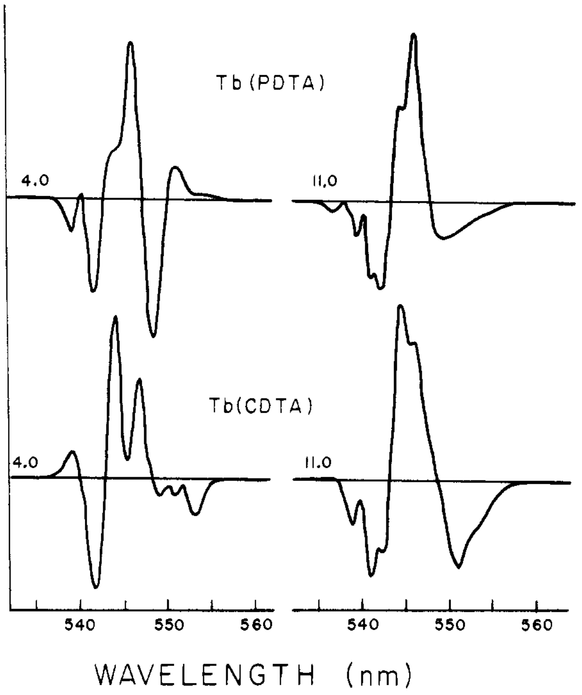

Figure 1. Circularly polarized luminescence spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition for the parent Tb(APC) compounds. Data are shown for Tb(PDTA)$(H_2O)_3$ [upper traces] and Tb(CDTA)$(H_2O)_3$ [lower traces], and the pH values at which the data were obtained accompany each spectrum.

Table I. Apparent Formation Constants Obtained for Interaction of Achiral Substrate Ligands with Tb(APC) Complexes[a]

	log K_1	
substrate	Tb(CDTA)	Tb(PDTA)
phthalic acid (PHT)	2.74	2.77
trimellitic acid (TML)	2.86	2.90
hemimellitic acid (HML)	2.70	2.74
pyromellitic acid (PML)	2.53	2.57
Tiron (TIR)	2.96	3.01
5-sulfosalicylic acid (SSA)	2.94	2.98
oxalic acid (OX)	4.0*	4.0*
malonic acid (MAL)	2.83	2.88
succinic acid (SUC)	2.15	2.19
glycolic acid (GLY)	2.91	2.95
oxydiacetic acid (ODA)	4.0*	4.0*
picolinic acid (PIC)	2.80	2.85
dipicolinic acid (DPA)	4.0*	4.0*

[a] An upper limit of K_1 = 10000 L/mol existed when Tb(III) luminescence lifetimes were used to determine the ternary formation constants. The error associated with each constant is ±0.03 log K unit. Asterisks signify that the association constant for these ligands exceeds the upper limit.

spectra that were different from those of the parent Tb(APC) compound. Within the high-pH region, should the substrate be capable of interfering with the oligomerization process, the perturbed CPL spectra would again be observed. Thus, the CPL spectra would appear to be ideal to elucidate details of adduct formation associated with the Tb(APC)(L) complexes.

Since the publication of the earlier work, the CPL spectrometer design has been significantly improved. Consequently, vastly superior CPL spectra for Tb(CDTA)$(H_2O)_3$ and Tb(PDTA)$(H_2O)_3$ have been obtained at low and high pH values. Since the spectra of these compounds will be used to evaluate the spectra obtained for ternary carboxylate species, the improved spectral line shapes are shown in Figure 1 for all the parent Tb(APC) compounds.

B. Ternary Complexes Containing Benzenecarboxylic Acids. The first group of ternary complexes were formed by Tb(PDTA) and Tb(CDTA) with several benzenecarboxylic acids. These ligands were chosen since they were known to bind lanthanide ions with reasonable efficiency[20] and also their steric requirements should be minor. Such properties ensure that these ligands are not likely to cause large perturbations in the aminopolycarboxylate structure; hence, the observed CPL spectra will provide a basis for later data interpretation.

CPL spectra were obtained for the Tb(CDTA) and Tb(PDTA) complexes with phthalic, trimellitic, hemimellitic, and pyromellitic acids. The low-pH CPL line shapes were generally stable between pH 3.5 and 9.5 and gradually changed into the high-pH line shapes between pH 9.5 and 10.0. The high-pH line shapes were stable between pH 10.5 and 11.5 and underwent drastic decompositions (due to complex hydrolysis) above this pH range.

Any stereochemical changes that accompany formation of the ternary compounds can be deduced by comparison of the benzenecarboxylate data with the corresponding data of the parent compounds. The CPL spectra obtained between pH 3 and 9 are essentially unchanged with respect to the corresponding parent Tb(PDTA) and Tb(CDTA) compounds. Some loss of peak resolution is observed in the spectra of the mixed-ligand compounds; however, these small differences are undoubtedly due to the presence of slightly different compounds having exceedingly similar stereochemistries. The luminescence dissymmetry factors obtained for corresponding bands are also quite similar, indicating that little perturbation of the APC ligand conformation has accompanied the binding of the benzenecarboxylate ligands.

With the exception of Tb(PDTA)(trimellitate), all the high-pH CPL spectra strongly resemble the spectra of the parent Tb(APC) compounds. These results are surprising since the CPL change observed above pH 10 is due to formation of polynuclear complexes, held together by hydroxy bridges.[19] The close correspondence of the data (both in line shape and in magnitude) indicates that the same association process must take place with the ternary Tb(APC)(benzenecarboxylate) complexes at elevated pH values. It is resonable to assume that these mixed-ligand compounds cannot form the same type of bridged species as do the parent compounds, since the polymers are undoubtedly held together by multiple hydroxide bridges.[13] Were the ternary ligand to remain bound, then formation of the bridges would not be possible. It may be concluded from these considerations that, during formation of the polynuclear, hydroxy-bridged compounds, the carboxylate ligands are simultaneously expelled from the Tb(III) coordination sphere.

This situation would require that the association constant for formation of a $[Tb(APC)]_x$ polymer complex would be greater than the corresponding formation constant governing the binding of the carboxylate ligands by the Tb(APC) complexes. In previous work, the association constants corresponding to formation of the $[Tb(APC)]_x$ were found to be pH-dependent, but near pH 11 (where the CPL data of the present work were obtained) a value of log K = 2.86 was obtained for Tb(PDTA) and a value of log K = 3.08 was obtained for Tb(CDTA).[19] Ternary formation constants were computed (by using the lifetime method discussed earlier) for the various Tb(APC)(L) complexes; these are given in Table I. Most of the constants do not exceed those for the oligomeric compounds, supporting the hypothesis that the ternary ligand is expelled at high pH values at the same time as the oligomerization process. The ternary constant observed for Tb(PDTA)(TML) is comparable to the oligomerization constant of $[Tb(PDTA)]_x$; hence, the CPL spectra indicate the existence of mixed species in solution.

C. Ternary Complexes Containing Sulfonated Benzene Derivatives. Significantly more information is available regarding the mixed-ligand complexes formed between Ln(APC) compounds and either 5-sulfosalicylic acid (SSA) or 1,2-dihydroxybenzene-3,5-sulfonic acid (Tiron, or TIR) since these compounds are used in fluorometric determinations of Tb(III).[21,22] Attempts have

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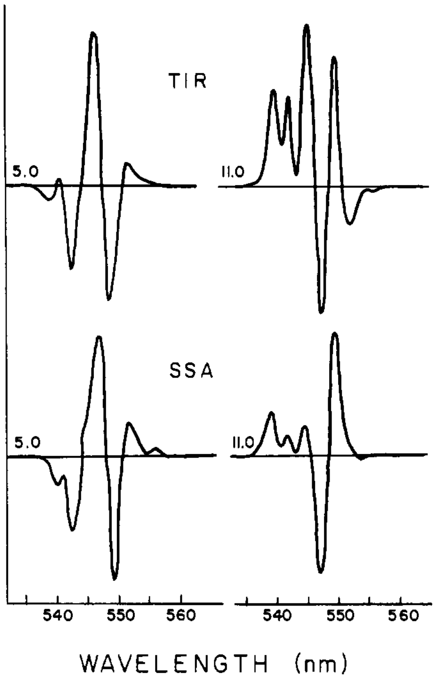

Figure 2. Circularly polarized luminescence spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition for Tb(PDTA) complexes with sulfonated benzene derivatives. Data are shown for Tiron (TIR) and 5-sulfosalicylic acid (SSA). The pH values at which the data were obtained accompany each spectrum.

been made to use various physical means to deduce the apparent association constants for Ln(EDTA) complexes with TIR or SSA, but while these results tend to differ by many orders of magnitude,[23-25] the values obtained were substantial.

Representative examples of low- and high-pH CPL line shapes obtained for the Tb(PDTA) complexes with TIR and SSA are shown in Figure 2. All low-pH line shapes are essentially unchanged relative to those of the parent Tb(CDTA) and Tb(PDTA) compounds, indicating that formation of the ternary compounds does not greatly perturb the basic APC stereochemistries. The Tb(III) emission intensities obtained in the Tb(APC)(SSA) or Tb(APC)(TIR) compounds were observed to be considerably higher than those of the parent Tb(APC) compounds, indicating that efficient energy transfer from the ligands to the Tb(III) ion could take place.

Somewhat different results were obtained within the high-pH region. The CPL spectra for Tb(CDTA)(TIR) and Tb(CDTA)(SSA) strongly resembled the corresponding high-pH spectra of the parent compounds. These results indicate that neither SSA nor TIR was capable of preventing formation of bridged Tb(APC)(hydroxy) compounds. On the other hand, large changes in the CPL line shapes were noted for the TIR and SSA ternary compounds with Tb(PDTA). The close similarity in the line shapes (and dissymmetry factors) obtained for Tb(PDTA)(TIR) and Tb(PDTA)(SSA) signifies that the compounds are very similar in their stereochemistry. Energy-transfer results obtained for Tb(EDTA)(TIR)[26] and Tb(EDTA)(SSA)[27] indicate that these mixed-ligand complexes are monomeric. Ternary formation constants were obtained for the SSA and TIR complexes, and these are consistent with the conclusions just outlined.

D. Ternary Complexes Containing Dicarboxylic Acids. Dicarboxylic acids are capable of binding lanthanide ions in a bidentate manner using both carboxylate groups. The complexes formed by oxalic acid (OX) are known to be the strongest, followed by the malonic acid (MAL) and succinic acid (SUC) complexes.[20] The Tb(III) aquo ion is usually precipitated by dicarboxylates (forming $Tb_2(L)_3$ compounds), but such precipitation does not take place with Tb(APC) compounds. The complexation between Ln(CDTA) and certain unsaturated dicarboxylic acids has been characterized by fairly strong formation constants.[28]

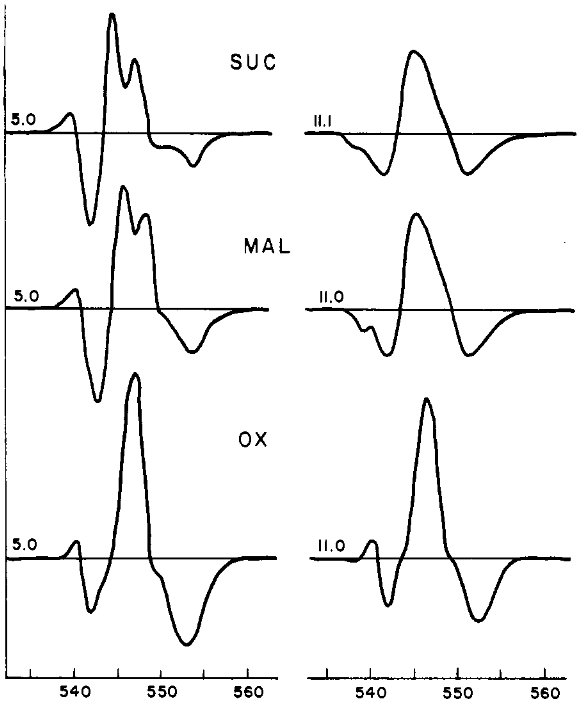

Figure 3. Circularly polarized luminescence spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition for Tb(CDTA) complexes with dicarboxylic acids. Data are shown for succinic acid (SUC), malonic acid (MAL), and oxalic acid (OX). The pH values at which the data were obtained accompany each spectrum.

Examples of the CPL spectra obtained at low and high pH are shown in Figure 3 for the Tb(CDTA)(dicarboxylate) compounds. Examination of Figure 3 reveals that the CPL spectra of Tb(CDTA)(SUC) and Tb(CDTA)(MAL) are not changed relative to the spectra of the parent Tb(CDTA) compound. This implies that the stereochemistry of the CDTA ligand is not changed upon formation of the simple adduct (low pH) and that the high-pH oligomerization process is not perturbed by the presence of either MAL or SUC. However, the situation for OX is very different. The low-pH spectrum of Tb(CDTA)(OX) is quite different from that of simple Tb(CDTA), indicating that binding of the OX ligand produces a strong alteration of the CDTA stereochemistry. No change in CPL pattern is noted at the high-pH conditions, indicating that the oxalate ligands cannot be displaced in the oligomerization process.

Somewhat similar trends were noted with the Tb(PDTA) compounds. Tb(PDTA)(SUC) behaves exactly as does Tb(CDTA)(SUC); hence, the same conclusions as stated above hold for this compound. In a similar vein, the same overall behavior was observed for Tb(PDTA)(OX), as was seen in the case of Tb(CDTA)(OX). Somewhat different behavior was observed for Tb(PDTA)(MAL), where the observed CPL spectra appeared to consist of a superimposition of Tb(PDTA)(OX) and Tb(PDTA)(SUC) spectra. We conclude from these considerations that a mixture of species is present for the Tb(PDTA)(MAL) compound.

The ternary formation constants shown in Table I again support these assignments. Only a lower limit could be calculated by the lifetime technique for the OX complexes, since the complexation

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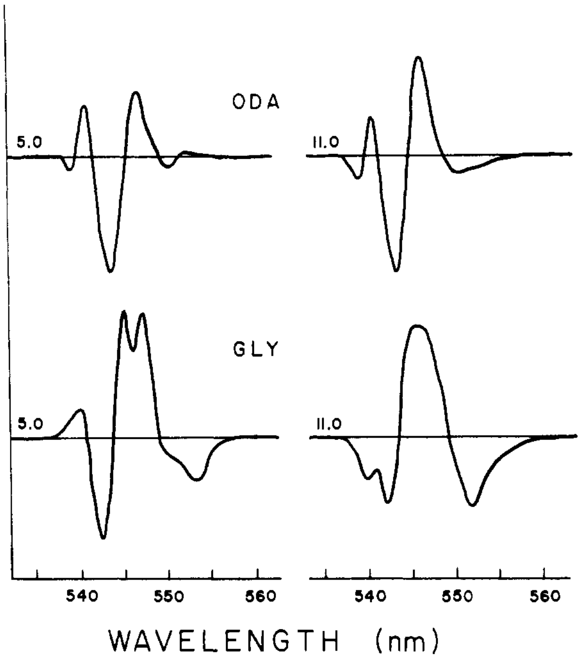

Figure 4. Circularly polarized luminescence spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition for Tb(CDTA) complexes with hydroxy carboxylic acids. Data are shown for oxydiacetic acid (ODA) and glycolic acid (GLY). The pH values at which the data were obtained accompany each spectrum.

was too strong to permit direct determinations. The values must be much larger than those for the oligomeric complexes; hence, the Tb(APC)(OX) compounds remain monomeric and unchanged over all pH values. With the CDTA ligand, the more weakly binding MAL and SUC cannot prevent the oligomer formation and must be expelled from the Tb(III) coordination sphere at high pH. With Tb(APC)(MAL), the association constant is comparable to that of the oligomer constant, thus the observation of the existence of multiple species. It is interesting to note that it is the smallest ligand which produces the largest changes in both the PDTA and CDTA stereochemistries upon formation of the ternary complexes. This observation implies that the larger dicarboxylate ligands (having more flexibility) are able to accommodate their structure to fit the available binding space in the Tb(APC) complex. The OX ligand has no such flexibility and must therefore enforce its steric requirements on the conformation of the APC ligands.

E. Ternary Complexes Containing Hydroxy Carboxylic Acids. The family of α-hydroxy carboxylic acids forms a sequence in which one may evaluate the relative strengths of Tb(III) complexation and relate these trends to observed CPL parameters. Attempts have been made to obtain the formation constants corresponding to the addition of hydroxy carboxylic acids to Ln(CDTA) complexes;[29,30] however, the computed constants were found to be larger than those reported for the simple binary complexes.[20]

CPL data were obtained on the simplest hydroxy carboxylic acid, glycolic acid (GLY), and on its dimer, oxydiacetic acid (ODA). The GLY ligand is known to bind lanthanide ions in a bidentate manner at the α-hydroxy carboxy grouping, while the ODA ligand binds in a tridentate manner using the two carboxylates and the ether oxygen. CPL spectra corresponding to the GLY and ODA complexes of Tb(CDTA) are found in Figure 4.

Examination of Figure 4 reveals that the low-pH CPL spectrum of Tb(CDTA)(GLY) is very much like that of the parent Tb(CDTA) compound. The low-pH spectrum of Tb(PDTA)(GLY) bears a strong resemblance to that of the parent Tb(PDTA) compound, but significant differences in minor peaks are evident.

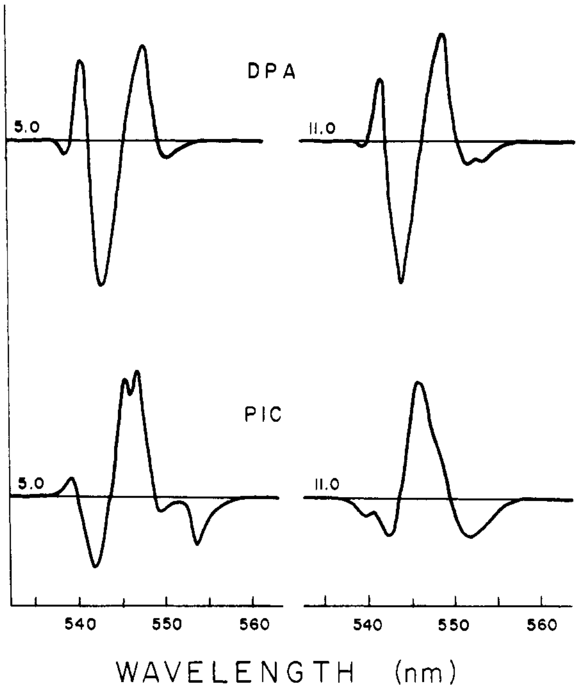

Figure 5. Circularly polarized luminescence spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition for Tb(CDTA) complexes with pyridinecarboxylic acids. Data are shown for dipicolinic acid (DPA) and picolinic acid (PIC).

These spectra indicate that a simple hydroxy carboxylic acid cannot perturb the stereochemistry of coordinated CDTA but that some steric interaction with PDTA is possible. These results are consistent with the overall observed trend that the PDTA ligand is more easily perturbed than the CDTA ligand. On the other hand, the CPL spectra obtained for the Tb(APC)(ODA) compounds are definitely altered relative to the parent Tb(APC) compounds. A very detailed inspection and interpretation of the spectra of Tb(CDTA)(ODA) and Tb(PDTA)(ODA) reveal that the two sets of CPL line shapes are really the same. The main difference between the two is that better peak resolution was obtained for the PDTA compound. The result would imply that only one mixed-ligand complex was present for Tb(PDTA)(ODA) and that at least two stereochemically similar species were observed with Tb(CDTA)(ODA).

When the solution pH is raised, the Tb(CDTA)(GLY) CPL line shape is indicative of the oligomeric species, while the Tb(PDTA)(GLY) line shape actually strongly resembles that of Tb(PDTA)(MAL). These results would imply that GLY cannot prevent the oligomerization of Tb(CDTA) but that some interference is possible for Tb(PDTA). Examination of the ternary formation constants of Table I indicates that these conclusions are exactly what one would anticipate. The high-pH spectra of the Tb(APC)(ODA) compounds are very much like those of the low-pH spectra, indicating that the tridentate ODA ligand definitely prevents formation of the Tb(APC) oligomers. This conclusion is in accord with the data of Table I, where it was found that the formation constants of the ODA complexes were too high to be measured by the lifetime method.

F. Ternary Complexes Containing Pyridinecarboxylic Acids. The final class of ternary ligands to be considered is that of the pyridinecarboxylic acids. The complexation of lanthanide ions by pyridine-2-carboxylic acid (picolinic acid, PIC) and pyridine-2,6-dicarboxylic acid (dipicolinic acid, DPA) has been well studied, and reliable association constants are available for the binding of PIC by Ln(EDTA) complexes.[31]

CPL spectra obtained on the PIC and DPA complexes of Tb(CDTA) are shown in Figure 5. Under low-pH conditions,

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(29) Rana, H. S.; Tadon, J. P. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1391.

(30) Tripathi, S. P.; Sharma, R. C.; Chaturvedi, G. K. *Z. Anorg. Allg. Chem.* **1980**, *462*, 226.

(31) Ekstrom, C.-G.; Nilsson, L.; Duncan, I. A.; Grenthe, I. *Inorg. Chim. Acta* **1980**, *40*, 91.

one finds that the PIC ligand induces some degree of change in the CPL line shapes of both Tb(PDTA) and Tb(CDTA). In both systems, a loss of peak resolution and the intensification of certain characteristic parent compound peaks are found. These observations imply that the PIC ligand requires a sufficiently larger binding site than the benzenecarboxylic acids. When the solution pH is raised to 11, interference with the oligomerization processes of both Tb(APC) compounds is observed. The relatively simple CPL line shape of the Tb(APC)(PIC) compound resembles that of the parent compound; however, significant wavelength differences exist. The complicated spectrum of the Tb(PDTA)(PIC) compound again is indicative of the presence of multiple species.

The situation is much simpler for the DPA mixed-ligand complexes. At low pH values, the spectra are strongly perturbed compared to the spectra of the parent compounds. No CPL line shape changes accompany raising of the solution pH to 11, indicating that the Tb(APC) oligomerizations cannot take place. It is quite significant to note that, aside from differences in minor sidebands, the CPL spectra of Tb(CDTA)(ODA), Tb(PDTA)(ODA), Tb(CDTA)(DPA), and Tb(PDTA)(DPA) are almost identical. We conclude from these observations that the two tridentate ligands bind Tb(III) so strongly (and dictate their own stereochemistry) that a particular conformation is forced upon the APC ligands. The observed Tb(III) chirality is a reflection of this enforced conformation.

These conclusions are supported by the known formation constants. According to Grenthe et al.,[31] log *K* of Gd(EDTA)(PIC) is 2.7 and log *K* of Dy(EDTA)(PIC) is 2.5. Our reported values (Table I) of log $K = 2.80$ for Tb(CDTA)(PIC) and log $K = 2.85$ for Tb(PDTA)(PIC) are in excellent agreement with those calculated by using the potentiometric method. These values are almost comparable to those we have reported for the Tb(PDTA) oligomer species, and one finds a significant degree of interference with formation of the $[\mathrm{Tb(PDTA)}]_x$ compounds. The values are also smaller than that of $[\mathrm{Tb(CDTA)}]_x$, and hence no interference with oligomerization is noted for Tb(CDTA)(PIC). The large ternary constants associated with the Tb(APC)(DPA) complexes are considerably larger than those for the corresponding oligomers, and thus only monomeric complexes can be formed.

Conclusions

Consideration of CPL spectra obtained for pure and mixed-ligand Tb(III) derivatives of (*R*)-(−)-PDTA and (*R*,*R*)-(−)-CDTA has enabled important conclusions to be drawn about the nature of these complexes. In the mixed-ligand complexes, one must separately consider the low- and high-pH situations. When the steric requirements of the ternary ligand are small, formation of the Tb(APC)(ligand) complex does not significantly perturb the stereochemistry of the APC ligand. However, should the ternary ligand require more space at the Tb(III) ion than is available after replacement of the three coordinated water molecules, then the APC ligand will adjust its conformation to suit the ternary ligand. For bulky tridentate ligands, such accommodations may require partial dissociation of one of the carboxylates of the APC ligand. Large ligands (e.g., succinate) that do not contain an inflexible aromatic ring system were found to adjust their own conformation, rather than induce a change in the APC ligand conformation.

At elevated pH values, two possible reactions may occur at the Tb(III) coordination sphere. If the association constant of the ternary ligand is smaller than the formation constant of the $[\mathrm{Tb(APC)}]_x$ polymer, the ternary ligand will be expelled and the oligomeric species will form. If the ternary ligand cannot be displaced, then the Tb(APC)(ligand) complex will remain monomeric even at the highest pH values. Should the two types of formation constants be equivalent in magnitude, then a mixture of compounds may result at high pH. The data indicate that the $[\mathrm{Tb(PDTA)}]_x$ species is more easily perturbed than is the $[\mathrm{Tb(CDTA)}]_x$ species, as would be expected from consideration of the apparent formation constants for polymeric association.

The results detailed in this work have important implications regarding the use of Ln(APC) compounds as aqueous shift reagents. If the steric nature of the substrate is such that it will become crowded by the APC ligand, then any conformational information deduced from analysis of the lanthanide-induced shifts may be misleading. The molecular conformation deduced in that situation would reflect the stereochemistry of the bound ligand, which could be substantially different from that of the free substrate. The results contained in this work indicate that one cannot simply assume a total lack of interaction between the APC ligand and a ternary substrate when these are both bound by a lanthanide ion. Any successful use of Ln(APC) compounds as aqueous shift reagents must consider the possible steric interactions of all ligands bound at the Ln(III) coordination sphere.

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Registry No. $\mathrm{Tb(PDTA)(H_2O)_3^-}$, 92389-75-8; $\mathrm{Tb(CDTA)(H_2O)_3^-}$, 92389-76-9; (*R*)-(−)-PDTA, 15456-17-4; Tb, 7440-27-9; (*R*,*R*)-(−)-CDTA, 28684-63-1; PHT, 88-99-3; TML, 528-44-9; HML, 569-51-7; PML, 89-05-4; TIR, 149-45-1; SSA, 97-05-2; OX, 144-62-7; MAL, 141-82-2; SUC, 110-15-6; GLY, 79-14-1; ODA, 110-99-6; PIC, 98-98-6; DPA, 499-83-2.

Supplementary Material Available: Figures showing additional CPL spectra obtained on Tb(CDTA) and Tb(PDTA) complexes with PML, HML, TML, PHT, TIR, SSA, SUC, MAL, OX, GLY, PIC, and DPA (8 pages). Ordering information is given on any current masthead page.