

## Circularly Polarized Luminescence Studies of the Ternary Complexes Formed by Tb(III) with (S,S)-Ethylenediamine-N,N'-disuccinic Acid and Achiral Substrate Ligands

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### Abstract

Circularly polarized luminescence spectroscopy has been used to study the ternary complexes formed by Tb(III) with (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS) and a series of achiral carboxylate ligands. The 1:1 Tb(EDDS) complexes form polynuclear species at low pH values, and only oxalic acid was able to interfere with this process. At elevated pH values the Tb(EDDS) compounds become monomeric, and are capable of forming ternary complexes. When the steric requirements of the substrate ligand were small, no perturbation of the EDDS stereochemistry was noted. However, certain strongly binding bidentate ligands with larger steric requirements were found to interact with the coordinated EDDS ligand. Evidence was also obtained which indicated that strongly binding terdentate ligands could partially displace one or more of the ligating carboxylates of the EDDS ligand.

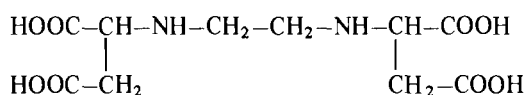
### Introduction

Studies of the stereochemical properties of lanthanide compounds are possible through the use of chiroptical techniques, and one may obtain important information regarding modes of metal–ligand bonding through such studies [1]. A significant literature has developed concerning lanthanide complexes with chiral aminopolycarboxylate ligands, with most workers concentrating on the lanthanide compounds with (R)-1,2-propanediamine tetraacetic acid (PDTA) [2–5] or (R,R)-*trans*-1,2-cyclohexanediamine tetraacetic acid (CDTA) [6, 7].

Circularly polarized luminescence (CPL) spectroscopy has been shown to be a valuable technique for the study of chiral lanthanide compounds [2, 8]. The CPL technique was used to detail the pH dependence of the conformational changes in the Tb(III)

and Eu(III) complexes of (R)-PDTA and (R,R)-CDTA [9]. In a subsequent study, the optical activity of ternary complexes containing Tb(III), either (R)-PDTA or (R,R)-CDTA, and an achiral substrate ligand was studied in an effort to detail any possible steric interactions which might exist among the various ligands [10]. In several instances, binding of the substrate led to drastic changes in the PDTA or CDTA conformational structure. The use of lanthanide aminopolycarboxylates as aqueous NMR shift reagents invariably assumes the lack of such interactions [11, 12], and with bulky substrate ligands such assumptions may not be reasonable [10].

The question of interactions among ligands in a lanthanide ternary complex has been addressed further during the course of the present work. Previously, the complexation of Tb(III) and Eu(III) by (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS):



was studied by means of CPL spectroscopy [13]. Earlier workers had noted that the circular dichroism spectra of lanthanide (S,S)-EDDS complexes exhibited variability with the solution pH and with the metal/ligand ratio [14, 15], and CPL spectral trends were used to deduce the details of the solution phase chemistry [13]. In the present work, the results of chiroptical studies on the nature of ternary Tb(EDDS) complexes with a series of achiral substrate ligands will be reported. The Tb(EDDS) complexes differ from the Tb(PDTA) and Tb(CDTA) compounds in that the solution phase chemistry is significantly more complicated, a fact undoubtedly due to the greater flexibility of the EDDS ligand.

### Experimental

(S,S)-EDDS was prepared by the condensation of two molecules of (S)-aspartic acid, using the method

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of Majer *et al.* [16] as modified by Neal and Rose [17]. In their work, Neal and Rose verified that the EDDS ligand forms with retention of configuration at each asymmetric atom of the L-ASP precursors. Stock solutions of Tb(III) perchlorate were prepared by dissolving the 99.9% oxide (Research Chemicals) in a stoichiometric amount of 70% HClO<sub>4</sub>, neutralizing to pH 3.5 with NaOH, and then diluting to the desired volume. The terbium and EDDS stock solutions were combined in such volumes so as to yield a Tb(III) ion concentration of 15 mM, and a Tb/EDDS ratio of 1:1 was used throughout.

The achiral substrate ligands were obtained from either Aldrich or Eastman, and were used as received. Stock solutions of these ligands were prepared, and a variety of Tb/EDDS/substrate ratios were studied. Limiting behavior in the CPL spectra was taken as an indication that the Tb(EDDS)(substrate) complex was fully formed. The pH of these solutions was varied between 3.0 and 11.5, with CPL data being obtained at approximate 0.5 intervals.

All CPL spectra were obtained on a spectrometer constructed for the purpose, and which is capable of simultaneously measuring total luminescence (TL) and CPL spectra at high resolution. The samples were excited either by the 365 nm output of a 1000W Xe arc lamp (selected by a combination of a 0.1 m grating monochromator and UV-transmitting filters), or by the UV output (350 nm) of an Ar-ion laser (Coherent model Innova 90-5). The emission was analyzed by a 0.5 m grating monochromator, and detected by an EMI 9798B photomultiplier tube (S-20 response). With the arc lamp, an excitation bandpass of 16 nm was used in combination with an emission bandpass of 2 nm; in this manner general trends involving spectra and solution pH were examined. More detailed analyses of the CPL lineshapes were obtained with the laser excitation, and these experiments were carried out at an emission bandpass of 0.2 nm.

In the CPL experiment, two observable quantities are produced. These are the total luminescence (TL) intensity, given as:

$$I = I_L + I_R$$

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

$$\Delta I = I_L - I_R$$

Most luminescence work concentrated on the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition at 545 nm, since it has been established that this particular transition exhibits the highest degree of both total and circularly polarized emission [18].

## Results and Discussion

UV excitation of a Tb(III) complex usually results in efficient population of the <sup>5</sup>D<sub>4</sub> excited state, and in the observation of emissive transitions to the <sup>7</sup>F<sub>6</sub> (490 nm), <sup>7</sup>F<sub>5</sub> (545 nm), <sup>7</sup>F<sub>4</sub> (585 nm), and <sup>7</sup>F<sub>3</sub> (625 nm) states of the ground manifold. Since it is only the J quantum number of a given state which is defined for a Tb(III) ion, then the spectroscopic transitions need only be labeled merely by the J quantum numbers of the initial and final states. 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.

### Tb(EDDS) Parent Compounds

The complexation of Tb(III) by (S,S)-EDDS is an efficient process, with a formation constant of log K = 13.51 being reported for the 1:1 complex [19]. However, the formation constant alone does not convey any details of the solution phase chemistry of the 1:1 Tb(EDDS) complex. pK<sub>a</sub> values for the EDDS ligand are available [20], but since the metal ion assists in the deprotonation steps, these particular values cannot be used to predict the protonation state of a particular Tb(EDDS) complex.

However, the details of the solution phase chemistry of the 1:1 Tb(EDDS) complex were deduced from a series of photophysical studies [13]. Below pH 8, extensive association of Tb(EDDS) complexes into polynuclear species was found to take place. At the same time, relatively few water molecules (approximately 2½ per metal ion) were bound at the inner coordination sphere of the Tb(III) ion. Since the coordination number of the lanthanide ion is normally 8 or higher, it was concluded that a considerable portion of each Tb(III) coordination sphere must be occupied by carboxylate groups of EDDS ligands. In these low pH polynuclear complexes, the EDDS ligands undoubtedly bridge Tb(III) centers. The CPL spectra obtained at low pH values for 1:1 Tb/EDDS ratios strongly resembled those obtained for Tb(III) complexes of (S)-aspartic acid [21], which would be consistent with sole carboxylate bonding.

Once pH 8 was exceeded, the complexes become totally monomeric and the number of coordinated water molecules increased to 4. This process apparently accompanied the full deprotonation of the EDDS ligand, which would then be expected to bind a single metal ion in a hexadentate manner. At 1:1 total ratios of metal/ligand, only the Ln(EDDS) complex would be formed. Since an average of 4 water molecules were shown to bind at the inner coordination sphere of the Tb(III) ion [13], the

monomeric Tb(EDDS) complex exhibits a coordination number of 10. These water molecules may be replaced by a substrate ligand:



in exactly the same manner as has been noted for other Tb(III) aminopoly carboxylate complexes [2].

#### Ternary Complexes Containing Benzene Carboxylic Acids

The first group of ternary complexes studied were those formed by Tb(EDDS) with several benzene carboxylic acids. These ligands were chosen since they were known to bind lanthanide ions with reasonable efficiency [22], and also since their steric requirements were anticipated to be minor. Such properties would insure that these ligands would not be likely to cause large perturbations in the conformation of the chelated EDDS ligand. Thus the observed CPL spectra would demonstrate that ternary complexes could be formed without altering the overall stereochemistry of the EDDS ligand.

Representative CPL spectra obtained for the Tb(EDDS) complexes with phthalic (PHT), trimellitic (TML), hemimellitic (HML), and pyromellitic (PML) acids are shown in Fig. 1. The low pH CPL lineshapes were generally stable between pH 3.5 and 8.0, and gradually changed into the high pH lineshapes between pH 8.5 and 9.0. The high pH lineshapes were stable between pH 9.5 and 10.5, and underwent drastic decompositions (due to complex hydrolysis)

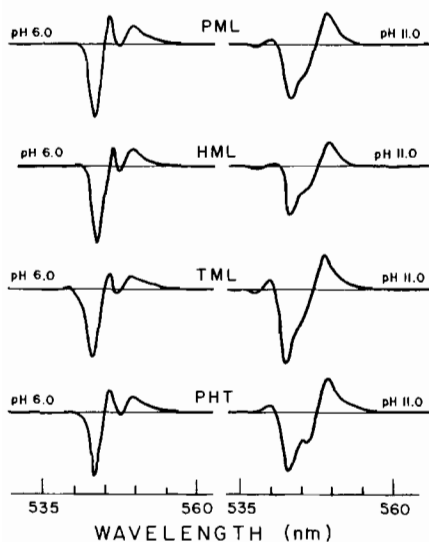


Fig. 1. Circularly polarized luminescence spectra obtained within the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  Tb(III) transition for Tb(EDDS) complexes with benzene carboxylic acids. Data are shown for pyromellitic acid [PML], hemimellitic acid [HML], trimellitic acid [TML], and phthalic acid [PHT]. The pH values at which the data were obtained accompany each spectrum.

above pH 11. These trends are essentially the same as those reported earlier for the parent Tb(EDDS) complex [13].

Comparison of the data in Fig. 1 with the corresponding data of the parent compounds (Fig. 2 of reference [13]) enables one to deduce whether any stereochemical changes accompany formation of the ternary compounds. The low pH CPL spectra are essentially superimposable with the corresponding spectra of the parent Tb(EDDS) compound. The luminescence dissymmetry factors obtained for corresponding bands are also quite similar, indicating that little perturbation of the APC ligand configuration has accompanied the interaction with the benzene carboxylate ligands.

These observations therefore indicate that the benzene carboxylic acids are incapable of interfering with the polynuclear association of the 1:1 Tb(EDDS) complexes. This situation could only arise if the low pH association constant governing formation of the Tb(EDDS)(BCA) complex was less than the corresponding value for the polynuclear  $[\text{Tb(EDDS)}]_x$  complex. In the earlier work [13], evaluation of the energy transfer data permitted a calculation of the formation constant of the donor/acceptor complex as  $K_c = 125 \pm 20$  liter/mol. Absolutely no mixed ligand formation constants have been measured for Tb(EDDS) with any ligand, but it is clear that these formation constants must be smaller than 125 liter/mol.

All of the high pH CPL spectra were also found to strongly resemble the spectra of the parent Tb(EDDS) compound. One may therefore conclude that formation of the ternary Tb(EDDS)(ligand) complexes is not accompanied by any perturbation in the steric nature of the EDDS ligand. This conclusion is exactly in accord with what had been anticipated, since in an earlier work it had been noted that benzene carboxylic acids are incapable of perturbing the stereochemistry of chelated (R)-PDTA or (R,R)-CDTA [10]. These results all indicate that the CPL technique can be successfully used to determine the extent of steric interactions in the ternary Tb(EDDS)-(ligand) complexes.

#### Ternary Complexes Containing Sulfonated Benzene Derivatives

Mixed-ligand complexes formed between lanthanide aminopolycarboxylate compounds and either 5-sulfosalicylic acid (SSA) or 1,2-dihydroxybenzene-3,5-sulfonic acid (tiron, or TIR) have received a great deal of attention, since these compounds may be used in fluorometric determinations of Tb(III) [23, 24]. Upon becoming bound in a ternary complex, the sulfonated benzene derivatives will function as extremely strong sensitizers of Tb(III) luminescence, unlike the benzene carboxylic acids for which such sensitization processes are only moderately strong.

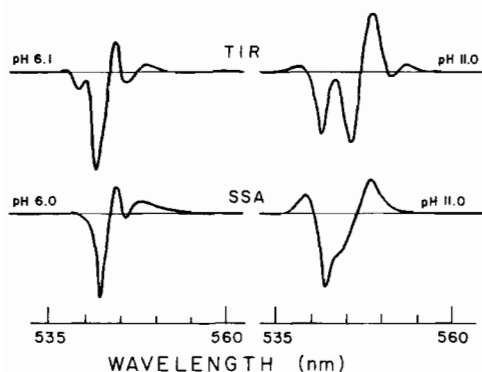


Fig. 2. Circularly polarized luminescence spectra obtained within the  $^5D_4 \rightarrow ^7F_5$  Tb(III) transition for Tb(EDDS) complexes with sulfonated benzene derivatives. Data are shown for tiron [TIR] and 5-sulfosalicylic acid [SSA]. The pH values at which the data were obtained accompany each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

Representative examples of low and high pH CPL lineshapes obtained for the Tb(EDDS) complexes with TIR and SSA are shown in Fig. 2. Once again, the low pH lineshapes are essentially unchanged relative to those of the parent Tb(EDDS) compound, although a very minor difference was noted for the Tb(EDDS)(TIR) compound. These observations indicate that formation of the ternary compounds does not greatly perturb the basic EDDS stereochemistry over the pH range for which the polynuclear species dominate the solution chemistry.

Somewhat different results were obtained within the high pH region. The CPL spectra obtained for Tb(EDDS)(SSA) strongly resembled the corresponding high pH spectra of the parent compounds. This result indicates that the SSA ligand does not alter the basic conformation of the bound EDDS ligand. On the other hand, large changes in the CPL lineshapes were noted for the TIR ternary compound with Tb(EDDS). The CPL spectrum of Tb(EDDS)(TIR) bears some resemblance to the Tb(EDDS)(SSA) spectrum, except that a major CPL peak is found at 547 nm (where only a shoulder was observed before). This observation actually suggests that the CPL spectrum of Tb(EDDS)(TIR) reflects contributions made by two different Tb(III) complexes, one of which represents a highly perturbed Tb(EDDS) species and one of which is an unperturbed species.

It is quite significant to note that the ligand which yielded the largest spectral change was the catechol derivative, and similar results were obtained earlier for the tiron complexes with Tb(PDTA) and Tb(CDTA) [10]. Upon deprotonation of the hydroxyl groups, tiron represents a ligand which forms a small, planar chelate ring when it binds to the Tb(III) ion. The bulky phenyl group is then bound much closer to the Tb(III) ion, and the inflexible ligand would be unable to twist so as to relieve its steric interactions

with the EDDS ligand. Even though the SSA ligand contains basically the same phenyl group, the larger (and more flexible) chelate ring which can be formed by the salicylate functionality clearly can accommodate itself on the Tb(III) coordination sphere without interacting with the coordinated EDDS ligand.

#### Ternary Complexes Containing Dicarboxylic Acids

Dicarboxylic acids are capable of binding lanthanide ions in a bidentate manner, as long as the chelate ring does not contain more than seven members. Relatively strong complexes are formed by oxalic acid (OX), malonic acid (MAL), and succinic acid (SUC), but glutaric acid does not form chelates. The Tb(III) aquo ion is usually precipitated by dicarboxylates (forming  $Tb_2(L)_3$  compounds), but such precipitation does not necessarily take place with ternary Tb(III) aminopolycarboxylate compounds. The complexation between Ln(CDTA) and certain unsaturated dicarboxylic acids has been characterized by fairly strong formation constants [25].

Examples of the CPL spectra obtained at low and high pH are shown in Fig. 3 for the Tb(EDDS)(di-

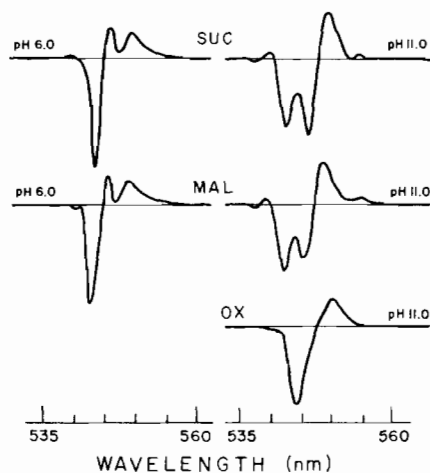


Fig. 3. Circularly polarized luminescence spectra obtained within the  $^5D_4 \rightarrow ^7F_5$  Tb(III) transition for Tb(EDDS) complexes with dicarboxylic acids. Data are shown for succinic acid [SUC], malonic acid [MAL], and oxalic acid [OX]. The pH values at which the data were obtained accompany each spectrum. No data are illustrated for Tb(EDDS)(OX) at low pH values due to the extensive precipitation observed in the solutions.

carboxylate) compounds. No data could be obtained at low pH values for the Tb(EDDS)(OX) system due to the presence of extensive precipitation of Tb(III) oxalate complexes. However, examination of Fig. 3 reveals that the low pH CPL spectra of Tb(EDDS)(SUC) and Tb(EDDS)(MAL) each are not changed relative to the spectra of the parent Tb(EDDS) com-

pound. This result implies that these dicarboxylate ligands cannot interfere with the formation of polymeric  $[\text{Tb}(\text{EDDS})_x]$  complexes within the low pH region. That the oxalate ligand is capable of interfering with this polymerization process is self-evident in that OX is capable of pulling the Tb(III) ion out of the Tb(EDDS) complex.

The high pH CPL spectra of the Tb(EDDS)(dicarboxylate) complexes all represent varying degrees of perturbation upon the basic Tb(EDDS) lineshape. The CPL spectrum of Tb(EDDS)(SUC) is essentially superimposable with that of Tb(EDDS)(TIR), which may be taken as indicating the presence of equal amounts of perturbed and unperturbed complexes. The high pH CPL spectrum of Tb(EDDS)(MAL) much more closely resembles that of Tb(EDDS), although the peak due to the perturbed species is still somewhat prominent. The spectrum of the perturbed Tb(EDDS) species is given clearly for Tb(EDDS)(OX); this compound is freely soluble at high pH values. Thus, the strong binding of the oxalate ligand yields a single ternary Tb(EDDS)(OX) compound, whose major CPL component (the negative peak at 547 nm) is seen to exist in the Tb(EDDS) derivatives with TIR, SUC, and MAL.

Unfortunately, no thermodynamic quantities are available for OX, MAL, or SUC in these mixed-ligand complexes, but comparison with data obtained on simpler complexes enables a rationalization of the data. The following formation constants have been reported for 1:1 Tb(dicarboxylate) complexes:  $\log K_1 = 5.5$  for OX,  $\log K_1 = 4.4$  for MAL, and  $\log K_1 = 3.2$  for SUC [22]. The CPL data are consistent with OX complexation as being the strongest in the ternary complexes. In addition to the strong binding, the OX ligand also contains the least degree of flexibility and forms a very small chelate ring. These properties are similar to those of the TIR ligand, and hence may be viewed as a general which promotes steric crowding of a coordinated EDDS ligand.

#### Ternary Complexes Containing Hydroxy Carboxylic Acids

The family of  $\alpha$ -hydroxy carboxylic acids forms an extensive sequence in which one may evaluate the relative strengths of Tb(III) complexation, and relate these trends to observed CPL parameters. 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  $\alpha$ -hydroxycarboxy grouping, while the ODA ligand binds in a terdentate manner using the two carboxylates and the ether oxygen. CPL spectra corresponding to the GLY and ODA complexes of Tb(EDDS) are found in Fig. 4.

Examination of Fig. 4 reveals that the low pH CPL spectrum of Tb(EDDS)(GLY) is very much like

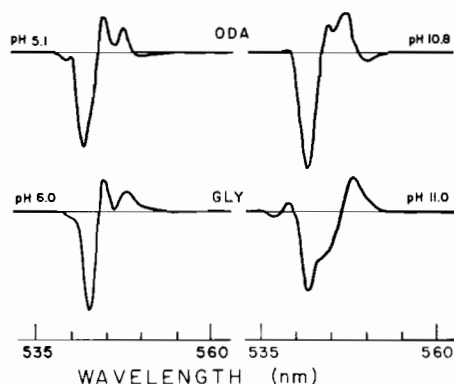


Fig. 4. Circularly polarized luminescence spectra obtained within the  $^5D_4 \rightarrow ^7F_5$  Tb(III) transition for Tb(EDDS) complexes with hydroxy carboxylic acids. Data are shown for oxydiacetic acid [ODA] and glycolic acid [GLY]. The pH values at which the data were obtained accompany each spectrum.

that of the parent Tb(EDDS) compound. In addition, the high pH spectrum of Tb(EDDS)(GLY) is also very similar to that of the parent Tb(EDDS) compound. These results imply that GLY cannot interfere with the low pH polymerization of the Tb(EDDS) complex. GLY also does not perturb the stereochemistry of coordinated EDDS in the Tb(III) complex, a feature undoubtedly due to the relatively minor steric requirement of the GLY ligand. Since the entire family of  $\alpha$ -hydroxycarboxylic acids should present similar steric requirements, one would anticipate that little steric interaction would exist for the other members of the family.

Somewhat different trends were noted in the CPL spectra of Tb(EDDS)(ODA). The low pH CPL spectrum was essentially that of the parent Tb(EDDS) complex, indicating again that no interference with the formation of low pH polynuclear complexes was possible. The high pH CPL spectrum of Tb(EDDS)(ODA) is distinctly different from that of the parent Tb(EDDS) compound, indicating the presence of substantial steric interactions in the ternary complex. Since the ODA ligand is certainly terdentate, a large steric interaction is not surprising. The low and high pH spectra bear a strong resemblance to each other, and this similarity persists in the other Tb(III) emission bands. In Fig. 5, data obtained within the  $^5D_4 \rightarrow ^7F_3$  band system are shown, and the correspondence between the spectra is evident. The data still resemble those of Tb/aspartate complexes, and this observation would be consistent with partial dissociation of the EDDS ligand (promoted by the multidentate bonding of the ODA ligand). Partial dissociation of the EDDS ligand would yield an aspartate-like chelate ring, and would also require quite strong lanthanide ion binding by the ODA ligand.

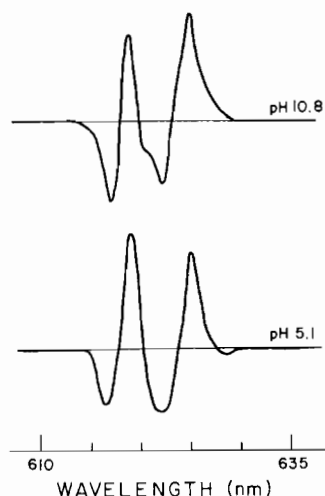


Fig. 5. Circularly polarized luminescence spectra obtained within the  $^5D_4 \rightarrow ^7F_3$  Tb(III) transition for the Tb(EDDS)-(ODA) complex. The pH values at which the data were obtained accompany each spectrum.

Since the formation constants of these mixed-ligand complexes are unavailable, one must consider the formation constants governing the binding of GLY and ODA by the Tb(III) aquo ion. These are reported as:  $\log K_1 = 4.8$  for Tb(GLY) and  $\log K_1 = 5.6$  for Tb(ODA) [22]. The ODA is seen to form much more robust complexes, as, would be required to displace a portion of the coordinated EDDS ligand.

#### Ternary Complexes Containing Pyridine Carboxylic Acids

The final class of ternary ligands to be considered are pyridine carboxylic acids, with data being obtained on the Tb(EDDS) complexes with pyridine-2-carboxylic acid (picolinic acid, PIC) and pyridine-2,6-dicarboxylic acid (dipicolinic acid, DPA). CPL spectra obtained within the  $^5D_4 \rightarrow ^7F_5$  band systems of the PIC and DPA complexes of Tb(EDDS) are found in Fig. 6. Under low pH conditions, one finds that the PIC ligand does not significantly perturb the low pH CPL lineshape of the parent Tb(EDDS) complex. Thus, it is concluded that the PIC ligand cannot significantly interfere with the formation of the low pH polynuclear complexes. At high pH values, the spectrum of Tb(EDDS)(PIC) is definitely changed relative to that of Tb(EDDS), and actually bears a close resemblance to the spectrum shown earlier for Tb(EDDS)(OX). It may therefore be concluded that the PIC ligand can interact with the EDDS ligand, and if the OX ligand does not lead to partial dissociation of the EDDS ligand then neither can the PIC ligand.

The data trends obtained for the Tb(EDDS)(DPA) complexes were found to be extremely similar to

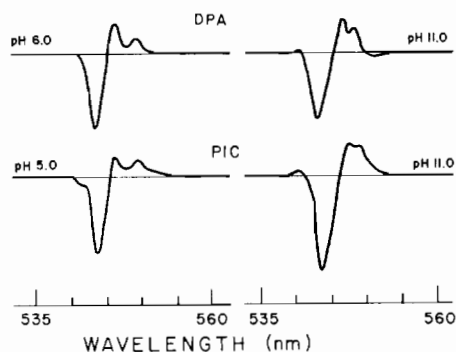


Fig. 6. Circularly polarized luminescence spectra obtained within the  $^5D_4 \rightarrow ^7F_5$  Tb(III) transition for Tb(EDDS) complexes with pyridine carboxylic acids. Data are shown for dipicolinic acid [DPA] and picolinic acid [PIC]. The pH values at which the data were obtained accompany each spectrum.

those just described for the ODA complexes. The low pH CPL lineshapes strongly resemble those of the parent Tb(EDDS) complex, indicating that the DPA ligand does not interfere with the oligomerization of the Tb(EDDS) complexes. The high pH spectra were found to be quite different from those of the parent complex, indicating the presence of strong steric interactions among the coordinated ligands. The high pH CPL spectra of the Tb(EDDS)(DPA) compound bear a strong resemblance to those of the Tb(EDDS)-(ODA) complex, and this similarity does carry over into the other Tb(III) band systems. Spectra obtained within the  $^5D_4 \rightarrow ^7F_3$  Tb(III) band system are shown in Fig. 7 for the Tb(EDDS)(DPA) compound, and a comparison with the data of Fig. 5 reveals the generality of the trend. These results imply that the

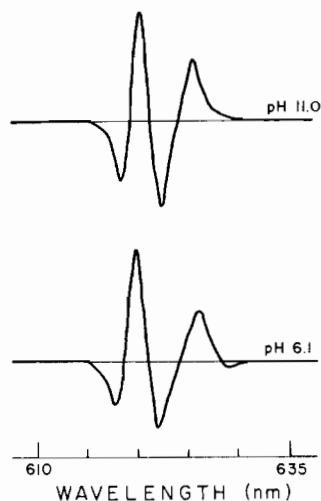


Fig. 7. Circularly polarized luminescence spectra obtained within the  $^5D_4 \rightarrow ^7F_3$  Tb(III) transition for the Tb(EDDS)-(DPA) complex. The pH values at which the data were obtained accompany each spectrum.

DPA ligand (which certainly forms very strong complexes with lanthanide ions [20]) also promotes partial dissociation of the EDDS ligand, since the observed CPL spectra are very similar to those of the S-aspartate complex.

## Conclusions

Consideration of CPL spectra obtained for pure and mixed-ligand Tb(III) derivatives of (S,S)-EDDS has enabled important conclusions to be drawn about the nature of these complexes. In the parent compounds, the low pH 1:1 Tb(EDDS) complexes were known to exist as oligomeric species of an ill-defined nature. At high pH values, final deprotonation of the EDDS ligand resulted in the formation of a well-defined, monomeric complex containing a hexadentate EDDS ligand and four bound water molecules.

In the mixed-ligand complexes, one must separately consider the low and high pH situations. Almost all of the achiral substrate ligands were not able to interfere with the low pH formation of polynuclear Tb(EDDS) complexes, indicating that the formation constants of these complexes were smaller than the association constants of the polymeric species. Only oxalic acid could perturb the association processes, and presumably the driving force for its reaction was the tendency to form insoluble oxalate compounds. In the polynuclear compounds, the CPL spectra were very similar to those of S-aspartic acid, indicating that the EDDS ligands probably bridge Tb(III) centers by means of bidentate, succinate-type ligation.

At high pH values, the coordinated water molecules of the monomeric Tb(EDDS) complex could be replaced by a variety of carboxylate ligands. When the ternary substrate ligands were small in size, or could form flexible chelate rings, then formation of the Tb(EDDS)(ligand) complex did not significantly perturb the stereochemistry of the EDDS ligand. However, when the ternary ligand required more space at the Tb(III) ion than was available after replacement of the four coordinated water molecules, then the EDDS ligand was found to adjust its conformation to suit the ternary ligand. For bulky terdentate ligands, such accommodations apparently required partial dissociation of one of the carboxylates of the EDDS ligand. Large ligands (e.g., succinate) which do not contain an inflexible aromatic ring system were found to adjust their own

conformation, rather than induce a major change in the EDDS ligand conformation.

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