

Solution Chemistry of Lanthanide Complexes. 7. Terbium(III) and Europium(III) Complexes of (*S,S*)-Ethylenediamine-*N,N'*-disuccinic Acid

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Received September 28, 1983

A variety of luminescence techniques have been used to study the complexes formed between the title compound (abbreviated as EDDS) and Tb(III) and Eu(III). The pH dependence of the luminescence intensity and lifetime was followed as a function of the metal:ligand ratio, and it was ascertained that different complex behavior existed on either side of pH 8. Below pH 8, the EDDS ligand was found to bind exclusively through the succinate functionalities. Extensive self-association of the Ln/EDDS complexes was noted at the 1:1 metal:ligand ratio, but this tendency was lost upon any increase in the metal:ligand ratio. Above pH 8, EDDS was found to bind in the anticipated hexadentate manner, and at metal:ligand ratios exceeding 1:1 the formation of a Ln(EDDS)₂ compound was deduced. The number of coordinated water molecules were counted spectroscopically for all metal:ligand ratios under conditions of low and high pH, and it appears that in most cases the lanthanide ion prefers a state of 10-coordination.

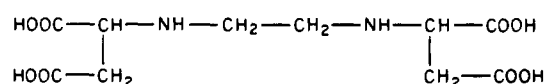
Introduction

Historically, the lanthanide complexes of aminopoly-carboxylic acids (APC) have been of great importance, since with these ligands the individual members of the series could be refined to any desired degree of purity.¹ Since that time, Ln(APC) complexes have continued to attract interest as aqueous shift reagents in NMR spectroscopy² and as compounds whose solution-phase stereochemistry is fairly simple to describe. Significant progress in understanding the dynamics associated with the complexes has come primarily from studies of NMR spectroscopy, and it is now established that the lifetime of the metal–nitrogen bonds is long on the NMR time scale, while the lifetime of the metal–oxygen bonds appears to be short in the same time scale.^{3,4}

Valuable information concerning the stereochemistry of these complexes is available from chiroptical investigations. But while the ethylenediaminetetraacetate complexes of kinetically inert transition-metal ions have been resolved chemically (and hence well characterized), the lanthanide derivatives of this ligand racemize too quickly to permit a chemical resolution.⁵ Consequently, the chiroptical investigations that have been carried out concern ligands in which chirality has been incorporated into the ligand framework. The optical rotatory dispersion (ORD) and circular dichroism (CD) spectra obtained for the free ligands and the lanthanide complexes of (*R*)-1,2-propylenediaminetetraacetic acid (PDTA)^{6–8} and (*R,R*)-*trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA)^{9,10} have been used to study the stereochemistry of these compounds. More recently, the Tb(III) and Eu(III) derivatives of (*R*)-PDTA and (*R,R*)-CDTA have been studied by means of circularly polarized luminescence (CPL) spectroscopy.¹¹

In the present work, we report the results of investigations detailing the complexation of Tb(III) and Eu(III) by (*S,S*)-

(*S,S*)-ethylenediamine-*N,N'*-disuccinic acid (EDDS)



as studied by means of CPL spectroscopy. Earlier workers had noted that the CD spectra of lanthanide (*S,S*)-EDDS complexes exhibited variability with pH and the metal:ligand ratio.^{12,13} Parallel observations were found in our (*R*)-PDTA and (*R,R*)-CDTA study.¹¹ The (*S,S*)-EDDS ligand was obtained upon condensation of two molecules of (*S*)-aspartic acid (ASP), and thus the present work may be considered to build on our earlier CPL studies of the lanthanide complexes formed with (*S*)-ASP.¹⁴

Experimental Section

Materials. (*S,S*)-EDDS was prepared by the condensation of two molecules of (*S*)-ASP, with use of the method of Majer et al.¹⁵ as modified by Neal and Rose.¹⁶ 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) and Eu(III) were prepared by dissolving the 99.9% oxides (Research Chemicals) in a stoichiometric amount of 70% HClO₄, neutralizing to pH 3.5 with NaOH, and then diluting to the desired volume. The lanthanide ion and EDDS stock solutions were combined in such volumes as to yield a Ln(III) ion concentration of 15 mM and metal:ligand ratios of 1:1, 1:2, 1:3, and 1:5.

Apparatus. Low-resolution total luminescence (TL) spectra were obtained on a fluorimeter constructed for this purpose. Samples were excited by the 365-nm output of a 100-W Hg arc lamp, with this wavelength being selected by a combination of a prism monochromator and UV-transmitting glass filters. The emission was analyzed at a 5-nm band-pass by the monochromator of a Beckman DU spectrometer (modified so as to permit wavelength scanning) and detected by an EMI 9781R photomultiplier tube (S-5 response). Daily fluctuations in emission intensities were dealt with by referencing all observed intensities to that of a standard sample of uranyl glass.

Emission lifetimes were obtained on the same basic system as described above, but with the replacement of the arc lamp by a nitrogen laser (PRA Associates, Model LN-100). The transient currents developed upon pulsed excitation of the sample were converted into voltages with a 220 kΩ load resistor, and these voltage pulses were captured on a storage oscilloscope. The emission lifetimes were obtained from the decay curves with use of a linear regression analysis of the $\ln I$ vs. time data points. Plots of $\ln I$ vs. time were invariably found to be linear and thus indicate the presence of only one emitting species.

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All CPL spectra were obtained on a different spectrometer, capable of simultaneously measuring TL and CPL spectra at much higher resolution. The samples were excited either by the 365-nm (Tb compounds) or 301-nm (Eu compounds) outputs of a 200-W Hg-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 band-pass of 16 nm was used in combination with an emission band-pass of 2 nm; in this manner general trends involving spectra and solution pH were examined. More detailed analyses of the CPL line shapes were obtained with the laser excitation, and these experiments were carried out at an emission band-pass of 0.2 nm.

Methods. TL and CPL spectra were recorded (at either medium or high resolution) for each metal:ligand ratio at selected pH values between 3.5 and 12.0. The solution pH was controlled by the addition of microliter amounts of standard NaOH or HClO₄ to 3.0 mL of the Ln/EDDS solution in the fluorescence cuvette. The pH was read on an Orion 701A pH meter employing a glass microcombination electrode, which was inserted directly into the cuvette. The electrode was calibrated daily by means of standardized phthalate and phosphate buffers. Emission lifetimes were recorded at each pH value, and hence complete plots of both photophysical parameters vs. pH were constructed.

In the energy-transfer experiments, small amounts of Eu/EDDS were added to Tb/EDDS solutions, with care being taken so that the overall metal:ligand ratio was not changed. The pH of each solution was then systematically varied between 3.5 and 12.0 as before, and the TL and emission lifetime were obtained at each pH value. Comparison of the intensity (or lifetime) vs. pH plots enabled a determination of these quantities at any desired pH value, and thus the quenching of the Tb(III) emission by Eu(III) could be evaluated as a function of pH.

The number of water molecules remaining attached to the lanthanide ions after formation of the Ln/EDDS complexes was determined by the method described by Horrocks and Sudnick.¹⁷ Tb/EDDS solutions were brought to dryness by heating at 110 °C in a vacuum desiccator and then redissolved in either H₂O or D₂O. The emission lifetime of the Tb(III) ion was measured in each solvent, and the reciprocal lifetime was used to estimate the number of coordinated water molecules.

Results and Discussion

A. pH Dependence of Luminescence. UV excitation of a Tb(EDDS) complex results in efficient population of the ⁵D₄ excited state and in the observation of emissive transitions to the ⁷F₆ (490 nm), ⁷F₅ (545 nm), ⁷F₄ (585 nm), and ⁷F₃ (625 nm) states of the ground manifold. The intensities and lifetimes of these bands were found to be dependent both on solution pH and on the metal:ligand ratio. However, it was noted that none of the observed trends depended on the particular band used to obtain the data, and consequently all attention focused on the ⁵D₄ → ⁷F₅ transition of the Tb(EDDS) complexes.

In the Eu(EDDS) complexes, the luminescence originates in the ⁵D₀ excited state and terminates in the ⁷F₀ (580 nm), ⁷F₁ (595 nm), and ⁷F₂ (615 nm) levels of the ground state. Again, the general trends were reproduced in each band system and consequently only luminescence obtained for the ⁵D₀ → ⁷F₂ transition was used for systematic studies. However, it was found that the trends noted with the various Eu(EDDS) complexes could not be distinguished from those of the Tb(EDDS) compounds. As a result, only the data obtained from study of the Tb(EDDS) complexes will be reported, but it should be remembered that the conclusions are of a general nature. These should be applicable to the lanthanide ions lying to the center of the series.

The dependence of Tb luminescence upon solution pH is illustrated in Figure 1, and all the curves may be subdivided into two areas. At low pH values (between pH 4 and 7), the

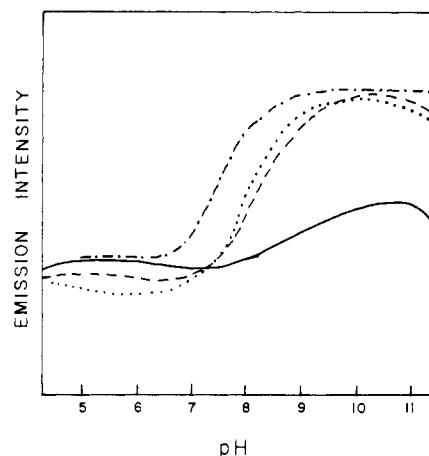
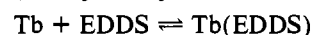


Figure 1. pH dependence of the total luminescence obtained from the Tb/EDDS complexes as a function of the metal:ligand ratio. The data were obtained at [Tb] = 15 mM and at metal:ligand ratios of 1:1 (—), 1:2 (---), 1:3 (···), and 1:5 (-·-·). The intensity scale is purely arbitrary, but the curves have been normalized so that they may be compared on a quantitative basis.

luminescence intensity of Tb/EDDS exhibits little variation with either pH or EDDS concentration. Above pH 7, the 1:1 Tb/EDDS solution exhibits only a modest increase in emission intensity, while a much sharper rise in luminescence is noted for the 1:2, 1:3, and 1:5 solutions. At the same time, little difference exists in the curves obtained at the higher metal:ligand ratios. Most of the curves exhibit a decrease in emission intensity above pH 11 (due undoubtedly to base-assisted hydrolysis of the complexes), but at the highest Tb:EDDS ratio such behavior is absent.

The emission lifetimes obtained for the same metal:ligand ratios exhibited pH trends that paralleled those just described for the emission intensities. At the 1:1 Tb:EDDS ratio the lifetime increased from 385 μs at pH 3.5 to 700 μs at pH 4.5. Between pH 4.5 and 8.0, the lifetime was observed to remain essentially constant at 720 μs but increased to 1030 μs in a regular fashion by pH 10.3. The lifetime was found to peak around pH 10.5 and decreased as the pH was raised further. In the low-pH region, Tb(III) emission lifetimes observed for the 1:2, 1:3, and 1:5 Tb/EDDS solutions did not differ appreciably from those obtained at the 1:1 ratio, but above pH 7 it was found that the lifetimes rose to significantly higher values. It was also noted that once the Tb:EDDS ratio exceeded 1:1, all solutions were found to exhibit a limiting lifetime of 1140 μs.

The trends just described provide strong evidence that different species must exist in the solutions at the various pH values and metal:ligand ratios. It is clear that formation of a 1:1 Ln(EDDS) complex is possible



since, for Eu(III), log *K* = 13.54 and, for Tb(III), log *K* = 13.51.¹⁸ The higher emission intensities and lifetimes observed at metal:ligand ratios exceeding 1:1 strongly suggest the formation of a 1:2 Ln(EDDS)₂ compound:



No formation constant values corresponding to the Ln(EDDS)₂ compounds have been reported.

B. Number of Coordinated Water Molecules. Very important probings of the inner coordination sphere of the Ln(III) ions are possible through the water-counting technique developed by Horrocks and Sudnick.¹⁷ It is well-known that the

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Table I. Photophysical Parameters Obtained for the Tb/EDDS Complexes

	pH 4	pH 10	pH 4	pH 10
(a) Tb:EDDS = 1:1				
$\tau(\text{H}_2\text{O}), \mu\text{s}$	485	795	$1/\tau(\text{D}_2\text{O}), \text{ms}^{-1}$	1.550
$\tau(\text{D}_2\text{O}), \mu\text{s}$	645	2350	$\Delta k_{\text{obsd}}, \text{ms}^{-1}$	0.512
$1/\tau(\text{H}_2\text{O}), \text{ms}^{-1}$	2.062	1.258	no. of waters ^a	2.1
(b) Tb:EDDS = 1:3				
$\tau(\text{H}_2\text{O}), \mu\text{s}$	490	1006	$1/\tau(\text{D}_2\text{O}), \text{ms}^{-1}$	0.458
$\tau(\text{D}_2\text{O}), \mu\text{s}$	2185	1835	$\Delta k_{\text{obsd}}, \text{ms}^{-1}$	1.583
$1/\tau(\text{H}_2\text{O}), \text{ms}^{-1}$	2.041	0.994	no. of waters ^a	6.6

^a This number represents the number of water molecules bound at the inner coordination sphere of the Tb(III) ion.

luminescence intensity and lifetime of emissive lanthanide compounds will increase significantly upon passing from H₂O to D₂O solvent, as long as one or more water molecules are present in the inner coordination sphere of the metal ion. One computes the reciprocal of the measured emission lifetime to obtain the radiative rate constant. The difference in rate constants obtained in H₂O and D₂O solvents is proportional to the number of coordinated water molecules. For Tb(III), the constant of proportionality equals 0.24 ms⁻¹.¹⁷

Tb/EDDS samples containing 1:1 and 1:3 metal:ligand ratios were obtained by removal of the solvent from aqueous solutions prepared in the usual manner, and then these solids were dissolved in either D₂O or H₂O. Luminescence lifetimes were recorded for each ratio in the two solvents at pH (or pD) values of 4 and 9, corresponding to the two different pH regions identified in the previous section. The pertinent data and computed results have been summarized in Table I. Even though the estimated error associated with the method is ± 0.5 H₂O molecule, it is quite clear that the natures of the Tb/EDDS complexes are entirely different under the four sets of conditions presented. These differences might be attributable to different degrees of ligand protonation or to varying Tb:EDDS stoichiometries.

C. Intermolecular Energy Transfer. It is entirely possible that, in aqueous solution, the Tb/EDDS complexes might exist as either monomeric or polymeric species. In the polymeric species, the EDDS ligands might bridge more than one metal center. If this were to be the case, then the differences in water coordination might be related to the state of association as well as the other factors mentioned earlier. We have developed a method based on the intermolecular transfer of electronic energy from Tb(III) species to analogous Eu(III) species that is capable of determining the conditions under which formation of polynuclear species takes place.¹⁹⁻²⁴ In one paper in the series, the self-association of the lanthanide complexes of PDTA and CDTA was examined, and it was found that at high pH (when ternary hydroxide compounds could be formed) the complexes underwent significant self-association.²⁴

Luminescence quenching in fluid solution proceeds via two mechanisms. One of these is termed dynamic quenching and refers to the situation where the energy transfer takes place as a result of a collision between the donor and quencher. With dynamic quenching, the energy-transfer process results in a decrease in the emission intensity and shortening of the emission lifetime. The other mechanism is termed static quenching and results when the donor and quencher molecules are chemically bound to each other. Formation of a Tb/Eu donor/acceptor will completely quench the emission of the

Table II. Stern-Volmer Quenching Constants Obtained from the Quenching of 1:1 Tb/EDDS by 1:1 Eu/EDDS

pH	K_{sv}^{ϕ}	K_{sv}^{τ}	pH	K_{sv}^{ϕ}	K_{sv}^{τ}
3.5	684	300	7.5	343	220
4.0	400	300	8.0	351	206
4.5	371	296	8.5	295	197
5.0	400	298	9.0	277	243
5.5	441	250	9.5	246	253
6.0	412	254	10.0	233	235
6.5	412	259	10.5	211	200
7.0	382	220	11.0	211	196

Tb(III) species, and the only emission observed will be that of the uncomplexed Tb compounds (if any are left). Such a process will result in a decrease in Tb emission intensity but will not affect the Tb lifetime. One may conclude that when the quenching mechanism is dynamic in nature, the lanthanide complexes must be monomeric. On the other hand, should the static mechanism be important, then one would conclude that significant self-association of the complexes was taking place.

If the emission intensity and lifetime of a Tb/EDDS solution are given as I_0 and τ_0 , respectively, and the corresponding values obtained in the presence of Eu/EDDS quencher (abbreviated as Q) are given by I and τ , then the quenching data may be placed on a quantitative basis through the usual Stern-Volmer equations:²⁵

$$\frac{I_0 - I}{I} = K_{\text{sv}}^{\phi}[\text{Q}] \quad \frac{\tau_0 - \tau}{\tau} = K_{\text{sv}}^{\tau}[\text{Q}]$$

The K_{sv} values are termed the Stern-Volmer quenching constants. For pure dynamic quenching it would follow that $K_{\text{sv}}^{\phi} = K_{\text{sv}}^{\tau}$, but if $K_{\text{sv}}^{\phi} > K_{\text{sv}}^{\tau}$, the presence of static quenching is indicated.

The presence of static quenching was noted at the 1:1 Ln:EDDS ratios, but at the 1:2, 1:3, and 1:5 ratios the quenching was completely dynamic in nature. The Stern-Volmer quenching constants obtained at the 1:1 ratio are collected in Table II. In the 1:1 solutions, extensive self-association exists up to pH 8.5, and above this pH value the polynuclear species break up into mononuclear complexes. At the higher metal:ligand ratios, the complexes are thus determined to be completely monomeric at all pH values.

In situations characterized by the presence of both static and dynamic quenching mechanisms, a more complicated Stern-Volmer equation is needed to describe the data:²⁵

$$\frac{I_0 - I}{I} = (K_{\text{sv}}^{\tau} + K_{\text{c}})[\text{Q}] + K_{\text{sv}}^{\phi}K_{\text{c}}[\text{Q}]^2$$

Knowledge of the K_{sv}^{τ} values thus permits a calculation of the association constant, K_{c} , for the donor/acceptor complex. Computation of such values for the 1:1 solutions below pH 8 yielded $K_{\text{c}} = 125 \pm 20$. The degree of association is considerably less than that observed for EDTA, PDTA, or CDTA complexes²⁴ but is unique in that the self-association is most pronounced at low pH values. This evidence suggests that, in the low-pH region, the EDDS ligands have a tendency to bridge between metal centers. Above pH 8, the bridges are broken and the complexes become exclusively monomeric.

D. Nature of the Ln/EDDS Complexes in Solution. The results presented in the preceding sections permit a discussion regarding plausible bonding modes in the Ln/EDDS solutions. It is now clear that the complexes existing at the 1:1 metal:ligand ratios are significantly different from those formed at the higher ratios, and thus each situation will be discussed in turn. Only after we understand the nature of the species

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present in solution can the chiroptical investigations be discussed in a rational manner.

While the pK_a values of EDDS are available,¹⁸ these will not be of much help since it is certain that the lanthanide ions will assist in the deprotonation of the ligand. However, it is known that, with lanthanide complexes of EDTA, formation of the $\text{LnH}(\text{EDTA})$ complex is essentially complete by pH 3 and that full deprotonation of the coordination EDTA ligand is complete by pH 8.¹¹ Above pH 8 the EDTA ligand binds the lanthanide ions in a hexadentate manner, and the complexes are observed to be monomeric.²⁴

At a $\text{Ln}:\text{EDDS}$ ratio of 1:1, it was noted that below pH 8 extensive association of complex species took place. At the same time, relatively few water molecules (approximately $2^{1/2}$ per metal ion) are bound at the metal's inner coordination sphere. Since the coordination number of the lanthanide ion is certainly 8 or higher, one must conclude that a considerable portion of each inner coordination sphere must be occupied by carboxylate groups of the EDDS ligands. The equal amounts of EDDS ligands and Ln ions may thus be seen as promoting the observed self-association.

Once pH 8 is exceeded and the ligand becomes fully deprotonated, the complexes become totally monomeric and the number of coordinated water molecules increases to 4. Once deprotonated, the EDDS ligand would be expected to bind a single metal ion in a hexadentate manner and ample evidence exists confirming such a tendency.^{16,26-28} At 1:1 total ratios of metal:ligand, one would expect that only the $\text{Ln}(\text{EDDS})$ complex could be formed. In a monomeric complex, the metal ion would thus exhibit 10-coordination.

The behaviors, of the complexes at the 1:2, 1:3, and 1:5 metal:ligand ratios are all similar, all species formed are monomeric, and the presence of both $\text{Ln}(\text{EDDS})$ and $\text{Ln}(\text{EDDS})_2$ complexes must be considered. The large number of water molecules bound by the Ln ions under low-pH conditions (found to be 7 at the 1:3 ratio) suggests that only the $\text{Ln}(\text{EDDS})$ complex is important below pH 8. The similar photophysical parameters observed at the 1:1 ratio support such a conclusion. The major complex species thus expected would be $\text{LnH}(\text{EDDS})$, with the ligand binding in a tridentate manner if the EDTA analogy may be applied. We again reach the conclusion that the lanthanide species are 10-coordinate under these conditions.

Once the pH was raised above 8, the emission intensities and lifetimes were found to increase significantly over the values observed at the 1:1 ratio. Since we have concluded that the $\text{Ln}(\text{EDDS})$ complex forms in the 1:1 solutions above pH 8, it must follow that $\text{Ln}(\text{EDDS})_2$ complexes exist at higher metal:ligand ratios. However, since we have determined that two water molecules are still bound at the inner coordination sphere of the Ln ion, it is clear that the two EDDS ligands cannot each bind in a hexadentate manner. It is most likely that one EDDS ligand binds in the conventional hexadentate fashion and that the other binds in a bidentate manner at one of the succinate portions of the EDDS ligand.

E. Circularly Polarized Luminescence Studies of Tb(III) and Eu(III) EDDS Complexes. Even though significant conclusions regarding the $\text{Ln}(\text{EDDS})$ complexes were deduced from investigations probing the total luminescence behavior of the Ln/EDDS solutions, the greatest degree of stereochemical information would be available from chiroptical studies. It has become clear that circularly polarized luminescence spectroscopy is the chiroptical method of choice in the study of emissive Tb(III) and Eu(III) complexes,^{29,30}

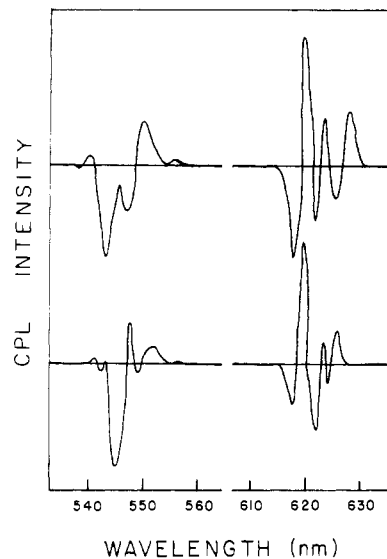


Figure 2. CPL spectra obtained at pH 5 (lower trace) and pH 10 (upper trace) from a 1:1 solution of Tb/EDDS. Data recorded within the $^5D_4 \rightarrow ^7F_5$ transition are located on the left side of the figure, and data obtained within the $^5D_4 \rightarrow ^7F_3$ transition are found on the right side of the figure. The spectra are shown in arbitrary units, with the intensities of the $^5D_4 \rightarrow ^7F_3$ spectra being approximately 1 order of magnitude smaller than those of the $^5D_4 \rightarrow ^7F_5$ spectra.

and consequently all data obtained in the present work employ CPL spectroscopy.

Strong CPL spectra were observed within the $^5D_4 \rightarrow ^7F_6$, 7F_5 , 7F_4 , 7F_3 transitions of Tb/EDDS and within the $^5D_0 \rightarrow ^7F_1$, 7F_2 transitions of Eu/EDDS. As might be anticipated from the work discussed in the preceding sections, the spectra were found to be dependent on both solution pH and metal:ligand ratio. The data obtained at the 1:1 metal:ligand ratios tended to differ greatly from those observed at the 1:2, 1:3, and 1:5 ratios, but the spectral line shapes observed at the higher metal:ligand ratios were not found to differ significantly from each other. In addition, the CPL spectra observed for each metal:ligand ratio were found to undergo drastic alterations in both line shape and magnitude as the solution pH was raised. These CPL changes were found to take place at the same transition points noted in the TL work, and thus the pH trends may again be divided into observations made at low and high pH values. Since the CPL spectra should be most sensitive to changes in complex structure, it follows that the bonding conclusions reached in earlier sections would find their most severe test in attempted correlations with the chiroptical results.

With the Tb/EDDS solutions the largest degrees of optical activity were obtained within the $^5D_4 \rightarrow ^7F_5$, 7F_3 transitions, and for the Eu/EDDS solutions the greatest CPL was observed within the $^5D_0 \rightarrow ^7F_1$, 7F_2 transitions. These observations support the theoretical conclusions made earlier by Richardson,³¹ and all CPL trends were therefore studied within these bands. Representative CPL spectra obtained at 1:1 and 1:3 $\text{Ln}:\text{EDDS}$ ratios are presented in Figures 2-5, and data obtained at pH 5 and 10 are given for each metal:ligand ratio.

The CPL spectra obtained from the Tb/EDDS complexes were found to be totally unlike the spectra observed for either the (R)-PDTA or (R,R)-CDTA complexes of Tb(III)¹¹ but in a few instances did strongly resemble the CPL spectra obtained with Tb(III) complexes of (S)-ASP.¹⁴ For instance, the CPL spectra observed for 1:1 Tb:EDDS at pH 5 are es-

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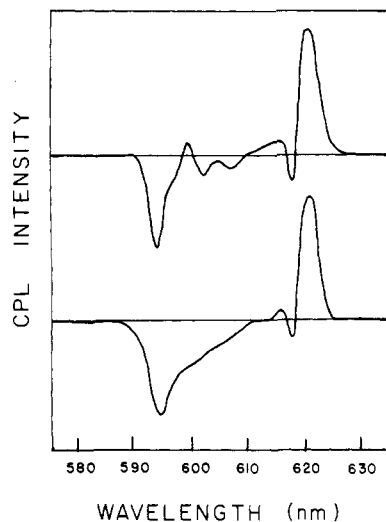


Figure 3. CPL spectra obtained within the ${}^5D_0 \rightarrow {}^7F_1, {}^7F_2$ transitions of a 1:1 Eu/EDDS solution. The spectra at the top of the figure were obtained at pH 10, while those at the bottom of the figure were recorded at pH 5.

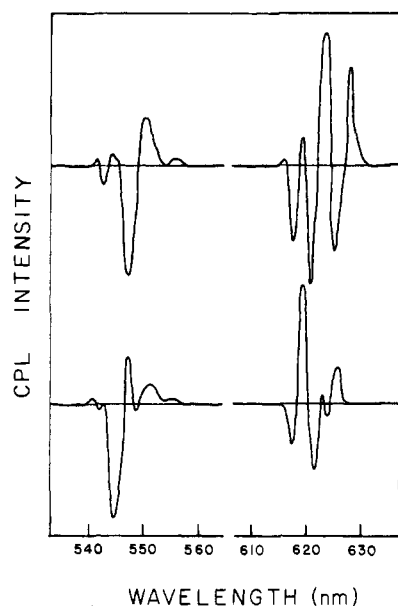


Figure 4. CPL spectra obtained within the ${}^5D_4 \rightarrow {}^7F_3, {}^7F_3$ transitions of a 1:3 Tb/EDDS solution. Data were obtained at pH 5 (lower trace) and pH 10 (upper trace), and all other conditions are as described for Figure 2.

essentially superimposable with that found for 1:1 Tb:ASP. This result would imply that, in the 1:1 solutions at low pH, binding through the carboxylate groups of the succinate moieties predominates. Since it was determined earlier that the EDDS complexes were polymeric under these conditions, the CPL data indicate that the bridging EDDS ligands contain essentially two independent ASP units. Raising the pH of the 1:1 Tb/EDDS solution results in the formation of monomeric $Tb(EDDS)(H_2O)_4$ complexes, with the evident changes in the CPL spectra.

Turning to the higher metal:ligand ratios, one observes that the low-pH spectra are again essentially the same as those observed for Tb/ASP. Quantitative examinations of the data reveal that the luminescence dissymmetry factors²⁹ calculated for the 1:1 and 1:3 Tb:EDDS ratios were equal as well. These observations indicate that, below pH 8, all binding again only involves the succinate functionalities of the EDDS ligands. The dissymmetry factors indicate that only one EDDS is bound per metal ion (even at the 1:5 metal:ligand ratios), a conclusion

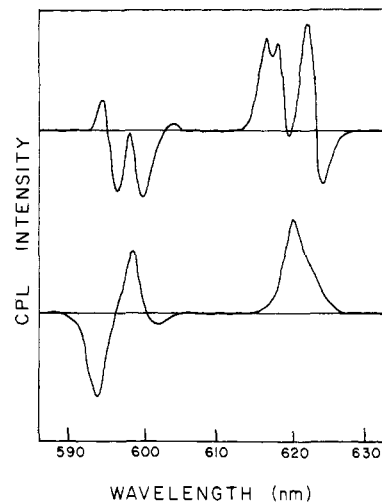


Figure 5. CPL spectra obtained within the ${}^5D_0 \rightarrow {}^7F_1, {}^7F_2$ transitions of a 1:3 Eu/EDDS solution. The upper spectra were obtained at pH 10, while the lower spectra were obtained at pH 5.

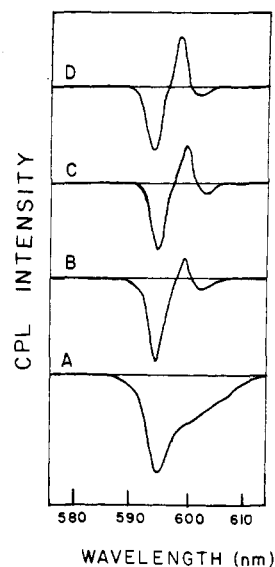


Figure 6. Dependence of the CPL within the ${}^5D_0 \rightarrow {}^7F_1$ transition of Eu/EDDS upon the metal:ligand ratio. The data correspond to Eu:EDDS ratios of 1:1 (A), 1:2 (B), 1:3 (C), and 1:5 (D).

reached earlier in the water-counting experiments.

Upon raising the pH of a 1:3 Tb/EDDS solution (for example) to 10, one finds a completely new set of CPL spectra. This would in turn indicate the formation of some new complex, which was determined before to be the $Tb(EDDS)_2(H_2O)_2$ complex. The difference in CPL noted for the 1:1 and 1:3 Tb/EDDS solutions at pH 10 reflects the additional chirality provided at the Tb(III) ion by the extra EDDS ligand.

The same general trends may be observed in the Eu/EDDS CPL spectra, but one important difference was observed. As the metal:ligand ratio was increased, the CPL associated with the ${}^5D_0 \rightarrow {}^7F_1$ band were found to change (see Figure 6). This observation indicates the presence of a new compound whose concentration increased with the metal:ligand ratio. It seems likely that the new peak arises from formation of an $Eu(EDDS)_2$ species, but where both ligands still bind only through the two carboxylates of a succinate functionality. The Tb/EDDS solutions do not exhibit this feature, and this difference between Tb and Eu may be a reflection of the somewhat higher basicity of the Eu(III) ion relative to that of the Tb(III) ion.

F. Other EDDS-Type Ligands. The preceding sections have shown that, in EDDS, the ligand often coordinates as if it were

an ASP ligand. To test this hypothesis, the same synthetic procedure used to link two ASP units was used to prepare the analogous ligands prepared from either (*S*)-alanine or (*S*)-glutamic acid. It has been shown that the two carboxylate groups of glutamic acid are too far apart to form a simple chelate ring,³² and of course alanine only contains a single carboxyl. Neither compound was observed to yield appreciable optical activity at low pH at any metal:ligand ratio, even though significant metal-ligand bonding is known to take place.¹⁸

It has also been shown that observation of strong optical activity requires the presence of a conformational effect (where the asymmetric atom of the ligand is bound in a chelate ring),³³ and such effects cannot exist in the ligands derived from alanine or glutamic acid. On the other hand, the CPL spectra observed for the Tb/ASP and Tb/EDDS complexes were both of a type indicative of conformational effects.^{32,33} The CPL data thus provide very strong evidence for concluding that, under low-pH conditions, the EDDS ligand forms complexes via its two carboxylate groups. There apparently is no tendency for the two carboxylate groups of an ASP functionality on EDDS to bind metal centers independently.

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G. Summary. The luminescence techniques used during the course of the present work have proved to be capable of providing rather detailed information regarding the nature of the Ln/EDDS complexes. The presence of polymeric and monomeric complexation was deduced from energy-transfer experiments, and water-counting experiments were used to obtain information on the inner coordination sphere of the lanthanide ions. CPL spectroscopy could be used to obtain further information regarding how the various functionalities of the EDDS ligand could be used to bind a metal ion, and taken together, all the techniques provide a detailed look into this aspect of lanthanide solution chemistry.

It is undoubtedly true that the nature of the Ln/EDDS binding might allow for the presence of more than one type of compound under any given set of experimental conditions. However, the specific nature of the information obtained within certain well-defined pH regions indicates that the conclusions obtained pertain to a majority species in solution. Thus, effects due to small amounts of other species may be neglected. The strengths of the luminescence techniques as means for the study of lanthanide complexes in solution are self-evident, and further work along these lines is currently being pursued.

Acknowledgment. This work was supported by the Camille and Henry Dreyfus Foundation, through a Teacher-Scholar award to H.G.B.

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Iron(III) Complexation by Desferrioxamine B in Acidic Aqueous Solutions. Kinetics and Mechanism of the Formation and Hydrolysis of the Binuclear Complex Diferrioxamine B

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Received September 8, 1983

Ferrioxamine B ($\text{Fe}(\text{HDFB})^+$), a complex of iron(III) with the linear trihydroxamic acid siderophore desferrioxamine B (H_4DFB^+), yields in the presence of an excess of ferric ions in aqueous acid the binuclear complex diferrioxamine B ($\text{Fe}_2(\text{HDFB})^{4+}$) by two parallel pathways involving fully aquated (Fe^{3+}) and hydrolyzed (FeOH^{2+}) iron(III) ions. The observed rate constants for two paths at 25 ± 0.1 °C and 1.00 M ionic strength (NaCl) are $k_4 = 52 \text{ M}^{-1} \text{ s}^{-1}$ and $k_4' = 3500 \text{ M}^{-1} \text{ s}^{-1}$, respectively. When the ferrioxamine B acid solution is mixed with a ferric ion solution of acidity higher than that of the ferrioxamine B solution, the binuclear complex formation reaction is preceded by a reversible process in which the partial unraveling of the desferrioxamine B ligand from the inner coordination sphere of the iron(III) center occurs. The acid hydrolysis of diferrioxamine B complex to the ferrioxamine B complex proceeds also by two parallel pathways: an acid-dependent and an acid-independent path exhibiting the rate constants $k_{-4} = 0.91 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-4}' = 0.105 \text{ s}^{-1}$, respectively. Mechanistic implications are discussed.

Introduction

Naturally occurring iron chelating agents called siderophores have attracted a remarkable interest because of their role in iron bioavailability in microorganisms,¹⁻³ where three limiting types among many mechanisms for siderophore-mediated microbial iron transport have been advanced.⁴ Of prime importance for the understanding of the molecular basis for iron bioavailability continues to be the kinetic and thermo-

dynamic information relating to the complexation of iron(III) by various siderophore chelating agents. The three types of siderophores—the hydroxamates, thiohydroxamates, and catecholates—have been recognized to form extremely stable, highly specific, high-spin d^5 octahedral coordination compounds with iron(III). The hydroxamate group ($\text{HON}(\text{R}_1)(\text{C}(\text{=O})\text{R}_2)$) is considered to be the most common functional group of siderophores produced by molds, fungi, and yeasts.⁵

Particularly important appears to be the linear trihydroxamic acid siderophore desferrioxamine B (H_4DFB^+) with the molecular formula $^+\text{NH}_3(\text{CH}_2)_5[\text{N}(\text{OH})\text{C}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})-$

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