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Solution Phase Chemistry of Lanthanide Complexes.
8. Tb(III) Complexes of 1,2-Dihydroxybenzene-3,5-Disulfonic Acid (Tiron)

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Abstract

The solution phase chemistry associated with lanthanide complexes of the title compound has been studied by means of luminescence spectroscopy. The nature of the tiron complexes was found to vary with the particular metal/ligand ratio present in the solution. In 1:1 Tb/tiron solutions, no evidence for a monomeric Tb(tiron) complex could be obtained, and instead all evidence pointed toward the existence of associated complexes. These $[Tb(tiron)]_x$ complexes could exist in protonated and deprotonated forms. At metal/ligand ratios of 1:2 and 1:3, monomeric $Tb(tiron)_2$ complexes were found to exist. At the highest ratios of metal/ligand (1:5 and 1:10), evidence was obtained which indicated the existence of monomeric $Tb(tiron)_3$ complexes. These results were not found to agree totally with conclusions drawn in two earlier, conflicting, works employing potentiometic titration methods, but instead demonstrated that the best interpretation actually contains elements of each complexation scheme.

Introduction

1,2-dihydroxybenzene-3,5-disulfonic acid (tiron) has found use as a fluorimetric reagent for the determination of lanthanide ions. While it is known that formation of the 1:1 lanthanide/tiron complex leads to the observation of sensitized emission [1], the most useful analytical procedures have involved the use of mixed-ligand complexes [2, 3]. The solution phase properties of these complexes have not been probed beyond determinations of the formation constants associated with the pure [4, 5] and mixed-ligand [6, 7] species. Further characterization of lanthanide/catechol complexes is desirable since Raymond and coworkers have investigated the possibility of using polycatechol ligands as specific sequestering agents for members of the actinide series [8, 9].

From these considerations, it is clear that additional knowledge regarding the solution phase chemistry of tiron complexes would be immensely useful. Since most Tb(III) complexes exhibit luminescence in aqueous solution upon UV excitation, one may apply techniques associated with emission spectroscopy toward the study of Tb/tiron complexation. The emission intensities and lifetimes of the Tb/tiron complexes may be followed as a function of pH, and this information can be used to deduce structural changes. Spectroscopic techniques exist whereby one may determine the number of water molecules coordinated to the Tb(III) ion, and through this method the coordination number of the Tb(III) ion can be estimated.

The application of these methods requires that one work exclusively with monomeric complexes whose structure can be described with a reasonable degree of certainity. Intermolecular energy transfer between lanthanide complexes can be used as a method whereby one may deduce the self-association state of a particular lanthanide complex [10]. It is fairly well known that many lanthanide carboxylate complexes exhibit a tendency to form polymeric species in solution, and this property is most prevalent at high pH values where μ-hydroxy bridges may be formed [11]. Recently, we have used the energy transfer method to deduce information regarding the lanthanide complexes of important complexing agents, citric acid [12] and the family of aminopolycarboxylic acids [13]. It is of importance to deduce the presence of any self-association of the Tb/tiron complexes.

In the present work, we wish to report the results of investigations in which luminescence spectroscopy was used to characterize the solution phase chemistry of lanthanide complexes of tiron.

Experimental

Tiron and ethylenediamine tetraacetic acid (EDTA) were obtained from Aldrich Chemicals, and each was used as received. Stock solutions of the lanthanide ions were prepared by dissolving the

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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. In the usual practice, stoichiometric amounts of lanthanide ion and tiron stock solutions were combined to yield Ln(III)/tiron molar ratios of 1:1, 1:2, 1:3, 1:5, and 1:10. The Tb(III) concentration in these studies was normally 15 mM. For the energy transfer experiments, microliter amounts of a stock Eu(III) solution (50 mM) were added to 3.0 ml of the Tb/tiron solutions. A sufficient amount of extra tiron ligand was also added so as to keep the total ratio of metal/ligand constant.

The pH of each of these solutions was varied between 3.0 and 11.5, and the required photophysical measurements were made at each pH value. 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 obtained using a glass microcombination electrode which could be inserted directly into the cuvette, and read on an Orion 701A pH meter. The system was calibrated daily with phosphate buffers.

The luminescence intensity of the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission band (545 nm) was recorded at each pH value on a low-resolution fluorimeter constructed in our laboratory. Samples were excited by the 365 nm output of a 100 W Hg-Xe arc lamp, with this excitation being selected by a combination of a prism monochromator and UV-transmitting glass filters. At 365 nm, Tb(III) may be excited with reasonable efficiency, but the quantum yield for Eu(III) emission is much less. The emission was analyzed by the monochromator of a Beckman DU spectrophotometer, and detected by an EMI 9781R photomultiplier tube (S-5 response). All measurements were obtained at an emission bandpass of approximately 5 nm, and under ambient temperature conditions. Daily fluctuations in emission intensities were eliminated by referencing all observed intensities to that of a standard piece of uranyl glass.

Emission lifetimes were obtained on a system similar to that 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 using a 220 K load resistor, and these voltage pulses were captured for viewing on a storage oscilloscope. At the same time, the data were digitized at 4 μsec intervals via a homebuilt analog/digital converter, and the digitized data fed directly into a Commodore PET 4032 microcomputer. Our program calculates the baseline from data points taken before the laser pulse, and subtracts the baseline from the decay data. The corrected decay curves were then analyzed using 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.

Results and Discussion

While the two sulfonic acid groups of tiron are quite acidic, ionization of the hydroxyl groups takes place at fairly high pH levels. At an ionic strength of 0.5 M, Lajunen [4] has determined that $pK_1 = 7.3$ and $pK_2 = 12.0$. It is known that tiron forms strong complexes with the members of the lanthanide series, although there appears to be some disagreement regarding the nature of the compounds in aqueous solutions. Lajunen [4] has determined from potentiometric measurements that complexes having 1:1 and 1:2 stoichiometries are possible:

$$\mathrm{Ln^{3+} + tiron^{4-} \rightleftharpoons Ln(tiron)^{-}} \qquad (1)$$

$$\mathrm{Ln(tiron)^{-} + tiron^{4-} \rightleftharpoons Ln(tiron)_2{}^{5-}} \qquad (2)$$

For Tb(III), Lajunen has found that $\log K_1 = 13.5$ and $\log K_2 = 9.0$, while for Eu(III) $\log K_1 = 13.3$ and $\log K_2 = 8.4$. In addition, Lajunen has also determined that the 1:2 complex may exist in a protonated form:

$$\mathrm{LnH(tiron)^{4-} \rightleftharpoons Ln(tiron)^{5-} + H^{+}} \qquad (3)$$

For the Tb(III) complex, the pK_a of this compound appears to be 7.8, while for Eu(III) $pK_a = 7.9$ [4].

In another study, Bhuyan and Dubey [5] determined the stability constants of the lanthanide/tiron complexes by the same general potentiometric method. These workers found evidence for the 1:1 and 1:2 Ln/tiron complexes, but also concluded that a 1:3 stoichiometry could exist:

$$\mathrm{Ln(tiron)_2{}^{5-} + tiron^{4-} \rightleftharpoons Ln(tiron)_3{}^{9-}} \qquad (4)$$

No mention was made regarding the existence of any protonated forms of Ln/tiron complexes.

In the following sections, a sequence of luminescence techniques will be used to probe the solution phase chemistry of the Ln/tiron complexes.

pH Dependence of Tb(III) Emission Intensity and Lifetime

UV excitation of a Tb/tiron complex 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. The intensities and lifetimes of these bands were found to exhibit dependencies on both the 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 was focused on the $^5D_4 \rightarrow {}^7F_5$ transition of the Tb/tiron complexes.

It is well known that the photophysical properties of coordinated Tb(III) are determined primarily by the inner coordination sphere of the complexed ion, and therefore luminescence intensity and lifetime trends ought to provide information regarding the nature of the Tb/tiron complexes. In Fig. 1, the pH dependence of Tb(III) emission intensity is illustrated as a function of the metal/ligand ratio, and Fig. 2 details analogous studies involving emission lifetimes.

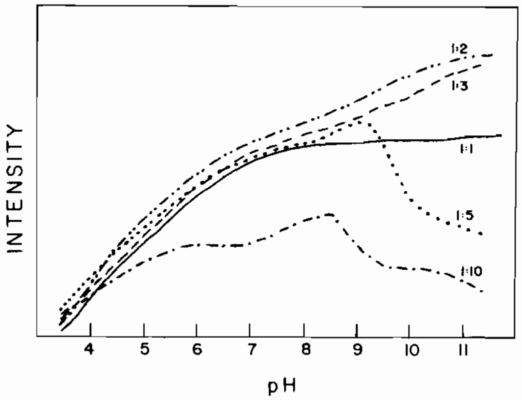

Fig. 1. pH dependence of the Tb(III) luminescence intensity as a function of the Tb/tiron ratio (indicated for each trace). All intensity data were obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission band, and are shown in arbitrary units.

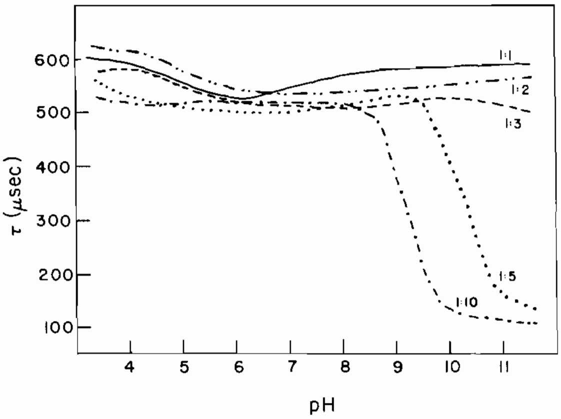

Fig. 2. pH dependence of the Tb(III) luminescence lifetimes as a function of the Tb/tiron ratio (indicated for each trace). The lifetime data were obtained in H_2O solution, within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission band.

It is immediately clear from consideration of Figs. 1 and 2 that the photophysical properties of the Tb/tiron solutions exhibit profound dependencies on the metal/ligand ratio used to make up the solution. When the metal/ligand ratio ranged between 1:1 and 1:3, the observed parameters varied in a well behaved manner. The emission intensities rose gradually between pH 3.5 and 7, remained fairly constant up to pH 10, and then rose slightly as the pH was raised up to 11.5. The emission lifetimes remained essentially constant over the entire pH range. It is significant to note that at a given pH value, the value observed for either the emission intensity or lifetime did not really depend on the particular metal/ligand ratio. This result would imply that the same type of complex was responsible for the observed luminescence, and that the makeup of this complex was not a function of the metal/ligand ratio.

At the higher metal/ligand ratios, quite different behavior was observed. The curves obtained for the 1:5 and 1:10 Tb/tiron ratios resembled those obtained at lower ratios as long as the pH remained below 8.5, but between pH 8.5 and 11 a sharp decrease in Tb(III) emission lifetime and intensity was observed. This tendency was found to be most pronounced for the 1/10 Tb/tiron ratio. In addition, the entire emission intensity curve of the 1:10 ratio was found to be smaller than those observed for the other ratios, but this effect is undoubtably due to an inner filter effect caused by the presence of a large excess of unbound tiron. This conclusion is supported by the observation that below pH 8.5, the lifetime measured for the Tb/tiron complex (as existing at the 1:10 metal/ligand ratio) did not differ from the lifetimes obtained for the lower metal/ligand ratios. The decrease observed for the 1:5 and 1:10 ratios above pH 8.5 cannot be ascribed to an inner filter effect, since the emission lifetime exhibits the same sharp decrease as does the emission intensity.

Intermolecular Energy Transfer Between Tb(III) and Eu(III) Tiron Complexes

No speculation regarding possible structural origins for the observed luminescence trends can be advanced until questions regarding possible self-association of the complexes are answered. To achieve this end, a series of energy transfer studies were carried out. In these works, the efficiency associated with the nonradiative transfer of electronic energy from Tb/tiron donor complexes to Eu/tiron acceptor complexes was followed as a function of pH.

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 complex will completely quench the emission of the 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/tiron solution is given as I_0 and τ_0 respectively, and the corresponding values obtained in the presence of Eu/tiron 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 [14]:

$$\frac{I_0 - I}{I} = K_{sv}{}^{\phi}[Q] \tag{5}$$

$$\frac{\tau_0 - \tau}{\tau} = K_{sv}{}^{\tau}[Q] \tag{6}$$

The K values are termed the Stern-Volmer quenching constants. For pure dynamic quenching it would follow that $K_{sv}{}^{\phi} = K_{sv}{}^{\tau}$, but if $K_{sv}{}^{\phi} > K_{sv}{}^{\tau}$ the presence of static quenching is indicated. 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 [15, 16]:

$$\frac{I_0 - I}{I} = (K_{sv}{}^{\tau} + K_c)[Q] + K_{sv}{}^{\tau}K_c[Q]^2 \tag{7}$$

Knowledge of the $K_{sv}{}^{\tau}$ values thus permits a calculation of the association constant, K_c, for the donor/acceptor complex.

The results obtained from the energy transfer experiments were found to be quite different from those obtained in earlier studies of Tb–Eu energy transfer [10]. Normally, a dynamic contribution to the energy transfer is observed, but with Tb/tiron/Eu complexes no such contribution was noted. The lifetimes measured at given metal/ligand ratios for the Tb/tiron/Eu compounds were not found to depend on the presence of Eu(III) quencher.

For the 1:2, 1:3, 1:5, and 1:10 metal/ligand ratios, the emission intensities of the Tb/tiron complexes were found to be the same (within experimental error) as those of the Tb/tiron/Eu complexes. We conclude from these observations that for these metal/ligand ratios, static quenching does not contribute to the energy transfer process. The sole exception to this general trend was noted for the 1:1 metal/ligand ratios, where a small degree of intensity quenching was noted. The pH dependence associated with this quenching is shown in Fig. 3. With the lifetime data indicating the lack of dynamic quenching, eqn. (7) becomes:

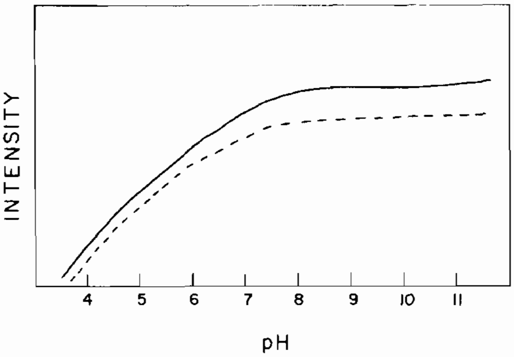

Fig. 3. Intensity quenching of 1:1 Tb/tiron by 1:1 Eu/tiron as a function of pH. The solid trace represents the emission intensity in the absence of quencher, and the dotted line shows the intensity in the presence of quencher.

$$\frac{I_0 - I}{I} = K_c[Q] \tag{8}$$

The Stern-Volmer quenching constant calculated between pH 4 and 10 was found to be 420 ± 15 l/mol, and thus represents the association constant of the donor/acceptor complex.

The sharp decrease in emission intensities and lifetimes noted for the 1:5 and 1:10 metal/ligand ratios at high pH was not found to result from self-association processes. No evidence could be obtained from the energy transfer data to indicate that any formation of mixed Tb/tiron/Eu complexes did take place. Consequently, we conclude that the quenching which takes place at high pH represents collisional quenching of the Tb(III) emission by unbound, ionized tiron molecules. The onset of this quenching mode accompanies the final deprotonation of free tiron.

Determination of the Number of Water Molecules Bound by Tb(III) in the Tiron Complexes

A determination of the number of solvent molecules bound by the Tb(III) ion in the tiron complexes should enable a rational interpretation of the coordination chemistry associated with these complexes. In particular, any variation in the number of bound water molecules with pH and metal/ligand ratio would provide evidence for a structural change. Since the photophysical data provided thus far have indicated a remarkable invariance in the nature of the Tb/tiron complexes, additional information is required to complete the picture.

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 luminescence intensity and lifetime of emissive lanthanide compounds will increase significantly upon passing from H_2O to D_2O 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 H_2O and D_2O solvents is proportional to the number of coordinated water molecules. For Tb(III), the constant of proportionality equals 0.24 $msec^{-1}$ [17].

The emission lifetimes associated with the Tb/tiron complexes were obtained as a function of pD in D_2O, using DCl and NaOD to adjust the pD. The pD dependence of the observed lifetimes are shown in Fig. 4 for the various metal/ligand ratios. The reciprocal of the observed lifetime was calculated, and taken as the observed rate constant for the radiative process. The difference in observed rate constants obtained in H_2O and D_2O solvents is proportional to the number of coordinated solvent molecules [17]. These calculated hydration numbers have been collected in Table I.

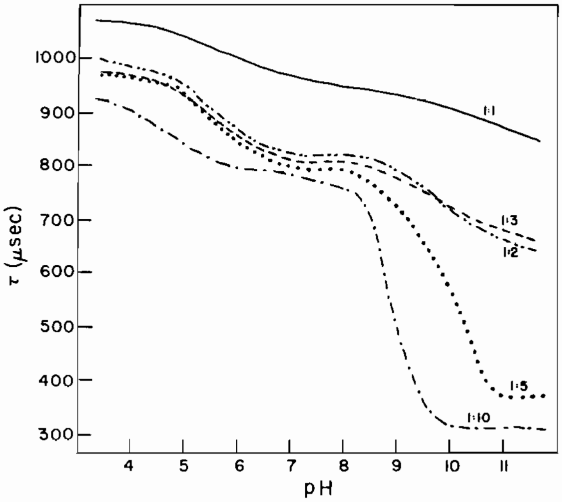

Fig. 4. pH dependence of the Tb(III) luminescence lifetimes as a function of the Tb/tiron ratio (indicated for each trace). The lifetime data were obtained in D_2O solution, within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission band.

One observes in the data of Table I that the number of coordinated solvent molecules does not exhibit wide variations. The maximum number of coordinated waters was found to be 3.5 at the 1:1 metal/ligand ratio, and values as small as 1 coordinated water were found for the 1:10 ratios. These results are consistent with the earlier observations that the nature of the Tb/tiron complexes is not overly dependent on either the solution pH or on the metal/ligand ratio.

Nature of the Tb/Tiron Complexes

If one now views all the photophysical data as a whole, it becomes possible to deduce a number of conclusions regarding the chemical nature of the Tb/tiron complexes. These conclusions in turn allow an evaluation of the results obtained as a result of the potentiometric titrations [4, 5]. At the 1:1 metal ligand ratio, the large formation constant of Tb(tiron) would insure that this compound would form quantitatively. In that case, one would anticipate that at least 5 water molecules would be required to give the normal lanthanide coordination number of 8–9. Instead, one finds that the number of coordinated waters never exceeds 3.5. However, the energy transfer measurements have shown that the 1:1 Tb/tiron complexes associate to a significant extent, and we conclude from these observations that the existence of ligand bridges reduces the number of bound solvent molecules. The number of coordinated waters was found to decrease above pH 7.5, and this feature happens to coincide exactly with the predicted deprotonation of the TbH(tiron) complex [4]. Thus, the existence of a protonated complex in the 1:1 Tb/tiron solutions appears to be confirmed.

TABLE I. Number of Coordinated Water Molecules in the Tb/Tiron Complexes.

Metal/ligand ratio					
pH	1:1	1:2	1:3	1:5	1:10
3.5	2.7	2.6	2.6	2.0	2.0
4.0	2.8	2.8	2.7	2.4	2.3
4.5	3.0	2.8	2.9	2.6	2.2
5.0	3.5	2.8	3.1	2.7	1.9
5.5	3.7	2.9	3.1	2.5	1.8
6.0	3.6	2.9	3.1	2.3	1.8
6.5	3.4	2.8	3.1	2.3	2.0
7.0	2.8	2.8	2.8	2.1	2.0
7.5	2.2	2.7	3.0	2.1	1.9
8.0	2.0	2.7	3.1	2.0	1.2
8.5	1.9	2.7	3.0	2.6	1.0
9.0	2.0	2.6	2.7	1.8	–
9.5	2.2	2.2	2.4	1.7	–
10.0	2.4	1.9	2.1	–	–
10.5	2.5	1.6	1.4	–	–
11.0	2.4	1.4	–	–	–

At the 1:2 metal ligand ratios, the formation of $Tb(tiron)_2$ complexes should also be fairly extensive. The water counting experiments indicate the presence of three bound solvent molecules in complexes where energy transfer studies have demonstrated the existence of monomeric species. With the assumption that each tiron ligand would bind in a bidentate manner at the catechol functionality, one finds then that the Tb(III) ion in $Tb(tiron)_2(H_2O)_3$ would be 7-coordinate. No decrease in the number of coordinated waters was noted near pH 7.5–8, and thus it appears that the protonated TbH(tiron) complex does not form at the higher metal/ligand ratios.

All results observed for the 1:3 metal/ligand ratios appear to be virtually identical with those found for the 1:2 ratio, and consequently the same general conclusions may be drawn. We conclude from these studies that even though the solution may contain additional tiron, only the $Tb(tiron)_2$ complex is formed.

At the 1:5 and 1:10 metal/ligand ratios, the number of coordinated water molecules decreases relative to the numbers calculated for the lower ratios, and it would appear that only 2 solvent molecules are bound per Tb/tiron complex. This observation would suggest that at the highest metal/ligand ratios, $Tb(tiron)_3$ complexes are formed. This observation would agree with the potentiometric results of Bhuyan and Dubey [5]. In such complexes, the presence of 2 coordinated solvent molecules and 3 bound tiron ligands would yield an overall coordination number of 8. No hydration numbers could be obtained at high pH values, as the quenching of the Tb/tiron complexes by ionized tiron complicates the lifetime data and prevents application of the Horrocks technique.

At the low metal/ligand ratios, the number of coordinated water molecules appears to decrease above pH 10. This observation probably does not represent a genuine structural change, but instead signifies the deprotonation of coordinated waters. This would in turn result in formation of hydroxo complexes.

Studies of Tb(EDTA)(tiron) Complexes

One method whereby the coordination equilibria associated with the Tb/tiron complexes may be simplified is to work with mixed-ligand complexes. From a consideration of formation constants, it is not possible that a tiron ligand could displace a bound molecule of ethylene diamine tetraacetate (EDTA). Consequently with Tb(EDTA)(tiron) mixed-ligand complexes the solution phase equilibria would necessarily be limited to:

$$\mathrm{Tb(EDTA)} + \mathrm{tiron} \rightleftharpoons \mathrm{Tb(EDTA)(tiron)} \qquad (9)$$

Such predictions have already been verified [3, 7]. In addition, we have verified that Tb(EDTA) complexes are invariably monomeric [13].

One intriguing feature of the Tb/tiron studies just described concerns what appeared to be quenching of $Tb(tiron)_3$ by ionized tiron. It was thus of interest to learn whether this phenemon was general in its nature, or whether it was peculiar to the $Tb(tiron)_3$ complex. Consequently, the pH dependence associated with Tb(III) lifetimes of Tb(EDTA)(tiron) complexes was investigated. These trends are illustrated in Fig. 5.

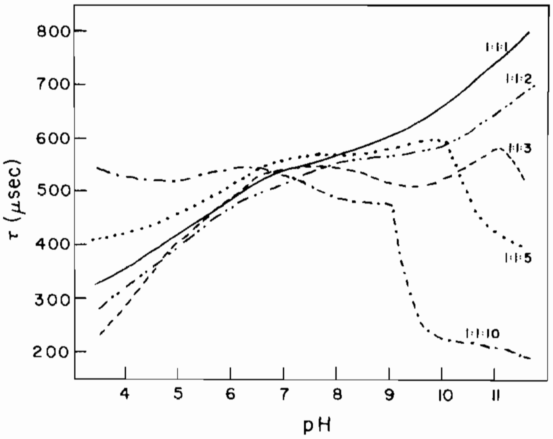

Fig. 5. pH dependence of the Tb(III) luminescence lifetimes as a function of the Tb/tiron ratio (indicated for each trace) in the Tb(EDTA)(tiron) complexes. These lifetime data were obtained in H_2O solution, within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission band.

From the data, it is clear that the Tb(III) quenching by ionized tiron is indeed a general phenomenon. The quenching is most apparent at the 1:5 and 1:10 metal/ligand ratios. Measurements of emission intensities reveal the same general trends, and it is most likely that the energy transfer arises solely froma dynamic mechanism. It is apparent that ionized tiron contains an energy level (probably a triplet) which is lower in energy than the $^5D_4$ level of the Tb(III) ion, and thus may act as an energy acceptor. Protonated tiron (or tiron binding a metal ion) would then have its corresponding level above the $^5D_4$ level of Tb(III), and would act as a sensitizer. It would appear that the final deprotonation of the tiron results in a destabilization of this level.

Conclusions

The results presented in the preceding sections illustrate how luminescence spectroscopy may be used to obtain details of the solution phase chemistry of lanthanide complexes. Information complementary to that obtained from potentiometric titrations is easily obtained, and the results obtained in this manner may be used to independently verify the conclusions drawn from such studies.

In 1:1 Tb/tiron solutions, no evidence for a monomeric Tb(tiron) complex could be obtained, and instead all evidence pointed toward the existence of associated complexes. These $[Tb(tiron)]_x$ complexes could exist in protonated and deprotonated forms. At metal/ligand ratios of 1:2 and 1:3, monomeric $Tb(tiron)_2$ complexes were found to exist. At the highest ratios of metal/ligand (1:5 and 1:10), evidence was obtained which indicated the existence of monomeric $Tb(tiron)_3$ complexes.

This type of structural information is also available from analysis of potentiometric titrations, but it is clear that the many observable parameters associated with the luminescence methods provide more detailed analyses of the solution equilibria. While the two potentiometric studies of lanthanide tiron complexes differed significantly in their conclusions, the results obtained during the course of the present work have shown that neither scheme was entirely correct. The best available interpretation of the data actually contains elements of both complexation schemes, but such concusions were only available after consideration of many parameters.

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