Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

Spectroscopic Studies of Lanthanide Ion Binding to Multidentate Ligands in Aqueous Solution. 1. Malic Acid

SIMON SALAMA and F. S. RICHARDSON*

Received July 25, 1979

Absorption spectra and luminescence lifetime and intensity measurements are reported for 1:3 Tb^{3+}:malic acid in aqueous solution under variable pH conditions. Luminescence decay measurements in H_2O/D_2O solvent mixtures are used to determine the number of bound water molecules (or OH^- ions) as a function of pH. These measurements along with absorption and luminescence intensity spectra reveal stepwise changes in the coordination environment of the lanthanide ion as pH is raised from 1.5 to 11.0. These changes are interpreted in terms of Tb(malic acid) complex formation and alterations in the number and nature of the coordinated solvent molecules. Oscillator strengths for the Tb^{3+} $^5D_4 \leftarrow {}^7F_6$ transition are reported along with pH-dependent quantum yields for the $^5D_4 \rightarrow {}^7F_6$ transition in H_2O and D_2O. Quenching of terbium luminescence by Eu^{3+} in Tb^{3+}/Eu^{3+}/malic acid/H_2O solutions was studied to characterize the nature of Ln^{3+}–Ln^{3+} interactions and to probe the existence of polynuclear complex species in solution. The dominant quenching mechanism was found to be dynamic, involving Tb → Eu energy transfer whose rate is collisionally controlled. Comparisons of Stern–Volmer quenching constants for Tb(L-malic acid) vs. Tb(DL-malic acid) revealed some small stereoselective influence on the quenching mechanism at pH <9.

Introduction

The coordination properties of trivalent lanthanide ions (Ln^{3+}) with multidentate ligands in aqueous solution have been the subject of numerous physicochemical studies. The search for effective Ln^{3+} sequestering agents has motivated many of these studies, and the use of Ln^{3+} ions as spectroscopic probes of ligand conformation in solution media has dictated that detailed information be obtained regarding the stoichiometric and structural aspects of the Ln^{3+}–ligand complexes formed under a variety of solution conditions. Additionally, there remains strong interest in the intrinsic coordinative (bonding) properties of the Ln^{3+} ions to various ligand donor moieties and in the stereochemical features of Ln^{3+}–ligand complex species. Nearly all Ln^{3+} complexes are labile in aqueous solution, and the extent of their formation or dissociation in water generally depends critically upon solution pH. Structural studies of Ln^{3+}–ligand complexes in aqueous solution are made difficult by the fact that Ln^{3+} ions have variable coordination numbers (7–10 depending upon ligand characteristics and solution properties), the propensity for Ln^{3+} ions to form dimeric and polymeric species in solution, and the fact that Ln^{3+}–H_2O and Ln^{3+}–OH^- interactions are relatively strong. To characterize Ln^{3+}–ligand complexes in aqueous solution, one must generally use a variety of spectroscopic techniques which are diagnostic of coordination number, donor atom type, dimer or polymer formation, and ligand stereochemistry. Although magnetic resonance techniques may be useful in studying certain aspects of Ln^{3+}–ligand complex structures (in D_2O solution), the sensitivity limits of these techniques generally require concentrations of Ln^{3+} and ligand in a range where dimer and polymer formation become dominant. Similarly, absorption spectra studies in the Ln^{3+} f–f transition regions are of limited utility because of the very weak absorptivities (oscillator strengths) exhibited by the transitions. On the other hand, the inherent sensitivity of emission (luminescence) spectroscopy makes the use of f–f luminescence particularly attractive as a probe of Ln^{3+}–ligand interactions in solution.

In the present study, a variety of luminescence intensity and lifetime techniques are used in conjunction with potentiometric titration data to investigate the complex species formed by malic acid with Tb^{3+} and/or Eu^{3+} ions in aqueous solution at various pH values. Malic acid is a potentially terdentate ligand which at high pH presents two carboxylato donor moieties plus a hydroxyl (or hydroxylato) donor group to the metal ion. Ln^{3+}–malic acid complexes in aqueous solution have been the subject of a number of previous studies reported in the literature.[1-4] However, none of these previous studies have yielded definitive and conclusive results regarding the detailed structural properties of the Ln^{3+}–malic acid species formed in aqueous solution as a function of pH.

The primary focus of the present study is on the malic acid complexes of Tb^{3+} formed in aqueous solution. The Tb^{3+} ion has an f^8 electron configuration in its ground electronic state and in its f–f excited electronic states. The emitting state of Tb^{3+} in aqueous solution is $^5D_4$. The luminescence spectrum of Tb^{3+} in aqueous solution generally consists of a series of bands assignable to crystal-field components of the $^5D_4 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4, 5, 6$) free-ion transitions, with the bands of $^5D_4 \rightarrow {}^7F_5$ free-ion parentage being the most intense. Both the intensities and decay times of these emissive transitions are sensitive to the ligand environment about the Tb^{3+} ion. Furthermore, the crystal-field-induced splittings within each free-ion $^5D_4 \rightarrow {}^7F_J$ transition reflect ligand structure and Tb^{3+}–ligand interaction details. In the present study, we use both emission lifetime data and emission intensity spectra to probe the coordination environment about the Tb^{3+} ion in Tb^{3+}/malic acid/water solutions. The Tb^{3+} $^7F_6 \rightarrow {}^5D_4$ absorption spectra are also considered.

To probe the interactions *between* Ln^{3+} ions in the Ln^{3+}/malic acid/water solutions, we have studied the quenching influence of Eu^{3+} ions on Tb^{3+} luminescence in such solutions. The $^5D_0$ and $^5D_1$ excited states of Eu^{3+} both lie lower in energy than the Tb^{3+} $^5D_4$ emitting state. Furthermore, the crystal-field levels of the Eu^{3+} $^5D_2$ excited state are nearly isoenergetic with the Tb^{3+} $^5D_4$ energy levels. This suggests that if the Eu^{3+} and Tb^{3+} ions of a Tb^{3+}/Eu^{3+}/malic acid/water solution are interacting within the lifetime of the Tb^{3+} $^5D_4$ emitting state (excited directly by the light source), then $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer by a radiationless mechanism may be expected, resulting in a quenching of Tb^{3+} luminescence and a concomitant rise in Eu^{3+} luminescence (from the $^5D_0$ Eu^{3+} excited state to the manifold of ^7F_J levels). The static vs. dynamic nature of the Tb^{3+}–Eu^{3+} quenching interactions may be further probed by comparing the Stern–Volmer quenching constants as determined from luminescence intensity vs. luminescence lifetime measurements. This information may then be used to ascertain the extent of complex association or polymerization in solution at various pH values and the extent to which individual com-

---

(1) L. I. Katzin, *Inorg. Chem.*, **7**, 1183 (1968).
(2) C. K. Luk and F. S. Richardson, *J. Am. Chem. Soc.*, **97**, 6666 (1975).
(3) R. Prados, L. G. Stadtherr, H. Donato, and R. B. Martin, *J. Inorg. Nucl. Chem.*, **36**, 689 (1974).
(4) H. G. Brittain and F. S. Richardson, *Inorg. Chem.*, **15**, 1507 (1976).

0020-1669/80/1319-0629$01.00/0

plexes maintain their monomeric stoichiometric identities. In the present study, additional evidence regarding the static vs. dynamic nature of the quenching mechanism was obtained by investigating the Tb^{3+} and Eu^{3+} luminescence spectra of Tb^{3+}/Eu^{3+}/malic acid/7 M LiCl aqueous solutions in the glassy state at liquid-nitrogen temperature. In the glassy state at 77 K, it is presumed that only static quenching mechanisms are operative.

Malic acid contains one asymmetric carbon atom and is, therefore, optically active. In our studies of $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer, we carried out measurements on two types of systems: Tb^{3+}/Eu^{3+}/L-malic acid/water and Tb^{3+}/Eu^{3+}/DL-malic acid/water. Comparisons between the results obtained in these two sets of measurements are used to determine stereoselective influences on the $Tb^{3+} \rightarrow Eu^{3+}$ energy-transfer mechanisms.

Previous studies in this laboratory have shown that the coordination chemistry of Ln^{3+} ions in aqueous solution with carboxylic acids cannot be characterized unambiguously from spectroscopic data alone. Since the metal ions generally have a profound influence on the pK_a's of the donor moieties of these ligands,[3] potentiometric titration data are of essential value in characterizing the Ln^{3+}–ligand coordination properties. In the present study, potentiometric titration data are reported for the Tb^{3+}/malic acid/water solutions, and the conclusions drawn from these data are then used in interpreting the spectroscopic results.

Experimental Section

$TbCl_3 \cdot 6H_2O$ and $EuCl_3 \cdot 6H_2O$ (each of 99% purity) were purchased from Alfa-Ventron. L-Malic acid, DL-malic acid, and D_2O were purchased from Aldrich. Reagent grade LiCl and NaOH were supplied by Mallinckrodt.

Potentiometric titrations were performed with a Radiometer automatic titrator, Model TTT-2, using AgCl/Ag combination electrodes. Absorption spectra were obtained on a Cary 17 spectrophotometer using sample cells of 10-cm path length. These spectra were obtained on H_2O solutions which were 210 mM in ligand (malic acid) and 70 mM in Ln^{3+}. Luminescence intensity spectra on the Tb^{3+}–malic acid systems were obtained by using emission instrumentation constructed in this laboratory and described elsewhere.[2] These measurements were carried out on H_2O solutions of Tb^{3+}–malic acid in which the $[Tb^{3+}]$:[malic acid] concentration ratio was held fixed at 1:3. Irradiation was at 360 nm ($\Delta\lambda_{ex} \simeq$ 20 nm) using a 1000-W Hg–Xe arc lamp. All pH adjustments were made by using either NaOH or HCl solutions.

In the $Tb^{3+} \rightarrow Eu^{3+}$ energy-transfer experiments, selective excitation of Tb^{3+} was accomplished by irradiating with the 488-nm line of an argon ion CW laser. In these experiments, the $[Ln^{3+}]$:[malic acid] concentration ratio was held fixed at 1:3 where $[Ln^{3+}] = [Eu^{3+}] + [Tb^{3+}]$. The solutions were ~40 mM in $[Tb^{3+}]$. For the energy-transfer studies at liquid-nitrogen temperature (77 K), the Ln^{3+}:malic acid (1:3) was dissolved in 7 M LiCl solution (aqueous) which forms a clear glass at 77 K.

All intensity data reported here were obtained by measuring the *areas* under the observed emission/absorption spectra. Since the bandwidths and band shapes observed in the emission and absorption spectra were observed to vary significantly with solution pH, peak heights and the positions of band maxima were not useful in the analysis. Therefore, only integrated band intensities were used.

Luminescence lifetime measurements were carried out by using a Molectron UV-14 pulsed N_2 laser with a 400-kW pulse peak power and a Molectron DL-II dye laser. In these experiments, the sample luminescence was passed through a Jobin-Yvon H-10 monochromator for emission-band selection and onto a RCA C7164R photomultiplier tube. Luminescence decay curves were plotted on a Hewlett-Packard 180 AR storage oscilloscope and photographed on Polaroid film type 46-L.

Results and Discussion

Qualitative evidence for the formation of rather strong Tb^{3+}–malic acid complexes in aqueous solution is provided by the observation that precipitation of $Tb(OH)_3$ from Tb^{3+}/malic acid solutions remains negligible up to at least pH 12. $TbCl_3$ in aqueous solution begins to precipitate out $Tb(OH)_3$ at pH ~6.5. Additional evidence for strong Tb^{3+}–malic acid coordination in aqueous solution is given by the very strong circularly polarized luminescence (CPL) observed in the Tb^{3+} $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3, 2) emissive transitions over the pH range 3–12 when an optically active form of the ligand is used.[2,4,5]

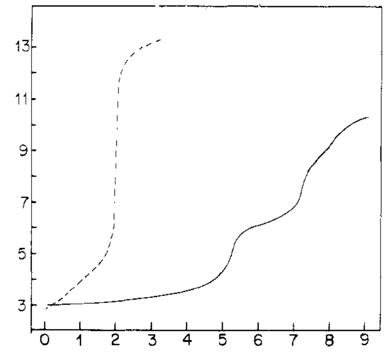

Figure 1. Potentiometric titration curves for free L-malic acid (- - -) and for 1:3 Tb^{3+}:L-malic acid (—) in aqueous solution.

Potentiometric Titrations. The potentiometric titration curves for free L-malic acid and for a 1:3 Tb^{3+}:L-malic acid solution (aqueous) are displayed in Figure 1. The data shown in this figure clearly demonstrate the influence of the metal ion upon the ligand pK_a's. For the free ligand, the two carboxyl group protons are titrated by pH 4.9, and a single end point is observed. On the other hand, the 1:3 Tb^{3+}:L-malic acid titration curve shows three end points at pH values of 4.8, 7.5, and 9.4. The observed end points correspond, respectively, to the titration of 5, 7, and 8 equiv of acid/equiv of Tb(L-malic acid)$_3$. We interpret the titration curve of the 1:3 Tb^{3+}:L-malic acid system in the following way. By pH 4.8, tris(bidentate) complexes of Tb(L-malic acid)$_3^{3-}$ have formed via Tb^{3+} coordination to six carboxylate groups (two from each of three malic acid ligands). Since the end point at pH 4.8 is reached after the addition of only 5 (rather than 6) equiv of base, it is assumed that on the average one ligand carboxyl group/equiv of Tb(L-malic acid)$_3$ is already deprotonated and bound at the start of the titration (pH ~3). Thus only 5 equiv of base needs to be added to generate six deprotonated carboxylate groups/equiv of Tb^{3+} in the 1:3 Tb^{3+}:L-malic acid system. Evidence for unidentate binding of one malic acid ligand (via a carboxylate group) at very low pH (<3) is provided by spectroscopic results to be discussed later (vide infra).

The second titration end point at pH 7.5 marks the deprotonation of two water molecules coordinated directly to the terbium ion. The last end point at pH 9.4 is attributed to the deprotonation of a ligand hydroxyl group which binds directly to the terbium ion. The basis for our assignments of the last three protons involved in the titration will be discussed after the spectroscopic results have been presented.

Luminescence Decay Measurements (Tb^{3+} $^5D_4 \rightarrow {}^7F_5$ Emission). Luminescence decay measurements were carried out on 1:3 Tb^{3+}:L-malic acid solutions in which the solvent was a H_2O/D_2O mixture. These measurements were carried out as a function of χ_{H_2O} (mole fraction of H_2O in the H_2O/D_2O solvent mixture) and as a function of solution pH. The emission monitored in these experiments was that due to the $^5D_4 \rightarrow {}^7F_5$ Tb^{3+} transition. The purpose of these measurements was to determine the number of water molecules or O–H groups coordinated directly to the Tb^{3+} ion under various

---

(5) F. S. Richardson and J. P. Riehl, *Chem. Rev.*, **77**, 773 (1977).

conditions of solution pH. At a given pH, these experiments are carried out by measuring the luminescence decay constant (k^{obsd}) as a function of χ_{H_2O} and then evaluating the slope of the resultant linear k^{obsd} vs. χ_{H_2O} plot. This slope may then be related in a straightforward way to the number of O–H groups (from H_2O or OH^-) coordinated directly to the Tb^{3+} ion.[6] These measurements are then repeated for additional pH values.

Measurements of the type described above for determining the number of water molecules coordinated to a Ln^{3+} ion in solution have been reported by several workers.[6] This technique exploits the fact that the rate constants observed for Ln^{3+} luminescence decay are extremely sensitive to the constitution of the metal ion coordination sphere. Furthermore, the luminescence decay constants, k^{obsd}, for Ln^{3+} ions in H_2O are greater than those observed for Ln^{3+} ions in D_2O. Previous work by Heller[7] and by Kropp and Windsor[8] established that the decay constant values for $Tb(aquo)^{3+}$ ions vary linearly with the mole fraction of H_2O in H_2O/D_2O mixtures and that the O–H oscillators of the bound H_2O molecules act independently in effecting radiationless deexcitation, with an efficiency which is unaffected by the nature and constitution of the remainder of the coordination sphere. Given these facts, the observed decay constants for Ln^{3+} emission in a H_2O/D_2O solution can be expressed as

$$k^{obsd} = k_r + k_x + k_w\chi_{H_2O} \quad (1)$$

where k_r is the inherent radiative decay constant, k_x is the decay constant for all radiationless decay processes *other than* H_2O-induced quenching, and k_w is the decay constant for the H_2O-induced deexcitation processes. The decay constant k_w is proportional to the number of water molecules bound directly to the metal ion and is determined as the slope of a k^{obsd} vs. χ_{H_2O} plot.

The proportionality constant, a, in the relationship

$$k_w = aW \quad (2)$$

where W = number of bound water molecules may be evaluated by determining k_w for a complex in which W is known. If we choose as our reference complex the $Ln(aquo)^{3+}$ system formed by dissolving $LnCl_3$ in water, we have

$$k_w(\text{aquo})/9 = a \quad (3)$$

where we have set $W = 9$ for this system.[6,9] Now for any other Ln^{3+} complex, we may write

$$W = k_w(\text{complex})/a = 9k_w(\text{complex})/k_w(\text{aquo}) \quad (4)$$

Measurements of the ratio $r = k_w(\text{complex})/k_w(\text{aquo})$ permit evaluation of W for the complex according to

$$W = 9r \quad (5)$$

The parameter r is just the ratio of the slopes of the straight-line plots of $k^{obsd}(\text{complex})$ vs. χ_{H_2O} and $k^{obsd}(\text{aquo})$ vs. χ_{H_2O} and is determined directly in our experiments. For our $Tb(\text{malic acid})_3$ complexes in aqueous solution

$$CN = W + l \quad (6)$$

where CN is the total coordination number for the Tb^{3+} ion and l is the number of malic acid donor groups coordinated to the Tb^{3+} ion.

The physical model underlying the analysis given above assumes that the deexcitation processes following k_w actually involve the action of *independent* O–H oscillators in the coordination sphere of the metal ion. Since each water molecule is assumed to consist of two independent O–H oscillators, the number of OH groups bound to the metal ion may be counted by $n_{OH} = 18r$. Each bound water molecule contributes 2 to n_{OH} and each bound OH^- group contributes 1 to n_{OH}.

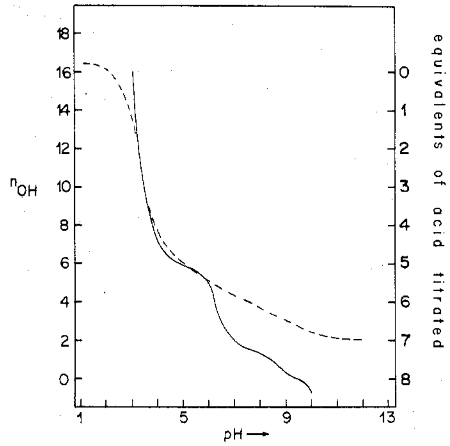

Figure 2. Solid curve: Equivalents of protons titrated vs. pH in a potentiometric titration of 1:3 Tb^{3+}:L-malic acid. Dashed curve: Number of bound O–H oscillators (n_{OH}) vs. pH as determined from luminescence decay measurements on 1:3 Tb^{3+}:L-malic acid in H_2O/D_2O mixtures.

In all of the luminescence decay experiments reported here, the $[Tb^{3+}]$:[L-malic acid] concentration ratio was held fixed at 1:3 and the solutions were ~40 mM in Tb^{3+}. Measurements were carried out over the pH range 1–12 to ascertain how n_{OH} varied with solution pH. In Figure 2, n_{OH} is plotted vs. pH. In this same figure we plot the number of equivalents of protons titrated vs. pH. The latter plot together with the former permits us to follow the change in composition of the Tb^{3+} coordination sphere as pH is varied. Four regions of the plots in Figure 2 are of special interest with regard to complex structure and complex formation. In the very low pH region (pH <3), we count eight coordinated water molecules (n_{OH} = 16, W = 8). Assuming a total coordination number of nine (CN = 9), we postulate that the remaining coordination site on Tb^{3+} in this pH region is occupied by a single ligand carboxylate group. We have, then, CN = 9, W = 8, and l = 1. That L-malic acid is bound at least unidentate at these low pH values is further suggested by the observation of weak circular polarization in the Tb^{3+} luminescence.[2,5]

Between pH 3 and pH 5, 5 equiv of protons is titrated and n_{OH} falls from 16 to 6. These results may be interpreted as showing the displacement of five water molecules (ten O–H oscillators) from the coordination sphere with the vacated sites being occupied by five malic acid carboxylate groups. By pH 5 we have, then, fully formed tris(bidentate) complexes of $Tb(\text{L-malic acid})_3{}^{3-}$ in which the Tb^{3+} coordination sphere is composed of six carboxylate groups (l = 6) and three water molecules (W = 3 or n_{OH} = 6). Between pH 5 and 7.5, two protons are titrated and n_{OH} is reduced by 2 (from 6 to 4). These results may be interpreted in terms of deprotonation of two bound water molecules with the consequent loss of two O–H deactivating oscillators in the Tb^{3+} coordination sphere. The total coordination number remains 9, and the malic acid ligands remain bidentate in their chelation to the metal ion.

An additional equivalent of acid is titrated between pH 7.5 and pH 9.5, and within this pH range n_{OH} is reduced from 4 to 3 (or slightly less). The most straightforward interpretation of this result would be that an additional bound water molecule is deprotonated with a consequent loss of one more O–H oscillator ($\Delta n_{OH} = -1$). However, an additional observation must be interjected here. The circularly polarized luminescence (CPL) spectrum of the Tb^{3+}/L-malic acid system exhibits a dramatic change (in sign pattern and intensity) in

---

(6) (a) W. D. Horrocks, Jr., G. F. Schmidt, D. R. Sudnick, C. Kittrell, and R. A. Bernheim, *J. Am. Chem. Soc.*, **99**, 2378 (1977); (b) W. D. Horrocks, Jr., and D. R. Sudnick, *ibid.*, **101**, 334 (1979).

(7) A. Heller, *J. Am. Chem. Soc.*, **88**, 2058 (1966).

(8) J. L. Kropp and M. W. Windsor, *J. Phys. Chem.*, **71**, 477 (1967).

(9) Y. Haas and G. Stein, *J. Phys. Chem.*, **75**, 3677 (1971).

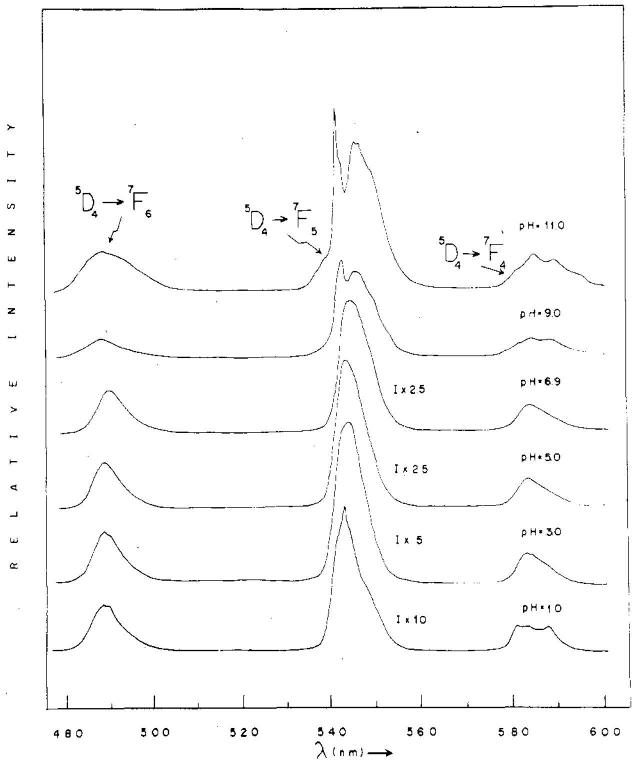

Figure 3. Luminescence spectra of 1:3 Tb^{3+}:L-malic acid in aqueous solution at various pH values. Excitation was centered at 360 nm ($\Delta\lambda_{ex} \simeq 20$ nm), and the spectral slit width for emission was $\Delta\lambda_{em} = 0.2$ nm.

this pH region, suggesting a major change in the stereochemical environment created by the ligands about the metal ion.[2,4] This suggests that at least one of the bound ligands is coordinating terdentate via two carboxylate groups and a hydroxylate group. If this is occurring, then the titrated proton is coming from a malic acid hydroxyl group and the hydroxylate group thus formed coordinates to Tb^{3+}, displacing a water molecule. In this case, assuming CN = 9, the value of l is 7 (six carboxylate groups plus one hydroxylate group) and $n_{OH} = 2$ (two bound OH^-) by pH 9.5. The observed value of n_{OH} at pH 9.5 is between 2 and 3, and it approaches 2 at pH 11. Thus the suggestion of hydroxylate binding at pH >7.5 is not greatly at variance with the experimental data, although it does not fit the n_{OH} data exactly. Further evidence for significant alterations in the ligand environment at pH >7.0 (possibly attributable to hydroxylate binding by a malic acid ligand) is provided by the observed structure in the Tb^{3+} $^5D_4 \rightarrow {}^7F_5$ emission band. Just as the $^5D_4 \rightarrow {}^7F_5$ CPL spectrum changes dramatically at pH >7.0, so does the total (unpolarized) emission spectrum. This is apparent from the spectra shown in Figure 3.

Absorption and Luminescence Decay Measurements (Tb^{3+} $^5D_4 \leftrightarrow {}^7F_6$ Transitions). The $^5D_4 \rightarrow {}^7F_6$ transition of Tb^{3+} exhibits a much weaker emission intensity than does the $^5D_4 \rightarrow {}^7F_5$ transition. However, the $^5D_4 \leftarrow {}^7F_6$ transition is accessible to absorption measurements whereas the $^5D_4 \leftarrow {}^7F_5$ transition is not. Absorption spectra were obtained for 1:3 Tb^{3+}:L-malic acid in H_2O in the $^5D_4 \leftarrow {}^7F_6$ Tb^{3+} transition region over the pH range 1.5–11.0. From these absorption data oscillator strengths were determined according to the expression[10]

$$f = 4.32 \times 10^{-9}\chi \int \epsilon(\bar{\nu})\, d\bar{\nu} \qquad (7)$$

Table I. Luminescence Decay Constants and $^5D_4 \leftarrow {}^7F_6$ Oscillator Strengths[a]

pH	$k^{obsd}(^5D_4 \rightarrow {}^7F_6)^b$		$k^{obsd}(^5D_4 \rightarrow {}^7F_5)^b$		$10^9 f(^5D_4 \leftarrow {}^7F_6)^c$
	H_2O	D_2O	H_2O	D_2O	
1.5	2080	187	2050	215	32.7
2.0	2110	206	2156	242	37.3
3.0	1860	284	1873	310	42.8
4.0	1232	366	1241	406	56.4
5.0	1098	359	1150	411	56.6
6.0	1071	336	1081	341	52.3
7.0	965	330	967	338	51.9
8.5	841	302	794	297	49.0
10.0	700	298	693	293	49.1
11.0	614	305	615	305	50.1

[a] All measurements were on 1:3 $[Tb^{3+}]$:[L-malic acid] solutions. [b] Given in s^{-1}. [c] Determined from eq 7 with $\chi = 0.84$.

where χ is the Lorentz field correction for the refractivity of the solvent medium ($\chi = 0.84$ for water), $\bar{\nu}$ is the spectral frequency variable expressed in cm^{-1}, $\epsilon(\bar{\nu})$ is the molar decadic extinction coefficient, and the integration is over the entire $^5D_4 \leftarrow {}^7F_6$ absorption region. The values determined for $f(^5D_4 \leftarrow {}^7F_6)$ are listed in Table I.

Luminescence decay measurements for the $^5D_4 \rightarrow {}^7F_6$ Tb^{3+} transition in 1:3 Tb^{3+}:L-malic acid solutions were also carried out. These measurements were carried out over the pH range 1.5–11.0 in both pure H_2O and pure D_2O solvent. The experimentally determined values of $k^{obsd}(^5D_4 \rightarrow {}^7F_6)$ are given in Table I along with the measured values of $k^{obsd}(^5D_4 \rightarrow {}^7F_5)$. In pure D_2O solution ($\chi_{H_2O} = 0$), eq 1 becomes

$$k^{obsd} = k_r + k_x \qquad (8)$$

where k_r is again the radiative decay constant and k_x is the radiationless decay constant. For the $^5D_4 \rightarrow {}^7F_6$ Tb^{3+} transition, the value of k_r may be determined indirectly from the absorption data obtained for the $^5D_4 \leftarrow {}^7F_6$ transition. This is accomplished by evaluating the expression[11]

$$k_r \simeq 2.88 \times 10^{-9} n^2 \langle \bar{\nu}_f^{-3} \rangle_{AV}^{-1} (g_l/g_u) \int \epsilon(\bar{\nu})\, d \ln \bar{\nu} \qquad (9)$$

where n is the refractive index of the medium, g_l/g_u is the ratio of the degeneracies of the lower (l) and upper (u) levels, the integration is over the $^5D_4 \leftarrow {}^7F_6$ absorptive region, and $\langle \bar{\nu}_f^{-3} \rangle_{AV}^{-1}$ is the reciprocal of the mean value of $\bar{\nu}$ in the $^5D_4 \rightarrow {}^7F_6$ luminescence spectrum. The $^5D_4 \leftarrow {}^7F_6$ absorption band spans the 20 100–20 900 cm^{-1} spectral region in nearly all of the spectra recorded. An approximation to eq 9 allows pulling a "mean" absorption frequency, $\bar{\nu}_0$, outside the integral so that

$$k_r \simeq 2.88 \times 10^{-9} n^2 \langle \bar{\nu}_f^{-3} \rangle_{AV}^{-1} (g_l/g_u) \bar{\nu}_0^{-1} \int \epsilon(\bar{\nu})\, d\bar{\nu} \qquad (10a)$$

or

$$k_r \simeq 0.67(n^2/\chi) \langle \bar{\nu}_f^{-3} \rangle_{AV}^{-1} (g_l/g_u) \bar{\nu}_0^{-1} f \qquad (10b)$$

Setting $\chi = 0.84$ and $n = 1.33$ (the refractive index of water), eq 10b may be rewritten as

$$k_r \simeq 1.4 \langle \bar{\nu}_f^{-3} \rangle_{AV}^{-1} (g_l/g_u) \bar{\nu}_0^{-1} f \qquad (11)$$

The approximate value of $\langle \bar{\nu}_f^{-3} \rangle_{AV}^{-1}$ for the $^5D_4 \rightarrow {}^7F_6$ emission spectra obtained at various solution pHs is 8.4×10^{12} cm^{-3}. Putting this number into eq 11 yields

$$k_r \simeq 1.2 \times 10^{13} (g_l/g_u) \bar{\nu}_0^{-1} f \qquad (12)$$

for the radiative decay constant (in s^{-1}) of the $^5D_4 \rightarrow {}^7F_6$ transition. Since the $^5D_4 \leftrightarrow {}^7F_6$ absorption and emission bands include transitions between many crystal-field components of the $^5D_4$ and $^7F_6$ free-ion states, it is not clear what value should

---

(10) Walter Kauzmann, "Quantum Chemistry", Academic Press, New York, 1957, p 581.

(11) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

Table II. Calculated Radiative and Nonradiative Decay Constants and Quantum Yields for the $^5D_4 \rightarrow {}^7F_6$ Transition[a]

pH	$10^{13} \times \bar{\nu}_0^{-1} f$[b]	$k_r(g_u/g_l)$[c]	Φ[d]		$k_x(D_2O)$[e]
			D_2O	H_2O	
1.5	15.9	19	0.10	0.009	168
2.0	18.2	22	0.11	0.010	184
3.0	20.8	25	0.09	0.013	259
4.0	27.5	33	0.09	0.027	333
5.0	27.6	33	0.09	0.030	326
6.0	25.5	31	0.09	0.029	305
7.0	25.4	31	0.09	0.032	299
8.5	23.9	29	0.10	0.034	273
10.0	23.8	29	0.10	0.041	269
11.0	24.3	29	0.10	0.047	276

[a] All measurements were on 1:3 [Tb^{3+}]:[L-malic acid] solutions. [b] Determined experimentally from absorption spectra. [c] Calculated from eq 12 and expressed in units of s^{-1}. [d] Quantum yield defined by $\Phi = k_r/k^{obsd}$. The values of k^{obsd} were obtained from Table I, and the values of k_r were calculated from eq 12 with $g_u/g_l = 1$. [e] Calculated from $k_x = k^{obsd} - k_r$, with $g_u/g_l = 1$.

be assigned to g_l/g_u. Given the low symmetries of the complex species involved, the $^5D_4 \leftrightarrow {}^7F_6$ transitions are most likely comprised of many nondegenerate crystal-field components in which case g_l/g_u may be set equal to unity. In Table II the experimentally determined values of $\bar{\nu}_0^{-1} f$ are listed along with $(g_u/g_l)k_r$ calculated from eq 12. Also listed in Table II are values of the $^5D_4 \rightarrow {}^7F_6$ luminescence quantum yields calculated from the observed $k^{obsd}(H_2O)$ and $k^{obsd}(D_2O)$ decay constants (given in Table I) and the calculated values of k_r with $g_u/g_l = 1$. Values for $k_x(D_2O)$ were calculated from $k_x = k^{obsd} - k_r$, and these too are given in Table II. Plots of oscillator strengths (f), k_r, and k_x vs. solution pH are shown in Figure 4.

An interpretation of the data in Table I and the plots in Figure 4 in terms of structural and photophysical details within the Tb^{3+}–malic acid complexes is beyond the scope of this study. However, several qualitative aspects of the plots shown in Figure 4 can be commented upon. In previous sections we have hypothesized that in going from pH ~2 to pH ~5 tris(bidentate) complexes of $Tb(\text{L-malic acid})_3^{3-}$ are formed with each malic acid coordinating to the Tb^{3+} via two carboxylate ligating groups. This formation of tris(bidentate) $Tb(\text{L-malic acid})_3^{3-}$ species should lead to dramatic changes in the Tb^{3+} crystal-field environment and these changes would be expected to be reflected in both k_r and k_x. Indeed the values of both k_r and k_x are found to change dramatically over the pH range 1.5 to ~4.5 (see Figure 4). The values of k_r and k_x are also seen to change significantly over the pH interval 4.5–6.0. This is just the pH interval over which we previously hypothesized that at least one and maybe two bound water molecules are being deprotonated (converting H_2O ligands to OH^- ligands). Again, this change in the nature of the bound ligands would be expected to alter the values of k_r and k_x via alterations in the Tb^{3+} crystal-field environment. Finally, between pH 7 and pH 8.5 we observe mild changes in the k_r and k_x values and this pH interval corresponds roughly to the region where we previously hypothesized that at least one of the three malic acid ligands is becoming terdentate (via two carboxylate groups and a hydroxylate group). The slight increase in both k_r and k_x as pH is raised above 9.5 can most likely be accounted for in terms of the onset of complex hydrolysis processes.

The qualitative interpretation given above for the pH dependence of k_r and k_x in terms of stepwise complex formation (or alteration) is by no means conclusive with respect to the identities and structural details of the complex species existing in solution. Suffice it to say that both k_r and k_x should be very sensitive to the nature and symmetry of the bound ligand groups, and the interpretation given above for their observed pH dependence is consistent with our previously stated interpretation of the potentiometric titration results and $^5D_4 \rightarrow {}^7F_5$ luminescence decay results (Figure 2).

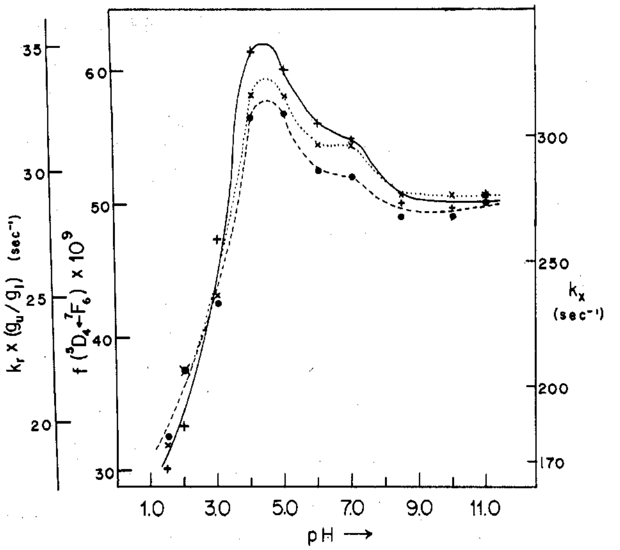

Figure 4. Solid curve: Plot of nonradiative decay constant (k_x) vs. pH for the $^5D_4 \rightarrow {}^7F_6$ transition of terbium in 1:3 Tb^{3+}:L-malic acid D_2O solution. Dotted curve: Plot of radiative decay constant ($k_r(g_u/g_l)$) vs. pH for the $^5D_4 \rightarrow {}^7F_6$ transition of terbium in 1:3 Tb^{3+}:L-malic acid D_2O solution. Dashed curve: Plot of oscillator strength (f) vs. pH for the $^5D_4 \leftarrow {}^7F_6$ transition of terbium in 1:3 Tb^{3+}:L-malic acid H_2O solution.

The last column in Table II gives approximate values for the quantum yield of the $^5D_4 \rightarrow {}^7F_6$ emission in D_2O solutions. We note that the quantum yield is nearly constant over the pH range 1.5–11.0, with a value of ~9% (or $\Phi \approx 0.09$).

Eu^{3+} Quenching of Tb^{3+} Emission in Tb^{3+}/Eu^{3+}/Malic Acid Solution. Terbium luminescence intensities and lifetimes were studied as a function of [Eu^{3+}]:[Tb^{3+}] concentration ratios in H_2O solutions of 1:3 [Ln^{3+}]:[malic acid], where [Ln^{3+}] = [Tb^{3+}] + [Eu^{3+}]. Measurements were carried out over the pH range 2.0–11.0, and for both L-malic acid and racemic DL-malic acid. The purpose of these studies was to probe the extent of Ln^{3+}–Ln^{3+} interactions and the nature of such interactions in solution under variable pH conditions.

A standard Stern–Volmer analysis was carried out in both the luminescence intensity and luminescence lifetime studies. For the intensity studies

$$I_0/I_M = 1 + K_{SV}^{\Phi}[Q] \tag{13}$$

where I_0 = Tb^{3+} luminescence intensity in the absence of quencher (Eu^{3+}), I_M = Tb^{3+} luminescence intensity in the presence of quencher at molar concentration M, [Q] = [Eu^{3+}], and K_{SV}^{Φ} is the Stern–Volmer quenching constant for Tb^{3+} luminescence intensity. The $^5D_4 \rightarrow {}^7F_5$ Tb^{3+} emission was used to monitor I_M. For the lifetime studies

$$\tau^0/\tau_M = 1 + K_{SV}^{\tau}[Q] \tag{14}$$

where τ^0 and τ_M are, respectively, the Tb^{3+} luminescence lifetime in the absence and presence of quencher (Eu^{3+}), $K_{SV}^{\tau} = \tau^0 k_q$, and k_q is the bimolecular (quenching) rate constant. The lifetime measurements, τ^0 and τ_M, were obtained on the $^5D_4 \rightarrow {}^7F_5$ Tb^{3+} emission. The experimentally determined values of K_{SV}^{Φ}, K_{SV}^{τ}, and k_q are listed in Table II.

All of the data given in Table III were obtained on fluid solutions at room temperature in which the total metal ion concentration, [Ln^{3+}] = [Tb^{3+}] + [Eu^{3+}], did not exceed 52 mM and the ligand:metal ratio was kept constant at 3:1. Under these relative and total concentration conditions, it

Table III. Stern–Volmer Quenching Constants[a] and Bimolecular (Quenching) Rate Constants[b]

	DL-malic acid	L-malic acid		
pH	$K_{SV}^{\Phi} \pm 2\sigma^c$	$K_{SV}^{\Phi} \pm 2\sigma^c$	$K_{SV}^{\tau} \pm 2\sigma^c$	$10^{-4}k_q$
4.0	457 ± 17	412 ± 13	607 ± 86	75.3
6.0	370 ± 14	304 ± 20	301 ± 32	32.5
8.0	289 ± 7	256 ± 9	157 ± 46	13.4
9.0	156 ± 11	152 ± 5	62 ± 18	4.7
10.0	114 ± 8	129 ± 8	14 ± 5	0.97
11.0	112 ± 11	105 ± 10		

[a] Expressed in L/mol. [b] Expressed in L/(mol·s). [c] σ = one standard deviation.

would seem unlikely that there would be significant Tb^{3+}–Eu^{3+} "mixed" complex formation at any of the pH values included in the study unless dimer or polymer formation was under very strong thermodynamic control. However, the small differences observed between K_{SV}^{Φ} and K_{SV}^{τ} for all pHs except pH 6.0 suggest some static quenching is taking place in solution. These differences are small, however, and cannot be taken as conclusive evidence for static quenching.

Luminescence quenching experiments were also carried out on Tb^{3+}/Eu^{3+}/malic acid dissolved in 7 M LiCl and frozen into a glassy state (solid solution) at liquid-nitrogen temperature. These experiments were carried out as a function of pH and as a function of Tb^{3+}:Eu^{3+} concentration ratios. Under these sample conditions (low-temperature solid solution), *no* quenching of Tb^{3+} luminescence by Eu^{3+} was observed. These low-temperature results in glasses would appear to rule out a static quenching mechanism for the fluid solution results. If, in fact, stable (long-lived) donor (Tb^{3+})–quencher (Eu^{3+}) complex species existed at significant concentration levels in solution at room temperature, they should persist in the formation of the glasses and this would lead to terbium luminescence quenching in the glassy state. The low-temperature results suggest, then, the dominance of a collision-controlled quenching mechanism in fluid solution which is "frozen out" in the solid solution at low temperature.

Assuming a pure dynamic (collisional) quenching mechanism, the ratio of k_q (the *observed* bimolecular quenching constant) to k_d (the diffusion rate constant for the solution) gives an estimate of the Tb → Eu energy-transfer probability per collision between a Tb^{3+} and a Eu^{3+} complex species. Taking a value of 5×10^9 s^{-1} for k_d, the values of k_q/k_d for several pHs are as follows [pH, $(k_q/k_d) \times 10^{-4}$]: 4.0, 151; 6.0, 65.0; 8.0, 26.8; 9.0, 9.40; 10.0, 1.94. The pH dependence of k_q can be interpreted in terms of two factors: (a) an increase in ligand "insulation" of the lanthanide ions as pH is raised and the malic acids become fully coordinated and (b) an increase in net negative charge on the interacting complexes as pH is raised. Both of these factors would serve to increase the Ln^{3+}–Ln^{3+} separation distance in an "encounter" complex and/or decrease the lifetime of the encounter complex, thus leading to a reduced efficiency in energy transfer.

Comparisons of K_{SV}^{Φ} for L-malic acid and DL-malic acid (see Table III) suggest some small stereoselective influence on the efficiency of Tb → Eu energy transfer. The differences between K_{SV}^{Φ}(L) and K_{SV}^{Φ}(DL) at pH 4, 6, and 8 are larger than can be accounted for in terms of experimental data scatter (as measured by the σ values given in Table III). No explanation can be offered as to why these differences are pH dependent.

So far in our discussion we have made the tacit assumption that the Eu^{3+} ions are acting as energy acceptors in the quenching process and that Tb → Eu energy transfer actually occurs. The alternative to this assumption is that the Eu^{3+} ions somehow interact with the terbium complexes to increase the rate of *direct* radiationless excited state to ground state deactivation in the Tb^{3+} ions. Proof that Tb → Eu energy transfer is the dominant quenching mechanism is given by the observation of strong europium emission. That is, europium emission is being sensitized by terbium excitation.

Conclusions

Spectroscopic absorption and luminescence measurements have been used in a variety of ways to investigate the formation and structural properties of Tb^{3+}–malic acid complexes in aqueous solution under variable pH conditions. Where possible, the pH dependence of these spectroscopic results has been compared to the potentiometric titration data obtained on the Tb^{3+}–malic acid system. Interpretation of the spectroscopic results focused primarily on changes occurring within the lanthanide ion coordination sphere as solution pH was raised from 1.5 to 11.0. These changes were attributed to stepwise formation of tris-chelated $Tb(malic\ acid)_3^{3-}$ complexes via Tb^{3+}–carboxylate group coordination, deprotonation of bound water molecules, and possible deprotonation and binding of a malic acid hydroxyl group. The luminescence decay measurements carried out in *mixed* H_2O/D_2O solutions provided a method for "counting" the number of water molecules (or O–H oscillators) bound to the lanthanide ion at various solution pH values. The absorption spectra and luminescence intensity spectra were used to follow changes occurring in the "crystal-field" environment of the lanthanide ion as evidenced by intensity changes and alterations in band splittings. The Tb → Eu energy-transfer experiments were used to probe the nature of Ln^{3+}–Ln^{3+} interactions in solution and to check for the possible formation of polynuclear complex species. In this latter regard, no evidence for polynuclear species was found at the concentration levels of metal ion and ligand used in these studies.

Taken all together, the spectroscopic results obtained in this study lead to a self-consistent interpretation of how the lanthanide ion coordination sphere changes as a function of pH in aqueous solutions of 1:3 [Tb^{3+}]:[malic acid]. However, considerable care must be taken as to how one views these results microscopically and macroscopically. Except at very low pH and very high pH, the terbium–malic acid interactions are most likely characterized by complex equilibria between multiple species. Under these conditions and in the absence of *dominant* species (at given pH values), the n_{OH} numbers given in Figure 2 are best considered "average" numbers of O–H oscillators bound to the metal ion. No attempt has been made in this study to sort out and characterize the detailed nature of the complex equilibria possibly existing throughout the pH range 3–8. Furthermore, our studies cannot address the question of how much lanthanide ion is bound to the malic acid ligands at a given pH. The spectroscopic experiments were designed to probe the nature of the bound Tb^{3+}–malic acid species but do not reveal formation constants.

The studies reported here demonstrate the efficacy of luminescence lifetime and intensity measurements for probing lanthanide ion complexes in aqueous solution and suggest the importance of using multiple techniques in characterizing such complexes. The spectroscopic techniques and results reported here should be transferable to both simpler and more complicated Ln^{3+}–ligand systems in aqueous solution.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE77-02150).

Registry No. Tb, 7440-27-9; DL-malic acid, 617-48-1; L-malic acid, 97-67-6; Eu, 7440-53-1.