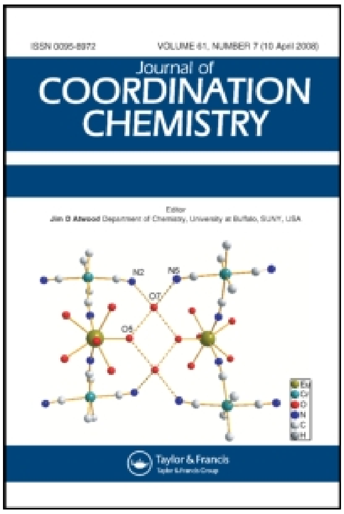

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SOLUTION PHASE CHEMISTRY OF LANTHANIDE COMPLEXES. 11.1:1 AND 1:2 LANTHANIDE COMPLEXES WITH NITRILOTRIACETIC ACID

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SOLUTION PHASE CHEMISTRY OF LANTHANIDE COMPLEXES.
11. 1:1 AND 1:2 LANTHANIDE COMPLEXES WITH NITRILOTRIACETIC ACID

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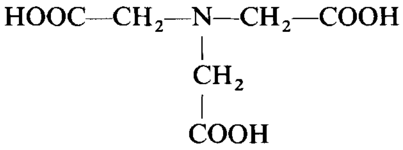
The solution phase coordination chemistry associated with the 1:1 and 1:2 complexes of lanthanide ions with nitrilotriacetic acid (NTA) has been studied by spectroscopic means. The Tb(III) luminescence intensities and lifetimes were found to be sensitive toward the solution phase properties, as was the hypersensitive absorption of the Ho(III) complexes. It was found that below neutral pH values, Ln(NTA) complexes were monomeric in nature and contained an average of 4.5 molecules of coordinated water. Above neutral pH, the Ln(NTA) complexes became self-associated into hydroxy bridged, oligomeric species. The Ln(NTA)$_2$ complexes remained monomeric at all pH values, and contained one coordinated solvent molecule. In all cases, the coordination number of the lanthanide species was approximately nine.

Keywords: lanthanide, nitrilotriacetic acid, luminescence, hydration

INTRODUCTION

The solution phase coordination chemistry associated with lanthanide ion complexes of aminopolycarboxylic acids remains an important area of investigation. Nitrilotriacetic acid (NTA) is a potentially tetradentate ligand, containing three carboxylate and one amine binding sites, as shown below.



$$\begin{array}{c} \mathrm{HOOC{-}CH_2{-}N{-}CH_2{-}COOH} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{COOH} \end{array}$$

It is known that NTA is capable of forming compounds having either 1:1 or 1:2 metal–ligand stoichiometry. The stability constants[1] and thermodynamic parameters[2] associated with the Ln(NTA) and Ln(NTA)$_2$ compounds have been documented. The free energies, enthalpies, and entropies of formation exhibit only slight variations as the metal ion is varied from La(III) to Lu(III).

The kinetics associated with lanthanide complexes of NTA have been studied in

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detail by ^1H nuclear magnetic resonance, where three pathways for intermolecular ligand exchange were detected.[3] The pH dependence of certain hypersensitive Ho(III) and Er(III) absorption bands has also been studied, and these workers attempted to deduce structural information from their spectral studies.[4] In all of these previous studies, the existence of monomeric lanthanide complexes was assumed, in spite of the fact that lanthanide compounds are often self-associated into oligomeric species under certain conditions.[5]

It is well established that the luminescence properties of lanthanide ions are extremely useful in deducing details of the solution phase coordination chemistry. To clarify the nature of lanthanide–NTA coordination chemistry, detailed spectral studies of the influence of solution pH on Ln(NTA) and $Ln(NTA)_2$ complexes were performed. The possible oligomerization of the complexes was investigated using the energy transfer method,[5] and the number of bound solvent molecules was established using the method of Horrocks.[6] Further characterization of the complexes was obtained through systematic investigations of Ho(III) hypersensititive absorption intensities and Tb(III) luminescence intensities and lifetimes.

EXPERIMENTAL

Nitrilotriacetic acid was used as received from Aldrich Chemicals, while hydrated $TbCl_3$ and $HoCl_3$ were used as received from Research Chemicals. Stock solutions were prepared by the dissolution of appropriate quantities of material, and solutions prepared by mixing stoichiometric amounts of the stock solutions. For the luminescence experiments, a final Tb(III) concentration of 10 mM was used. During the energy transfer studies, 10^{-3} cm^3 amounts of 50 mM Eu/NTA stock solutions (containing the same metal/ligand ratio as the Tb/NTA solution) were added to a Tb/NTA solution. The Ho/NTA experiments were performed at Ho(III) concentration levels of 50 mM. The ionic strength of the solutions was not controlled.

The pH of each solution was varied between pH 1.5 and 12, with the required photophysical measurements being obtained at each pH value. Variation of the solution pH of each solution was affected by the addition of 10^{-3} cm^3 amounts of standard NaOH or HCl directly into the cuvette. The pH was measured using a glass microcombination electrode which could be directly inserted into the cuvette. The pH meter was calibrated daily using phosphate buffers.

The Tb(III) luminescence intensity associated with the Tb(NTA) and $Tb(NTA)_2$ complexes was measured on a Spex Fluorolog II spectrometer. Luminescence lifetimes of the same solutions were obtained by exciting the samples with the pulsed 337 nm output of a nitrogen laser (model LN-1000, Photochemical Research Associates), and capturing the decay curve on a boxcar averager (model SR-265, Stanford Research Associates). The luminescence decay times and rate constants were obtained by fitting the decay curve to a single exponential function. The Ho(III) absorption experiments were carried out on a Cary 14 spectrophotometer. The reference cell in this series contained Ho(III) aquo-species at exactly the same concentration as the Ho/NTA solution, thus yielding a differential absorbance value.

RESULTS AND DISCUSSION

Detailed potentiometric studies of the lanthanide complexes with nitrilotriacetic acid have been reported,[1,2] with the ligand pK_a values being reported as 1.57, 2.64, and 9.57.[1] The binding of the first NTA ligand by a lanthanide ion to form the 1:1 complex, (*1*),

$$Ln^{3+} + NTA^{3-} \rightleftharpoons Ln(NTA) \qquad (1)$$

is known to be extremely efficient, with a log K_1 value of 11.25 being reported for the Tb(III) complex.[2] The addition of the second NTA ligand to form the 1:2 complex (*2*),

$$Ln(NTA) + NTA^{3-} \longleftrightarrow Ln(NTA)_2{}^{3-} \qquad (2)$$

is not as favourable, but a log K_2 value of 8.28 has been reported for the $Tb(NTA)_2$ complex.[3] The magnitude of these complex formation constants are such that the Tb(NTA) complex may be formed by the addition of one equivalent of Tb(III) and one equivalent of NTA, and the $Tb(NTA)_2$ complex may be formed by the addition of slightly more than two equivalents of NTA per equivalent of Tb(III).

A. pH Dependence of Tb(III) Emission Intensity

UV excitation of Tb(III) complexes results in reasonably efficient population of the luminescent $^5D_4$ excited state, and in subsequent 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 of the various emission bands were found to be a function of the solution pH, and of the complex stoichiometry investigated. The existence of a stable emission intensity over a defined pH range usually indicates the existence of a stable complex. Since it was noted that the trends associated with the pH dependence of each emission band system were identical, only results obtained within the $^5D_4 \rightarrow {}^7F_5$ transition will be discussed.

The pH dependence measured for the Tb(III) emission intensity in the Tb(NTA) and $Tb(NTA)_2$ complexes is shown in Figure 1. For the Tb(NTA) complex, the Tb(III) emission intensity increased rapidly up to pH 3.5 and remained stable up to 6.5. This observation implies that attachment of this first NTA ligand is complete by pH 3.5. A second inflection was observed between pH 6.5 and 8, indicating the formation of another species. This second species remained stable up to the highest pH values studied, although a slight systematic increase in emission intensity was observed.

The pH dependence associated with the $Tb(NTA)_2$ complex was quite different to that observed for the Tb(NTA) complex. An initial sharp increase in emission intensity was noted up to pH 6, whereupon a stable plateau was reached that remained up to pH 12. This latter observation indicates that once the $Tb(NTA)_2$ complex forms, no further coordination chemistry is accessible. The absence of any minor inflections within the initial increase indicate that both NTA ligands bind the Tb(III) ion independently, without cooperativity.

B. pH Dependence of Tb(III) Emission Lifetime

The mechanisms which lead to alteration of the luminescence lifetime of a Tb(III) species are similar to those which effect the emission intensity. High-energy vibrations (around 3500 cm^{-1}) are efficient promoters for deactivation of the excited

$^5D_4$ Tb(III) state, and consequent quenching the emission lifetime. The –OH stretching mode of coordinated water molecules is particularly effective in this regard.[6] Most ligands do not contain the required group vibrational frequencies which quench the excited state, and therefore are not efficient quenchers of Tb(III) emissive lifetimes. Since the binding of a ligand must result in the expulsion of some of the coordinated water molecules, then it follows that the Tb(III) emission lifetime is a good probe for the study of solution chemistry.

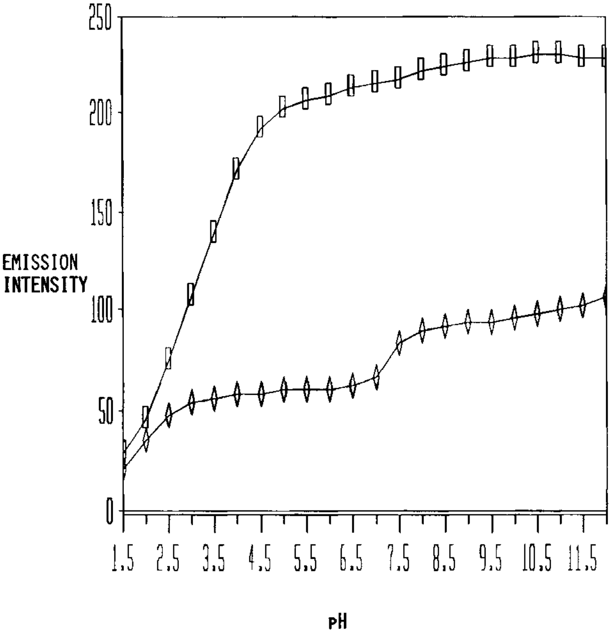

FIGURE 1 pH Dependence of Tb(III) luminescence intensities, obtained for Tb(NTA) {◇} and $Tb(NTA)_2$ {□} complexes. The data are shown in arbitrary units.

The pH dependences associated with the Tb(III) emission lifetimes of Tb(NTA) and $Tb(NTA)_2$ were found to closely parallel the trends noted for the emission intensities. For the Tb(NTA) complex, the initial increase in Tb(III) lifetime was observed to be modest, but the second inflection (pH 6.0 to 8.0) was quite substantial. The emission lifetimes also exhibited the same two regions of pH stability (pH 3 to 6, and 8 to 11) as had been noted in the emission intensity data. The $Tb(NTA)_2$ emission lifetimes were found to increase rapidly up to pH 6, where they levelled off and remained essentially unchanged up to pH 11. The data also do not indicate the existence of any cooperativity in the initial ligand binding region.

C. pH Dependence of Tb(III) Coordinated Water Molecules

The existence of a deuterium isotope effect in Tb(III) emission lifetimes has been known for some time.[6] While the –OH stretching mode of coordinated water ($3500\,cm^{-1}$) is effective at quenching the Tb(III) excited $^5D_4$ state, the analogous –OD stretching mode of coordinated deuterium oxide ($2800\,cm^{-1}$) is far less effective. Horrocks and Sudnick[7] have used this phenomenon to develop a spectroscopic method suitable for a determination of the number of water molecules bound at the inner coordination sphere of either Tb(III) or Eu(III). The luminescence lifetime of a given species is measured in both H_2O and D_2O, and the observed rate for luminescence decay obtained in each solvent system. The difference between the rate constants obtained in H_2O and D_2O is directly proportional to the number of coordinated water molecules, which is calculated using the proportionality constant provided by Horrocks and Sudnick.[7]

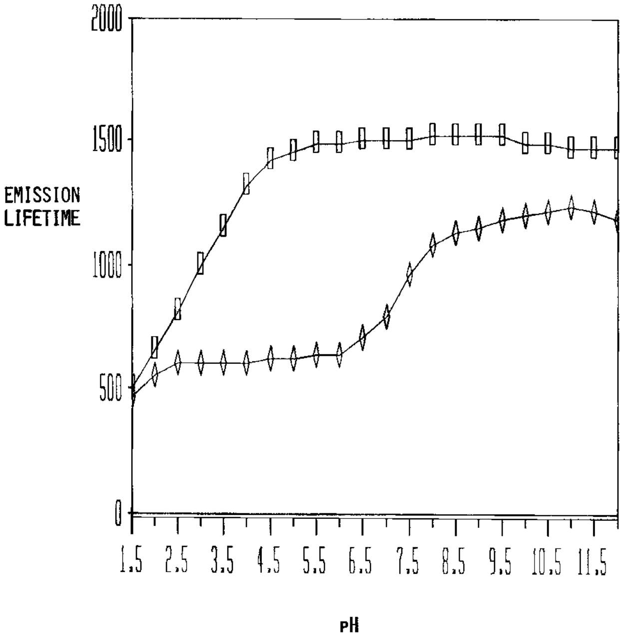

FIGURE 2 pH Dependence of Tb(III) luminescence lifetimes, obtained for Tb(NTA) {◇} and $Tb(NTA)_2$ {□} complexes. The lifetime data are shown in units of microseconds.

The pD dependence associated with the Tb(III) emission lifetimes of Tb(NTA) and $Tb(NTA)_2$ complexes dissolved in D_2O was obtained in a manner similar to that described above for the same complexes dissolved in H_2O. After correcting the pD values to the pH scale, the rate constants calculated at analogous acidity values were subtracted and the number of coordinated water molecules deduced at selected pH values. These data are plotted in Figure 3.

The existence of two types of Tb(III) complex were again noted in the results obtained for Tb(NTA). Between pH 1.5 and 2.5, a dramatic decrease in the number of bound water molecules takes place, and a stable plateau corresponding to 4.5 water molecules is observed. Such a non-integral hydration number would indicate that the equilibrium mixture consists of an approximately equal quantity of Tb(III) species featuring 4 waters of hydration, and an equal quantity containing 5 waters of hydration. These trends accompany the binding of the single NTA ligand, and the expulsion of an appropriate number of water molecules to provide adequate steric room for the NTA ligand. The Tb(NTA) $(H_2O)_4$ and Tb(NTA) $(H_2O)_5$ species exist unchanged up to pH 6. In the Tb(NTA) complexes, the Tb(III) ion therefore exists either in 9-fold or 8-fold coordination, with one tetradentate NTA ligand occupying 4 positions and water molecules making up the remainder of the coordination sphere.

Between pH 6 and 8, the number of coordinated water molecules decreases rapidly, even though no new ligand ionizations exist. This behaviour would indicate the formation of a new type of Tb(NTA) complex. The existence of this new species was detected in both the emission lifetime and intensity experiments, and it is observed to be stable between pH 8 and 11. According to the hydration data, the new species is characterized as containing between 1.5 and 2.0 water molecules of hydration.

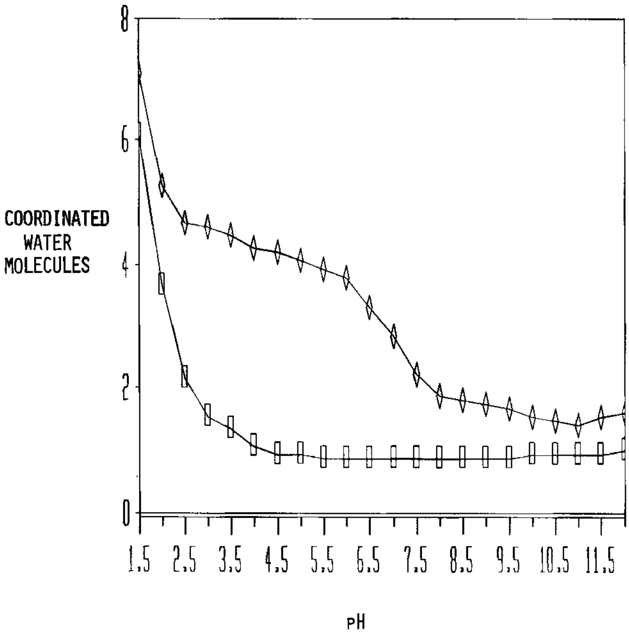

FIGURE 3 pH Dependence of the number of water molecules bound at the inner coordination sphere of Tb(III) in the Tb(NTA) {◇} and $Tb(NTA)_2$ {□} complexes.

Quite different behaviour was noted for the $Tb(NTA)_2$ complex. The initial decrease in water content was complete by pH 4.5, and the number of coordinated water molecules remained unchanged at 1 between pH 5 and 11. These data indicate the existence of 9-fold coordination in the $Tb(NTA)_2$ complex, with two tetradentate NTA ligands and one water of hydration being contained at the inner coordination sphere of the Tb(III) ion.

D. *pH Dependence of Ho(III) Hypersensitivity*

It is known that although the intensity of most lanthanide absorption bands are independent of the nature of the coordination sphere, certain bands exhibit absorptivities which are strongly dependent on the environment.[8] These are termed "hypersensititive" transitions, and are normally characterized by a change in the J quantum number of two. The $^5I_8 \rightarrow {}^5G_6$ transition of Ho(III) (located around 450 nm) is such a transition, and has been used in the past to obtain further characterization of lanthanide complexes in aqueous solution. Since the observed molar absorptivities are so small, the data are best displayed as the difference between the absorbance of the Ho(III) complex and the aquo-ion.

The pH dependence associated with the differential absorbance within the $^5I_8 \rightarrow {}^5G_6$ hypersensititive transition of Ho(III) in Ho(NTA) and $Ho(NTA)_2$ is illustrated in Figure 4. At very low pH values, the Ho(III) complexes are equally absorptive as the aquo-ion, but complexation with NTA ligands does lead to a modest enhancement of the absorption intensity. Both the Ho(NTA) and $Ho(NTA)_2$ complexes exhibit the same degree of absorption enhancement between pH 2.5 and 8, but important differences were noted above pH 8. The absorptivity of the Ho(NTA) complex was found to increase dramatically, while the absorbance of the $Ho(NTA)_2$ complex remained unchanged.

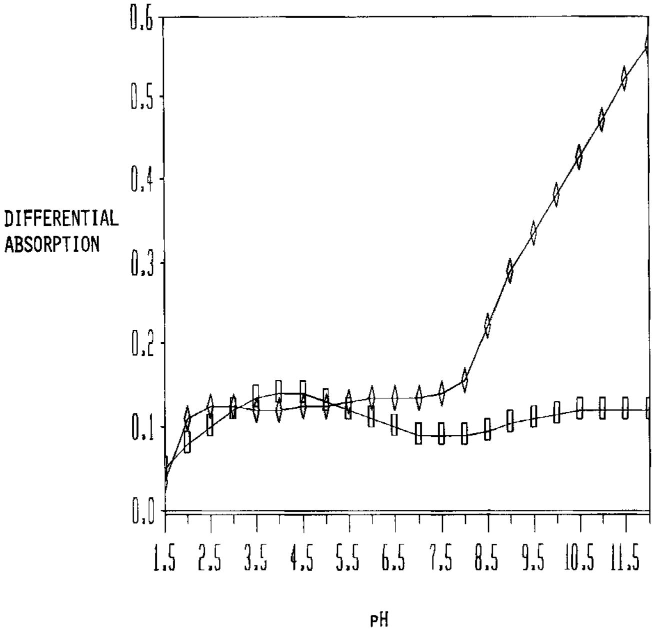

FIGURE 4 pH Dependence of Ho(III) differential absorption intensities, obtained for Ho(NTA) {◇} and $Ho(NTA)_2$ {□} complexes.

E. Energy Transfer Among Lanthanide NTA complexes

While the spectroscopic trends described thus far provide insight into the conditions under which Tb(NTA) and $Tb(NTA)_2$ complexes exist, full interpretation is not possible unless the oligomerization state of the complexes is determined. A method has been described in which intermolecular energy transfer among lanthanide complexes is used to analyze the possible self-association of the complexes.[5] The emission intensity and lifetime of a Tb(III) donor complex is monitored as a function of the concentration of added Eu(III) acceptor complex.

Luminescence quenching in fluid solution can proceed *via* two mechanisms, or some combination of these. In **dynamic quenching**, the energy transfer takes place as a result of collisons between the donor and quencher. This nonradiative transfer results in a concomitant decrease in emission intensity and shortening of the emission lifetime. An alternate mechanism is termed **static quenching**, and results when an actual complex is formed between the donor and quencher. Formation of a mixed Tb/Eu donor/acceptor species generates a non-emissive Tb(III) species, and thus the only observable emission parameters are associated with Tb/Tb or free Tb species. While static quenching results in a decrease in emission intensity (due to the removal of some emitting Tb species), the emission lifetime is unaffected (since the only species which are detectable are not quenched).

The intensity data are analyzed according to the Stern-Volmer equation, (*3*),

$$(I_o - I)/I = K_{sv}^{\varphi}\,[Q] \qquad (3)$$

where I_o is the Tb(III) emission intensity in the absence of Eu(III) quencher, I is the emission intensity obtained at a Eu(III) quencher concentration of [Q], and K_{sv}^{φ} is the Stern–Volmer quenching constant for intensity quenching. An analogous equation may be written for lifetime data, (*4*),

$$(\tau_o - \tau)/\tau = K_{sv}^{\tau}\,[Q] \qquad (4)$$

where τ_o is the Tb(III) emission lifetime in the absence of Eu(III) quencher, τ is the emission lifetime obtained at a Eu(III) quencher concentration of [Q], and K_{sv}^{τ} is the Stern–Volmer quenching constant for lifetime quenching.

If the complexes are purely monomeric in nature, then the energy transfer will take place by the collisional mechanism (dynamic quenching). In that case, the relationship between Stern–Volmer quenching constants will be as shown in (*5*)

$$K_{sv}^{\varphi} = K_{sv}^{\tau} \qquad (5)$$

When the complexes undergo self-association into oligomeric compounds, then the additional contribution from static quenching is observed. The situation usually results in the observation of extremely efficient energy transfer. When the energy transfer is characterized by either pure static or a combination of static and dynamic quenching, then (*6*) obtains.

$$K_{sv}^{\varphi} > K_{sv}^{\tau} \qquad (6)$$

When both static and dynamic mechanisms are possible, then the Stern–Volmer quenching kinetics are described[9] by (*7*).

$$(I_o - I)/I = (K_{sv}^{\tau} + K_c)\,[Q] + (K_{sv}^{\tau} * K_c)\,[Q]^2 \qquad (7)$$

The results of energy transfer studies performed on the Tb(NTA) complexes are collected in Table I, while analogous results obtained on the $Tb(NTA)_2$ complexes are given in Table II. The Tb(NTA) complexes were observed to be monomeric up to pH 6, but became heavily associated above this pH value. The existence of a fairly stable oligomeric species was noted between pH 8.5 and 10.5, characterized by a K_c value of approximately 2500. It is highly likely that the oligomeric species formed

TABLE I

Stern–Volmer quenching constants and intermolecular association constants for the Tb(NTA) complexes.

pH	K_{sv}^{φ}	K_{sv}^{τ}	K_c
1.5	225	220	4
2.0	315	300	12
2.5	350	325	19
3.0	425	400	18
3.5	450	425	18
4.0	555	525	20
4.5	630	610	12
5.0	880	700	106
5.5	1175	750	243
6.0	1500	800	389
6.5	1800	700	647
7.0	2410	650	1065
7.5	2760	625	1315
8.0	3525	600	1830
8.5	4055	550	2260
9.0	4215	500	2475
9.5	4180	450	2570
10.0	4200	400	2715
10.5	3995	425	2505
11.0	2955	450	1730
11.5	2230	475	1190
12.0	1890	500	927

TABLE II

Stern–Volmer quenching constants and intermolecular association constants for the $Tb(NTA)_2$ complexes.

pH	K_{sv}^{φ}	K_{sv}^{τ}	K_c
1.5	400	325	57
2.0	405	355	37
2.5	450	410	28
3.0	465	425	28
3.5	470	430	28
4.0	480	435	31
4.5	575	450	86
5.0	705	565	89
5.5	690	600	56
6.0	640	585	35
6.5	580	540	26
7.0	535	495	27
7.5	500	465	24
8.0	440	405	25
8.5	370	340	22
9.0	320	285	27
9.5	285	255	24
10.0	220	190	25
10.5	180	145	31
11.0	160	115	40
11.5	140	90	46
12.0	100	50	47

within this pH range represent hydroxy bridged dimer species, as has been noted by Martin and coworkers[10] during their titrations of lanthanide amino acid complexes.

On the other hand, the $Tb(NTA)_2$ complexes were found to be monomeric at all pH values, implying that hydroxy bridged dimers cannot form at the 1:2 metal-to-ligand ratio. An interesting feature was noted between pH 4 and 6, where a small degree of complex self-association was observed. Since it had been found with Tb(NTA) that the addition of the first NTA ligand was complete by pH 4, the feature observed for the $Tb(NTA)_2$ complex appears to be associated with the addition of the second NTA ligand. The data imply that the addition of the second NTA ligand is not as simple as the addition of the first NTA ligand, and a substantial pH increase is required to fully form the $Tb(NTA)_2$ complex.

CONCLUSIONS

When examined as a whole, the spectroscopic data provide a good description of the solution phase coordination chemistry of terbium complexes with tetradentate nitrilotriacetic acid. The 1:1 Tb(NTA) complex exists as a monomeric unit up to pH 6, with an average of 4.5 water molecules making up the remainder of the coordination sphere. This binding of a NTA ligand enhances the intensity and lifetime associated with Tb(III) luminescence (relative to the aquo-ion), and the hypersensititive absorptivity of the corresponding Ho(III) species. Above pH 6, the complexes become self-associated into oligomeric species, which probably are hydroxy bridged dimers. This process yields a modest increase in Tb(III) emission intensity, a doubling of the Tb(III) emission lifetime, and a major increase in Ho(III) hypersensitivity. The self-association constant of the oligomeric complexes is approximately 2500.

The 1:2 $Tb(NTA)_2$ complexes were found to be fully monomeric at all pH values, with only a single water molecule remaining in the Tb(III) inner coordination sphere. The $Tb(NTA)_2$ complex is fully formed by pH 4.5, with the Tb(III) emission lifetime and intensity, as well as Ho(III) hypersensitive absorption, being constant above this pH value. Although the complex is fully formed by pH 4.5, the energy transfer data do indicate that a small coordination sphere rearrangement takes place between pH 4 and 6.

These results imply that future investigations into the nature of 1:1 Ln(NTA) complexes above pH 6 must take the oligomerization of these complexes into consideration. Studies carried out on Ln(NTA) complexes below pH 6 can safely assume the existence of purely monomeric species. Studies on the nature of 1:2 $Tb(NTA)_2$ complexes can be carried out without consideration of the possible existence of polynuclear compounds.

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