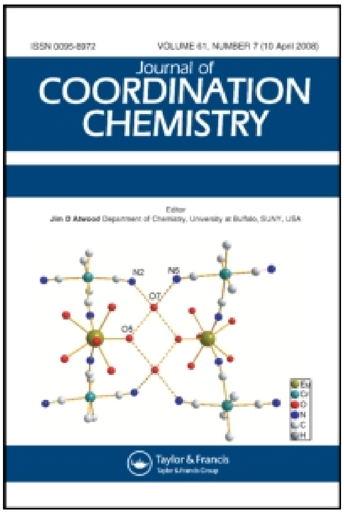

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INTERMOLECULAR ENERGY TRANSFER BETWEEN LANTHANIDE COMPLEXES. 10. Tb(III) DONOR AND Eu(III) ACCEPTOR COMPLEXES OF TRIETHYLENETETRAAMINEHEXAACETIC ACID

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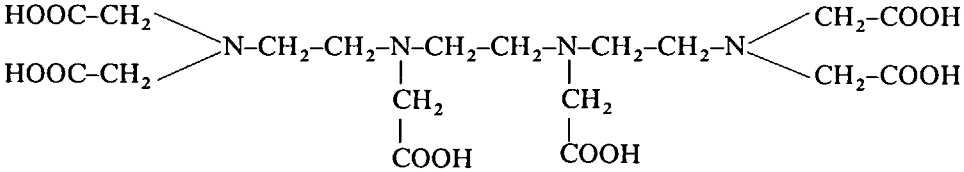
The solution phase coordination chemistry assoicated with the 1:1 complexes of lanthanide ions with triethylenetetraaminehexaacetic acid (TTHA) has been studied by spectroscopic means. It was found that in the pH region of 3 to 7.5, the partially protonated Ln(TTHA) complexes exist as oligomeric species. A well defined polynuclear species has been found to exist between pH 4 and 6, and this characterized by an association constant of 125. Between pH 6 and 8, the oligomeric species apparently dissociate, yielding monomeric lanthanide TTHA complexes above pH 8.

Keywords: Lanthanides, terbium, europium, multidentates, luminescence

INTRODUCTION

The solution phase coordination chemistry associated with lanthanide ion complexes of aminopolycarboxylic acids remains an important area of investigation. Triethylenetetraaminehexaacetic acid (TTHA) is a ligand of multiple denticity, containing six carboxylate and four amine binding sites.



$$\begin{array}{l}HOOC\text{-}CH_2\\HOOC\text{-}CH_2\end{array}\!>\!N\text{-}CH_2\text{-}CH_2\text{-}\underset{\substack{|\\CH_2\\|\\COOH}}{N}\text{-}CH_2\text{-}CH_2\text{-}\underset{\substack{|\\CH_2\\|\\COOH}}{N}\text{-}CH_2\text{-}CH_2\text{-}N\!<\!\begin{array}{l}CH_2\text{-}COOH\\CH_2\text{-}COOH\end{array}$$

The stabilities and thermodynamic properties of lanthanide complexes with TTHA have been studied by several groups,[1-5] since this ligand system has been proposed for a variety of analytical uses. Although slight differences in stability constants exist among the reported results, it is generally agreed that the association constant for 1:1 Ln(TTHA) complexes exceeds 10^{22}.

It is well established that the luminescence properties of lanthanide ions are extremely useful in deducing details of their solution phase coordination chemistry, and that studies on Tb(III) or Eu(III) complexes are most useful in this regard.[6] To clarify the nature of Ln(TTHA) coordination chemistry, detailed studies of the

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influence of solution pH on Tb(TTHA) luminescence intensities and lifetimes were carried out. The possible oligomerization of the complexes was also investigated using the energy transfer method.[7]

EXPERIMENTAL

Triethylenetetraaminehexaacetic acid was used as received from Aldrich Chemicals, while hydrated $TbCl_3$ or $EuCl_3$ were used as received from Research Chemicals. Stock solutions of these reagents were prepared by the dissolution of appropriate quantities of material, with the Ln(TTHA) complex solutions being prepared by mixing stoichiometric amounts of the stock solutions. For the luminescence experiments, a final Tb(TTHA) concentration of 10 mM was used. During the energy transfer studies, microlitre amounts of 50 mM Eu(TTHA) stock solutions were added to a Tb(TTHA) solution.

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 solution pH was effected by the addition of microlitre amounts of standardized NaOH or HCl directly to 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(TTHA) or Tb(TTHA)/Eu(TTHA) 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.

RESULTS

Using the potentiometric titration method, eight ligand pK_a values have been measured for TTHA: 1.5, 1.8, 2.2, 2.7, 4.1, 6.2, 9.5, and 10.5.[8] The large number of acid ionization processes, and the variety of pH values at which these take place, could certainly lead to variability in the binding of lanthanide ions by the TTHA ligand. The formation of the 1:1 Ln(TTHA) complex is known to be extremely efficient, with a log K_1 value of 23.08 being reported for the Tb(III) complex.[5]

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, and the luminescence lifetimes associated with them, were found to be a function of the solution pH. Variations in the photophysical properties are taken to be indicative of changes in coordination chemistry. Since it was noted that the trends associated with the pH dependence of each emission band system were identical, the results obtained within the ${}^5D_4 \rightarrow {}^7F_5$ transition will be taken as indicative of the overall luminescence phenomena.

The pH dependence associated with the Tb(III) emission intensity and lifetime in the Tb(TTHA) complex is shown in Figure 1. Both sets of parameters are essentially similar, and appear to indicate the existence of three diameter pH regions. In the first of these, both parameters increase linearly between pH 2 and 4. Between pH 4 and 8 another linear region is noted, but the rate of increase in either intensity of lifetime is less than that noted between pH 2 and 4. The final region exists between pH 8 and 11, where no change in either emission intensity or lifetime is observed.

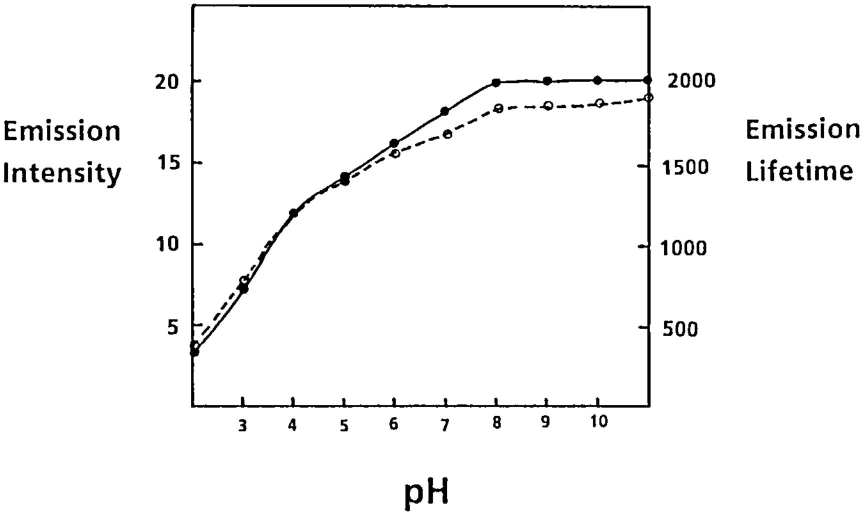

FIGURE 1 pH Dependence of Tb(III) luminescence intensities (solid trace, closed circles) and luminescence lifetimes (dashed trace, open circles) obtained for Tb(TTHA) complexes as a function of pH. The intensity data are shown in arbitrary units, while the lifetime data are shown in units of microseconds.

Although the spectroscopic trends provide insight into the coordination chemistry of Tb(TTHA), full interpretation is not possible unless the oligomerization state of the complex is determined. A method has been described in which intramolecular energy transfer among lanthanide complexes is used to analyze the possible self-association of the complexes.[7] In this method, 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, and the quenching data used to deduce the energy transfer mechanism.

Luminescence quenching in fluid solution can proceed *via* two mechanisms, or some combination of these. With dynamic quenching, the energy transfer takes place as a result of collision of donor and quencher. This non-radiative transfer results in a concomitant decrease in emission intensity and shortening of the emission lifetime. When the donor and quencher form an associated species, static quenching is observed. In static quenching, the donor emission intensity is found to decrease, while the emission lifetime is unaffected. Static quenching is normally much more effective in the deactivation of the donor species than is dynamic quenching.

The intensity data are analyzed according to the Stern–Volmer equation, (*1*),

$$(I_0 - I)/I = K_{sv}^{\Phi}[Q] \qquad (1)$$

where I_0 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], andK_{sv}^{Φ} is the Stern–Volmer quenching constant for intensity quenching. An analogous equation may be written for lifetime data as shown in (*2*),

$$(\tau_o - \tau)/\tau = K_{sv}{}^{\tau}[Q] \tag{2}$$

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 $K_{sv}{}^{\tau}$ 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 collision mechanism (dynamic quenching). In that case, the relationship between Stern–Volmer quenching constants will be that shown in (*3*).

$$K_{sv}{}^{\Phi} = K_{sv}{}^{\tau} \tag{3}$$

When the complexes undergo self-association to form oligomeric compounds, additional contribution from static quenching is observed. When the energy transfer is characterized by either pure static or a combination of static and dynamic quenching, then equation (*4*) holds

$$K_{sv}{}^{\Phi} > K_{sv}{}^{\tau} \tag{4}$$

When both static and dynamic mechanisms are possible, then the Stern–Volmer quenching kinetics are described[9] by (*5*).

$$(I_o - I)/I = (K_{sv}{}^{\tau} + K_c)[Q] + (K_{sv}{}^{\tau} * K_c)[Q]^2 \tag{5}$$

The results of energy transfer studies performed on the Tb(TTHA) complexes are collected in Table I. The data indicate that the Tb(TTHA) complexes are extensively associated below pH 8, but that monomeric species are formed above this pH. The existence of a stable oligomeric species was noted between pH 3.5 and 6.0, characterized by a K_c value of approximately 125. The pH ranges of these three oligomerization regions correspond quite well, with distinct pH ranges noted for the luminescence intensity and lifetime data.

TABLE I

pH Dependence of the Stern–Volmer quenching constants and computed donor/acceptor association constants.

pH	$K_{sv}{}^{\Phi}$	$K_{sv}{}^{\tau}$	K_c
2	684	138	229
3	490	136	150
4	398	117	130
5	382	121	118
6	375	107	130
7	250	116	62
8	115	112	3.4
9	129	121	3.6
10	119	109	4.8
11	114	107	3.4

DISCUSSION

It has been shown that the carboxylate groups located at the centre of TTHA remain protonated at significantly higher pH values when compared to the four terminal carboxylate groups.[8,10] It is therefore quite likely that as long as the ligand is partially deprotonated, the only available metal ion binding sites are at the terminal iminodiacetate groups. In that case, the oligomeric species formed within this pH range would represent the bridging of metal centres by opposite ends of the TTHA ligands. A similar conclusion was reached when considering the low pH oligomerization of the lanthanide complexes of (*S*,*S*)-ethylenediamine-*N*,*N*′-disuccinic acid.[11] This type of low pH oligomerization is distinctly different from the high pH oligomerization noted for simple aminopolycarboxylate complexes, which apparently involves formation of μ-hydroxy-bridged species.[12,13]

The existence of protonated lanthanide TTHA complexes has been demonstrated,[3-5] and it was concluded that these protonated species could be polynuclear in nature. The extreme length of the TTHA ligand backbone ensures that these sites remain independent, and thus promotes the formation of oligomeric species. The existence of such oligomer species has been demonstrated in the solid state.[14] Deprotonation of the central carboxylate groups (a process which begins at neutral pH values) apparently favours the formation of monomeric species, which become fully formed at pH 8.

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