Inorg. Chem. **2006**, *45*, 8026–8035

Inorganic Chemistry
Article

Coordination Modes in the Formation of the Ternary Am(III), Cm(III), and Eu(III) Complexes with EDTA and NTA: TRLFS, ^{13}C NMR, EXAFS, and Thermodynamics of the Complexation

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Received December 20, 2005

The formation and the structure of the ternary complexes of trivalent Am, Cm, and Eu with mixtures of EDTA+NTA (ethylenediamine tetraacetate and nitrilotriacetate) have been studied by time-resolved laser fluorescence spectroscopy, ^{13}C NMR, extended X-ray absorption fine structure, and two-phase metal ion equilibrium distribution at 6.60 m ($NaClO_4$) and a hydrogen ion concentration value (pcH) between 3.60 and 11.50. In the ternary complexes, EDTA binds via four carboxylates and two nitrogens, while the binding of the NTA varies with the hydrogen ion concentration, pcH, and the concentration ratios of the metal ion and the ligand. When the concentration ratios of the metal to ligand is low (1:1:1–1:1:2), two ternary complexes, $M(EDTA)(NTAH)^{3-}$ and $M(EDTA)(NTA)^{4-}$, are formed at pcH ca. 9.00 in which NTA binds via three carboxylates, via two carboxylates and one nitrogen, or via two carboxylates and a H_2O. At higher ratios (1:1:20 and 1:10:10) and pcH's of ca. 9.00 and 11.50, one ternary complex, $M(EDTA)(NTA)^{4-}$, is formed in which NTA binds via three carboxylates and not via nitrogen. The two-phase equilibrium distribution studies at tracer concentrations of Am, Cm, and Eu have also confirmed the formation of the ternary complex $M(EDTA)(NTA)^{4-}$ at temperatures between 0 and 60 °C. The stability constants (log β_{111}) for these metal ions increase with increasing temperature. The endothermic enthalpy and positive entropy indicated a significant effect of cation dehydration in the formation of the ternary complexes at high ionic strength.

Introduction

It is well established that the aminopolycarboxylate ligands ethylenendiamine tetraacetate (EDTA) and nitrilotriacetate (NTA) form strong aqueous complexes with trivalent actinides (Am^{3+} and Cm^{3+}) and lanthanides (Eu^{3+}).[1] These metal cations usually have a total coordination number, CN_T of 9.0 in the formation of the 1:1 complex $M(EDTA)^-$; six from EDTA (four carboxylates, two nitrogens) binding and three from waters of hydration.[2] Addition of a secondary ligand results in the formation of a ternary complex with displacement of the three waters of hydration. This complex has a high stability constant and is more resistant to hydrolysis than the binary complex. There are many reports on the formation of the ternary complexes of $Ln(EDTA)^-$ with ligands such as acetate (Ac), oxalate (Ox), diglycolate (Dgl), iminodiacetate (IDA), 8-hydroxyquilnoline-5-sulfonate (HQS), NTA, etc.[3−7] Studies of the formation of ternary complexes of actinides are relatively few. Those investigated include $UO_2(NTA)^-$ and $Th(NTA)^+$ with dicarboxylates,[8] $Th(EDTA)^0$ and $Th(CDTA)^0$ (CDTA = 1,2-cyclohexanedinitrilotetraacetate) with IDA, HQS, and salicylate (SA) etc.,[9,10] $Pu(HEDTA)^0$ (HEDTA = *N*-hydroxyethylethylene-

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10.1021/ic052166c CCC: $33.50

diaminetriacetate) or Pu(EDTA)$^-$ with NTA, IDA or Gly (glycinate),[11] and Pu(EDTA)^0 with Cit (citrate) and CO_3^{2-} (carbonate).[12] These studies reflect the importance of size of metal cations, ligand basicity, steric requirements of the ligands, and some specific metal to secondary ligand interactions on the formation of the ternary complexes. Further, most of these studies measured only the stability constant values for the formation of the ternary complex at $I \leq 1.0$ M. Little thermodynamic data and information on the coordination modes in the formation of the ternary complexes have been provided.

Safe disposal of nuclear waste has required study of the complexation of the actinides at high ionic strength and temperatures. Such data are useful to better understand some problems of the nuclear waste and can also improve the fundamental understanding of the coordination chemistry of the actinides. The organic ligands, i.e., EDTA, NTA, etc., which are present in nuclear waste (from reprocessing of the spent fuel) increase the solubility of the actinides on complexation.[13] Considering the high stability constants of the ternary complex of actinides and lanthanides, it is likely that the actinides in the waste solution may be present as ternary species. If this is correct, a more complete understanding of the effects of organic ligands on the solubility and aqueous speciation, including identification of ternary complexes and of mixed hydroxo-ternary complexes of the trivalent actinides at high ionic strength and temperatures would be valuable for establishing effective strategies for waste processing.

The present work describes the complexation thermodynamics and the coordination modes in the formation of the binary and the ternary complexes of Am^{3+}, Cm^{3+}, and Eu^{3+} with EDTA and NTA at $I = 6.60$ m ($NaClO_4$) and temperatures of 0−60 °C. Spectral studies (e.g., time-resolved laser fluorescence spectroscopy (TRLFS)) of Eu^{3+}, a chemical analogue of trivalent actinides, and ^{13}C NMR spectra of solutions of La^{3+}/Y^{3+} also the actinides analogues were used to gain understanding of hydration state and the binding and structural aspects of these ternary complexes. Extended X-ray absorption fine structure (EXAFS) studies were used to determine the binding modes of EDTA and NTA in the ternary complex.

Experimental Section

All chemicals used were reagent grade, and distilled deionized water (E-pure, Barnstead) was used for solution preparation. Sodium perchlorate (>98%, Sigma-Aldrich, ACS certified) solutions were prepared and filtered through 0.45 μm membrane. The solutions of EDTA (ACS certified Fisher Scientific) and NTA (Fluka) were prepared at a concentration of 6.60 m ($NaClO_4$) and standardized by potentiometric titration with standard carbonate free NaOH. $Eu(ClO_4)_3$, $La(ClO_4)_3$, and $Y(ClO_4)_3$ solutions were prepared from the oxides (99.99%, Aldrich) in perchloric acid (60%, Fisher Scientific) followed by dilution. The concentration of these solutions was estimated by complexometric titration with EDTA.[14] Di-(2-ethylhexyl) phosphoric acid, (D2EHPA, Sigma-Aldrich) and heptane (Fisher Scientific, ACS) were used as received.

The radioactive tracers ^{241}Am, ^{244}Cm, and ^{152,154}Eu (Oak Ridge National Laboratory) were purified and their purity checked by α- and/or γ-spectrometry. The working stock of each tracer was prepared in a solution of pH = 3.0 ($HClO_4$) with a concentration of ca. 50 000 cpm per 10.0 μL. The activities of ^{241}Am, ^{244}Cm, and ^{152,154}Eu were measured in a Beckman liquid scintillation counter using Ecolite cocktail (ICN, Research Product Division).

An Accumet 950 (Fisher Scientific) pH meter was used with glass electrode (corning semi-micro combination) to measure pH values. The KCl solution of the electrode was replaced with saturated NaCl solution to avoid the erratic readings by the pH meter due to the low solubility of $KClO_4$ at high ionic strengths. The electrode was calibrated with 4.00 ± 0.01 and 7.00 ± 0.01 standard pH buffers. The pH meter readings (pHr) were converted to hydrogen ion concentration values (pcH's) using calibration curves obtained from a series of $HClO_4$ and NaOH solutions of known [H^+] in $I = 6.60$ m ($NaClO_4$) and $T = 0-60$ °C. The correlation equations for pHr and pcH at $I = 6.60$ m ($NaClO_4$) and $T = 0-60$ °C are given in the Supporting Information.

TRLFS. Solutions were prepared at varying Eu^{3+}-to-NTA and -EDTA ratios (Eu/NTA, 1:1−1:50; Eu/EDTA, 1:1−1:10; and Eu/EDTA/NTA, 1:1:1−1:1:20 and 1:10:10) and pcH in the range of 3.60−11.50. The Eu^{3+} concentration was ca. 1×10^{-4} M in all solutions. The $^7F_0 \rightarrow {}^5D_0$ excitation spectra were recorded by scanning the tunable dye laser stepwise at regular wavenumber intervals through the absorption band 577.7−580.7 nm while monitoring the emission at 616 nm. The luminescence decay curves were acquired by exciting at the peak of the $^7F_0 \rightarrow {}^5D_0$ transition and monitoring the luminescence intensity at 616 nm. Experiments were conducted at room temperature in a quartz cell of 1.00 cm path length. The calculation $CN_C = 0.237\Delta\nu + 0.628$,[15] where $\Delta\nu$ is the shift of the spectral peak of $Eu^{3+}_{(aq)}$ upon complexation, was used to obtain the coordination number, CN_C, of the complex. The number of water molecules associated with the complex, N_{H2O} were calculated by the equation $N_{H2O} = 1.05K_{obs} - 0.70$,[16] where K_{obs} is the luminescence decay constant obtained by fitting the observed decay curves to an exponential function. N_{H2O} values have an uncertainty of ±0.5 in these experiments.[17] Spectral deconvolution of the overlapping peaks was done with Labspec software using Lorentzian + Gaussian shaped analysis.

^{13}C NMR. All the sample solutions were prepared in D_2O by adding required amounts of NaOD or DCl to EDTA, NTA, or their mixtures. The solutions were mixed thoroughly, and the required amounts of $La(ClO_4)_3$ or $Y(ClO_4)_3$ were added. The [La^{3+}] and [Y^{3+}] were fixed at 0.025 and 0.066 M, respectively. The spectra were recorded for (1) NTA at pcH 3.60 and 9.82 and (2) EDTA at pcH 3.60 and 9.63. For the binary system, spectral measurements were done for (1) La/NTA of 1:1 at pcH = 3.66; Y/NTA of 1:1 at pcH = 9.32; and La/NTA of 1:2 at pcH = 9.44 and (2) La- or Y/EDTA of 1:1 at pcH = 9.30. For the ternary systems, spectra were recorded for La- or Y/EDTA/NTA ratios of 1:1:1 at pcH's of ∼9.64 and 11.12. The values reported are direct pH-meter reading,

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and no corrections for D_2O were made. The spectra were measured at room temperature using a Bruker 300 spectrometer at 75 MHz, with a deviation of ±0.1 ppm. All chemical shifts values were reported with respect to sodium trimethylsilanolate, $\delta = 0.00$ ppm.

EXAFS. A concentration of 0.015 M of Eu(III) was used in all the solutions. The solutions of Eu/NTA 1:2 at pcH = 9.00 and Eu/EDTA 1:1 at pcH = 6.00 were used as the standards, as the complex species formed under these conditions would be $Eu(NTA)_2(H_2O)^{3-}$ and $Eu(EDTA)(H_2O)_3^{-}$. The other solutions prepared were Eu/EDTA of 1:10 at pcH = 11.50; Eu/EDTA/NTA of 1:1:2 at pcH's of 9.00 and 11.50; and Eu/EDTA/NTA of 1:10:10 at pcH = 11.50. EXAFS analysis to determine the association of europium with the complexants EDTA and NTA was performed at the Eu L_{III} absorption edge (6.977 keV) on beamline ×10C at the National Synchrotron Light Source (NSLS) (Brookhaven National Laboratory) with a Si (220) double flat crystal monochromator. The line width of the monochromator at this energy range (8 keV) is ca. 0.3 eV with a focusing/cutoff mirror placed after the monochromator to prevent second and third harmonic interference. The aqueous sample was placed in heat-sealed polypropylene bags and mounted on an Al sample holder having a geometry of 2 mm × 20 mm with a 1.5 mm thickness. Fluorescence data were collected using a 13-element Ge detector. The absorption edge energy was calibrated using the first inflection point of an Fe foil (7.112 keV). The EXAFS data were processed using the program Ifeffit.[18] The theoretical EXAFS modeling code FEFF6 was used to calculate the backscattering phase and amplitude information for individual neighboring atoms.[19] The phase and amplitude functions were determined using the crystal structure for europium teraphthalate.[20] A single-shell scattering path for Eu−N was included in the fitting. Four scans were collected per sample, and the data were averaged. The amplitude reduction factor (S_0^2) was fixed at 0.9 for all the fits. Fitting parameters for the samples were obtained by comparison with the standards.

Metal Ion Distribution Measurements. Distribution of the metal ions (Am^{3+}, Cm^{3+}, and Eu^{3+}) between the aqueous phase containing NTA alone or mixtures of EDTA+NTA in 6.60 m ($NaClO_4$) and the organic phase containing D2EHPA in heptane (2×10^{-4} M for Eu^{3+} and 5×10^{-4} M for Am^{3+} and Cm^{3+}) at pcH of 3.60 ± 0.02 were determined in duplicate in the temperature range of 0−60 ± 0.1 °C by measuring the concentration of ^{241}Am, ^{244}Cm, and ^{152,154}Eu radiometrically in both the phases at equilibrium. The metal ion distribution ratios, D, $(=[M]_{total,org}/[M]_{total,aq})$ defined as the ratio of the total concentrations of the metal ions in an organic and an aqueous phase. The organic phase was pre-equilibrated with $NaClO_4$ to ensure that the pcH's of the solutions were constant during the extraction experiments.

For experiments with NTA alone, its concentrations was varied between 1×10^{-4} and 5×10^{-4} M, whereas with mixtures of EDTA+NTA, the concentration of EDTA was fixed at 5×10^{-6} M, and NTA was varied between 1×10^{-4} and 7×10^{-4} M. Five milliliters each of aqueous phase (containing one of the radioactive metal tracers) without or with the ligands and the pre-equilibrated D2EHPA/heptane solution were placed in a 20 mL liquid scintillation vial. Details of the equilibrium experiments, counting procedure, measurement of equilibrium pHr, and the conversion of pHr to pcH at $I = 6.60$ m ($NaClO_4$) and at the four temperatures are described in the Supporting Information.

The stability constants of the complexes $M(NTA)^0$ (β_{101}) and $M(EDTA)(NTA)^{4-}$(β_{111}) were evaluated using the correlations:

$$D_0/D\text{-}1 = \beta_{101}[NTA^{3-}] \qquad (1)$$

$$D_1/D\text{-}1 = \beta_{111}[EDTA^{4-}][NTA^{3-}]/(1 + \beta_{101}[EDTA^{4-}]) \qquad (2)$$

where D_0 and D_1 are the distribution ratios of metal ions in the absence and the presence of EDTA, respectively. The detail derivations of these equations are included in the Supporting Information.

To compare the results at different temperatures, the stability constant values calculated in molarity (M) scale were converted to molality (m) scale according to the correlation:[21]

$$\log \beta_m = \log \beta_M + \Sigma_r \nu_r \log \theta \qquad (3)$$

where (β_M) and (β_m) are the stability constants in molarity and molality, respectively. θ is the ratio of the values of molality to molarity for the specific ionic medium, and $\Sigma_r \nu_r$ is the stoichiometric coefficient of the reactions $M^{3+} + NTA^{3-} \Leftrightarrow M(NTA)^0$ and $M^{3+} + EDTA^{4-} + NTA^{3-} \Leftrightarrow M(EDTA)(NTA)^{4-}$ (ν_r is positive for the products and negative for the reactants), which gives a value of $\Sigma_r \nu_r$ of −1 for the former and of −2 for the latter reactions. Density data of 6.60 m ($NaClO_4$) at four temperatures were taken from ref 22.

Potentiometric Titration. The protonation constants of EDTA and NTA in aqueous solutions of $I = 6.60$ m ($NaClO_4$) and at different temperatures were calculated from the potentiometric titration data obtained at 0−60 °C. The ligand solutions of EDTA or NTA (15 mL, 0.003 M for NTA and 0.001 M for EDTA in 6.60 m ($NaClO_4$)) were titrated automatically in a titration cup by an incremental addition of standardized 0.1000 M NaOH at the same ionic strength from the buret. The desired temperatures were maintained by the water circulation from a constant-temperature bath. To avoid water condensation underneath the lid at higher temperatures (45 and 60 °C), both the titration cup and the lid were water-jacketed. The experimental details have been described previously.[23] The PSEQUAD[24] program has been used to evaluate the pK_a values from the titration curve. The pK_a values of NTA and EDTA at $I = 6.60$ m ($NaClO_4$) and $T = 0{-}60$ °C are listed in Table 1.

Results and Discussion

TRLFS. The $^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu^{3+} at various metal-to-ligand concentration ratios and pcH are shown in Figure 1, and the peak positions, luminescence lifetimes and the calculated N_{H2O} values of the species are listed in Table 2. The spectral peak of Eu^{3+}(0.01 M) in 6.60 m ($NaClO_4$) had the same position as that observed in $I = 0.1$ m ($NaClO_4$) with a lifetime of 116 ± 3 μs and N_{H2O} =

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Table 1. Protonation Constants of NTA and EDTA at $I = 6.60$ m ($NaClO_4$); $T = 0-60$ °C

	temp (°C)	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}
NTA	0	2.07 ± 0.12	2.63 ± 0.09	9.01 ± 0.01	
	25	2.14 ± 0.09	2.71 ± 0.08	9.56 ± 0.01	
	45	2.18 ± 0.11	2.78 ± 0.05	9.68 ± 0.01	
	60	2.21 ± 0.12	2.82 ± 0.09	9.91 ± 0.01	
EDTA	0	2.18 ± 0.05	2.54 ± 0.04	6.82 ± 0.04	8.92 ± 0.07
	25	2.25 ± 0.12	2.64 ± 0.07	7.18 ± 0.05	9.26 ± 0.04
	45	2.28 ± 0.08	2.68 ± 0.06	7.51 ± 0.03	9.54 ± 0.04
	60	2.30 ± 0.10	2.72 ± 0.05	7.68 ± 0.08	10.06 ± 0.09

8.4, indicating that there is no effect of ionic medium on the $^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu^{3+}. This is consistent with previous report[25] in which no significant change in the $^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu^{3+} were observed in solutions of ca. 10 M $HClO_4$ and $NaClO_4$; however, above that concentration, a variation in the spectral pattern was observed.

At Eu/NTA of 1:1 and pcH 3.60, a peak at 579.37 nm with lifetime of 209 ± 5 μs and $N_{H2O} = 4.3$ indicates the formation of the 1:1 complex. At a higher ratio of 1:50 and pcH = 5.00−9.00, a sharp peak at 580.08 nm with a lifetime of 790 ± 15 μs and $N_{H2O} = 0.6$ reflects the formation of the 1:2 complex. The N_{H2O} values of 6.0 and 5.0 and 4.4 and 5.0 have been reported previously for the $Eu(NTA)^0$ and $Tb(NTA)^0$ complexes, respectively.[17,26] The lower N_{H2O} value of 4.3 in the present study is attributed to the change in the hydration number from 5 to 4 observed across the series for the $Ln(NTA)^0$ complex.[27] For $Eu(NTA)_2{}^{3-}$, the N_{H2O} values reported are in the range 1.0−1.3,[26] which is consistent with the tetradentate coordination of NTA. The X-ray crystal structure of $Sm(NTA)_2{}^{3-}$ also indicated the presence of one water molecule in the inner coordination shell of Sm^{3+}.[28] The formation of hydroxyl species was not observed in the present study; however, the formation of such species has been reported in highly basic solutions (0.05−0.10 M NaOH).[29]

The excitation spectra of the Eu/EDTA system at a ratio of 1:1 and pcH of 3.60−8.00 and at a concentration ratio of 1:10 and pcH = 3.60 showed two peaks at 579.64 and 580.18 nm with an average lifetime of 318 ± 13 μs and $N_{H2O} = 2.6$, which is consistent with the formation of the complex $Eu(EDTA)(H_2O)_3{}^-$.[22] The observance of two peaks for the Eu/EDTA complex is consistent with the measurement of Latva et al.[30] and is indicative of two different $Eu(EDTA)^-$ complexes, i.e., $Eu(EDTA)(H_2O)_3{}^-$, CN = 9.0; $Eu(EDTA)(H_2O)_2{}^-$, CN = 8.0. Since our studies cover the pcH range 3.60−11.50, the formation of a protonated complex of EDTA was not observed. However, the formation of protonated complex, $Eu(EDTAH)^0$, with a lifetime of 160 μs, has been reported at pcH $\leq$ 1.50.[20] At a higher pcH value of 9.00, formation of the hydroxyl species $Eu(OH)(EDTA)(H_2O)_2{}^{2-}$ with a longer lifetime was obtained.[22]

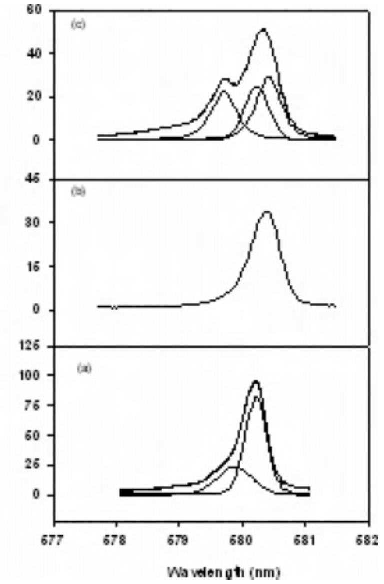

Figure 1. $^7F_0 \rightarrow {}_5D°$ excitation spectra of Eu(III) complexes with EDTA+NTA, $[Eu^{3+}] = 1 \times 10^{-4}$ M, $I = 6.60$ m ($NaClO_4$), Eu/EDTA/NTA, (a)1:10:10, pcH = 8.99; (b) 1:1:20, pcH = 9.03; and (c) 1:1:1, pcH = 8.99.

At Eu/EDTA of 1:10 and pcH = 6.85, in addition to the peaks at 579.66 and 580.11 nm, a new peak at 580.21 nm was observed with an average lifetime of 500 ± 7 μs and $N_{H2O} = 1.4$. The increased lifetime and decreased value of N_{H2O} indicates the formation of the 1:2 complex. The speciation calculations using the protonation constants of EDTA shows that $EDTAH^{3-}$ is a dominant species up to pcH $\approx$ 8.00. The complex most likely form at pcH 6.85 would be $Eu(EDTA)(EDTAH)(H_2O),^{4-}$ in which a second EDTA molecule binds via smaller number of coordination sites. On increasing the pcH from 6.85 to 8.99, the peak at 580.11 nm became a major peak and that at 579.66 nm was present as a shoulder. The lifetime of 576 ± 10 μs and $N_{H2O} = 1.1$ at 579.66 nm, and 665 ± 12 μs and $N_{H2O} = 0.8$ at 580.11 nm is consistent with the presence of two different species. With increased pcH from 6.65 to 8.99, the concentration of $EDTA^{4-}$ in solutions also increases and the complex $Eu(EDTA)_2(H_2O)^{5-}$ become dominant. The shoulder peak is due to the presence of small percentage of the complex $Eu(EDTA)(EDTAH)(H_2O)^{4-}$ (Supporting Information, Figure S1).

The excitation spectra of the Eu/EDTA/NTA system at concentration ratios of 1:1:1−1:1:2, had two peaks at 579.66 and 580.18 nm in the pcH range 3.60−5.00. The average lifetime of 291 ± 13 μs and of $N_{H2O} = 2.9$ are the same values as measured for $Eu(EDTA)(H_2O)_3{}^-$, indicating no formation of a ternary complex. On increasing the pcH of the solution to 7.03, the lifetime and N_{H2O} of the peak at 579.66 nm remain the same, while that at 580.18 nm increases to 422 ± 12 μs and the value of N_{H2O} decreases to 1.8. The increased lifetime and decreased value of N_{H2O}

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Table 2. Spectral Characteristics of Eu^{3+} Complexes with NTA, EDTA, and EDTA+NTA at $I = 6.60$ m ($NaClO_4$)

Eu/EDTA/NTA	species	pcH	peak positions (nm)	lifetime (μs)	N_{H2O}
1:0:0	Eu^{3+} (aq)	2.20	578.90	116 ± 3	8.4
1:0:1	$Eu(NTA)(H_2O)_5$	3.60	579.37	209 ± 5	4.3
1:0:50	$Eu(NTA)_2(H_2O)^{3-}$	5.00−9.00	580.08	790 ± 15	0.6
1:1:0	$Eu(EDTA)(H_2O)_3^{-}$	3.60−8.00	579.64, 580.18	318 ± 13	2.6
1:10:0	$Eu(EDTA)(H_2O)_3^{-}$	3.60	579.64, 580.18	318 ± 13	2.6
1:1:0	$Eu(EDTA)(OH)(H_2O)_2^{2-}$	9.00	579.64, 580.11	458 ± 6	1.7
1:10:0	$Eu(EDTA)(EDTAH)(H_2O)^{4-}$	6.85	579.66, 580.11 580.21	500 ± 7	1.4
1:10:0	$Eu(EDTA)(EDTAH)(H_2O)^{4-}$	8.99	579.66	576 ± 10	1.1
	$Eu(EDTA)_2(H_2O)^{5-}$		580.11	665 ± 12	0.8
1:1:1−1:1:2	$Eu(EDTA)(H_2O)_3^{-}$	3.60−5.00	579.66, 580.18	291 ± 13	2.9
1:1:2	$Eu(EDTA)(H_2O)_3^{-}$	7.03	579.66	300 ± 10	2.8
	$Eu(EDTA)(NTAH) (H_2O)^{3-}$		580.18	422 ± 12	1.8
1:1:2	$Eu(EDTA)(NTAH) (H_2O)^{3-}$	8.99	579.66	488 ± 15	1.4
	$Eu(EDTA)(NTA)^{4-}$/ $Eu(NTA)_2(H_2O)^{3-}$		580.21, 580.08	729 ± 17	0.7
1:1:2	$Eu(EDTA)(NTA)^{4-}$	11.50	580.21, 579.95	961 ± 11	0.4
			∼578.80	−	−
1:1:20	$Eu(EDTA)(NTAH)(H_2O)^{3-}$	7.40	579.66	422 ± 12	1.8
	$Eu(NTA)_2(H_2O)^{3-}$		580.16	781 ± 12	0.6
1:1:20	$Eu(EDTA)(NTA)^{4-}$	9.03	580.18	961 ± 12	0.4
1:1:20	$Eu(EDTA)(NTA)^{4-}$	11.50	580.21	1050 ± 12	0.3
			∼578.80	−	−
1:10:10	$Eu(EDTA)(H_2O)_3^{-}$	3.60−4.77	579.66, 580.16	331 ± 14	2.5
1:10:10	$Eu(EDTA)(EDTAH)(H_2O)^{4-}$	7.40	579.64	540 ± 12	1.2
	$Eu(EDTA)(NTA)^{4-}$/ $Eu(NTA)_2(H_2O)^{3-}$		580.08, 580.18	725 ± 12	0.7
1:10:10	$Eu(EDTA)(NTA)^{4-}$	8.99	579.93, 580.21	990 ± 30	0.3
1:10:10	$Eu(EDTA)(NTA)^{4-}$	11.50	580.21	983 ± 12	0.4
			∼578.80	−	−

indicates the beginning of formation of a ternary complex at pcH ca. 7.00. On further increasing the pcH to 8.99, the two peaks had the same position, but the intensity of the peak at 580.18 nm increases and that at 579.66 nm decreases. This on deconvolution resolved into three peaks at 580.21, 580.08, and 579.66 nm, indicating the presence of three different species. The peak at 580.08 nm corresponds to the formation of the complex $Eu(NTA)_2^{3-}$, while those at 580.21 and 579.66 nm are due to the formation of ternary complexes. Considering $CN_T = 9.0$ for Eu^{3+}, we assign the species at 579.66 nm with lifetime of 488 ± 15 μs and $N_{H2O} = 1.4$ as due to the ternary complex $Eu(EDTA)(NTAH)(H_2O)^{3-}$ and the peak at 580.21 nm as due to the formation of ternary complex $Eu(EDTA)(NTA)(H_2O)^{4-}$. The same average lifetime of 729 ± 17 μs and $N_{H2O} = 0.7$ for the peaks at 580.08 and 580.21 nm indicates that the ternary complex $Eu(EDTA)(NTA)(H_2O)^{4-}$ is in equilibrium with the binary $Eu(NTA)_2(H_2O)^{3-}$ complex. This is consistent with the previous reports on the formation the ternary complexes of lanthanides with EDTA+NTA by potentiometric titration, ^{1}H NMR, and absorption spectral methods.[3−7] At pcH = 11.50, the peak at 580.18 nm became a major peak and a new broad peak appeared at ∼578.80 nm. This on deconvolution resolved into three peaks at 580.21, 579.95, and 578.80 nm. The average lifetime of 961 ± 11 μs and $N_{H2O} = 0.4$ for the peaks at 580.21 and 579.95 nm, indicates that the ternary complexes $Eu(EDTA)(NTAH)^{3-}$ and $Eu(EDTA)(NTA)^{4-}$ are in fast equilibrium. The third peak at 578.80 nm is due to the complexation of EDTA and NTA with surface Eu(III) sites of the colloidal nanoparticles. In highly basic solutions and in the presence of strong complexing agent, the formation of such complexes have been reported previously for Eu(III) and Cm(III) by TRLFS.[29]

At Eu/EDTA/NTA of 1:1:20 and pcH = 7.40, two peaks at 579.66 and 580.16 nm were present. The lifetime and N_{H2O} value at 580.16 nm correspond to the formation of the complex $Eu(NTA)_2(H_2O)^{3-}$, while that at 579.66 nm is consistent with the formation of the ternary complex $Eu(EDTA)(NTAH)(H_2O)^{3-}$ (Table 2). The spectroscopic study of Tananaeva et al.,[7] also reported the existence of a 1:2 complex of NTA plus a ternary complex at Nd/EDTA/NTA ratios of 1:1:10−1:1:50. At pcH 9.03, a sharp peak at 580.18 nm (Supporting Information, Figure S2) with a lifetime of 961 ± 12 μs and N_{H2O} of 0.4 is due to the formation of a ternary complex $Eu(EDTA)(NTA).^{4-}$ On further raising pcH to 11.50, a sharp peak at 580.21 nm with lifetime of 1050 ± 12 μs and N_{H2O} value of 0.3, indicating the predominance of a ternary complex $Eu(EDTA)(NTA)^{4-}$ (Supporting Information, Figure S2). The broad peak at ∼578.80 nm was also present in the spectra but in low dominance.

At a solution ratio of 1:10:10, two peaks at 579.66 and 580.16 nm had the same position in the pcH range 3.60−4.77. The average lifetime of 331 ± 14 μs and $N_{H2O} = 2.5$ indicate no formation of a ternary complex. On increasing the pcH to 7.40, the peaks had the same position, but the intensity of the peak at 580.16 nm increases and that at 579.64 nm decreases. This on deconvolution gave three peaks at 580.18, 580.08, and 579.64 nm. The peak at 579.64 nm with a lifetime of 540 ± 12 μs corresponds to the formation of the complex $Eu(EDTA)(EDTAH)(H_2O)^{4-}$, while that at 580.08 and 580.18 nm with an average lifetime of 725 ±

Table 3. Assigned Chemical Shifts of Carboxylate Groups and Species Proposed in the ^{13}C NMR Spectra of La^{3+}/Y^{3+} with EDTA and NTA at $I = 6.60$ m($NaClO_4$)

species	M:components	pcH	chemical shifts δ (ppm) C=O	$-CH_2$
NTA	–	3.60	174.9	61.6
		9.82	182.7	62.4
EDTA	–	3.60	174.9	62.4
		9.63	185.2	64.1
$La(NTA)^0$	1:1	3.66	185.7	68.9
$La(NTA)_2^{3-}$	1:2	9.44	185.9	69.1
$Y(NTA)^0$	1:1	9.32	185.5	68.7, 68.9
$La(EDTA)^-$	1:1	9.30	185.7, 174.0	65.2, 57.8
				64.4, 57.5
$Y(EDTA)^-$	1:1	9.58	185.5	67.4
$La(EDTA)(NTA)^{4-}$	1:1:1	9.64	185.8, 185.4	67.7, 64.1
			185.1, 173.4	60.8, 57.2
	1:1:1	11.12	186.1, 185.7,	68.7, 64.6
			174.6	
				61.0, 57.6
$Y(EDTA)(NTA)^{4-}$	1:1:1	9.60	183.4, 183.2	67.6, 66.2
				65.0

12 μs is due to the formation of a ternary complex $Eu(EDTA)(NTA)^{4-}$ which is in equilibrium with the $Eu(NTA)_2(H_2O)^{3-}$ complex. At pcH 8.99, an asymmetrical peak centered at 580.21 nm was resolved into two peaks at 579.93 and 580.21 nm (Figure 1). The average lifetime of 990 ± 30 μs and $N_{H2O} = 0.3$ suggest that the ternary complexes $Eu(EDTA)(NTAH)^{3-}$ and $Eu(EDTA)(NTA)^{4-}$ are in fast equilibrium on the time scale of the excited-state lifetime, and therefore, these two species cannot be time resolved. The ^{1}H NMR studies of Southwood-Jones et al., [6] also detected the formation of a 1:2 complex of EDTA plus a ternary complex $Eu(EDTA)(NTA)^{4-}$ at pcH $\approx$ 7.0, but the formation of ternary complex is dominant at pcH > 8.4. At pcH 11.50, a single sharp peak at 580.21 nm with a lifetime of 983 ± 12 μs and $N_{H2O} = 0.4$ is consistent with the formation of a ternary complex $Eu(EDTA)(NTA)^{4-}$. A broad peak at ~578.80 nm was also present in the spectra (Supporting Information, Figure S3).

Luminescence lifetime measurements, especially with measured excited-state lifetime and $^7F_0 \rightarrow {}^5D_0$ spectroscopy provides good estimation of the coordination environment around the Eu^{3+} ion. However, often there are several species present in solutions and their rate of chemical interchange is fast, or there are energy-transfer processes among them. In such cases, we can observe different peaks in the $^7F_0 \rightarrow {}^5D_0$ spectra but it is not possible to measure the accurate lifetime of the individual species. Only a weighted average of the lifetime of the individual species could be obtained.

^{13}C NMR Spectroscopy. The ^{13}C NMR spectra of NTA, EDTA, La−NTA, La−EDTA, and La− or Y−EDTA−NTA were recorded to further substantiate the findings of TRLFS studies. The species formed and the assigned chemical shifts are given in Table 3. For NTA carboxylates, the carbon atom peak of 174.9 ppm at pcH 3.60 is shifted to 182.7 ppm at pcH 9.82. For EDTA carboxylates, the peak of 174.9 ppm at pcH 3.60 is shifted to 185.2 ppm at pcH 9.63, reflecting the presence of different anionic species at these pcH values (Supporting Information, Figure S4). The $-CH_2$ carbons of NTA and EDTA also showed an expected shift of signal downfield with increased pcH values (Table 3). The chemical shifts for EDTA and NTA will serve as a reference for the changes that occur on complexation with La^{3+} and Y^{3+}.

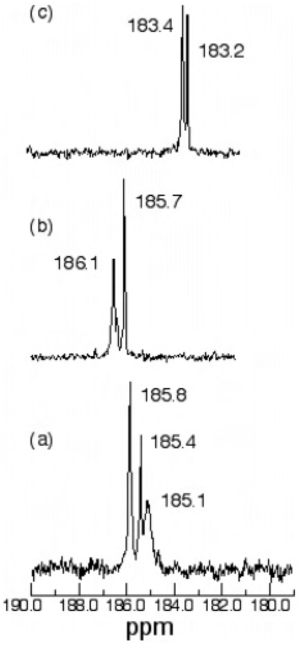

Figure 2. ^{13}C NMR spectra in 6.60 m ($NaClO_4$) at different pcH values (a) La−EDTA−NTA, 1:1:1, pcH = 9.64; (b) La−EDTA−NTA, 1:1:1, pcH = 11.12; (c) Y−EDTA−NTA, 1:1:1, pcH = 9.60.

For the La−NTA system (Supporting Information, Figure S4), the carboxylates peak showed a downfield shift for both La/NTA of 1:1 (pcH 3.66) and 1:2 (pcH 9.44). The peak intensity for $La(NTA)_2^{3-}$ was about twice as that of La-$(NTA)^0$, indicating binding of six carboxylates in the former and only three in the latter complex. Similarly, downfield shift of carboxylates and $-CH_2$ carbon signals indicated the formation of $Y(NTA)^0$. The formation of $M(NTA)^0$ and $M(NTA)_2^{3-}$ for Eu(III) and other rare earths have been reported previously under these conditions.[6] In case of La−EDTA, a small downfield shift of the EDTA (carboxylates + ethylene) signals are consistent with the formation of the complex $La(EDTA)^-$ at pcH 9.30. An additional carboxylates peak at 174.0 ppm and the $-CH_2$ carbons peaks at 64.4 and 57.5 ppm in the spectra of La-EDTA are due to the weak complexing of Na^+ with EDTA.[31]

The peaks at 185.8, 185.4, and 185.1 ppm in the spectra of La−EDTA−NTA, 1:1:1 at pcH 9.64, suggest three types of carboxylate carbons having different chemical environments and abundance (Figure 2). The ratio of the integration area of ca. 4:2:3 is consistent with the binding of four carboxylate carbons of EDTA (185.8 ppm), and two or three carboxylate carbons of NTA (185.4 and 185.1 ppm), respectively. The two different chemical shifts for carboxylate carbons indicates that NTA has two binding modes, i.e., (1) via three carboxylates and (2) via two carboxylates. The speciation calculations using the protonation constants of NTA show that $NTAH^{2-}$ and NTA^{3-} are dominant species in solutions at pcH $\approx$ 9.0−10, and the two different chemical

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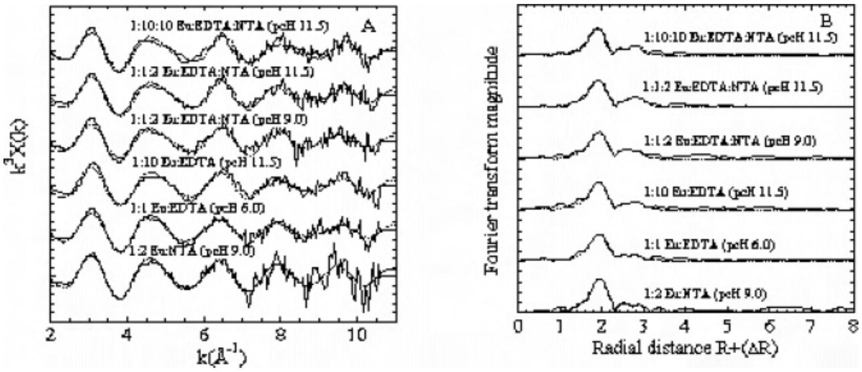

Figure 3. Fitted and k^3-weighted (2.0−10.6A^{-1}) and Fourier transformed spectra showing Eu(III) association with EDTA and NTA in $I = 6.60$ m (NaClO$_4$). Experimental data (−); fitted data (− − −)

shifts for carboxylates carbon peak of NTA is consistent with the formation of the two ternary complexes, La(EDTA)(NTAH)$^{3-}$ and La(EDTA)(NTA)$^{4-}$, in which NTA binds via two carboxylates in the former and via three carboxylates in the latter complex. The −CH$_2$ carbons of EDTA and NTA showed a small shift of signals on formation of the ternary complexes. The above results were also confirmed by taking the spectra of the solution at pcH 11.12 where NTA^{3-} is the dominant anion (∼98%). The two carboxylate peaks (instead of three observed at pcH 9.64) at 186.1 and 185.7 ppm with integrated peaks areas in the ratio of ca. 4:3 indicate the formation of a ternary complex La(EDTA)(NTA)$^{4-}$ in which NTA binds via three carboxylates. A small shoulder peak at 186.0 ppm suggests the presence of La(EDTA)(NTAH)$^{3-}$ as a minor species, which is consistent with the results of the TRLFS study.

The spectra of Y−EDTA−NTA at pcH 9.60 (Figure 2) has two peaks at 183.4 and 183.2 ppm for carboxylate carbons of EDTA and NTA. The integrated peak areas ratio of ca. 4:2 suggest that NTA binds via two of its three carboxylate carbons in the formation of Y(EDTA)(NTA)$^{4-}$. A further downfield shift of carboxylates carbon signal relative to that of Y(EDTA)$^-$ on formation of the ternary complex indicated that the EDTA molecules undergo structural reconstruction due to the steric hindrance caused by the binding of the EDTA and NTA molecules to the smaller Y^{3+}. The −CH$_2$ carbons peak of EDTA appears as a sharp peak at 67.6 ppm, while those of NTA at 66.2 and 65.0 ppm show a significant broadening on formation of the ternary complex. The increased values of the stability constant of the ternary complex of the EDTA+NTA for 9-coordinated lanthanides (La−Gd) and a decreasing trend for eight-coordinated lanthanides (Tb−Lu) also supports two different mechanisms for the formation of the ternary complex of the lanthanides along the series.[5] The two carboxylate carbon peaks were also observed in the ^{13}C NMR spectra of Y−EDTA−NTA at pcH 11.12, consistent with the CN = 8.0 for Y^{3+}, (6EDTA +2NTA). These observations indicate that, for the nine-coordinated lanthanides and actinides such as La^{3+}, Eu^{3+}, Am^{3+}, Cm^{3+}, etc., the coordination modes of NTA (two or three carboxylates) varies with the pcH of the solution and that for the eight-coordinated metal ions (Y^{3+}, Lu^{3+}, etc.), NTA binds via two carboxylates and their coordination modes are independent of pcH.

EXAFS. The fitted and k^3-weighted (2.0−10.6Å^{-1}) L$_{111}$ edge EXAFS spectra for Eu/NTA 1:2 (pcH, 9.00), Eu/EDTA 1:1 (pcH, 6.00), Eu/EDTA 1:10 (pcH, 11.5), Eu/EDTA/NTA 1:1:2 (pcH, 9.00 and 11.50), and Eu/EDTA/NTA 1:10:10 (pcH, 11.50) and their corresponding Fourier transformed spectra in 6.60 m (NaClO$_4$) solutions are shown in Figure 3. The molar ratio for the metal−ligand complexes are presented for the initial ratio of metal to ligand and do not reflect the actual stoichiometry for the complexes. The low k range for the data set is due to interference from the L$_{II}$ edge at 7.617 keV. The spectra show similarity in both phase and amplitude, which is to be expected from the similarity in the bonding ligand carboxylates and nitrogens. A summary of the fitting parameters and the corresponding Debye−Waller factors are given in Table 4.

The nearest neighbors of Eu are the oxygens with Eu−O distances generally at 2.41 ± 0.01Å, except in the solution of Eu/EDTA/NTA of 1:10:10 where it is 2.36 ± 0.03Å. The Eu−O distances agree well with 2.40 ± 0.01Å, reported by XRD for Eu−EDTA[32] and Eu−NTA,[33] and by EXAFS for the Eu−thenoyltrifluoroacetone[34] complexes. The Eu−N bonding distances are between 2.76 ± 0.01Å for Eu/EDTA 1:1 (pcH, 6.00), Eu/EDTA 1:10 (pcH, 11.50), and Eu/EDTA/NTA 1:10:10 (pcH, 11.50), and 2.81 ± 0.04 Å for the rest of the complexes studied. However, the Eu−N distances of 2.64 ± 0.01Å reported by XRD for Eu−EDTA[32] and Eu−NTA[33] are smaller than the present values, probably due to the differences in the structure in the bulk sample solutions (EXAFS) as against that in the crystal (XRD). Similar differences in U−O bond distances have been observed for the uranyl−oxydiacetate complex[35] by EXAFS (2.95 Å) and XRD (2.6 Å).

For Eu/NTA of 1:2 and pcH 9.00 (Table 4), it is confirmed that the complex formed is Eu(NTA)$_2$(H$_2$O)$^{3-}$, in which each NTA binds via three carboxylates and one nitrogen. Further, it has been confirmed that with Eu/EDTA, 1:1 and pcH 6.00, the complex formed is Eu(EDTA)(H$_2$O)$_3{}^-$ in which the

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Table 4. EXAFS Fitting Parameters Showing the Association of NTA and EDTA with Eu^{3+} at $I = 6.60$ m ($NaClO_4$)

sample	pcH	atom	N	R(Å)	σ^2	E_0	R
Eu/NTA, 1:2	9.00	Eu−O	6.8 ± 0.5	2.41 ± 0.01	0.006 ± 0.001	1.9 ± 0.2	0.019
		Eu−N	1.6 ± 0.3	2.84 ± 0.02	0.004 ± 0.003	8.2 ± 0.6	
		Eu−C	6.0 ± 0.6	3.35 ± 0.02	0.010 ± 0.003	2.1 ± 0.4	
Eu/EDTA, 1:1	6.00	Eu−O	6.7 ± 0.4	2.41 ± 0.00	0.008 ± 0.001	2.0 ± 0.4	0.036
		Eu−N	2.0 ± 0.8	2.76 ± 0.02	0.007 ± 0.002	8.9 ± 1.1	
		Eu−C	5.0 ± 1.7	3.31 ± 0.03	0.008 ± 0.003	3.2 ± 1.0	
Eu/EDTA, 1:10	11.50	Eu−O	6.9 ± 0.8	2.41 ± 0.01	0.008 ± 0.001	2.0 ± 0.4	0.065
		Eu−N	1.4 ± 0.8	2.78 ± 0.02	0.009 ± 0.003	7.5 ± 2.3	
		Eu−C	7.0 ± 1.3	3.33 ± 0.02	0.008 ± 0.004	4.2 ± 1.1	
Eu/EDTA/NTA, 1:1:2	9.00	Eu−O	5.8 ± 0.5	2.41 ± 0.01	0.006 ± 0.001	2.0 ± 0.5	0.070
		Eu−N	2.6 ± 0.8	2.81 ± 0.04	0.007 ± 0.002	8.5 ± 2.3	
		Eu−C	6.2 ± 1.4	3.34 ± 0.04	0.010 ± 0.003	2.0 ± 1.3	
Eu/EDTA/NTA, 1:1:2	11.50	Eu−O	7.5 ± 0.5	2.40 ± 0.01	0.009 ± 0.002	2.1 ± 1.0	0.049
		Eu−N	1.5 ± 0.5	2.84 ± 0.02	0.008 ± 0.001	8.5 ± 2.0	
		Eu−C	6.4 ± 1.7	3.34 ± 0.02	0.005 ± 0.002	2.0 ± 1.3	
Eu/EDTA/NTA, 1:10:10	11.50	Eu−O	7.0 ± 0.7	2.36 ± 0.03	0.008 ± 0.001	1.0 ± 0.9	0.110
		Eu−N	1.7 ± 0.6	2.75 ± 0.01	0.009 ± 0.002	8.0 ± 1.9	
		Eu−C	7.2 ± 1.5	3.35 ± 0.03	0.007 ± 0.002	1.5 ± 1.0	

EDTA binds with four carboxylates and two nitrogens. For Eu/EDTA of 1:10 and pcH 11.50, the formation of $Eu(EDTA)_2^{5-}$ has been established, in which the first EDTA molecule binds with its four carboxylates and two nitrogens and the second EDTA molecule with three carboxylate groups. For Eu/EDTA/NTA of 1:1:2, the pcH of the solution was adjusted to 11.50, at which both EDTA and NTA are highly ionized. The EXAFS data confirmed the formation of a ternary complex $Eu(EDTA)(NTA)^{4-}$ in which EDTA binds via four carboxylate groups and two nitrogens plus NTA via three carboxylate groups. At pcH of 9.00, with the same Eu/EDTA/NTA ratio, where the TRLFS indicate the presence of the two ternary complexes and the 1:2 complex of NTA, the EXAFS result suggests Eu^{3+} binding to six to seven carboxylates and two to three nitogens. Since the EXAFS cannot distinguish among the carboxylate and nitrogen of NTA and EDTA, the results are average ligand number observed by EXAFS. However, as the other systems studied by EXAFS at varying ratio and pcH values have EDTA binding via four carboxylate groups and two nitrogens, the binding of NTA molecule has several possibilities such as (a) three carboxylates (b) two carboxylates and one H_2O, and (c) two carboxylates and one nitrogen. We conclude that at pcH ca. 9.00 two ternary species and the 1:2 complex of NTA are formed and the EXAFS value are the average of the three values. It should be noted that the above assignments are the most reasonable representation of the EXAFS data and are consistent with the results of the TRLFS and the ^{13}C NMR studies. Further research on crystal structure of the solid compounds and/or solution is required to reveal the exact structure.

At Eu/EDTA/NTA 1:10:10 and pcH 11.50, a ternary complex $Eu(EDTA)(NTA)^{4-}$ is formed in which EDTA binds via four carboxylates and two nitrogens and NTA via three carboxylates. Figure 4 shows the molecular structure of the ternary complex $Eu(EDTA)(NTA)^{4-}$.

Complexation and Thermodynamics. The formation of 1:1 Am^{3+}−, Cm^{3+}−, and Eu^{3+}−NTA complex at temperatures of 0−60 °C was concluded from the linear plots of $1/D$ vs $[NTA^{3-}]$ (Figure S5, a representative graph for Am^{3+}, Cm^{3+}, and Eu^{3+} at 25 °C) under the experimental conditions.

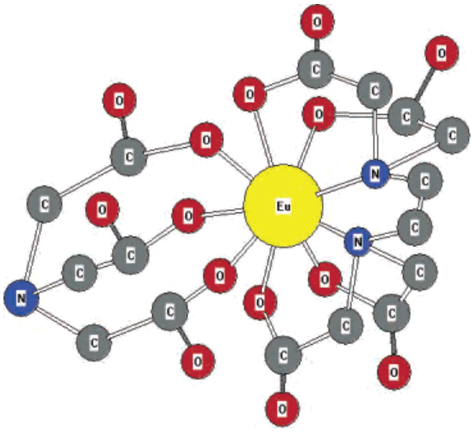

Figure 4. Model showing the binding modes of the formation of the ternary complex $Eu(EDTA)(NTA)^{4-}$ at Eu/EDTA/NTA of 1:10:10 and pcH = 11.5. The EDTA is bound to Eu^{3+} via two nitrogens and four carboxylate groups and NTA via three carboxylate groups. The nitrogen of NTA is not involved in the bonding.

Table 5. Stability Constants of Am^{3+}, Cm^{3+}, and Eu^{3+} with NTA (log β_{101}) at pcH = 3.60, $I = 6.60$ m ($NaClO_4$), $T = 0-60$ °C

temp (°C)	I (m)	Am	Cm	Eu	ref[a]
0	6.60 $NaClO_4$	9.71 ± 0.08	9.85 ± 0.08	9.62 ± 0.07	p.w
25	6.60 $NaClO_4$	10.48 ± 0.09	10.82 ± 0.08	10.52 ± 0.08	p.w
25	0.5 $NaClO_4$	11.19 ± 0.05	11.29 ± 0.07	11.15 ± 0.09	40
25	0.1	11.79 ± 0.03	11.91 ± 0.08	11.52 ± 0.05	41
45	6.60 $NaClO_4$	10.83 ± 0.08	11.08 ± 0.09	11.91 ± 0.09	p.w
40	0.1 KNO_3	−	−	11.55 ± 0.06	41
60	6.60 $NaClO_4$	11.33 ± 0.10	11.66 ± 0.10	11.38 ± 0.08	p.w

[a] p.w. = present work.

The complexation of M^{3+} with NTA^{3-} is so strong that even at pcH ca. 3.60 the metal ion is essentially completely complexed if $[NTA]_{total} \geq [M^{3+}]_{total}$. The stability constants of the formation of 1:1 complex (β_{101}) at different temperatures are given in Table 5 plus the constants reported for these metal ions at $I \leq 1.0$ M. The stability of the 1:1 complex of these metal ions at $I = 6.60$ m ($NaClO_4$) is slightly lower than those at $I = 0.1$ and 0.5 m, reflecting the effect of the ionic media. With increased temperatures, the stability of the 1:1 complex has increased values. The formation of the 1:2 complex of NTA is not observed in our experimental conditions; however, the formation of such complexes have been reported at high concentrations ratio and pcH.[1]

Table 6. Stability Constants of Am^{3+}, Cm^{3+}, and Eu^{3+} with EDTA+NTA (log β_{111}) at pcH = 3.60, I = 6.60 m ($NaClO_4$), T = 0−60 °C[a]

temp (°C)	I (m)	method	Am	Cm	Eu	ref
0	6.60 $NaClO_4$	sx	23.73 ± 0.08	23.80 ± 0.09	24.40 ± 0.10	p.w
25	6.60 $NaClO_4$	sx	25.73 ± 0.09	25.91 ± 0.08	25.96 ± 0.09	p.w
25	0.5 KNO_3	pot	−	−	21.08 ± 0.18*	3
20	1.0 KCl	abs	−	−	20.4 ± 0.20	7
20	0.1 KNO_3	pot	−	−	22.38 ± 0.09	5
20	0.1 KNO_3	^{1}H NMR	−	−	22.40 ± 0.09	6
45	6.60 $NaClO_4$	sx	26.82 ± 0.11	27.39 ± 0.10	27.44 ± 0.11	p.w
60	6.60 $NaClO_4$	sx	28.06 ± 0.11	28.80 ± 0.10	28.71 ± 0.11	p.w

[a] Sm, sx = solvent extraction, pot = potentiometric titration, abs = absorption spectroscopy, p.w. = present work.

Table 7. Thermodynamics of Complexation of Am^{3+}, Cm^{3+}, and Eu^{3+} with NTA and EDTA+NTA at 25 °C, pcH = 3.60, I = 6.60 m ($NaClO_4$)

M	ΔG_{101} (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔS_{101} (J K^{-1} mol^{-1})	ΔG_{111} (kJ mol^{-1})	ΔH_{111} (kJ mol^{-1})	ΔS_{111} (J K^{-1} mol^{-1})
Am	−59.6 ± 0.5	23.3 ± 2.7	279 ± 9	−146.29 ± 0.46	40.0 ± 4.2	626 ± 65
	−63.9 ± 0.3	−12.6 ± 0.6	172 ± 2[a]			
Cm	−61.5 ± 0.5	24.7 ± 2.5	290 ± 8	−147.31 ± 0.48	41.3 ± 3.7	633 ± 58
	−64.4 ± 0.4	−11.5 ± 2.2	178 ± 8[a]			
Eu	−59.8 ± 0.5	24.5 ± 2.5	283 ± 10	−147.59 ± 0.51	41.4 ± 5.5	630 ± 68
	−63.6 ± 0.5	−7.5 ± 1.7	188 ± 6[a]	−125.73 ± 0.54	−40.8 ± 1.7	290 ± 8[b]

[a] Reference 36. [b] Reference 5.

Linear plots of 1/D vs [NTA^{3-}] with mixtures of EDTA+NTA, (at fixed EDTA and varying NTA concentrations) and at T = 0−60 °C suggest involvement of one NTA molecule in the formation of the ternary complex M(EDTA)-$(NTA)^{4-}$ (Supporting Information Figure S6, a representative graph for Am^{3+}, Cm^{3+}, and Eu^{3+} at 25 °C). The measured stability constant (log β_{111}) plus the constants reported earlier for the formation of the ternary complexes of lanthanides are listed in Table 6. The difference of ca. 4−5 log units between our value of log β_{111} for Eu^{3+} at 25 °C and those of the literature values at 20−25 °C and I = 0.1 m reflects the effect of the ionic media and the different reactions viz. $M^{3+} + EDTA^{4-} + NTA^{3-} = M(EDTA)(NTA)^{4-}$ in our case and the reaction $M(EDTA)^{-} + NTA^{3-} = M(EDTA)(NTA)^{4-}$ used in the literature to evaluate the constants. For Am^{3+} and Cm^{3+}, no such constants are available. However, log β_{111} of 20.80 ± 0.02 has been measured for the ternary complex, $Pu(EDTA)(NTA)^{4-}$ at I = 1.0 m (KCl) and T = 25 °C.[11]

A linear correlation exists between the log β_{101}/log β_{111} of Am^{3+} with the ΣpK_a of the ligands (Supporting Information, Figure S7) indicating ionic nature of bonding in the binary 1:1 and the ternary 1:1:1 complexes. Figure 5 shows the observed trend of the stability constants of the binary 1:1 and the ternary 1:1:1 complexes of Am^{3+} with the number of carboxylate groups present in the ligand backbone. The straight line supports the participation of all available carboxylates groups in the bond formation with Am^{3+}. The stability constant value of Ac^- at I = 6.60 m ($NaClO_4$) extrapolated from the data at (I = 0.1 and 2.0 m[1,36]), the values of IDA, EDTA, DTPA, EDTA+IDA, and EDTA+Ox were taken from refs 37 and 38 and that of NTA and EDTA+NTA from this study.

The thermodynamic parameters for the formation of $M(NTA)^0$ at 6.60 m ($NaClO_4$) are listed in Table 7 (after applying corrections for the heat of deprotonation, ΔH = 25.1 kJ mol^{-1} of the third proton of NTA) indicate that the complexation of M^{3+} with NTA is largely endothermic. The positive values of ΔH_{101} reflect a significant effect of cation dehydration contributions over the cation−ligand interaction contributions in the formation of these complexes. This is consistent with the strong dehydration of cations at such high ionic strength.[39] By contrast, an exothermic enthalpy for these complexes reflects, at lower ionic strength, the predominance of metal−ligand interaction contributions upon complexation.[36]

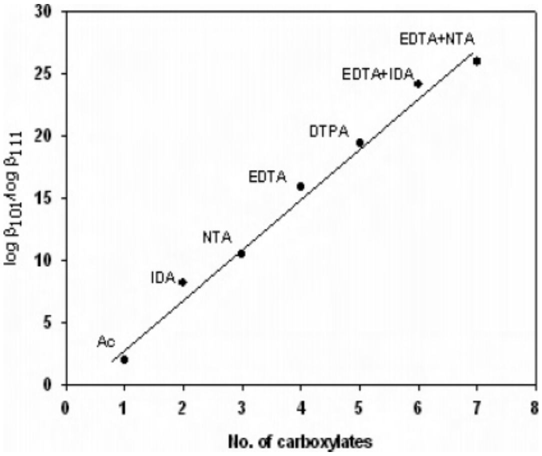

Figure 5. Relation between log β_{101}/log β_{111} of Am^{3+}−aminopolycarboxylates vs number of carboxylates groups; T = 25 °C and I = 6.60 m ($NaClO_4$).

The thermodynamic parameters for the formation of the ternary complex $M(EDTA)(NTA)^{4-}$ in 6.60 m ($NaClO_4$) are listed in Table 7 (after subtracting the heats of deprotonation

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of the last two protons for EDTA, 56.9 kJ mol^{-1} and the third proton of number of NTA, 25.1 kJ mol^{-1} due to the ionic media). The data in Table 7 are consistent with the predominant effect of the dehydration contributions over the cation−ligand interaction contributions in the formation of the ternary complex. The endothermic enthalpies for the formation of the ternary complex of these metal ions at $I =$ 6.60 m ($NaClO_4$) is in contrast to those of exothermic enthalpy measured for these complexes at $I = 0.1$ m (KNO_3). The difference, $\delta\Delta H$ ($\Delta H_{EDTA+NTA} - \Delta H_{NTA} = 41.4-24.5 = +16.9$ kJ mol^{-1} at $I = 6.60$ m ($NaClO_4$) and $\delta\Delta H$ ($\Delta H_{EDTA+NTA} - \Delta H_{\ NTA} = -40.75\ (-4.2)) = -36.5$ kJ mol^{-1} at $I = 0.1$ m (KNO_3) reflect the predominant effect of the dehydration of the cations in the former and the strong cation−ligand interaction in the latter process.

Conclusion

The first systematic study on the ternary complexation of Am^{3+}, Cm^{3+}, and Eu^{3+} at $I = 6.60$ m ($NaClO_4$) with EDTA and NTA provides a complete information on the complexation thermodynamics and gives insight into the binding modes of EDTA and NTA in the ternary complexes. The formation of the ternary complex $M(EDTA)(NTA)^{4-}$ depends on the concentration ratios (Eu/EDTA/NTA) and the pcH of the solutions. At low Eu/EDTA/NTA ratios of 1:1:1−1:1:2 and at pcH ca. 9.00, two complexes $M(EDTA)(NTAH)^{3-}$ and $M(EDTA)(NTA)^{4-}$ exist together in which NTA binds via three donor groups with competition between donor groups such as three carboxylates, two carboxylates and one nitrogen, and two carboxylates and one H_2O. Thus, the ternary complexes formed at Eu/EDTA/NTA of 1:1:2 and pcH ca. 9.00 are mixtures of two complexes and NTA has several possibilities for binding to the metal cations. One ternary complex $M(EDTA)(NTA)^{4-}$ is formed for M/EDTA/NTA of 1:1:20 and 1:10:10 at pcH ca. 9.00 and 11.50 and at concentrations ratios of 1:1:1−1:1:2 and pcH ca. 11.50, in which NTA binds via three carboxylates and not with nitrogen. When the concentrations of EDTA and NTA are higher than the metal, the formation of the 1:2 complexes of EDTA and NTA complicates the formation of the ternary complex at pcH ca. 7.00.

The two-phase equilibrium distribution measurements of Am^{3+}, Cm^{3+}, and Eu^{3+} (tracer concentrations) with EDTA and NTA in 6.60 m ($NaClO_4$) also established the formation of a ternary complex $M(EDTA)(NTA)^{4-}$ with stability constant values, log $\beta_{111} \approx 25.8$. The enthalpy and entropy of complexation suggest the predominant effect of cation dehydration in the formation of these complexes at high ionic strengths. The high stability of the ternary complex $M(EDTA)(NTA)^{4-}$ indicates that the ternary species plus the mixed chelate hydroxyl complexes can significantly increase the solubility of the trivalent lanthanides and, by analogy, trivalent actinides in the waste tanks, and can significantly impact the strategies for the waste processing.

Acknowledgment. This research was supported by an USDOE-EMSP contact. We gratefully acknowledge Dr. Bert Van De Burgt of chemistry Department Laser Facility and Dr. Thomas Gedris of NMR facility for their assistance.

Supporting Information Available: Data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

IC052166C