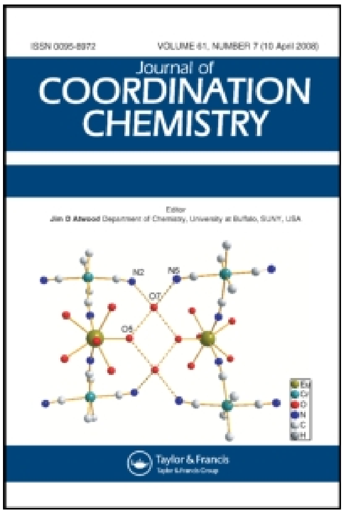

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Complexation and the laser luminescence studies of Eu(III), Am(III), and Cm(III) with EDTA, CDTA, and PDTA and their ternary complexation with dicarboxylates

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Complexation and the laser luminescence studies of Eu(III), Am(III), and Cm(III) with EDTA, CDTA, and PDTA and their ternary complexation with dicarboxylates

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Spectroscopy has been used to determine the number of coordinated water molecules bound to Eu(III) and Cm(III) in a series of binary complexes of polyaminocarboxylate and their ternary complexes with dicarboxylates as well as with similar ligands with additional O-, N-, and S-donors. Complexes of Eu(III) and Cm(III) with polyaminocarboxylate alone contain *ca.* 2.5–3.0 waters of hydration. Increasing the steric requirement of a polyaminocarboxylate by increasing the number of groups in the ligand backbone does not appreciably change the hydration of these cations. The stability constants of the binary and ternary complexes of Cm(III), Am(III), and Eu(III) with these ligands were measured by solvent extraction in a solution of 0.1 M ($NaClO_4$). The size, basicity, specific M^{3+}-second ligand interactions, and steric requirement of the ligands are the factors which affect the ternary complexation. Knowledge of the chemical species formed by actinide cations with organic ligands (carboxylates and aminocarboxylates), which are present in all nuclear waste, is important to understand the behavior of waste forms and the migration behavior of actinides in the environment.

Keywords: Complexation; Eu(III); Am(III); Cm(III); TRLFS; Aminopolycarboxylates

1. Introduction

The most significant features of the f-cations in aqueous solution are stability of the trivalent state and the strongly ionic character of their bonding [1]. Because of strong ionic nature of the bonding, these cations do not display the restricted stereochemistry typical of transition elements. The stereochemistries in f-cations complexation in solution are determined primarily by the electrostatic and spatial requirements of the ligands and can frequently be difficult to predict [2]. Although many techniques have been used to determine the coordination number of these cations in complexes, Ln(III) luminescence (Ln = Eu and Tb) has been applied extensively to study coordination chemistry of the lanthanides [3–5].

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An interesting aspect of the $^7F_0 \rightarrow {}^5D_0$ transition is that the excited and ground states are non-degenerate and each peak in the spectrum corresponds to a distinct Eu(III) environment [6]. Previous work has shown that a linear relation exists between the frequency shifts of the $^7F_0 \rightarrow {}^5D_0$ transition of Eu(III) complexes and the maximum coordination number, CN_L, of the ligand in the complex, allowing determination of the ligand coordination number in the inner sphere of Eu(III) [5]. This shift reflects either an increase of the M–L bond covalency or a decrease of the effective charge of the metal cation upon complexation [5]. Albin and Horrocks [7] established a relationship between the $^7F_0 \rightarrow {}^5D_0$ band frequency and the ligand charge of a number of complexes and attributed the frequency shift of the $^7F_0 \rightarrow {}^5D_0$ band to a decrease in the effective nuclear charge on the lanthanide as the negative charge of the ligands increases. As for Eu(III) and Tb(III), a linear correlation was found for Cm(III) between the reciprocal of the excited-state lifetime and the number of water molecules in the first coordination sphere [8, 9]. The high sensitivity of Cm(III)-TRLFS (Time Resolved Laser Fluorescence Spectroscopy) allows study of the complexation reactions over a wide range of concentrations and pH values with no significant effect from the hydrolysis reaction [10].

Trivalent lanthanide and actinide cations bind with as many as nine ligand donor sites in their coordination sphere. The ligands EDTA (ethylenediaminetetraacetate), CDTA (trans-1,2 diaminocyclohexane tetraacetate), and PDTA (1,2 diamino propanetetracetate) are hexadentate, and, upon complexation with Eu^{3+}, all the donor groups are coordinated with three waters of hydration [6]. Luminescence lifetime measurements in solution and the solid state indicate the presence of three waters of hydration in these complexes [6, 11–13]. Addition of a second ligand results in displacement of the residual waters of hydration by formation of a ternary complex. The interactions of $M(EDTA)^-$ ($M(III) = Am$, Cm, and Eu) with malonate, succinate, glutarate, and adipate show the effect of chelate ring size in the formation of the ternary complexes.

In this study, luminescence of Cm(III) and of Eu(III) (as a reference ion) was used to assess the relationship between the lifetime and the hydration number of Cm(III) in the ternary complexes formed between a series of simple aminopolycarboxylates and dicarboxylates as well as with ligands having additional O-, N-, and S-donors.

Knowledge of the chemical species formed by actinide cations with organic ligands (carboxylates and aminocarboxylates), which are present in all nuclear waste, is important to understand the behavior of waste forms and the migration behavior of actinides in the environment. Since the properties of f-element metal ion complexes are determined principally by ionic and steric effects, comparison of the complexation of these ligands provides insight into the role of different donor groups and, how steric differences between ligands affects the ternary complexation. The stability of these complexes was measured by solvent extraction.

2. Experimental

All chemicals were reagent grade and their solutions were prepared in distilled deionized water. Solutions of oxalate (Ox), oxydiacetate (ODA), thiodiacetate (TDA), iminodiacetate (IDA), methyliminodiacetate (MIDA), N-hydroxyethyliminodiacetate (HIDA), nitrilotriacetate (NTA), EDTA, CDTA, and PDTA (all ACS certified, from

Fisher Scientific or Sigma-Aldrich) were prepared in 0.1 M ($NaClO_4$) and standardized by potentiometric titration with standard carbonate free NaOH. The Eu(III) stock solution was prepared from Eu_2O_3 (99.99%, Aldrich) in perchloric acid and the concentration was determined by EDTA titration using xylenol orange as indicator [14]. The extractant di-(2-ethylhexyl) phosphoric acid, (D2EHPA, Sigma-Aldrich) and reagent grade heptane (Fisher Scientific, ACS) were used as received.

^{241}Am, ^{244}Cm, and $^{152,\ 154}$Eu were obtained from Oak Ridge National Laboratory. The ^{244}Cm was purified from its daughter nuclide ^{240}Pu by passage in 7.5 M HNO_3 solution through a column of Dowex-1 anion exchange resin [15]. The tracer solutions were prepared in $pH = 3.0$ ($HClO_4$) with an activity of *ca.* 50,000 counts per minute (cpm) per 10.0 μL. ^{248}Cm for the luminescence studies was purified in a similar manner. The purity of the tracers was confirmed by α- and/or β-spectrometry. Activities of ^{241}Am, ^{244}Cm, and $^{152,\ 154}$Eu were measured with a Beckman Liquid Scintillation Counter (LSC) using Ecolite cocktail (ICN Research Product Division).

An Accumet 950 (Fisher Scientific) pH meter was used with glass electrodes (Corning semi-micro combination) to measure the change in pH. The electrode was calibrated with 4.00 ± 0.01 and 7.00 ± 0.01 standard pH buffer (Fisher Scientific). The pH meter readings, pHr were converted to hydrogen ion concentrations, pcH, using the calibration curves obtained by a series of measurements of $HClO_4$ and NaOH solutions of known H^+ concentrations in $NaClO_4$. The hydrogen ion concentration, pcH, was calculated from the measured pH using the relation $pcH = pH + 0.259(\pm 0.025)^* C_{NaClO_4}$, where C is the concentration of $NaClO_4$. The base solutions were standardized by potassium acid phthalate, KHP, titration. Prior to use, KHP was dried at 100°C for at least 2 h and cooled in a desiccator over silica gel.

2.1. *Solvent extraction experiments*

The distribution ratio, $D = [M]_{total,\,org}/[M]_{total,\,aq}$, of Am(III), Cm(III), and Eu(III) between the aqueous ($I = 0.1$ M $NaClO_4$) and the organic (D2EHPA in heptane) phases was measured using solvent extraction [15]. For measurement of the binary constants, the concentration of EDTA, CDTA, and PDTA were varied from 1.0 to 5.0 ($\times 10^{-7}$ M). For measurement of the ternary constants, the concentration of EDTA, CDTA, and PDTA were 1.0×10^{-7} M and that of Ox varied from 1.0×10^{-4} to 1.0×10^{-3} M, of HIDA from 1.0 to 5.0 ($\times 10^{-5}$ M), of TDA from 0.04 to 0.18 M, of ODA from 0.20 to 4.0 ($\times 10^{-4}$ M), of IDA, and MIDA from 0.02 to 0.12 M. Details of the distribution experiments, pre-equilibration of the organic phase, counting procedures, and equilibrium pH measurements are as described [15].

2.2. *Data analysis*

Extraction of M(III) (M = Am, Cm, and Eu) between the aqueous phase 0.1 M ($NaClO_4$) and the organic phase (D2EHPA, represented as the dimer H_2A_2) can be expressed by:

$$M^{3+}_{(a)} + 3H_2A_{2(o)} \Leftrightarrow M(HA_2)_{3(o)} + 3H^+_{(a)} \qquad (1)$$

where (a) and (o) represent the aqueous and organic phases, respectively. In the presence of ligands (L^{m-}) in the aqueous phase, the complexation reaction of the metal ions can be described by the reaction,

$$M^{3+}_{(a)} + L^{m-}_{(a)} \overset{\beta_{101}}{\Leftrightarrow} ML^{3-m} \tag{2}$$

where β_{101} is the stability constant of the complex formed, L = EDTA, CDTA, and PDTA. The polynomial correlating D values with $[L^{m-}]$ and $\log \beta_{101}$ were calculated from plots of:

$$1/D = 1/D_0(1 + \beta_{101}[L^{m-}]) \tag{3}$$

or

$$D_0/D - 1 = \beta_{101}[L^{m-}] \tag{4}$$

where D_0 is the distribution ratio of metal ions for aqueous solutions in the absence of complexing ligands.

2.3. *Ternary systems*

The formation of ternary complexes with M + L + P can be written as:

$$M^{3+}_{(a)} + L^{4-}_{(a)} + nP^{m-}_{(a)} \overset{\beta_{1011}}{\Leftrightarrow} M(EDTA)(P)_n^{(1+nm)-} \tag{5}$$

where $n = 1$ and 2 for Ox and $n = 1$ for NTA, IDA, ODA, TDA, MIDA, HIDA. The stability constant, β_{101n} of the ternary complex can be described in two steps. The first step is a variation of $[L^{4-}]$ concentration in the absence of P^{m-} by equation (6) and the second step is the variation of $[P^{m-}]$ at a fixed concentration of $[L^{4-}]$ by equation (7),

$$D_1 = \left[M^{3+}\right]_{(o)} / \left[M^{3+}\right]_{(a)} \left(1 + \beta_{101}\left[L^{4-}\right]\right) \tag{6}$$

where D_1 is the distribution ratio in the presence of $[L^{4-}]$ but no ternary ligand.

$$D = \left[M^{3+}\right]_{(o)} / \left[M^{3+}\right]_{(a)} \left(1 + \beta_{101}\left[L^{4-}\right] + \beta_{101n}\left[L^{4-}\right][P^{m-}]^n\right) / \left(1 + \beta_{101}\left[L^{4-}\right]\right) \tag{7}$$

Equations (6) and (7) can be combined, and simplified to

$$D_1/D - 1 = \beta_{101n}\left[L^{4-}\right][P^{m-}]^n / \left(1 + \beta_{101}\left[L^{4-}\right]\right) \tag{8}$$

The stability constants (β_{1011} and β_{1012}) of the ternary complex were evaluated using the equation:

$$\begin{aligned} D_1/D - 1 = {} & \beta_{1011}\left[L^{4-}\right][P^{m-}] / \left(1 + \beta_{101}\left[L^{4-}\right]\right) \\ & + \beta_{1012}\left[L^{4-}\right][P^{m-}]2 / \left(1 + \beta_{101}\left[L^{4-}\right]\right) \end{aligned} \tag{9}$$

2.4. *TRLFS experiments*

The pumped dye laser systems for the spectral experiments were as described previously [15]. The excitation spectra of the Cm(III) complexes were measured by scanning the dye laser spectrum of the $^8S_{7/2} \rightarrow {}^6I_{17/2,11/2}$ band, while monitoring the luminescence emission intensity at 600 nm to measure the luminescence lifetime. The details of the instrumental setup were as described [8, 9]. The excitation was achieved with a pulsed (10 Hz) 532 nm beam of a Nd-YAG laser (Quanta Ray DCR 3A, Spectra-Physics) pumping DCM (Exciton, Inc.) in methanol in a Quanta Ray PDL 2 (Spectra-Physics) dye laser head. The laser beam was converted to the desired wavelength (388–410 nm range) by mixing the dye laser output with the 1064 nm fundamental in a wavelength extender module (Quanta Ray WEX-1). The deconvolution of the excitation spectra was performed using Lorentzian–Gaussian functions. The concentration of Cm(III) was $2.0–4.0 \times 10^{-6}$ M, while that of Eu(III) was 1.0×10^{-4} M.

The equations $N_{H_2O} = 1.05k_{obs} – 0.70$, where k_{obs} is the luminescence decay constant [5], were used to calculate the number of water molecules associated with the Eu(III) complex. For Cm(III), the correlation $N_{H_2O} = 0.65k_{obs} – 0.88$ [8, 9] was used to calculate the number of bound water molecules. An uncertainty of ±0.5 is assigned for N_{H_2O} in these measurements [5].

3. Results and discussion

For aqueous complexes of Cm(III) and Eu(III), the luminescence lifetime of 64 ± 3 and 113 ± 5 μs, and the N_{H_2O} values of 9.1 and 8.6, respectively, are consistent with the values of 9.4 and 8.7 reported previously [5, 9].

The simple aminocarboxylates EDTA, PDTA, and CDTA form 1 : 1 complexes over the pH range 3.6–8.0. The two peaks in the spectra of these complexes (figure 1) result from the presence of two different complex species which differ by one coordinated water [4]. The third peak at *ca.* 396.00 nm in the spectra of Cm-L results from the large ligand field splitting by the stronger metal–ligand interaction [16]. The N_{H_2O} data in table 1 indicate that the additional groups in the ligand backbone do not remove extra waters of hydration from the inner coordination shell of cations. At pH > 9.0 the N_{H_2O} values of the peaks decrease, indicating formation of a ternary hydroxyl complex. The complexation strength of these aminocarboxylates follows the order: CDTA > EDTA > PDTA (table 2 and figure 2). Substitution of a cyclohexane ring for the ethylene group of EDTA increased the stability constants of the $M(CDTA)^-$ complexes by *ca.* one log unit, while additional methyl group in the ethylenediamine backbone slightly decreased the stability constant of the $M(PDTA)^-$ complexes relative to $Ln(EDTA)^-$.

The addition of tridentate IDA and MIDA to ML^- results in the formation of a ternary complex with displacement of remaining waters of hydration from the inner hydration shell of the metal cations (M = Cm(III), Eu(III) and L = EDTA, PDTA or CDTA). At pH 3.60, no formation of a ternary complex is observed for these systems. As the pH is raised to 9.0, the increased lifetime and decreased N_{H_2O} values indicate formation of a ternary complex (table 3). The three excitation peaks in the spectra of Eu(III) with EDTA + IDA, CDTA + IDA and PDTA + IDA are consistent with the formation of $M(L)(OH)^{2-}$ and the ternary complex as observed in absorption spectra of $Eu(EDTA)(IDA)^{3-}$ (figure 3). Displacement of *ca.* three waters of hydration by IDA on formation of the ternary complexes indicates tridentate coordination. These ternary complexes remain stable in solution to pH of 9.0–11.5. However, the size and rigidity of

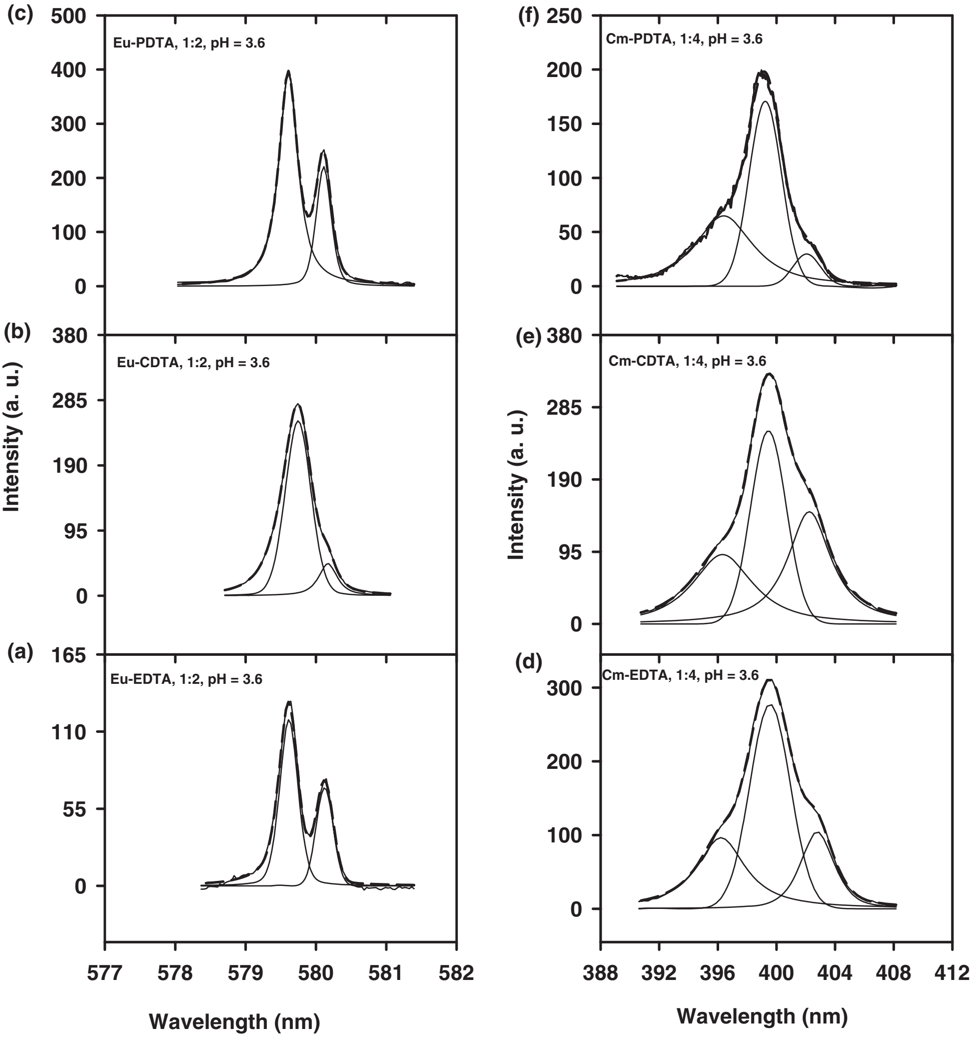

Figure 1. The excitation spectra of (a) Eu-EDTA; (b) Eu-CDTA; (c) Eu-PDTA; (d) Cm-EDTA; (e) Cm-CDTA and (f) Cm-PDTA at pH 3.6, Cm(III) $= 4.0 \times 10^{-6}$; Eu(III) $= 1 \times 10^{-4}$ M; $I = 0.1$ M (NaClO$_4$) and $T = 25°$C.

CDTA and PDTA affect the binding mode of IDA in the ternary complexation; the three peaks are due to formation of Eu(L)$^-$ and of the ternary complexes Eu(L)(IDA)(H$_2$O)$^{3-}$ and Eu(L)(IDA)$^{3-}$. The three absorption bands (429.2 nm for Nd(CDTA)$^-$ and 429.7 and 430.2 nm for formation of two ternary complexes) are also present in absorption spectra of Nd(CDTA)(IDA)$^{3-}$ [17]. Stability constants of the ternary complex measured by solvent extraction are listed in table 2. The order of complexation strength (CDTA + IDA > EDTA + IDA > PDTA + IDA) is the same as that of the 1 : 1 complexes of these metal ions (figure 2) [18]. The presence of AB patterns in the ^{1}H NMR of spectra of Ln(EDTA)(IDA)$^{3-}$ (Ln(III) = La and Eu) for the acetate protons of EDTA indicates that in the ternary complex M–N bonds remain long-lived, while collapse of the AB pattern for the Y and Lu indicates short-lived M–N

Table 1. Spectral characteristics of binary complexation of Cm(III) and Eu(III) with EDTA, CDTA, and PDTA; $I = 0.1$ M ($NaClO_4$), $T = 25$°C.

Component	Ratio	pH	Peak position (nm)	Species	Lifetime (μs)	N_{H_2O} (±0.5)
Cm-EDTA	1 : 4	3.6–8.0	402.75, 399.58, 396.27	Cm(EDTA)$^{-}$	138 ± 5	3.8
		9.0	401.38, 399.35, 396.85	Cm(EDTA)(OH)$^{2-}$	212 ± 5	2.2
Cm-CDTA	1 : 4	3.6–8.0	402.23, 399.45, 396.32	Cm(CDTA)$^{-}$	157 ± 5	3.2
	1 : 4	9.0	401.67, 399.55, 395.29	Cm(CDTA)(OH)^{2}	209 ± 5	2.3
Cm-PDTA	1 : 4	3.6–8.0	402.06, 399.24, 396.40	Cm(PDTA)$^{-}$	147 ± 5	3.5
	1 : 4	9.0	402.00, 399.44, 396.67	Cm(PDTA)(OH)$^{2-}$	154 ± 6	3.3
Eu-EDTA	1 : 2	3.6–8.0	579.64, 580.18	Eu(EDTA)$^{-}$	309 ± 5	2.7
	1 : 2	9.0	579.64, 580.11	Eu(EDTA)(OH)$^{2-}$	459 ± 6	1.7
Eu-CDTA	1 : 2	3.6–8.0	579.74, 580.18	Eu(CDTA)$^{-}$	339 ± 5	2.4
	1 : 2	10	579.88, 578.97	Eu(CDTA)(OH)$^{2-}$	478 ± 5	1.5
Eu-PDTA	1 : 2	3.6	579.61, 580.11	Eu(PDTA)$^{-}$	348 ± 5	2.3
	1 : 2	9.0	579.61, 580.11	Eu(PDTA)(OH)$^{2-}$	381 ± 7	2.0
	1 : 2	13.0		Eu(PDTA)(OH)$^{2-}$	495 ± 3	1.4

Table 2. Stability constants of the binary and the ternary complexes of Am(III), Cm(III) and Eu(III) at $I = 0.1$ M ($NaClO_4$), $T = 25$°C.

Ligands	Am(III)	Cm(III)	Eu(III)
EDTA	17.92 ± 0.03	17.86 ± 0.04	17.52 ± 0.03
CDTA	18.85 ± 0.06	18.72 ± 0.05	18.59 ± 0.06
PDTA	17.48 ± 0.05	17.70 ± 0.03	17.38 ± 0.06
EDTA + IDA	23.90 ± 0.08	23.81 ± 0.09	23.56 ± 0.1
CDTA + IDA	24.67 ± 0.09	24.34 ± 0.08	24.36 ± 0.08
PDTA + IDA	23.52 ± 0.09	23.62 ± 0.07	23.45 ± 0.08
EDTA + MIDA	23.78 ± 0.07	23.68 ± 0.06	23.58 ± 0.09
CDTA + MIDA	24.85 ± 0.10	24.75 ± 0.09	24.54 ± 0.08
PDTA + MIDA	23.52 ± 0.08	23.65 ± 0.08	23.75 ± 0.09
EDTA + Ox	22.88 ± 0.08 (26.77 ± 0.10)	22.81 ± 0.08 (26.78 ± 0.11)	22.73 ± 0.09 (26.64 ± 0.11)
CDTA + Ox	23.63 ± 0.08 (27.67 ± 0.11)	23.61 ± 0.08 (27.61 ± 0.12)	23.48 ± 0.09 (27.57 ± 0.11)
PDTA + Ox	22.07 ± 0.07 (26.33 ± 0.10)	22.70 ± 0.08 (26.65 ± 0.11)	22.66 ± 0.07 (26.49 ± 0.09)
EDTA + ODA	22.94 ± 0.09	22.89 ± 0.09	22.37 ± 0.09
CDTA + ODA	23.41 ± 0.08	23.64 ± 0.08	23.88 ± 0.08
PDTA + ODA	22.61 ± 0.07	22.75 ± 0.08	22.93 ± 0.09
EDTA + TDA	20.17 ± 0.08	20.24 ± 0.08	19.62 ± 0.08
CDTA + TDA	21.06 ± 0.09	21.17 ± 0.08	20.77 ± 0.07
PDTA + TDA	19.74 ± 0.08	20.08 ± 0.07	19.48 ± 0.07
EDTA + NTA	26.98 ± 0.08	26.94 ± 0.07	26.84 ± 0.09
CDTA + NTA	27.85 ± 0.09	27.78 ± 0.08	27.65 ± 0.09
PDTA + NTA	26.52 ± 0.08	26.62 ± 0.09	26.39 ± 0.10
EDTA + HIDA	–	–	24.78 ± 0.10
CDTA + HIDA	–	–	25.45 ± 0.11
PDTA + HIDA	–	–	24.52 ± 0.10

Note: Values in parentheses are for $\log \beta_{1012}$.

bonds [19, 20]. The results imply that EDTA and IDA undergo structural reconstruction due to the steric hindrance caused by binding of these molecules to the smaller Ln(III) cations. The increased stability constant values of the ternary complexes of EDTA + IDA for nine-coordinate lanthanides (La–Gd) and the decreasing trend for

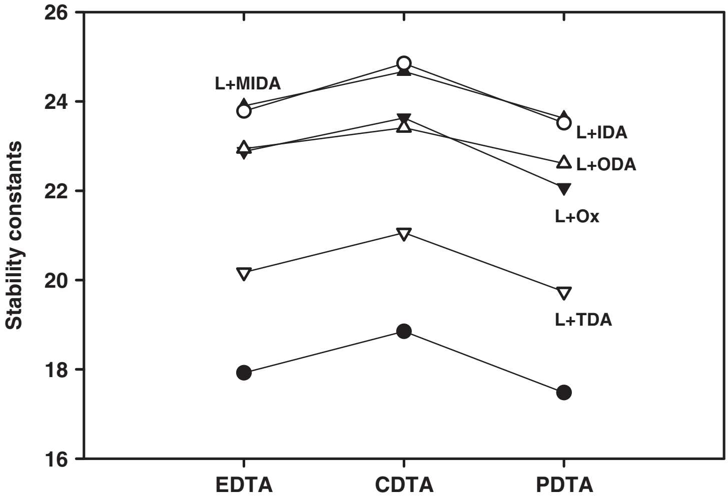

Figure 2. Variation of stability constant of 1 : 1 and 1 : 1 : 1 ternary complexes of Am(III) at 25°C.

eight-coordinate lanthanides (Tb–Lu) supports two different mechanisms for formation of the ternary complexes. The lack of data prevents such conclusions for the CDTA + IDA and PDTA + IDA.

MIDA, in which a proton attached to nitrogen is replaced by methyl, like IDA, has tridentate coordination in the ternary complex. The N_{H_2O} values of 0.5 ± 0.5 on formation of the ternary complex $M(L)(MIDA)^{3-}$ are consistent with the hexa- and tridentate coordination for L and MIDA, respectively (figure 4 and table 4). The stability constant values of M-L-IDA and M-L-MIDA are the same because of the similarity of the ligands, or slightly higher for the MIDA complex because of greater basicity of the ligand (figure 2). This suggests that incorporation of the methyl group has not altered significantly the nature and strength of complexation.

ODA, like IDA, is tridentate and forms a ternary complex with replacement of *ca.* three waters of hydration. The lifetime and N_{H_2O} values of the complexes are summarized in table 5 and the deconvoluted spectra are presented in figure 5. The ternary complex formed by IDA is more stable than the corresponding complex of ODA (table 2). This difference in stability reflects difference in ligand basicities as seen, for example, in 1 : 1 complexes of M-ODA and M-IDA [18]. TDA has a sulfur donor which interacts weakly, if at all, with hard acid cations such as lanthanide and actinides. With these metal cations TDA forms a ternary complex with displacement of *ca.* two waters of hydration, consistent with bidentate coordination with no binding of the sulfur.

HIDA and NTA both are tetradentate, displacing *ca.* four waters of hydration in the formation of 1 : 1 and 1 : 2 complexes [21, 22]. As expected the stability constant of the 1 : 1-HIDA complex is lower than that for the 1 : 1-NTA complex due to the lower basicity of HIDA [18]. However, in the formation of ternary complexes, displacement of less than four waters of hydration indicates that the steric requirements of the bulky HIDA and NTA prevent tetradentate coordination for HIDA and NTA as observed in the corresponding binary complexes (table 6). Formation of $M(NTA)_2^{3-}$ and $M(HIDA)_2^{3-}$ plus the ternary complexes are observed at high concentration ratios of

Table 3. Spectral characteristics of ternary complexes of Eu(III) and Cm(III) with L + IDA (L = EDTA, CDTA, and PDTA); $I = 0.1$ M ($NaClO_4$), $T = 25°C$.

Component	Ratio	pH	Peak position (nm)	Species	Lifetime (μs)	N_{H_2O} (±0.5)
Cm-EDTA-IDA	1 : 1 : 20	9.0	404.02, 400.43, 396.18	$Cm(EDTA)(IDA)^{3-}$	471 ± 10	0.5
	1 : 1 : 30	9.0	404.01, 400.60, 396.27	$Cm(EDTA)(IDA)^{3-}$	492 ± 8	0.5
	1 : 1 : 20	11.5	404.05, 400.79, 398.16	$Cm(EDTA)(IDA)^{3-}$	440 ± 15	0.6
Cm-CDTA-IDA	1 : 1 : 20	9.0	403.73	$Cm(CDTA)(IDA)(H_2O)^{3-}$	379 ± 7	0.9
			405.86	$Cm(CDTA)(IDA)^{3-}$	438 ± 8	0.6
			401.20, 399.32, 396.01	$Cm(CDTA)(OH)^{2-}$	–	–
	1 : 1 : 50	9.0	403.82	$Cm(CDTA)(IDA)(H_2O)^{3-}$	366 ± 8	0.9
			405.90	$Cm(CDTA)(IDA)^{3-}$	442 ± 9	0.6
			401.15, 399.55, 396.71	$Cm(CDTA)(OH)^{2-}$		–
	1 : 1 : 20	11.5	403.71	$Cm(CDTA)(IDA)(H_2O)^{3-}$	304 ± 7	1.2
			405.92	$Cm(CDTA)(IDA)^{3-}$	315 ± 9	1.3
			401.02, 399.24, 396.00	$Cm(CDTA)(OH)^{2-}$	–	–
Cm-PDTA-IDA	1 : 1 : 50	3.60	402.06, 399.24, 396.40	$Cm(PDTA)^{-}$	150 ± 4	3.6
	1 : 1 : 50	9.0	403.88, 400.44, 397.94	$Cm(PDTA)(IDA)^{3-}$	361 ± 9	0.9
	1 : 1 : 50	11.5	403.82, 400.47, 397.85	$Cm(PDTA)(IDA)^{3-}$	381 ± 8	0.8
Eu-EDTA-IDA	1 : 1 : 1	9.0	580.55	$Eu(EDTA)(IDA)^{3-}$	831 ± 6	0.5
			579.71, 580.18	$Eu(EDTA)(OH)^{2-}$	525 ± 5	1.3
	1 : 1 : 5	9.0	580.55	$Eu(EDTA)(IDA)^{3-}$	879 ± 5	0.5
	1 : 1 : 5	11.5	580.55	$Eu(EDTA)(IDA)^{3-}$	778 ± 9	0.6
Eu-CDTA-IDA	1 : 1 : 2	9.0	580.31, 579.84	$Eu(CDTA)(IDA)(H_2O)^{3-}$	761 ± 10	0.8
			580.62	$Cm(CDTA)(IDA)^{3-}$	800 ± 10	0.6
	1 : 1 : 5	9.0	580.35, 579.84	$Eu(CDTA)(IDA)(H_2O)^{3-}$	769 ± 12	0.8
			580.62	$Cm(CDTA)(IDA)^{3-}$	854 ± 10	0.5
	1 : 1 : 5	11.5	580.58	$Eu(CDTA)(IDA)(H_2O)^{3-}$	473 ± 9	1.5
			579.88, 578.97	$Eu(CDTA)(OH)^{2-}$	409 ± 10	1.9
Eu-PDTA-IDA	1 : 1 : 10	9.0	580.11, 579.61	$Eu(PDTA)(OH)^{2-}$	432 ± 9	1.7
			580.43, ~579.31	$Eu(PDTA)(IDA)^{3-}$	1051 ± 12	0.3
	1 : 1 : 100	9.0	580.15, 579.61	$Eu(PDTA)(IDA)(H_2O)^{3-}$	676 ± 10	0.9
			580.43	$Eu(PDTA)(IDA)^{3-}$	870 ± 8	0.5
	1 : 1 : 100	11.5	579.93	$Eu(PDTA)(OH)^{2-}$	469 ± 2	1.5
			580.43	$Eu(PDTA)(IDA)^{3-}$	870 ± 8	0.5

NTA and HIDA (figure 6). The L + HIDA ternary complex is less stable than the L + IDA and L + NTA complexes due to decreased basicity of nitrogen caused by the inductive effect of the hydroxyl. Additionally, the hydroxyethyl group in HIDA could serve to reduce the stability constants. EXAFS studies of $Eu(EDTA)(NTA)^{3-}$ at pH ~ 9.0 confirmed three binding possibilities for NTA, such as: (1) via three carboxylates, (2) via two carboxylates and a H_2O, and (3) via two carboxylates and a nitrogen. This is supported by the TRLFS and ^{13}C NMR data [21]. At pH 11.5 NTA binds via three carboxylates but not nitrogen, with EDTA hexadentate. Unfortunately with EDTA, CDTA, or PDTA + EDDA, the relatively large size of the EDDA results in steric hindrance and fails to form ternary complexes. However, for the first five lanthanides, formation of a ternary complex is reported for HEDTA + EDDA [23]

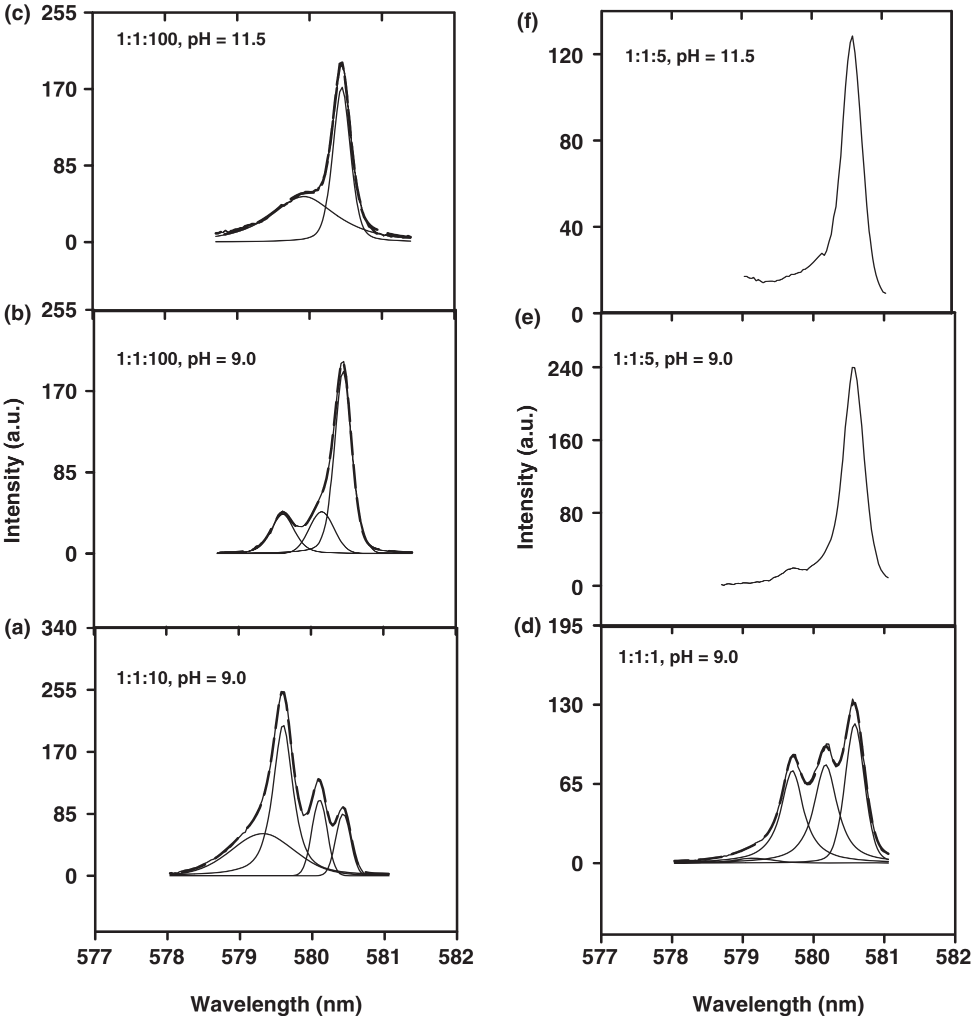

Figure 3. The $^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu(III) complexes with PDTA + IDA; (a) 1 : 1: 10, pH = 9.0; (b) 1 : 1 : 100, pH = 9.0; (c) 1 : 1 : 100, pH = 11.5; and Eu-EDTA-IDA; (d) 1 : 1 : 1, pH = 9.0; (e) 1 : 1 : 5, pH = 9.0 and (f) 1 : 1 : 5, pH = 11.5; Eu(III) = 1.0×10^{-4} M, I = 0.1 M ($NaClO_4$).

(HEDTA = hydroxyethylethylenediamine triacetate). The ternary complexes are less stable except for La(III) and the stability decreases with increasing Z. Stability of lanthanides has the pattern HEDTA + HIDA > HEDTA + EDDA > HEDTA + IDA. The above trend in stability reflects the steric effect, size, and complexing ability of the lanthanides, which are dominant factors in the stability of complexation.

With the smaller Ox, formation of two ternary complexes 1 : 1 : 1 and 1 : 1 : 2 is observed (table 7). The 1 : 1 : 1 ternary complexes are reported for Nd and Er at a ratio of 1 : 1 : 3 by TRLFS and by potentiometric titration for the lanthanides series [19, 24]. Their stability order increases in the same order as the stability constant of the corresponding binary complex, i.e., log β_{1011} (CDTA + Ox) > log β_{1011} (EDTA + Ox) > log β_{1011} (PDTA + Ox) (figure 7). The N_{H_2O} value of *ca.* 2.2 for $Cm(L)(Ox)^{3-}$ is

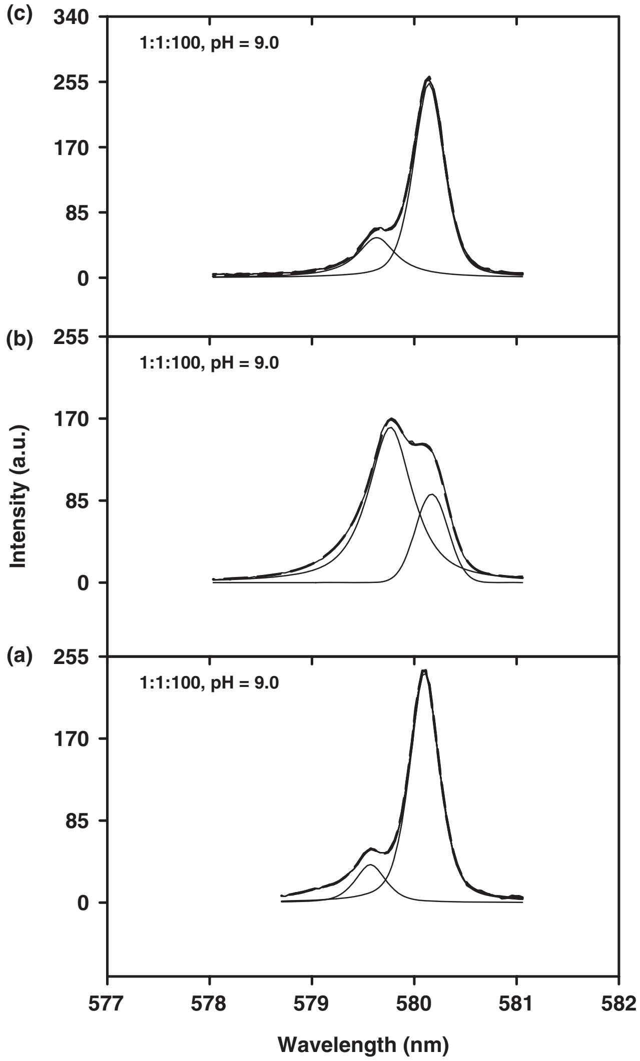

Figure 4. The $^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu(III) complexes with L + MIDA; (a) Eu-EDTA-MIDA, 1 : 1 : 100, pH = 9.0; (b) Eu-CDTA-MIDA, 1 : 1 : 100, pH = 9.0; (c) Eu-PDTA-MIDA, 1 : 1 : 100, pH = 9.0; Eu(III) = 1.0×10^{-4} M, $I = 0.1$ M ($NaClO_4$).

consistent with hexadentate and bidentate coordination for the L and Ox, respectively, with one water of hydration remaining attached to the metal. NMR and EXAFS data of $Eu(EDTA)(Ox)^{3-}$ confirmed such coordination in the 1 : 1 : 1 ternary complex [25]. The AB pattern of the acetate protons of EDTA in the ternary complex implies that the metal-nitrogen bond is long-lived [25]. For $Cm(EDTA)(Ox)_2^{5-}$ an N_{H_2O} value of 1.6 indicates a CN_T of 10 (6EDTA + 4Ox + 1 or $0H_2O$), which has been reported earlier for these f-cations [26]. Since both EDTA and Ox are hard base anions and have great affinity for hard acid cations such as Cm(III), it is reasonable to assume that the ternary complex has no waters of hydration. EXAFS data of $Eu(EDTA)(Ox)_2^{5-}$ suggest that one carboxylate group, either from EDTA or Ox, is unbound and the complex has no

Table 4. Spectral characteristics of ternary complexes of Eu(III) and Cm(III) with L + MIDA (L = EDTA, CDTA, and PDTA); $I = 0.1$ M ($NaClO_4$), $T = 25°C$.

Component	Ratio	pH	Peak position (nm)	Species	Lifetime (μs)	N_{H_2O} (±0.5)
Eu-EDTA-MIDA	1 : 1 : 10	9.0	579.61	$Eu(EDTA)(OH)^{2-}$	361 ± 2	2.2
			580.11	$Eu(EDTA)(MIDA)(H_2O)^{3-}$	500 ± 2	1.4
	1 : 1 : 100	9.0	580.11, 579.58	$Eu(EDTA)(MIDA)^{3-}$	1048 ± 12	0.3
	1 : 1 : 10	11.5	580.11, 579.64, 579.24	$Eu(EDTA)(MIDA)^{3-}$	775 ± 9	0.7
Eu-CDTA-MIDA	1 : 1 : 10	9.0	579.50, 579.74, 580.14	$Eu(CDTA)(OH)^{2-}$	380 ± 8	2.1
				$Eu(CDTA)(MIDA)(H_2O)^{3-}$	409 ± 6	1.8
				$Eu(CDTA)(MIDA)^{3-}$	–	–
	1 : 1 : 100	9.0	580.17, 579.77	$Eu(CDTA)(MIDA)^{3-}$	840 ± 5	0.6
				$Eu(CDTA)(MIDA)(H_2O)^{3-}$		
Eu-PDTA:MIDA	1 : 1 : 10	9.0	579.61	$Eu(PDTA)(OH)^{2-}$	342 ± 8	2.4
			580.11	$Eu(PDTA)(MIDA)(H_2O)^{3-}$	595 ± 10	1.1
	1 : 1 : 100	9.0	580.11, 579.58	$Eu(PDTA)(MIDA)^{3-}$	1036 ± 10	0.3

Table 5. Spectral characteristics of ternary complexes of Eu(III) with L + ODA and TDA (L = EDTA, CDTA, and PDTA); $I = 0.1$ M ($NaClO_4$), $T = 25°C$.

Component	Ratio	pH	Peak position (nm)	Species	Lifetime (μs)	N_{H_2O} (±0.5)
Eu-EDTA-ODA	1 : 1 : 100	9.0	579.64, 580.11 580.01	$Eu(EDTA)(ODA)^{3-}$	662 ± 3	0.9
Eu-CDTA-ODA	1 : 1 : 10	9.0	579.68, 580.04	$Eu(CDTA)(ODA)^{3-}$	769 ± 8	0.7
Eu-PDTA-ODA	1 : 1 : 10	9.0	579.64, 580.08 578.98	$Eu(PDTA)(ODA)^{3-}$	662 ± 6	0.9
	1 : 1 : 50	9.0	579.64, 580.08 578.98	$Eu(PDTA)(ODA)^{3-}$	813 ± 7	0.6
Eu:EDTA:TDA	1 : 1 : 100	9.0	579.64, 580.11	$Eu(EDTA)(OH)^{2-}$	478 ± 8	1.5
			580.01	$Eu(EDTA)(TDA)^{3-}$	529 ± 10	1.3
Eu-CDTA-TDA	1 : 1 : 100	9.0	579.80, 579.28	$Eu(CDTA)(OH)^{2-}$	388 ± 9	2.0
			580.16	$Eu(CDTA)(TDA)^{3-}$	781 ± 6	0.6
Eu-PDTA-TDA	1 : 1 : 100	9.0	579.61, 579.04	$Eu(PDTA)(OH)^{2-}$	421 ± 7	1.8
			580.08	$Eu(PDTA)(TDA)^{3-}$	840 ± 7	0.6

water of hydration [25]. A similar decrease in N_{H_2O} for the ternary complexes (table 7) of $M(EDTA)^-$, $M(CDTA)^-$, and $M(PDTA)^-$ with Ox indicates that the binding modes of the ligands in these complexes are the same. The residual hydration of the ternary complexes of Cm(III) is, in general, larger than for the corresponding Eu(III) complexes, consistent with the larger average coordination of Cm(III) compared to Eu(III) [8].

4. Conclusion

Both the decay constants and stability constant measurements indicate that under the conditions of this study EDTA, CDTA, and PDTA form 1 : 1 complexes. The formation of ternary hydroxyl complexes are observed at $pH > 9.0$. Complexation strength follows the order: CDTA > EDTA > PDTA. Addition of a

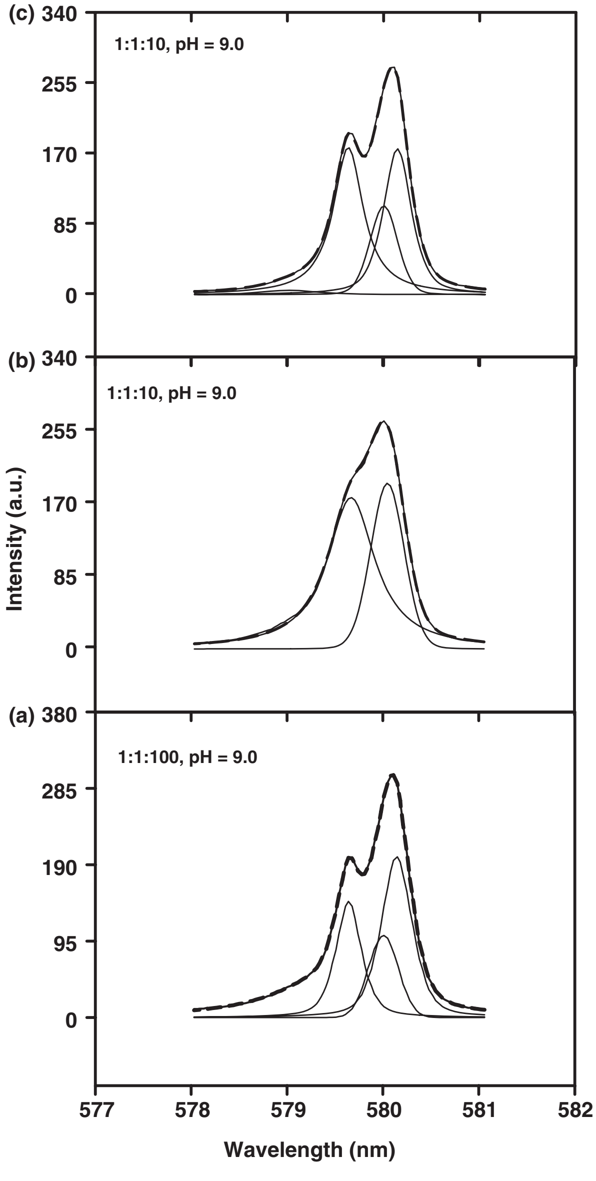

Figure 5. The $^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu(III) complexes with L + ODA; (a) Eu-EDTA-ODA, 1 : 1 : 100, pH = 9.0; (b) Eu-CDTA-ODA, 1 : 1 : 10, pH = 9.0; (c) Eu-PDTA-ODA, 1 : 1 : 10, pH = 9.0; Eu(III) = 1.0×10^{-4} M, $I = 0.1$ M ($NaClO_4$).

secondary ligand results in the formation of ternary complexes for all these systems. The dicarboxylates IDA, MIDA, ODA, and TDA form 1 : 1 : 1 ternary complexes. In all these complexes, the primary ligands (L = EDTA, CDTA or PDTA) retain hexadentate coordination with IDA, MIDA, and ODA binding via tridentate coordination for a CN_T of 9. The stability order L + MIDA > L + IDA > L + ODA reflects the importance of ligand basicity on formation of ternary complexes. TDA has a sulfur which is not involved in complexation and the complexes have a water of hydration for $CN_T = 9$.

Table 6. Spectral characteristics of ternary complexation of Cm(III) and Eu(III) with IDA, EDTA, CDTA, and PDTA + L (L = NTA and HIDA); $I = 0.1$ M ($NaClO_4$), $T = 25°C$.

Component	Ratio	pH	Peak position (nm)	Species	Lifetime (μs)	N_{H2O} (±0.5)
Cm-EDTA-NTA	1 : 1 : 20	9.0	401.98, 400.00, 397.36	$\mathrm{Cm(EDTA)(NTA)^{4-}}$	388 ± 12	0.8
			404.44	$\mathrm{Cm(EDTA)(HNTA)^{3-}}$	326 ± 15	1.1
				$\mathrm{Cm(NTA)_2^{3-}}$		
	1 : 1 : 50	9.0	401.63, 400.07, 396.98	$\mathrm{Cm(EDTA)(NTA)^{4-}}$	384 ± 15	0.8
			404.51	$\mathrm{Cm(EDTA)(HNTA)^{3-}}$	330 ± 15	1.1
				$\mathrm{Cm(NTA)_2^{3-}}$		
	1 : 1 : 50	11.5	402.05, 400.15, 397.28	$\mathrm{Cm(EDTA)(NTA)^{4-}}$	401 ± 15	0.7
			404.49	$\mathrm{Cm(NTA)_2^{3-}}$	337 ± 15	1.1
Cm-CDTA-NTA	1 : 1 : 20	3.6	401.64, 399.50, 396.18	$\mathrm{Cm(CDTA)^{-}}$	153 ± 6	3.1
	1 : 1 : 20	9.0	402.25, 400.08, 396.59	$\mathrm{Cm(CDTA)(NTA)^{4-}}$	383 ± 8	0.8
			404.45	$\mathrm{Cm(CDTA)(HNTA)^{3-}}$	323 ± 8	1.1
				$\mathrm{Cm(NTA)_2^{3-}}$		
	1 : 1 : 50	9.0	402.28, 400.22, 397.21	$\mathrm{Cm(CDTA)(NTA)^{4-}}$	387 ± 7	0.8
			404.45	$\mathrm{Cm(CDTA)(HNTA)^{3-}}$	323 ± 8	1.1
				$\mathrm{Cm(NTA)_2^{3-}}$		
Cm-PDTA-NTA	1 : 1 : 50	3.6	402.03, 399.24, 396.48	$\mathrm{Cm(PDTA)^{-}}$	145 ± 5	3.5
	1 : 1 : 50	9.0	401.98, 400.12, 397.56	$\mathrm{Cm(PDTA)(NTA)^{4-}}$	345 ± 5	1.0
			404.31	$\mathrm{Cm(PDTA)(HNTA)^{3-}}$	319 ± 6	1.1
				$\mathrm{Cm(NTA)_2^{3-}}$		
	1 : 1 : 50	11.5	402.05, 400.19, 397.30	$\mathrm{Cm(PDTA)(NTA)^{4-}}$	343 ± 5	1.2
			404.25	$\mathrm{Cm(PDTA)(HNTA)^{3-}}$	324 ± 6	1.1
				$\mathrm{Cm(NTA)_2^{3-}}$		
Eu-EDTA-NTA	1 : 1 : 2	9.0	579.66	$\mathrm{Eu(EDTA)(NTAH)^{3-}}$	488 ± 15	1.4
			580.21, 580.08	$\mathrm{Eu(EDTA)(NTA)^{4-}}$	729 ± 17	0.7
				$\mathrm{Eu(NTA)_2^{3-}}$		
	1 : 1 : 2	11.5	579.95	$\mathrm{Eu(EDTA)(NTAH)^{3-}}$	961 ± 11	0.4
			580.21, ~578.80	$\mathrm{Eu(EDTA)(NTA)^{4-}}$		
	1 : 1 : 20	7.0	579.66	$\mathrm{Eu(EDTA)(NTAH)^{3-}}$	422 ± 12	1.8
			580.16	$\mathrm{Eu(NTA)_2^{3-}}$	781 ± 12	0.6

	1 : 1 : 20	9.0	580.18	$Eu(EDTA)(NTA)^{4-}$	961 ± 12	0.4
	1 : 1 : 20	11.5	580.18	$Eu(EDTA)(NTA)^{4-}$	1050 ± 12	0.3
Eu-CDTA-NTA	1 : 1 : 2-1 :1 :5	9.0	579.84	$Eu(CDTA)(HNTA)^{3-}$	704 ± 7	0.8
			580.18, 579.14	$Eu(CDTA)(NTA)^{4-}$	730 ± 8	0.7
				$Eu(NTA)_2^{3-}$		
	1 : 1 : 2-1 : 1 : 5	11.5	579.84, 578.87	$Eu(CDTA)(OH)^{2-}$	476 ± 6	1.5
	1 : 1 : 20	9.0	579.84	$Eu(CDTA)(HNTA)^{3-}$	740 ± 8	0.7
			580.15, 578.97	$Eu(CDTA)(NTA)^{4-}$	704 ± 5	0.8
				$Eu(NTA)_2^{3-}$		
	1 : 10 : 10	9.0	579.84	$Eu(CDTA)(HNTA)^{3-}$	724 ± 8	0.7
			580.18	$Eu(CDTA)(NTA)^{4-}$	662 ± 10	0.9
				$Eu(NTA)_2^{3-}$		
Eu-PDTA-NTA	1 : 1 : 2	3.6	579.61, 580.16	$Eu(PDTA)^{-}$	336 ± 6	2.4
	1 : 1 : 2	9.0	579.61	$Eu(PDTA)(NTAH)^{3-}$	589 ± 9	1.1
			580.17, 580.04	$Eu(PDTA)(NTA)^{4-}$	909 ± 10	0.5
				$Eu(NTA)_2^{3-}$		
	1 : 1 : 2	11.5	579.62	$Eu(PDTA)(NTAH)^{3-}$	574 ± 8	1.1
			580.18, 580.04	$Eu(PDTA)(NTA)^{4-}$	892 ± 10	0.5
				$Eu(NTA)_2^{3-}$		
Eu-EDTA-HIDA	1 : 1 : 5–10	9.0	580.08, 579.61	$Eu(EDTA)^{-}$	337 ± 5	2.7
	1 : 1 : 100	9.0	580.11, 579.97, 579.61	$Eu(EDTA)(HIDA)^{3-}$	752 ± 8	0.7
				$Eu(HIDA)_2^{-}$		
	1 : 1 : 10	11.5	579.61	$Eu(EDTA)(OH)^{2-}$	423 ± 5	1.8
			580.11	$Eu(EDTA)(HIDA)^{3-}$	621 ± 5	1.0
Eu-CDTA-HIDA	1 : 1 : 10	9.0	579.74	$Eu(CDTA)^{-}$	308 ± 6	2.7
			580.11	$Eu(CDTA)(HIDA)^{3-}$	444 ± 8	1.7
	1 : 1 : 100	9.0	580.11, 579.81	$Eu(CDTA)(HIDA)^{3}$	581 ± 10	1.1
				$Eu(HIDA)_2^{-}$		
Eu-PDTA-HIDA	1 : 1 : 10	9.0	580.11, 579.61	$Eu(PDTA)(OH)^{2-}$	358 ± 7	2.2
	1 : 1 : 100	9.0	580.09, 579.96, 579.61	$Eu(PDTA)(HIDA)^{3}$	549 ± 6	1.2
				$Eu(HIDA)_2^{-}$		

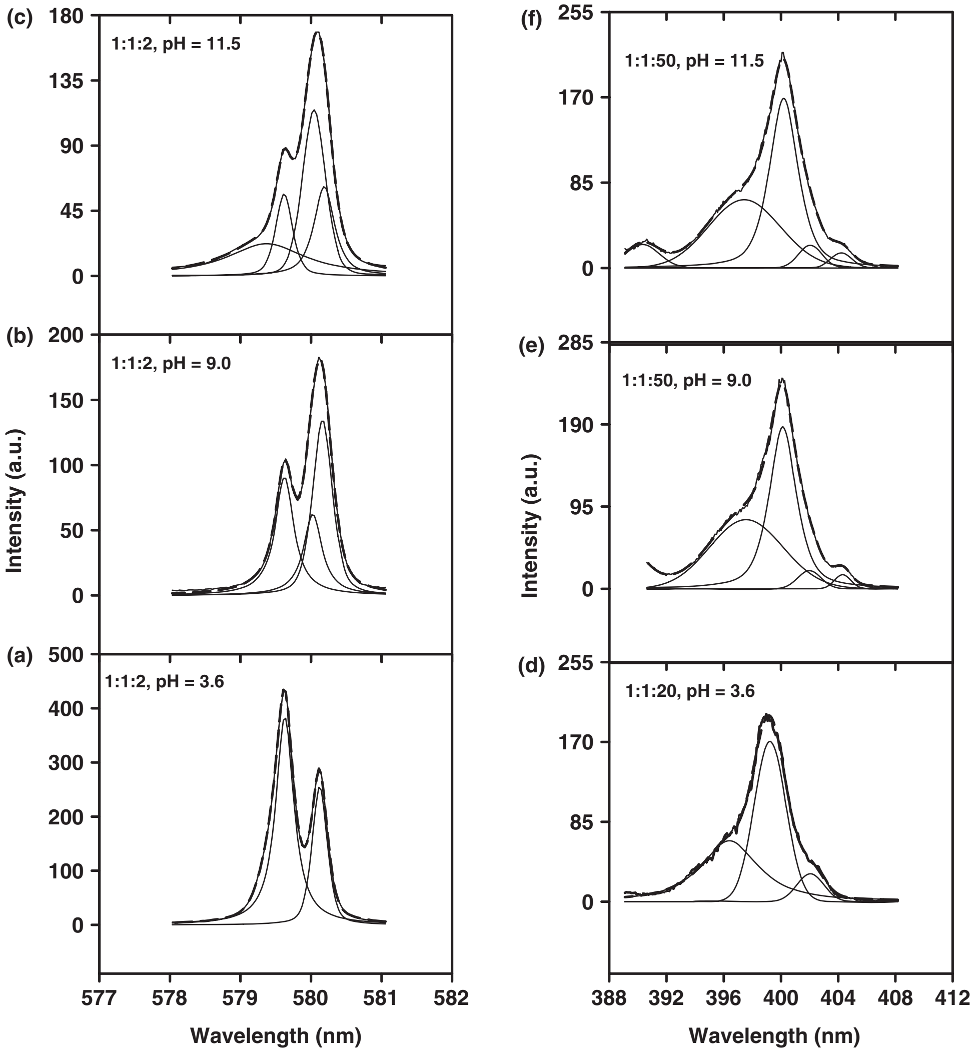

Figure 6. The excitation spectra of Eu-PDTA-NTA (a) 1 : 1 : 2; pH = 3.60; (b) 1 : 1 : 2, pH = 9.0; (c) 1 : 1 : 2, pH = 11.5 and Cm-PDTA-NTA (d) 1 : 1 : 20, pH = 3.60; (e) 1 : 1 : 50, pH = 9.0 and (f) 1 : 1 : 50, pH = 11.5; Cm(III) = 4.0×10^{-6}; Eu(III) = 1.0×10^{-4} M; $I = 0.1$ M ($NaClO_4$) and $T = 25°C$.

The tetradentate HIDA and NTA form 1 : 1 : 1 ternary complexes. Due to steric hindrance the HIDA and NTA molecules bind via a smaller number of coordination sites in the ternary complexes. Low stability of the L + HIDA complexes reflects non-coordination of hydroxyl groups in ternary complexation. In contrast, low stability of the ternary complexes of L + NTA is due to tridentate coordination of NTA with competition between donor groups such as (a) three carboxylates (b) two carboxylates and one H_2O, and (c) two carboxylates and one nitrogen.

The bidentate Ox forms 1 : 1 : 1 and 1 : 1 : 2 ternary complexes. In the formation of 1 : 1 : 1 complexes, the L retained hexadentate coordination with Ox binding via two carboxylates and one residual water of hydration. In the 1 : 1 : 2 complex, one nitrogen

Table 7. Spectral characteristics of ternary complexes of Eu(III) with L + Ox (L = EDTA, CDTA, and PDTA); $I = 0.1$ M ($NaClO_4$), $T = 25$°C.

Component	Ratio	pH	Peak position (nm)	Species	Lifetime (μs)	N_{H_2O} (±0.5)
Cm-EDTA-Ox	1 : 1 : 50	9.0	402.55, 400.76, 399.26, 396.88	$Cm(EDTA)(Ox)^{3-}$	199 ± 7	2.4
	1 : 1 : 200	7.0	402.77, 400.80, 399.23, 396.83	$Cm(EDTA)(Ox)^{3-}$	189 ± 8	2.5
	1 : 1 : 200	9.0	403.04, 401.39, 399.49, 396.68	$Cm(EDTA)(Ox)_2^{5-}$	262 ± 8	1.6
Cm-CDTA-Ox	1 : 1 : 25	9.0	403.94, 402.16, 399.62, 396.55	$Cm(CDTA)(Ox)^{3-}$	189 ± 5	2.6
	1 : 1 : 50	9.0	403.92, 402.13, 399.58, 396.25	$Cm(CDTA)(Ox)^{3-}$	192 ± 7	2.5
	1 : 1 : 200	9.0	403.94, 402.19, 399.70, 396.52	$Cm(CDTA)(Ox)_2^{5-}$	248 ± 10	1.7
Cm-PDTA-Ox	1 : 1 : 50	9.0	401.90, 399.31, 396.61	$Cm(PDTA)(Ox)^{3-}$	204 ± 8	2.3
	1 : 1 : 100	9.0	401.90, 399.39, 396.82	$Cm(PDTA)(Ox)^{3-}$	200 ± 8	2.4
	1 : 1 : 500	9.0	402.29, 399.46, 396.50	$Cm(PDTA)(Ox)_2^{5-}$	252 ± 6	1.7
Eu-EDTA-Ox	1 : 1 : 2	3.6	579.64, 580.18	$Eu(EDTA)^{-}$	354 ± 6	2.3
			580.04	$Eu(EDTA)(Ox)^{3-}$	482 ± 8	1.5
	1 : 1 : 5	9.0	579.81, 580.01	$Eu(EDTA)(Ox)^{3-}$	485 ± 10	1.4
	1 : 1 : 9.4	6.0–9.0	579.64, 580.01	$Eu(EDTA)(Ox)_2^{5-}$	625 ± 12	0.9
Eu-CDTA-Ox	1 : 1 : 1	3.6	580.25, 579.81	$Eu(CDTA)^{-}$	389 ± 10	2.0
			580.05	$Eu(CDTA)(Ox)^{3-}$	438 ± 10	1.7
	1 : 1 : 1	6.0–9.0	580.05, 579.81	$Eu(CDTA)(Ox)^{3-}$	568 ± 8	1.1
	1 : 1 : 2	3.6	579.81	$Eu(CDTA)^{-}$	410 ± 9	1.9
			580.05	$Eu(CDTA)(Ox)^{3-}$	500 ± 9	1.4
Eu-PDTA-Ox	1 : 1 : 10	9.0	580.01, 579.54	$Eu(PDTA)(Ox)^{3-}$	386 ± 9	2.0
	1 : 1 : 40	9.0	580.01, 579.54	$Eu(PDTA)(Ox)^{3-}$	440 ± 12	1.7
	1 : 1 : 200	9.0	580.01, 579.61, 579.34	$Eu(PDTA)(Ox)_2^{5-}$	595 ± 15	1.0

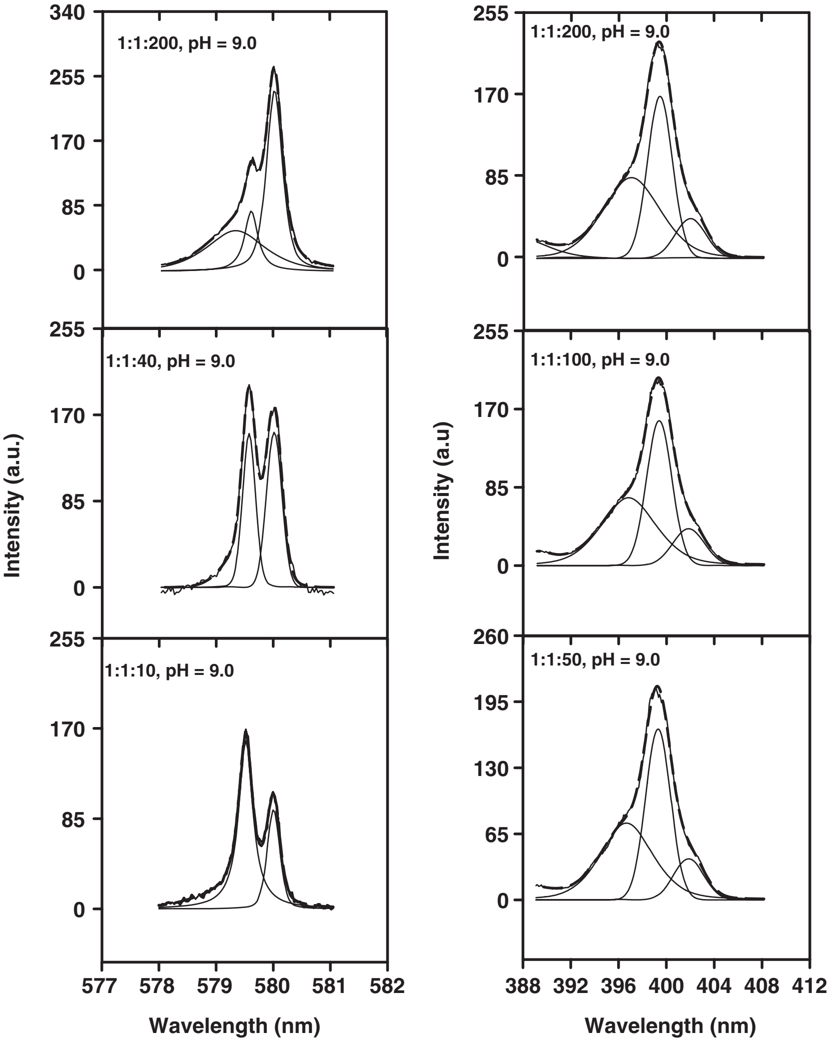

Figure 7. The excitation spectra of Eu-PDTA-Ox (a) 1 : 1 : 10; pH = 9.0; (b) 1 : 1 : 40, pH = 9.0; (c) 1 : 1 : 200, pH = 9.0 and Cm-PDTA-Ox (d) 1 : 1 : 50, pH = 9.0; (e) 1 : 1 : 100, pH = 9.0 and (f) 1 : 1 : 200, pH = 9.0; Cm(III) = 4.0×10^{-6}; Eu(III) = 1.0×10^{-4} M; $I = 0.1$ M ($NaClO_4$) and $T = 25°C$.

or one of the carboxylates of L is displaced by the second Ox group for a total CN of 9 or both L and Ox retain their full coordination for a total CN of 10. The data presented give insight into the role of the size of the cations, the steric requirements of the secondary ligands, the basicity of the ligands, and the interaction of the metal cations with the ligands. The composition of the complexes of Cm(III) and Eu(III) are the same. The hydration number of Cm(III) in these complexes is larger than that of Eu(III), consistent with the larger average coordination of Cm(III) as compared to Eu(III).

Such data has relevance for isolation of actinides present in nuclear waste stored in tanks. Organic ligands such as EDTA, CDTA, NTA etc. form strong aqueous complexes with the actinide cations, which increases the solubilities in such waste.

Because of the high stability of the ternary complexes, some fraction of the actinides in the storage tanks may be present as ternary complexes. Consequently, more complete understanding of the effects of organic ligands on the aqueous speciation, including ternary complexation, is necessary in developing effective waste processing strategies. The higher stability of the ternary complexes relative to that of the binary complexes may allow more effective use of multi-ligand reagents in ion exchange separations.

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