

Thermodynamics and the structural aspects of the ternary complexes of Am(III), Cm(III) and Eu(III) with Ox and EDTA + Ox[†]

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The stability constants and the associated thermodynamic parameters of formation of the binary and the ternary complexes of Am³⁺, Cm³⁺ and Eu³⁺ were determined by a solvent extraction to measure the variation in the distribution coefficient with temperature (0–60 °C) for aqueous solutions of $I = 6.60$ m (NaClO₄). The formation of ternary complexes is favored by both the enthalpy (exothermic) and the entropy (endothermic) values. ¹³C NMR, TRLFS and EXAFS spectral data was used to study the coordination modes of the ternary complexes. In the formation of the complex M(EDTA)(Ox)³⁻, the EDTA retained all its coordination sites with Ox binding *via* two carboxylates and with one water of hydration remaining attached to the M³⁺. In the complex M(EDTA)(Ox)₂⁵⁻, one carboxylate, either from EDTA or Ox, is not bounded to M³⁺ and there were no water of hydration attached to these cations

Introduction

The trivalent actinide and lanthanide cations Am³⁺, Cm³⁺ and Eu³⁺ in a binary M(EDTA) complex have a total coordination number, CN of 9, CN = 6 for binding EDTA⁴⁻ anion and CN = 3 for the waters of hydration. Addition of a second ligand, such as oxalate, results in the formation of a ternary complex, for which there are many reports for lanthanides at $I \leq 1.0$ M,^{1–7} but fewer for actinide complexation.^{8–13}

The stability trends of the formation of ternary complexes of lanthanides with EDTA and monodentate fluoride, bidentate HQS (8-hydroxyquinoline-5-sulfonate) and Ox (oxalate), tridentate IDA (iminodiacetate) and tetradentate NTA (nitrilotriacetate) reflect the role of several factors; *e.g.*, size of the metal cations, spatial requirements of the ligands, steric hindrance on coordination, specific Ln³⁺–second ligand interactions, basicity of the donor atom and the change in conformation of the coordinated EDTA in the formation of the ternary complexes.^{1,2,6} The stability constants and thermodynamic parameters of the structure of the ternary complex, M(EDTA)(NTA)⁴⁻, (M³⁺ = Am³⁺, Cm³⁺ and Eu³⁺) indicate that EDTA binds *via* four carboxylates and two nitrogens, while the nature of the binding of NTA varies with the hydrogen ion concentrations.¹¹

The problem of nuclear wastes disposal has generated significant interest in the study of the coordination chemistry of actinides in solution at high temperatures and ionic strengths. Organic ligands such as EDTA, NTA, oxalic acid, citric acid *etc.*, form strong complexes with actinides and lanthanides which can be present in nuclear wastes. Such complexation results in increased solubility

of Am³⁺ and Cm³⁺ in the high level waste storage tanks (~1 M OH⁻ concentration).¹⁴

The present study measured the stability constants of the binary and ternary complexation of Am³⁺, Cm³⁺ and Eu³⁺ with Ox and EDTA + Ox at $I = 6.60$ m and $T = 0–60$ °C by the solvent extraction method. The thermodynamic parameters were determined by the temperature dependence of the stability constants. Spectroscopic techniques, (*i.e.*, time resolved laser fluorescence spectroscopy (TRLFS), ¹³C NMR and EXAFS (extended X-ray absorption fine structure)) were used to establish the coordination modes in the complexes. An understanding of fundamental aspects of actinides coordination in high ionic strength and in strongly basic solution is necessary to resolve some issues of nuclear wastes treatment for disposal.

Experimental

All chemicals were reagent grade and distilled, deionized water was used for solution preparation. Stock solutions of NaClO₄ (>98%, Sigma-Aldrich, ACS certified) were prepared and filtered through 0.45 μm membranes. The solutions of EDTA and Ox (Fisher Scientific) were prepared in 6.60 m (NaClO₄) and standardized by potentiometric titration. The Eu(ClO₄)₃ and La(ClO₄)₃ solutions were prepared from the oxides (99.99%, Aldrich) in perchloric acid (60%, Fisher Scientific), followed by dilution to the desired concentrations. The concentrations of solutions were determined by EDTA titration. Di-(2-ethylhexyl) phosphoric acid, (HDEHP, Sigma-Aldrich) and heptane (Fisher Scientific, ACS) were used as received.

After preparation in the desired solution, the radiochemical purity of the tracers ²⁴¹Am, ²⁴⁴Cm and ^{152,154}Eu (Oak Ridge National laboratory) was checked by α- and/or γ-spectrometry. The working stock of each tracer has a concentration of *ca.* 50 000 cpm per 10.0 μL. The activities of ²⁴¹Am, ²⁴⁴Cm and ^{152,154}Eu were measured in a Beckman Liquid Scintillation Counter (LSC) using Ecolite cocktail (ICN, Research Product Division).

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An Accumet 950 (Fisher Scientific) pH meter was used with glass electrodes (Corning semi-micro combination) to measure the change in pH values. The KCl solution in the salt bridge was replaced with saturated NaCl solution to avoid erratic readings by the pH-meter due to the low solubility of KClO₄ at high ionic strengths. The electrode was calibrated with 4.00 ± 0.01 and 7.00 ± 0.01 standard pH buffer. The pH meter readings (pHr) were converted to hydrogen ion concentration values (pcH) using calibration curves obtained from a series of HClO₄ and NaOH solutions of known [H⁺] in *I* = 6.60 m (NaClO₄) and *T* = 0–60 °C. The correlation equations for pHr and pcH at *I* = 6.60 m (NaClO₄) and *T* = 0–60 °C in ref. 15 were used.

Metal ion distribution experiments

The distribution ratios, ($D = [M]_{\text{total, org}}/[M]_{\text{total, aq}}$) of Am³⁺, Cm³⁺ and Eu³⁺ for aqueous phases containing Ox (1.0–6.5 (×10⁻⁴ M)) or a mixture of EDTA + Ox (EDTA, 5.0 × 10⁻⁶ M, and Ox, 1.0–7.5 (×10⁻⁴ M)) in 6.60 m (NaClO₄) solution and organic phases containing pre-equilibrated HDEHP (2 × 10⁻⁴ M for Eu³⁺ and 5 × 10⁻⁴ M for Am³⁺ and Cm³⁺) in heptane were determined in duplicate at pcH 3.60 ± 0.02 and temperature for 0 to 60 ± 0.1 °C. The details of the distribution experiments, pre-equilibration of the organic phase, counting procedures, equilibrium pH measurements and conversion of pH-meter readings (pHr) to pcH at *I* = 6.60 m (NaClO₄) and *T* = 0–60 °C are described in ref. 15.

The stability constants (β) were determined from the variation in the values of *D* as described in ref. 15. β values, in molarity, were converted to molality as discussed in ref. 11 and 15. The p*K*_a values of EDTA and Ox at *I* = 6.60 m (NaClO₄) and *T* = 0–60 °C temperatures were taken from ref. 16. The details of the data analysis for the computation of the stability constants and the thermodynamic parameters of the equilibrium reaction of complex formation and of the conversion of stability constants from molarity to molality are further described in the supplemental material.† The stability constant values (log β_{101}) of M(EDTA)⁻ at *I* = 6.60 m (NaClO₄) and *T* = 0–60 °C are also listed in Table S1 (ESI).†

¹³C NMR

All sample solutions for ¹H and ¹³C NMR were prepared in D₂O. Due to the precipitation of La³⁺/Y³⁺, a constant ionic strength of *I* = 6.60 m (NaClO₄) was not maintained in these solutions. The spectra were measured at room temperature for (1) Ox (0.025 M), (2) EDTA (0.025 M), (3) La/Y : EDTA (1 : 1), (4) La/Y : EDTA : Ox (1 : 1 : 1), and (5) La/Y : EDTA : Ox (1 : 1 : 2). The La³⁺/Y³⁺ concentrations were ~0.025 M and the pcH of the each solution were adjusted to a range of 8.2–9.3 with NaOD or DCl. The solutions of La/Y-EDTA-Ox were prepared by a dropwise addition of La³⁺/Y³⁺ to a solution of the ligands (EDTA + Ox), with care taken to increase the pcH of the solution to *ca.* 6–7 before addition of the next drop of metal ions to avoid precipitation. The spectra were measured at room temperature using a Bruker AC 300 spectrometer at 300.13 MHz for ¹H and at 75 MHz for ¹³C NMR with a deviation of ± 0.1 ppm. All chemical shift values were reported with respect to sodium trimethylsilanolate $\delta = 0.00$ ppm.

TRLFS

All fluorescence spectroscopic measurements were done in 6.60 m (NaClO₄) solution in the pcH range of 3.6 to 9.0 except for Eu : Ox. The [Eu³⁺] concentration was fixed at ~1 × 10⁻⁴ M. The luminescence spectra were measured for (1) Eu : Ox, 1 : 1, pcH = 3.6 and (2) Eu : EDTA, 1 : 1, pcH = 3.6–9.0. For the ternary system the ratios of Eu/EDTA/Ox varied between 1 : 1 : 1 to 1 : 1 : 9.4, pcH = 3.6–9.0; and (3) 1 : 10 : 10, pcH = 3.6–11.5. The low solubility of Eu-oxalate limited the study of the Eu–Ox system to low pcH and concentration ratios. The ⁷F₀ → ⁵D₀ excitation spectra of the Eu solutions were measured in 1.00 cm quartz fluorimeter cells using the instrumental setup and the data processing described in ref. 15 and 17. The coordination number CN_C, of the complex was calculated by the equation CN_C = 0.237Δ*v* + 0.628,¹⁸ where Δ*v* is the shift in excitation spectra peak of Eu³⁺_(aq) upon complexation. The number of water molecules attached to the complex were calculated by the equation *N*_{H₂O} = 1.05 *K*_{obs} – 0.70,¹⁹ where *K*_{obs} is the luminescence decay constant. *N*_{H₂O} values have an uncertainty of ±0.5.¹⁹ Spectral deconvolution of the overlapping peaks was done on Labspec software.

EXAFS

Two solutions, (1) Eu : EDTA : Ox, 1 : 1 : 1, pcH = 9.0 and (2) Eu : EDTA : Ox, 1 : 1 : 2, pcH ~ 9.0 were used for the EXAFS experiments. The concentration of europium was ~ 0.015 M in all solutions. The Eu : EDTA of 1 : 1 at pcH 6.5 was used as the standard since, under these conditions, the complex species formed is Eu(EDTA)(H₂O)₃⁻. EXAFS analysis was performed at the EuL_{III} absorption edge (6.977 keV) to determine the association of europium with the complexants EDTA and Ox. The aqueous sample (1.0 mL) was placed in heat sealed polypropylene bags and mounted on an Al sample holder having a geometry of 2 mm (H) × 20 mm (L) with a 1.5 mm thickness. Fluorescence data were collected using a 13 element Ge detector on beamline X10C at the National Synchrotron Light Source (NSLS) (Brookhaven National Laboratory). The absorption edge energy was calibrated using the first inflection point of the spectrum of an Fe foil (7.112 keV). The EXAFS data were processed using the program Ifeffit.²⁰ The theoretical EXAFS modeling code FEFF6 was used to calculate the back-scattering phase and amplitude information for individual neighboring atoms.²¹ The phase and amplitude functions were determined using the crystal structure for europium terephthalate.²² Four scans were collected per sample and the data were averaged. The amplitude reduction factor (*S*₀²) was fixed at 1.0 for all of the fits. Fitting parameters for the samples were obtained by comparison with the standards.

Results and discussion

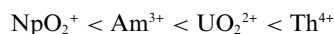
Complexation and thermodynamics

The formation of the 1 : 1 and 1 : 2 complexes of Am³⁺, Cm³⁺ and Eu³⁺ at pcH = 3.60, *I* = 6.60 m (NaClO₄) and the temperature range of 0–60 °C was calculated using eqn (1) (Fig. S1 and ESI S1–S3)†

$$D_0/D - 1 = \beta_{101}[L] + \beta_{102}[L]^2 \quad (1)$$

where $L = \text{Ox}^{2-}$, as calculated from the protonation constants of oxalic acid.¹⁶ The stability constants at 25 °C in Table 1 may be compared with existing literature data.^{23–24} For Am^{3+} , the $\log \beta_{101}$ values reported in the literature vary from 5.25–4.54 and the corresponding $\log \beta_{102}$, from 8.85–8.77 for $I = 0.1$ –14.1 m (NaClO_4) and $I = 0.1$ –5.0 m (NaCl). Our $\log \beta_{101}$ value at 25 °C is higher than the value reported in ref. 23, but the corresponding $\log \beta_{102}$ is in fair agreement with the literature data. For Cm^{3+} and Eu^{3+} no such data are reported in the literature at higher ionic strengths for comparison.

Oxalate is known to form complexes higher than 1 : 2 with these metal ions.²⁵ In the present study, the concentration of the Ox was chosen to allow formation of only the 1 : 1 and 1 : 2 complexes. For the 1 : 1 complexes, the values of the stability constant increased in the order²⁴



in accordance with the metal charge density,²⁶ reflecting strong ionic bonding. The effect of temperature on the formation constants of the complexes between hard acid cations (*e.g.*, lanthanides and actinides) and hard base anions (*e.g.*, oxygen donor ligands such as oxalate) can be estimated by the modified Born type electrostatic model^{27,28} which has a temperature dependent dielectric constant. The temperature effect of complexes is expressed as:

$$\delta(\log \beta)/\delta T = Ne^2 Z_1 Z_2 / (0.2303 R d_{12}) (1/T - 1/\theta) / (\epsilon T) \quad (2)$$

where the symbols have usual their meaning and are discussed in ref. 27. The electrostatic model predicts $\delta(\log \beta)/\delta T > 0$ if $Z_1 Z_2 < 0$, and the magnitude of the temperature coefficient, $\delta(\log \beta)/\delta T$, is proportional to $|Z_1 Z_2|$; *i.e.*, the interaction between species of opposite charges is stronger with increased temperature. Table 2 shows the effect of temperature on the formation of the 1 : 1 and 1 : 2 complexes of Am^{3+} , Cm^{3+} and Eu^{3+} with Ox, which agree well with the prediction based on the electrostatic model. This is also the case of the temperature effect on complexation of Nd^{3+} -acetate,²⁹ UO_2^{2+} -acetate,²⁸ Sm^{3+} and UO_2^{2+} -oxydiacetate³⁰ and UO_2^{2+} -malonate.³¹

With mixtures of EDTA + Ox, a plot of $1/D$ vs. $[\text{Ox}^{2-}]$ at a fixed concentration of EDTA shows a nonlinear curve indicating the presence of more than one ternary complex (Fig. 1). The stability

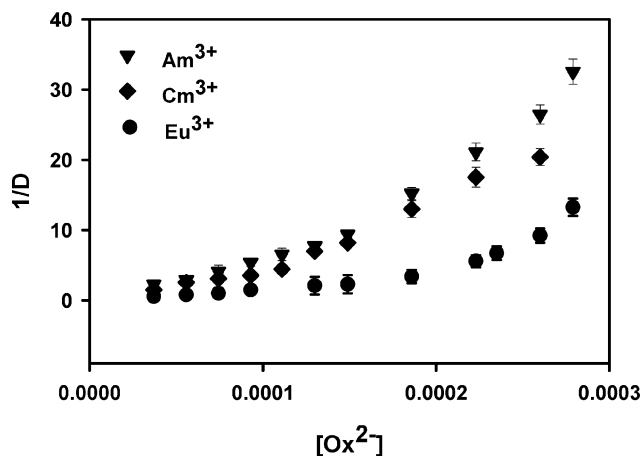


Fig. 1 Plots of $1/D$ vs. $[\text{Ox}^{2-}]$ for Am^{3+} , Cm^{3+} and Eu^{3+} at $I = 6.60$ m (NaClO_4), $T = 25$ °C and $\text{pcH} = 3.60$.

Table 1 Stability constants of Am^{3+} , Cm^{3+} and Eu^{3+} with Ox ($\log \beta_{101}$) and EDTA + Ox ($\log \beta_{111, m}$ and $(\log \beta_{112, m})$) at $\text{pcH} = 3.60$, $I = 6.60$ m (NaClO_4), $T = 0$ –60 °C

Temp/°C	Am	Eu	Temp/°C	Am	Eu
0	5.18 ± 0.08 (8.52 ± 0.08)	4.72 ± 0.07 (8.54 ± 0.10)	0	20.44 ± 0.12 (24.16 ± 0.13)	20.18 ± 0.11 (23.99 ± 0.11)
25	5.37 ± 0.09 (9.04 ± 0.09)	5.03 ± 0.08 (8.93 ± 0.09)	10	20.51 ± 0.11 (24.21 ± 0.12)	20.30 ± 0.11 (24.09 ± 0.12)
45	5.65 ± 0.08 (9.21 ± 0.11)	5.33 ± 0.09 (9.30 ± 0.11)	25	20.58 ± 0.11 (24.26 ± 0.12)	20.35 ± 0.10 (24.15 ± 0.11)
60	5.85 ± 0.09 (9.41 ± 0.11)	5.49 ± 0.08 (9.50 ± 0.11)	35	20.64 ± 0.11 (24.40 ± 0.12)	20.38 ± 0.12 (24.35 ± 0.13)
			log β_{101}/Cm		
			0	20.40 ± 0.09 (24.16 ± 0.10)	
			10	20.43 ± 0.11 (24.21 ± 0.12)	
			25	20.52 ± 0.10 (24.30 ± 0.11)	
			35	20.59 ± 0.12 (24.38 ± 0.12)	

Values in parentheses are $\log \beta_{102}$ and $\log \beta_{112}$. The values of $\log \beta_{101}$ were either taken from ref. 15 or measured (Table S1, ESI).†

Table 2 Temperature effect on the formation of the 1 : 1 and 1 : 2 complexes of Am³⁺, Cm³⁺ and Eu³⁺ with oxalate; p.w. = present work

Reaction	Z ₁ Z ₂	β ₆₀ /β ₀	Ref.
Am ³⁺ + Ox ²⁻ ⇌ Am(Ox) ⁺	-6	4.8	p.w.
Am(Ox) ⁺ + Ox ²⁻ ⇌ Am(Ox) ₂ ³⁻	-2	1.7	p.w.
Cm ³⁺ + Ox ²⁻ ⇌ Cm(Ox) ⁺	-6	5.3	p.w.
Cm(Ox) ⁺ + Ox ²⁻ ⇌ Cm(Ox) ₂ ³⁻	-2	1.4	p.w.
Eu ³⁺ + Ox ²⁻ ⇌ Eu(Ox) ⁺	-6	5.9	p.w.
Eu(Ox) ⁺ + Ox ²⁻ ⇌ Eu(Ox) ₂ ³⁻	-2	1.5	p.w.
Nd ³⁺ + Ac ⁻ ⇌ Nd(Ac) ₂ ⁺	-3	2.1 ^a	29

β₆₀/β₀ = ratio of stepwise formation constants of M(Ox)⁺ and M(Ox)₂³⁻ at T = 60 and 0 °C.^a β₇₅/β₂₅.

constants (log β₁₁₁ and log β₁₁₂) at different temperatures (evaluated using the polynomial, ESI S1–S3) are listed in Table 1. The stability constants of the 1 : 1 : 1 and 1 : 1 : 2 ternary complexes follow linear relationships with temperature. The log β₁₁₁ values of 18.94 ± 0.1 for Nd(EDTA)(Ox)₂³⁻ and 20.36 ± 0.08 for Er(EDTA)(Ox)₂³⁻, measured by Kostromina *et al.*³² for I = 0.2 m and T = 20 °C, are in fair agreement with the values of 19.13 ± 0.1 and 20.5 ± 0.1 reported by Kiraly *et al.*¹ at 25 °C and I = 1.0 m. A difference of ~1.4 log units is found for our value for Eu³⁺ at 25 °C, I = 6.60 m and the value at I = 1.0 m, reflecting the effect of the ionic media. The formation of the 1 : 1 : 2 ternary complexes were not observed in the study of Kostromina *et al.*³² but Kiraly *et al.*¹ suggested its formation for lighter lanthanides (La, Ce, Sm) in the presence of excess Ox; however, no stability constants were reported.

The thermodynamic parameters for the formation of M(Ox)⁺ and M(Ox)₂³⁻ in 6.60 m (NaClO₄) are listed in Table 3 along with the thermodynamic data of the analogous dicarboxylic ligands. The data in Table 3 indicate that the complexation of M³⁺ ions with oxalate is due to the positive entropy change since the endothermic enthalpy opposes complexation, which is the trend commonly found for the interactions between hard acid cations and hard base anions. This reflects the effects of the change in cation hydration upon complexation.³³ ΔH₁₀₂ is more endothermic than ΔH₁₀₁ while ΔS₁₀₂ is smaller than ΔS₁₀₁, reflecting the decreasing importance of the disruption of hydration of the cation relative to that of the overall enthalpies and entropies of complexation.³³ The data on the enthalpy and entropy changes (by temperature coefficient method) are reported only for Eu³⁺-oxalate system³⁴ at I = 1.0 M (NaClO₄), which is *ca.* 15.2 kJ mol⁻¹ less endothermic than our value at I = 6.60 m (NaClO₄).

The thermodynamic parameters for the formation of M(EDTA)(Ox)₂³⁻ and M(EDTA)(Ox)₂⁵⁻ in 6.60 m (NaClO₄) are listed in Table 4 (after applying corrections for the heat of deprotonation of the second proton of Ox and the last two

protons of EDTA for the ionic media). The data in Table 4 are consistent with formation of the ternary complexes being stabilized by both the enthalpy (exothermic) and the entropy (positive). The exothermic enthalpy reflects the fact that the metal–ligand interaction energy is more important than dehydration contribution. However, dehydration dominates the entropy term and is more extensive than for the formation of M(Ox)⁺ and M(Ox)₂³⁻. Within the experimental error, the values of ΔH₁₁₁ and ΔH₁₁₂ are approximately the same, reflecting decreasing importance of the disruption of the hydration sphere of the metal ions in the enthalpies of complexation.³⁴

The observed trend (*i.e.*, exothermic enthalpy for the ternary complexes M(EDTA)(Ox)₂³⁻ and M(EDTA)(Ox)₂⁵⁻ and the endothermic enthalpy for the binary complexes M(Ox)⁺ and M(Ox)₂³⁻) are also reported for the ternary complexation of lanthanides with EDTA + F at I = 1.0 m (KCl).² The negative difference in, δΔH (ΔH_{111, EDTA + F} - ΔH_{101, F} = -37.17 kJ mol⁻¹) and δΔH (ΔH_{111, EDTA + Ox} - ΔH_{101, Ox} = -72.5 kJ mol⁻¹) reflects the predominance of interaction energy in these ternary systems (where both Ox²⁻ and F⁻ are hard donor ligands with high electronegativity F and O atoms).

The exothermic enthalpy in the formation of ternary complexation of Am³⁺, Cm³⁺ and Eu³⁺ with EDTA + Ox is in contrast to that of endothermic enthalpy measured for these metal ions with EDTA + NTA and EDTA + Cit in the same ionic strength.^{11,12} In I = 6.60 m (NaClO₄), the formation of the complex M(EDTA)⁻ is a weakly endothermic process (+14.7 kJ mol⁻¹), which becomes strongly endothermic in the formation of the ternary complexes M(EDTA)(NTA)⁴⁻ (~+40 kJ mol⁻¹) and M(EDTA)(Cit)³⁻ (~90 kJ mol⁻¹, estimated from log β₁₁₁ at 25 and 60 °C). By contrast, at I = 0.1 m (KNO₃), the formation of M(EDTA)⁻ is accompanied by a less exothermic enthalpy (~10–12 kJ mol), while that of M(EDTA)(NTA)⁴⁻ and M(EDTA)(IDA)³⁻,⁶ by more exothermic enthalpies (~34–40 kJ mol). This reflects the predominant effect of the dehydration of the cation in the former and the stronger metal–ligand interaction in the latter reaction.

¹H and ¹³C NMR

The ¹H NMR spectra of La-EDTA and La-EDTA-Ox systems are shown in Fig. S2 (ESI)[†] and the assigned chemical shifts are given in Table 5. In free EDTA, the four ethylene protons and the eight acetate protons are equivalent and result in two singlets of relative intensities 1 : 2, which is consistent with the previous study.³⁵ For the La-EDTA complex, an AB quartet centered at 3.24 ppm (J_{AB} = 18.0 ± 1.0 Hz) for acetate protons and a singlet for the ethylene protons was observed. This indicates a long

Table 3 Thermodynamics of complexation of Am³⁺, Cm³⁺ and Eu³⁺ with aliphatic dicarboxylate ligands at 25 °C; p.w. = present work

	I/m (NaClO ₄)	ΔG ₁₀₁ /kJ mol ⁻¹	ΔH ₁₀₁ /kJ mol ⁻¹	ΔS ₁₀₁ /J K ⁻¹ mol ⁻¹	ΔG ₁₀₂ /kJ mol ⁻¹	ΔH ₁₀₂ /kJ mol ⁻¹	ΔS ₁₀₂ /J K ⁻¹ mol ⁻¹	Ref.
Am-oxalate	6.60	-30.53 ± 0.60	19.3 ± 4.7	167 ± 12	-51.40 ± 0.46	25.1 ± 4.2	257 ± 65	p.w.
Cm-oxalate	6.60	-30.36 ± 0.58	20.6 ± 3.5	171 ± 14	-48.95 ± 0.48	26.1 ± 4.7	252 ± 58	p.w.
Eu-oxalate	6.60	-28.60 ± 0.52	22.5 ± 4.5	171 ± 11	-50.77 ± 0.51	28.1 ± 5.5	265 ± 68	p.w.
Eu-oxalate	1.0	-30.30 ± 0.17	13.6 ± 2.5	147 ± 8.0	—	—	—	34
Eu-malonate	1.0	-26.36 ± 0.06	13.5 ± 0.09	134 ± 1.2	—	—	—	34
Eu-succinate	1.0	-20.20 ± 0.15	12.2 ± 0.15	109 ± 1.2	—	—	—	34
Eu-glutarate	1.0	-18.40 ± 0.15	13.5 ± 0.09	107 ± 1.2	—	—	—	34
Eu-adipate	1.0	-17.50 ± 0.15	10.5 ± 0.15	94 ± 1.2	—	—	—	34

Table 4 Thermodynamics of complexation of Am³⁺, Cm³⁺ and Eu³⁺ with EDTA + Ox at 25 °C, pcH = 3.60, I = 6.60 m (NaClO₄)

M ³⁺	$\Delta G_{111}/\text{kJ mol}^{-1}$	$\Delta H_{111}/\text{kJ mol}^{-1}$	$\Delta S_{111}/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta G_{112}/\text{kJ mol}^{-1}$	$\Delta H_{112}/\text{kJ mol}^{-1}$	$\Delta S_{112}/\text{J K}^{-1} \text{mol}^{-1}$
Am	-117.00 ± 0.65	9.0 ± 3.8	423 ± 10	-137.92 ± 0.73	10.1 ± 4.2	497 ± 22
Cm	-116.66 ± 0.68	-43.4 ± 5.2^a	247 ± 13^a	-138.14 ± 0.73	-34.8 ± 5.0^a	346 ± 31^a
		8.9 ± 4.2	421 ± 12		10.0 ± 3.7	497 ± 24
Eu	-115.69 ± 0.66	-43.5 ± 6.0^a	245 ± 14^a	-137.29 ± 0.73	-37.9 ± 4.6^a	336 ± 32^a
		8.7 ± 4.5	418 ± 11		11.1 ± 5.5	498 ± 25
		-43.7 ± 5.8^a	242 ± 14^a		-36.8 ± 6.2^a	337 ± 33^a

^a Residual values after applying correction for ligand deprotonation heat.

Table 5 Assigned chemical shifts (δ/ppm) of carboxylate groups and species proposed in the ¹³C NMR spectra of La³⁺/Y³⁺ with EDTA, Ox and EDTA + Ox in D₂O

Species	pcH	¹ H	¹³ C	
			-C=O	-CH ₂
Ox	8.2	—	173.5	
EDTA	9.0	2.97, 2.41	178.4	56.3, 51.7
La-EDTA, 1 : 1	9.3	2.55, AB(q)	180.0	61.6, 54.1
Y-EDTA, 1 : 1	9.2	2.67, AB(q)	180.1	62.7, 57.5
La-EDTA-Ox, 1 : 1 : 1	9.1	2.53, AB(q)	180.0, 172.2	61.3, 54.3
Y-EDTA-Ox, 1 : 1 : 1	9.3	2.69, AB(q)	180.1, 179.9	63.0, 58.9
				57.7, 52.1
La-EDTA-Ox, 1 : 1 : 2	9.2	2.52, AB(q)	180.0, 172.8	61.3, 58.7
				53.9, 51.6
Y-EDTA-Ox, 1 : 1 : 2	9.3	2.69, AB(q)	180.1, 179.9	63.0, 58.9
				57.8, 52.0

lifetime for the metal–nitrogen bond and a short lifetime for the metal–oxygen (carboxylate) bond. The observance of only one AB quartet supports equal average distances for all four Ln–O bonds and two Ln–N bonds in the Ln(EDTA)[−] complex.³⁵

The ¹H NMR spectra of the La : EDTA : Ox at a ratio of 1 : 1 : 1 and pcH = 9.1 consists of a slightly broadened AB quartet centered at 3.20 ppm with very weak side peaks and a broad peak for the ethylene protons. Oxalate does not give ¹H NMR signals. The AB pattern of the acetate protons of EDTA in the ternary complex implies that the metal–nitrogen bond is long-lived (non-labile). The metal–nitrogen bond is also observed to be long-lived in the formation of the ternary complex La(EDTA)(IDA)^{3−}.¹ The lack of significant shifts of the EDTA signals in the formation of the ternary complex La(EDTA)(Ox)^{3−}, reflects the lacks of any additional steric crowding on coordination of the smaller and less spatially demanding oxalate groups, consistent with similar observations in ref. 1 and 36 for the chemical shift of ¹H NMR spectra for EDTA in the ternary complexes La(EDTA)(Ox)^{3−} and La(EDTA)(IDA)^{3−}. At high concentration ratios of 1 : 1 : 2, the chemical shifts of acetate and ethylene protons remained the same, except for two broad signals at 2.98 and 2.42 ppm due to the slow rate of exchange between free and coordinated ligand.

The ¹H NMR spectra of Y³⁺ which usually has a CN = 8.0 showed expected shifts of signal downfield on complexation with EDTA. The AB pattern ($J_{AB} = 18.0 \pm 1.0$ Hz) for the acetate protons is consistent with the earlier report and reflects the long-lived metal–nitrogen bond. For Y(EDTA)(Ox)^{3−}, the AB quartet pattern of the acetate protons remained the same. Two separate peaks at 2.96 and 2.40 ppm due to the slow rate of exchange between free and coordinated ligand were present. At La : EDTA : Ox of 1 : 1 : 2 and pcH = 9.2, no further chemical shift was observed.

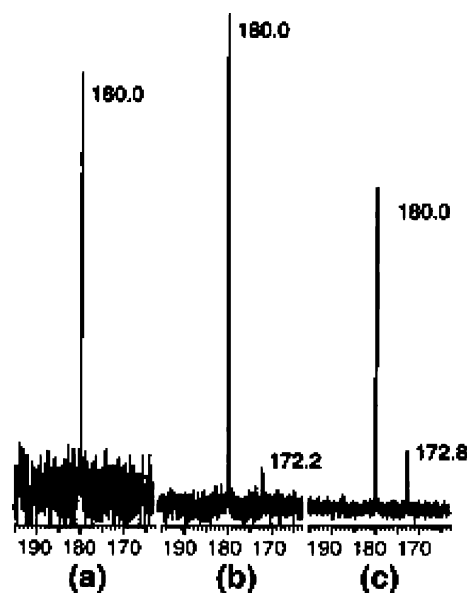


Fig. 2 ¹³C NMR spectra of (from left to right) (a) La : EDTA, 1 : 1, pcH = 9.3, (b) La : EDTA : Ox, 1 : 1 : 1, pcH = 9.1, and (c) La : EDTA : Ox, 1 : 1 : 2, pcH = 9.2.

The ¹³C NMR spectra of the binary La-EDTA and the ternary complexes of La-EDTA-Ox (Fig. 2) also support the finding of the TRLFS and ¹H NMR studies. The carboxylate carbon peak of free EDTA and Ox appeared at 178.4 and 173.5 ppm. The shift of the EDTA peak to 180.0 ppm in La : EDTA of 1 : 1 at pcH = 9.2, indicating the formation of the complex La(EDTA)[−] is consistent with data in ref. 11. At La : EDTA : Ox of 1 : 1 : 1 and pcH = 9.1, although the carboxylate carbons of EDTA show no further chemical shift, a new peak at 172.2 ppm indicates the formation of the ternary complex La(EDTA)(Ox)^{3−}. With increased concentrations of oxalate in solution (1 : 1 : 2), the position of the new peak shifted to 172.8 ppm, but the position of the carboxylate carbon peak of EDTA remains unchanged. This shift in carboxylate carbon peak of oxalate can be assigned to the second oxalate group resulting in the formation of the ternary complex La(EDTA)(Ox)₂^{5−}. The lack of additional chemical shift of carboxylate carbon of EDTA in the ternary complex reflects the absence of additional steric hindrance on coordination of oxalate groups, consistent with the results of ¹H NMR and the observations in ref. 1 and 36. However, Kiraly *et al.*¹ suggested some displacement of the functional groups of EDTA by oxalate in the formation of the complex Ln(EDTA)(Ox)₂^{5−} (Ln = La, Ce, Sm).

The ^{13}C NMR spectra of Y^{3+} indicated the formation of the ternary complex $\text{Y}(\text{EDTA})(\text{Ox})^{3-}$ at a ratio of 1 : 1 : 1 and $\text{pH} = 9.3$. However, no additional change in the chemical shift of carboxylates carbon peaks of oxalate at concentrations ratios of 1 : 1 : 2 and 1 : 1 : 3 were observed, which is in agreement with the observation in ref. 1.

The stability constants order of the ternary $\text{Ln}(\text{EDTA})(\text{Ox})^{3-}$ ($\text{Ln} = \text{Tm-Lu}$) are higher than those of the corresponding $\text{Ln}(\text{EDTA})(\text{IDA})^{3-}$ complex, indicating that there is no additional steric hindrance on coordination of the smaller oxalate in the formation of the ternary complex. However, the similarity of the stability constants order of ternary $\text{Ln}(\text{EDTA})(\text{Ox})^{3-}$ and the binary $\text{Ln}(\text{Ox})^+$ complex¹ with ionic radii indicates that some specific metal-secondary ligand interactions may play an important role in addition to that of the steric effect in the formation of the ternary complex. A similar conclusion was drawn on formation of the ternary complexes $\text{Ln}(\text{EDTA})(\text{F})^{2-}$.²

TRLFS

The $^7\text{F}_0 \rightarrow ^5\text{D}_0$ excitation spectra of Eu^{3+} at various metal-to-ligand concentration ratios and pH values are shown in Fig. 3 and the peak position, luminescence lifetime and the calculated $N_{\text{H}_2\text{O}}$ are listed in Table 6. 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 $116 \pm 3 \mu\text{s}$ and $N_{\text{H}_2\text{O}} = 8.4$, indicating that there is no effect of ionic medium on the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ excitation spectra of Eu^{3+} . This is consistent with previous reports³⁷ in which no significant effects were observed on the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ excitation spectra of Eu^{3+} in solutions of *ca.* 10 M HClO_4 and NaClO_4 ; however, above that concentration, a variation in the spectral pattern was observed.

The excitation spectra of Eu-Ox system at a ratio of 1 : 1 and $\text{pH} = 3.6$, had a single peak at 578.94 nm with a lifetime of $139 \pm 3 \mu\text{s}$ and $N_{\text{H}_2\text{O}} = 6.8$, indicating the formation of the complex $\text{Eu}(\text{Ox})^+$. Excitation spectra of Eu-Ox at higher concentrations ratios and pH 's values could not be obtained due to precipitation of Eu-oxalate .

The excitation spectra of Eu-EDTA in a solution ratio of 1 : 1 and $\text{pH} = 3.6-8.0$ has two peaks at 579.64 and 580.18 nm with an average lifetime of $311 \pm 5 \mu\text{s}$ and $N_{\text{H}_2\text{O}} = 2.7$, which

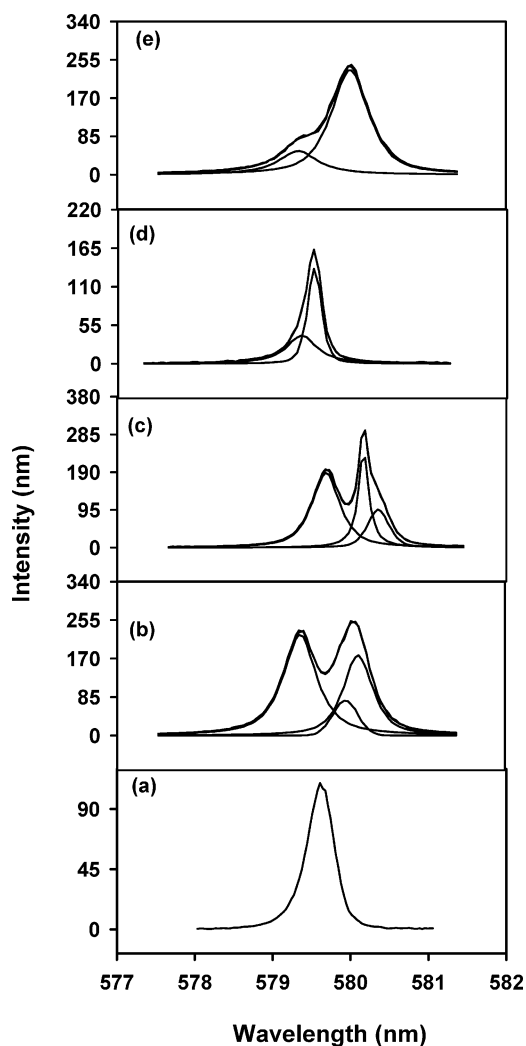


Fig. 4 The $^5\text{F}_0 \rightarrow ^7\text{D}_0$ excitation spectra of $\text{Eu}(\text{III})$ complexes with Ox and $\text{EDTA} + \text{Ox}$ [$\text{Eu}^{3+}] = 1 \times 10^{-4}$ M, $I = 6.60$ m (NaClO_4), (a) $\text{Eu} : \text{Ox}$, 1 : 1, and $\text{Eu} : \text{EDTA} : \text{Ox}$, (b) 1 : 1 : 1, $\text{pH} = 9.0$ (c) 1 : 1 : 2, $\text{pH} = 3.6$, (d) 1 : 1 : 9.4, $\text{pH} = 3.6$, (e) 1 : 1 : 9.4, $\text{pH} = 9.0$.

is consistent with the earlier report.¹⁵ At higher pH (~ 9.0), formation of hydroxyl species $\text{Eu}(\text{OH})(\text{EDTA})(\text{H}_2\text{O})_2$ with longer

Table 6 Spectral characteristics of Eu^{3+} complexes with Ox and $\text{EDTA} + \text{Ox}$ at $I = 6.60$ m (NaClO_4)

$\text{Eu} : \text{EDTA} : \text{Ox}$	Species	pH	Peak position/nm	Lifetime/ μs	$N_{\text{H}_2\text{O}}$ (± 0.5)
1 : 0 : 0	Eu^{3+} (aq)	2.2	578.90	116 ± 3	8.4
1 : 0 : 1 ^a	$\text{Eu}(\text{Ox})^+$	3.6	578.94	139 ± 3	6.8
1 : 1 : 0	$\text{Eu}(\text{EDTA})^-$	3.6–8.0	579.64, 580.18	311 ± 5	2.7
1 : 1 : 0	$\text{Eu}(\text{EDTA})(\text{OH})^{2-}$	9.0	579.64, 580.11	458 ± 6	1.7
1 : 1 : 1	$\text{Eu}(\text{EDTA})^-$	3.6	579.64, 580.18	325 ± 5	2.5
1 : 1 : 1	$\text{Eu}(\text{EDTA})(\text{Ox})^{3-}$	6.0–9.0	579.64, 580.18	453 ± 10	1.6
1 : 1 : 2	$\text{Eu}(\text{EDTA})^-$	3.6	579.64, 580.18	354 ± 4	2.3
	$\text{Eu}(\text{EDTA})(\text{Ox})^{3-}$		580.04	482 ± 6	1.5
1 : 1 : 5–1 : 1 : 9.4	$\text{Eu}(\text{EDTA})(\text{Ox})^{3-}$	3.6	579.81, 580.01	485 ± 5	1.4
1 : 1 : 9.4	$\text{Eu}(\text{EDTA})(\text{Ox})_2^{5-}$	6.0–9.0	579.64, 580.01	625 ± 12	0.9
1 : 10 : 10	$\text{Eu}(\text{EDTA})(\text{Ox})_2^{5-}$	3.6	579.84, 580.01	628 ± 15	0.9
	$\text{Eu}(\text{EDTA})(\text{Ox})_2^{5-}$	6.0–9.0	579.64, 580.14	520 ± 5	1.3
			580.01	641 ± 5	0.9

^a Constant ionic strength of $I = 6.60$ m (NaClO_4) was not maintained.

lifetime was observed.¹⁵ The two peaks observed for $\text{Eu}(\text{EDTA})^-$ complex are indicative of two different $\text{Eu}(\text{EDTA})^-$ complexes, *i.e.*, $\text{Eu}(\text{EDTA})(\text{H}_2\text{O})_3^-$, CN = 9.0 and $\text{Eu}(\text{EDTA})(\text{H}_2\text{O})_2^-$, CN = 8.0.³⁸ The formation of a protonated complex of EDTA was not observed in the pcH range (3.6–9.0) of our studies. However, at lower pcH (≤ 1.5) the formation of such species, $\text{Eu}(\text{EDTAH})^0$, with a lifetime of 160 μs has been reported.³⁸

The excitation spectra of $\text{Eu} : \text{EDTA} : \text{Ox}$ of 1 : 1 : 1 and pcH of 3.6 had two peaks at 579.64 and 580.18 nm with an average lifetime of $325 \pm 5 \mu\text{s}$ and $N_{\text{H}_2\text{O}} = 2.5$. Since these values are the same as those for the $\text{Eu}(\text{EDTA})(\text{H}_2\text{O})_3^-$,^{11,39} it can be concluded that there is no formation of a ternary complex at pcH = 3.6. In the pcH range between 6.0–9.0, the position of the peaks remain the same, but the intensity of the peak at 580.18 nm increases with increased pcH values. These were deconvoluted into three peaks at 579.64, 580.04 and 580.18 nm with an average lifetime of $453 \pm 10 \mu\text{s}$ and an $N_{\text{H}_2\text{O}}$ value of 1.6 which indicates the formation of a ternary complex $\text{Eu}(\text{EDTA})(\text{Ox})^{3-}$. Kostromina *et al.*³² also reported the formation of ternary complex $\text{Ln}(\text{EDTA})(\text{Ox})^{3-}$ (Ln = Nd and Er) at a Nd : EDTA : Ox ratio of 1 : 1 : 3 and pcH = 8.6.

At a ratio of 1 : 1 : 2 and pcH = 3.6, the two peaks had the same position, but the intensity of the peak at 580.18 nm increases and that at 579.64 nm decreases. Deconvolution of the spectra gave three peaks at 579.64, 580.18 and 580.04 nm with an average lifetime of $354 \pm 4 \mu\text{s}$ and $N_{\text{H}_2\text{O}} = 2.3$ at 579.64 and 580.18 nm, consistent with the formation of the complex $\text{Eu}(\text{EDTA})^-$. The lifetime of $482 \pm 6 \mu\text{s}$ and $N_{\text{H}_2\text{O}} = 1.5$ at 580.04 nm is different from the lifetime measured for the $\text{Eu}(\text{EDTA})^-$ complex, indicating the formation of a ternary complex $\text{Eu}(\text{EDTA})(\text{Ox})(\text{H}_2\text{O})^{3-}$.

For $\text{Eu}/\text{EDTA}/\text{Ox}$ ratios of 1 : 1 : 5 to 1 : 1 : 9.4 and pcH = 3.6, a single asymmetrical peak at 580.01 nm on deconvolution resolved into two peaks at 579.81 and 580.01 nm. The average lifetime of $485 \pm 5 \mu\text{s}$ and $N_{\text{H}_2\text{O}} = 1.4$ indicates the dominance of a ternary complex $\text{Eu}(\text{EDTA})(\text{Ox})(\text{H}_2\text{O})^{3-}$. With increased pcH between 6.0 to 9.0, an asymmetrical peak centered at 580.08 nm was resolved into two peaks at 579.64 and 580.01 nm with an average lifetime of $625 \pm 12 \mu\text{s}$ and $N_{\text{H}_2\text{O}} = 0.9$. The increased lifetime and decreased values of $N_{\text{H}_2\text{O}}$ indicate the formation of a second ternary complex $\text{Eu}(\text{EDTA})(\text{Ox})_2(\text{H}_2\text{O})^{5-}$. Since Ox is a

bidentate ligand, these values give CN = 11 (6 EDTA + 4 Ox + H_2O), which has been reported earlier for solution chemistry of lanthanides.⁴⁰ However, it is also possible that there is a change in the conformation of coordinated EDTA as this also has been reported in the formation of ternary complexes.¹

At a ratio of 1 : 10 : 10 and pcH = 3.6, a single peak at 580.01 nm was resolved into two peaks at 579.84 and 580.01 nm with an average lifetime of $628 \pm 15 \mu\text{s}$ and $N_{\text{H}_2\text{O}} = 0.9$. With increased pcH between 6.0–9.0, an asymmetrical broad peak centered at 580.01 nm was observed. This on deconvolution gave three peaks at 579.64, 580.04 and 580.14 nm. The lifetime of $641 \pm 5 \mu\text{s}$ and $N_{\text{H}_2\text{O}} = 0.9$ at 580.04 nm is consistent with the formation of a ternary complex $\text{Eu}(\text{EDTA})(\text{Ox})_2(\text{H}_2\text{O})^{5-}$, while an average lifetime of $520 \pm 10 \mu\text{s}$ and the $N_{\text{H}_2\text{O}}$ value of 1.3 at 579.64 and 580.14 nm are due to the formation of 1 : 2 complex of EDTA.³⁸ At pcH ~ 11.5 , the intensity of the peak decreased by a factor of *ca.* 5 and a new broad peak at ~ 578.90 nm (free Eu^{3+}) was observed. This on deconvolution gave three peaks at 578.87, 579.71 and 580.11 nm (Fig. S3, ESI).[†] The decreased lifetimes and the increased values of $N_{\text{H}_2\text{O}}$ indicate that the ternary complex is not stable at ~ 11.5 or that a hydroxyl species is competing for the coordination sites. The successive loss of one water of hydration from the inner coordination sphere of $\text{Eu}(\text{EDTA})^-$ on coordination of an Ox molecule indicates that either Ox behaves as a monodentate ligand or that a sterically less demanding Ox molecule displaces a smaller number of waters of hydration on formation of the ternary complex.

EXAFS

To confirm the existence of the ternary complexes predicted by ¹³C NMR and TRLFS studies, selected systems were studied by EXAFS to unambiguously determine the coordination environment of Eu^{3+} in these ternary complexes. Fig. 4 shows the fitted and k^3 -weighted (2.0–11.0 Å) L_{111} edge EXAFS spectra for $\text{Eu} : \text{EDTA}$ (1 : 1, pcH = 6.0), $\text{Eu} : \text{EDTA} : \text{Ox}$ (1 : 1 : 1, pcH = 9.4) and $\text{Eu} : \text{EDTA} : \text{Ox}$ (1 : 1 : 2, pcH = 9.3) and their Fourier transformed spectra in deionized water. The spectra show similarity both in phase and amplitude, supporting the similarity in the bonding

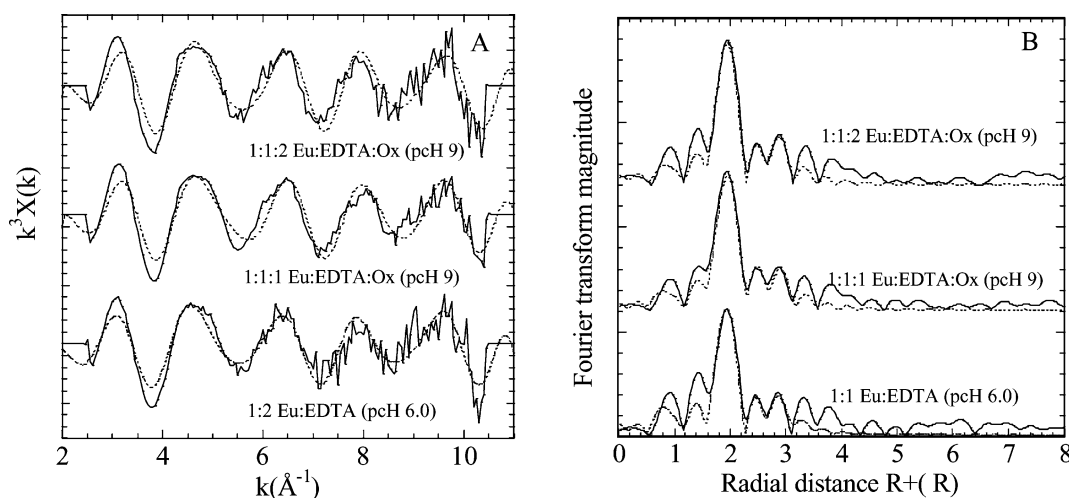


Fig. 3 The fitted k^3 -weighted (2.0–11.0 Å⁻¹) and Fourier transformed spectra showing association of Eu^{3+} with EDTA and Ox. Experimental data (—); fitted data (---).

Table 7 EXAFS fitting parameters showing the association of EDTA and oxalic acid with Eu^{3+}

Sample	Bond	N	$R/\text{\AA}$	σ^2	E_0	R
Eu : EDTA, 1 : 1	Eu–O	7.0 ± 1.2	2.45 ± 0.01	0.008 ± 0.001	5.0 ± 0.4	0.10
	Eu–N	2.0 ± 0.5	2.77 ± 0.03	0.004 ± 0.002	8.0 ± 1.1	
	Eu–C	4.0 ± 1.3	3.24 ± 0.03	0.005 ± 0.003	3.1 ± 1.0	
Eu : EDTA : Ox, 1 : 1 : 1	Eu–O	7.0 ± 1.2	2.43 ± 0.01	0.009 ± 0.002	5.0 ± 0.5	0.09
	Eu–N	1.8 ± 0.4	2.80 ± 0.05	0.002 ± 0.001	9.5 ± 2.3	
	Eu–C	6.3 ± 1.5	3.24 ± 0.04	0.006 ± 0.002	1.2 ± 1.0	
Eu : EDTA : Ox, 1 : 1 : 2	Eu–O	7.2 ± 1.4	2.43 ± 0.02	0.008 ± 0.002	2.0 ± 0.9	0.11
	Eu–N	2.0 ± 0.5	2.78 ± 0.04	0.008 ± 0.002	6.0 ± 1.9	
	Eu–C	7.5 ± 1.5	3.22 ± 0.03	0.005 ± 0.002	1.5 ± 1.0	

N = the number of atoms in each coordination shell; R is the radial distance between the two atoms of each atomic pair in Angstroms; σ^2 = the relative mean square displacement from the average path length (Debye–Waller factor); E_0 = the energy shift for the photoelectron; and R is the goodness of fit value.

of carboxylates and nitrogens. The best fit parameters and the corresponding Debye–Waller factors are given in Table 7.

The nearest neighbors of Eu in the Eu : EDTA complex are the 7.00 ± 1.20 oxygens with Eu–O distances of 2.45 ± 0.01 Å and 2.00 ± 0.5 nitrogens at a distance of 2.77 ± 0.03 Å. The Eu–O distances are the same as reported from XRD data for Eu–EDTA⁴¹ and Eu–NTA,⁴² and by EXAFS data analysis for Eu–EDTA, Eu–NTA, Eu–EDTA–NTA¹¹ and Eu–thenoyltrifluoroacetone complexes.⁴³ The Eu–N bonding distance of 2.77 ± 0.03 Å for Eu : EDTA also agrees with the distance reported previously for this complex.¹¹

The EXAFS data analysis (Table 7) confirmed the formation of $\text{Eu}(\text{EDTA})(\text{H}_2\text{O})_3^-$ in which EDTA binds *via* four carboxylate and two nitrogens which is consistent with the XRD analysis.⁴¹ The best fit of the EXAFS data for the 1 : 1 : 1.

Eu–EDTA–Ox complex indicates 7.0 ± 1.2 oxygens at 2.43 ± 0.01 Å, 6.3 ± 1.5 carbons at 3.24 ± 0.04 Å and 1.8 ± 0.04 nitrogen atoms at 2.80 ± 0.05 Å. These data lead to a total coordination number, $\text{CN} = 8.8$ (1EDTA (4 carboxylates + 2 nitrogens) + 1 Ox (2 carboxylates) + 1 H_2O) for Eu^{3+} in $\text{Eu}(\text{EDTA})(\text{Ox})(\text{H}_2\text{O})_3^-$. The TRLFS data of *ca.* 1.5 ± 0.5 waters of hydration in the complex $\text{Eu}(\text{EDTA})(\text{Ox})_3^-$ is substantiated by the EXAFS data.

At Eu : EDTA : Ox of 1 : 1 : 2, the EXAFS analysis establishes the formation of a ternary complex $\text{Eu}(\text{EDTA})(\text{Ox})_2^{5-}$. The EXAFS best fit data of 7.2 ± 1.4 oxygens at 2.43 ± 0.02 Å, 7.5 ± 1.5 carboxylate carbons at 3.22 ± 0.03 Å and 2.0 ± 0.5 N atoms at 2.78 ± 0.04 Å suggest a total $\text{CN} = 9.2$ for Eu^{3+} in $\text{Eu}(\text{EDTA})(\text{Ox})_2^{5-}$. The presence of 7.5 ± 1.5 carboxylate carbons indicates that one of the carboxylate group of either EDTA or of oxalate remains unbound in the ternary complex, $\text{Eu}(\text{EDTA})(\text{Ox})_2^{5-}$. Although the EXAFS data are consistent with the results of TRLFS and NMR (¹H and ¹³C), the TRLFS results of *ca.* 0.9 ± 0.5 water of hydration in the ternary complex $\text{Eu}(\text{EDTA})(\text{Ox})_2^{5-}$ are contrary to those of the EXAFS studies. Since both EDTA and oxalate are hard base donors and show greater preferences for the hard acid cation like Eu^{3+} , it is reasonable to assume that the ternary complex $\text{Eu}(\text{EDTA})(\text{Ox})_2^{5-}$ has no water of hydration attached to the inner coordination sphere of Eu^{3+} . It may be likely that the usually hexadentate EDTA behaves as a pentadentate ligand, allowing higher coordination for the oxalate ligands in the ternary complex. Fig. 5 shows the association of Eu^{3+} with EDTA and oxalate in the formation of ternary 1 : 1 : 1 complex, $\text{Eu}(\text{EDTA})(\text{Ox})(\text{H}_2\text{O})_3^-$. We cannot unambiguously assign the structure of the ternary 1 : 1 : 2

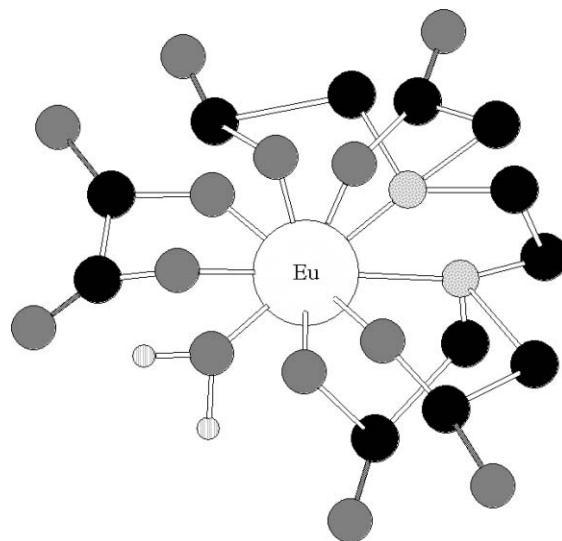


Fig. 5 Proposed structure for $\text{Eu}(\text{EDTA})(\text{Ox})(\text{H}_2\text{O})$ ternary complex; atoms: gray, O; black, C; light gray, N; vertical line, H.

complex based on this study, however, it has been proposed that the coordination modes of the ternary 1 : 1 : 2 complex are similar to that of the 1 : 1 : 1 complex; with one of the carboxylates from EDTA or oxalate remaining unbound and no water of hydration associated with the Eu^{3+} . Further research on the crystal structure of the solid compounds and/or solution is required to determine the exact structure.

Speciation calculations of Am^{3+} and Cm^{3+} in the radioactive waste storage tank solutions in the presence of large concentrations of EDTA, Cit, NTA and Ox in the pH range of 3–10, were done using the stability constants of $\text{Eu}(\text{EDTA})(\text{Ox})_3^-$, $\text{Eu}(\text{EDTA})(\text{Ox})_2^{5-}$ (present work), $\text{Eu}(\text{EDTA})(\text{NTA})_4^- = 25.96$,¹¹ $\text{Eu}(\text{EDTA})(\text{Cit})_4^- = 20.93$,¹² $\text{Eu}(\text{EDTA})_2^{5-} = 19.2$ (extrapolated from the values at $I = 0.1$ M for $\text{Eu}(\text{EDTA})^-$ and $\text{Eu}(\text{EDTA})_2^{5-}$ and of $\text{Eu}(\text{EDTA})^-$ at 6.60 m (NaClO_4) from ref. 15). At pH > 7.0 the complexes $\text{Eu}(\text{EDTA})(\text{NTA})_4^-$ and $\text{Eu}(\text{EDTA})(\text{Ox})_2^{5-}$ are present in high concentrations (Fig. 6).

Conclusion

The combined results of ¹³C NMR, TRLFS and EXAFS studies establish the formation and coordination modes of the ternary

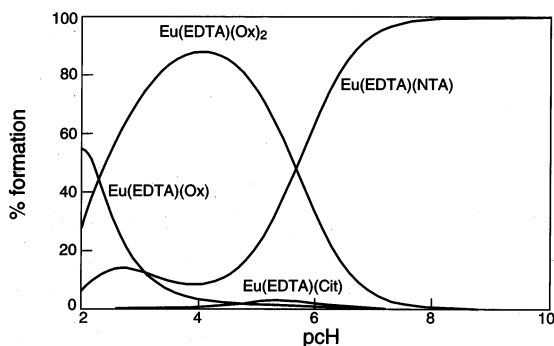


Fig. 6 Speciation diagram of trivalent Eu with mixtures of EDTA + Ox, Cit and NTA at a ratio of 1 : 10 : 10.

complexes $M(EDTA)(Ox)^{3-}$ and $M(EDTA)(Ox)_2^{5-}$. In the formation of the ternary complexes, $M(EDTA)(Ox)^{3-}$, the metal cations show a total coordination number, $CN \sim 9$ (EDTA (4 carboxylates + 2 nitrogens) + Ox (2 carboxylates) + 1 H_2O), while in the ternary complex $M(EDTA)(Ox)^{3-}$, the cations also retain a CN of ca. 9 as EDTA or oxalate undergo some structural reconstruction to allow better coordination for each other and with no water of hydration associated to the metal cations. As in the binary 1 : 1 complex, the metal–nitrogen bond remains long-lived (non-labile) in the ternary 1 : 1 : 1 and 1 : 1 : 2 complexes.

The two phase equilibrium distribution measurements of Am^{3+} , Cm^{3+} and Eu^{3+} (tracer concentrations) with EDTA and Ox provide evidence for formation of the ternary complexes $M(EDTA)(Ox)^{3-}$ and $M(EDTA)(Ox)_2^{5-}$. The associated enthalpy (exothermic) and entropy (positive) values also support formation of the ternary complexes. Increases in temperature greatly enhance the stability of the binary and the ternary complexes for which the Born type electrostatic model provides a satisfactory explanation. The relatively high concentration of the ternary complexes in the speciation profile suggests that the greater solubility of the actinides in high level waste storage tanks could be due to such ternary complexation of Am and Cm. For the treatment of the large volumes of the waste solutions, either decomposition or transmetalation of such complexes with some highly complexing nonradioactive metal ions could be useful.

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