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Review

Complexation thermodynamics and structural aspects of actinide–aminopolycarboxylates

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Contents

Abstract

The interaction of trivalent actinides with aminopolycarboxylate ligands in aqueous solution is reviewed. The strength of complexation to form binary and ternary complexes is interpreted in terms of cationic hydration and structural effects in the interaction of metal cations with aminopolycarboxylate ligands. The trends in the enthalpies and entropies of complexation of actinide and lanthanide cations are compared and discussed in terms of those effects. The results of the spectral measurements, TRLFS, ^{13}C NMR and EXAFS, provide information on the binding modes and structural aspects of the complexation. These results reflect the progress in recent years in understanding the factors determining the complexation thermodynamics and the structural aspects of the interaction of f-element cations with aminopolycarboxylates ligands.

Keywords: Actinides; Aminopolycarboxylates; Complexation thermodynamics; Ternary complexations; Spectral aspects

1. Introduction

Complexation of aminopolycarboxylates has been an active area of research in f-elements cation chemistry for over five decades. Aminopolycarboxylates such as EDTA and HEDTA were first used in the ion exchange separations of actinides from lanthanides [1,2]. An important characteristic of the f-element cations in aqueous solution is the strong ionic nature of their bonding with ligands, including the aminopolycarboxylates. The primary focus of this review is actinide–aminopolycarboxylate complexation but comparable lanthanide complexation is also discussed for comparative value.

The actinides are hard acid cations and interact preferentially with hard base donors such as fluoride or oxygen rather than with softer bases, such as nitrogen, sulfur or phosphorus atoms [3]. The interaction of actinides with aminopolycarboxylate ligands involves bonding to one or more oxygen atoms plus the nitrogen atoms in the aminopolycarboxylate ligands as such chelation

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provides greater stability. The strength of actinide bonding follows the order $AnO_2^+ < An^{3+} < AnO_2^{2+} < An^{4+}$ [4], which is the order of the effective charge density of the metal ions, i.e., +2.2 for AnO_2^+ and +3.3 for AnO_2^{2+}.

Aminopolycarboxylates form multidentate complexes with actinides, resulting in large stability constants [5,6]. The high separation factors for actinides and lanthanides and for individual actinides of the same valence state in aminopolycarboxylate complexes have been of great interest in nuclear reactor processing activities, including the disposal of highly radioactive waste solutions [5–10]. The chemistry of actinide and lanthanide complexation in solution has been extensively studied and the results of earlier research have been reviewed often [11–14]. However, the degree and the role of covalency in the bonding of the actinides remains a subject of controversy.

There is evidence of covalent bonding in actinide chemistry in the formation of the linear actinyl ions, AnO_2^+ and AnO_2^{2+}, in which participation of both f and d orbitals have been proposed in the An–O bonds. The use of sophisticated spectroscopy (e.g., two-photon laser and oxygen k-edge X-ray absorption) and advanced theoretical calculations based on the hybrid Density Functional Approach (DFA) have provided convincing evidence of covalent (An–O) interactions in actinyl ions [15]. The presence of a small amount of covalency in lanthanide bonds has been attributed to involvement of lanthanide 6s orbitals rather than of the 4f orbitals [16,17]. From a thermodynamic study, Alzuhairi and Siekierski, concluded that the covalency contributions in both series of cations varied in the order $Y^{3+} < Ln^{3+} < Am^{3+}$, which was assumed to reflect the increasing participation of 4f and 5f orbitals, respectively [18]. The larger spectral shifts (f–f absorption bands) and the higher thermodynamic stability of the Am(III)–aminopolycarboxylates than for the analogous lanthanides have been attributed to less shielding of 5f orbitals than of 4f orbitals resulting in a slightly greater degree of covalency in actinide compared to lanthanide bonding [14]. Other studies [12] also were interpreted to reflect that actinide bonding has a larger degree of covalency relative to that for lanthanide complexes; however, the f orbitals were considered as unlikely to be involved in the covalency in either group of elements.

The formation and thermodynamics of binary and ternary complexation of the transuranium (TRU) actinides with IDA, NTA, HEDTA, EDTA, CDTA, TMDTA and DTPA is also reviewed. The structural formulae of these aminopolycarboxylates are given in Fig. 1, together with those of other ligands mentioned in this review. Critically selected data for lanthanide complexation with these ligands have been used to establish trends in stability constants, thermodynamic parameters of complexation and degree of covalency in bonding of actinides. The results of TRLFS, NMR and EXAFS studies on the structural aspect of these complexes in solution are also reviewed.

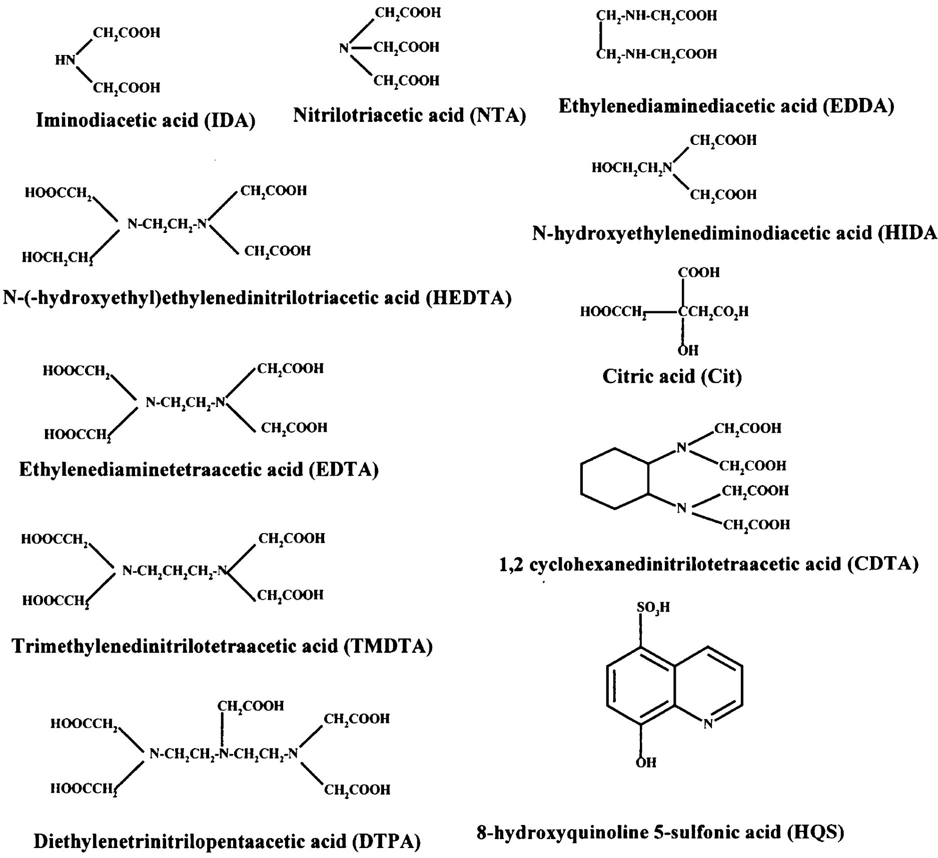

Fig. 1. Abbreviation and structural formula for ligands.

2. Binary systems

2.1. Complexation of trivalent TRU

The interactions of actinides with aminopolycarboxylates are predominantly electrostatic in nature. Consequently, the kinetics of complexation are relatively rapid and conform to the Eigen–Tamm mechanism [19]. The reaction can be described in three steps:

$$\mathrm{An}_{(\mathrm{aq})} + \mathrm{L}_{(\mathrm{aq})} \underset{(1)}{\overset{k_1}{\Leftrightarrow}} \mathrm{An}_{(\mathrm{aq})}\mathrm{L}_{(\mathrm{aq})} \underset{(2)}{\overset{k_2}{\Leftrightarrow}} \mathrm{An}(\mathrm{H_2O})_n\mathrm{L}_{(\mathrm{aq})} \underset{(3)}{\overset{k_3}{\Leftrightarrow}} \mathrm{AnL}_{(\mathrm{aq})}$$

where $k_1 > k_2 > k_3$. Step 1 represents the interaction of ligands with actinide cations in solution leading to the formation (step 2) of outer sphere ion pairs. The third step involves conversion to inner sphere An–aminopolycarboxylate complexes. This step also involves the partial or full displacement of hydration from the actinide cations to allow ligand bonding. For most aminopolycarboxylate ligands, the bonding of cation retains a partial hydration in the 1:1 complex. The stability constants of the actinides of a particular oxidation state complexed with aminopolycarboxylate ligands normally increase with increasing actinide atomic number. This reflects the increased strength of the ionic interaction with the ligand due to the decrease in ionic radii of the actinide cations as the atomic number increases. The decreased hydration caused by complexation results in a positive increase in the entropy of the system. However, as dehydration of the actinide ions requires energy to break the cation–water and water–water bonding of the hydration layers, the result is a significant endothermic contribution to the enthalpy values associated with the complexation reactions.

Direct calorimetric measurements of the heats of complexation of actinide cations have been, with rare exception, limited to elements of $Z \leq 96$, because of the problems of radiolysis involved with microconcentrations of the higher Z actinides. Temperature dependent solvent extraction experiments can be used for studies of the $Z \geq 96$ actinide cations at tracer concentrations [4,6].

Selected stability constants, log β_{101} and log β_{102}, for complexation of trivalent TRU elements with the aminopolycarboxylates are listed in Table 1.These trivalent cations generally form

Table 1
Log β_{101} and log β_{102} (in parentheses) of complexes of trivalent actinides with aminopolycarboxylates at different ionic strengths; $T = 25\ ^\circ\mathrm{C}$

Ligands	Ionic strength (m)	Pu^{3+}	Am^{3+}	Cm^{3+}	Bk^{3+}	Cf^{3+}	Es^{3+}	Fm^{3+}	Md^{3+}
IDA	0.1[a]	–	6.94[b]	7.20	–	–	–	–	–
		–	(11.4)[c]	–	–	–	–	–	–
	0.5[d]	–	7.87	7.89	–	–	–	–	–
	1.0[e]	–	6.15	–	–	–	–	–	–
NTA	0.1[a]	11.38[f]	12.01	12.29	12.50	11.89	11.30[f]	–	–
		–	(21.09)	(21.30)	(21.49)	–	–	–	–
	0.5[d]	–	11.20	11.29	11.37	11.83	11.57	–	–
	1.0[e]	10.26	–	–	–	–	–	–	–
		(19.62)	–	–	–	–	–	–	–
	6.60[d]	–	10.48	10.82	–	–	–	–	–
HEDTA	0.1[b]	15.85[f]	15.69	15.91	–	16.30	–	–	–
		–	(27.39)	(27.19)	–	(28.51)	–	–	–
	1.0[e]	14.70	–	–	–	–	–	–	–
		(21.77)	–	–	–	–	–	–	–
EDTA	0.1[a]	17.19	18.09	18.41	18.79	19.09	–	–	–
	0.5[d]	–	16.77	16.86	–	–	–	–	–
	1.0[e]	16.04	–	–	–	–	–	–	–
		(20.31)			–	–	–	–	–
	6.60[d]	–	15.88	16.06	–	–	–	–	–
CDTA	0.1[a]	–	19.52	19.61	19.91	20.19	20.18	20.19	20.19
	0.5[d]	–	18.21	18.11	–	–	–	–	–
	1.0[e]	17.70	–	–	–	–	–	–	–
TMDTA	0.1[g]	–	13.45	13.79	14.36	14.66	–	–	–
	0.5[d]	–	12.92	13.06	–	–	–	–	–
DTPA	0.1[a]	22.59	23.11	23.18	23.00	22.71	22.79	22.91	–
	0.5[d]	–	21.14	21.26	–	–	–	–	–
	1.0[e]	21.47	–	–	–	–	–	–	–

[a] 0.1 m data from ref. [6].

[b] NH_4ClO_4.

[c] Extrapolated to 0.1 m.

[d] $NaClO_4$.

[e] KCl.

[f] Extrapolated to 0.1 m KCl.

[g] NaCl, log β_{102} values in parenthesis.

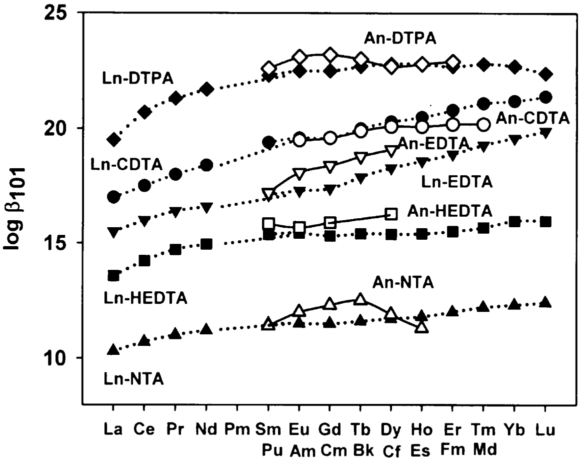

Fig. 2. Trends in log β_{101} of trivalent actinides and lanthanides with aminopolycarboxylates at $I = 0.1$ m.

1:1 and 1:2 complexes with ligands having four or fewer coordinating sites (IDA, NTA), and 1:1 complexes with ligands of $CN \geq 6$. HEDTA and EDTA are exceptions to this as they form 1:2 complexes.

IDA (CN = 3) is reported to form 1:3 complexes [6,20]. For IDA complexation, stability constants are reported only for Am^{3+} and Cm^{3+} with values in relatively close agreement with those of the analogous lanthanide complexes. Spectrophotometric studies [21] confirmed the formation of AmL^+ and AmL_2^- (L = IDA) complexes, but only the value of the 1:1 complex ($\log \beta_{101} = 6.94$ at $I = 0.10$ m (NH_4ClO_4)) was reported. The log β_{101} values of Am^{3+} by solvent extraction studies at $I = 0.5$ m ($NaClO_4$) [9] are about 1 log unit higher than that at 0.10 m (NH_4ClO_4) [21]. The 1:2 complex of IDA forms at high pH and IDA concentrations, with a $\log \beta_{102} = 11.4$ for Am^{3+} [6]. The log β_{101} and log β_{102} values of the corresponding lanthanides follow an order of increasing Z [7].

The log β_{101} values for the 1:1 complexation of the Am^{3+}, Cm^{3+}, Bk^{3+}, Cf^{3+} and Es^{3+} with NTA reported at $I = 0.1$ and 0.5 m ($NaClO_4$) [6,9] (Table 1) have a pattern of $Am^{3+} < Cm^{3+} < Bk^{3+} > Cf^{3+} > Es^{3+}$ which, with the exception of Cf^{3+} and Es^{3+}, is the trend for the order of decreasing ionic radii (Fig. 2). Due to the scarcity of data for Bk^{3+}, Cf^{3+} and Es^{3+} complexation, it is not possible to offer an explanation of the failure of Cf^{3+} and Es^{3+} to conform. The values of log β_{101} for Am^{3+} and Cm^{3+} decrease with increased ionic strength from 0.10 to 6.60 m (Table 1). In excess concentrations of ligands, formation of the 1:2 complexes occurs; the log β_{102} varies in the order $Am^{3+} < Cm^{3+} < Bk^{3+}$. The stability of the analogous lanthanide complexes has a pattern of increased log β_{101} with increased Z.

The log β_{101} values of An^{3+} with HEDTA at $I = 0.1$ m (Table 1) follow the trend $Am^{3+} < Cm^{3+} < Cf^{3+}$ which is consistent with an expected increase in stability with decreasing ionic radii. The log β_{101} values of HEDTA are about 2 log units lower than the corresponding values for EDTA complexes which is expected from the difference in the $\sum pK_a$ values for EDTA and HEDTA [22]. The formation of the 1:2 complexes was reported for Pu^{3+}, Am^{3+}, Cm^{3+} and Cf^{3+} in the presence of excess concentrations of the ligand [6]. With the exception of Cm^{3+}, the increase in stability of the 1:2 complex follows the order of decreasing ionic radii.

The hexadentate ligand EDTA forms a 1:1 complex with An^{3+} for which the stability constant is higher than those of the 1:1 complexes with IDA, NTA and HEDTA, reflecting the increase in polydentate character of the ligand. The log β_{101} of actinides with EDTA at $I = 0.1$ m (Fig. 2), follows the trend $Pu^{3+} < Am^{3+} < Cm^{3+} < Bk^{3+} < Cf^{3+}$. The 1:1 complexes of Am^{3+} and Cm^{3+} with EDTA decrease with increasing ionic strength from 0.1 to 6.60 m (Table 1). The 1:2 complex with EDTA has been reported only for Pu^{3+} [23]. The relatively low stability of the $Pu(EDTA)_2{}^{5-}$ complex is significant and is due to the second EDTA molecule binding via only two or three carboxylates [23] while the net charge on the complex becomes −5. The stability of the analogous 1:2 lanthanides complexes is also low and follows an increasing trend with Z to Eu^{3+}, with decreasing values from Eu to Tm, and no 1:2 complexation for Yb^{3+} and Lu^{3+} [20]. This trend of log β_{102} is consistent with the increasing steric hindrance of coordination of the second EDTA molecule as the cationic radii decrease with increasing atomic number.

CDTA is one of the more studied aminopolycarboxylates with known values of the stability constants of the trivalent actinides through Md^{3+} [6]. CDTA is a hexadentate ligand in which a cyclohexane ring replaces the ethylene group in EDTA, making CDTA a more rigid ligand than EDTA. Initially, it was expected that the stability constants of the actinides with CDTA would be larger from those of EDTA, resulting larger separation factors for the trivalent actinides. The values of log β_{101} increase from Am^{3+} through Cf^{3+}, and remain essentially constant from Cf^{3+} through Md^{3+} (Table 1). The $\Delta \log \beta_{101}$ (=log β_{101} CDTA − log β_{101} EDTA) for Am^{3+}, Cm^{3+}, Bk^{3+} and Cf^{3+} are in the range of 1.4–1.0 whereas for the Ln^{3+} the values vary from 1.5 (La^{3+}, Ce^{3+}), to 2.3 (Sm^{3+}, Eu^{3+}), 2.2 (Gd^{3+}), 1.9(Ho^{3+}, Er^{3+}) and 1.5 (Lu^{3+}) [7]. The values of log β_{101} of the Am^{3+}, Cm^{3+} and Bk^{3+} complexes are very similar to those of Eu^{3+}, Gd^{3+} and Tb^{3+}, while, for the higher Z actinides, the values are lower than for the corresponding lanthanides. This is in contrast to the more common trend of log β_{101} (An) > log β_{101} (Ln).

TMDTA is a hexadentate ligand with a trimethylene group in place of the ethylene group in EDTA. The log β_{101} values of Am^{3+}, Cm^{3+}, Bk^{3+} and Cf^{3+} reported for $I = 0.1$ m (NaCl) (Table 1) have an increasing order with increased Z of the actinides and are comparable to the corresponding values of the lanthanides reported also for 0.1 m [6]. TMDTA forms weaker complexes with the actinides and lanthanides than expected from the $\sum pK_a$ (i.e., the values of log β_{101} are about 6 log units lower than the value of 19.2 expected for the $\sum pK_a$ of TMDTA, 24.4 [24]). The stability constant order EDTA > TMDTA reflects that TMDTA forms weaker, six-membered $\widehat{\text{N-M-N}}$ chelate rings compared to the analogous five-membered rings with EDTA [14]. NMR data also indicates weakening of the Ln–N interaction upon expansion of the size of the chelate ring from 5 (EDTA) to 6 (TMDTA) [25].

The values of log β_{101} for complexation of trivalent actinides with the octadentate ligand DTPA increase from Pu through Cm which is consistent with the common trend for increasing Z of the An^{3+} cations. The values of $\log \beta_{101}$ decrease for Bk^{3+} and Cf^{3+}, while the Cf^{3+} and Es^{3+} complexes have similar values. The corresponding values for the lanthanides show an increasing trend to Dy^{3+}, and then have almost constant values to Yb^{3+} with a decrease for Lu^{3+}. The $\Delta\log \beta_{101} = \log \beta_{101}$ (An) − $\log \beta_{101}$ (Ln), varies from 0.3 for Pu^{3+}/Sm^{3+} to 0.6 for Am^{3+}/Eu^{3+}, 0.7 for Cm^{3+}/Gd^{3+}, 0.3 for Bk^{3+}/Tb^{3+}, 0.1 for Cf^{3+}/Dy^{3+}, 0.0 for Es^{3+}/Ho^{3+} and 0.2 for Fm^{3+}/Er^{3+}. Actinide–DTPA complexes have larger separation factors relative to those for the lanthanide–DTPA complexes compared to the difference in such values for other aminopolycarboxylate complexes. As a result, this ligand is used in the radiochemical separation of Am^{3+} and Cm^{3+} from the lanthanide fission products by solvent extraction [26]. DTPA is the main component in the Trivalent Actinide Lanthanide Separation by Phosphorus Extractants and Aqueous Komplexes (TALSPEAK) process [27]. In the TALSPEAK process, the trivalent lanthanides are extracted into the organic phase of di-(2-ethylhexyl) phosphoric acid/diisopropyl benzene from an aqueous solution containing both lactic acid and DTPA at pH 2.5–3.0 while the trivalent actinides remain in the aqueous phase.

The stability of An^{3+}–aminopolycarboxylate complexation increases with increasing polydentate character of the ligands. The complexes have common coordination numbers of 8 and 9 due to ligand coordination and residual hydration [14]. The ligands IDA, NTA, HEDTA and EDTA form 1:1 and 1:2 complexes with trivalent actinides while CDTA, TMDTA and DTPA form only 1:1 complexes. The number and the structures of the complexes are determined primarily by steric and electrostatic factors. Comparison of the $\log \beta_{101}$ values of the trivalent actinides with those of the trivalent lanthanides, Fig. 2, shows a slight enhancement in the stabilities of the actinide complexation with the aminopolycarboxylates, except for CDTA. This enhancement in stability of the actinide complexes relative to the stability of the lanthanides complexes may be a reflection of a slightly greater covalency in the actinide bonds. However, the difference in stability is relatively small and further research is needed to resolve the question of such an enhanced covalent effect in the bonding of actinides relative to lanthanide bonding and the role of such enhanced covalency in the increased separation factors for actinides. Studies based on complexation by soft donor ligands [12], synergism for actinides in solvent extraction with soft donor systems [28,29], Mossbauer and spectral chemical shifts of soft donor complexes [28] and complexation thermodynamics [28] are consistent but not definitive that a small degree of enhanced covalency is present in the bonding of trivalent actinides with soft donor ligands when compared to that in the bonding of lanthanides.

2.2. Complexation of tetra-, penta- and hexavalent TRU

Relatively few stability constants for the formation of M^{4+}, $MO_2{}^+$ and $MO_2{}^{2+}$ actinide complexes with aminopolycarboxylates ligands have been reported (Table 2).

The trend in the $\log \beta_{101}$ for tetravalent actinides is similar to that observed for the trivalent actinides (increasing $\log \beta_{101}$ values with Z). The $\log \beta_{101}$ values of Np^{4+} and Pu^{4+} complexation with NTA, HEDTA and EDTA are about 6 log units higher than those of the trivalent actinides while, for DTPA, they are about 10 units higher. The large variations in the $\log \beta_{101}$ values of Np^{4+} and Pu^{4+} with aminopolycarboxylates are most likely due to the different ionic medium and the experimental conditions used in the studies. These variations may also reflect the difficulty of maintaining Np and Pu in the tetravalent state at pH ~ 4.0.

Table 2
$\log \beta_{101}$ of complexes of tetra-, penta- and hexavalent actinides with aminopolycarboxylates at $I = 0.1$ m; $T = 25\,°C$

Ligand	Np^{4+}	Pu^{4+}	$NpO_2{}^+$	$PuO_2{}^+$	$NpO_2{}^{2+}$	$PuO_2{}^{2+}$
IDA	–	–	6.3	6.2	8.72[a]	8.50
NTA	18.5	–	6.80	6.91	–	–
HEDTA	20.8	–	–	–	6.9	–
	(33.6)	–	–	–	–	–
EDTA	26.2	27.0	7.33	–	–	–
DTPA	32.3	29.4[b]	–	–	–	–

[a] 1.0 m Na^+ salt.
[b] $T = 20\,°C$, ref. [59].

The few stability constants available for the penta- and hexavalent dioxoactinide cations indicate that the constants change little with increases in the atomic number. A small increase in $\log \beta_{101}$ is seen for the NTA complexes of $NpO_2{}^+$ and $PuO_2{}^+$, consistent with a small decrease in the ionic radii of the actinides with increasing atomic number.

2.3. Thermodynamics of complexation

The thermodynamics of formation of 1:1 complexes of trivalent actinides with aminopolycarboxylates at different ionic strengths are listed in Table 3. The thermodynamic data obtained by temperature variation measurements have larger uncertainties than those from calorimetric studies. Normally, the uncertainties of such experimental data are less from studies over wider temperature ranges. The enthalpy data obtained by solvent extraction have been corrected for the heat of protonation of ligands (for those ligands for which heat of protonation are available) at different temperatures and ionic strengths as described in ref. [30]. The positive values of enthalpies obtained from solvent extraction experiments initially becomes negative upon such corrections and are comparable to the values from calorimetric data with similar corrections. However, in some cases wide differences in data from these two studies are observed even after applying corrections.

With the exception of EDTA and NTA, the thermodynamic parameters of actinide complexation with aminopolycarboxylates are reported only for Am^{3+} and Cm^{3+} (Table 3). Within error limits, the ΔH values of 1:1 complexation of Am^{3+} and Cm^{3+} with aminopolycarboxylates are the same. For NTA, the ΔH values of actinides follow an order of decreased exothermicity from Am^{3+} through Es^{3+} (Fig. 3). The corresponding values for the lanthanides are more exothermic to Sm^{3+}; at Eu^{3+}, this trend reverses and the values become less exothermic through the remainder of the series except for Dy^{3+} through Er^{3+} which have slightly endothermic enthalpies of

Table 3
Thermodynamic parameters of Pu^{3+}, Am^{3+}, Cm^{3+} and Eu^{3+}–IDA, NTA, CDTA, EDTA, TMDTA, EDTA and DTPA complexation at 25 °C

M^{3+}–ligand	ΔG_{101} (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔS_{101} (J K^{-1} mol^{-1})	Method	*I* (m)	Ref.
Am–IDA	−44.9 ± 0.3	−4.5 ± 0.7	136 ± 3	cal	0.5[a]	[31]
	−44.9 ± 0.3	−18 ± 1[b]	90 ± 5	sx	0.5[a]	[21]
Cm–IDA	−45.0 ± 0.5	−14 ± 1	104 ± 7	sx	0.5[a]	[21]
Eu–IDA	−35.9 ± 0.3	−4.0 ± 0.9	107 ± 3	cal	0.5[a]	[31]
Am–NTA	−63.9 ± 0.3	−12.6 ± 0.6	172 ± 2	cal	0.5[a]	[31]
	−63.9 ± 0.3	−8.6 ± 0.9[b]	185 ± 4[b]	sx	0.5[a]	[21]
	−59.8 ± 0.5	+23.3 ± 2.7	279 ± 9	sx	6.60[a]	[45]
Cm–NTA	−64.4 ± 0.4	−11.5 ± 2.2	178 ± 8	cal	0.5[a]	[31]
	−64.4 ± 0.4	−3.2 ± 2[b]	205 ± 7[b]	sx	0.5[a]	[21]
	−61.7 ± 0.5	+24.7 ± 2.5	290 ± 8	sx	6.60[a]	[45]
Cf–NTA	−67.5 ± 0.3	+0.8 ± 2[b]	229 ± 2[b]	sx	0.5[a]	[21]
Es–NTA	−66.0 ± 0.3	+1.8 ± 2[b]	227 ± 2[b]	sx	0.5[a]	[21]
Eu–NTA	−63.6 ± 0.5	−7.5 ± 1.7	188 ± 6	cal	0.5[a]	[31]
	−60.0 ± 0.5	+24.5 ± 2.5	294 ± 10	sx	6.60[a]	[45]
Pu–EDTA	−103.1 ± 0.4	−17.7 ± 1	287 ± 8	cal	0.1[c]	[60]
Am–EDTA	−103.7 ± 0.5	−19.54 ± 1.0	282 ± 8	cal	0.1[c]	[60]
	−95.7 ± 0.6	−23.9 ± 1.0	241 ± 4	cal	0.5[a]	[31]
	−95.7 ± 0.6	−32.3 ± 1.5[b]	212 ± 7[b]	sx	0.5[a]	[21]
	−90.3 ± 0.5	+14.7 ± 3	352 ± 10	sx	6.60[a]	[30]
Cm–EDTA	−96.2 ± 0.5	−29.3 ± 1.3	225 ± 6	cal	0.5[a]	[34]
	−96.2 ± 0.5	−28.8 ± 2[b]	226 ± 8[b]	sx	0.5[a]	[9]
Eu–EDTA	−92.6 ± 0.4	−22.9 ± 1.3	234 ± 6	cal	0.5[a]	[34]
	−92.63 ± 0.4	−24.9 ± 0.3	227 ± 2	cal	0.5[a]	[33]
	−97.5 ± 0.2	−10.7 ± 0.2	295 ± 3	cal	0.1[d]	[43]
	–	−21.2 ± 0.1	–	cal	1.0[a]	[61]
	−95.1 ± 0.5	−10.7 ± 0.2	283 ± 3	cal	0.1[d]	[62]
	−95.1 ± 0.5	−42.5[b]	176[b]	sx	0.1[d]	[63]
Am–CDTA	−103.9 ± 0.6	−10.8 ± 0.8	312 ± 3	cal	0.5[a]	[31]
Cm–CDTA	−103.3 ± 0.6	−9.7 ± 1.9	314 ± 7	cal	0.5[a]	[31]
Eu–CDTA	−103.3 ± 0.3	−6.2 ± 0.9	326 ± 3	cal	0.5[a]	[31]
Am–TMDTA	−73.7 ± 0.3	−13.3 ± 1.0	292 ± 4	cal	0.5[a]	[31]
Cm–TMDTA	−74.5 ± 0.3	−12.7 ± 1.5	293 ± 5	cal	0.5[a]	[31,34]
Eu–TMDTA	−74.7 ± 0.3	−13.6 ± 0.7	296 ± 3	cal	0.5[a]	[31]
Am–DTPA	−120.6 ± 0.3	−39.5 ± 1	272 ± 5	cal	0.5[a]	[31]
	−120.6 ± 0.6	−16 ± 2[b]	350 ± 9[b]	sx	0.5[a]	[21]
Cm–DTPA	−121.3 ± 0.6	−14 ± 2[b]	360 ± 9[b]	sx	0.5[a]	[21]
Eu–DTPA	−119.1 ± 0.4	−39.8 ± 1.5	266 ± 5	cal	0.5[a]	[31]

[a] $NaClO_4$.
[b] Values corrected for the heat of deprotonation of the ligands.
[c] KCl.
[d] KNO_3.

complexation [7]. By contrast, at high ionic strength, the value becomes more endothermic for Am^{3+}, $Cm^{3+}$and Eu^{3+} reflecting extensive dehydration of the actinide cations as more energy is required to break the M^{3+}–H_2O bonds than the energy released during the formation of the An^{3+}–L bonds.

In Fig. 4, the enthalpies of complexation of Am^{3+} with aminopolycarboxylates are plotted versus the total number of ligand coordination sites (carboxylate + nitrogen) at $I = 0.5$ and 6.60 m [31,32]. The straight line plot supports the participation of all available carboxylate and nitrogen donors in the bond formation with M^{3+} [31]. The deviation of CDTA and TMDTA from the linear plots reflects extra dehydration of Am^{3+} for these ligands than occurs for EDTA complexation [33].

The enthalpy value of formation of $Am(Ac)^{2+}$ (Ac = acetate) is endothermic (with no M–N bond); however, the value becomes more exothermic with increasing number of metal–nitrogen bonds from one in $Am(IDA)^+$ to three in $Am(DTPA)^{2-}$ formation. This confirms the exothermic enthalpic contribution of the metal–nitrogen interactions [31,33–35]. This, also, is in agreement with ^1H NMR spectra of LnEDTA complex, which indicate long-lived Ln–N bonds, increasing from La–Lu, and short-lived Ln–O bonds [36]. However, at $I = 6.60$ m, the values of Am^{3+}, Cm^{3+} and Eu^{3+} with EDTA and NTA are endothermic. The smaller endothermicity of $Am(EDTA)^-$ complexation (with two M–N bonds) than that of the $Am(NTA)^0$ complexation (with one M–N bond) (Table 3) suggests that the endoergic dehydration effect overcomes the exoergic metal–nitrogen interactions at high ionic strength.

Fig. 5 illustrates the correlation between the residual enthalpy contribution for the interaction of metal–nitrogen bonding, cal-

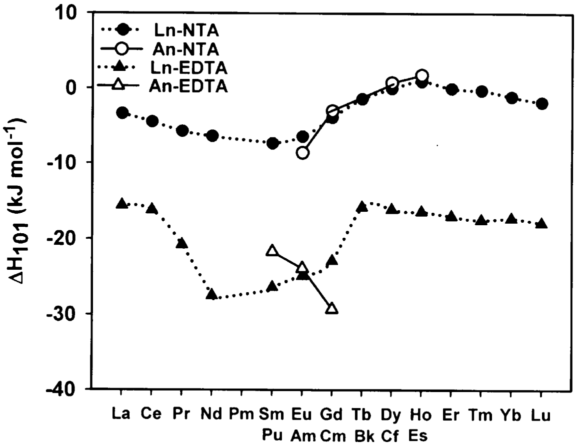

Fig. 3. Trends in enthalpies of complexation of trivalent actinides and lanthanides with NTA and EDTA at $I = 0.5$ m ($NaClO_4$).

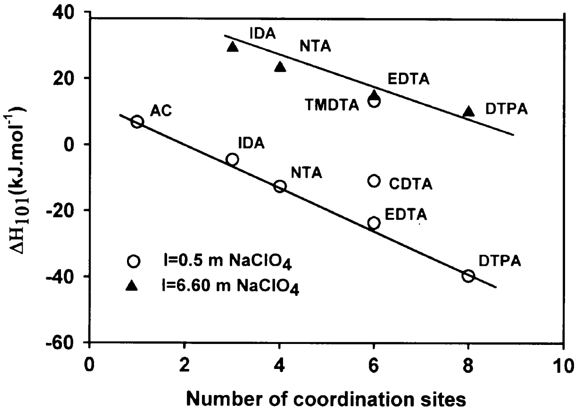

Fig. 4. Correlation between enthalpy of complexation of Am^{3+} and the number of coordination sites (carboxylates + nitrogens) of aminopolycarboxylates.

culated using the relationship $\delta(\Delta H_N) = \Delta H_{101} - n\,\Delta H_{Ac}$ versus $\sum pK(N)$, where n is the number of binding acetate groups in the ligand and ΔH_{Ac} is the enthalpy change for complexation of $Am(Ac)^{2+}$ [31,33].

This relationship is seen for all ligands (including CDTA, after correction for the excess ligand dehydration). The deviations of the IDA and TMDTA complexation from the linear pattern reflects the weaker interaction of Am–N bonds, similar to that observed for the Ln–N interaction in IDA and TMDTA complexes [31]. The residual enthalpy, $\delta(\Delta H_N)$, of AmL (L = aminopolycarboxylates) complexes plotted versus that of the corresponding EuL and CmL complexes (Fig. 6) is linear with a slope of unity, indicating no significant variations in M–N bonding of Cm^{3+} and Eu^{3+} relative to that of Am^{3+}. This indicates that the thermodynamic data for complexation of Am^{3+}, Cm^{3+} and Eu^{3+} with aminopolycarboxylates reflect no enhanced covalency in the metal–nitrogen bonds for the actinides complexes compared to that in the corresponding lanthanide complexes [31].

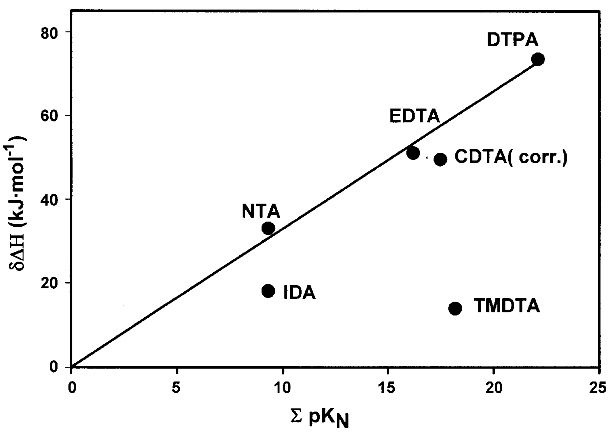

Fig. 5. Relation between the residual enthalpy $\delta(\Delta H)$ and the total basicity of the nitrogen donors ($\sum pK_N$) of the ligands for Am^{3+}-aminopolycarboxylates complex Reproduced from Ref. [31].

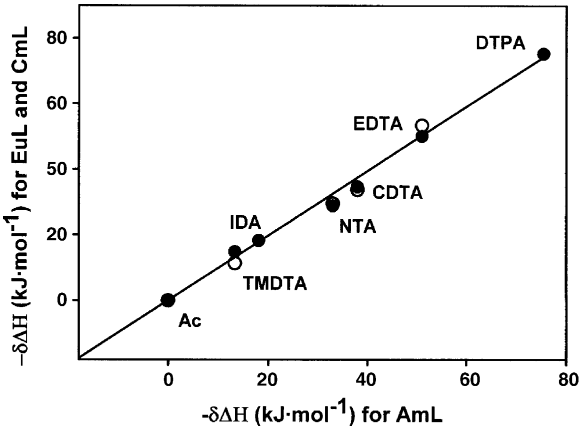

Fig. 6. Relation between $\delta(\Delta H)$ for AmL complexes and those for EuL (solid circles) and CmL (open circles) for acetate and a series of aminopolycarboxylate ligands from Ref. [31].

The entropy change for the 1:1 complexation of Am^{3+} and Eu^{3+} with aminopolycarboxylates versus n (the number of carboxylate groups) (Fig. 7) has a linear relationship with a slope of ca. 57 J K^{-1} mol^{-1}. The slope of this line is close to the value of entropy change, ca. ~60 J K^{-1} mol^{-1}, for the formation of the 1:1 complex of $Am(Ac)^{2+}$ and supports a relationship $\Delta S \approx n\,\Delta S_{Ac}$ for the entropy change [14]. The deviation of the values of CDTA and TMDTA from this relationship again reflects extra dehydration of the metal ions upon complexation

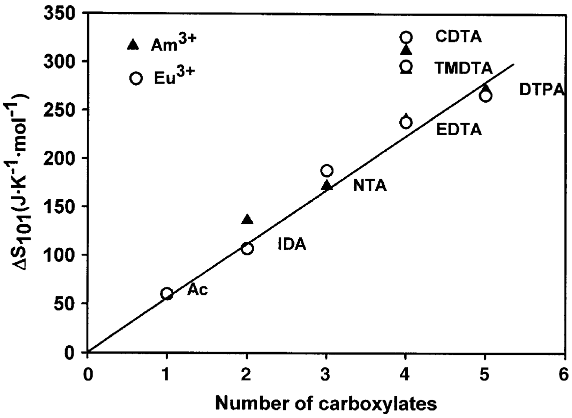

Fig. 7. Relationship between entropy of complexation and the number of ligand carboxylate groups.

with these ligands, which can be attributed to the presence of additional steric effects (cyclohexane ring in CDTA and an extra methylene group in TMDTA) in the ligand backbone [33].

3. Ternary systems

3.1. Ternary complexation of actinides

The An^{3+}cations can coordinate to as many as nine monodentate donor sites in their inner coordination sphere. In the formation of the $An(EDTA)^-$ complex, six coordination sites of an An^{3+} are occupied by EDTA; binding of water and/or secondary ligands are required to satisfy the cation coordination number of 9. Although there are a number of reports on ternary complexation of the lanthanides [37–43], formation of ternary complexes of the actinides is reported only for Pu^{4+} [44], Pu^{3+} [23], Am^{3+} and Cm^{3+} [45,46]. The $\log \beta_{111}$ values of trivalent actinides and lanthanides with EDTA, CDTA, HEDTA and DTPA as primary ligands and Cit, IDA, NTA, HIDA, HQS, HEDTA and EDDA as secondary ligands are summarized in Table 4. The values of $\log \beta_{111}$ for ternary chelate ligands are generally ca. 5 log units higher than the corresponding values of $\log \beta_{101}$ for EDTA, CDTA, HEDTA and DTPA, the values of $\log \beta_{111}$ do vary for the different primary and secondary ligand combinations. The $\log \beta_{111}$ values of Am^{3+} and Cm^{3+} with EDTA + NTA show an increasing trend with *Z* and temperature. The analogous lanthanide ternary complexes with EDTA + HQS also have an increasing trend across the series with increasing *Z*. However, the values of the ternary complexation of EDTA + IDA and EDTA + NTA show an increasing trend to Ho^{3+} and Dy^{3+}, respectively, with almost constant values from Dy^{3+} to Yb^{3+}, and an increase for Lu^{3+}. The EDTA binds via four carboxylates and two nitrogen atoms and NTA via three carboxylates [43] which is consistent with EXAFS studies which confirmed the binding of NTA via three carboxylates but not via nitrogen [45]. The stability constant order reported by Geier and Karlen [43], EDTA + NTA > EDTA + IDA is opposite to that of the stability order, EDTA + IDA > EDTA + NTA, reported by Titova et al. [47] for the ternary complexes of Sm^{3+}. The authors in ref. [47] argued the low value for the stability of EDTA + IDA complex in [43] possibly is due to the failure to include the equilibrium constant for the formation of the protonated species $SmEDTAHIDA^{2-}$ in the calculation. The low stability of the EDTA + NTA ternary complex is likely due to the binding of NTA via three donor groups with competition between complexes using one nitrogen + two carboxylates of NTA versus those simply using three carboxylates. The EXAFS studies of $Eu(EDTA)(NTA)^{4-}$ confirmed three binding possibilities for NTA at pH ~ 9.0 [45]. The lack of definitive data on the ternary complexation of EDTA + IDA and EDTA + NTA leaves this question open.

The stability sequences of the ternary complexation of HEDTA + NTA, HEDTA + HIDA and HEDTA + IDA have an increasing trend to Ho^{3+} and Dy^{3+}, with a decreasing trend to Lu^{3+}. Due to the formation of $Ln(HEDTA)(OH)^-$ for Ln^{3+} of $Z > 63$; the formation of ternary complexation with HEDTA + EDDA has been reported only for the first five lanthanides; however, their stability values, except for La^{3+}, have

Table 4
Log β_{111} for the formation of the ternary complexation of Pu^{3+}, Am^{3+}, Cm^{3+} and Eu^{3+} at 25 °C

Ligand mixture	$\log \beta_{111}$ (M^{3+})				*I* (m)	Ref.
	Pu^{3+}	Am^{3+}	Cm^{3+}	Eu^{3+}		
EDTA + Cit	–	–	21.32 ± 0.12	20.93 ± 0.13	6.60[a]	[46]
	–	–	24.38 ± 0.15[b]	23.28 ± 0.15[b]		[46]
EDTA + Cit	–	–	–	19.52 ± 0.02[c]	1.0	[65]
EDTA + NTA	–	25.73 ± 0.09	25.91 ± 0.09	25.96 ± 0.08	6.60[a]	[45]
	–	28.06 ± 0.11[b]	28.71 ± 0.11[b]	28.80 ± 0.10[b]		[45]
EDTA + NTA	21.80 ± 0.02	–	–	–	1.0[d]	[23]
	–	–	–	22.39 ± 0.52	0.1[e]	[43]
EDTA + HEDTA	21.38 ± 0.03	–	–	19.57 ± 0.02	1.0[d]	[23]
EDTA + IDA	20.68 ± 0.05	–	–	–	1.0[d]	[23]
	–	–	–	21.58 ± 0.05	0.1[e]	[43]
EDTA + HQS	–	–	–	21.76 ± 0.05	0.1[e]	[43]
DTPA + IDA	–	–	–	26.50 ± 0.03	0.2[a]	[64]
CDTA + IDA	–	–	–	21.6 ± 0.02[c]	0.3	[49]
				23.99 ± 0.02	0.2[a]	[64]
HEDTA + IDA	20.20 ± 0.05	–	–	19.60 ± 0.04	1.0[d]	[23,48]
	–	–	–	20.22 ± 0.06	0.1[e]	[37]
				20.98 ± 0.02	0.2[a]	[64]
HEDTA + NTA	19.33 ± 0.32	–	–	20.68 ± 0.04	1.0[d]	[23,48]
HEDTA + HIDA	–	–	–	20.06 ± 0.05	0.1[e]	[37]
HEDTA + EDDA	–	–	–	18.72 ± 0.05[c]	0.1[e]	[37]

[a] $NaClO_4$.
[b] 60 °C.
[c] Nd^{3+}.
[d] KCl.
[e] KNO_3.

Table 5
Thermodynamic parameters of the formation of the ternary complexes of Am^{3+}, Cm^{3+} and Eu^{3+} at 25 °C

System	ΔG_{111} (kJ mol^{-1})	ΔH_{111} (kJ mol^{-1})	ΔS_{111} (J K^{-1} mol^{-1})	Method	I (m)	Ref.
Am + EDTA + NTA	−146.29 ± 0.46	+40.0 ± 4.2	625 ± 65	sx	6.60[a]	[45]
Cm + EDTA + NTA	−147.31 ± 0.48	+41.3 ± 3.7	633 ± 58	sx	6.60[a]	[45]
Eu + EDTA + NTA	−147.59 ± 0.50	+41.4 ± 5.5	634 ± 68	sx	6.60[a]	[45]
Eu + EDTA + NTA	−125.73 ± 0.51	−40.75 ± 1.7	289 ± 7	cal	0.1[b]	[43]
Eu + EDTA + IDA	−121.21 ± 0.54	−34.02 ± 1.5	297 ± 8	cal	0.1[b]	[43]
Eu + EDTA + HQS	−122.21 ± 0.54	−34.85 ± 1.7	298 ± 8	cal	0.1[b]	[43]

[a] $NaClO_4$.
[b] KNO_3.

an increasing trend with Z. The increasing trends in stability values of the ternary complexes of EDTA + HEDTA are observed through Eu^{3+}, with the values showing a decreasing trend from Eu^{3+} to Lu^{3+}. The relatively low stability of EDTA + HEDTA ternary complexes is consistent with the steric hindrance such that the HEDTA binds only via three coordination groups [48].

The stability constant order DTPA + IDA > CDTA + IDA > EDTA + IDA > HEDTA + IDA (Table 4) is in agreement with the stability sequence order of log β_{101} of DTPA, CDTA, EDTA and HEDTA complexes of lanthanides. However, the large size and rigid structure of CDTA interferes with the tridentate binding mode and IDA has a bidentate coordination in the ternary complex $Nd(CDTA)(IDA)^{3-}$, in contrast to $Nd(EDTA)(IDA)^{3-}$, in which IDA is tridentate [49].The larger value of Pu^{4+} complex, $Pu(EDTA)(Cit)^{3-}$ (log $\beta_{111} = 33.46$) [44] relative to that of the Pu^{3+} complex $Pu(EDTA)(NTA)^{4-}$ (21.80) (Table 4) is consistent with the stronger complexing ability of the tetravalent actinides relative to that of the trivalent cations. In summary, the formation and the stability of the ternary complexes are dependent on the size and the steric requirements of the ligands and the complexing ability of the cations.

3.2. Thermodynamics of ternary complexation

The enthalpies of the ternary complexation of Am^{3+}, Cm^{3+} and Eu^{3+} with EDTA + NTA are large and positive, similar to those of the 1:1 complexation of $M(EDTA)^{-1}$ and $M(NTA)^0$ at $I = 6.60$ m (Table 5) [30,45]. This is consistent with the extensive dehydration of metal ions at such high ionic strength. Within the error uncertainty, the enthalpies of the ternary complexation of Am^{3+} follow the relationship $\Delta H_{111}(EDTA + NTA) = \Delta H_{101}(EDTA) + \Delta H_{101}(NTA)$, which indicates that the enthalpy of ternary complexation at high ionic strength is dominated by dehydration effects. By contrast, the enthalpies of ternary complexation of lanthanides are more exothermic across the series for EDTA + IDA and EDTA + NTA than for the 1:1 complexation with IDA, NTA and EDTA at $I = 0.1$ m. The large exothermicity of the ternary complexation at lower ionic strength suggests that the Ln–N interactions are predominant over dehydration effects of the lanthanide cations.

4. Structural aspects of complexation

Knowledge of the structure of the actinides and aminopolycarboxylate complexes in solution has increased significantly in the past two decades. NMR and EXAFS spectral studies have provided information on the coordination geometry, and TRLFS has given information on the number of water molecules (N_{H_2O}) in the first hydration sphere of Cm^{3+}. Nanomolar concentrations of Cm^{3+} are used for such TRLFS studies because of the high fluorescence spectroscopic sensitivity of Cm^{3+}. The peak positions of the different species of Cm^{3+} or Eu^{3+} formed with IDA, NTA, HEDTA, EDTA, CDTA, TMDTA, DTPA, and EDTA + NTA and EDTA + Cit, their lifetimes, N_{H_2O} values and assignment of the species present in solution are summarized in Table 6.

The TRLFS study established the formation of $Eu(IDA)(H_2O)_6{}^+$ and $Eu(IDA)_2(H_2O)_3{}^-$ complexes between pH 5.0 and 9.0 in which IDA binds via two carboxylates and one nitrogen [50,51]. At a ratio of Eu:IDA of 1:4 and pH 11.1, the IDA forms the complex $Eu(IDA)_3{}^{3-}$ [50]. The data indicate that the Cm^{3+} retains the same CN in these complexes (CN = 9.0) as hydrated $Cm(H_2O)_9{}^{3+}$ [52].

At pH 4.6 and a [NTA]:[Cm^{3+}] ratio of 1, the lifetime and N_{H_2O} correspond to the formation of $Cm(NTA)(H_2O)_5$ [52]. The formation of the complexes $Cm(NTA)(H_2O)_5$ and $Cm(NTA)_2(H_2O)^{3-}$ have been reported at a higher [NTA]/[Cm^{3+}] ratio of ∼10–100 at pH 4.6 [52]. The formation of both 1:1 and 1:2 complexes with one or more hydroxyl group(s) in the inner coordination of Cm^{3+} has been reported at a higher [NTA]/[Cm^{3+}] ratio of $\sim 1 \times 10^6$ in 0.1–1.0 M NaOH [53]. The formation of the 1:1 and 1:2 complex species have been observed for Eu^{3+} by TRLFS, ^{13}C NMR and EXAFS studies at pH 3.6–9.0, with NTA binding via three carboxylates and one nitrogen [45]. At high NaOH concentrations (>5.0 M), a spectral peak at 613.2 nm with a short lifetime of 66 μs, and $N_{H_2O} = 9.0$ has been attributed to the formation of (a) an oxo-bridged dimeric NTA–Cm-O-Cm complex, (b) an insoluble hydroxyl species (i.e., $Cm(OH)_4{}^-$) in solution and/or (c) formation of strong complexes of NTA with surface Cm^{3+} sites of the colloidal nanoparticles [53].

For HEDTA, the TRLFS study indicates the formation of $Cm(HEDTA)(H_2O)_4$, at a [HEDTA]:[Cm^{3+}] ratio of 1 and pH 4.6 [52]. The formation of 1:1 and 1:2 complexes Cm(HEDTA) and $Cm(HEDTA)_2{}^{3-}$ occurs at higher [HEDTA]:[Cm^{3+}] ratios of ∼10–100 at pH 4.6. In 0.1–1.0 M NaOH and a higher [HEDTA]:[Cm^{3+}] ratio of $\sim 1 \times 10^6$, the formation of 1:1 and 1:2 complexes with one or more hydroxyl group(s) in the primary coordination sphere of Cm^{3+} ion have been observed [53]. HEDTA acts as a pentadentate ligand in the formation of the $Cm(HEDTA)(H_2O)_4$, in which Cm^{3+} binds via three carboxy-

Table 6
Spectroscopic characteristics of Cm^{3+} or Eu^{3+} complexes with aminopolycarboxylates

Medium (M), ligand	Assigned species	Peak position (nm)	Lifetime (μs)	N_{H_2O}	Ref.
0.1–1.0 HCl, $HClO_4$, $NaClO_4$	Cm^{3+}	593.0, 594.0	66 ± 3[a]	9.2	[52,53]
	Eu^{3+}		109 ± 3	8.9	[52]
IDA, pH 8.48	$Eu(IDA)^+$	–	158	6.3	[50]
pH 9.62	$Eu(IDA)_2^-$	–	265	3.6	[50]
pH 11.1	$Eu(IDA)_3^{3-}$	–	423	2.1	[50]
NTA, pH 4.6	Cm(NTA)	–	91	6.3	[52]
	Eu(NTA)	–	128	4.5	[52]
0.01–7.5, NaOH	Cm(NTA)	596.4	220	2.1	[53]
	$Cm(NTA)_2^{3-}$	606.1	336	1.1	[53]
	NTA–Cm-O-Cm-	613.2	66	9.0	[53]
HEDTA, pH 4.6	Cm(HEDTA)	–	128	4.2	[52]
	Eu(HEDTA)		280	3.1	[52]
	Cm(HEDTA)	600.4	227	2.0	[53]
	$Cm(HEDTA)_2^{3-}$	607.0	456	0.3	[53]
	HEDTA–Cm-O-Cm-	616.0	82	7.1	[53]
EDTA, pH 4.6	$Cm(EDTA)^-$	–	141	3.7	[52]
pH 3.0	–	603.8	126	4.3	[55]
pH 3.7	$Eu(EDTA)^-$	–	327	2.6	[52]
0.01–7.5 NaOH	$Cm(EDTA)^-$	599.4	234	1.9	[53]
	$Cm(EDTA)_2^{5-}$	609.1	347	1.0	[53]
	EDTA–Cm-O-Cm-	616.6	95	5.9	[53]
CDTA, pH 4.6	$Cm(CDTA)^-$	–	139	3.8	[52]
	$Eu(CDTA)^-$	–	366	2.3	[52]
TMDTA, pH 4.5	$Eu(TMDTA)^-$	–	354	2.4	[54]
DTPA, pH 4.6	$Cm(DTPA)^{2-}$	588.0	271	1.6	[52]
	$Eu(DTPA)^{2-}$	–	680	0.9	[52]
Eu–EDTA–Cit, pH 5.0–9.0	$Eu(EDTA)(Cit)^{4-}$	580.39	926	0.4	[46]
Eu–EDTA–NTA, pH 8.99	$Eu(EDTA)(NTA)^{4-}$	580.16	729	0.7	[45]

Absolute uncertainty in N_{H_2O} is ±0.5.

[a] Average value.

lates and two nitrogen atoms. The $Cm(HEDTA)_2^{3-}$, has the second HEDTA binding via three carboxylates and one nitrogen or via two carboxylates and two nitrogen atoms. At high NaOH concentrations (>5.0 M), a spectral peak at 616.0 nm with a lifetime of 82 μs is similar to that of the hydrated Cm^{3+}–NTA system.

For lanthanides the formation of $Ln(HEDTA)(H_2O)_3$ (Ln = Eu^{3+} and Tb^{3+}) in the pH range of 3.0–8.0 has been reported [54]. The low average hydration of lanthanide–HEDTA complexes (Table 6) indicates that the hydroxylethyl group of the HEDTA ligand most likely participates in the cation binding. At pH > 8.5, further decrease in hydration state of Ln^{3+} indicates the formation of hydroxo species.

The lifetime and N_{H_2O} support the formation of $Cm(EDTA)(H_2O)_3^-$ at pH 4.6 for [EDTA]:[Cm^{3+}] ratio of ∼1 [52] and at pH 3.0 for a [EDTA]:[Cm^{3+}] ratio of $\sim 1 \times 10^3$ [55]. The TRLFS, ^{13}C NMR and EXAFS studies confirmed the binding of the EDTA molecule via four carboxylates and two nitrogen atoms [45]. The decrease in hydration state of Cm^{3+} at a [EDTA]:[Cm^{3+}] ratio of $\sim 1 \times 10^6$ and, in dilute NaOH (<0.1 M), reflects the formation of 1:1 complex $Cm(EDTA)^-$ with one or more hydroxyl groups coordinated to the Cm^{3+} ion [53] and the 1:2 complex $Cm(EDTA)_2^{5-}$. The formation of ternary hydroxo species have also been reported for Eu–EDTA [30] and Eu–(DTPA Dien) complexes [56] at pH ∼ 9.0. The EXAFS data for a [EDTA]:[Eu^{3+}] ratio of 10 at pH 11.5 confirmed that in the complex $Eu(EDTA)_2^{5-}$, one EDTA molecule binds via four carboxylates and two nitrogen and the second via three carboxylates [45]. At high NaOH concentrations (>5.0 M), spectral changes of the Cm–EDTA is similar to that described for the Cm–NTA and Cm–HEDTA systems [53].

For CDTA, the TRLFS study confirmed the formation of $Cm(CDTA)(H_2O)_3^-$ at pH 4.6 for [CDTA]:[Cm^{3+}] ratio of ∼1 [52]. The formation of such species with Eu^{3+} and Tb^{3+} between pH 3.0–8.0 with average values of $N_{H_2O} = 2.3$, is attributed to the additional steric effects of the CDTA ligand relative to EDTA [54]. However, a similar decrease in hydration state is not observed for Cm^{3+} and the N_{H_2O} measured for Cm–CDTA is similar to those of the Cm–EDTA complex [52]. At high pH region (10.0–11.5), a further decrease in N_{H_2O} is consistent with the formation of ternary hydroxo species [54].

For TMDTA, the TRLFS study indicates the formation of the 1:1 complex Ln $(TMDTA)(H_2O)_3$ (Ln = Eu^{3+} and Tb^{3+}) at pH ∼ 4.5 [54]. Such data for the complexation of Cm^{3+} with TMDTA are lacking. The average values of $N_{H_2O} = 2.4$ is essentially identical with the values for Ln(EDTA) and Ln(CDTA), indicating that the extra methylene group in the ligand backbone of TMDTA does not displace additional waters from the coordination sphere. No further decrease in N_{H_2O} of lanthanide ions for pH as high as 11.5 indicates that the extra methylene group of TMDTA prevents the formation of ternary hydroxo species at higher pH [54].

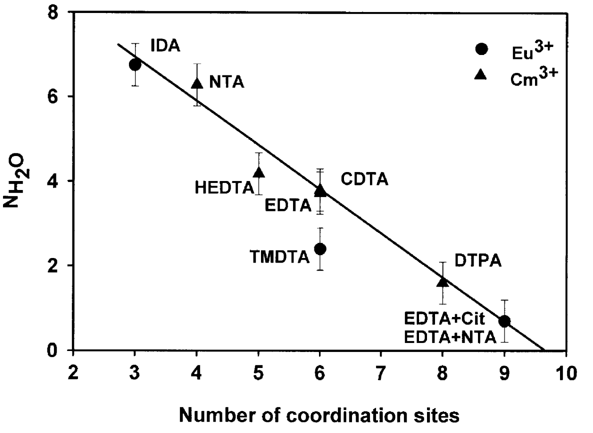

Fig. 8. Correlation of the residual N_{H_2O} and CN_L of the aminopolycarboxylates for the Cm^{3+}/Eu^{3+}. The identity of the aminopolycarboxylates is shown with the data points.

The TRLFS study support the formation of $Cm(DTPA)(H_2O)^{2-}$ at pH 4.6 for [DTPA]:[Cm^{3+}] ratio of ~1 [52]. Formation of such species has been reported also for Eu^{3+} and Tb^{3+} in the pH region 2.0–11.0 with the inclusion of a single water of hydration in the inner coordination sphere [54]. The lack of change in N_{H_2O} up to pH 11.0 indicates that octadentate DTPA forms a 1:1 complex over this pH range [54].

In all these systems, despite the similar thermodynamic parameters of complexation (Table 3) for Cm^{3+} and Eu^{3+} complexes, the N_{H_2O} for Cm^{3+} is larger than that of the Eu^{3+} for the same system (Table 6). This is consistent with the total average coordination of Cm^{3+}, which is ca. 0.5 unit larger than that of Eu^{3+} in aminopolycarboxylates [52].

For the ternary complex, $Eu(EDTA)(Cit)^{4-}$ at pH of 5.0–9.0, the TRLFS study established a binding of EDTA via four carboxylates and two nitrogen atoms and of Cit via three carboxylates [46]. For $Eu(EDTA)(NTA)^{4-}$, the TRLFS, ^{13}C NMR and EXAFS studies confirmed the similar binding modes for EDTA; however, for Eu^{3+}, NTA binds via three carboxylates but not via nitrogen [45]. The EXAFS data indicate a greater Eu–N distance (2.84 Å) in $Eu(EDTA)(NTA)^{4-}$ than in $Eu(EDTA)^{-}$ (2.76 Å). These structural changes minimize the electrostatic repulsions between ligands and provide room for larger NTA coordination. NTA with a tripodal structure binds via three carboxylates, probably because the carboxylate groups are easily approachable to the Eu^{3+} ion and their binding causes less steric hindrance compared to binding via one nitrogen and two carboxylates in which more molecular bending is required. The formation of complexation with an eight-membered ring structure is reported for UO_2^{2+} with IDA or oxydiacetic acid (ODA) [57] and also in the 1:2 complexation of trivalent lanthanides with benzene-1,2-dioxydiacetic acid [58].

An inverse linear relationship (Fig. 8) exists between the number of coordination sites (carboxylates + nitrogen) of aminopolycarboxylates versus N_{H_2O} calculated for the formation of binary and ternary complexes of Cm^{3+} and Eu^{3+}. The decrease in N_{H_2O} with increasing number of occupied coordination sites by aminopolycarboxylates is consistent with the increased dehydration of the metal ions upon complexation. A similar correlation was found between the entropy change in the formation of 1:1 complexation with aminopolycarboxylates and N_{H_2O} which was interpreted as reflecting the strong influence on the entropy of complexation by the dehydration of the cations [54].

5. Conclusion

This review provides information on the thermodynamics and structural aspects of actinide complexes with aminopolycarboxylates. Almost five decades of research on trivalent actinide aminopolycarboxylates have generated information on the stability constants and other aspects of the coordination chemistry. Unfortunately, much of this data is limited to actinides of $Z \leq 96$. The data reviewed supports a strongly ionic interaction between actinides and aminopolycarboxylates. The high stability of actinide–aminopolycarboxylates reflects the strong contributions of the An–N bonding similar to that of the Ln–N bond in Ln–aminopolycarboxylate complexes. There may be a slightly greater degree of covalency in the bonding of the actinides over that of lanthanides. However, calorimetric data for complexation of Am^{3+}, Cm^{3+} and Eu^{3+} with aminopolycarboxylates indicated no significant differences in the Eu–N and An–N bond strengths. The thermodynamics of formation of the binary 1:1 and the ternary 1:1:1 complexation reflects the effect of reduced water activity at high ionic strength.

TRLFS, NMR and EXAFS measurements provided better understanding of the role of hydration and coordination modes of actinide–aminocarboxylates interaction in the formation of the binary and ternary complexation. Although the study of the behavior of actinides in aqueous solution has progressed rapidly in the past several decades, the question of covalency in the actinides bonding requires more study. The lack of adequate data on the complexation thermodynamics and the structural aspects of their complexation for $Z \leq 96$, and the very few stability constant values for $Z > 96$ cations with aminopolycarboxylates also reflect the need for further research of these systems.

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