Revisiting Complexation Thermodynamics of Transplutonium Elements Up to Einsteinium

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Literature casts einsteinium as a departure from earlier transplutonium actinides, with a decrease in stability constants with aminopolycarboxylate ligands. This report studies transplutonium chemistry – including Am, Bk, Cf, and Es – with aminopolycarboxylate ligands. Es complexation follows similar thermodynamic and structural trends established by the earlier actinides, consistent with first-principle calculations.

Einsteinium (Es) is among the heaviest elements for which off-line experimental studies are possible. The number of metal-ligand stability constant measurements with Es is limited.[1] Previously reported data for Es^{3+} with NTA, CDTA, and EDTA suggest that Es interactions with aminopolycarboxylate (APC) ligands are unexpectedly much weaker than lanthanide (Ln) interactions with the same ligands.[2] This manuscript reports on experimentally determined actinide-APC binding for americium (Am), berkelium (Bk), californium (Cf) and einsteinium (Es). Computational stability constant studies of the same actinides with diethylenetriamine-pentaacetic acid (DTPA; Figure 1) are also completed. The experimental and computational results of actinide complexation are compared to each other and with previous Ln-APC complexation results.

Observations of weaker Es-APC interactions are in contradiction with recent work on the complexation of Bk and Cf. These reports suggest orbital energy degeneracy driven covalency involving the 5*f* orbitals could be a relevant feature of transplutonium actinide (An) chemistry.[3-6] This was shown to be the case in transplutonium actinide complexation by dipicolinate (DPA), which showed an increase in complex stability between Am and Cf as well as a decrease in An-DPA distances.[7-10] The current disagreement in complexation trends for Es relative to Bk and Cf indicates a revaluation of transplutonium complexation thermodynamics elements is appropriate.

In addition to examining systematic changes across the transplutonium actinides, understanding the differences between trivalent actinide and lanthanide complexation is important since these differences have direct applications in nuclear fuel management and heavy element production.[11] Actinide fission always produces lanthanides which, due to their similar chemistry to the trivalent actinides, can make purification of the minor actinides a challenge. Separations of trivalent actinides from the lanthanides usually rely on soft donor complexants that preferentially interact with the actinides. With An selectivity frequently attributed to greater covalency in the An-ligand interaction compared to the lanthanides.[12]

Aliphatic APCs represent one of the largest classes of complexants characterized for the trivalent actinides based both on the number of different complexants and actinides considered.[2] Stability constants with aliphatic APCs have been measured for actinides as heavy as fermium. A review completed by Choppin[13] showed An-APC stability constants decreasing at Bk for transplutonium actinides with DTPA and NTA, inconsistent with the slight increases observed in DTPA and NTA interactions across the lanthanide series.[14, 15] This decrease in An-NTA or An-DTPA stability constants could be suggestive of a decrease in covalent interaction for the heavier actinides. This decrease in covalent interaction would be in better agreement with the classical understanding of heavy actinide chemistry, that actinide ions become more lanthanide

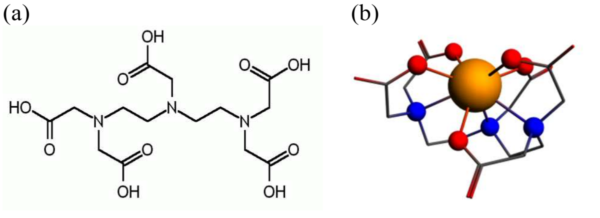

Figure 1. (a) The protonated DTPA ligand. (b) The $[EsDTPA]^{2-}$ complex. An ions form bonds with 5 oxygen (red) carboxylate groups and the 3 nitrogen (blue). Only Es and connected atoms are shown as balls; other atoms as sticks with hydrogen atoms hidden for clarity.

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like as their orbitals contract across the series[16], than recent reports of actinide covalency and stability constant patterns.[3, 9, 17]

The APCs considered in this report are NTA, 2-hydroxyethylethylenediamine-triacetic acid (HEDTA), CDTA, and DTPA. Thermodynamic data for Es-DPA complexes are also reported and compared with previously studied trivalent An-DPA thermodynamic data. Actinide-DTPA complexes are used as a model to assess the electronic structure of aliphatic APC-An complexes, as previous work has verified computationally computed transplutonium-DTPA structures.[18]

Distribution ratio measurements and UV-Vis spectrophometric titrations have been well described in previous manuscripts[3, 19] and more detailed information is provided in the ESI. Minimum energy structures of the aqueous An(III) ions and their deprotonated 1:1 DTPA and 1:3 DPA complexes were computed with density functional theory (DFT). Frequency calculations were carried out to calculate complexation thermodynamics. Computational details can be found in the ESI.

The stability constants measured in this study are presented in Table 1. Only 1:1 metal:ligand species were observed for the actinides with CDTA, HEDTA and DTPA. For NTA, a 1:1 and 1:2 metal:ligand species could be resolved with Bk, Cf and Es. The Am studies were completed at a slightly higher acid concentration (pH ~ 2.1 vs 2.5) since the Am radiotracer spike was at a higher acid concentration (3 M) than for the heavier actinides (0.1 M). This led to the presence of less NTA^{3-}, possibly hindering observation of the $Am(NTA)_2^{3-}$ species. Einsteinium-DPA stability constants were also assessed for the first time. Consistent with earlier actinides and lanthanides, Es can form 1:1, 1:2 and 1:3 metal:ligand species.

Table 1. Aminopolycarboxylate stability constants with Am, Bk, Cf and Es in 0.5 M $NaClO_4$. Error is annotated parenthetically, reported at the 1σ level and corresponds to the last digit of a given stability constant.

		Am	Bk	Cf	Es
NTA	log β_{101}	11.6(1)	11.8(1)	11.76(1)	12.07(2)
	log β_{102}	*	22.2(2)	22.3(1)	22.80(3)
HEDTA	log β_{101}	15.8(1) 15.6(2)‡	15.5(1)	16.12(2)	16.17(1)
CDTA	log β_{101}	--	20.1(1)	20.95(5)	20.69(7)
DTPA	log β_{101}	22.71(5)	23.4(1)	23.8(1)	24.04(1)
DPA	log β_{101}	9.14(7)†	9.07(7)†	9.1(1)†	9.2(4)†
	log β_{102}	16.4(1)†	17.2(2)†	17.3(4)†	17.47(4)†
	log β_{103}	22.65(1)	23.14(5)	23.29(3)	23.44(5)

*Did not refine

†Previously reported[6]

‡Determined using visible spectroscopy

The data in Table 1 shows a small but significant trend of stronger binding constants for the later actinides (Bk-Es) compared to Am, a trend that is more apparent when the data are plotted relative to Am as in Figure S3. This increase is larger for the larger ligands. For example, the change in logβ_{101} between Am and Es is 0.47 for NTA (a tetradentate chelator), while it is 1.33 for DTPA (an octadentate chelator).

The same trend of increasing complex strength with heavier actinides was observed with DPA in our previous work. The newly measured Es-DPA stability constants are in line with our previous observations of Bk and Cf-DPA complexes.[3] The slight increase in Es-DPA interactions relative to Cf-DPA interactions (Table 1) is consistent with the increase in stability constant observed between adjacent Bk and Cf complexes and suggests similar chemistry is driving An-DPA interactions in the transcurium part of the periodic table. Although Es is anticipated to prefer a hydration number of eight based on previous calculations with the earlier actinides and this work (*vide infra*),[3] the preorganized geometry of the DPA complexant enforces an expanded coordination number (CN) of nine when the 1:3 Es:DPA complex is formed. This expanded CN is similar to heavy lanthanide-DPA complexes where hydration numbers also generally trend towards eight.[3]

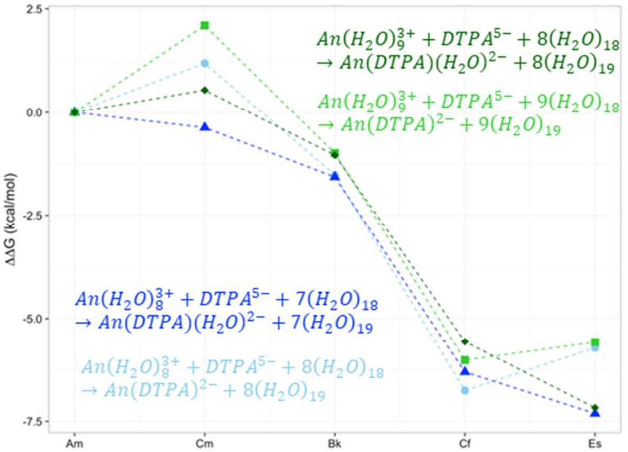

Figure 2. Gibbs free energies of An-DTPA complexation. Reactions with differing coordination numbers (CN) for the aqueous ions and DTPA complexes are given: (◆) CN 9 to CN 9, (🟩) CN 9 to CN 8, (▲) CN 8 to CN 9, (●) CN 8 to CN 8 (see reactions S10-S13 in the ESI). Energies are plotted as ΔΔG relative to the complexation free energy of Am.

The DFT calculated thermodynamics of DTPA complexation (following equations S10-S13 in the ESI) are shown in Figure 2. As in previous DPA work, the An-DTPA qualitatively match quite well with the experimental results described above. Einsteinium follows the trend of decreasing ΔG (increasing complexation) set by earlier transplutonium actinides, both thermodynamically and structurally. The addition of an extra water molecule to the An-DTPA complexes causes only a small perturbation in ΔG. As with DPA, the decrease in complexation energy coincides with the An *5f* orbitals on average becoming more degenerate with the 2*p* orbitals of the coordinating O or N atoms from the ligand, as seen in Figure S5. The coordinating O and N 2p orbitals are close in energy, with O slightly higher on average in the DTPA complexes. This suggests any effects from orbital energy degeneracy driven covalency are present in both systems, and the differences in complexation between DTPA and DPA are likely attributable to electrostatic and steric considerations. This is well captured in examining closer proximity of the DTPA oxygen relative to those of DPA (see Figure S6).

While ionic interactions dominate An-DTPA and An-DPA bonding, these results suggest the degree of covalent interaction impacts trends across the series. To demonstrate this point, an energy decomposition analysis[20-22] was completed to understand the nature of the metal-ligand bonding interaction in the $[Cm(DPTA)]^{2-}$ and $[Cm(DPA)_3]^{3-}$ complexes. Curium was chosen due to its easy-to-calculate $5f^7$ electron configuration. Though comparisons between the two ligands are not feasible due to the difference in charge of their complexes, the energy decomposition analysis breaks down energetic contributions to bonding within the complexes. The results of this analysis show orbital interactions are a minor component of the bonding interaction between Cm and both ligands. Orbital contributes between 36% and 39% of the bonding interaction. The other 61-64% are contributed by electrostatic effects or Pauli repulsion. This confirms the strong ionic character in the An-DTPA and An-DPA systems.

The stability constants patterns for NTA and DTPA with the transplutonium actinides measured here are not in agreement with previous data.[13-15, 23] Instead, the DTPA stability constants are in reasonable agreement with more recent stability constant data[24] and with EXAFS observations by Abergel.[18] DFT calculations on complexation thermodynamics, electronic structures, and complex geometries all show Es as a continuation of the transplutonium actinide series, with similar forces to those seen in Bk and Cf driving Es chemistry.

The assessment of Es extraction constants with various APCs allows for more accurate comparison to trivalent lanthanide chemistry. When the previously reported Es-APC stability constants were considered against lanthanides of similar ionic radii in a linear free energy relationship (LFER), the composite data suggested the Es-APC interactions were comparable to those of the lanthanides.[2] Heavy actinide DTPA data was assessed by two separate groups and neither study accounted for the DTPA formation of protonated $M(HDTPA)^-$ species.[25, 26] The data collected in this report shows Es interactions with aliphatic APCs are stronger than APC interactions with comparably sized lanthanides.

Linear free energy relationships (LFERs) have long been used to evaluate the selectivity of APCs for actinides over the lanthanides.[2, 27] Past LFER reports suggest a decrease in An-APC selectivity across the series, though no significant changes could be quantified due to the high error in previous measurements.[2] While this decrease in selectivity is potentially at odds with more recent work on the chemistry of the transplutonium actinides[3, 9, 17], the data available, in particular for Bk and Es, were comparatively sparse.[1] If stability constants were interpreted consistently across the group and more stability constants were collected, perhaps the data could be sufficiently refined to show differences in selectivity across the series.

The linear free energy relationship arising from this work which, normalized An/Ln pairs by their ionic radii,[28] is presented in Figure 4. Comparisons were made between Ln-APC stability constants at 0.5 M and 0.1 M ionic strength (Table S11). The 0.5 M ionic strength lanthanide stability constants assessed by Choppin only used the first four and five stability constants for CDTA and DTPA, respectively.[15] To account for this, actinide stability constants refined and compared to 0.5 M ionic strength lanthanide data used the same acid dissociation constants. Stability constants derived from this treatment are smaller since the additional proton competition is not considered. Lanthanide stability constants from 0.1 M ionic strength used all known acid dissociation constants for CDTA and DTPA. Acid dissociation constants used can be found in Tables S1 through S4.

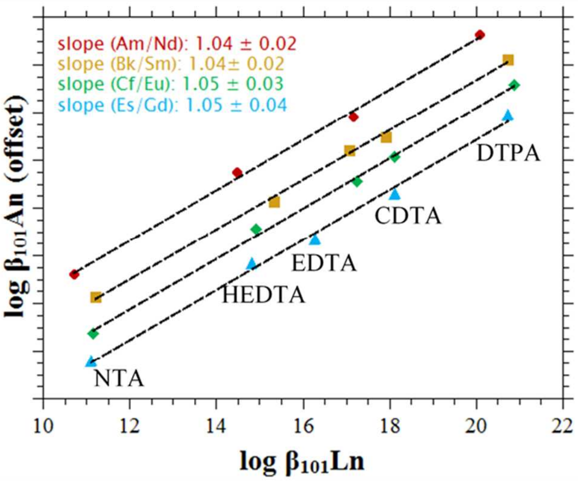

Figure 4. Linear free energy relationships for f-element binding with aminipolycarboxylates. Actinide stability constants are offset from each other to allow visualization of individual trends.

The uncertainty associated with the linear free energy relationships is improved relative to the uncertainty reported in previous linear free energy relationships.[2] The smaller uncertainties could be related to consistency in acid dissociation constants between actinide and lanthanide stability constants and longer equilibration times that allowed for larger APCs than previous literature reports,[25, 26, 29, 30] which additionally did not note the specific solution pH used for stability constant assessments. The extraction kinetics for the lanthanides and actinides, particularly the heavier actinides, from aqueous media containing APCs are known to be acid catalyzed;[31-37] for the larger APCs, such as CDTA or DTPA, at least one-hour contacts under acidic conditions were completed with the Labteck Shaker, and Es contacts used 2.5 hour contacts. These times were used for contacts after preliminary studies under these conditions suggested equilibrium had been obtained.

The APC ligands examined here are selective for transplutonium actinides over similarly sized lanthanides, suggesting participation from the 5*f* electrons not shared by the 4*f* electrons. A significant difference in the selectivity observed across the actinide series from Am to Es is not observed, with any differences being within error of the experimental measurements. The inability for the LFER to assess changes in An-APC selectivity and possible shifts in covalency suggests slight changes in stability constants arising from changes in covalent interactions, a junior partner to the ionic interaction in the overall binding, are masked by the uncertainties associated with the bulk assessment of so many stability constants.

Our experimental measurements and DFT calculations depict Es complexation as a clear continuation of transplutonium actinide chemistry for APC ligands. This is in contrast with earlier work. Rather than decreasing as previously reported, Es-APC stability constants continue to increase relative to earlier actinides, retaining their selectivity for An over Ln ions deep into the actinide series.

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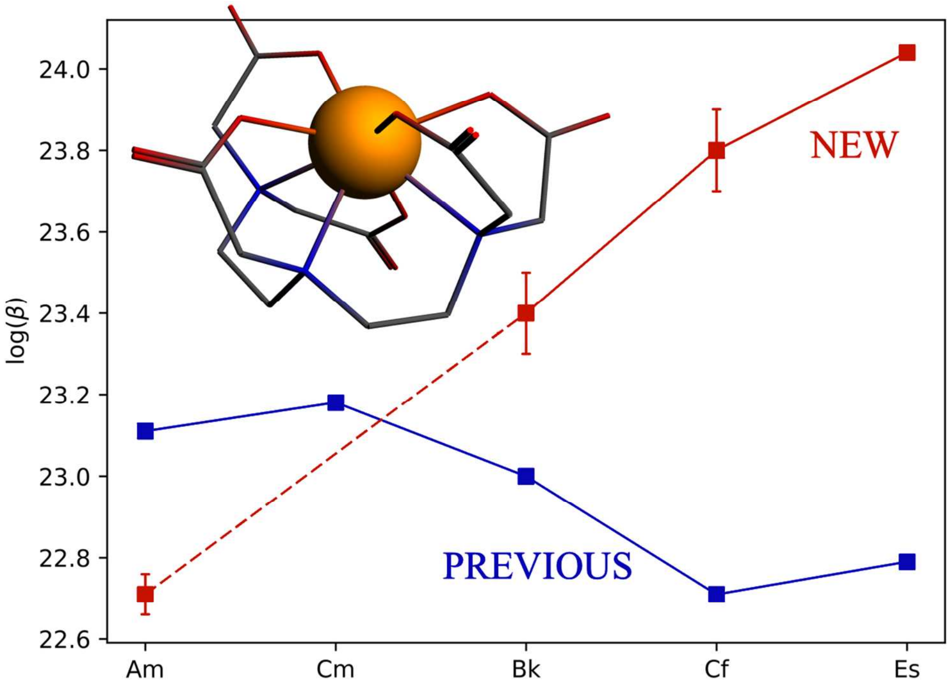
Conflicts of interest

There are no conflicts to declare.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23.8
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Am
Cm
Bk
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Es
NEW
PREVIOUS