## Supplemental Information

# Revisiting complexation thermodynamics of transplutonium elements up to Es 

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## Supplemental Information

## Table of Contents

1. Acid Dissociation Constants Used for Stability Constant
Determination ..... 3
2. HDEHP concentrations $-\mathrm{K}_{\mathrm{Ex}}$ determinations ..... 4
3. Contact Times $-\mathrm{K}_{\mathrm{Ex}}$ Determination ..... 4
4. Contact Times - Stability Constant Determination ..... 4
5. DTPA Concentrations - DTPA $\beta_{111}$ Stability Constant Determinations ..... 4
6. Aminopolycarboxylate Concentrations - Stability Constant Determination ..... 5
7. HDEHP Concentrations - Stability Constant Determination ..... 5
8. Lanthanide Stability Constants for Linear Free Energy Relationships ..... 6
9. HDEHP Actinide Extraction - Assessment \& Constants ..... 8
10. Stability Constant Assessment - Methodology ..... 9
11. Computational Methods ..... 11
12. Computational Thermodynamics ..... 12
13. Computed Structures ..... 15
14. Optimized Geometries ..... 16
15. References ..... 20

## Supplemental Information

Table S1. Acid Dissociation Constants and Thermodynamic Information for NTA at Standard Conditions I $=0.5 \mathrm{M}$ Ionic Strength and $25^{\circ} \mathrm{C} .{ }^{1}$

| Protonated Ligand | $\mathbf{p K a}$ | $\Delta \mathbf{H}[\mathbf{K J} / \mathbf{m o l}]$ |
| :---: | :---: | :---: |
| $\mathrm{H}_{1} \mathrm{NTA}$ | $9.57 \pm 0.01$ | $24.2 \pm 0.02$ |
| $\mathrm{H}_{2} \mathrm{NTA}$ | $2.64 \pm 0.01$ | 0 |
| $\mathrm{H}_{3} \mathrm{NTA}$ | $1.57 \pm 0.06$ | 2 |

Table S2. Acid Dissociation Constants and Thermodynamic Information for HEDTA at Standard Conditions I $=0.5 \mathrm{M}$ Ionic Strength and $25^{\circ} \mathrm{C} .{ }^{1}$

| Protonated Ligand | $\mathbf{p K a}$ | $\mathbf{\Delta H}[\mathbf{K J} / \mathbf{m o l}]$ |
| :---: | :---: | :---: |
| $\mathrm{H}_{1} \mathrm{HEDTA}$ | $9.90 \pm 0.04$ | $-28 \pm 0.03$ |
| $\mathrm{H}_{2} \mathrm{HEDTA}$ | $5.54 \pm 0.02$ | $-12(\mathrm{I}=0.1)$ |
| $\mathrm{H}_{3} \mathrm{HEDTA}$ | $2.83 \pm 0.06$ | $4.6(\mathrm{I}=0.1)$ |

Table S3. Acid Dissociation Constants and Thermodynamic Information for CDTA at Standard Conditions I $=0.5 \mathrm{M}$ Ionic Strength and $25^{\circ} \mathrm{C} .{ }^{1}$

| Protonated Ligand | $\mathbf{p K a}$ | $\mathbf{\Delta H}[\mathbf{K J} / \mathbf{m o l}]$ |
| :---: | :---: | :---: |
| $\mathrm{H}_{1} \mathrm{CDTA}$ | $11.30 \pm 0.07$ | -38.8 |
| $\mathrm{H}_{2} \mathrm{CDTA}$ | $6.51 \pm 0.06$ | -10.7 |
| $\mathrm{H}_{3} \mathrm{CDTA}$ | $3.01 \pm 0.06$ | -1.4 |
| $\mathrm{H}_{4} \mathrm{CDTA}$ | $2.38 \pm 0.06$ | -1.7 |
| $\mathrm{H}_{5} \mathrm{CDTA}$ | 1.65 | 0 |

Table S4. Acid Dissociation Constants and Thermodynamic Information for DTPA at Standard Conditions I $=0.5 \mathrm{M}$ Ionic Strength and $25^{\circ} \mathrm{C} .{ }^{1}$

| Protonated Ligand | $\mathbf{p K a}$ | $\mathbf{\Delta H}[\mathbf{K J} / \mathbf{m o l}]$ |
| :---: | :---: | :---: |
| $\mathrm{H}_{4} \mathrm{DTPA}$ | $9.9 \pm 0.1$ | -33 |
| $\mathrm{H}_{2}$ DTPA | $8.32 \pm 0.08$ | -17 |
| $\mathrm{H}_{3} \mathrm{DTPA}$ | $4.12 \pm 0.07$ | -6.2 |
| $\mathrm{H}_{4}$ DTPA | $2.85 \pm 0.06$ | -1 |
| $\mathrm{H}_{5}$ DTPA | $1.95 \pm 0.06$ | 2 |
| $\mathrm{H}_{6} \mathrm{DTPA}$ | 1.60 | 0 |

## Supplemental Information

Table S5. HDEHP concentrations - $\mathrm{K}_{\mathrm{Ex}}$ determinations

| Radiotracer | HDEHP Concentrations (mM) |
| :---: | :---: |
| Am-241 | $1,2,3,5$ |
| Bk-249 | $0.5,0.6,0.7,0.8,0.9$ |
| Cf-249 | $0.1,0.2,0.3,0.4,0.5$ |
| Es-253/254 | $0.1,0.2,0.3,0.4,0.5$ |

Table S6. Contact Times - $\mathrm{K}_{\mathrm{Ex}}$ Determination

| Radiotracer | Temperature | Contact Time |
| :--- | :--- | :--- |
| Am-241 | $15^{\circ} \mathrm{C}, 25^{\circ} \mathrm{C}, 35^{\circ} \mathrm{C}, 45^{\circ} \mathrm{C}, 55^{\circ} \mathrm{C}$ | 1 hr |
| Bk-249 | $15^{\circ} \mathrm{C}, 25^{\circ} \mathrm{C}, 35^{\circ} \mathrm{C}, 45^{\circ} \mathrm{C}, 55^{\circ} \mathrm{C}$ | 1 hr |
| Cf-249 | $25^{\circ} \mathrm{C}, 35^{\circ} \mathrm{C}, 45^{\circ} \mathrm{C}, 55^{\circ} \mathrm{C}$ | 30 min |
| Cf-249 | $15^{\circ} \mathrm{C}$ | 45 min |
| Es-253/254 | $25^{\circ} \mathrm{C}, 35^{\circ} \mathrm{C}, 45^{\circ} \mathrm{C}, 55^{\circ} \mathrm{C}$ | 30 min |
| Es-253/254 | $15^{\circ} \mathrm{C}$ | 45 min |

Table S7. Contact Times - Stability Constant Determination

| Radiotracer | APC | Contact Times |
| :---: | :---: | :---: |
| Am-241 | NTA, HEDTA | 2 hr |
| Bk-249 | NTA, HEDTA | 2 hr |
| Cf-249 | All | 1 hr |
| Es-253/254 | NTA, HEDTA, \& |  |
|  | CDTA | 2.5 hr |
|  | DTPA |  |

Table S8. DTPA Concentrations - DTPA $\beta_{111}$ Stability Constant Determinations

| Radiotracer | $\mathbf{p c H ~ 1 . 9}(\mathbf{m M})$ | $\mathbf{p c H} 2.1(\mathbf{m M})$ | $\mathbf{p c H} 2.3(\mathbf{m M})$ | $\mathbf{p c H} \mathbf{2 . 5}(\mathbf{m M})$ |
| :--- | :---: | :---: | :---: | :---: |
| Bk-249 | $0.01,0.05,0.1$, | $0.1,0.5,1,2,3,4$, | $0.01,0.05,0.1$, | $0.01,0.05,0.1$, |
|  | $0.3,0.5$ | 5 | $0.3,0.5$ | $0.3,0.5$ |
| Cf-249 | $0.1,0.3,0.5,0.7,1$ | $0.1,0.3,0.5,0.7,1$ | $0.1,0.3,0.5,0.7,1$ | $0.1,0.3,0.5,0.7,1$ |
| Es-253/254 | $0.1,0.3,0.5,0.7,1$ | $0.1,0.3,0.5,0.7,1$ | $0.1,0.3,0.5,0.7,1$ |  |

## Supplemental Information

Table S9. Aminopolycarboxylate Concentrations - Stability Constant Determination

| Radiotracer | NTA (mM) | HEDTA (mM) | CDTA (mM) |
| :---: | :---: | :---: | :---: |
| Am-241 | $0.05,0.075,0.1,0.2$, | $0.01,0.025,0.05$, | not studied |
|  | $0.3,0.4,0.5,1$ | $0.075,0.1,0.25,0.35$, |  |
| Bk-249 | $0.1,0.25,0.4,0.5,0.6$, | $0.05,0.1,0.3,0.5,0.7$, | $0.01,0.03,0.05,0.1$, |
|  | $0.75,1,1.1,1.2,1.5$ | $1,2,3,4,5$ | $0.3,0.5,1$ |
| Cf-249 | $0.1,0.5,0.75,1,2,3,4$, | $0.1,0.25,0.5,0.75,1$, | $0.01,0.03,0.05,0.07$, |
|  | 5 | $3,5,7$ | $0.1,0.5$ |
| Es-253/254 | $1,2,3,4,5$ | $0.5,0.75,1,3,5,7$ | $0.03,0.05,0.07,0.1$, |
|  |  |  | 0.2 |

Table S10. HDEHP Concentrations - Stability Constant Determination

| Radiotracer | Ligand Study | HDEHP Concentration (mM) |
| :---: | :---: | :---: |
| Am-241 | NTA | 5.0 |
|  | HEDTA | 5.0 |
|  | NTA | 4.25 |
|  | HEDTA | 5.0 |
|  | CDTA | 20.0 |
| Cf-249 | DTPA | 20.0 |
|  | NTA | 1.365 |
|  | HEDTA | 5.193 |
|  | CDTA | 20.0 |
|  | DTPA | 20.0 |
| Es-253/254 | NTA | 1.365 |
|  | HEDTA | 5.193 |
|  | CDTA | 15.0 |
|  | DTPA | 20.0 |

## Supplemental Information

Table S11. Lanthanide stability constants for linear free energy relationships ${ }^{1,2}$

| Ligand | 0.5 M ionic strength | 0.1 M ionic strength |
| :---: | :---: | :---: |
| $\boldsymbol{N T \boldsymbol { A }}$ | 10.71 | 11.1 |
| Nd | 11.21 | 11.32 |
| Sm | 11.15 | 11.32 |
| Eu | 11.11 | 11.35 |
| Gd |  |  |
| $\boldsymbol{H E D T A}$ | 14.47 | 15.16 |
| Nd | 14.85 | 14.85 |
| Sm | 14.9 | 15.6 |
| Eu | 14.8 | 15.44 |
| Gd | 16.51 | 15.75 |
| $\boldsymbol{E D T A}$ | 17.06 | 16.20 |
| Nd | 17.25 | 16.23 |
| Sm | 17.35 | 16.28 |
| Eu |  |  |
| Gd | 17.16 | 18.3 |
| $\boldsymbol{C D T A}$ | 17.91 | 19.1 |
| Nd | 18.1 | 19.4 |
| Sm | 18.12 | 19.5 |
| Eu |  |  |
| Gd | 20.09 | 22.62 |
| $\boldsymbol{D T P A}$ | 20.72 | 22.35 |
| Nd | 20.87 |  |
| Sm | 20.73 |  |
| Eu |  |  |
| Gd |  |  |
|  |  |  |

# Supplemental Information 

## Solvent Extraction Methodology

All complexation thermodynamics were assessed by using competitive solvent extraction investigations with bis-2-ethyl phosphoric acid (HDEHP) dissolved in ndodecane. The distribution ratios are calculated as $D=[M]_{\text {org }} /[\mathrm{M}]_{\text {aq }}$. The HDEHP extraction constants used for calculation of actinide-aminopolycarboxylates were either previously reported $^{3}$ or are reported in this manuscript, SI Table 12. To assess metalaminopolycarboxylate stability constants, metal partitioning between an HDEHP organic phase and an aqueous phase with increasing aminopolycarboxylate concentration was measured. The ionic strength of the aqueous phase was maintained at 0.5 M using $\mathrm{NaClO}_{4}$. All phases were pre-equilibrated with an appropriate aqueous or organic phase prior to use in the distribution study at the temperature of a given study. Pre-equilibration contact times were five minutes and contact times for thermodynamic measurements varied depending on the results of kinetics experiments that considered actinide partitioning as a function of time SI Table 6. Contacts were completed using a Labteck shaker with aluminum temperature block fabricated in house.

The pcH of the aqueous phase was measured after contact by using a series of standardized acid solutions at $0.5 \mathrm{M} \mathrm{NaClO}_{4}$. Conversions from molality to were afforded by density determinations at $22^{\circ} \mathrm{C}$. Partitioning of ${ }^{249} \mathrm{Bk}$ and ${ }^{253} \mathrm{Es}$ was monitored using a HIDEX 300 SL liquid scintillation counter in alpha-beta discrimination mode. Partitioning of ${ }^{249} \mathrm{Cf}$ and ${ }^{241} \mathrm{Am}$ was monitored using Packard Cobra II Auto-gamma counter. Radionuclides were provided by the Department of Energy ( ${ }^{249} \mathrm{Bk}$ and ${ }^{253} \mathrm{Es}$ ) and available stocks from Florida State University $\left({ }^{241} \mathrm{Am}\right.$ and $\left.{ }^{249} \mathrm{Cf}\right)$. All thermodynamic constants were fit in QtiPlot using nonlinear regression model weighting the distribution data using $\mathrm{w}=$ $1 / \sigma^{2}$ weighting. Metal $\mathrm{K}_{\mathrm{Ex}}$ values were fit assuming equilibria and mass balance relationships previously established in the literature, SI Equations 1-9.4, 5 Stability constant fits included the error in the extraction constant and distribution ratios.

## Radionuclide Purity

The purity of the Am, Bk, Cf and Es was assayed using alpha, liquid scintillation and gamma spectroscopy as appropriate.

Am-241 - The americium stock acquired from FSU had a yellow impurity that was accompanied by beta emission. This stock was purified using an HDEHP extraction. Upon contact and stripping, no yellow color or beta impurity remained. Alpha and gamma emissions arising from the sample indicated the exclusive presence of Am-241.

Cf-249 - The Cf-249 stock from FSU had a $1 \%$ contamination from Bk-249 (presumably arising from the purification of the material). This did not interfere with the Cf- 249 measurements as the Cf-249 measurements were completed using gamma spectroscopy.

Bk-249 - The Bk-249 stock from ORNL had no other discernable radionuclides.

## Supplemental Information

Es-253 - The alpha spectroscopic assay of Es-253 indicated $>99.98 \%$ purity of Es.

## Spectrophotometric Titration Methodology

UV-Vis spectrophotometric measurements of the Am-HEDTA system, Figure S1, were made on a 400-series charge-coupled device array spectrophotometer (Spectral Instruments Inc.) with a $200-950 \mathrm{~nm}$ scanning range with a 0.35 nm resolution. The solutions were held in quartz $1-\mathrm{cm}$ cuvettes. The temperature was not controlled but the ambient room temperature was established to be $22 \pm 1^{\circ} \mathrm{C}$. All solution spectra were referenced to a blank solution containing the supporting electrolyte ( $1.0 \mathrm{~mol} \cdot \mathrm{~L}-1 \mathrm{NaCl}$ ). Spectra provided are the baselined average of four thousand scans (four saved files at 1000 scans per file). Chloride was selected as the primary supporting anion to minimize potential spectral interferences that may be associated with high concentrations of nitrate or perchlorate. Spectrophotometric titrations were performed by first introducing a single portion of the starting metal solution. directly into the cuvette. The ligand then was introduced by adding aliquots of HEDTA solution. The change in pH was evaluated by performing a separate experiment in which the pH was measured between HEDTA additions.


Figure S1. Spectrophotometric titration of americium by HEDTA.
HypSpec ${ }^{6}$ was employed to refine stability constants and deconvolute molar absorptivities of light absorbing species using non-linear least square (NLLS) statistics. This code utilizes wavelength and absorbance information initially provided in an ASCII format from the Ocean Optics software. Data from 490 to 525 nm was used to fit the americium peak transition arising from complexation. Alternative species considered in the fitting routine of the ternary experiment included $\mathrm{Am}(\mathrm{HEDTA}) \mathrm{OH}, \mathrm{Am}(\mathrm{HEDTA})_{2}, \mathrm{Am}\left(\mathrm{H}^{*} \mathrm{HEDTA}\right)$ and the exclusive

## Supplemental Information

presence of Am(HEDTA). The HypSpec program could only minimize a fit when the Am(HEDTA) species was exclusively present.

## HDEHP Actinide Extraction - Assessment \& Constants

The van't Hoff relationships and extraction constants for Am, Bk, Cf and Es with HDEHP are presented in Figure S2 and Table S12. Extraction constants were calculated by assuming the following equilibrium, equation S 1 , where M is a metal ion and an overbar denotes an organic phase species.

$$
\begin{equation*}
M^{3+}+3 H D E H P_{2} \rightleftharpoons M \cdot\left(H(\overline{D E H P})_{2}\right)_{3}+3 H^{+} \tag{S1}
\end{equation*}
$$

The slopes derived from the $\log \mathrm{D}$ versus $\log$ [HDEHP] plots are all greater than 2.5 and largely consistent with the extraction equilibrium assumed above. The extraction constants increase with increasing atomic number.


Figure S2. HDEHP van't Hoff relationships for actinide-HDEHP extraction.

Table S12. HDEHP extraction constants used in aminopolycarboxylic acid stability constant

| Metal | Am | Cm | Bk | Cf | Es |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{K}_{\mathrm{Ex}}$ | $8.3 \pm 0.5$ | $8.8 \pm 0.7$ | $95 \pm 5$ | $1137 \pm 2$ | $5300 \pm 300$ |
| $\Delta \mathrm{H}$ | $-16 \pm 1$ | $-19 \pm 3$ | $-21 \pm 1$ | $-14 \pm 1$ | $-13 \pm 1$ |

## Stability Constant Assessment - Methodology

Metal complexes can be modeled using the following equilibria, equations S1 and S2,

## Supplemental Information

$$
\begin{align*}
M^{3+}+L^{3-} \rightleftharpoons M L & \beta_{101}=\frac{[M L]}{\left[M^{3+}\right]\left[L^{3-}\right]}  \tag{S1}\\
M^{3+}+2 L^{3-} \rightleftharpoons M L^{3-} & \beta_{102}=\frac{\left[M L_{2}^{3-}\right]}{\left\lceil M^{3+}\right\rceil\left[L^{3-}\right\rceil^{2}} \tag{S2}
\end{align*}
$$

where $L^{3-}$ represents the fully deprotonated ligand anion, either NTA, CDTA, or HEDTA ${ }^{1}$. An aqueous phase mass balance expression may be used, along with the stability constant models, to calculate the free metal ion concentrations, equation 3.

$$
\begin{equation*}
\left[M^{3+}\right]_{a q}=\left[M^{3+}\right]_{\text {free }}+[M L]+\left[M L_{2}^{3+}\right] \tag{S3}
\end{equation*}
$$

Substitution of the stability constants provides equation 4.

$$
\begin{equation*}
\left[M^{3+}\right]_{a q}=\left[M^{3+}\right]_{\text {free }}\left(1+\beta_{101}\left[L^{3-}\right]+\beta_{102}\left[L^{3-}\right]^{2}\right) \tag{S4}
\end{equation*}
$$

Another substitution of the mass balance into the extraction equation provides equations 5 or 6 which are appropriate for stability constant minimization when either 1:1 or 1:2 metal:ligand species are present, respectively. In equations 5 or $6, D_{0}$ is the distribution of a metal in the absence of a competitive, aqueous phase complexant. These were the relationships considered for assessing for stability constants of NTA, HEDTA, and CDTA.

$$
\begin{align*}
& \frac{D_{o}}{D}-1=\beta_{101}\left[L^{3-}\right]  \tag{S5}\\
& \frac{D_{o}}{D}-1=\beta_{101}\left[L^{3-}\right]+\beta_{102}\left[L^{3-}\right]^{2} \tag{S6}
\end{align*}
$$

This expression relies on the assumptions that the ligand concentration is in excess of the metal ion concentration, and the ligand does not partition into the organic phase. The first assumption works well due to the use of radiotracers in all experiments, ensuring that ligand concentrations will be well above metal ion concentrations. The studied ligands also poorly partition into the organic phase due to the poor organic solubility of the carboxylic acid functional groups present on all studied ligands. Metal-protonated ligand species were assumed to not form at the pcHs studied save for DTPA. To test for metal protonated species with DTPA, solvent extraction studies at different pcHs were conducted.

DTPA requires additional relationships to account for the presence of protonated, M(HDTPA)-, deprotonated, M(DTPA) $)^{2-}$, species form complexes with metal cations. Shanbhag and Choppin describe the method to solve for the protonated and unprotonated stability constants ${ }^{5}$. Equation 6 must be modified by accounting for both species. Equation 7 shows the modification of the addition of the $\beta_{111}$ stability constant.

$$
\begin{equation*}
\frac{D_{o}}{D}-1=\left(\beta_{101}+\beta_{111}\left[H^{+}\right]\right)\left[L^{3-}\right] \tag{S7}
\end{equation*}
$$

To solve for each stability constant, an overall conditional constant, called $\beta_{1}$, must first be solved for. This constant is defined in equation 8 .
$\beta_{1}=\beta_{101}+\beta_{111}\left[H^{+}\right]$
This conditional constant is solved for using non-linear least squares analysis of equation 9 .

## Supplemental Information

$$
\begin{equation*}
\frac{D_{o}}{D}-1=\beta_{1}\left[L^{3-}\right] \tag{S9}
\end{equation*}
$$

By completing competition experiments over a range of hydrogen ion concentrations and solving for $\beta_{1}$ for each set, a plot of $\beta_{1}$ vs. hydrogen ion concentration may be created. The slope of this plot is the stability constant for the protonated complex while the intercept is the stability constant for the deprotonated complex.


Figure S3. Stability constants for actinide ions with NTA, HEDTA, DTPA, and for the 1:3 DPA complex plotted relative to the Am value for each ligand, to help identify trends across the series from Figure 1. Error bars are 10 .

## Supplemental Information

## Computational Methods

Structures of the $\left[\mathrm{An}^{\text {III }} \mathrm{DTPA}\right]^{2-}$, $\left[\mathrm{An}^{\text {III }} \mathrm{DTPA}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2-},\left[\mathrm{An}^{\text {III }}(\mathrm{DPA})_{3}\right]^{3--},\left[\mathrm{An}^{\text {III }}\left(\mathrm{H}_{2} \mathrm{O}\right)_{8}\right]^{3+}$, and $\left[\mathrm{An}^{\text {III }}\left(\mathrm{H}_{2} \mathrm{O}\right)_{9}\right]^{3+}$ complexes were optimized using density functional theory (DFT) with the hybrid PBE0 functional, ${ }^{7,8}$ relativistic ZORA Hamiltonian, and triple- $\zeta$ plus two polarization function (TZ2P) basis sets with the frozen core approximation applied to the inner shells $\left[1 \mathrm{~s}^{2}-4 \mathrm{f}^{14}\right]$ for actinide atoms and $\left[1 \mathrm{~s}^{2}\right]$ for $\mathrm{C}, \mathrm{N}$ and O atoms. ${ }^{9}$, ${ }^{10}$ Frequency calculations were performed to determine thermodynamic properties of each structure; all computed structures were local minima with no imaginary frequencies. The COSMO implicit solvation model ${ }^{11-14}$ was used to model the complexes in an aqueous environment, using a radius of $2.224 \AA$ for the actinide ions. Frequency calculations were performed at 1354 atm when calculating reaction energies; this standard state correction is necessary because molecules under standard state conditions ( 1 atm ) have more freedom prior to complexation than they do subsequently, which is not the case in solution. The pressure of 1354 atm was determined from the density of liquid water at the standard state. ${ }^{15}$ All calculations were performed using ADF 2016. ${ }^{16,17}$

To calculate reaction energies, large water clusters were used. Globally minimized clusters of 18 and 19 water molecules were taken from Su et al. ${ }^{18}$ These geometries were reoptimized to remove imaginary frequencies at the PBE0 level; all imaginary frequencies were removed from the $\left(\mathrm{H}_{2} \mathrm{O}\right)_{18}$ geometry, while a single imaginary frequency at $-21.6 \mathrm{~cm}^{-1}$ remained in and could not be removed from the $\left(\mathrm{H}_{2} \mathrm{O}\right)_{19}$ geometry. Reactions energies for DTPA complexation were calculated following the reactions in Equations S10-S13 below, depending on the coordination numbers of the aqueous ion and the complex:

$$
\begin{align*}
& A n\left(\mathrm{H}_{2} \mathrm{O}\right)_{8}^{3+}+\mathrm{DTPA}^{5-}+8\left(\mathrm{H}_{2} \mathrm{O}\right)_{18} \rightarrow \mathrm{An}(\mathrm{DTPA})^{2-}+8\left(\mathrm{H}_{2} \mathrm{O}\right)_{19}  \tag{S10}\\
& \mathrm{An}\left(\mathrm{H}_{2} \mathrm{O}\right)_{8}^{3+}+\mathrm{DTPA}^{5-}+7\left(\mathrm{H}_{2} \mathrm{O}\right)_{18} \rightarrow \mathrm{An}(\mathrm{DTPA})\left(\mathrm{H}_{2} \mathrm{O}\right)^{2-}+7\left(\mathrm{H}_{2} \mathrm{O}\right)_{19}  \tag{S11}\\
& \mathrm{An}\left(\mathrm{H}_{2} \mathrm{O}\right)_{9}^{3+}+\mathrm{DTPA}^{5-}+9\left(\mathrm{H}_{2} \mathrm{O}\right)_{18} \rightarrow \mathrm{An}(\mathrm{DTPA})^{2-}+9\left(\mathrm{H}_{2} \mathrm{O}\right)_{19}  \tag{S12}\\
& \mathrm{An}\left(\mathrm{H}_{2} \mathrm{O}\right)_{9}^{3+}+\mathrm{DTPA}^{5-}+8\left(\mathrm{H}_{2} \mathrm{O}\right)_{18} \rightarrow \mathrm{An}(\mathrm{DTPA})\left(\mathrm{H}_{2} \mathrm{O}\right)^{2-}+8\left(\mathrm{H}_{2} \mathrm{O}\right)_{19} \tag{S13}
\end{align*}
$$

## Supplemental Information

## Computational Thermodynamics



Figure S4. Gibbs free energies of actinide-DTPA complexation. Reactions with differing coordination
 CN 9 to CN 8, ( $\infty$ ) CN 8 to CN 8 (see reactions S10-S13 in the ESI). Same data as Figure 2, plotted nonrelative.

## Supplemental Information



Figure S5. Average energy levels of the An 5 f (blue) and 6d (red) orbitals in the [An(DTPA)] ${ }^{2-}$ complexes. The average energy levels of the 2 p orbitals of coordinating DTPA O and N atoms are also shown (grey). Darker lines represent the average energy value of the orbitals, while the shaded regions give the standard deviation. Averages and standard deviations of the orbital energies are weighted by MO composition.

## Computed Structures



Figure S6. Average An-DPA and An-DTPA distances for coordinating nitrogen and oxygen atoms in optimized DFT structures.

## Supplemental Information

## Optimized Geometries

$[\mathrm{Es}(\mathrm{DTPA})]^{2-}$

|  |
| :---: |
|  |
| O 1.730511-1.544006-1.470955 |
| 2108 -1.782736 1. 124546 |
| -0.481273-3.214088 2.673249 |
|  |
| O -2.224031 3.692214-0.702553 |
| O $1.2931231 .556423-1.560353$ |
| 8,8608 |
| .207389 -0.611993 0.82534 |
| 7 |
| N 2.4190540 .1467090 .556397 |
| C -2.841403-1.355371-1.47190 |
| -3.279156-0.660469 |
| -2.349789 0.4997921 .781259 |
| 2.371062 |
| 8521.7907371 .98 |
| C 2.1378370 .5692551 .938446 |
| 3.052803-1.173314 0.495015 |
| $2.777374-1.89606-0.831692$ |
| -1.906878 1.505456 |
| C -0.661983-2.334383 1.81738 |
| 832.8342060 .860105 |
| -1.539989 $2.70476-0.384271$ |
| , |
| $2.4738861 .925214-1.267432$ |
| -1.79066-2.226898 |
| 55555-2.799567-1.178624 |
| 2.484142 -2.691034 0.84634 |
| -3.009723 0.2156242 .614491 |
| 2410.1269672.845574 |
| 407461.331819 |
| 2383361.6990253 .164514 |
| 1.2031713 .3834731 .637341 |
| 730743.4786210 .548469 |
| 1326932.124763 .028373 |
| 132282.6095621 .443729 |
| $1.671004-0.2754852 .451946$ |
| Н 3.0671040 .8119132 .478281 |
| H 2.618047 -1.809636 1.270784 |
| $36115-1.121650 .666345$ |
| $4.0351190 .628401-0.708307$ |
| H 3.6989091 .8479990 .494777 |
| H -2.699656-1.936903 2.420758 |
| 4.186087-1.148178 0.208553 |
| 35 |

## Supplemental Information

$\left[\mathrm{Es}(\mathrm{DTPA})\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2-}$
Es 0.031672-0.148409-0.625775
O -1.690432 -1.55781-1.593746
O 1.805565-1.566634-1.463833
O 0.023568-0.348668-3.218911
O 0.240636-1.808408 1.035308
O -0.436034-3.233466 2.61431
O -1.50836 1.596583-1.047781
O - 2.25109 3.675924-0.720721
O $1.3168451 .686798-1.411418$
O 3.133051 2.974493-1.568535
N -2.215361-0.583536 0.872094
N -0.098116 1.5802351 .350569
N 2.4197050 .1050530 .571412
C - $2.938438-1.451304-1.340318$
C - $3.318285-0.654878-0.085602$
C -2.341569 0.5444881 .805596
C-1.003055 1.0026392 .367499
C 1.2412881 .8034331 .943622
С 2.1232740 .5644081 .936322
C 3.041451 -1.220388 0.558457
C $2.799151-1.955942-0.765878$
C -2.079069-1.862305 1.57773
C - $0.642621-2.3364951 .779342$
C -0.649728 2.8374680 .820042
C - $1.556062 .693828-0.408023$
С $3.258241 .0586-0.167608$
C $2.5113791 .995551-1.116434$
H -0.708355 -0.988322 -3.193771
Н $0.824851-0.883403-3.30918$
O -3.850584-1.908243-2.045343
O 3.553624-2.898724-1.059814
H -2.555191-2.652633 0.986168
H -2.996876 0.2840142 .650922
H - 0.4915780 .160552 .843029
H -2.829074 1.3721821 .284571
H -1.193171 1.7473853 .156468
H -1.184593 3.4027381 .595723
H 0.1762833 .4708110 .48325
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H 4.12011-1.175881 0.761496
H $3.9524820 .503595-0.808394$
H 3.8835261 .6533930 .511835
H -2.598641-1.846903 2.544959
H -4.230682-1.083889 0.351582
H -3.559495 0.354142 -0.433387

## Supplemental Information

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[Es(DPA)}\mp@subsup{)}{3}{}\mp@subsup{]}{}{3-
C -22.094836 -47.073076 0.94648
C -23.093929 -47.360823-0.165882
C -22.846497 -48.267216-1.1956
C -23.830372 -48.456748-2.163565
C -25.021168 -47.739187-2.073451
C -25.183915 -46.854228-1.008877
C -26.442478 -46.02082-0.80479
O -22.47724 -46.230956 1.813597
H -24.955066 -48.319675 6.319144
H -23.546572 -46.922355 7.867674
H -22.56817 -44.775598 6.990721
N -25.415597 -42.6743191.369874
O -26.435791 -45.270299 0.216901
O -25.644152 -47.166329 2.528133
C -25.553861 -47.706239 3.672
C -24.717212 -46.94111694.688664
C -24.509035-47.385848 5.993407
C -23.728061 -46.60627 6.843862
C -23.182423 -45.41659 6.366834
C -23.440922-45.049939 5.047158
C -22.898202 -43.774173 4.41769
O -23.233022-43.580218 3.210589
H -27.769352 -40.51506 2.38434
H -26.592102 -39.07514 0.688981
H -24.6274 -40.043027-0.550208
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C -26.917269 -40.881899 1.82169
C -26.259732-40.091799 0.881389
C -25.171069 -40.619663 0.19079
C -24.779494-41.928404 0.469071
C -23.605153-42.610178-0.221394
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O -22.182491 -43.028229 5.110656
H -25.816241 -47.852664-2.802929
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N -24.236485 -46.6814-0.089412
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N -24.190487-45.802264 4.243774
Es -24.620757-45.057452 1.840379
H -21.903292-48.80278-1.223155
H -23.670804 -49.156379-2.979639
```


## Supplemental Information

## Supplemental Information

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