# Aqueous Complexation of Thorium(IV), Uranium(IV), Neptunium(IV), Plutonium(III/IV), and Cerium(III/IV) with DTPA

M. Alex Brown,[†] Alena Paulenova,[‡] and Artem V. Gelis*[,§]

[†]Department of Chemistry and [‡]Department of Nuclear Engineering and Radiation Health Physics, Oregon State University, Corvallis, Oregon 97330, United States
[§]Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, United States

S *Supporting Information*

ABSTRACT: Aqueous complexation of Th(IV), U(IV), Np(IV), Pu(III/IV), and Ce(III/IV) with DTPA was studied by potentiometry, absorption spectrophotometry, and cyclic voltammetry at 1 M ionic strength and 25 °C. The stability constants for the 1:1 complex of each trivalent and tetravalent metal were calculated. From the potentiometric data, we report stability constant values for Ce(III)DTPA, Ce(III)HDTPA, and Th(IV)DTPA of $\log \beta_{101} = 20.01 \pm 0.02$, $\log \beta_{111} = 22.0 \pm 0.2$, and $\log \beta_{101} = 29.6 \pm 1$, respectively. From the absorption spectrophotometry data, we report stability constant values for U(IV)DTPA, Np(IV)DTPA, and Pu(IV)DTPA of $\log \beta_{101} = 31.8 \pm 0.1$, 32.3 ± 0.1, and 33.67 ± 0.02, respectively. From the cyclic voltammetry data, we report stability constant values for Ce(IV) and Pu(III) of $\log \beta_{101} = 34.04 \pm 0.04$ and 20.58 ± 0.04, respectively. The values obtained in this work are compared and discussed with respect to the ionic radius of each cationic metal.
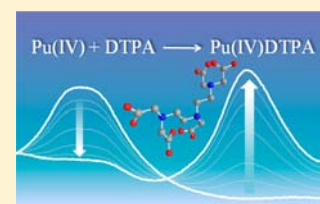
INTRODUCTION

Diethylenetriaminepentaacetic acid (DTPA) complexes with actinide and lanthanide elements play a relevant role in nuclear medicine and the processing of used nuclear fuels. DTPA's strong affinity for positively charged metal ions in solution has made it one of the most propitious agents for actinide removal (particularly plutonium) via chelation therapy from a biological system after internal contamination.[1,2] Gadolinium complexes with DTPA are applicable in the field of magnetic resonance imaging because of their low toxicity and accelerated relaxation rates.[3] DTPA is also one of the key components used in solvent extraction separations of trivalent lanthanides (Ln(III)) from trivalent actinides (An(III)) with respect to reduction of long-term radioactive hazards and heat contribution from nuclear wastes.[4] Advanced separations of used nuclear fuels which utilize similar techniques and materials have been extended to the tetravalent actinides (An(IV)) as well.[5]

In each case, chelation therapy and in solvent extraction separations of metals, it is desirable to construct a thermodynamic model that is based on the stability constants of relevant ligands with specific metal ions at certain temperatures and ionic media.[6a] The need for efficient separations of Ln(III) from An(III) with regard to nuclear reprocessing sparked in-depth investigations of the aqueous equilibria of Ln(III) and An(III) with DTPA, and thus, the literature of these stability constant values for trivalent metals is much more prolific and continues to be researched at the present day.[7,8] Of particular interest in this work is the 1:1 complex of An(IV) and Ce(IV) with DTPA (where An = Th, U, Np, or Pu). The stability of this complex can dictate the nature of the formation of the succeeding complexes such as the hydrolyzed species (An(IV)DTPA(OH)) which forms at

neutral pH. The first complex of An(IV) with DTPA, however, forms under relatively strong acidic conditions. This species was first studied in the early 1970s by potentiometric and spectrophotometric methods.[9−12] Traditionally, potentiometric methods are the preferred and most reliable methods of investigating metal−ligand equilibria.[13] However, without careful consideration of the junction potential of a pH electrode, strong acidic conditions (typically below pH 2) render potentiometry unreliable in determining stability constant values.[6]

In this work we investigate the complexation of DTPA with Ce(III/IV), Th(IV), U(IV), Np(IV), and Pu(III/IV) by potentiometry, spectrophotometry, and cyclic volatammetry at 1 M ionic strength and 25 °C with the objective of constructing a more reliable database of An(IV) complexes with DTPA and examine trends in the complexation nature as a function of ionic radii. The results and discrepancies from the accepted literature are discussed.

EXPERIMENTAL SECTION

Caution: Thorium, uranium, neptunium, and plutonium all contain alpha-emitting radioactive isotopes. Health physics supervision should be employed when handling these radionuclides.

Materials. Chemicals used were of ACS specifications. All aqueous solutions were prepared using Milli-Q (18.1 mΩ) deionized (DI) water. Solutions containing hydrochloric acid were prepared by dilution of a 1 or 6 M standardized solution (Sigma-Aldrich).

Ce(III). A cerium stock solution was prepared by dissolving cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.9%) in dilute HCl.

Th(IV). A thorium stock solution was prepared by dissolving thorium nitrate ($Th(NO_3)_4 \cdot 4H_2O$, 99%) in standardized 1 M HCl.

U(IV). Depleted uranium metal was dissolved in warm 6 M HCl and then filtered to remove the insoluble oxide compounds. The uranium concentration was determined by thermal ionization mass spectrometry (TIMS).[14] The solution was maintained under a constant nitrogen gas stream, and the tetravalent oxidation state was confirmed throughout the set of experiments by visible spectroscopy.

Np(IV). A ^{237}Np stock was purified using an anion exchanger with 7 M HNO_3. Neptunium was reduced to Np(IV) by hydrogen peroxide and sorbed on a Reillex HPQ resin as a hexanitrato complex. The complex was washed by 20 bed volumes of 5.5 M HNO_3 to remove cations and eluted with 0.3 M HNO_3 as NpO_2^+. To convert the aqueous matrix to HCl, the solution was evaporated to dryness three times in concentrated HCl. No NO_x gas was observed after the first evaporation. The stock solution was diluted with DI water to obtain the desired acid concentration and analyzed by ICP-MS; no major cationic impurities were found. A working solution of Np(IV) in 2 M HCl was prepared by taking an aliquot of the house stock of Np(V) and electrochemically reducing it using a platinum mesh cathode vs saturated calomel electrode (SCE) at −0.1 V for 20 min. The tetravalent oxidation state was confirmed by the absorption peaks at 724 and 960 nm and the absence of a Np(V) absorption peak at 980 nm. The neptunium concentration was determined by liquid scintillation (PerkinElmer TriCarb, α/β discrimination) and γ spectroscopy (GeLi Canberra detector with Ortec software). The solution was maintained under a constant nitrogen gas stream throughout the set of experiments and periodically checked by visible spectroscopy for consistency of the tetravalent oxidation state.

Pu(IV). A solution of ^{242}Pu was purified by an anion-exchange method using Reillex HPQ resin in the nitrate form.[15] Plutonium was adsorbed on the column in 7 M HNO_3 as $Pu(NO_3)_6^{2-}$; then the column was washed with at least 20 bed volumes of 5.5 M HNO_3 to remove major cationic impurities. Plutonium was eluted by 0.3 M HNO_3 at 60 °C. Approximately 10 mL of concentrated TraceGrade HNO_3 was added to the eluate. The solution was evaporated slowly in concentrated HNO_3 (~15.9 M) until approximately 8 mL remained. Then a known volume fraction was diluted with standardized 0.5 M HNO_3 in a volumetric flask to prepare a final stock solution in 2.0 M HNO_3. Stock solution was stored for approximately 3 years before usage. Prior to use, it was analyzed by α spectroscopy (Ortec) and γ spectroscopy. The isotope composition (by α activity) was 78% ^{242}Pu, 5% ^{239}Pu, and 17% $^{238}Pu/^{241}Am$ (>99% Pu by mass). The americium content was calculated by γ spectroscopy and found to be less than 5% of the total alpha radioactivity. The plutonium concentration in both the stock and the working solutions was determined by liquid scintillation considering the fraction of ^{242}Pu (0.78). The stock solution was also analyzed by ICP-MS to confirm the isotopic ratios and concentrations. The tetravalent oxidation state was verified by visible spectroscopy; no Pu(IV) polymer, Pu(III), or Pu(VI) was detected.

Cyclic Voltammetry. A 3-electrode cell was connected to a CH Instruments CHI660B potentiostat. A thermostatted cell from BioAnalytical Systems (BAS) and a circulating water bath was used to maintain the temperature 25.0 ± 0.1 °C, which was verified by a Fisher Scientific thermometer, traceable to NIST. A CHI102 Pt disk working electrode ($d = 2$ mm), Pt wire auxiliary electrode, and Ag/AgCl/KCl$_{satd}$ reference electrodes were used ($E = 0.1999$ V/NHE).[16] The Ag/AgCl/KCl$_{satd}$ reference electrode was prepared from the BAS Ag/AgCl/3 M NaCl solution by substituting the electrolyte with saturated KCl (with added solid AgCl). The reference electrode was checked against two SCEs by Radiometer and EG&G Princeton. The cell potential (E_{cell}) was found to be −0.045 V, consistent with the literature data.[16]

A Pt working electrode was pretreated in 0.5 M H_2SO_4 by first applying an oxidizing potential (10 cycles from 0 to 2.4) and then a reducing potential (20 cycles from 0 to −1 V/SCE). The electrode was polished between tests using 0.05 μm alumina−water paste. High-purity N_2 gas was used to purge the solution for at least 20 min prior to each experiment. Peak potentials and peak currents for the cyclic

voltammetry experiments were determined by the CH Instruments operating software from the experimental graphs.

An aliquot of plutonium stock solution was added to a certain amount of DTPA/electrolyte solution to obtain desired concentrations. The pH was adjusted by adding either corresponding acid or base. On several occasions, a precipitate was formed upon alkali addition. In these cases, the solution was filtered through a Duapore 0.1 μm syrince filter (Millipore). To verify the absence of colloidal species in solution, an aliquot was filtered through a Millipore Ultrafree MC Biomax 10 000 NMWL centrifuge filter with ~1.5 nm pore size.[17] The alpha activities of the initial solution and the filtrate were the same within 1%, and it was thus concluded that no colloidal plutonium species were present. The working solution was stored for 12 h before use to ensure no formation of any precipitate. An alpha energy spectrum was collected to confirm the ratio of ^{242}Pu activity to the total alpha activity. No significant changes (<1%) were observed. Visible spectra were collected at certain pH points.

Potentiometric Titrations. Potentiometric titrations were carried out with a Metrohm automated titrator, Titrando 836. Solutions were maintained at 25.0 ± 0.1 °C using a circulating water-jacketed titration vessel that had been calibrated using a NIST traceable thermometer. Analyte solution was bubbled with N_2 gas in each set of experiments. The titrant was prepared by dilution of 50% NaOH (precipitated of insoluble Na_2CO_3) with boiled DI water and additional NaCl or KNO_3 electrolyte to correct for the ionic strength. Titrations of Th:DTPA used standardized HCl as the titrant (Sigma-Aldrich). The pH electrode (Metrohm, equipped with Metrohm combination electrode in 3 M KCl) was calibrated to measure p[H] (hydrogen ion concentration) by titrating a standardized strong acid with the prepared alkali and using *GLEE* software; the carbonate content, as determined by a Gran plot, did not exceed 2%.[18] For experiments concerning strong acid concentrations, the electrode was calibrated by titrating solutions containing 1 M NaCl with 1 M HCl to the acid concentration of interest. Electromotive force readings (mV) were input to the program *VlpH*[18] to calibrate and adjust for the junction potential of the electrode. Calibration data can be found in the Supporting Information, Figure S1. These readings were used in the *Hyperquad* refinements.[19] The linear trends in mV adjustments from these blank experiments were then applied to the titrations containing thorium and DTPA. Potentiometric experiments consisted of no less than 50 mV readings, and multiple titrations were performed at various Th:DTPA ratios: [Th(IV)] = 2 mM:[DTPA] = 4 mM and [Th(IV)] = 2 mM:[DTPA] = 2 mM in NaCl media. Ce:DTPA solutions were titrated in KNO_3 media and at concentration ratios of [Ce(III)] = 1 mM:[DTPA] = 1 mM, [Ce(III)] = 0.7 mM:[DTPA] = 1 mM, and [Ce(III)] = 0.4 mM:[DTPA] = 1 mM. DTPA titrations were carried out at 4 and 7 mM in NaCl or KNO_3. No precipitation was observed.

Spectrophotometric Titrations. All solutions were prepared in a 1.00 mL volumetric flask and rigorously agitated on a vortex mixer. Measurements were made on a Varian Cary 5E UV−vis−NIR spectrophotometer using a 10.00 mm quartz cuvette with a Teflon cap. The temperature of the solutions in the cuvette was maintained at 25.0 ± 0.1 °C using a circulating temperature bath which had previously been calibrated with a Fisher Scientific temperature probe. The data interval for each measurement was set to 0.1 nm, and the scan range was typically within ±200 nm of the peaks of interest. The slit width was set to 0.2 nm for all measurements. Reference solutions for each set of experiments contained DTPA, the background electrolyte (NaCl), and the appropriate concentration of HCl. For the set of uranium titrations, the DTPA concentration ranged from 0 to 7.2 mM, with a constant uranium concentration of 5 mM, 0.6 M H^+, and 0.4 M NaCl. Neptunium titrations were carried out at 0.6 M H^+, 0.4 M NaCl, a DTPA concentration range of 0−5 mM, and a constant neptunium concentration of 4.5 mM. At a constant plutonium concentration of 4 mM, titrations were carried out within a DTPA concentration range of 0−5 mM, 0.9 M H^+, and 0.1 M NaCl. For each set of An(IV) solutions, no precipitation was observed. The stability constants and spectral deconvolution were refined using the least-squares fitting program *HypSpec*.[20]

■ RESULTS

Aqueous metals (M) and their complexes with organic ligands (L) can be described as (charges omitted)

$$iM + jH + kL \rightleftharpoons M_iH_jL_k \qquad (1)$$

and their corresponding equilibrium on the molarity scale at a constant ionic strength is defined as

$$\beta_{ijk} = [M_iH_jL_k]/[M]^i[H]^j[L]^k \qquad (2)$$

Hydrolysis of tetravalent actinides, particularly plutonium, has been thoroughly studied and can occur even in relatively acidic solutions.[21a] The first hydrolysis constant for the tetravalent actinides was included in the each model.[22] Formation of the very stable and soluble 1:1 complex of An(IV) with DTPA occurs under relatively high acidic conditions.

$$An^{4+} + DTPA^{5-} \rightleftharpoons AnDTPA^- \qquad (3)$$

$$\beta_{101} = [AnDTPA^-]/[An^{4+}][DTPA^{5-}] \qquad (4)$$

Anionic and cationic charges written in the text are here omitted. DTPA also forms a hydroxide metal complex with tetravalent actinides (An(IV)DTPAOH).[22] However, this species was not included in the refinement models since it forms at near-neutral pH conditions.

DTPA Dissociation Constants. An example of a DTPA potentiometric titration curve is shown in Figure 1. Table 1 lists
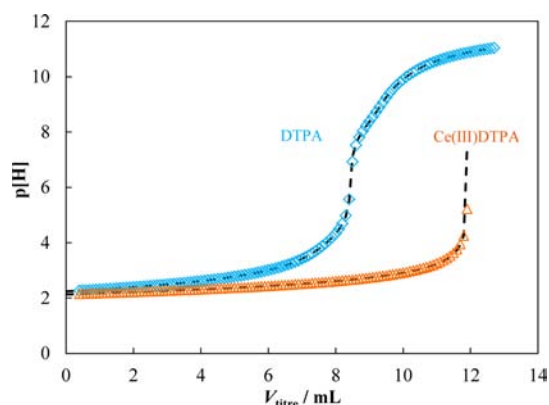

Figure 1. Potentiometric titration of DTPA, [DTPA] = 4.0 mM, [KNO$_3$] = 1M, T = 25.0 ± 0.1 °C, V_0 = 125 mL, titrant =0.1066 M NaOH + 0.9 M KNO$_3$ (diamonds). Potentiometric titration of Ce(III)DTPA, [Ce(III)] = 0.38 mM, [DTPA] = 0.95 mM, [KNO$_3$] = 1M, T = 25.0 ± 0.1 °C, V_0 = 125 mL, titrant [NaOH] = 0.1066 M + 0.9 M KNO$_3$ (squares). Symbols represent experimental data, and dashed curve represents the model fit.

the protonation equilibria of DTPA used in this work. For simplicity, DTPA will refer to the deprotonated (5−) charged anion. Protonation equilibria of DTPA on the molarity scale are defined as

$$nH^+ + H_{n-1}DTPA^{5-} \rightleftharpoons H_nDTPA^{n-5} \qquad (5)$$

$$K_n = [H_nDTPA^{5-n}]/[H^+][H^{n-1}DTPA^{5-}] \qquad (6)$$

where n = 1−8. DTPA has five acidic carboxylic groups and three amine groups capable of protonation. Protonation constants used in this work were determined by p[H] titration and compared with the NIST Critical Stability Constant Database values (referred to as NIST).[22] Best fits were obtained

Table 1. Thermodynamic Data for DTPA and Ce(III/IV), Th(IV), U(IV), Np(IV), and Pu(III/IV) at I = 1 M (H, NaCl or H, KNO$_3$) and 25.0 ± 0.1 °C (unless otherwise noted)[a]

equilibria	log β
DTPA	
H$^+$ + DTPA^{5-} ⇌ HDTPA^{4-}	9.50 ± 0.01 (1 M Na$^+$);[b] 9.92 ± 0.01 (1 M K$^+$)[b]
2H$^+$ + DTPA^{5-} ⇌ H$_2$DTPA^{3-}	17.65 ± 0.01 (1 M Na$^+$);[b] 18.16 ± 0.02 (1 M K$^+$)[b]
3H$^+$ + DTPA^{5-} ⇌ H$_3$DTPA^{2-}	21.76 ± 0.02 (1 M Na$^+$);[b] 22.29 ± 0.02 (1 M K$^+$)[b]
4H$^+$ + DTPA^{5-} ⇌ H$_4$DTPA$^-$	24.46 ± 0.04 (1 M Na$^+$);[b] 25.11 ± 0.02 (1 M K$^+$)[b]
5H$^+$ + DTPA^{5-} ⇌ H$_5$DTPA	26.65 ± 0.06 (1 M Na$^+$);[b] 26.66 ± 0.08 (1 M K$^+$)[b]
6H$^+$ + DTPA^{5-} ⇌ H$_6$DTPA$^+$	28.52 ± 0.08 (1 M Na$^+$);[b] 28.67 ± 0.07 (1 M K$^+$)[b]
7H$^+$ + DTPA^{5-} ⇌ H$_7$DTPA^{2+}	29.3[c]
8H$^+$ + DTPA^{5-} ⇌ H$_8$DTPA^{3+}	29.2[c]
Cerium	
Ce^{3+} + NO$_3^-$ ⇌ CeNO$_3^{2-}$	0.2[c]
Ce^{3+} + DTPA^{5-} ⇌ CeDTPA^{2-}	20.01 ± 0.01 (1 M K$^+$)[b]
Ce^{3+} + H$^+$ + DTPA^{5-} ⇌ CeHDTPA$^-$	22.0 ± 0.2 (1 M K$^+$)[b]
Ce^{4+} + DTPA^{5-} ⇌ CeDTPA$^-$	34.04 ± 0.04 (1 M K$^+$)[e]
Thorium	
Th^{4+} + H$_2$O ⇌ Th(OH)$^{3+}$ + H$^+$	−4.1[c]
Th^{4+} + NO$_3^-$ ⇌ ThNO$_3^{3+}$	0.67[c]
Th^{4+} + Cl$^-$ ⇌ ThCl^{3+}	0.18[c]
Th^{4+} + DTPA^{5-} ⇌ ThDTPA$^-$	29.6 ± 1 (1 M Na$^+$)[b]; 26.6[c]
Th^{4+} + H$^+$ + DTPA^{5-} ⇌ ThHDTPA	29.8 ± 1 (1 M Na$^+$)[b]; 30.8 (μ = 0.1)[c]
Uranium	
U^{4+} + H$_2$O ⇌ U(OH)$^{3+}$ + H$^+$	−1.9[c]
U^{4+} + Cl$^-$ ⇌ UCl^{3+}	0.3[c]
U^{4+} + DTPA^{5-} ⇌ UDTPA$^-$	31.8 ± 0.1 (1 M Na$^+$)[d]; 28.8[c]
Neptunium	
Np^{4+} + H$_2$O ⇌ Np(OH)$^{3+}$ + H$^+$	−2.22[c]
Np^{4+} + DTPA^{5-} ⇌ NpDTPA$^-$	32.3 ± 0.1 (1 M Na$^+$)[d]; 30.3[c]
Plutonium	
Pu^{3+} + DTPA^{5-} ⇌ PuDTPA^{2-}	20.58 ± 0.04 (1 M H$^+$)[e]; 21.5[c]
Pu^{4+} + H$_2$O ⇌ Pu(OH)$^{3+}$ + H$^+$	−1.52[c]
Pu^{4+} + Cl$^-$ ⇌ PuCl^{3+}	0.14[c]
Pu^{4+} + NO$_3^-$ ⇌ PuNO$_3^{3+}$	0.74[c]
Pu^{4+} + 2NO$_3^-$ ⇌ Pu(NO$_3$)$_2^{2+}$	1.37[c]
Pu^{4+} + DTPA^{5-} ⇌ PuDTPA$^-$	33.67 ± 0.02 (1 M Na$^+$)[d]; 29.5[c]

[a]Uncertainties are reported at 95% confidence. [b]Determined by potentiometry. [c]NIST database. [d]Determined by spectrophotometry. [e]Determined by cyclic voltammetry.

when constants K_n = 1−6 were refined. With the exception of pK_{a6}, the values were calculated to be within the standard

deviation of the NIST values, though the ionic medium is ambivalent in the database for pK_{a3-8}. Refinement of the seventh protonation constant resulted in excessive error, and the eighth protonation constant could not be determined in this set of experiments. The NIST database reports values of $pK_{a7} = 0.8$ and $pK_{a8} = -0.1$, which were also sequentially mapped and quantified using ^{1}H NMR chemical shift data;[23,24] these values were used in our models.

Ce(III)DTPA Complex. Figure 1 shows a typical Ce:DTPA titration curve. Best results were obtained when the species CeDTPA, CeHDTPA, and CeNO$_3$ were included in the refinement model. We report a CeDTPA stability constant value of $\log \beta_{101} = 20.01 \pm 0.02$ (1 M K, 25 °C, 2σ uncertainty). Protonated metal complex species have previously been observed for An(III) and Ln(III).[8,22] The species CeHDPTA refined successfully within the model; we report $\log \beta_{111} = 22.0 \pm 0.2$ (1 M K, 25 °C, 2σ uncertainty). The uncertainty in each value was taken from an average and a standard deviation of the results of three titrations.

Th(IV)DTPA Complex. Figure 2 shows a representative $p[H]$ titration curve of a Th:DTPA solution. Near the end
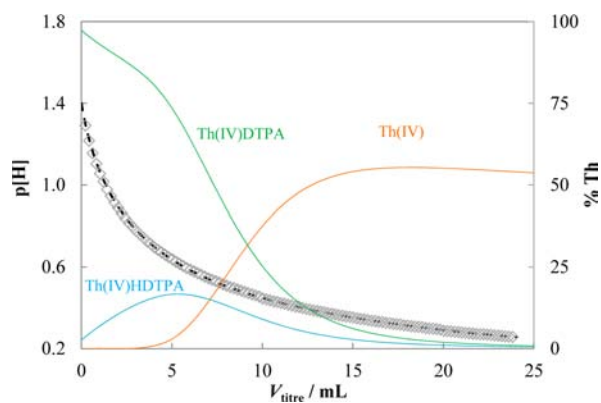

Figure 2. Potentiometric titration of Th(IV)DTPA. Symbols represent experimental data; dashed curve represents the model fit; [Th(IV)] = 2.0 mM; [DTPA] = 4.0 mM; [NaCl] = 1 M; titrant [HCl] = 1.00 M; V_0 = 20 mL; T = 25.0 ± 0.1 °C. Th(IV) represents a mixture of Th^{4+} and ThCl^{3+}.

point of the titration, the $p[H]$ values approached the region in which the junction potential of the electrode became significant. The best fit of the data by *Hyperquad* yielded two complexes, ThDTPA and ThHDTPA. Chloride and nitrate contributions were included; the complete model is listed in Table 1. The reported stability constants of $\log \beta_{101} = 29.6 \pm 1.0$ (1 M Na; 25 °C; 2σ uncertainty) and $\log \beta_{111} = 29.8 \pm 1.0$ (1 M Na; 25 °C; 2σ uncertainty) were taken from the average of two titrations performed at different Th:DTPA ratios.

U(IV)DTPA Complex. Figure 3a shows the absorption spectra of U(IV) and the effect of additions of DTPA. Table 1 shows the complete model used for stability constant calculations. Factor analysis by the *HypSpec* software was implemented to characterize the number of species present in solution. Using the assumption that the total absorbance is the sum of the individual absorbances, subjecting the absorbance data to singular value decomposition and identifying the number of singular values that are positive, the software alluded to the possibility of two absorbing species. The majority of the absorbance was due to the U(IV) cation and the U(IV)DTPA complex. Including the monomeric UCl complex into the
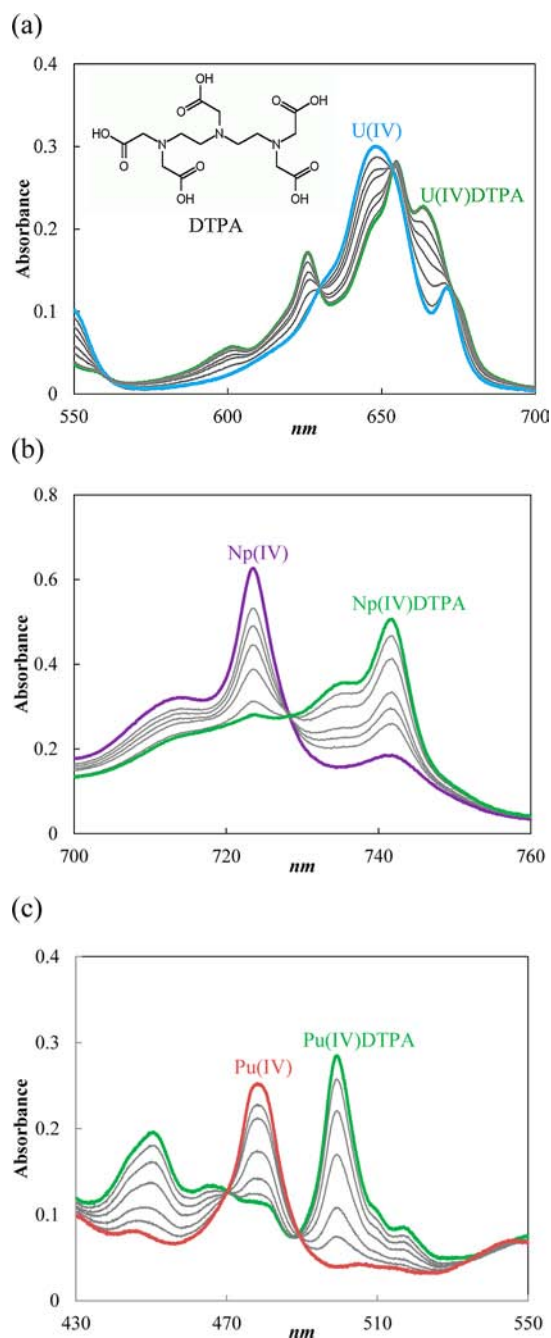

Figure 3. Spectrophotometric titrations of (a) U(IV), (b) Np(IV), and (c) Pu(IV) as a function of DTPA concentration. Conditions are as follows: (a) [U(IV)] = 5.0 mM for all spectra, [DTPA] = 0 (labeled U(IV)), 0.49, 1.48, 3.46, 4.45, 6.44, and 7.23 mM (labeled U(IV)DTPA), [HCl] = 0.6 M, [NaCl] = 0.4 M; (b) [Np(IV)] = 4.5 mM for all spectra, [DTPA] = 0 (labeled Np(IV)), 0.99, 1.25, 1.48, 2.97, 3.96, and 4.95 mM (labeled Np(IV)DTPA), [HCl] = 0.6 M, [NaCl] = 0.4 M; (c) [Pu(IV)] = 4.0 mM for all spectra, [DTPA] = 0 (labeled Pu(IV)), 0.51, 0.99, 1.98, 2.97, 3.96, and 4.95 mM (labeled Pu(IV)DTPA), [HCl] = 0.9 M, [NaCl] = 0.1 M. Solutions were maintained at 25.0 ± 0.1 °C in a 10.00 mm quartz cuvette.

model gave the best fit of the spectral data ($\log \beta_{101} = 0.4$).[22] A red shift in the spectrum of U(IV) occurred upon addition of DTPA. A more characteristic U(IV)DTPA peak at 627 nm appeared when the concentration of DTPA was in excess to uranium. This peak was followed by an isosbestic point at about 630 nm. From spectral deconvolution of the data, the molar

absorbance for this peak was calculated to be ε_{627} = 34.0 M^{-1} cm^{-1}. Refinement of the spectra (range 600−700 nm) by *HypSpec* calculated a U(IV)DTPA stability constant of log β_{101} = 31.8 ± 0.1 (1 M Na; 25 °C; 2σ uncertainty).

Np(IV)DTPA Complex. Figure 3b shows the absorbance spectra of Np(IV) and Np(IV)DTPA. An isosbestic point followed by a characteristic Np(IV)DTPA peak occurred at 729 and 742 nm, respectively. Factor analysis calculated two absorbing species. The contributions of chloride ions were neglected since the best fit of the spectral data was obtained in the absence of the NpCl species (log β = −0.04). By spectral deconvolution, the molar absorptivity of NpDTPA was calculated to be ε_{742} = 118.0 M^{-1} cm^{-1} and refinement of the spectra (range 700−760 nm) calculated a stability constant value of log β_{101} = 32.3 ± 0.1 (1 M Na; 25 °C; 2σ uncertainty).

Pu(IV)DTPA Complex: Spectrophotometry. Visible spectra of tetravalent plutonium and its DTPA complex are shown in Figure 3c. Two isosbestic points were observed at 471 and 490 nm. The major Pu(IV)DTPA peak grew in at 499 nm. Very similar absorption spectra were observed for a Pu/EDTA system.[25] The majority of the absorbance was due to the Pu(IV) and Pu(IV)DTPA ions. Since the stock solution of plutonium was maintained in nitric acid and modification of this solvent proved to be problematic in previous experiments, nitrate complexation was included in the refinement model (log β_{101} = 0.74, log β_{102} = 1.37).[22] The major extinction coefficient of Pu(IV) in nitric acid (474 nm) is significantly larger[26] than that of a less complexing medium such as chloride or perchlorate.[27] Thus, monomeric $PuNO_3$ was included as an additional colored species in the model and resulted in the best fit of the data. Chloride complexes were also included in the model but contributed no change to the visible spectrum. Deconvolution and refinement of the data yielded an extinction coefficient for the species PuDTPA of ε_{499} = 80.4 M^{-1} cm^{-1} and a stability constant value of log β_{101} = 33.67 ± 0.02 (I = 1 M Na; 25 °C; 2σ uncertainty).

Pu(IV)DTPA Complex: Cyclic Voltammetry. CV was applied to measure the formal redox potential of the Pu(IV)/Pu(III) couple and estimate the stability constant of Pu(IV) with DTPA. A cyclic voltammogram of the Pu(IV)/Pu(III) couple in a DTPA/1 M KCl at pH 3.48 solution is shown in Figure 4. The liquid-junction potential between saturated KCl and 1 M KCl is less than 1 mV.[16] Tests at various scanning
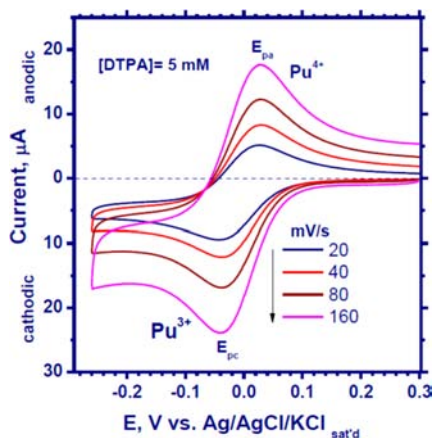

Figure 4. Cyclic voltammograms of a Pu(III)DTPA and Pu(IV)DTPA couple; [Pu(IV)] = 2.2 mM; [DTPA] = 5.0 mM; pH = 3.48; T = 25.0 ± 0.1 °C; 1 M KCl.

rates revealed reversible behavior of the couples. The peak current ratio, i_{pa}/i_{pc}, was approximately equal to 1, randomly varying in the range from 0.93 to 0.97, and the peak separation, $\Delta E = E_{pa} - E_{pc}$, was essentially independent of the scan rate. Thus, ΔE was found to be 66 mV for 40, 80, and 160 mV/s, which is close to the theoretical value of 59 mV for a one-electron transfer of a reversible reaction.[28] Cyclic voltammograms were collected at several pH points. The Pu(IV)/Pu(III) couple showed quasi-reversible behavior between pH 2 and 3 with the peak current ratio changing from 0.8 to 0.85; $E_{1/2}$ = 7.5 mV/ref. The couple was reversible in the pH range from 3.4 to 6. A slight negative shift of potential was observed at pH 5.80 and 6.83. A quasi-reversible electron transfer was found at pH 6.83, and the peak current ratio is about 0.8, although independent of the scan rate. At pH 7.9 a precipitate was observed. Tests were repeated at three different Pu:DTPA ratios, always in an excess of DTPA. The reversibility was observed in the tests in the same pH range between 3.4 and 6. Speciation diagrams that included Pu(III)DTPA (log β = 21.5)[22] and Pu(IV)DTPA (log β = 34) suggested that at excess amounts of DTPA, the coordination structures of Pu(III)-DTPA and Pu(IV)DTPA should be the same in the pH range of 4−6. However, two protonated Pu(III)DTPA species have been reported in the literature.[29] The reversible cyclic voltammogram at pH 3.48 does not confirm the presence of multiple Pu(III)DTPA species as seen by Figure 4. Therefore, based on the reversibility of the couple and the experimental and literature data on An(IV) and An(III) complexation with DTPA, we can write the following reaction for the redox process taking place at the working electrode

$$PuDTPA^- + e^- \rightleftharpoons PuDTPA^{2-} \quad (7)$$
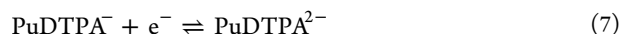
The formal potential of the Pu(IV)/Pu(III) couple in DTPA/1 M KCl can be determined from CV and is approximately equal to the numerical average of the anodic and cathodic peak potentials.[30] The formal potential was found to be about −3 mV vs Ag/AgCl/KCl$_{satd}$ or 196 mV vs NHE. For a simple reaction such as eq 7, the formal potential of the plutonium couple in the DTPA solution is expressed through the formal potential of the couple in a noncomplexing medium with the ratio of the stability constants related by eq 8[31]

$$E^{0'}_{DTPA} = E^{0'}_{f} - 59.15 \log(\beta^{PuIV}/\beta^{PuIII}) \quad (8)$$

where $E^{0'}$ is the formal potential of the Pu(IV)/Pu(III) couple in the corresponding electrolyte in the absence of the complexing agent. Due to Pu(IV) hydrolysis at low acid concentrations, the formal potential in 1 M KCl cannot be directly measured. Instead, the formal potential in 1 M HCl can be used to account for the complexation of Pu(IV) and Pu(III) with 1 M Cl^-. However, the difference in the Pu(IV) and Pu(III) activity coefficients in 1 M KCl and HCl remains unaccounted for and therefore the following calculations are to be considered approximate. If we use $E^{0'}_{HCl}$ = 970 mV,[21c] our experimental value of log β^{PuIV} = 33.67 and $E^{0'}_{DTPA}$ = 196 mV, then log β^{PuIII} is approximately equal to 20.58. This value is in good agreement with the literature value of 21.5 reported by Merciny et al.[29] and the NIST database.[22] Consequently, if the literature value of 21.5 is used, the calculated log β^{PuIV} is equal to 34.58, close to our experimental value but significantly higher than 29.5, which is reported in the database.[22] Due to the approximate character of these calculations and the presence of the junction potential, the uncertainty in each value of the half-wave potentials was estimated to be ±3 mV.

Ce(III/IV)DTPA Complex: Cyclic Voltammetry. There are two values reported for the Ce(IV)DTPA stability constant: 34.1[32] and 30.[33] Using similar considerations as Pu(III/IV) described previously, we can estimate the Ce(IV)DTPA constant using the experimental value of the Ce(III)DTPA stability constant and the formal potentials of the Ce(IV)/Ce(III) couple, $E^{0'}$, in DTPA and 1 M HNO$_3$.

The Ce(IV)/Ce(III) formal potential in 1 M HNO$_3$ is equal to 1.61 V/NHE.[28] The cyclic voltammogram of Ce(III) in the presence of DTPA at pH 4.19 is shown in Figure 5. The couple

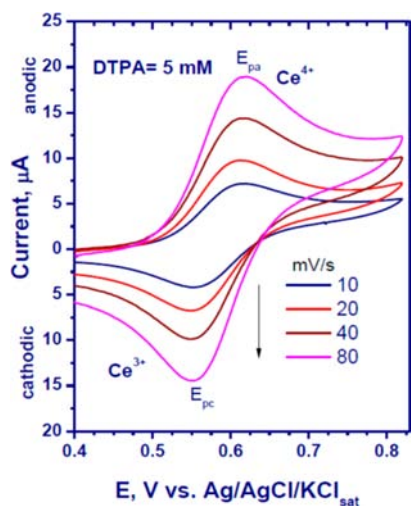**Figure 5.** Cyclic voltammograms of a Ce(III)DTPA and Ce(IV)-DTPA couple; [Ce(III)] = 2 mM; [DTPA] = 5 mM; pH = 4.19; T = 25.0 ± 0.1 °C; 1 M KNO$_3$.

shows nearly reversible behavior: the peak separation $\Delta E = E_{pa} - E_{pc}$ is 66 mV for 10, 20, and 40 mV/s; however, the i_{pa}/i_{pc} is decreasing from 1.25 to ~1.1 as the scan rate increases from 10 to 80 mV/s. This indicates a complication on the Pt electrode surface likely caused by the interaction of Pt with DTPA in the working potential range. On the basis of the speciation diagram shown in Figure S2, Supporting Information, at pH 4.19 the deprotonated Ce(III)DTPA complex becomes predominant and eqs 7 and 8 can be used to calculate log β for Ce(IV)DTPA. By increasing the scan rate, the currents from the Ce(III)−Ce(IV) electron transfer become more dominant, improving the peak current ratio. It should be noted that in order to collect these data the Pt working electrode was polished before each scan; otherwise, the couple showed irreversible behavior. $E_{1/2}$ is equal to 581 mV/ref or 780 mV/NHE. Using eq 8, the log β for Ce(III)DTPA as 20.01, and the formal potential in 1 M HNO$_3$, we can calculate a stability constant for Ce(IV)DTPA as log β = 34.04, which is in remarkable agreement with the value reported in one of the published reports.[32]

■ DISCUSSION

Because thorium does not exhibit optical absorption in the visible region and formation of the 1:1 complex of DTPA occurs at very low pH values where it can be difficult for glass electrodes to perform, determination of the ThDTPA stability constant value proved to be more difficult than the subsequent actinides. Spectroscopic studies have been conducted on the complexation chemistry of Th(IV) with desferrioxamine and several of its derivatives that targeted absorption of the ligand in

the UV range.[34] However, since DTPA does not exhibit good absorbance below 400 nm and a small presence of nitrate can easily mask the UV region,[35] potentiometric titrations were performed in order to study the ThDTPA complex. Th^{4+} has an ionic radius of 0.97 Å;[21b] therefore, ThDTPA should be the least stable complex (relative to the actinides investigated in this work) and should begin formation at higher pH values. Below pH 1, small changes in pH readings were difficult to extract. Numerous Th:DTPA titrations were performed at various metal/ligand ratios and electrode junction potential characteristics, but only several titrations converged successfully. Potentiometric titrations of U(IV) and Np(IV) with DTPA were attempted but ineffective in analyzing the stability constants because the complex begins to form under increasingly strong acid conditions. However, refinement of the spectrophotometric titrations of the An(IV)DTPA complexes proved to be much more successful. The most encouraging results were the values obtained for PuDTPA by spectrophotometric titration and cyclic voltammetry. Method validation of stability constant determination emphasizes the importance of investigating a given system by more than one method to enhance the reliability and understanding of the equilibria.[13] The two independent techniques used to investigate Pu(IV)DTPA agree within 1 order of magnitude of stability. Furthermore, the Pu(III)DTPA value obtained in this work, 20.58, is in good agreement with stability constants and ionic radii of Am(III)DTPA (21.2, 0.975 Å) and Cm(III)DTPA (21.3, 0.970 Å).[21b,22] This decrease in stability is expected due to the fact that Pu(III) has a significantly larger ionic radius (1.00 Å).[21b] The previously reported value for Pu(III)DTPA was determined using plutonium in a maintained trivalent state. As it follows from the formal potential in DTPA and the complicated oxidation−reduction equilibria of plutonium, any trace amounts of oxygen or moderate oxidants may oxidize Pu(III) to Pu(IV). It is also well known that multiple oxidation states of plutonium can exist simultaneously in solution, which would considerably affect the overall complexation nature.[21b]

DTPA is an octadentate ligand,[7] while the aqueous tetravalent metals Th(IV)−Pu(IV) can range between 8 and 10 coordination.[36,37] The limits of complexation of An(IV) with DTPA are restricted to mononuclear complexes,[7] and similar boundaries most likely apply to An(IV) as well. Protonated metal complexes with DTPA, as mentioned earlier, are plausible, particularly for An(III) and Ln(III). A recent investigation of Nd(III)DTPA and Eu(III)DTPA complexes concluded that the DTPA ligand can still be protonated when fully coordinated with a metal ion.[8] The protonated complex was successfully calculated in this work for Ce(III). Refinement of the Th(IV)HDTPA complex by potentiometry was less successful (as indicated by the standard deviation) but converged nonetheless to a value that was nearly identical to the Th(IV)DTPA value. For the remainder of the An(IV) titrations (U−Pu) the *HypSpec* program rejected the protonated An(IV)HDTPA species.

As the An(IV) series is traversed from thorium to plutonium, the stability of aqueous complexes should generally increase since the ionic radius decreases and the effective charge grows. A linear relationship between the logarithm stability constant of An(IV) with DTPA and inverse cationic radii would coincide with the modified Born equation that relates the charge Z with a radius r ($M^{Z+} \propto Z^2/r$).[38] This relationship holds for many ligands with An(IV), though steric effects or solvent

interactions can considerably affect the linearity. Our results present a reasonably linear relationship ($R^2 = 0.98$ for a given set of ionic radii,[21b] Figure S3, Supporting Information) as a function of An(IV) radii. Attempts were made to compare the complexation of DTPA with An(IV) and Ln(III) as a function of ionic radius since the Born equation predicts a slope ratio of the two valence states of 1.7 ($4^2/3^2$) assuming no variations in the dielectric constant and no steric or solvent complications. An approximate ratio value of 1.5 was calculated for the Ln(III)/An(III)DTPA series, though the La−Gd(III)DTPA stability constant values failed to yield a sufficient linear relationship as a function of radii.[22] The same behavior was observed for EDTA. A plot of stability constants for An(IV)DTPA/EDTA and Ln(III)DTPA/EDTA versus ionic radii can be found in Figure S3, Supporting Information. Behaviors such as the tetrad effect of the 4f group render the ionic radii of Ln(III) less substantial in analyzing their complexation nature,[39] though this effect is still often debated.[40] Theory predicts analogous quantum mechanical interelectron repulsion behavior at the 1/4-, 1/2-, and 3/4-filled shell in both Ln(III) and An(III).[41] Whether or not the tetrad effect is reflected in the 5f group is still undecided, partially because of their low availability and inherent difficulties in handling.

The reported stability constants of An(IV) with DTPA in this work are significantly larger than those reported in the literature.[22] In some cases, we report values that are almost 3 orders of magnitude larger. Corrections for ionic strength are almost negligible between 0.5 and 1.0 M.[6b] Further investigation of the literature shows a discrepancy in the calculations regarding the active sites of DTPA. In most previous studies, DTPA was treated as a hexa-active carboxylic acid.[9−12] NMR studies of the ligand have definitively confirmed the presence of eight active binding sites and even mapped the protonation sequence to some extent; a more detailed review of DTPA protonation was done by Moulin et al.[42] Speciation diagrams of DTPA show that starting below pH 0 eight protonation sites must be overcome to reach the bare 5−charged ligand. A study on Th(IV)DTPA concluded that the five carboxylic groups and three nitrogens are coordinated to the Th(IV) ion in acidic solution.[43] Furthermore, when the An(IV)DTPA titration experiments in this work were negated of $pK_{a(6−8)}$ in the refinement model, the data for each actinide successfully converged to about two or three log units lower than the values that we report, thus reducing the gap between our values and the reported literature that used only six active protonation sites for DTPA. It is therefore concluded that all eight activation sites must be included in the model.

■ SUMMARY

The aqueous complexation thermodynamics of DTPA with Ce(III/IV), Th(IV), U(IV), Np(IV), and Pu(III/IV) has been studied at 25 °C and $I = 1$ M by various methods. Quantification of the complexes shows a linear increase in stability as the An(IV) series is traversed. A comparison of the data presented here and that with previous studies conclude that all eight coordination sites of DTPA must be considered, especially when working at low pH.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Calibration data for the glass electrode in strong acid concentrations, speciation diagram for Ce(III) and DTPA, and DTPA/EDTA stability constant values for selected f elements as a function of ionic radii. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: guelis@anl.gov.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Serandour, A. L.; Gremy, O.; Frechou, M.; Renault, D.; Poncy, J. L.; Fritsch, P. *Radiat. Res.* **2008**, *170*, 208−215.
(2) Stradling, G. N. *J. Alloys Compd.* **1998**, *271−273*, 72−77.
(3) Micskei, K.; Helm, L.; Brücher, E.; Merbach, A. E. *Inorg. Chem.* **1993**, *32*, 3844−3850.
(4) Weaver, B.; Kappelmann, F. A. *J. Inorg. Nucl. Chem.* **1968**, *30*, 263−272.
(5) Gelis, A. V.; Vandegrift, G. F.; Bakel, A.; Bowers, D. L.; Hebden, A. S.; Pereira, C.; Regalbuto, M. *Radiochim. Acta* **2009**, *97*, 231−232.
(6) (a) Martell, A. E.; Motekaitis, R. J. *Determination and Use of Stability Constants*, 2nd ed.; VCH Publishers, Inc.: New York, 1992; p 195. (b) Martell, A. E.; Motekaitis, R. J. *Determination and Use of Stability Constants*, 2nd ed.; VCH Publishers, Inc.: New York, 1992; p 122.
(7) Choppin, G. R.; Thakur, P.; Mathur, J. N. *Coord. Chem. Rev.* **2006**, *250*, 936−947.
(8) Tian, G.; Martin, L. R.; Zhang, Z.; Rao, L. *Inorg. Chem.* **2011**, *50*, 3087−3096.
(9) Piskunov, E. M.; Rykov, A. G. *Sov. Radiochem.* **1972**, *14*, 270−274.
(10) Piskunov, E. M.; Rykov, A. G. *Sov. Radiochem.* **1972**, *14*, 275−278.
(11) Piskunov, E. M.; Rykov, A. G. *Sov. Radiochem.* **1972**, *14*, 342−344.
(12) Moskvin, A. I. *Sov. Radiochem.* **1971**, *13*, 641−643.
(13) Hartley, F. R.; Burgess, C.; Alcock, R. M. *Solution Equilibria*; Ellis Horwood Limited: England, 1980.
(14) Dietz, L. A.; Pachucki, C. F.; Land, G. A. *Anal. Chem.* **1962**, *34*, 709−710.
(15) Cleveland, J. M. *The Chemistry of Plutonium*; Gordon & Breach Science Publishers, Inc.: New York, 1970; p 148.
(16) Sawyer, D. T.; Sobkowiak, A. J.; Roberts, J., Jr. *Electrochemistry for Chemists*, 2nd ed.; John Wiley & Sons: New York, 1995; Section 5.2
(17) Novikov, A. P.; Kalmykov, S. N.; Utsunomiya, S.; Ewing, R. C.; Horreard, F.; Merkulov, A.; Clark, S. B.; Tkachev, V. V.; Myasoedov, B. F. *Science* **2006**, *314*, 638−641.
(18) www.hyperquad.co.uk.
(19) Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739−1753.
(20) Gans, P.; Sabatini, A.; Vacca, A. *Ann. Chim.* **1999**, *89*, 45−49.
(21) (a) Weigel, F.; Katz, J. J.; Seaborg, G. T. Plutonium. *The Chemistry of the Actinide Elements*, 2nd ed.; Chapman and Hall: London, 1986; Vol. *1*, Ch. 7, p 790. (b) Burns, J. H. Structural Chemistry. *The Chemistry of the Actinide Elements*, 2nd ed.; Chapman

and Hall: London, 1986; Vol. 2, Chapter 20, p 1512. (c) Weigel, F.; Katz, J. J.; Seaborg, G. T. Plutonium. *The Chemistry of the Actinide Elements*, 2nd ed.; Chapman and Hall: London, 1986; Vol. 1, Chapter 7, p 818.

(22) NIST Standard Reference Database 46; *NIST Critically Selected Stability Constants of Metal Complexes Database*, version 8.0; U.S. Department of Commerce: Washington, DC, 2004.

(23) Sudmeier, J. L.; Reilley, C. N. *Anal. Chem.* **1964**, *36*, 1698−1706.

(24) Lammers, H.; van der Heijden, A. M.; van Bekkum, H.; Geraldes, C. G. F. C.; Peters, J. A. *Inorg. Chim. Acta* **1998**, *277*, 193−201.

(25) Boukhalfa, H.; Reilly, S. D.; Smith, W. H.; Neu, M. P. *Inorg. Chem.* **2004**, *43*, 5816−5823.

(26) Sinkov, S. I.; Rapko, B. M.; Lumetta, G. J.; Hay, B. P.; Hutchison, J. E.; Parks, B. W. *Inorg. Chem.* **2004**, *43*, 8404−8413.

(27) Cohen, D. *J. Inorg. Nucl. Chem.* **1961**, *18*, 211−218.

(28) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; John Wiley & Sons: New York, 2001.

(29) Merciny, E.; Gatez, J. M.; Duyckaerts, G. *Anal. Chim. Acta* **1978**, *100*, 329−342.

(30) Barnard, G. M.; Boddington, T.; Gregor, J. E.; Pettit, L. D.; Taylor, N. *Talanta* **1990**, *37*, 219−228.

(31) Laitinen, H.; Harris, W. E. *Chemical Analysis*, 2nd ed.; McGraw-Hill, Inc.: New York, 1975.

(32) Malinina, E. A.; Martynenko, L. I.; Pechurova, N. I.; Spitsyn, V. I. *Bull. Acad. Sci. USSR Chem. Sci.* **1970**, *19*, 2060−2063.

(33) Petschurowa, N. I.; Marynenko, L. I.; Spitsyn, V. I.; Malinina, E. A. *Z. Anorg. Allg. Chem.* **1971**, *380*, 202−205.

(34) Whisenhunt, D. W.; Neu, M. P.; Hou, Z.; Xu, J.; Hoffman, D. C.; Raymond, K. R. *Inorg. Chem.* **1996**, *35*, 4128−4136.

(35) Chlistunoff, J.; Ziegler, K. J.; Lasdon, L.; Johnston, K. P. *J Phys. Chem. A* **1999**, *103*, 1678−1688.

(36) Szabó, A.; Toraishi, T.; Vallet, V.; Grenthe, I. *Coord. Chem. Rev.* **2006**, *250*, 784−815.

(37) Cotton, S. *Lanthanide and Actinide Chemistry*; John Wiley & Sons, Ltd.: Chichester, U.K., 2006.

(38) Choppin, G. R.; Jensen, M. P. Actinides in Solution: Complexation and Kinetics. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Katz, J. J., Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Netherlands, 2006; Vol. 4, Chapter 23.

(39) Peppard, D. F.; Mason, G. W.; Lewey, S. *J. Inorg. Nucl. Chem.* **1960**, *31*, 2271−2272.

(40) Bau, M. *Contrib. Mineral Petrol.* **1997**, *128*, 409−412.

(41) Nugent, L. J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3485−3491.

(42) Moulin, C.; Amekraz, B.; Steiner, V.; Plancque, G.; Ansoborlo, E. *Appl. Spectrosc.* **2003**, *9*, 1151−1161.

(43) Fried, A. R.; Martell, A. E. *J. Am. Chem. Soc.* **1971**, *93:19*, 4695−4700.