# Structural Periodicity in the Coordination Chemistry of Aqueous Pu(IV) Sulfates

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ABSTRACT: Extended X-ray absorption fine structure measurements have been conducted on solutions of Pu(IV) with varying concentrations of sulfate anion in aqueous solution. Data support the periodic progression to primarily bidentate sulfate coordination about An(IV) centers when moving heavier in the actinides. This observation is attributed to the increase in Lewis acidity of the tetravalent actinides across the series, a consequence of the filling of the 5f orbitals and the actinide contraction. Though the changes in the chemical formation energies of the An(IV) complexes between Th and Pu are small, it is these small energetic differences that are critical to understanding how to effect more efficient and effective chemical separations among isovalent metal ions.
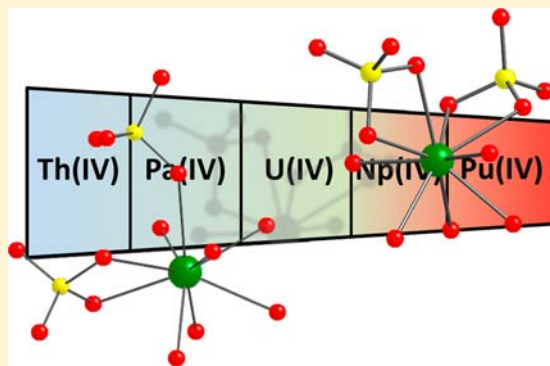
INTRODUCTION

The horizontal arrangement of the lanthanides and actinides in the modern periodic table provides a framework allowing for coarse prediction of chemical behavior across the series in ways similar to the predictive trends established in the vertical groups of the transition metals and main group elements. In the actinide series the early members of this period share a common accessible tetravalent oxidation state in aqueous solution. In their tetravalent oxidation states these elements are classified as strong Lewis acids, their Lewis acidities increasing with their concomitant decrease in ionic radii. Alternatively, in aqueous solution the tetravalent actinides can be described in terms of their Bronsted acidities as aquated cations using the stability constants derived for their hydrolysis reactions showing a steady increase in the acidity from Th to Pu.[1,2] Unlike the transition metals, these ions share similar chemistries despite the different electron configurations of the ions (i.e., [Rn] at Th(IV) and $[Rn]5f^4$ at Pu(IV)) owing to the limited participation of the mostly shielded 5f electrons and orbitals. Periodic chemical trends are observed beyond the acidities in aqueous solution and hold across many ligand sets, usually showing an increase in the formation constant, a consequence of the filling of the 5f electronic shell and thus the actinide contraction.

Macroscopic trends are clearly established in both the solution thermodynamics and the structural chemistry for the tetravalent actinides. It was the isostructural series of binary oxides characterized by Zachariasen that allowed Seaborg to develop his actinide hypothesis.[3] However, these macroscopic thermodynamic quantities do not tell us much regarding the molecular level structural chemistry occurring and whether or not it is possible to correlate changes in their structural chemistry in solution with their chemical or periodic properties. An equilibrium constant of formation does not explicitly provide information on the particular coordination mode of a ligand to a metal at the molecular level. The importance of understanding molecular level changes in the chemistry and structure of these ions and correlating them with their thermochemical properties is well demonstrated in the application of this chemistry to separations science.[4−7]

In order to investigate the structural periodicity in An(IV) solution coordination I have chosen to complete the series of An(IV) sulfate complexes extensively studied for Th(IV), U(IV), and Np(IV) by Hennig et al.[8−10] The macroscopic thermodynamic properties of An(IV) sulfate complexes have been studied and reviewed with reliable quantities available across the entire early actinide series.[1,2] Coordination of bisulfate/sulfate to a metal cation in aqueous solution generally occurs in two modes for mononuclear metal complexes, a corner-sharing monodentate binding or an edge-sharing bidentate binding mode. In the experiments reported in this manuscript the dominating form of the sulfate ligand in solution is bisulfate, HSO_4^-.

Generally speaking, it is expected that for a given metal−polydentate ligand system, the chelate complex would be lower in energy than the monodentate complex, a concept known as the chelate effect. However, observation of the chelate effect across different metals within the same ligand system, in this case bisulfate/sulfate, may reveal other chemical factors which may influence the coordination chemistry and structure of metal−ligand complexes. This makes sulfate a useful ligand to investigate whether the changing Lewis acidity and therefore chemistry of the An(IV) ion influences the sulfate coordination mode and vice versa.

Table 1. Sample Composition and Metrical Fit Data from the EXAFS Spectra[a]

[Pu(IV)], mmol·L⁻¹	(NH₄)₂SO₄, mol·L⁻¹	Pu–O (N_{Pu-O})	Pu–O, d, Å	σ^2, Å²	Pu–S (N_{Pu-S}) {calcd}	Pu–S, d, Å	σ^2, Å²	R, X^2
10	0.0	8.5	2.384(7)	0.010	0.0 {0.0}	0.0	0.0	0.06, 3.48
10	0.1	8.8	2.391(10)	0.010	1.3 {1.0}	3.060(10)	0.005	0.03, 9.28
10	0.2	9.1	2.390(6)	0.009	1.8 {1.3}	3.063(10)	0.005	0.03, 14.43
10	0.5	9.0	2.392(6)	0.008	2.3 {1.6}	3.064(10)	0.002	0.03, 11.38
10	0.5	9.0	2.392(6)	0.008	2.0 {1.6}	3.062(10)	0.005[b]	0.03,11.48
[Pu(IV)], mmol·L⁻¹	H₂SO₄, mol·L⁻¹	Pu–O (N_{Pu-O})	Pu–O, d, Å	σ^2, Å²	Pu–S (N_{Pu-S}) {calcd}	Pu–S, d, Å	σ^2, Å²	R, X^2
10	1.0	8.7	2.401(6)	0.008	2.0 {1.6}	3.062(7)	0.002	0.03 1.98
10	1.0	8.9	2.401(6)	0.008	2.6 {1.6}	3.064(7)	0.005[b]	0.04 2.01
10	2.0	9.2	2.389(6)	0.008	2.6 {1.7}	3.068(8)	0.005	0.04, 15.3

[a]Average sulfate coordination numbers calculated from available experimental stability constants taken from ref 1 presented in {}. Fit statistics expressed as R, % misfit, and X^2, reduced chi square.[16,17] [b]Parameter fixed during the fit.

In their X-ray absorption spectroscopy (XAS) studies of three members of this series, Hennig et al. observed a periodic shift in the coordination mode of the sulfate anions as the actinide ion was changed from Th(IV) to U(IV) to Np(IV). The sulfate anion coordination mode was observed to change from primarily monodentate at Th to a mixture of predominantly bidentate at Np(IV).[8,10] Moreover, bidentate sulfate dominates at higher concentrations of sulfate, despite what could be a steric pushback against such coordination as the mean sulfate coordination number increases about the metal center and the metals become smaller.[8–10] Recently, such trends were investigated in the synthesis of a series of Pu(IV) sulfate salts and compared to other An(IV) and Group IV metal sulfate complexes.[11] The solid state complexes of the series of An(IV) sulfate complexes could not be easily correlated, if at all, with the structural observations in solution.

Building on my previous report of plutonium(IV) sulfate complexes in the solid state, I present here a study of the solution structure of Pu(IV) sulfate complexes using X-ray absorption spectroscopy. X-ray absorption spectroscopy is a powerful structural probe of the average near-neighbor coordination environment of metal ions in condensed phases.[12] This study completes, sans Pa, the periodic series of the stable tetravalent ions in aqueous solution and demonstrates the changing coordination modes of sulfate across the An(IV) series, preserving the periodic trends in this series at the molecular level.

■ EXPERIMENTAL METHODS

Caution! ²⁴²Pu is an alpha-emitting radionuclide and should be handled only in a laboratory appropriately equipped with radiological fume hoods and gloveboxes.

²⁴²Pu Stock Solution. The working stock solution of ²⁴²Pu was prepared by precipitation of an aliquot of ²⁴²Pu(III) from a hydrochloric acid solution that had been previously prepared and purified using standard methods.[13] This precipitate was washed three times with distilled water and dissolved with an appropriate volume of perchloric acid, providing a stock solution of 0.025 M Pu(IV) in 5 M HClO₄. The oxidation state and concentration of the Pu stock solution were confirmed by optical absorption spectroscopy and liquid scintillation counting, respectively.[14] Samples of 10 mM Pu(IV) with varying concentrations of sulfate were prepared by dilution of this stock solution and appropriate addition of either (NH₄)₂SO₄ or H₂SO₄. Details of sample compositions are provided in Table 1.

EXAFS Data Collection and Analysis. Extended X-ray absorption fine structure (EXAFS) spectra were collected at the bending magnet beamline, 12BM-B, at the Advanced Photon Source, Argonne National Laboratory.[15] Data were collected at the Pu(L_III) absorption edge (18.054 keV) by monitoring the L_α X-ray fluorescence signal at 90° to the samples using a Canberra 13-element germanium detector. Data were collected at room temperature. Samples were encapsulated in 1 mm ID Kapton capillaries sealed with epoxy and further packaged in heat-sealed polyethylene bags, which were contained in a sealed motorized sample box as required for measurement of these radiological samples at the APS. Data reduction, background subtraction, normalization, and Fourier transformations (FT) were performed using the SIXPACK software suite.[16,17] Fits to the EXAFS data were performed in r space using SIXPACK with scattering paths chosen from single-crystal structures and calculated using FEFF8.0 using an amplitude reduction factor, $S_o^2 = 1.0$.[18] All data reductions and fits were conducted identically in order to minimize errors associated with disparate data analysis.

■ RESULTS

EXAFS data were collected on 10 mM Pu(IV) solutions in 2 M HClO₄ with varying sulfate concentrations, with Pu:SO₄ ratios ranging from 1:0 to 1:50 using (NH₄)₂SO₄ to adjust the sulfate concentration. The high perchloric acid concentration was chosen to negate any possibility of Pu(IV) hydrolysis in this system, as well as to correlate the chemistry of these samples with previous structural and thermodynamic studies with Pu(IV) sulfates.[1] Additionally, data were collected on samples of Pu(IV) in 1 and 2 M H₂SO₄ in the absence of perchlorate, representing 1:100 and 1:200 Pu:SO₄ ratios. Sample compositions are summarized in Table 1 along with the results of the fits to the EXAFS spectra. Graphic presentations of the EXAFS spectra and the fits in both k and r space are shown in Figures 1–3.

Pu(IV) in 2 M HClO₄. The EXAFS spectrum of 10 mM Pu(IV) in 2 M HClO₄ is shown in Figure 1. The r-space FT of the EXAFS shows a single peak that can be satisfactorily fit with a single-shell model representing a Pu–O scattering path, Table 1. This Pu–O path is attributed to the first hydration sphere of the Pu(IV) ion. These data demonstrate 8.5 water molecules at an average distance of 2.384(7) Å. The error generally associated with the coordination number derived from fits to EXAFS data is approximately 10%. The observed coordination number of 8.5 is in good agreement with previously reported values of 9–10 water molecules for An(IV) using EXAFS.[19,20] The only benchmark in the solid state for an aquated tetravalent cation is the 10-coordinate [Th(H₂O)₁₀]Br₄ compound.[21] The reduction in the ionic radius of An(IV) ions between Th and Pu drives a shift in the hydration equilibrium to lower coordination numbers as observed in Ln(III) and An(III) ions.[5,22–25]

Pu(IV) Sulfate EXAFS. Shown in Figure 2 are the k^3-weighted EXAFS spectra and their Fourier transformations of the samples containing 10 mM Pu in 2 M HClO₄ with addition of sulfate as the ammonium salt. The resulting metrical data
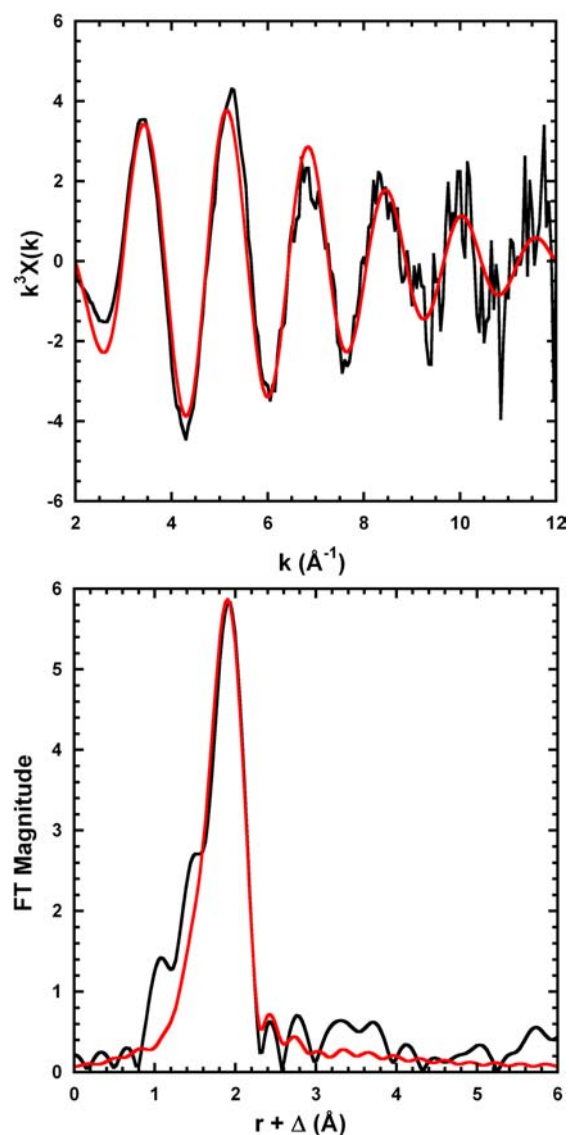
Figure 1. EXAFS, $k^3X(k)$, and FT from 10 mM Pu(IV) in 2 M HClO$_4$. Data are given in black and fits in red.

Figure 2. EXAFS, $k^3X(k)$, and FT of 10 mM Pu(IV) in 2 M HClO$_4$ with varying concentrations of ammonium sulfate. Data are given in black and fits in red.

from the fits are presented in Table 1. Analysis of the spectra reveals that the first coordination sphere remains fairly constant in its value of approximately 9 oxygen atoms across the series of samples. The contribution to the first coordination sphere of Pu(IV) comes from both hydrating water molecules, as shown in the sample containing only Pu(IV) in 2 M HClO$_4$, and those arising because of coordination of bisulfate/sulfate anions.

The average sulfate coordination number in the measured samples spans 1.3−2.3, suggesting inclusion of cationic, neutral, and potentially anionic Pu sulfate complexes. The mean sulfate coordination number is derived from a fit of the Pu−S scattering path highlighted with the broken line in the phase-shifted r-space plots at ∼2.7 Å in Figures 2 and 3. The distance of 3.06 Å is a good indicator of the bidentate Pu−S scattering pair, consistent with the bidentate Pu−S distances observed in single-crystal structures previously reported.[11] The change in the Debye−Waller factor for the sample containing 0.5 M (NH$_4$)$_2$SO$_4$ in an unconstrained fit was approximately one-half the value refined in the other two sulfate-containing samples. Inspection of the correlation coefficients of the fit to this spectrum revealed that the Pu−S amplitude and Debye−Waller
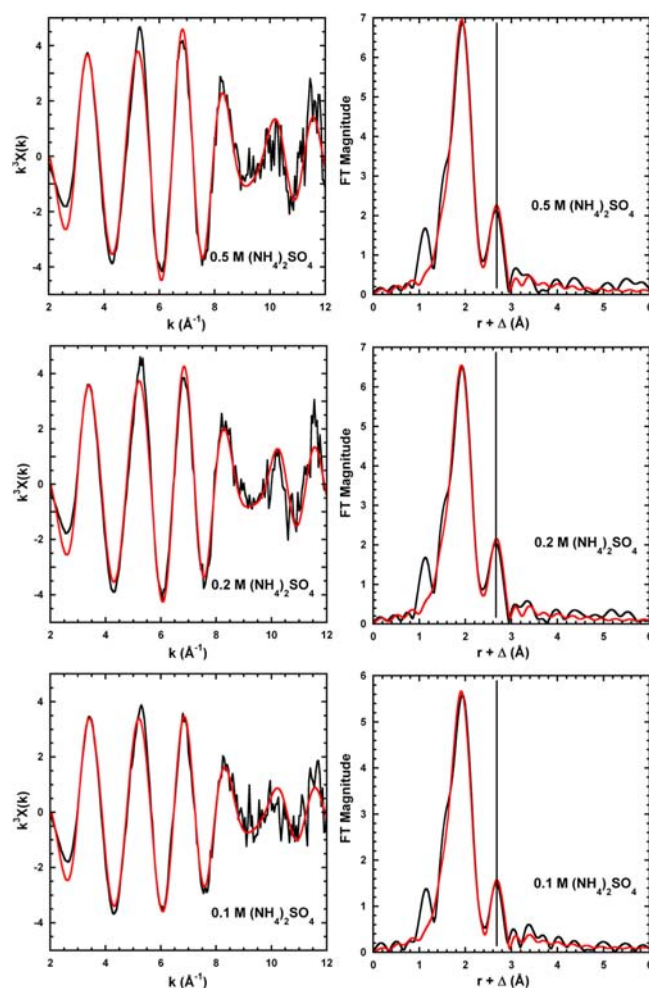
factor were strongly correlated, 90%. An additional fit to the data using a Debye−Waller factor identical to the others and constrained to 0.005 Å^2 resulted in a decrease in the Pu−S amplitude to 2.0 with no statistical difference to the fit results, Table 1.

Unlike the data reported by Hennig for Th(IV), U(IV), and Np(IV), efforts to include a second, longer Pu−S scattering pair as a monodentate sulfate species (Pu−S, ∼3.5−3.6 Å) were not successful, even when constraining the Debye−Waller factors and/or Pu−S correlation distances. The observed increase in the mean coordination number for sulfate across this series of samples can be rationalized by mass action considerations on the Pu−sulfate equilibria, Table 2. Calculation of the mean sulfate coordination from available experimental thermochemical data show moderate agreement with the values determined from EXAFS at lower sulfate concentrations but sharp disagreement with the measurements reported here at higher sulfate concentrations. However, current thermodynamic data do not provide a value for anionic sulfate complexes of U(IV), Np(IV), and Pu(IV) cations or complexes with more than two sulfuric acid based ligands, despite evidence here of their existence and by others for the lighter actinides.[1,2,8−10] The lack of experimental thermodynamic data for anionic complexes or sulfate complexes with more than two sulfuric acid based ligands is more likely a limitation of the methods used to
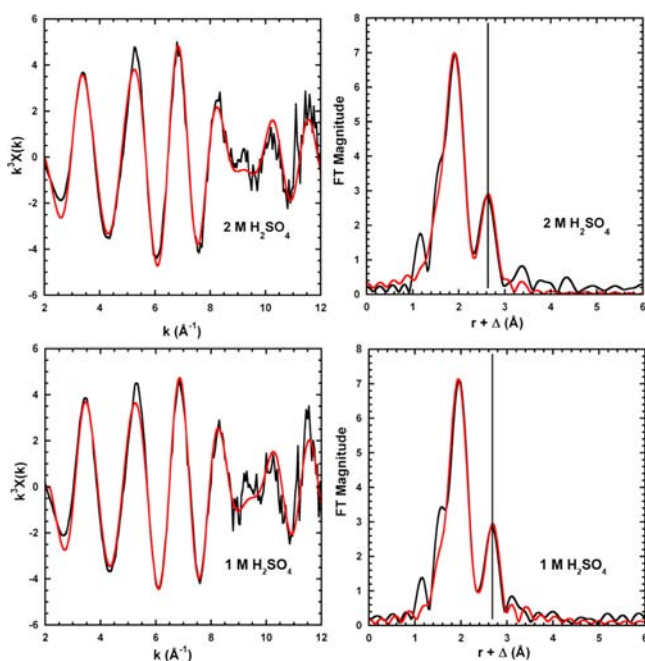
Figure 3. EXAFS, $k^3X(k)$, and FT of 10 mM Pu(IV) in 1 M H_2SO_4 (bottom) and 2 M H_2SO_4 (top).

Table 2. Thermodynamic Complex Formation Constants Expressed as log β ($I = 0$) for Reactions $An^{4+} + xHSO_4^- \leftrightarrow An(IV)(SO4)_x^{(4-2x)+} + xH^{+a}$

actinide (radius Å)	log β_1	log β_2	$\Delta_r G_1$ and $\Delta_r G_2$ (kJ mol^{-1})
Th(IV) 1.05	4.19(32)	5.73(25)	−24(2), −33(1)
U(IV) 1.00	4.58(19)	6.51(20)	−26(1), −37(1)
Np(IV) 0.98	4.87(15)	7.09(25)	−28(1), −40(1)
Pu(IV) 0.96	4.91(22)	7.18(32)	−28(1), −41(2)

[a]The free energy of reaction for the complexes is calculated from the stability constants using $\Delta G^\circ = -RT \ln \beta$. The values for the ionic radii are taken from Shannon;[30] complex formation constants and their uncertainties are taken from refs 1 and 2.

quantify these species than an expectation of their non-existence. Thermodynamic values for such complexes are available for Th but not the heavier actinides.[2]

Under the conditions of this experiment, 2 M $HClO_4$, the dominant sulfuric acid species is bisulfate, potentially minimizing the likelihood of predominant bidentate sulfate coordination about the plutonium metal cation. Data here do not support inclusion of any significant fraction of mono-dentate-coordinated sulfate as either bisulfate or sulfate but cannot provide evidence of whether or not the bidentate-coordinated sulfate group is in fact a protonated bisulfate chelate (Pu–η^2-O_2SO_2H).

The EXAFS from Pu(IV) in 1 and 2 M H_2SO_4 do not support inclusion of monodentate sulfate species either. Here the reasoning was to push the equilibrium even more strongly to favor bisulfate using sulfuric acid as the source of the sulfate anion, presuming, albeit incorrectly,[26] that bisulfate will not form bidentate chelate complexes. The mean coordination number in these complexes, where the Pu:SO_4 ratio is now 1:100 and 1:200, respectively, demonstrates similar bond distances and coordination numbers in the first coordination spheres as in previous examples. The mean sulfate coordination increases from 2.0 (a neutral or cationic complex depending on
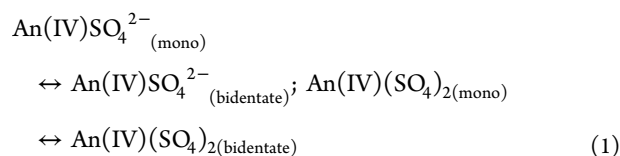
the protonation state of the sulfate ligand) in the 1 M H_2SO_4 sample, when all parameters were allowed to vary, and 2.6, when the Debye−Waller factor was constrained to a value of 0.005 Å^2 as done in the ammonium sulfate samples, to 2.6 in the 2 M H_2SO_4 sample, both samples supporting the potential existence of anionic complexes of Pu(IV) and sulfate in these samples if the sulfate is bound as a fully deprotonated ligand.

■ DISCUSSION

The available thermodynamic data ($I = 0$) for An(IV) sulfate coordination for the 1:1 and 1:2 metal:ligand complexes are presented in Table 2.[1,2] Shown in this table are clear correlations between the ionic radius of the metal ion and the increasing complex formation constants for the complexes. In the lighter actinides, Th[10], U[9], and Np[9], it was shown by Hennig et al. using both XAS and DFT that a change from predominantly monodentate sulfate coordination at Th to predominantly bidentate sulfate coordination at Np occurred when transiting the series.[8]

Data presented in this study show that the trend to increased bidentate sulfate coordination holds at Pu(IV), our data supporting *only* inclusion of bidentate sulfate coordination in the plutonium system. Only a minor fraction of the sulfuric acid is present as sulfate versus the larger concentration of bisulfate, suggesting either deprotonation of the bisulfate anion to sulfate well below the pK_a of the bisulfate−sulfate equilibrium (pK_a = 1.92) or formation of a bisulfate or sulfate chelate complex of the form Pu(η^2-O_2SO_2H)$^{3+}$ or Pu($\eta^2O_2SO_2$)$^{2+}$. Data here cannot discriminate between the bisulfate and the sulfate chelates nor do we know the pK_a of the Pu(η^2-O_2SO_2H)$^{3+}$ ↔ Pu($\eta^2O_2SO_2$)$^{2+}$ + H$^+$ equilibria.

In their DFT calculations, Hennig et al. (Table 5 in ref 8) showed the preference for bidentate coordination of sulfate to the An(IV) ions in the gas phase and solvated systems from Th and Np, eq 1.[8]

$$An(IV)SO_4^{2-}{}_{(mono)}$$
$$\leftrightarrow An(IV)SO_4^{2-}{}_{(bidentate)}; \quad An(IV)(SO_4)_{2(mono)}$$
$$\leftrightarrow An(IV)(SO_4)_{2(bidentate)} \qquad (1)$$

They calculated that the bidentate complexes are more stable than the monodentate complexes in the gas phase by more than 95 and 109 kJ mol^{-1} in the monosulfate complexes of Th(IV) and Np(IV), respectively. The bidentate bis-sulfate complexes are 144−173 kJ mol^{-1} more stable in the gas phase. Upon solvation of these complexes, the preference for bidentate sulfate coordination remains across the An(IV) ions but the relative energy differences are decreased to 17 (Th) and 21 kJ mol^{-1} (Np) for the mono-sulfate complex and 56 (Th) and 94 (Np) kJ mol^{-1} for the bis-sulfato complexes.

These results are not entirely unexpected in consideration of the empirical "chelate effect" where, when sterically possible and available to the ligand, a chelate complex will be more stable than the monodentate nonchelate complex. However, in the tetravalent actinides where the steric degrees of freedom are likely becoming limited as the size of the ions decreases from Th to Pu the invocation of the chelate effect as the cause for these phenomena might not be wholly appropriate or sufficient to explain the trend across the entire An(IV) series. This is based on the experimental data that show a dynamic partition between the amount of monodentate sulfate and bidentate

sulfate across the series with a concomitant decrease in metal cation size that could offset the favorability of chelation: one would expect at least an equal tendency or greater at Th to bidentate sulfate coordination since because of its size it is the least sterically encumbered. All other factors being equal, the degree of chelate formation, the preference for bidentate sulfate coordination, seems to be driven by the chemical properties of the actinide ion separate from their ability to accommodate more ligands.

Using the thermodynamic relationship $\Delta G^0 = -RT \ln K$, the calculated free energies for the equilibrium between monodentate and bidentate sulfate coordination (eq 1) and the experimentally measured complex formation constants at the standard state, Table 2, may be evaluated. Using the same thermochemical rationale for chelate ring closure as that employed in the quantum chemical study of the chelate effect by Vallet, Wahlgren, and Grenthe, the energetics associated with chelate ring closure (monodentate to bidentate) and opening (bidentate to monodentate) must be less negative than the experimentally determined free energy of formation of the complex.[27] The calculated free energy for the monodentate and bidentate equilibria, eq 1, and experimentally measured free energies for complex formation of the 1:1 complexes are approximately the same. The calculated equilibrium constants for the change in sulfate coordination from mono- to bidentate for the 1:2 complexes are more negative than the experimentally determined formation constants for the complexes themselves. DFT calculations demonstrate a relative trend but call into question the chemical explanations for this trend considering the energetics of the equilibria are equal to or larger than the experimentally determined total free energy of complex formation for the aqueous complexes.

The observed trend toward bidentate sulfate coordination is not clearly explained by previous DFT calculations.[8] In the analysis of their calculations Hennig et al.[8] state that the actinide–ligand polarization is greater at Th than at Np but that the contributions to the solvation energy at Np make the bidentate complex more stable than that for Th, a give and take between the actinide ligand polarization and the resulting size of the solvation cavity used in their calculation. An alternate explanation for these effects is suggested.

Experimentally determined enthalpies of complex formation for An(IV) ions with sulfate are available for all but Pa(IV).[1,2,28] The uncertainties associated with the experimentally determined absolute values of the enthalpies and free energies of reactions make identification of a clear quantifiable thermodynamic trend and explanation uncertain when partitioning the free energy between its enthalpic and entropic components. However, what is clear from the data is that the coordination of sulfate to tetravalent actinide ions is an entropically driven process, the enthalpies of reactions being modestly positive in their values and the corresponding entropies relatively large and positive.[1,2,28] The underlying cause of the entropically dominated energetics may result from the increased tendency toward bidentate sulfate coordination, which would necessarily result in the displacement of water molecules from the An(IV) center, more so as the steric crowding about the smaller transuranic actinides becomes pronounced. Though this may argue in favor of the chelate effect as a reason for the trend toward bidentate sulfate coordination, the chelate effect has been shown to be more complicated and nuanced with contributions arising from both reaction enthalpy as well as both translational and rotational entropic components of the

chemical system.[27] In addition, the observed changing distribution between bidentate and monodentate coordination across the actinide series suggests that the equilibria are changing as a function of the metal ion and that the energetics associated with the equilibria in eq 1 are probably fairly small, being least favored for Th and most favorable for Pu.

The increased tendency toward bidentate sulfate coordination moving from Th to Pu can be qualitatively explained as a consequence of the increased Lewis acidity of the actinide ions. This is supported by the calculated Mulliken populations of Hennig,[8] where the charge on the Th center in the sulfate complexes is *more* positive than the charge on the corresponding Np sulfate complexes. This indicates a greater electronic interaction, or larger charge transfer, between the sulfate oxygen atoms and the more acidic Np(IV) ion versus the more basic Th(IV) ion, a trend that based on our observations should continue to plutonium. A comprehensive quantum chemical treatment of this chemical series, as done in ref 27, would provide significant insight here.

The differences in the free energies of complex formation between mono- and bis-sulfate/bisulfate Th and Pu are approximately 4 and 9 kJ mol^{-1}, respectively, Table 2. This is a quantity very near the limits of computational chemistry to parse. These small energy differences are sufficient to carry out a chemical separation. Every order of magnitude in a separation factor corresponds to a 5.7 kJ mol^{-1} difference in free energy, $\Delta G^\circ = -RT \ln K$. These seemingly tiny energetic quantities highlight the importance of understanding and quantifying these chemical periodic trends both experimentally and computationally as pointed out by Wipff et al. in their study of lanthanide nitrate coordination modes in solvent extraction systems.[29] This is especially true if technologies are to be developed to chemically exploit and parse even smaller energetic differences such as those encountered in the classical chemical problem of trivalent lanthanide and actinide separations.

■ CONCLUSION

Experimental data have been provided for Pu, completing the changing trend in the sulfate coordination mode between Th and Pu in the early actinide(IV) ions first highlighted by Hennig. This trend is attributed to the increase in Lewis acidity progressing from Th to Pu, a result of the filling of the 5f orbitals and the resulting contraction in the ionic radii of the actinide ions. Previous thermochemical measurements have demonstrated that these effects are primarily entropically driven in solution. Recent quantum chemical calculations highlight the need for additional inspection of this system, particularly with regard to the underlying energetics associated with the chelate effect across varying actinide ions within the same ligand system The systematic change in the coordination environment as a function of the metal cation and the relatively small changes in energy from Th to Pu, ~5 kJ mol^{-1}, highlights the necessity of studying the origin and effects of these small changes in energy both computationally and experimentally. Understanding these seemingly small energetic differences is critically important in the development of chemical separations where such changes in energy can result in substantial enhancements in the effectiveness of the separation.

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