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Molecular Models for Actinide Speciation

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Glossary

NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared
UV	Ultraviolet
NIR	Near Infrared
An	Actinide
OR	Alkoxide
OAr	Aryloxide
THF	Tetrahydrofuran, C_4H_8O
i-Pr	Isopropyl, $CH(CH_3)_2$
t-Bu	Tertiary butyl, $C(CH_3)_3$
Ph	Phenyl, C_6H_5
Me	Methyl, CH_3
R	Alkyl, C_nH_m
Ar	Aryl, C_6H_5
L	Ligand
dmpe	Bis(dimethylphosphino)ethane, $(CH_3)_2PCH_2CH_2P(CH_3)_2$
py	pyridine, C_5H_5N

MOLECULAR MODELS FOR ACTINIDE SPECIATION

by

David L. Clark, John G. Watkin, David E. Morris, and John M. Berg

ABSTRACT

Much effort has been devoted to the development of sensitive spectroscopic techniques for the study of actinide speciation based on the sensitivity of f-f electronic absorption bands to oxidation state and ligation of the actinide ions. These efforts assume that data obtained in such studies will be interpretable in terms of changes in complexation of the metal center. However, our current understanding of 5f electronic structure is based on data from solid state doped single crystals. In those studies, the local coordination geometry about the central actinide ion is maintained in an almost perfect high-symmetry environment and will have little relevance for species in solution where deviations from perfect high symmetry tend to be the rule rather than the exception. We have developed a vigorous research program in the systematic preparation and spectroscopic characterization of synthetic actinide complexes (Th, U, Np, and Pu) in which we can control nuclearity, oxidation state, and molecular structure. These complexes have been used to determine how observable electronic transitions are perturbed in response to structural changes in the complex in solution. From the spectra obtained for these model complexes, we have found that the f-f transitions naturally fall into obvious groupings by coordination number and symmetry by which we can now differentiate between monomeric, dimeric, and trimeric species in solution.

Introduction

The study of radionuclide speciation is fundamentally important to the determination of radionuclide solubility in the groundwater at Yucca Mountain. Radionuclide speciation is strictly defined as (1) the identification of the radionuclide, (2) the determination of oxidation state, and (3) the formula and molecular structure of the ionic and/or solid complex (i.e., the stoichiometry and structure of the metal ion as complexed by ions and/or other ligands). Although direct solubility measurements will provide limits for the concentrations of important radionuclides under certain specific groundwater conditions, they cannot possibly provide concentration limits for all foreseeable groundwater conditions. Therefore, a basic thermodynamic characterization of radionuclide speciation is needed to bridge any gaps in the data acquired from direct solubility

determinations and to provide the fundamental thermodynamic constants needed for modeling solubility under conditions that are not specifically considered in the solubility determination. In the speciation study, we need to identify the important complexes of the radionuclides that may exist under conditions likely to be encountered at the potential Yucca Mountain Repository, and determine their formation constants.

It is difficult to study many of the complex equilibria in solution directly using conventional methods because, at environmentally-relevant pH values, the concentration of important actinide ions is extremely low. These experimental difficulties can be overcome in several ways. We are currently developing an approach that uses modern, ultrasensitive, laser-based spectroscopic techniques. These techniques include the absorption-based probes known as photoacoustic spectroscopy (PAS), the related method of photothermal deflection spectroscopy (PDS), and the complementary, emission-based probe known as laser-induced fluorescence (LIF) spectroscopy. Because of the extreme sensitivity of these methods, electronic spectral data can be obtained directly for solutions having site-specific characteristics.

These ultrasensitive spectroscopic techniques rely on information contained in the electronic absorption band structure of the radionuclide complexes to characterize speciation. The principal electronic transitions that give rise to these characteristic absorption bands are Laporte-forbidden f-f transitions within the manifold of 5f electronic states of an actinide complex. Although these transitions do not involve bonding electrons, the energies, intensities, and numbers of transitions in the total absorption spectrum change in a very sensitive way in response to perturbations induced by the coordination environment (i.e., the ligand field) of the radionuclide ion. Thus, different species of the same metal ions possess distinctive absorption spectra. However, because the spectral transitions are parity-forbidden, the intensities are extremely low, and molar extinction coefficients (ϵ) below $50 \text{ M}^{-1} \text{ cm}^{-1}$ are not uncommon. This fact, coupled with the inherent low solubility of these species under solution conditions in the groundwater is the cause of a formidable experimental challenge to the characterization of speciation in these actinide systems.

Photoacoustic and photothermal deflection spectroscopies and LIF have extraordinary sensitivity. For example, it has been demonstrated that LIF can detect as few as eight molecules of a substance in solution. However, most of these measurements involve probing electronic spectroscopic transitions and, as such, the spectra are notoriously difficult to relate *a priori* to specific structural features. The spectra are quite sensitive to structure, but the relationships between spectral signatures and molecular structures must generally be established empirically. It is assumed that the data obtained with this new instrumentation, showing changes in peak positions and intensities with varying conditions, will be interpretable in terms of changes in complexation of the metal center. Most recent published work in the chemistry and chemical physics literature in condensed media focuses on actinide-doped crystalline systems. These studies are of fundamental importance but have limited applicability to speciation studies because only a few systems have been successfully synthesized and characterized. The ability to fine-tune changes in structure and ligand-field strengths has not been available in any previous solid state or solution work. Accordingly, part of our task has been to establish these spectral signatures for the actinide species extant under environmentally relevant conditions.

Spectroscopic Signatures: The Model Compound Approach

In order to establish spectroscopic signatures that are applicable to interpretation of actinide solution spectra, we need the ability to fine-tune changes in structure and ligand-field strengths. The most convenient way to achieve this fine-tuning is through synthetically-tailored actinide complexes. Therefore, we have adopted a model compound approach that exploits the versatility of synthetic actinide chemistry to enable this fine-tuning of structural and electronic effects so that a clearer correlation of molecular and electronic structure can be established. Speciation information can then be extracted from subsequent spectral data (e.g., from environmental samples) with greater likelihood of success, perhaps making it possible to obtain the fundamental molecular-level characterization required to fully understand and model actinide transport and transformation processes.

Experimental activities in this model complex investigation have been proceeding along two paths. One involves the refinement of synthetic strategies and ligand sets to make available a wide range of actinide complexes with varying structural and electronic perturbations. The second is acquisition and interpretation of the electronic spectral data for these synthetically-tailored model complexes. The synthetic work has focused on alkoxide (OR^-) and alkylcarbonate (O_2COR^-) ligands. These ligands are ideal structural and electronic analogues of hydroxide (OH^-) and carbonate (O_2CO^{2-}) or bicarbonate (O_2COH^-) ligands; three ubiquitous ligands in the aqueous systems relevant to Yucca Mountain. Therefore, these synthetically-prepared complexes of the actinides should be directly related to actual environmental actinide species, both structurally and spectroscopically. The advantage afforded by the synthetic model complexes is that they provide unambiguous structures of a single species under well-controlled conditions and can be readily characterized by a suite of spectroscopic techniques. We have utilized pulse NMR, Raman, and FTIR for the characterization of molecular speciation and structure of the complexes in solution and single crystal X-ray diffraction for unambiguous structural characterization of solids when applicable.

The relationship between hydroxide/alkoxide and bicarbonate/alkylcarbonate ligands is illustrated qualitatively below in Figure 1. It can be seen from this figure that the hydroxide ligand is the simplest member of a large series of ligands known as alkoxides, and as such, the alkoxide ligand should serve as an ideal model for the effects of hydroxide ligation on f-element electronic structure. In a similar fashion, it can be seen from Figure 1 that the bicarbonate ligand is a simple prototype of a large series of ligands known as alkylcarbonates. Thus, alkylcarbonates should serve as ideal models for the effects on carbonate/bicarbonate ligation on f-element electronic structure. A major advantage afforded by alkoxide and alkylcarbonate ligands is that, by varying the attendant alkyl group (R), tremendous versatility is achieved in controlling the nuclearity, structure, oxidation state, and inductive electronic effects in actinide complexes. This, in turn, will have important implications in the interpretation of electronic spectroscopic data for actinide species under environmentally-relevant conditions.

Figure 1. A comparison of actinide alkoxide and hydroxide ligands (left) and actinide carbonate, bicarbonate and alkylcarbonate ligands (right).

The electronic structure determinations for these model compounds have been derived principally from UV-visible-near-IR electronic absorption or emission data. Attention has been devoted to understanding how the observable electronic transitions are perturbed in response to structural changes in the complexes. Additional experimental strategies will be implemented as required to clarify electronic band assignments and enhance the quality of the data. These include using low temperature glasses or doped single crystals to improve spectral resolution, and implementation of magnetic perturbations, polarization techniques, and multiphoton spectroscopies to manipulate selection rules so that detailed assignments become possible. An iterative process is evolving between spectroscopic and synthetic efforts in which new synthetic strategies will be driven by the need to tune specific spectroscopic perturbations.

It should be stressed that this model complex work is of a scoping nature and not effecting quality of the potential Yucca Mountain Repository in any way. This work will establish the fundamental baseline spectroscopic signatures that will be used as interpretive aids in the speciation studies of actinide ions under conditions relevant to the potential Yucca Mountain Repository. Therefore, we have made use of known actinide alkoxide structures present in the literature, as well as new complexes developed in our laboratory. Our original experimental work has focused on thorium and uranium compounds due to the ease of handling and, hence, rapidity of experimental procedures. The similarity that we have observed in the chemistry of thorium and uranium is excellent evidence that our preparative strategies will work well for neptunium and

plutonium complexes. Much of the spectroscopic data on uranium complexes have been collected by one of the authors of this work, Dr. John M. Berg, a Director's Funded postdoctoral fellow. Dr. Berg's collaboration in this effort has been invaluable, and his feedback on how structural perturbations affect spectroscopic band shifts has allowed us to move quickly through the prescreening process. From these preliminary data it is clear that small structural perturbations on the synthetic compounds give rise to fairly large spectroscopic perturbations, and it appears that we are now able to identify monomeric, dimeric and trimeric uranium (IV) species in solution.

Synthesis and Characterization of Actinide Alkoxide Complexes

Alkoxide complexes of the actinides were first reported in the mid-1950s during the search for volatile complexes for uranium isotope separation.¹ Much of the early work on these complexes is due to the pioneering efforts of Don Bradley whose group prepared an extensive series of tetravalent actinide alkoxides of empirical formula $An(OR)_4$ ($An = Th, U$).² Over the last decade, much new information on compounds of this type has emerged, and these new results have cleared up many earlier misinterpretations of the exact nature of these compounds in solution and in the solid state.^{1c}

Our entry into compounds of this class has come about principally as a result of the discovery of large-scale synthetic routes to soluble Lewis base adducts of uranium and thorium.^{3,4} We have employed these starting materials on a routine basis for the preparation of new and known tetravalent actinide alkoxide complexes.

Tetravalent Aryloxide Complexes

Monomeric uranium(IV) and thorium(IV) aryloxide complexes, $An(OAr)_4$, have been sought for some time. The first members of this class were prepared by Lappert and coworkers.⁵ Metathesis reactions of thorium or uranium tetrachloride with lithium aryloxides gave "double alkoxide" salts, $[Li(THF)_4][An(O-2,6-i-Pr_2C_6H_3)_5]$, or incomplete metathesis products such as $AnCl(O-2,4,6-t-Bu_3C_6H_2)_3$ ($An = Th, U$) in good yields. In the latter case, an excess of lithium

aryloxide failed to provide the homoleptic thorium complex of general formula $\text{Th}(\text{OAr})_4$. A blue homoleptic thorium aryloxide, $\text{Th}(\text{O}-2,6\text{-Ph}_2\text{C}_6\text{H}_3)_4$, obtained from the reaction of the tetrachloride with 4 equivalents of $\text{LiO}-2,6\text{-Ph}_2\text{C}_6\text{H}_3$ in THF solution, has also been described, but no structural data were presented.

Lappert and coworkers have also examined the alcoholysis reactions of $[\text{U}(\text{NEt}_2)_4]_2$ with excess phenol. These reactions were unsuccessful vis-à-vis the preparation of $\text{U}(\text{O}-2,6\text{-t-Bu}_2\text{C}_6\text{H}_3)_4$; only $\text{U}(\text{NEt}_2)(\text{O}-2,6\text{-t-Bu}_2\text{C}_6\text{H}_3)_3$ could be isolated. This reaction has recently been repeated, and it was found that even in refluxing toluene, the fourth diethylamide ligand is not susceptible to alcoholysis.⁶ Several years ago, Dormond *et al.*⁷ described the reactions of the uranium(IV) metallacycle $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{U}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)$ ⁸ with both HO-t-Bu and $\text{HO}-2,6\text{-Me}_2\text{C}_6\text{H}_3$. They observed rapid protonation of the uranium carbon bond and isolated two complexes of general formula $\text{U}(\text{OR})[\text{N}(\text{SiMe}_3)_2]_3$. They also noted that cleavage of uranium-nitrogen bonds occurred but was not competitive with attack on the metal-carbon bond. In agreement with Dormond *et al.*, we observed that the reaction of one equivalent of $\text{HO}-2,6\text{-t-Bu}_2\text{C}_6\text{H}_3$ with $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{U}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)$ ($\text{An} = \text{Th}, \text{U}$) in hexane at room temperature for 1 hour provides orange ($\text{An} = \text{U}$)⁶ or colorless ($\text{An} = \text{Th}$)⁹ $\text{An}(\text{O}-2,6\text{-t-Bu}_2\text{C}_6\text{H}_3)[\text{N}(\text{SiMe}_3)_2]_3$ in essentially quantitative yield as shown in Equation 1. These compounds have been characterized by elemental analyses and ^1H NMR spectroscopy. The room temperature ^1H NMR spectrum of the uranium complex shows nonequivalent silylamide ligands indicative of restricted rotation about the $\text{U}-\text{O}$ and/or $\text{U}-\text{N}$ bonds.⁶ Similar behavior is not observed for the thorium complex, and may reflect the greater size of the $\text{Th}(\text{IV})$ center.⁹

For the uranium metallacycle, reaction with slightly greater than 4 equivalents of HO-2,6-*t*-Bu₂C₆H₃ in toluene at 100°C for 6 hour provides, after solvent removal and recrystallization, orange, crystalline U(OAr)₄ in 80% yield according to Equation 2.⁶ However, the analogous reaction for thorium fails to give the homoleptic thorium aryloxy product, even after prolonged (36 hour) reflux with excess disubstituted phenol.⁹ The incomplete substitution product Th[(N(SiMe₃)₂)[O-2,6-*t*-Bu₂C₆H₃]₃ can be isolated in *ca.* 80% yield as outlined in Equation 3.⁹

Upon decreasing the steric bulk of the substituted phenol HO-2,6-R₂C₆H₃ (R = *i*-Pr, Me), the alcoholysis proceeds smoothly to give the homoleptic Th(OAr)₄ complexes as shown (Eq. 2) for uranium. Our inability to prepare the homoleptic Th(O-2,6-*t*-Bu₂C₆H₃)₄ complex *via* this simple protonolysis reaction cannot be due to the steric requirements of the resulting Th(OAr)₄ compound, since the reaction of ThI₄(THF)₄ with four equivalents of potassium 2,6-di-*tert*-butylphenoxide in THF solution results in the formation of Th(O-2,6-*t*-Bu₂C₆H₃)₄, in *ca.* 90% isolated yield according to Equation 4.⁹ In these reactions, the formation of insoluble KI may act

as a driving force, and we observe complete metathesis of iodide ligands and no formation of "ate" complexes. It is noteworthy that while this reaction is conducted in THF solution, the experimental work-up procedures yield $\text{Th}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)_4$ as a base-free complex, presumably due to the steric demands of the bulky 2,6-di-*tert*-butylphenoxide ligand.

For less sterically-demanding aryloxy ligands, the reaction of $\text{ThI}_4(\text{THF})_4$ with four equivalents of $\text{KO}-2,6\text{-R}_2\text{C}_6\text{H}_3$ ($\text{R} = i\text{-Pr}$ or Me) in THF solution results in the formation of bis-THF adducts $\text{Th}(\text{O}-2,6\text{-R}_2\text{C}_6\text{H}_3)_4(\text{THF})_2$ in *ca.* 60% to 70% yield according to Equation 5. The THF adducts readily exchange with other Lewis bases such as pyridine to give $\text{Th}(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_4(\text{L})_2$ complexes according to Equation 6. We note that Andersen has isolated and structurally characterized a related phosphine adduct of formula $\text{Th}(\text{OPh})_4(\text{dmpe})_2$.¹⁰

Single crystal X-ray structures have been determined for both the uranium⁶ and thorium⁹ $\text{An}(\text{O-2,6-}i\text{-Bu}_2\text{C}_6\text{H}_3)_4$ complexes. The compounds are isostructural and possess crystallographic $\bar{4}$ (S_4) symmetry. A view of the basic molecular structure emphasizing the S_4 symmetry is shown in Figure 2. Both sets of four An-O bond lengths are identical (2.189(6) Å, Th; and 2.135(4) Å, U), and the O-An-O angles are of two types, four of 110.46(15)° (An = Th) and two of 107.5(3)° (An = Th); the latter angles are those bisected by the C_2 (S_4) axis and correspond to a slight flattening of the central AnO_4 core from T_d to D_{2d} symmetry. Other parameters show a strong similarity between the two structures. The structural similarity between thorium and uranium compounds leaves little doubt that we will be able to prepare the neptunium and plutonium analogues following the strategy outlined in Equations 2 or 4.

Figure 2. A drawing of the crystal structure of $\text{An}(\text{O}-2,6\text{-t-Bu}_2\text{C}_6\text{H}_3)_4$ viewed perpendicular to the S_4 axis, emphasizing S_4 symmetry. Important bond distances [Å] and angles [°]: (An = Th) Th(1)-O(2) 2.189(6), Th(1)-O(2)-C(3) 153.5(10), O(2)-Th(1)-O(2b) 110.46(15), O(2)-Th(1)-O(2a) 107.5(3). (An = U) U(1)-O(2) 2.135(4), U(1)-O(2)-C(3) 154.0(6), O(2)-U(1)-O(2b) 110.2(1), O(2)-U(1)-O(2a) 108.0(2).

The low-temperature (185K) solution ^1H NMR spectra of $\text{An}(\text{O}-2,6\text{-t-Bu}_2\text{C}_6\text{H}_3)_4$ complexes reveal chemically-inequivalent *t*-Bu and *meta* proton resonances, yet a single *para* proton resonance for the 2,6-di-*tert*-butylphenoxide ligand. This is indicative of S_4 symmetry in solution at low temperature in agreement with expectations based on the solid state structures. Upon raising the temperature, the *para* proton remains a sharp triplet, while the *t*-Bu and *meta* proton (doublet) resonances coalesce into single sharp (doublet) resonances with average chemical shift values consistent with rapid rotation about An-O or O-C bonds ($\Delta G^\ddagger = 11.6 \pm 0.1 \text{ kcal mol}^{-1}$, An = Th).⁹ This variable temperature behavior is shown in Figure 3 for the thorium complex and illustrates the usefulness of variable temperature NMR spectroscopy for determination of actinide speciation in solution. While the NMR serves as confirmation of molecular structure for these well-characterized model compounds in solution, it can serve as a structure determination tool (and, hence speciation tool) for uncharacterized actinide complexes in solution.

Figure 3. ^1H NMR spectra showing the variable temperature behavior of the arene (left) and t-Bu resonances (right) for $\text{Th}(\text{O}-2,6\text{-t-Bu}_2\text{C}_6\text{H}_3)_4$. The limiting spectrum obtained at low temperatures is consistent with S_4 symmetry as observed in the solid state molecular structure.

A single crystal X-ray structure of the pyridine adduct $\text{Th}(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_4\text{py}_2$ displays a pseudooctahedral geometry about the central thorium atom with the two pyridine ligands occupying *cis* positions on the octahedron (Figure 4).⁹ The Th-N distances average 2.679 Å. Two different Th-O bond lengths are seen in the molecule; 2.186 Å (ave) for the aryloxy ligands *trans* to pyridine and 2.209 Å (ave) for aryloxy ligands *trans* to one another. These Th-O distances are in the same range as seen in the solid state structure of $\text{Th}(\text{OAr})_4$ and both display relatively large Th-O-C angles. The aryloxy ligands *trans* to pyridine display the shorter Th-O distances and exhibit the greater Th-O-C angles of 176.0° (ave), while those *trans* to one another are found to have slightly longer Th-O distances and smaller Th-O-C angles of 170.6° (ave).

Figure 4. A drawing of the crystal structure of $\text{Th}(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_4(\text{py})_2$ emphasizing the *cis* psuedo-octahedral symmetry. Important bond distances [$\text{\AA}$] and angles [$^\circ$]: $\text{Th}(1)\text{-O}(2)$ 2.211(6), $\text{Th}(1)\text{-O}(20)$ 2.206(6), $\text{Th}(1)\text{-O}(11)$ 2.188(6), $\text{Th}(1)\text{-O}(29)$ 2.183(6), $\text{Th}(1)\text{-N}(38)$ 2.662(8), $\text{Th}(1)\text{-N}(44)$ 2.696(8), $\text{Th}(1)\text{-O}(2)\text{-C}(3)$ 169.1(7), $\text{Th}(1)\text{-O}(20)\text{-C}(21)$ 172.0(6), $\text{Th}(1)\text{-O}(11)\text{-C}(12)$ 175.8(6), $\text{Th}(1)\text{-O}(29)\text{-C}(30)$ 176.2(6), $\text{N}(38)\text{-Th}(1)\text{-N}(44)$ 78.40(24), $\text{O}(2)\text{-Th}(1)\text{-O}(11)$ 94.37(24), $\text{O}(2)\text{-Th}(1)\text{-O}(29)$ 93.76(23), $\text{O}(11)\text{-Th}(1)\text{-O}(20)$ 94.99(24)

Aliphatic Alkoxide Complexes

A number of homoleptic actinide alkoxide complexes of composition $\text{An}(\text{OR})_4$ ($\text{An} = \text{Th}$, U ; $\text{R} = \text{Me}$, Et , $i\text{-Pr}$, $n\text{-Pr}$, $n\text{-Bu}$ etc.) have been reported previously,² but their characterization has been limited to elemental analysis and solution molecular weight determination. We have discovered that treatment of the thorium metallacycle $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Th}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)$ **8** with four equivalents of either di-*iso*-propylmethanol or dimethyl-*tert*-butylsilanol in hexane at room temperature yields colorless crystals of $\text{Th}_2(\text{OR})_8$ ($\text{R} = \text{CH-}i\text{-Pr}_2$, $\text{SiMe}_2\text{-}t\text{-Bu}$) in good yield according to Equation 7.

A similar dimeric compound has been prepared for uranium. Although by a somewhat different synthetic route, alcoholysis of $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$ ¹¹ with $\text{HOSiMe}_2\text{-}t\text{-Bu}$ leads to oxidation of the uranium(III) center and isolation of a uranium(IV) product of formula $\text{U}_2(\text{OSiMe}_2\text{-}t\text{-Bu})_8$. In order to account for oxidation of uranium(III) to uranium(IV), it is assumed that hydrogen is evolved in the reaction (Eq. 8); work is in progress to resolve this question.

Single crystal X-ray structures have been determined for both $\text{Th}_2(\text{OCH-}i\text{-Pr}_2)_8$ and $\text{U}_2(\text{OSiMe}_2\text{-}t\text{-Bu})_8$. The structure of $\text{Th}_2(\text{OCH-}i\text{-Pr}_2)_8$ is shown in Figure 5.⁹ The compound crystallizes in the monoclinic space group $\text{P}2_1/\text{n}$ with two molecules per unit cell which reside on centers of inversion. Each thorium atom adopts a distorted trigonal bipyramidal geometry, and the Th_2O_8 core can be viewed as two ThO_5 trigonal bipyramids joined along a common axial-equatorial edge. The three equatorial bonds are distorted from the ideal (120°) trigonal angles, the actual values being $129.2(4)$, $111.8(4)$, and $116.2(4)$; the deviation of the trigonal ThO_3 unit from

planarity is 2.8 degrees. The axial O-Th-O unit is distorted (158.2°) from the idealized 180° and may be due to steric demands of the bridging alkoxide unit. Terminal Th-O distances are rather short at 2.154 Å (ave) and virtually identical to the Th-O distance (2.154(8) Å) observed for the 2-butene-2,3-diolate ligand in the X-ray structure of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\mu\text{-O}_2\text{C}_2\text{Me}_2)]_2$.¹² The corresponding Th-O-C angles are large and range from $167.4 - 171.5^\circ$.

Figure 5. A view of the molecular structure of $\text{Th}_2(\text{OCH-i-Pr})_8$ emphasizing the fused trigonal bipyramidal coordination geometry. Methyl carbons of the $\text{OCH}(\text{CHMe}_2)_2$ ligands are omitted for clarity. Important bond lengths [Å] and angles [$^\circ$]: Th(1)-O(2) 2.160(11), Th(1)-O(10) 2.141(11), Th(1)-O(18) 2.161(11), Th(1)-O(26) 2.408(10), Th(1)-O(26a) 2.463(11); O(2)-Th(1)-O(10) $98.2(4)$, O(2)-Th(1)-O(18) $94.8(5)$, O(2)-Th(1)-O(26) $93.9(4)$, O(2)-Th(1)-O(26a) $158.2(4)$, O(10)-Th(1)-O(18) $111.8(4)$, O(10)-Th(1)-O(26) $116.2(4)$, O(10)-Th(1)-O(26a) $98.7(4)$, O(18)-Th(1)-O(26) $129.2(4)$, O(18)-Th(1)-O(26a) $91.7(4)$, Th(1)-O(26)-Th(1a) $113.8(4)$, O(26)-Th(1)-O(26a) $66.2(4)$.

The structure of $\text{U}_2(\text{OSiMe}_2\text{-t-Bu})_8$ is similar to that seen for $\text{Th}_2(\text{OCH-i-Pr})_8$ and is shown in Figure 6. Each uranium atom adopts a distorted trigonal bipyramidal coordination geometry, and the U_2O_8 core can be viewed as two UO_5 trigonal bipyramids joined along a common axial-equatorial edge. The molecule is distorted relative to $\text{Th}_2(\text{OCH-i-Pr})_8$, with the distortion arising from a puckering in the $\text{U}_2(\mu\text{-O})_2$ bridge, presumably due to steric interactions of the bulky $\text{OSiMe}_2\text{-t-Bu}$ ligands. From Figure 6 the local trigonal bipyramidal coordination

environment around each uranium atom can readily be seen. For U(1), oxygen atoms O(3) and O(43) occupy apical positions, while O(11), O(59) and O(51) lie in the equatorial plane. The three equatorial bonds are distorted from the ideal (120°) trigonal angles, the actual values being 129.4 , 120.6 , and 107.9 ; the deviation of the trigonal UO_3 unit from planarity is 2.1 degrees. The axial O(3)-U(1)-O(43) unit is distorted (162.2°) from the ideal 180° , again probably a result of steric interactions with the bridge. In a similar fashion, O(35)-U(2)-O(11) make up the principal (axial) axis, while O(27), O(19), and O(3) lie in the trigonal plane. The two trigonal bipyramids are joined through the agency of bridging alkoxide ligands with an average U-O distance of $2.401 \text{ \AA}$; the terminal U-O bonds average $2.118 \text{ \AA}$. The terminal U-O-Si angles are rather large, ranging from 156.8° to 174.3° , with an average value of 165.2° .

Figure 6. A view of the molecular structure of $\text{U}_2(\text{OSiMe}_2\text{-t-Bu})_8$ emphasizing the fused trigonal bipyramidal coordination geometry. Carbon atoms of the $\text{OSiMe}_2\text{-t-Bu}$ ligands are omitted for clarity. Important bond lengths [$\text{\AA}$] and angles [$^\circ$]: U(1) - U(2) $3.819(2)$, U(1)-O(3) $2.372(17)$, U(1)-O(11) $2.401(17)$, U(1)-O(43) $2.106(18)$, U(1)-O(51) $2.166(19)$, U(1)-O(59) $2.101(18)$, O(3)-U(1)-O(43) $162.2(6)$, O(3)-U(1)-O(51) $102.5(7)$, O(3)-U(1)-O(59) $88.7(7)$, O(11)-U(1)-O(43) $95.4(6)$, O(11)-U(1)-O(51) $134.3(7)$, O(11)-U(1)-O(59) $116.6(7)$.

In solution, ^1H NMR spectroscopy reveals only one ligand environment for the $\text{OSiMe}_2\text{-t-Bu}$ ligands in the $\text{An}_2(\text{OSiMe}_2\text{-t-Bu})_8$ compounds ($\text{An} = \text{Th}, \text{U}$) indicative of rapid bridge-terminal site exchange on the NMR time scale. In contrast, room temperature ^1H NMR spectra of $\text{Th}_2(\text{OCH-i-Pr}_2)_8$ reveal resonances consistent with two species present in solution, and suggest an equilibrium between monomeric $[\text{Th}(\text{OCH-i-Pr}_2)_4]$, and its dimer $[\text{Th}(\text{OCH-i-Pr}_2)_4]_2$ as shown in Equation 9.⁹ The important features (of the methine regions) of the ^1H NMR spectrum are shown in Figure 7.⁹ There is one set of broadened methine resonances (indicated by numeral 1 in Figure 7) consistent with only one type of alkoxide ligand, suggesting a rapid bridge-terminal exchange process for $\text{Th}_2(\text{OCH-i-Pr}_2)_8$. A smaller, sharp set of resonances, indicative of a single alkoxide environment, is also present (labeled as numeral 2 in Figure 7). Integrated intensities of *ca.* 9:1 preclude any assignment of these resonances to $\text{Th}_2(\text{OCH-i-Pr}_2)_8$ alone. Upon heating the solution, the resonances assignable to $\text{Th}_2(\text{OCH-i-Pr}_2)_8$ (1) diminish and those assigned to $\text{Th}(\text{OCH-i-Pr}_2)_4$ (2) increase, and at $+60^\circ\text{C}$, the monomer predominates in solution (Figure 7). Upon cooling, the resonances of the dimer reappear rapidly, implying a low barrier to dimerization (Eq. 9). Low temperature ^1H NMR spectra show a further increase in the concentration of dimer (1) relative to monomer (2) as expected for an equilibrium mixture. In addition, those NMR resonances assignable to the dimer (1) broaden and split out into two separate resonances in a 3:1 ratio consistent with maintenance of the dimeric structure in solution.

The observation of the dynamic equilibrium for this thorium complex in solution is particularly exciting in terms of spectroscopic signatures. We are presently working on preparation of the corresponding uranium system, since it's electronic spectrum will provide a unique

opportunity to measure and deconvolute an equilibrium mixture in which the molecular structure of both equilibrium components are known.

The addition of an excess of pyridine or THF to solutions of $\text{Th}_2(\text{OCH-}i\text{-Pr}_2)_8$ results in the formation of monomeric Lewis base adducts $\text{Th}(\text{OCH-}i\text{-Pr}_2)_4\text{L}_2$ ($\text{L} = \text{py}$ or THF), which may be isolated as colorless crystals in good yield.⁹ We assume that Lewis bases react with monomeric $\text{Th}(\text{OCH-}i\text{-Pr}_2)_4$, shifting the equilibrium until all the dimer is consumed (Eq. 9).

Figure 7. ¹H NMR spectra of the methine region of a mixture of $\text{Th}_2(\text{OCH-}i\text{-Pr}_2)_8$ (1) and $\text{Th}(\text{OCH-}i\text{-Pr}_2)_4$ (2) at 293K (bottom) and 333K (top). Left and right spectra not to scale. The resonance marked with an asterisk denotes the ¹H impurity in toluene-d₈. Methine resonances assigned to 1 and 2 are labeled.

Lewis base adducts of general formula $\text{Th}(\text{OR})_4\text{py}_2$ may also be prepared directly by the addition of four equivalents of potassium alkoxide to $\text{ThX}_4(\text{THF})_4$ ($\text{X} = \text{Br}, \text{I}$)⁴ in THF or THF/pyridine, followed by crystallization as indicated in Equation 10.⁹

For example, reaction of the tetrahydrofuran adduct of thorium tetraiodide with four equivalents of potassium *tert*-butoxide in the presence of pyridine leads to the isolation of $\text{Th}(\text{O-t-Bu})_4(\text{py})_2$. A single crystal X-ray diffraction study on $\text{Th}(\text{O-t-Bu})_4(\text{py})_2$ revealed a pseudooctahedral geometry about the central thorium atom with the two pyridine ligands occupying *cis* positions. The molecular structure of $\text{Th}(\text{O-t-Bu})_4(\text{py})_2$ is shown in Figure 8. Like its aryloxide analogue, two significantly different Th - O bond lengths are seen in the molecule; 2.16 Å for the *tert*-butoxide ligands *trans* to pyridine and 2.20 Å for the *tert*-butoxide ligands *trans* to one another. The two pyridine ligands exhibit a thorium - nitrogen distance of 2.76 Å. The relatively large Th-O-C angles are indicative of a significant degree of π -donation from oxygen lone pairs to the thorium metal center and are dependent on the *trans* influence and π -donor properties of the *trans* ligand. Thus the *tert*-butoxide ligands *trans* to pyridine (which has a relatively weak *trans* influence) exhibit Th - O - C angles of 172° while those *trans* to one another are found to have smaller Th - O - C angles of 163°.

Room-temperature ^1H NMR spectra reveal only one type of alkoxide ligand for $\text{Th}(\text{OR})_4\text{py}_2$, presumably due to a dynamic exchange process in solution. The dynamic exchange is so facile that low temperature NMR spectroscopy is unable to freeze out a limiting structure, even at -185 K. We note the isolation, by Bradley *et al.*, of the complex $\text{Th}(\text{OCMe}_2\text{CCl}_3)_4\text{py}_2$,^{2e} although no mention was made of the stereochemistry of the molecule, and we also note the preparation by Andersen and coworkers of the related uranium species $\text{U}\{\text{OCH}(\text{CF}_3)_2\}_4(\text{THF})_2$,¹⁶ $\text{U}\{\text{OC}(\text{CF}_3)_3\}_4(\text{THF})_2$ ¹⁶ and $\text{U}(\text{OCH-t-Bu})_4$.¹⁷

Figure 8. A drawing of the molecular structure of $\text{Th}(\text{O}-t\text{-Bu})_4(\text{py})_2$ emphasizing the cis pseudo-octahedral symmetry about the central thorium atom. Important bond distances [Å] and angles [°]: $\text{Th}(1)\text{-O}(1)$ 2.194(6), $\text{Th}(1)\text{-O}(2)$ 2.157(6), $\text{Th}(1)\text{-N}(1)$ 2.753(8), $\text{Th}(1)\text{-O}(1)\text{-C}(1)$ 163.0(7), $\text{Th}(1)\text{-O}(2)\text{-C}(5)$ 172.1(6)

Treatment of the metallacyclic species $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{U}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)]$ with four equivalents of *tert*-butanol in toluene at room temperature produces the dimeric alcoholate formulated as $\text{An}_2(\text{O}-t\text{-Bu})_8(\text{HO}-t\text{-Bu})$ for both $\text{An} = \text{Th}^9$ and U^{13} as outlined in Equation 11. The compound is formulated as $\text{An}_2(\text{O}-t\text{-Bu})_8(\text{HO}-t\text{-Bu})$ based on elemental analyses, solution NMR, IR, and UV-visible-NIR spectroscopy. The combined data are all consistent with a fused confacial bioctahedral coordination geometry as illustrated in Equation 11. Deprotonation of the alcoholate complex with alkali metal hydride or alkoxide generates the corresponding alkali metal salt $\text{M}'\text{An}_2(\text{O}-t\text{-Bu})_9$ where $\text{An} = \text{Th}$ and $\text{M}' = \text{Na}^9$ or $\text{An} = \text{U}$, and $\text{M}' = \text{K}^{13}$ as shown in Equation 12.

Solution ^1H NMR data displayed four types of alkoxide ligands in a 4:2:2:1 ratio consistent with a static confacial bioctahedral $\text{Th}_2(\text{O-t-Bu})_9^-$ anion bridged by a sodium cation as illustrated in Equation 12. This structural hypothesis was confirmed by a single-crystal X-ray structure determination on $\text{NaTh}_2(\text{O-t-Bu})_9$, and a view of the solid state structure is shown in Figure 9. Thorium - oxygen bond lengths are found to be 2.15 and 2.23 Å for the terminal *tert*-butoxide ligands and 2.48 Å (average) for the bridging alkoxide ligands. The sodium ion is coordinated to four oxygen atoms of the *tert*-butoxide ligands, two of these occupying bridging positions and two being terminal ligands, with sodium - oxygen distances of 2.42 and 2.61 Å, respectively. The isostructural uranium analogue of formula $\text{KU}_2(\text{O-t-Bu})_9$ has been reported by Cotton and coworkers.¹⁴ The uranium analogue can also be prepared in good yield directly from uranium tetrachloride and 4.5 equivalents of potassium *tert*butoxide.

Figure 9. A drawing of the molecular structure of $\text{NaTh}_2(\text{O-}t\text{-Bu})_9$ emphasizing the confacial biotetrahedral dimeric structure, with the sodium ion cradled by two bridging and two terminal oxygen atoms. Important bond distances [Å] and angles [°]: Th(1)-O(1) 2.448(8), Th(1)-O(2) 2.498(8), Th(1)-O(6) 2.477(8), Th(1)-O(3) 2.146(9), Th(1)-O(4) 2.266(12), Th(1)-O(5) 2.164(9), Na(1)-O(4) 2.61 Na(1)-O(2) 2.42.

If the actinide metallacycle $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{U}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)$ is treated with an excess of *tert*-butanol (6 equivalents) in refluxing toluene, the trimeric complex $\text{An}_3\text{O}(\text{O-}t\text{-Bu})_{10}$ may be obtained according to Equation 13. For the uranium analogue, it has been shown that hydrolysis via one equivalent of H_2O will also generate the trimer shown in Equation 13. ^1H NMR spectroscopy reveals a characteristic 3:3:3:1 pattern of *tert*-butoxide resonances indicative of an M_3X_{11} structure as indicated in Equation 13. An X-ray structure determination has been reported for the uranium analogue by Cotton and coworkers.¹⁵ A drawing of the molecular structure of $\text{U}_3\text{O}(\text{O-}t\text{-Bu})_9$ is shown in Figure 10.

Figure 10. A drawing of the molecular structure of $\text{An}_3\text{O}(\text{O}-t\text{-Bu})_9$ emphasizing the octahedral coordination environment around each actinide atom. The structure reveals six terminal alkoxide oxygens, three doubly bridging oxygens, one triply bridging alkoxide oxygen, and one triply bridging oxo ligand on the front of the molecule as shown here.

Summary of Model Compound Synthesis

In environmental groundwaters, the slow polymerization of actinide ions may be attributed to the kinetically slow polymerization of metal-oxygen bonds in direct analogy to the slow polymerization observed in many metal alkoxide complexes in nonaqueous solution. We have shown that, in general, a decrease in the steric bulk about the actinide metal center will promote oligomerization of metal-oxygen bonds. Thus, by careful control of steric bulk on the supporting alkyl group in the actinide alkoxide, one can control oligomerization in the model complexes as exemplified by the X-ray structures of $\text{An}(\text{OAr})_4$, $\text{An}_2(\text{OR})_8$ and $\text{An}_3\text{O}(\text{OR})_{10}$. Many of the same structural types have been prepared and characterized for both Th(IV) and U(IV), indicating a high likelihood for success in preparation of analogous Np(IV) and Pu(IV) complexes for spectroscopic study.

Spectroscopic Study of Actinide Electronic Structure

The synthetic studies have established that we can indeed control the local coordination geometry about the central actinide ion, and we have built a fairly extensive database of X-ray structural data. Solution NMR studies have demonstrated that these structural types are maintained in solution and, thus, electronic absorption spectra obtained on pure compounds will be indicative of each structural type in solution. For the discussion of optical spectroscopic data, we have chosen representative examples from the variety of structures discussed in the earlier section. The structural types chosen for a discussion of spectroscopic signatures include four-coordinate monomers of structural type **1**, six-coordinate dimeric species of structural types **2** and **3**, and the six-coordinate trimer of structural type **4**. These important structural types are indicated for reference below.

For the electronic spectra of the actinide model compounds, the narrow absorption peaks observed in visible and near-infrared spectra are due to transitions between states which are predominantly metal $5f^n$ in origin. A large number of states originate from this manifold even for cases such as U(IV) which has only two f electrons. Figures 11 and 12 show representative spectra that we have obtained for six synthetically-tailored U(IV) model complexes of the four structural types listed above. Since one must consider ligand field effects in addition to the strong interactions within the $5f^n$ manifold in interpreting spectra, the problem of understanding the electronic structure of all but the most simple actinide complexes begins to appear forbiddingly difficult.

Fortunately, the energies of the states within the $5f^n$ configuration are determined principally by electron-electron repulsion and spin-orbit interactions, which are heavily dependent on the metal ion and its oxidation state. This leads to a qualitative similarity of spectra of actinide complexes in the same oxidation state and makes low-level assignments of the gross peak structure possible. Indeed the spectra shown in Figure 11 share many common characteristics with each other and with U(IV) doped in crystalline systems and in aqueous solution. Ligand-field effects, which are weaker than in transition metal complexes, can be approached initially as perturbations on this dominant structure. The synthetic control discussed above allows us to manipulate these perturbations with a subtlety not approached by other classes of complexes, such as crystalline halide salts. Thus we have a unique opportunity to provide one key to an integrated understanding of overall electronic structure of light actinide complexes in solution.

Figure 11. Room temperature UV-VIS-NIR spectra for six uranium (IV) model complexes obtained at 293 K. Compounds are as follows: a = $\text{U}(\text{OAr}^*)_4$, b = $\text{U}[\text{N}(\text{SiMe}_3)_2](\text{OAr}^*)_3$, c = $\text{U}_2(\text{O-t-Bu})_8(\text{HO-t-Bu})$, d = $\text{KU}_2(\text{O-t-Bu})_9$, e = $(\text{NBu}_4)\text{U}_2(\text{O-t-Bu})_9$, f = $\text{U}_3\text{O}(\text{O-t-Bu})_{10}$.

The differences between the spectra shown in Figures 11 and 12 already illustrate interesting aspects of the influence of the ligand field on the structure of the $5f^n$ configuration. The top two spectra (a and b) in Figure 11 are of monomeric complexes with approximately tetrahedral symmetry about the U(IV) center (structure type 1). The third, fourth, and fifth spectra (c, d, and e) are of dimeric complexes with 6-coordinate U(IV) centers and approximately octahedral symmetry (structure types 2 and 3). The last spectrum (f) is of the trimer with 6-coordinate U(IV) centers which are slightly distorted from octahedral symmetry (structure type 4). We submit that the spectra in Figure 11 naturally fall into groupings by coordination number and symmetry, with a and b having similar appearances which are distinct from c-e, and with the trimer f showing qualitative differences from all the others. The low-temperature spectra in Figure 12 accentuate these differences. Within these groupings by symmetry, changes due to different ligand identities

are evident. For instance, the shift to higher energies of the major peaks in spectra **c-e** correlates with decreasing ligand polarizability.

Figure 12. Low-temperature UV-VIS-NIR spectra for three uranium (IV) model complexes obtained at 77 K. Compounds are as follows: **a** = $\text{U}(\text{OAr}^*)_4$, **d** = $\text{KU}_2(\text{O-t-Bu})_9$, **f** = $\text{U}_3\text{O}(\text{O-t-Bu})_{10}$.

Further design and synthesis of similar complexes with controlled variation in the factors which influence the absorption spectra will enable us to strengthen and fine-tune correlations between spectra and ligation to the point where absorption-based spectroscopic techniques become more useful molecular structure tools. The degree of control within our existing synthetic capabilities gives this work unique promise to provide a level of understanding of actinide electronic structure which will compliment and, in many ways, exceed that which has been achieved through the studies of doped crystalline systems.

Concluding Remarks

A great deal of effort has been devoted to the development of sensitive spectroscopic techniques for the study of actinide speciation based on the sensitivity of f-f electronic absorption bands to oxidation state and ligation of the actinide ions. These efforts assume that data obtained in such studies will be interpretable in terms of changes in complexation of the metal center. However, our current understanding of 5f electronic structure is based on data from solid state doped single crystals. In these studies the local coordination geometry about the central actinide ion is maintained in an almost perfect high-symmetry environment, and this has little relevance for species in solution where deviations from perfect high symmetry tend to be the rule rather than the exception. Accordingly, part of our task has been to establish these spectral signatures in building a spectral database for the actinide species extant under environmentally relevant conditions.

In order to establish spectroscopic signatures that are applicable to interpretation of actinide solution spectra, we need the ability to fine-tune changes in structure and ligand-field strengths. The most convenient way to achieve this fine-tuning is through synthetically-tailored actinide complexes. Therefore, we have adopted a model compound approach that exploits the versatility of synthetic actinide chemistry to enable this fine-tuning of structural and electronic effects so that a clearer correlation of molecular and electronic structure can be established. Speciation information can then be extracted from subsequent spectral data (e.g., from environmental samples) with greater likelihood of success, perhaps making it possible to obtain the fundamental molecular-level characterization required to fully understand and model actinide transport and transformation processes.

Experimental activities in this model complex investigation have involved both the refinement of synthetic strategies to make available a wide range of actinide complexes with varying structural and electronic perturbations and acquisition and interpretation of the electronic spectral data for these synthetically-tailored model complexes. We have synthesized and characterized well over 40 new actinide alkoxide complexes and are confident that our methodology will be applicable to the preparation of the analogous neptunium and plutonium

complexes. The neptunium and plutonium synthetic chemistry efforts are expected to be underway with completion of a new hotlab chemistry facility and the lifting of a laboratory-wide moratorium on producing mixed waste.

These model complexes have been used to determine how observable electronic transitions are perturbed in response to structural changes in the complex in solution. From the spectra obtained for these model complexes, we have found that the f-f transitions naturally fall into obvious groupings by coordination number and symmetry by which we can now differentiate between monomeric, dimeric, and trimeric actinide species in solution. It is noteworthy that the f-f transitions in the homoleptic alkoxide complexes differ from those observed in a mixed oxo-alkoxide complex of the same coordination number and local site symmetry.

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