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Oxidation State Delineation via U L_{III}-Edge XANES in a Series of Isostructural Uranium Coordination Complexes

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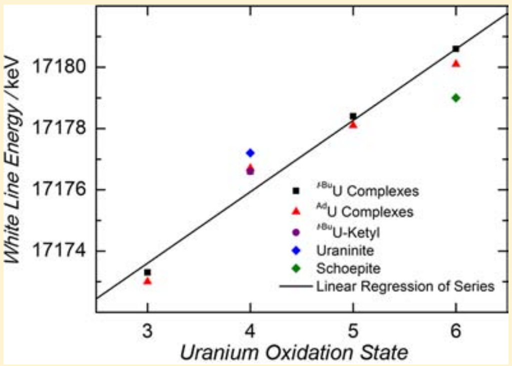
Supporting Information

ABSTRACT: We present an X-ray absorption near-edge structure (XANES) study of a series of uranium coordination complexes that possess nearly identical first coordination spheres and geometries in a range of oxidation states from U^{III} to U^{VI}. These compounds were obtained through the activation of small molecules, such as ketones, azides, and carbon dioxide, and upon oxidation of a high-valent $U^{V}{\equiv}O$ to $[U^{VI}{\equiv}O]^+$. Most of the compounds have been reported previously. All of them are fully characterized and their oxidation states have been confirmed by various spectroscopic methods (SQUID, ^{1}H NMR, and UV/vis/near-IR). Each uranium complex consists of a triazacyclononane anchor bearing three aryloxide side arms with bulky *tert*-butyl (*t*-Bu) or adamantyl (Ad) ortho substituents. All complexes have approximate C_3 symmetry and possess an axial cavity that is either empty (U^{III}) or occupied by a seventh ligand, namely, terminal oxygen (U^{V} and U^{VI}) or an oxygen-containing ligand (U^{IV}). The only exception is $[((^{t\text{-Bu}}ArO)_3tacnU^{VI}(O)][SbF_6]$, which is the rare case of a complex that shows a strong inverse trans influence. The determined correlation between the uranium oxidation state and the U L_{III}-edge XANES absorption in this series includes a single terminal oxo ligand bonded uranium(V,VI), for which data are essentially nonexistent. The correct assignment of the uranium valence in a $U^{IV}{-}L^{\bullet-}$ compound ($L^{\bullet-}$ = ketyl radical) is shown to be only possible by a comparison to structurally similar compounds.



INTRODUCTION

In the course of our studies of small-molecule activation by uranium complexes supported by the $(^{R}ArO)_3tacn^{3-}$ ligand system [for R = *t*-Bu (*tert*-butyl), **1-*t*-Bu**,[1] and for R = Ad (1-adamantyl), **1-Ad**[2]], we have prepared a series of isostructural hexa- and heptacoordinate uranium complexes that possess nearly identical first-coordination spheres and geometries in the full range of oxidation states from U^{III} to U^{VI}.

Only recently, we have completed this series with the synthesis of uranium(V)[3] and uranium(VI)[4] complexes, featuring a single terminal oxo ligand. The electronic and molecular structure of most of these complexes has been fully characterized previously by standard methods, such as SQUID magnetometry (superconducting quantum interference device), EPR spectroscopy (electron paramagnetic resonance), ^{1}H NMR and UV/vis/NIR spectroscopy, as well as XRD (X-ray diffraction).The characterization of **4-*t*-Bu** and **4-Ad** is included in the Supporting Information (SI). Each complex consists of a triazacyclononane anchor bearing three aryloxide side arms with *t*-Bu or Ad ortho substituents. All complexes have approximate C_3 symmetry (except for $[((^{t\text{-Bu}}ArO)_3tacn)U^{VI}(O)][SbF_6]$ (**6-*t*-Bu**),[4] which has C_s symmetry) and possess an axial cavity, which is either empty (U^{III}, **1-R**) or occupied by a seventh ligand, namely, a terminal oxo (U^{V}, **5-R**;[3] U^{VI}, **6-R**[4]), an alkoxide [U^{IV}, **3**;[5] **4-R** (see the SI)], or a ketyl radical ($U^{IV}{-}L^{\bullet-}$, **2**;[5] Scheme 1).

For the crystallographically characterized η^1-ketyl complex **2**, four different resonance structures can be considered (Scheme 2). While three of them are charge-separated compounds, where the metal can be assigned to a formal oxidation state of U^{IV} with a radical on an anionic ketyl ligand, one has a formal U^{III} center and a neutral benzophenone ligand. Quantum-chemical density functional theory studies on complex **2** suggested that the unpaired electron is located and resonance stabilized on both the metal and ligand.[5] Similarly, temperature-dependent SQUID magnetization measurements revealed a U^{IV} center with an uncoupled ligand radical and magnetic moments of ~1.7 μ_B at 4 K.[5] In contrast, uranium(IV) complexes with closed-shell ligands have a non-magnetic singlet ground state and typically exhibit magnetic moments of approximately 0.4 μ_B.[6] In this report, we use the U L_{III}-edge X-ray absorption near-edge structure (XANES) energies of the other near-isostructural uranium complexes and of hexa- and tetravalent

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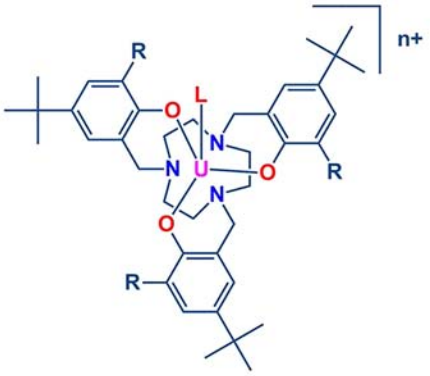
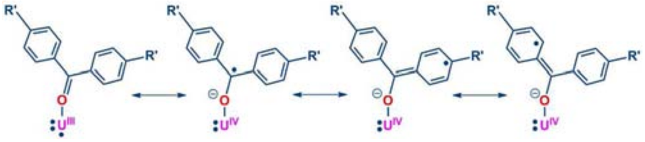
Scheme 1. Schematic Representation of Complexes of the General Type $[((^{R}ArO)_3tacn)U{-}L]^{n+}$ and Table of Compounds



L	R = *t*-Bu	R = Ad	Ox. State
–	**1-*t*-Bu**, n=0	**1-Ad**, n=0	III
$O\text{-}C\text{-}(^{t\text{-}Bu}Ar)_2^{\bullet -}$	**2**, n=0	–	IV
$O\text{-}CH\text{-}(^{t\text{-}Bu}Ar)_2$	**3**, n=0	–	IV
$O\text{-}CH_3$	**4-*t*-Bu**, n=0	**4-Ad**, n=0	IV
O	**5-*t*-Bu**, n=0	**5-Ad**, n=0	V
O	**6-*t*-Bu**, n=1	**6-Ad**, n=1	VI

Scheme 2. Different Possible Resonance Structures for a Uranium Ketyl Complex[a]



[a] In **2**, R and R′ = *t*-Bu. The chelating $(^{t\text{-}Bu}ArO)_3tacn^{3-}$ ligand is omitted. Only one of the possible resonance structures of the para and ortho radical forms is depicted.

oxide reference compounds to determine the oxidation state of the open-shell, charge-separated uranium ketyl complex **2**. Notably, a comparison to the closed-shell alkoxo derivative **3** and the methoxide complex **4** assists in the potentially ambiguous assignment of **2**.

X-ray absorption fine structure (XAFS)[7] spectroscopy is a helpful tool to characterize the near-ordered structure surrounding of a selected element in systems in varying physical states, i.e., everything from solids, including nanoparticles and amorphous materials, to liquids and gases. It is applicable where no long-range order exists and XRD structure determinations are not possible.[7] Detailed analysis of the extended XAFS (EXAFS) is used to characterize the coordination structure, including determination of the coordination numbers and bond distances.[8−11] Analysis of the XAFS region at energies near an element's ionization energy (XANES)[12] is an exceptionally powerful tool for determining the oxidation states. Recent studies combine XANES from both the metal ion and the coordinating ligand absorption edges with results from theoretical tools to define the degree of covalency in metal–ligand bonds in transition-metal and actinide complexes.[13−22]

Metal and metal-ion oxidation-state determinations using XANES spectroscopy rest on the fact that the binding energy for exciting a core photoelectron increases with the charge of the metal center; the transition energy, observed as an "edge" or rise in the measured absorption coefficient, shifts to higher energy upon increasing valence of the absorbing metal ion.[12] The XANES edge energy is, however, not solely a function of the formal oxidation state. The chemical environment and other factors contributing to the electron density or shielding of empty final states involved in the photoelectron transition also play an important role. As a result, edge energies for compounds possessing highly covalent, π-bonded metal–ligand multiple bonds most often differ from those for compounds of the same formal valence but exhibiting solely σ-bound ligands. Filled π orbitals decrease the effective charge on the metal center and, as a result, a linear correlation between the metal formal oxidation state and edge energy for such systems no longer strictly holds. For the lighter actinide elements in particular, this phenomenon complicates determination of the oxidation states with XANES because their higher-valent complexes almost invariably form actinyl compounds, $[O{=}An{=}O]^{n+}$, with multiple bonds between the $An^{(m-n)+}$ cation and its oxo ligands.[23] For example, the energy position of the Np L_{III} edge for neptunium(IV) compounds generally lies *above* that of their neptunyl $[O{=}Np^{V}{=}O]^{+}$ counterparts because of the relatively higher charge on the Np^{V} center with two π-bonded terminal oxo ligands. This is in reverse order of an expected straightforward increase in the ionization energy with increasing valence state of the absorbing atom.[24] Such behavior renders disentangling correlations between the oxidation state and XANES absorption energies challenging for these elements, whose chemistry is critical in environmental and energy areas.

To date, few studies of penta- and hexavalent uranium coordination compounds without the abundant uranyl $[O{=}U^{VI}{=}O]^{2+}$ moiety have been reported.[25,26] A limiting factor in such studies is the paucity of high-valent uranium complexes stabilized by a single terminal oxo ligand.[3,4,27−30] The systematic U L_{III}-edge XANES investigation presented here will add to the present scarce database for such compounds. In addition, the results for our isostructural series of uranium(III) to uranium(VI) complexes to probe the uranium valence are not only useful to determine the correct resonance structure for **2**; moreover, they can serve as a benchmark for the further advancement of quantum-chemical tools for modeling these heavy, highly correlated, and relativistic systems in general and can help aid in challenging oxidation-state assignments in particular.

■ RESULTS AND DISCUSSION

The background-subtracted, normalized U L_{III}-edge XANES spectra of the complexes **1-R**, **2**, **3**, **4-R**, **5-R**, and **6-R** are shown in Figure 1 (top). The first derivative of the normalized absorption versus energy plot is also shown (bottom), where the zero crossing corresponds to the primary spectral XANES peak (white line) energy for each compound. These energy values are listed in Table 1.

The observed energy increase with the uranium valence is consistent with the expectation that the increased formal charge

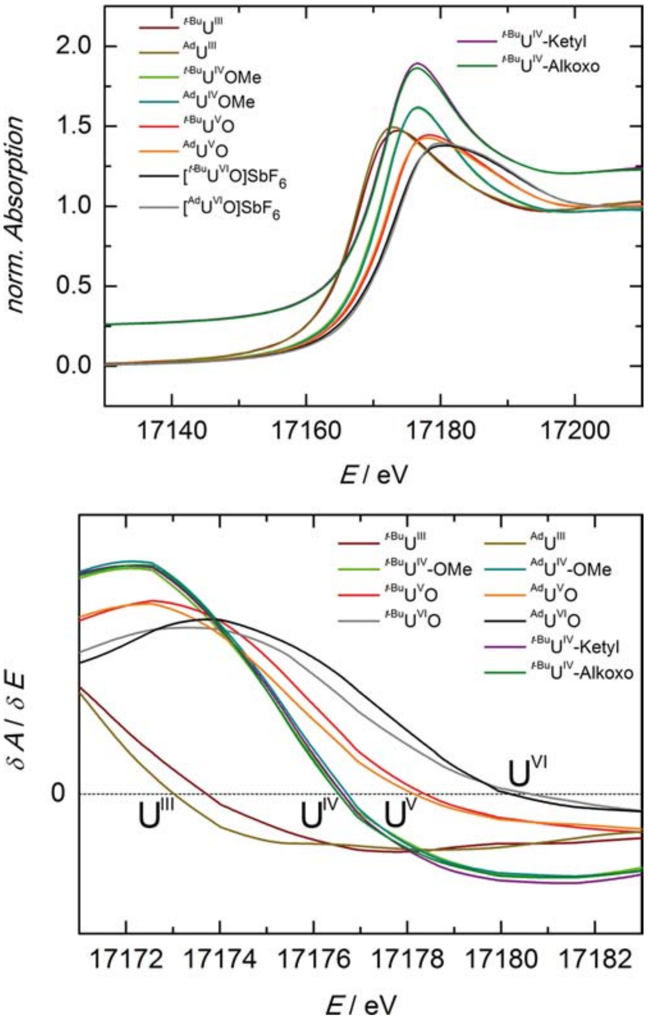


Figure 1. Normalized U L_{III}-edge XANES (top) and their corresponding first derivatives (bottom) for compounds **1-R** (brown, ocre), **4-R** (light green, blue), **5-R** (red, orange), and **6-R** (black, gray) for both ligand systems (R = *t*-Bu, Ad) and for compounds **2** (purple) and **3** (dark green). In the upper plot, the last two spectra are shifted along the *y* axis by 0.25 for clarity.

Table 1. Energies for U L_{III}-Edge XANES White-Line Maxima of the Samples Studied and of Synthetic Oxide Minerals Uraninite and Schoepite

compound	oxidation state	edge energy
1-*t*-Bu, **1-Ad**	III	17173.6, 17173.0
4-*t*-Bu, **4-Ad**	IV	17176.6, 17176.7
5-*t*-Bu, **5-Ad**	V	17178.4, 17178.1
6-*t*-Bu, **6-Ad**	VI	17180.6, 17180.1
schoepite	VI	17179.0
UO_2	IV	17177.2
2, **3**	IV	17176.6, 17176.6

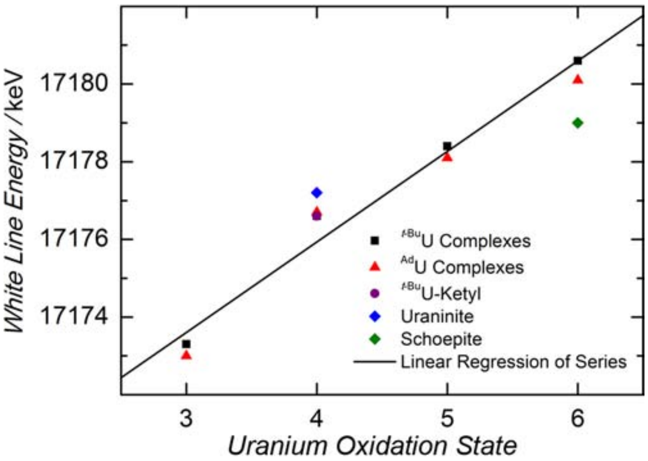


Figure 2. Uranium oxidation state versus of U L_{III}-edge XANES white-line energy for the **1-R**, **4-R**, **5-R**, and **6-R** (R = ***t*-Bu** or **Ad**) samples and the associated trend (determined as linear regression through the data points). The data for compound **2** and for the oxide minerals uraninite and schoepite are added for comparison. Note the slope of the trend using the oxide mineral data is much smaller than the trend for the samples of this study (0.9 instead of 2.32).

correlates with a higher core electron binding energy and a concomitant upward shift in the XANES edge energies. The observed L_{III}-edge energy dependence on the uranium valence for this series is not strictly linear (Table 1 and Figure 2) because the energy shifts associated with unit valence changes are not constant. The edge energy differences associated with a change of one formal charge from U^{III} to U^{IV} (**1-R** vs **4-R**) are 3.0 eV (***t*-Bu**) and 3.7 eV (**Ad**). This separation is substantially larger than the energy difference between U^{IV} and U^{V} (**4-R** vs **5-R**), 1.8 (***t*-Bu**), and 1.4 eV (**Ad**). The shift of the white line for U^{V} to U^{VI} (**5-R** vs **6-R**) is intermediate to the other two pairs and exhibits a shift of 2.2 (***t*-Bu**) and 2.0 eV (**Ad**). The non-linearity of the edge energy with formal charge in this series is partially due to the terminal oxo ligand present in the **5-R** and **6-R** compounds, which leads to a relative reduction of the effective U charge.

The white-line energies for **5-R** and **6-R** are higher than those generally observed for dioxouranyl(V,VI) species. For example, the white line maximum for uranyl in the spectrum of the mineral schoepite lies well below 1 eV from that for the uranium(VI) compounds in this series. Obviously, the singly π-bonded terminal oxo **6-R** compounds have a higher effective charge on uranium than the *trans*-dioxo $[O{=}U{=}O]^{2+}$ moiety.

The spectra in Figure 1 exhibit the XANES features known for light actinides: strong white lines for the tri- and tetravalent uranium compounds and a lowering of the white line intensity for higher-valent uranium with π-bonded terminal oxo ligands.[31] An extensively studied feature of the $L_{II/III}$-edge XANES of light actinides is the multiple-scattering feature appearing as a shoulder on the high-energy side of the white line for the actinyl(V/VI) complexes.[32−39] While the white line peak shape in the spectra of **1-R** and **4-R** can be described as asymmetric Gaussian-like, the uranium(V) and uranium(VI) terminal oxo complexes **5-R** and **6-R** exhibit broader white lines with a shoulder on the high-energy side, reminiscent of spectra for actinyl complexes but comparatively less resolved. Notably, the peak forms for **6-*t*-Bu** and **6-Ad** are similar but not identical, which might reflect their differences in ground-state coordination geometry (C_s vs C_3, vide supra).

Fits to these two XANES spectra using two asymmetric Lorentz functions to model the white line (see the SI) reveal the primary difference in these spectra to lie in the energy splitting of the white line modeled by these two functions. This splitting is smaller for the low-symmetry **6-*t*-Bu** than for **6-Ad**. The shoulder in the **5-R** and **6-R** spectra might be considered due to multiple scattering on the *mono*-oxo ligand, analogous to the white line and its multiple-scattering feature observed in U

L_{III}-edge XANES of uranyl compounds. Generally, an increase in the energy difference between the white line and high-energy shoulder (ΔE) in uranyl compounds with smaller U−O distances is observed due to the relation $\Delta E \propto 1/R(\text{U–O})^2$.[40] For example, the observed value for ΔE in the schoepite L_{III} spectrum is around 13 eV, which is 1−2 eV larger than that for the **6-R** compounds. This reflects the differences in R(U−O) in these systems, which is shorter in schoepite (1.78 Å)[41] than in **6-*t*-Bu** or **6-Ad** (1.81 and 1.84 Å, respectively).[4] We also explored whether the shoulder on the white line in **6-R** spectra might also result from photoelectron transitions to split d-like final states near continuum by calculating the angular momentum projected density of states (*l*DOS) for dipole-allowed final d-states in the $2p_{3/2} \rightarrow 5d$ transition using the FEFF8.4 code[42,43] (see the SI). The calculations for both compounds reveal a strong unoccupied dDOS associated with the spectral white lines. This main d-state shows an asymmetric doublet for **6-Ad**, which is not found for **6-*t*-Bu**; however, no correlation between calculated dDOS and the shoulder features in the experimental XANES is evident.

The shape of the XANES spectra and the edge energy of the closed-shell ligand uranium(IV) methoxide and alkoxide (**4-*t*-Bu** and **3**) are identical, which shows that the different alkyl groups on the axial ligand do not affect the ligand-to-metal charge transfer, peak position, or shape. Therefore, the spectrum of the open-shell ketyl complex **2** can be directly compared to both of these spectra. The edge energy for **2** is the same as and its peak shape nearly identical with these two other uranium(IV) species, allowing unambiguous assignment of **2** as a tetravalent uranium(IV) complex. In other words, the uranium(III) resonance structure does not significantly contribute to the oxidation state of this compound. Note that if we had compared the edge energy for **2** with oxide reference compounds uraninite (UO_2) and schoepite, we would have, via extrapolation, erroneously come to the conclusion that the mean oxidation state in **2** is 3.3, falsely indicating a contribution of the uranium(III) resonance structure.

CONCLUSION

We have characterized the spectroscopic oxidation state in a series of isostructural hexa- and heptacoordinate uranium complexes by means of U L_{III}-edge XANES. The oxidation states of the compounds in the U^{III} to U^{VI} series are correlated to defined edge energies, and this information is used to successfully identify the oxidation state in the isostructural open-shell uranium ketyl complex **2**, clearly shown to be tetravalent. A comparison of edge energies of structurally similar compounds proved to be essential. This series of complexes also exhibits subtle differences in various spectral features for compounds in the same oxidation state. Further investigation of this series with higher energy resolution, such as PFY-XANES (partial fluorescent yield XANES), and combining results with quantum-chemical studies, will provide quantified information concerning the effective metal-ion charge and associated electronic structure of uranium coordination complexes. This will allow quantitative evaluation of geometry effects compared to electronic effects, thereby enabling refinement of oxidation-state determinations, notably for systems lacking structurally similar reference compounds. With increasing interest in uranium coordination chemistry, these investigations promise to become a prominent tool in the elucidation of structure−reactivity relationships and be an indispensable probe of the electronic structure of novel molecules, thereby assisting in elucidating the origins of their reactivity. For example, in the complexes NaU_2Cl_6,[44] $K_2[\{(R,R'C{=}N)_3U\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_{10}H_8)]$,[45] $[\{(Ar[R]N)_2U\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_7H_8)]$,[46] $[\{(C_5Me_5)_2U\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)]$,[47] or $[\{(BIPM^{TMS}H)U(I)\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_5CH_3)]$,[48] the U center has the rare formal oxidation state of II+, reportedly an unstable oxidation state for uranium. Uranium in the unusual arene-bridged complex $[\{(Ts^{Xy})U\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_5Me)]$[49] has an oxidation state of V+. XANES information would have been helpful in the characterization of its electronic structure. Nevertheless, structurally similar compounds are presently needed as reference samples, as we show in this manuscript. Such novel compounds generally have rather unique coordination geometries, and appropriate references may not be readily available. Further investigation combined with the development of robust quantum-chemical tools should advance our understanding of XANES to a level allowing accurate prediction and thus help to solve cases lacking structurally similar references. The determination of the uranium oxidation state and characterization of the electronic structure of such complexes therefore hinges on the application of such refined spectroscopic techniques.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectroscopic and crystallographic details for **4-R**, and details of XAFS measurements and *l*DOS calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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