Inorg. Chem. **2001,** *40,* 2835−2841 **2835**

Structural Studies of Uranium and Thorium Complexes with 4,5-Dihydroxy-3,5-benzenesdisulfonate (Tiron) at Low and Neutral pH by X-ray Absorption Spectroscopy

E. R. Sylwester, P. G. Allen,* U. R. Dharmawardana, and M. Sutton

Glenn T. Seaborg Institute for Transactinium Science, Lawrence Livermore National Laboratory,
P.O. Box 808, MS L-231, Livermore, California 94551

Received November 6, 2000

We have determined the structure of uranyl, UO_2^{2+}, and Th^{4+} complexes formed in aqueous solution with 4,5-dihydroxy-3,5-benzenedisulfonate (Tiron) as function of pH and concentration. At equimolar concentrations of 0.05 M UO_2^{2+} and Tiron, the predominant species was found to be aqueous uranyl at pH = 2.0. At pH = 6.0, the formation of a 3:3 UO_2^{2+}:Tiron trimer (proposed in earlier studies) was observed. In this structure, bidentate catecholate complexation to Tiron as well as oxygen bridging between uranyl units is detected. Th^{4+} structural changes were observed both as a function of pH and Th:L (L = Tiron) ratio. At Th:L = 1:1 and pH = 1.4, a monomeric complex is observed with each Th center complexing monodentate to ∼2 sulfonate functional groups. At pH 4.0 similar sulfonate ligation is observed along with oligomer formation. At pH 6.0 thorium hydrolysis products are detected, with little evidence for inner-sphere Tiron coordination. When the Th:L is changed to 1:2 at pH = 6.0, a stable oligomeric complex is formed that dominates the speciation for Th:L ratios up to 1:5. This complex is characterized by bidentate catechol and monodentate sulfonate ligation to Tiron along with oxygen bridging between Th^{4+} atoms and is consistent with the formation of the 2:3 Th:L polymeric species proposed from earlier work. At a Th:L ratio of 1:10, Th^{4+} complexation is dominated by bidentate catechol ligation and the formation of a monomeric $Th(Tiron)_x$ species, where $x \geq 2$.

Introduction

Over the past 60 years the nuclear industries have produced a large volume of radioactive waste scattered over multiple sites and contained in a variety of waste forms. Efforts to reduce the amount of waste and to remediate waste sites have focused on pretreatment to separate the radioisotopes from the bulk chemicals, followed by further separation by chemical form and half-life. For uranium, concern lies primarily in the stable, highly soluble, and mobile aqueous uranyl ion. In the cases of Np and Pu, the tetra- and pentavalent forms represent the more important environmental species.

The uranyl unit consists of a uranium center with a formal charge of +6 coordinated to two double-bonded oxygen atoms to form a linear dioxo cation, UO_2^{2+}. This unit is highly stable and binds to other ligands via the formation of U−O bonds in a plane perpendicular to the axis of the uranyl ion. The "equatorial" oxygen coordination number may vary from 4 to 6 depending on the chemical environment, and these equatorial bonds are the sole means of complexation available for uranyl units under normal conditions. Complexing agents that preferentially bind to the equatorial sites in the uranyl unit have proven effective in laboratory studies for separation of uranyl from mixed wastes and chemicals. Previous studies have looked at the structure and properties of actinyl complexes with organic materials such as humic acids, citrates,[1] EDTA,[2] and catechols.[3] Inorganic complexes such as carbonate[4,5] have also been studied. In most of these complexes, binding occurs through the sharing of one (monodentate), two (bidentate), or more equatorial oxygen atoms between the uranyl ion and the ligand. Multiple ligands may also be observed to complex to each uranyl center via both monodentate or bidentate bonds.

The compound 4,5-dihydroxy-3,5-benzenedisulfonate, known as DHBSA or Tiron, consists of a catechol unit with two additional *meta*-sulfonate groups. This compound has been postulated to form binary (2:2)[3] and ternary (3:3)[6] complexes with uranyl, where the catechol oxygens are bound bidentate and equatorially to the uranyl ion while the other uranyl centers are connected via equatorial oxygen bridges. When the tetravalent ion Th^{4+} is coordinated to Tiron, a stable 2:3 (Th^{4+}:Tiron) complex is expected to form at metal-to-ligand ratios of 1:1.5 and above.[7−9] In addition, bidentate catechol binding to Th^{4+} has been previously observed,[10] providing an indication that the catechol oxygens in Tiron are the sole active complexing groups.

---

* Corresponding author. E-mail: allen42@llnl.gov.

(1) Allen, P. G.; Shuh, D. K.; Bucher, J. J.; Edelstein, N. M.; Reich, T.; Denecke, M. A.; Nitsche, H. *Inorg. Chem.* **1996**, *35*, 784−787.

(2) Pokrovsky, O. S.; Bronikowski, M. G.; Moore, R. C.; Choppin, G. R. *Radiochim. Acta* **1998**, *80*, 23−29.

(3) Bartušek, M.; Sommer, L. *J. Inorg. Nucl. Chem.* **1965,** *27*, 2397−2412.

(4) Clark, D. L.; Hobart, D. E.; Neu, M. P. *Chem. Rev.* **1995**, *95*, 25−48.

(5) Allen, P. G.; Bucher, J. J.; Clark, D. L.; Edelstein, N. M.; Ekberg, S. A.; Gohdes, J. W.; Hudson, E. A.; Kaltsoyannis, N.; Lukens, W. W.; Neu, M. P.; Palmer, P. D.; Reich, T.; Shuh, D. K.; Tait, C. D.; Zwick, B. D. *Inorg. Chem.* **1995**, *34*, 4797−4807.

(6) Gustafson, R. L.; Richard, C.; Martell, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 1526−1534.

(7) Murakami, Y.; Martell, A. E. *J. Am. Chem. Soc.* **1966**, *88*, 1077−1079.

(8) Bogucki, R. F.; Murakami, Y.; Martell, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 5608−5610.

(9) Gustafson, R. L.; Richard, C.; Martell, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 5610−5616.

(10) Sofen, S. R.; Abu-Dari, K.; Freyberg, D. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 7882−7887.

10.1021/ic001223t

Table 1. Summary of Sample Preparations

actinide ion	[An^{x+}], mol/L	[Tiron], mol/L	pH
UO_2^{2+}	0.100		2[a]
UO_2^{2+}	0.050	0.050	2.0
UO_2^{2+}	0.050	0.050	3.5
UO_2^{2+}	0.050	0.050	6.0
Th^{4+}	0.024	0.024	1.4
Th^{4+}	0.024	0.024	4.0
Th^{4+}	0.024	0.024	6.0
Th^{4+}	0.024	0.048	6.0
Th^{4+}	0.024	0.096	6.0
Th^{4+}	0.024	0.120	6.0
Th^{4+}	0.024	0.240	6.0

[a] Taken from Allen et al.[13]

The addition of sulfonate groups to the catechol unit makes this ligand attractive for study since these groups can be used to attach Tiron to other substrates as well as change its solvation characteristics. This in turn makes Tiron an attractive ligand for use in filtration schemes[11] or chromatographic separations.

We have studied the structure of UO_2^{2+} and Th^{4+} complexed with Tiron in aqueous solution at low and near-neutral pH by X-ray absorption spectroscopy (XAS). Thorium(IV) was selected as a surrogate for the An(IV) states since the lower radioactivity affords relative ease in working with at higher concentrations.

Analysis of the extended X-ray absorption fine structure (EXAFS) has allowed us to directly characterize the local structure and metrical parameters around the uranium and thorium centers in these systems. Comparison of the results with model structures and those predicted from the literature has allowed us to elucidate the probable structure of aqueous UO_2^{2+} and Th^{4+} complexes with Tiron.

Experimental Section

Sample Preparation. The compound 4,5-dihydroxy-3,5-benzenedisulfonate disodium salt monohydrate [$(OH)_2C_6H_2(SO_3Na)_2 \cdot H_2O$], commercially known as Tiron, was obtained from Aldrich Co. and was used without further purification. Uranyl nitrate hexahydrate obtained from Strem Chemical Inc. without purification was used as the source of UO_2^{2+} ions. A standardized $ThCl_4$ stock solution was obtained from the Glenn T. Seaborg Institute for Transactinium Science at Lawrence Livermore National Laboratory and used as the source of Th^{4+} ions.

The Tiron was analyzed directly by UV spectrophotometry at 292 nm. The uranium stock solution was analyzed colorimetrically using arsenazo III reagent in perchloric acid medium as described previously.[12] The thorium stock solution was determined using the same colorimetric reagent in hydrochloric acid medium. All spectrophotometric experiments were performed using the HP-8456 diode array spectrophotometer or the Guided Wave model 260 spectrophotometer equipped with fiber optics lines.

After analysis of the starting materials, aqueous uranium samples were prepared at 0.05 M ^{238}U with a UO_2^{2+}:Tiron ratio of 1:1 and varying pH values of 2.0, 3.5, and 6.0. Aqueous Th^{4+} samples were prepared at 0.024 M ^{nat}Th with a 1:1 Th^{4+}:Tiron molar ratio and varying pH values of 1.4, 4.0, and 6.0. Additional samples with Th:Tiron ratios of 1:2, 1:4, 1:5, and 1:10 were also prepared at pH 6.0 in order to study the affect of relative Tiron concentration on complexation. Table 1 lists the sample details as well as preparation data for a uranyl aquo ion reference sample taken from Allen et al.[13]

X-ray Absorption Spectroscopy (XAS). Uranium and thorium L_{III}-edge X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL). All samples were studied on beam line 4-1, using a Si(220) double-crystal monochromator. The beam size was 10 mm (horizontal) by 0.5 mm (vertical). All spectra were collected at room temperature, in transmission mode using argon-filled ionization chambers or in fluorescence mode using a Ge solid-state detector developed at Lawrence Berkeley National Laboratory.[14] Samples were energy calibrated by simultaneous measurement of the transmission spectrum of either a UO_2(s) or ThO_2(s) sample. The energies of the first inflection points for the U L_{III} and Th L_{III} reference sample absorption edges, E_r, were defined as 17166.0 and 16300.0 eV, respectively (based on reference values taken from actinide metal standards).

Rejection of higher order harmonics of the beam at SSRL was achieved by detuning the monochromator crystals so that the incident flux was reduced to 50% of the maximum. The XANES and EXAFS data were extracted from the raw absorption spectra by standard methods described elsewhere,[15] using the suite of programs EXAFSPAK, developed by Graham George of SSRL.[16] Nonlinear least-squares curve-fitting analysis was performed using EXAFSPAK to fit the raw k^3-weighted data based on neighboring shells of atoms. Single and multiple scattering (SS, MS) EXAFS paths were calculated from model compounds using FEFF7.2,[17] with the amplitude reduction factor (S_0^2) value fixed at 1.0. Input files for FEFF7.2 were prepared using the structural modeling code ATOMS 2.46b.[18] The model compounds used in this study include α-$UO_2(OH)_2$[19] ($U-O_{ax,eq}$, U−U), tetrakis(catecholato)uranate(IV) and -thorate(IV)[10] ($An-C_{SS,MS}$), ThO_2[20] (Th−O, Th−Th), and diaqua(oxydiacetato)sulfatothorium(IV) monohydrate[21] ($Th-S_{SS,MS}$).

Equilibrium Calculations. Solution model calculations were performed using the program MINTEQA2 v4.0,[22] a geochemical equilibrium speciation modeling program for dilute aqueous systems. The program is capable of calculating aqueous speciation, adsorption, gas-phase partitioning, solid-phase saturation states, and precipitation−dissolution of metals. Internal databases were modified to contain equilibrium constants (log K) for the following UO_2^{2+} and Th^{4+} iron complexes[23] as well as U and Th hydroxides and polymers:[24,25] for uranyl, HL^-, H_2L, UO_2L, UO_2HL^+, $(UO_2)_2(OH)L_2^-$, $(UO_2)_3(OH)_2L_3^{2-}$, and $(UO_2)_3(OH)_2L_4^{4-}$; for thorium, HL^-, H_2L, $Th(OH)_4$, $Th(OH)_3^+$, $Th(OH)_2^{2+}$, $Th(OH)^{3+}$, $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$, $Th_6(OH)_{15}^{9+}$, $Th_2L_3^{2+}$, and $Th_2(OH)_2L_3$. The log K value for Th(catechol)$^{2+}$ [26] was included as a surrogate for ThL^{2+}. In all cases L represents the doubly dissociated form of the Tiron ligand, $[C_6H_2(SO_3H)_2O_2]^{2-}$.

---

(11) Bhattacharyya, D.; Schaaf, D. P.; Grieves, R. B. *Can. J. Chem. Eng.* **1976**, *54*, 185−189.

(12) Dharmawardana, U. R.; Christian, S. D.; Taylor, R. W.; Scamehorn, J. F.; Palmer, C. D.; Hoffman, D. C. Presented at the American Chemical Society National Meeting, Aug 1999, New Orleans, La.

(13) Allen, P. G.; Bucher, J. J.; Shuh, D. K.; Edelstein, N. M.; Reich, T. *Inorg. Chem.* **1997**, *36*, 4676−4683.

(14) Bucher, J. J.; Edelstein, N. M.; Osborne, K. P.; Shuh, D. K.; Madden, N.; Luke, P.; Pehl, D.; Cork, C.; Malone, D.; Allen, P. G. SRI Conf. Proc. *Rev. Sci. Instrum.* **1996**, *67*, 1.

(15) Prins, R., Koningsberger, D. E., Eds. *X-ray Absorption: Principles, Applications, Techniques for EXAFS, SEXAFS, and XANES*; Wiley: New York, 1988.

(16) George, G. N.; Pickering, I. J. *EXAFSPAK, a suite of computer programs for analysis of X-ray absorption spectra*; SSRL: Stanford, CA, 1995.

(17) de Leon, J. M.; Rehr, J. J.; Zabinsky, S.; Albers, R. C. *Phys. Rev.* B **1991**, *44*, 4146−4156.

(18) Ravel, B. *ATOMS, a program to generate atom lists for XAFS analysis from crystallographic data*; University of Washington: Seattle, WA, 1996.

(19) Taylor, J. C.; Hurst, H. J. *Acta Crystallogr. B* **1971**, *22*, 2018−2022.

(20) Wyckoff, R. W. G. *Cryst. Struct.* **1963**, *1*, 241.

(21) Graziani, R.; Battiston, G. A.; Casellato, U.; Sbrignadello, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1−7.

(22) MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.11. EPA/600/3-91/021, NTIS accession No. PB91 182 469.

(23) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1976.

(24) Allard, B.; Kipatsi, H.; Liljenzin, J. O. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1015−1027.

(25) Ekberg, C.; Albinsson, Y.; Comarmond, M. J.; Brown, P. L. *J. Soution. Chem.* **2000**, *29* (1), 63−86.

(26) Baisden, P. A.; Torres, R. A.; Choppin, C. R *Complexes of Thorium with Inorganic and Organic Ligands*; Report UCRL-96588; Lawrence Livermore National Laboratory: Livermore, CA, 1987.

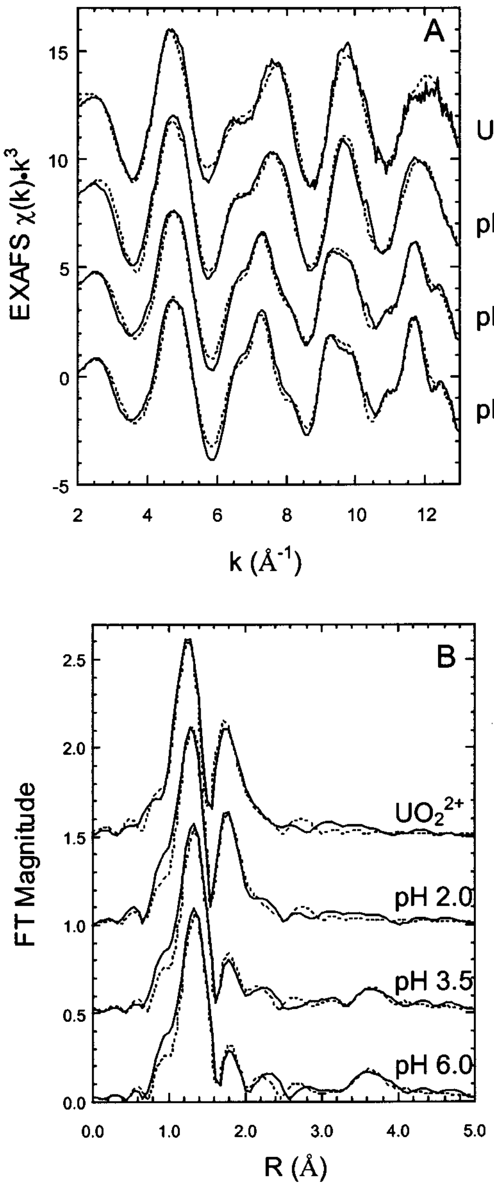

Figure 1. (A) Raw k^3-weighted and (B) Fourier transformed ($k = 2-13$ Å^{-1}) U L$_{\text{III}}$-edge EXAFS data for the aqueous uranyl standard and uranyl:Tiron samples at pH 2.0, pH 3.5, and pH 6.0. The solid line represents the experimental data, and the dashed line represents the best theoretical fit to the data.

Table 2. EXAFS Structural Results for Aqueous UO_2^{2+}:Tiron Mixtures

sample	shell^g	N^a	R (Å)^a	σ^2 (Å^2)^{b,c}
UO_2^{2+}	U−O$_{ax}$*	2	1.76	0.00180^d
	U−O$_{eq}$	5.3	2.41	0.00700
pH 2.0	U−O$_{ax}$*	2	1.78	0.00170
	U−O$_{eq}$	5.7	2.42	0.00996
pH 3.5	U−O$_{ax}$*	2	1.80	0.00232
	U−O$_{eq1}$	1.9	2.30	0.00594
	U−O$_{eq2}$	2.9	2.47	0.00594
	U−C*	1.5	3.46	0.00390^e
	U−U	1.3	3.82	0.00540^f
pH 6	U−O$_{ax}$*	2	1.80	0.00204
	U−O$_{eq1}$	2.3	2.30	0.00724
	U−O$_{eq2}$	2.9	2.47	0.00724
	U−C*	1.4	3.45	0.00390^e
	U−U	1.7	3.84	0.00540^f

[a] The 95% confidence limits for the bond lengths (R) and coordination numbers (N) for each shell are (pH 6)the following: U−O$_{ax}$, ±0.0020 Å; U−O$_{eq1,eq2}$, ±0.012 Å and ±19%; U−C, ±0.030 Å and ±54%; U−U, ±0.007 Å and ±15%, respectively. [b] σ is the EXAFS Debye−Waller term which accounts for the effects of thermal and static disorder through damping of the EXAFS oscillations by the factor $\exp(-2k^2\sigma^2)$. [c] Fixed Debye−Waller factors are shown in italics. [d] Allen et al.[13] [e] Allen et al.[5] [f] Thompson et al.[27] [g] Asterisk indicates a dependent MS paths for these SS paths not shown.

Results

Uranium.Analysis of the near edge (XANES) spectra (not shown) confirmed the presence of the stable UO_2^{2+} moiety in all Tiron samples (i.e., no uranate or redox transformations had occurred). The raw k^3-weighted EXAFS data and Fourier transforms (FTs) for all samples along with the corresponding least-squares curve-fits are shown in Figure 1 over the k-range 2−13 Å^{-1}. In the raw EXAFS there is clear evidence for a change in structure as a function of pH, with the pH 2.0 sample resembling the aqueous uranyl standard and the pH 6.0 sample showing a more complex high-k structure. All samples are observed to contain a low-frequency oscillation attributable to backscattering from the oxygen atoms contained in the uranyl structure. The pH 2.0 sample shows a second oscillation appearing predominantly at $k \sim 6.5$ Å^{-1} which can also be found in the aqueous uranyl spectrum. At pH 3.5 and 6.0 a smaller high-frequency oscillation becomes apparent beginning at $k \sim 8$ Å^{-1} which can tentatively be assigned to backscattering from distant high-Z atoms (i.e. uranium) and may be evidence for oligomer formation.

These interactions are more easily observed in the FTs. The FT spectra represent a pseudoradial distribution of atoms near the central atom, with observed atomic distances reduced by ~0.2−0.5 Å compared to true atomic distances due to the EXAFS phase shift. An increase in the U peak at ~3.6 Å is observed for the pH 3.5 and 6.0 samples, signifying the presence of U−U interactions indicative of oligomer or polymer formation. A split in the equatorial oxygen shell which would indicate inner-sphere complex formation is also observed at both pH 3.5 and pH 6.0.

Quantitative analysis of the U(VI)−Tiron structure has been performed through nonlinear least-squares fitting of the raw EXAFS spectra using the independent paths listed in Table 2. The interactions detected include U−O (axial), U−O (equatorial), U−C, and U−U. Due to correlation effects between the coordination number (N) and the Debye−Waller factor (σ^2), the latter was held fixed for all shells beyond the (2nd) equatorial oxygen shell (see Table 2) in order to systematically monitor changes in ligand number (i.e., N) as a function of pH. Fixed σ^2 values for U−C and U−U interactions were derived from Allen et al.[5] and Thompson et al,[27] respectively.

Although the U−C contribution is not directly apparent in the pH = 3.5 or 6.0 FT spectra, inclusion of catechol U−C single scattering (SS) and multiple scattering (MS) paths yields a ~17% increase in the goodness of fit when normalized for the larger number of variables (measured as reduced chi-squared; χ^2r). The U−C−C MS paths chosen include the 3-leg and 4-leg U−C$_1$−C$_2$ paths expected from catechol binding (see Figure 2). These MS interactions are detectable contributors to the EXAFS spectra as the result of the nearly linear arrangement between the three atoms ($\angle$U−C$_1$−C$_2$ = 160°), which has a focusing affect on the backscattered wave as discussed by Stern in ref 15. The 4-legged uranyl MS interaction (along the O=U=O vector) was also included in the fits, since it has previously

---

(27) Thompson, H. A.; Brown, G. E.; Parks, G. A. *Am. Mineral.* **1997**, *82*, 483−496.

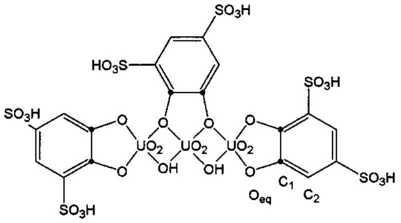

Figure 2. Structure of 3:3 UO_2^{2+}:Tiron trimer proposed by Gustafson et al.[5] An equatorial oxygen atom and carbon atoms contributing to SS and MS interactions are identified. Solvation oxygens (i.e. water molecules) bound to the uranyl are not shown.

been observed to contribute significantly to the uranyl EXAFS signal.[1,5,28]

Both N and σ^2 for all MS paths were kept dependent on the SS path parameters. For the axial U−O_{MS} path, the path length (R, Å) was fixed at twice the SS path length. However, R values for the U−C_1–C_2 MS paths were allowed to vary due to their nonlinearity. This variation resulted in values physically consistent with bidentate bonding of a catechol group to uranium (U−C_1–C_2, $R \sim 4.59$ Å, compared to $R \sim 4.61$ Å reported[10] in U^{IV}(catecholate)$_4$). Parameters for all dependent MS shells have been excluded from Tables2 and 3 for brevity.

Thorium. Figure 3 shows the raw k^3-weighted EXAFS data and FTs for all samples along with the corresponding nonlinear least-squares fits over the k-range 2−13 Å^{-1}. All of the EXAFS spectra are dominated by a single high-amplitude oscillation indicative of backscattering from first shell oxygen atoms. Differences between the individual EXAFS spectra are detected at $k \sim 6$ Å^{-1}, with some samples (e.g., the 1:1 M:L at pH = 6) clearly displaying a high-frequency oscillatory pattern extending out to relatively high k values.

These differences become more apparent in the FT spectra. If one moves outward from the central Th^{4+} ion, all samples show a single large peak at $R \sim 1.9$ Å which corresponds to the nearest neighbor Th−O interactions. All samples are observed to contain a peak at ~3.1 Å. The 1:2, 1:4, and 1:5 M:L samples all display similar structure over the range 3.0−3.8 Å, which may indicate the formation of the same species in all three samples. Another point to note is that the pH = 6.0 (1:1) sample is markedly different and contains a large interaction at ~3.8 Å. This interaction could correspond to Th−Th interactions similar to those present in $Th^{IV}O_2$(s) or hydrolysis products such as $Th_x(OH)_y^{4-y}$(aq). Finally, the 1:10 M:L sample displays yet another bonding pattern over the range of 2.3−2.7 Å.

The Th EXAFS curve fitting results over the range $k = 2-13$ Å^{-1} are shown in Table 3. Interactions detected in the seven samples include Th−O, catechol Th−C and Th−C−C (SS and MS, respectively), monodentate sulfonate Th−S and Th−O−S (SS and MS, respectively), and Th−Th backscattered paths. As with the uranyl samples, σ^2 values for specific shells were held constant to avoid correlation effects between N and σ^2 and monitor ligand coordination number changes (see Table 3). Appropriate values for σ^2 were taken from Allen et al.[5] (Th−C), Thompson et al.[27] (Th−Th), and Karabulut et al.[29] (Th−S, from analogous U−P interactions).

Fitting confirmed the presence of two separate Th−O shells contributing to the first FT peak in all spectra. These shells have a total coordination number $N \sim 8-10$ and are located at distances of ~2.40 and ~2.54 Å. Initial attempts to fit the second major peak (~3.1 Å) in the pH 1.4 sample using catechol binding signatures (C atoms at ~3.28 Å) similar to that observed in the uranyl samples failed to yield a good fit. The peak was best fit with SS Th−S and dependent 3-leg and 4-leg MS Th−O−S paths. The resulting R_S of ~3.72 Å corresponds closely to An(IV)−S bond lengths found for monodentate sulfonate ligation in the crystal data for Th(IV)[21] and U(IV)[30] sulfate compounds (3.79 and 3.68 Å, respectively). The peak at ~3.1 Å in the pH 4.0 sample was also best fit using monodentate SS and MS Th−S paths. A third peak at ~3.6−3.8 Å is observed in this spectrum, which was identified as a Th−Th interaction, indicating polymeric species formation.

For the pH 6.0, 1:1 M:L sample, a single Th−Th shell at 4.04 Å with $N \sim 2$ was sufficient to describe the single major peak in the spectrum past the first (O shell) peaks. It is noteworthy that the 4.04 Å Th−Th interaction also contributes a small FT amplitude at ~3.1 Å, due to the complex EXAFS phase and amplitude functions produced by a high-Z backscatterer such as Th. However with the exception of the hydrolyzed pH 6.0, 1:1 M:L sample, this secondary low-R FT structure is insufficient to provide a good fit to the 3.1 Å peak in any of the remaining spectra.

The 1:2, 1:4, and 1:5 M:L samples required both monodentate Th−O−S interactions similar to those used for the pH 1.4 and 4.0 samples, along with Th−C catechol interactions similar to those used in the uranyl fits in order to effectively model the FT structure between ~2.8 and 3.1 Å. Approximately 2 C are detected in each case. The third peak in these samples was found to be best fit using a Th−Th interaction with $R \sim 3.91$ Å and $N \sim 1$. This Th−Th bond length is consistent with the Th−Th bond length of 3.96 Å observed in ThO_2(s).[20] For the 1:10 sample, the broad double peak between ~2.8 and 3.2 Å also required both Th−C catechol and Th−S monodentate sulfonate interactions. In contrast to the samples with lower Tiron concentrations, ~4 C are detected and no Th−Th interactions are observed.

Discussion

Uranium. The coordination numbers observed for both U−C and U−U interactions are consistent with a trend of increasing formation of an oligomeric complex (i.e., a 3:3 complex) as the pH increases. Additionally, our results are consistent within experimental error with calculations performed with MINTEQA2 for these experimental conditions, shown in Figure 4, which predict the predominant species to be aqueous uranyl at pH = 2.0, ~90% trimer at pH = 3.5, and 100% trimer at pH = 6.0.

With this trend, we would expect to see the following trends in the EXAFS data. When the uranyl group does not interact with the Tiron ligand, the EXAFS spectra will represent that of aqueous uranyl. With the formation of a UO_2^{2+}:Tiron monomer, two U−C (SS) interactions would be observed along with a split in the equatorial oxygen shells due to the bonding of two equatorial oxygens to the benzene unit of the ligand. No U−U interactions would be observed. Formation of the dimeric species could be observed in the EXAFS spectra through the appearance of a U−U interaction having an average $N_U = 1$, as each uranyl group is bridged with a single uranyl near-neighbor. The U−C

---

(28) Allen, P. G.; Shuh, D. K.; Bucher, J. J.; Edelstein, N. M.; Palmer, C. E. A.; Silva, R. J.; Nguyen, S. N.; Marquez, L. N.; Hudson, E. A. *Radiochim. Acta* **1996**, *75*, 47−55.

(29) Karabulut, M.; Marasinghe, G. K.; Ray, C. S.; Day, D. E.; Waddill, G. D.; Allen, P. G.; Booth, C. S.; Bucher, J. J.; Caulder, D. L.; Shuh, D. K.; Grimsditch, M.; Saboungi, M.-L. *J. Mater. Res.* **2000**, *15*, 1972−1984.

(30) Kierkegaard, P. *Acta Chem. Scand.* **1956**, *10*, 599−616.

Table 3. EXAFS Structural Results for Aqueous Th(IV):Tiron Mixtures

sample	shell^g	N^a	R (Å)^a	σ^2 (Å^2)^{b,c}
pH 1.4, 1:1	Th−O	5.0	2.43	0.00742
	Th−O	4.5	2.53	0.00742
	Th−S*	2.0	3.72	0.00750^e
pH 4, 1:1	Th−O	4.6	2.42	0.00712
	Th−O	4.5	2.55	0.00712
	Th−S*	1.9	3.71	0.00750^e
	Th−Th	0.5	3.85	0.00540^f
pH 6, 1:1	Th−O	3.9	2.39	0.00474
	Th−O	4.1	2.53	0.00474
	Th−Th	2.3	4.06	0.00540^f
pH 6, 1:2	Th−O	4.4	2.41	0.00725
	Th−O	4.1	2.54	0.00725
	Th−C*	2.1	3.35	0.00390^d
	Th−S*	2.3	3.71	0.00750^e
	Th−Th	1.0	3.93	0.00540^f
pH 6, 1:4	Th−O	4.7	2.40	0.00656
	Th−O	3.9	2.56	0.00656
	Th−C*	1.9	3.33	0.00390^d
	Th−S*	2.6	3.73	0.00750^e
	Th−Th	1.1	3.93	0.00540^f
pH 6, 1:5	Th−O	4.7	2.40	0.00574
	Th−O	3.7	2.56	0.00574
	Th−C*	2.2	3.32	0.00390^d
	Th−S*	2.6	3.74	0.00750^e
	Th−Th	1.1	3.94	0.00540^f
pH 6, 1:10	Th−O	5.2	2.40	0.00352
	Th−O	2.4	2.52	0.00352
	Th−C*	4.5	3.30	0.00390^d
	Th−S*	2.0	3.78	0.00750^e

[a] The 95% confidence limits for the bond lengths (R) and coordination numbers (N) for each shell are (based on pH 6, 1:5 Th:Tiron) are as follows: Th−O$_1$, ±0.010 Å and ±8%; Th−O$_2$, ±0.007 Å and ±10%; Th−C, ±0.018 Å and ±28%; Th−S, ±0.016 Å and ±30%; Th−Th, ±0.011 Å and ±25%, respectively. [b] σ, EXAFS Debye−Waller term. [c] Fixed Debye−Waller factors are shown in italics. [d] Allen et al.[5] [e] Karabulut et al.[29] [f] Thompson et al.[27] [g] Asterisk indicates dependent MS paths for these SS paths not shown.

(SS) coordination number would remain at 2, and the equatorial oxygen shells would remain split. The trimer structure given by Gustafson et al.[6] and shown in Figure 2 would be expected to have an average U−U coordination number of 1.33 (two-thirds of uranium atoms have one near-neighbor uranium, one-third of uranium atoms have two near-neighbors), a U−C (SS) coordination number of 2, and a split equatorial oxygen shell consisting of catechol O groups and most probably water ligands.

These general trends are in fact observed in the EXAFS data. The curve-fitting results suggest the predominant species to be aqueous uranyl at pH = 2.0, the 2:2 dimer or a mix of trimer and aqueous uranyl at pH = 3.5, and the 3:3 trimer at pH = 6.0. The uncertainty associated with N_U makes calculation of a meaningful "% trimerization" at pH 3.5 difficult. It should also be noted that only the average of all uranium structures can be seen using EXAFS spectroscopy, making it difficult to distinguish between the presence of an intermediate form, such as a dimer, and a mix of aqueous uranyl and the 3:3 UO_2^{2+}:Tiron trimer.

Thorium. The total Th−O coordination of ∼8−10 found by curve-fitting is consistent with previous EXAFS studies on aqueous Th(IV)[31,32] and Np(IV)[13] complexes. The split into two distinct shells provides evidence for the presence of oxygens utilized in inner-sphere complexation under all conditions, in addition to the presence of hydration oxygens (i.e. water). At pH 1.4, the detection of Th−S interactions indicate that the Tiron groups bind through a single monodentate sulfonate oxygen. The Th(IV) complexes formed are observed to be primarily monomeric. At pH 4.0 similar sulfonate bonds are observed, but there appears to be a mix of oligomeric and monomeric structures as evidenced by the detection of Th−Th interactions.

At pH 6.0 and a 1:1 Th:L ratio, no inner-sphere Th−S interactions are observed. The spectrum beyond the first shell oxygen peak is instead dominated by ∼2 Th−Th interactions. This confirms the presence of polymeric species (e.g., $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$) which result from Th(IV) hydrolysis in this regime.

Figure 5 shows the results of speciation calculations performed with MINTEQA2 for the 1:1 system as a function of pH. No complexation is predicted at pH 1.4. Both the pH 4.0 and pH 6.0 samples are predicted to contain a percentage of mixed polymeric thorium hydroxide species, agreeing with the observation of Th−Th shells in the EXAFS spectra.

Murakami and Martell[7] report evidence for nearly complete formation of 1:1 Th:Tiron complex at pH = 2.0, which is consistent with the EXAFS evidence for complexation at pH = 1.4. However, the speciation calculation predicts <10% Th complexation in the 1:1 species. This discrepancy may result from using an artificially low log K value for Th(Tiron)$^{2+}$, taken from the complex Th(Catechol)$^{2+}$, rather than the true log K value which was not available in the literature. This would result in the underestimation of complex formation as seen in the calculation. In terms of treating the formation of oligomeric species, the EXAFS results at pH = 6.0 (1:1 ratio) as well as the speciation calculations both illustrate the formation of Th hydrolysis products.

Speciation as a Function of M:L. When the pH is held constant at 6.0 and the M:L ratio is increased from 1:1 to 1:2, we observe the formation of a distinct Th(IV)−Tiron oligomeric complex. Curve-fitting results indicate the formation of a Th−Th bridged compound which includes bidentate catechol complexation between Th^{4+} and one Tiron unit and monodentate sulfonate complexation. The invariant curve fit results for M:L ratios of 1:2, 1:4, and 1:5 confirm that the speciation is the same under these conditions.

These results are in qualitative agreement with the work of Martell and co-workers[7−9,33] which showed that a single, unique Th(IV)−Tiron complex (with M:L = 2:3) is formed at a molar ratio of 1:1.5 Th:Tiron and persists when the ligand concentration is increased up to the highest M:L ratio tested, 1:4. Murakami and Martell[7] proposed a structure for this complex shown in Figure 6A. It consists of two thorium(IV) atoms each complexed to a Tiron unit with bidentate catechol groups, with a third Tiron acting (with additional oxygens) as a bridging ligand and bound via one catechol oxygen to each thorium atom. This structure, if observed by EXAFS, would display no Th−S interactions.

---

(31) Moll, H.; Denecke, M. A.; Jalilehvand, F.; Sandström, M.; Grenthe, I. *Inorg. Chem.* **1999**, *38*, 1795−1799.

(32) Johansson, G.; Magini, M.; Ohtaki, H. *J. Solution Chem.* **1991**, *20*, 775−792.

(33) Murakami, Y.; Martell, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 5−5607.

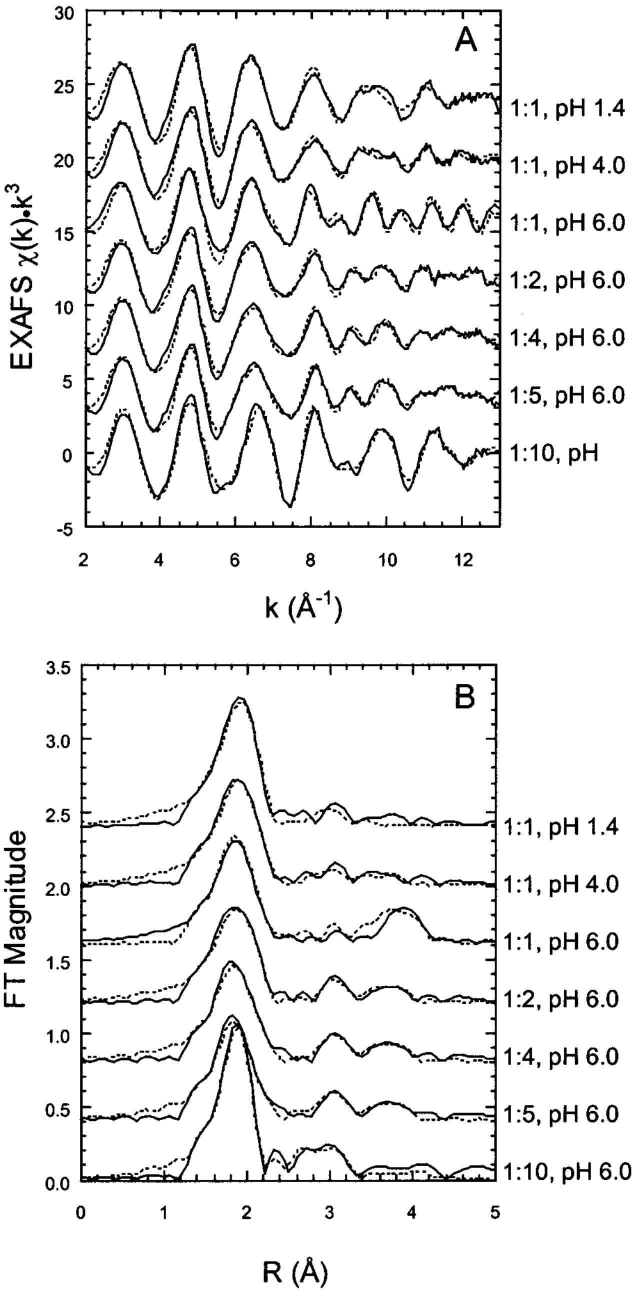

Figure 3. (A) Raw k^3-weighted and (b) Fourier transformed ($k = 2-13$ Å^{-1}) Th L_{III}-edge EXAFS data for Th:Tiron samples as a function of pH. The solid line represents the experimental data while the dashed line represents the best theoretical fit to the data.

In contrast, monodentate Th−sulfonate bonds are detected in the EXAFS data, thereby indicating that the structure shown in Figure 6A may be incorrect. For these conditions (pH 6.0, M:L = 1:2 up to 1:5), our results are more consistent with the local structure found in the compound Tb_2Tiron_2•4DMF reported by Sun et al.[34] A variation of this structure with Th replacing Tb is shown in Figure 6B. Interestingly, the Tb complex is only formed at ligand concentrations at or exceeding the M:L molar ratio of 2:3 where Sun et al. propose the formation of a polymer with the formula $[(M_2L_2)L]_n$. This proposed dimeric subunit would yield an expected EXAFS signature containing 1 Th−Th and 2 Th−S interactions per Th center.

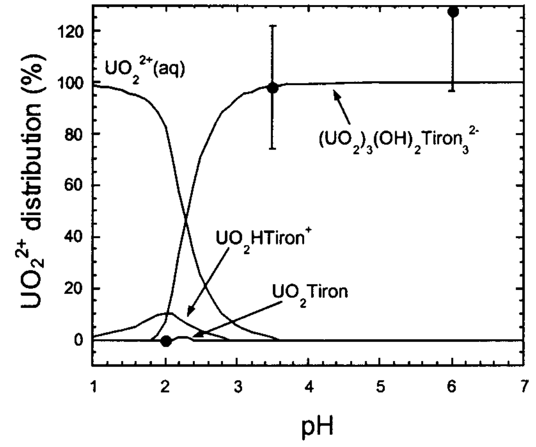

Figure 4. Figure 4. MINTEQA2 calculation of % distribution of UO_2^{2+} (lines) as a function of pH, superimposed with the "% trimer" (data points) calculated from data for N_U. Data are shown with $3\sigma_N$ errors (99.7% confidence). "Tiron" represents the doubly dissociated form of the Tiron ligand, $[C_6H_2(SO_3H)_2O_2]^{2-}$.

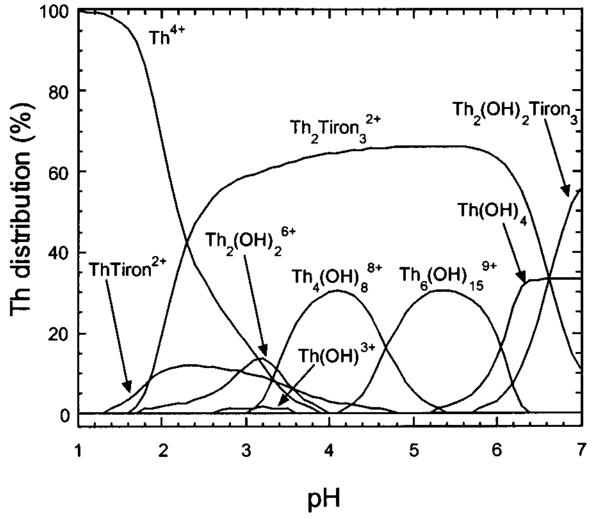

Figure 5. MINTEQA2 calculation of % distribution of Th^{4+} as a function of pH. "Tiron" represents the doubly dissociated form of the Tiron ligand, $[C_6H_2(SO_3H)_2O_2]^{2-}$.

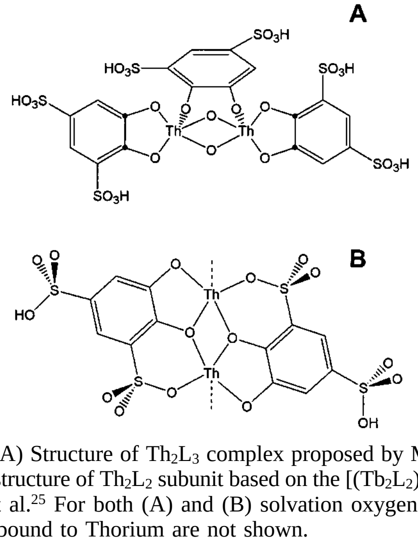

Figure 6. (A) Structure of Th_2L_3 complex proposed by Murakami et al.[6] and (b) structure of Th_2L_2 subunit based on the $[(Tb_2L_2)$•L] structure from Sun et al.[25] For both (A) and (B) solvation oxygens (i.e. water molecules) bound to Thorium are not shown.

Since the EXAFS technique can only observe average structure, some consideration must also be given to the possibility that these three samples contain a mixture of Th(IV)−Tiron

---

[34] Sun, H.; Huang, C.; Xu, G.; Ma, Z.; Shi, N. *Polyhedron* **1995**, 947−951.

complexes and polymeric thorium(IV) hydroxides. However, the presence of polymeric hydrolysis products would tend to increase the average Th−Th coordination number while decreasing the average Th−C and Th−S coordination numbers. Also, speciation calculations performed at pH 6.0 as a function of Tiron concentration (not shown) predict that, at M:L ratios between 1:2 and 1:10, greater than 98% of all Th will occur as the 2:3 Th:Tiron complex.

At a M:L = 1:10, the number of Th−C interactions observed increases to 4−5, Th−S interactions are retained, and the Th−Th interactions disappear. These results suggest that the large excess of ligand ultimately destroys the 2:3 Th:Tiron complex and allows bidentate catechol binding to the Th^{4+} ion to dominate. Under these conditions, this most probably results in the formation of mixed monomeric $Th(Tiron)_x$ ($x \geq 2$) species possessing both bidentate catechol and monodentate sulfonate ligation.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. This work was done (partially) at SSRL, which is operated by the Department of Energy, Division of Chemical Sciences.

Supporting Information Available: Figures of individual shell contributions to the calculated fits for each sample. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001223T