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Structures of Dimeric Hydrolysis Products of Thorium

Richard E. Wilson,[†] S. Skanthakumar,[†] Ginger Sigmon,[‡] Peter C. Burns,[†,‡] and L. Soderholm*,[†,‡]

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana 46556

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Three unique thorium dimeric compounds have been crystallized from either direct hydrolysis of Th^{4+}(aq)/HCl or titration of $Th(OH)_4$(am) with $Th(NO_3)_4$(aq) and their structures determined using single-crystal X-ray diffraction. The compound $[Th_2(\mu_2\text{-}OH)_2(NO_3)_6(H_2O)_6]H_2O$ (**1**) is identical to that identified previously by Johansson. Two additional unreported compounds have been identified, $[Th_2(\mu_2\text{-}OH)_2(NO_3)_4(H_2O)_8](NO_3)_2$ (**2**) and $[Th_2(\mu_2\text{-}OH)_2Cl_2(H_2O)_{12}]Cl_4\cdot 2H_2O$ (**3**). **1** crystallizes in the monoclinic space group $P2_1/c$, with $a = 6.792(2)$ Å, $b = 11.710(4)$ Å, $c = 13.778(5)$ Å, and $\beta = 102.714(5)°$ and **2** crystallizes in the monoclinic space group $P2_1/n$, with $a = 6.926(5)$ Å, $b = 7.207(1)$ Å, $c = 21.502(1)$ Å, and $\beta = 96.380(1)°$. The chloride-containing dimer, **3**, crystallizes in triclinic $P\bar{1}$, with $a = 8.080(2)$ Å, $b = 8.880(2)$ Å, $c = 9.013(2)$ Å, $\alpha = 97.41(3)°$, $\beta = 91.00(3)$, and $\gamma = 116.54(3)°$. We also present high-energy X-ray scattering data demonstrating the presence of the hydroxo-bridged moiety in solution and discuss our findings in the context of known solid-state structures. The three structures demonstrate 11-, 10-, and 9-coordinate thorium, respectively, and coupled with the scattering experiments provide additional structural and chemical insight into tetravalent actinide hydrolysis.

Introduction

Hydrolysis reactions of dissolved metal ions are some of the most fundamental and perhaps most important reactions in aqueous chemistry. These hydrolysis reactions affect properties such as acid−base chemistry, solubility, and redox reactions in solution. The results of thermodynamic studies of thorium hydrolysis provide the stability constants for successive hydrolysis reactions that produce a variety of complexes, from monomeric hydroxides to ill-defined polynuclear species and colloids.[1−8] For concentrations of thorium greater than millimolar, it is demonstrated that polynuclear complexes dominate the speciation at low pH.[6] At slightly more neutral pH these small polynuclear species are understood to be precursors to larger polynuclear complexes of the actinides, possibly including tetramers, hexamers, and ultimately much larger complexes familiarly known as colloids or polymers.

The complex stoichiometries identified from solution thermodynamics have little or no grounding in structural studies. The studies of hydrolysis reactions in solution rely on potentiometric titration data usually complemented by a spectroscopic probe to identify or confirm the species involved in the system. In the particular case of thorium, optical spectroscopy is uninformative because its $[Rn]^0$ electronic configuration produces no f−f transitions. Previous experimental studies of Th hydrolysis reactions have relied on curve fitting of potentiometric data to extract stability constants or, more recently, X-ray absorption spectroscopy (XAS),[9,10] which provides information about metal-ion near-neighbor coordination. In the solid state, previous binuclear structures containing extended chains have been presented

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* To whom correspondence should be addressed. E-mail: ls@anl.gov.
[†] Argonne National Laboratory.
[‡] University of Notre Dame.

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for thorium, mostly silicates, sulfates, and phosphates,[11] with only one previous report for a discrete molecular hydroxo-bridged complex of thorium with nitrate[12] and none for chlorine-containing dimers. Multimeric compounds reported for uranium and neptunium are more numerous, with many of the crystal structures containing infinite chains of edge-sharing polyhedra, though molecular multimeric hydroxo- and peroxo-bridged complexes of uranium have been identified in both the solid and solution states.[13,14]

To more fully understand thorium hydrolysis reactions, we have undertaken a study to isolate molecular, polynuclear products that crystallize from these reactions and to develop a structural relationship between the structures isolated in the solid state and those in solution. Furthermore, by identifying the polynuclear structures in solution we hope to more fully understand the relationship between tetravalent actinide colloids, smaller polynuclear complexes, and the chemistry by which they are formed.

To draw a correlation between the single-crystal structures and the structure of the complex in solution, we have used high-energy X-ray scattering (HEXS) as a probe of the dissolved thorium complexation in the solution from which crystals were grown. High-energy X-ray scattering data provides information regarding local and intermediate range atomic correlations (≤ 50 Å).[15] Such information is not available with other X-ray or optical techniques and allows direct quantification of monomeric, dimeric, and larger oligomers in solution. Furthermore, HEXS lends itself particularly to the investigation of large *Z* atoms (i.e., actinides) because of the multiplicative dependency of the scattered intensity with electron number. The HEXS experiments allow us to probe atomic correlations in solution, thereby assessing the relative similarity of solution and solid-state coordination. Comparison of the scattering data with a model calculated using the dimer structure provides a means to further assess the presence of similar moieties in solution, which should ultimately provide the metrical information necessary to realize a molecular level understanding of the formation and structure of amorphous hydrolysis products.

Together with our comparative diffraction and HEXS results on $[Th_2(\mu_2\text{-}OH)_2Cl_2(H_2O)_{12}]Cl_4$ (**3**), we present new structural characterization of the dimer $[Th_2(\mu_2\text{-}OH)_2(NO_3)_4(H_2O)_8](NO_3)_2$ (**2**), along with the compound previously reported by Johansson for comparison, $[Th_2(\mu_2\text{-}OH)_2(NO_3)_6(H_2O)_4]H_2O$ (**1**).[12] These binuclear thorium complexes are bridged by two coplanar hydroxyl groups with either two or three nitrate anions coordinated on each thorium atom. In the chlorine-containing dimer, there is only one chlorine atom coordinated to each thorium atom, the balance of each coordination sphere completed by coordinated water. The structures contain only cations of thorium.

Experimental Methods

Caution! *^{232}Th is a radioactive element with a half-life of 14.1 × 10^9 years and is in radioactive equilibrium with its daughters of Ac, Ra, and Rn, which contribute beta and photon radiation to the Th alpha radiation. Additionally, evaporation and crystallization promote the dispersal of recoiling daughter nuclei. The quantities used in the syntheses below should be handled in a fume hood using standard precautions for working with radioactive materials.*

$[Th_2(\mu_2\text{-}OH)_2(NO_3)_6(H_2O)_4]H_2O$ (1). This compound was prepared following the methods of Johansson[16] using $Th(NO_3)_4{\cdot}(H_2O)_x$ dissolved in water, $[Th^{4+}] = 0.7$ M. The $Th(OH)_4$ compound described by Johansson was prepared by precipitation of $Th(NO_3)_4$ solution with NH_4OH and subsequent washings of the precipitate with distilled water until the pH of the supernatant was neutral as determined by paper.

$[Th_2(\mu_2\text{-}OH)_2(NO_3)_4(H_2O)_8](NO_3)_2$ (2). **2** was formed similarly to **1** with the adjustment of the Th/NO_3 ratio and by consequence of the sample acidity. The solution of $Th(NO_3)_4$ from which the complex was prepared was initially 0.7 M in $Th(NO_3)_4$, and **2** was precipitated and washed with a process identical to that of **1**. To this precipitate was added 2 mL of the original $Th(NO_3)_4$ solution from which elongated rectangular plates of **2** formed after several days.

$[Th_2(\mu_2\text{-}OH)_2Cl_2(H_2O)_{12}]Cl_4{\cdot}2H_2O$ (3). **3** was prepared by the precipitation of 1 mL of a solution of 0.7 M $Th(NO_3)_4$ with NH_4OH and subsequent washing of the $Th(OH)_4$ precipitate with distilled water until the pH of the supernatant was neutral. To this precipitate cake, 1 mL of 1 M HCl was added, resulting in a final volume of ~1.5 mL. Large plates of **3** form (>1 mm on edge) after several days.

Structure Determinations X-ray diffraction data were collected using a Bruker AXS SMART diffractometer equipped with an APEX II CCD detector. Crystals were manipulated under oil and were mounted on hollow glass fibers using a fast-drying epoxy. Absorption corrections were performed using SADABS,[17] and data reduction and structure refinements were done using SHELXTL.[18] A summary of crystallographic and refinement details is found in Table 1 and in the Supporting Information in CIF format.

High-Energy X-ray Scattering (HEXS) The high-energy X-ray scattering data were collected at the Advanced Photon Source, Argonne National Laboratory (wiggler beamline 11-ID-B, BESSRC-CAT). The incident beam of 91 keV corresponds to a wavelength of 0.13702 Å, with the scattered intensity measured using a General Electric amorphous silicon flat panel X-ray detector (GE Healthcare) mounted in a static position ($2\theta = 0°$) providing detection in momentum transfer space Q (Å^{-1}) up to 32 Å^{-1} at this fixed geometry. Samples of both liquid and solids were enclosed in Kapton capillaries with epoxy plugs and further contained as required for actinide samples. Data were treated as described previously.[19,20]

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Table 1. Crystallographic and Major Structural Details for the Thorium Dimers

	1	**2**	**3**
		Crystal Data	
a (Å)	6.792(2)	6.925(1)	8.080(2)
b (Å)	11.710(4)	7.207(1)	8.880(2)
c (Å)	13.778(5)	21.502(1)	9.013(2)
α (deg)	90.00	90.00	97.41(3)
β (deg)	102.714(5)	96.380(1)	102.714(5)
γ (deg)	90.00	90.00	116.54(3)
V (Å^3)	1068.9(6)	1066.55(9)	571.6(2)
Z	2	2	1
mol wt (g·mol^{-1})	980.27	982.28	932.78
space group	$P2_1/c$ monoclinic	$P2_1/n$ monoclinic	$P\bar{1}$ triclinic
T (°C)	25	25	25
λ (Å) (Mo Kα)	0.71073	0.71073	0.71073
ρ_{calc} (g·cm^{-3})	3.046	3.059	2.709
μ (mm^{-1})	14.028	14.059	13.746
R(F_o), wR2(F_o^2)^a	0.0745, 0.1276	0.0397, 0.0612	0.0379, 0.0885
		Bond Distances (Å)	
	Th−O(1) 2.356(9)	Th−O(1) 2.333(3)	Th−O(1) 2.351(4)
	Th−O(1A) 2.375(8)	Th−O(1A) 2.369(3)	Th−O(1A) 2.360(4)
	Th−O(2) 2.566(9)	Th−O(2) 2.482(3)	Th−O(2) 2.497(5)
	Th−O(3) 2.496(9)	Th−O(3) 2.544(3)	Th−O(3) 2.493(5)
	Th−O(4) 2.528(9)	Th−O(4) 2.485(3)	Th−O(4) 2.498(5)
	Th−O$_N$(5) 2.581(9)	Th−O(5) 2.521(3)	Th−O(5) 2.523(4)
	Th−O$_N$(6) 2.707(9)	Th−O$_N$(6) 2.585(3)	Th−O(6) 2.554(4)
	Th−O$_N$(7) 2.586(8)	Th−O$_N$(7) 2.596(3)	Th−O(7) 2.503(5)
	Th−O$_N$(8) 2.760(10)	Th−O$_N$(8) 2.633(3)	Th−Cl(1) 2.850(2)
	Th−O$_N$(9) 2.683(8)	Th−O$_N$(9) 2.579(3)	Th−Th 4.020(2)
	Th−O$_N$(10) 2.601(9)	Th−Th 3.981(2)	
	Th−Th 3.998(2)		

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, F on all data, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

Results and Discussion

Single-Crystal Structures. The structure of **1** is presented in Figure 1, and the relevant bond distances and angles are in Table 1. The dimer of thorium polyhedra contains two hydroxyl groups, with six coordinating nitrate groups and six coordinating water molecules. The nitrate groups are bidentate, giving each thorium atom a coordination number of 11. The dimer is made of two edge-sharing thorium polyhedra. The shortest Th−O bond is between the Th and bridging hydroxyl groups, 2.356(9) and 2.375(8) Å, respectively, creating a parallelogram with O−Th−O and Th−O−Th angles of 64.63° and 115.37°. The Th−Th distance is 3.998(2) Å, and the Th atoms are perfectly coplanar with the hydroxyl groups, indicating that the structure is not bent or puckered. The coordinating water occupies a trigonal face behind the bidentate nitrate groups in the coordination sphere. The Th−O bond distances for the coordinating water are 2.496(9), 2.528(9), and 2.566(9) Å. The nitrate oxygen bonds range from 2.581(9) to 2.760(10) Å. About the inversion center, the two nitrate ligands that are trans to each other necessarily lie in a plane; however, the oxygen atoms of the nitrate ligands perpendicular to the hydroxo-bridge form a torsion angle of 21.61° as presented in Figure 2, moving them slightly out of an eclipsing arrangement. The apical oxygens of the trans-nitrato groups are coplanar with the thorium atoms and relative to this, the plane created by the bridging hydroxyl groups and Th is rotated 8.67° as demonstrated in Figure 2.

The structure of **2** is presented in Figure 1 and also given as a summary of bond distances in Table 1. In this structure each thorium atom is coordinated by 10 oxygen atoms, with the two oxygen atoms of the trans nitrate group in **1** replaced by one coordinating water molecule. The charges of the thorium clusters are balanced by an interstitial nitrate anion. The Th−Th bond distance in **2** is 3.981(2) Å. The two hydroxyl groups have bond distances to the thorium atom of 2.333(3) and 2.369(3) Å, forming O−Th−O and Th−O−Th bond angles of 64.28° and 115.71°, respectively. The bond distances for the four crystallographically unique coordinating oxygen atoms of water are 2.482(3), 2.485(3), 2.521(3), and 2.545(3) Å, generally shorter than those observed in **1**. The range of Th−O bond distances to the nitrate oxygen encompasses 2.579(3) to 2.633(3) Å. Interestingly, the nitrate configuration perpendicular to the $Th_2(\mu_2\text{-}OH)_2$ plane is similar to **1** despite the absence of the third nitrate anion. Regardless, the apical nitrate oxygen atoms are only slightly rotated from fully eclipsed with a O−Th−Th−O torsion angle of 15.54°. The rotation of the bridging hydroxyl groups out of the plane of the symmetry-generated O(2)−Th−Th−O(2A) plane and the O(4)−Th−Th−O(4A) plane results in a rotation of the O(1)−Th(1)−O(1) plane 6.27° and 4.53°, respectively, as can be seen in Figure 2, the rotation between the two reference planes being 1.73° from coplanar.

The structure for **3** contains nine-coordinate thorium (Figure 3). In this structure the thorium atom is almost completely hydrated and coordinated by only one chlorine atom. The Th−Th distance is 4.020(2) Å, which is only slightly longer than those observed in the nitrate-containing dimer compounds, and the bridging hydroxyl bond distances are similar to those of the nitrate complexes, 2.351(4) and 2.360(4) Å. The coordinating water molecules have bond

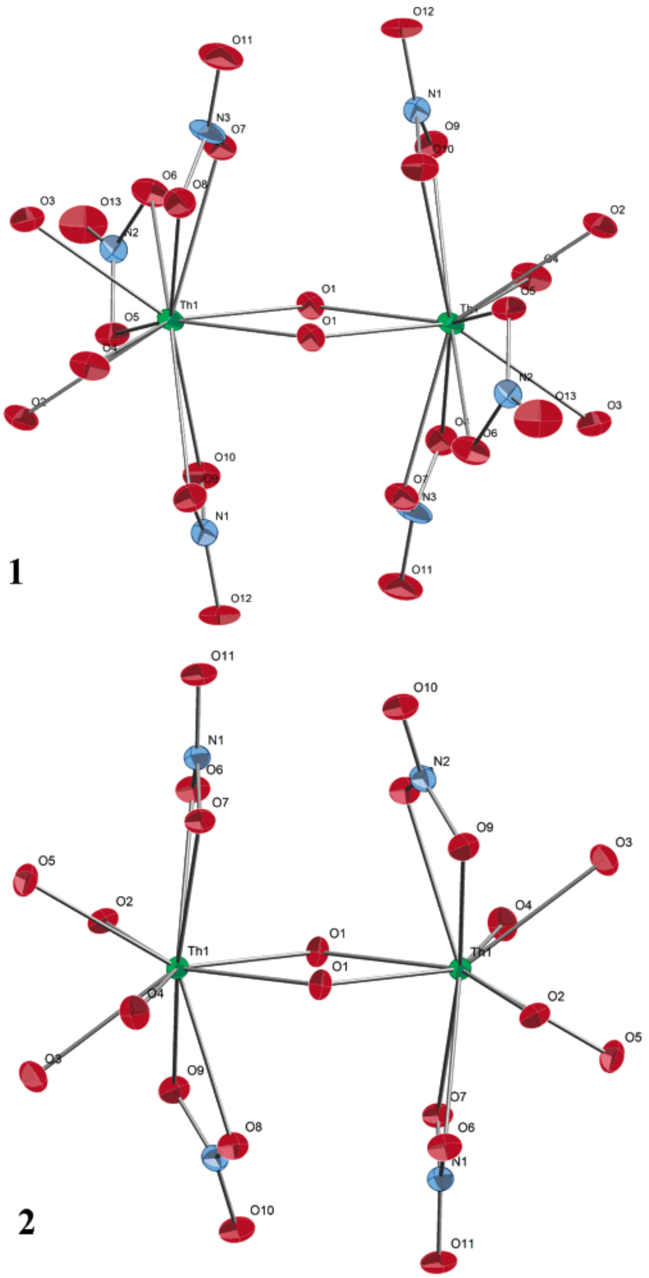

Figure 1. Thermal ellipsoid plot of the molecule (**1**) $[Th_2(\mu_2\text{-}OH)_2(NO_3)_6(H_2O)_4]H_2O$ and (**2**) $[Th_2(\mu_2\text{-}OH)_2(NO_3)_4(H_2O)_8](NO_3)_2$; ellipsoids presented at 50% probability. The water and nitrates of crystallization have been removed for clarity.

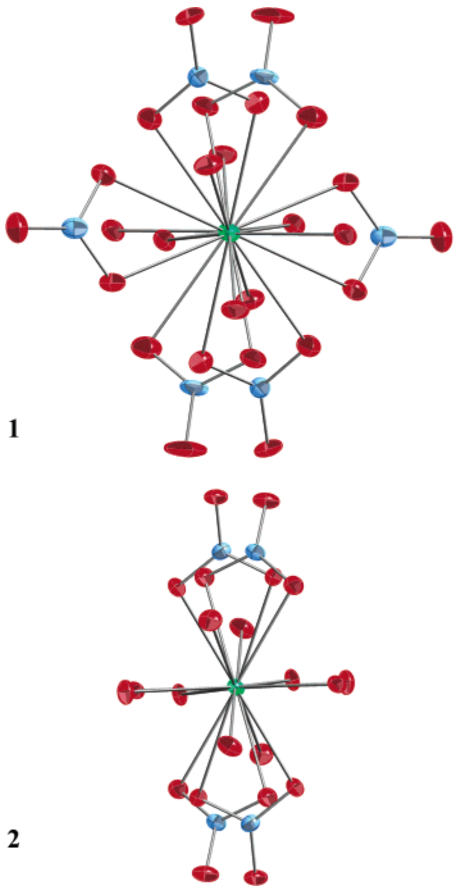

Figure 2. Projection of **1** and **2** demonstrating the nearly eclipsed character of the apical nitrate groups in both structures and the relative rotation of the coplanar $Th_2(\mu_2\text{-}OH)_2$ plane compared to the plane created by O(8)−Th−Th−O(8) (with angles of 12.47° for **1** and 10.35° for **2**).

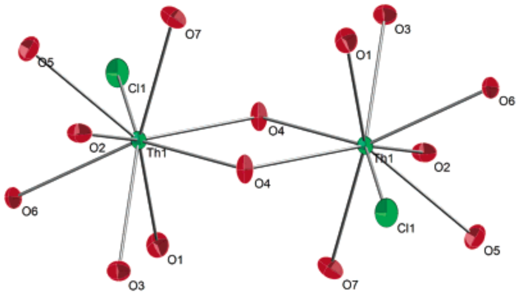

Figure 3. Thermal ellipsoid plot for (**3**) $[Th_2(\mu_2\text{-}OH)_2Cl_2(H_2O)_{12}]Cl_4\cdot 2H_2O$, representing 50% probability. The charge-balancing chloride anions and water of crystallization have been removed for clarity.

distances to thorium that cover the range of 2.493(5)−2.554(4) Å, in good agreement with the Th−O bond distances determined for the nitrate complexes. The Th−Cl bond distance is 2.850(20) Å, within the range of Th−Cl distances in the tetra- and hexachloride complexes $ThCl_4$ and Cs_2ThCl_6.[21] The chlorine atoms are in a trans arrangement, nearly coplanar with the bridging hydroxyl atoms, differing only by 1.96°.

Atomic Correlations in Solution. The precipitation of Th dimers from the chloride solution raises the question of Th speciation in solution, specifically with respect to the presence of chloride complexation and oligomerization. X-ray scattering data obtained from a solution with the same composition and stoichiometery as that from which the chloride dimers (**3**) were crystallized is shown in Figure 3. These solution data are compared with scattering data collected under the same conditions from a pulverized solid sample of the Th−Cl dimer. Also included in the figure is a spectrum calculated assuming contributions only from the $Th_2(\mu_2\text{-}OH)_2Cl_2(H_2O)_{12}$ moiety itself. A direct comparison between these three spectra reveals that the rather intense peak in the solution spectrum at 2.477 Å arises from the Th first coordination sphere. It is shifted to a lower *r* than that seen in the spectrum for the solid-phase material, a result that is not inconsistent with comparisons of solution and

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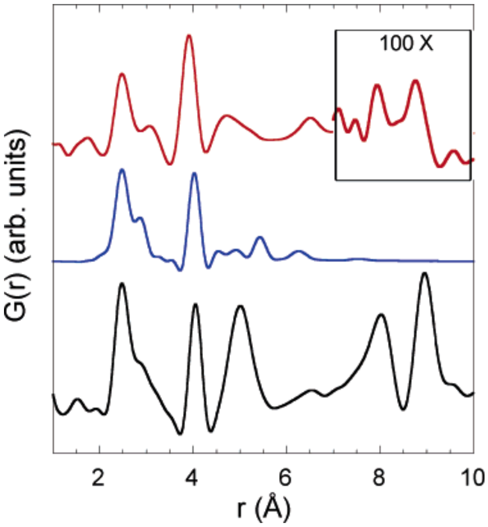

Figure 4. Pair-distribution functions obtained from HEXS data. (top) Function obtained from a solution out of which $[Th_2(\mu_2\text{-}OH)_2Cl_2(H_2O)_{12}]Cl_4\cdot 2H_2O$ crystallizes. The inset is a blow-up of the intensity over the distance range of 7−10 Å showing the peaks at 7.9 and 8.8 Å. (middle) Calculated function assuming only the correlations within a single $Th_2(\mu_2\text{-}OH)_2Cl_2(H_2O)_{12}$ dimer unit. (bottom) Function obtained from a powdered solid-phase sample of (**3**) $[Th_2(\mu_2\text{-}OH)_2Cl_2(H_2O)_{12}]Cl_4\cdot 2H_2O$. The large peaks at 8.0 and 8.9 Å arise from Th−Th interdimer correlations.

solid-phase coordination environments.[22] However, the profile of the peak on the higher *r* side indicates a change in coordination environment. The Th−Cl interaction is exemplified by the calculated spectrum as a shoulder at 2.85 Å and visible as a shoulder in the solid sample. It is not apparent in the solution data but instead is replaced by a peak centered at 3.05 Å. The peak at 4.05 Å in the solid-phase spectrum primarily represents the Th−Th interaction within the dimer. This peak is also present in the solution data, indicating the presence of dimers in solution.

The solid-phase spectrum has a large peak at about 5 Å that corresponds primarily to correlations between Th and interstitial Cl atoms. This peak is significantly decreased and shifted to slightly shorter correlation lengths in the solution, reflecting the disordering of the Cl^- not directly bound to the Th in solution but incorporated into the solid-state lattice. Also present in the solid-phase spectrum are two strong peaks at about 8 and 9 Å. These peaks correspond to the correlation between a Th in one dimer unit with a Th in a neighboring dimer. Surprisingly, similar correlations are also observed in the solution at about 8 and 8.8 Å. Whereas these more distant interactions may signal the presence of higher order oligomers, the similarity with the solid-phase data suggests that the solution correlations may represent dimer−dimer preformed interactions in solution. Further studies are needed to understand this information.

Conclusions

We provide two new crystal structures of thorium hydroxo-bridged dimers isolated from aqueous solution. The single-crystal structural data, together with the HEXS spectrum from the solid, allow the interpretation of the HEXS correlations seen in solution and lead us to suggest the presence of preformed Th^{4+} dimers in solution. Dimer−dimer correlations are also suggested by the solution results.

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Supporting Information Available: Additional crystallographic and refinement details via a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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