

Hydration and Hydrolysis of Thorium(IV) in Aqueous Solution and the Structures of Two Crystalline Thorium(IV) Hydrates

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Received September 4, 2009

Solid octaqua(κ^2 O-perchlorato)thorium(IV) perchlorate hydrate, $[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, **1**, and aquaoxonium hexaaquatrakis(κ O-trifluoromethanesulfonato)thorium(IV) trisaqua-hexakis(κ O-trifluoromethanesulfonato)thorinate(IV), $\text{H}_5\text{O}_2[\text{Th}(\text{H}_2\text{O})_6(\text{OSO}_2\text{CF}_3)_3][\text{Th}(\text{H}_2\text{O})_3(\text{OSO}_2\text{CF}_3)_6]$, **2**, were crystallized from concentrated perchloric and trifluoromethanesulfonic acid solutions, respectively. **1** adopts a severely distorted tricapped trigonal prismatic configuration with an additional oxygen from the perchlorate ion at a longer distance. **2** consists of individual hexaaquatrakis(κ O-trifluoromethanesulfonato)thorium(IV) and trisaqua-hexakis(κ O-trifluoromethanesulfonato)thorinate(IV) ions and an aquaoxonium ion bridging these two ions through hydrogen bonding. The hydrated thorium(IV) ion is nine-coordinated in aqueous solution as determined by extended X-ray absorption fine structure (EXAFS) and large angle X-ray scattering (LAXS). The LAXS studies also showed a second hydration sphere of about 18 water molecules, and traces of a 3rd hydration sphere. Structural studies in aqueous solution of the hydrolysis products of thorium(IV) have identified three different types of hydrolysis species: a μ^2 O-hydroxo dimer, $[\text{Th}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$, a μ^2 O-hydroxo tetramer, $[\text{Th}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$, and a μ^3 O-oxo hexamer, $[\text{Th}_6\text{O}_8(\text{H}_2\text{O})_n]^{8+}$. Detailed structures of these three hydrolysis species are given. A compilation of reported solid state structures of actinoid(IV) compounds with oxygen donor ligands show a strong correlation between the An—O bond distance and the coordination number. The earlier reported U—O bond distance in the hydrated uranium(IV) ion in aqueous solution, confirmed in this study, is related to nine-coordination. The hydrated tri- and tetravalent actinoid ions in aqueous solution all seem to be nine-coordinated. The trivalent ions show a significant difference in bond distance to prismatic and capping water molecules in assumed tricapped trigonal prismatic configuration, while the tetravalent ions seem to form more regular structures, probably because of higher polarization.

Introduction

Thorium belongs to the actinoid series, and all its isotopes are radioactive; nevertheless, ^{232}Th is naturally occurring because of its very long half-life, $1.405 \cdot 10^{10}$ years.¹ Thorium(IV) has an ionic radius of 1.09 Å in nine-coordination² making it the largest stable tetravalent metal ion and, in spite of its high valence, fairly resistant to hydrolysis. These properties make it more easy to work with thorium(IV) than the other actinoids, and it is often used as a model for the actinoid chemistry even though the only stable oxidation

state, +IV, is lacking 5f electrons. A large number of hydrolysis studies of thorium(IV) in aqueous solution has been reported using mainly potentiometric, solubility, and liquid–liquid extraction methods.³ The reported data are fairly scattered, and unusually dependent on ionic medium and strength with reported stability constants varying several orders of magnitude by changing the ionic strength from 0 to $3 \text{ mol} \cdot \text{dm}^{-3}$.³ Thorium(IV) starts to hydrolyze around pH = 4 at micromolar concentrations, while the hydrolysis is significant at pH = 1 for concentrated solutions.

The determination of the hydrolysis species present in aqueous solution becomes difficult as the monomeric hydrolysis complexes have a strong tendency to polymerize. This leads to a situation where the monomeric complexes are only predominating at micromolar concentrations where the measurements tend to have lower accuracy and precision. The first monomeric hydrolysis complex, $[\text{ThOH}(\text{H}_2\text{O})_n]^{3+}$, with $n = 7$ or 8, easily dimerizes to $[\text{Th}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$, while larger polymers with an $\text{OH}^-/\text{Th}^{4+}$ ratio in the complex of 1.0 do not seem to form. The second hydrolysis

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complex, $[\text{Th}(\text{OH})_2(\text{H}_2\text{O})_n]^{2+}$, readily polymerizes to a tetramer and at higher concentrations to a hexamer, while formation of other kinds of hydrolyzed clusters do not seem to take place at an $\text{OH}^-/\text{Th}^{4+}$ ratio of 2.0. At higher $\text{OH}^-/\text{Th}^{4+}$ ratios in the complex hexameric hydrolysis clusters as $[\text{Th}_6(\text{OH})_n]^{(24-n)+}$, $n = 14$ or 15 , are reported to form.³ It is very uncertain if the higher monomeric hydrolysis complexes, $\text{Th}(\text{OH})_3^+$ and $\text{Th}(\text{OH})_4$, even exist in measurable amounts in aqueous solution. At higher pH values, thorium(IV) precipitates as hydrated thorium(IV) hydroxide which over time is transferred to thorium(IV) oxide, the most thermodynamically stable form, which is almost insoluble in acid.⁴ A summary of some important acidic and polymerization constants is given in Supporting Information, Table S1, and an overview and evaluation of the proposed hydrolysis products and their equilibrium constants are found in reference 3.

Even though the thorium(IV)/hydroxide system is thoroughly studied from a thermodynamic point of view, the number of structural investigations of the hydrated thorium(IV) ion and its hydrolysis products in aqueous solution is limited. Only one crystal structure containing a fully hydrated thorium(IV) ion has been reported, $[\text{Th}(\text{H}_2\text{O})_{10}]\text{Br}_4$, with a mean Th–O bond distance of 2.498 Å in a dicationic square antiprismatic (*d-sap*) configuration.⁵ Two large angle X-ray scattering (LAXS) studies report the hydrated thorium(IV) ion in strongly acidic aqueous solution as eleven-coordinated with mean Th–O bond lengths of 2.49(1) and 2.45(1) Å, respectively.^{6,7} A LAXS study using synchrotron light of the hydrated thorium(IV) ion in aqueous solution has reported a mean Th–O bond distance of 2.46 Å with a coordination number of 10.⁵

Johansson has reported that the shortest mean Th···Th distance in polynuclear hydrolysis complexes in aqueous solution is 3.94 Å.⁸ A couple of solid state structures containing the hydrolyzed dimer with a double hydroxo bridge, $[\text{Th}(\text{OH})_2\text{Th}]^{6+}$, have been reported including potassium decaaquabis(μ^2 -*O*-hydroxo)dithorium(IV) tetrakis(μ^3 -*S*-sulfido)(μ^2 -*O*-oxalato)tris(μ^2 -*S*-disulfido)bis(oxalato)tristungsten hydrate, $[\text{Th}_2(\text{OH})_2(\text{H}_2\text{O})_{10}(\text{W}_3\text{S}_7(\text{C}_2\text{O}_4)_2) \cdot 14.3\text{H}_2\text{O}$,⁹ decaaquabis(μ^2 -*O*-hydroxo)dithorium(IV)bis(κ -*O*-picrate) picrate decahydrate, $[(\text{Th}_2(\text{OH})_2(\text{H}_2\text{O})_{10}(\text{OC}_6\text{H}_2(\text{NO}_2)_3)_2)(\text{OC}_6\text{H}_2(\text{NO}_2)_3)_4 \cdot 10\text{H}_2\text{O}$,¹⁰ hexaquaahexanitratato(μ^2 -*O*-hydroxo)dithorium(IV) dihydrate, $[\text{Th}_2(\text{OH})_2(\text{NO}_3)_6(\text{H}_2\text{O})_8] \cdot 2\text{H}_2\text{O}$,¹¹ and dodecaaquabischloro(μ^2 -*O*-hydroxo)dithorium(IV) chloride monohydrate 18-crown-6, $[\text{Th}_2(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_{12}]\text{Cl} \cdot \text{H}_2\text{O} \cdot \text{C}_{12}\text{H}_{24}\text{O}_6$.¹² The Th···Th distance is just below 4.0 Å in all compounds except in the picrate compound

where it is 4.07 Å. The Th–O bond distances to the bridging hydroxides, about 2.36 Å, are 0.10–0.15 Å shorter than to terminal water molecules or other oxygen donor ligands.^{5,9–12}

It is well established that there is a strong correlation between coordination number and ionic radius for a specific metal ion.² Structure determination of metal complexes in solution using X-ray methods as extended X-ray absorption fine structure (EXAFS) and LAXS normally yields accurate distances, while the number of equal distances is much more uncertain and, more importantly, strongly correlated with the Debye–Waller factor coefficient.¹³ A more accurate way to estimate the mean coordination number from measurements in solution is to correlate the obtained distance with mean bond distances in different configurations from crystallographically determined compounds only binding to ligands with a certain donor atom, for example, oxygen, in monodentate neutral ligands, see section “Overview of the structures of the hydrated actinoid(IV) ions” below.

The aims of this study are to determine the structure of the hydrated thorium(IV) ion in aqueous solution using the EXAFS and LAXS methods, to determine the crystal structures of the hydrated thorium(IV) ion in the solid perchlorate and trifluoromethanesulfonate salts, to determine the structures of hydrolyzed thorium(IV) complexes in aqueous solution, and ultimately to discuss the structures of tri- and tetravalent actinoid ions in aqueous solution reported in this study and the literature.

Experimental Section

Chemicals. Thorium(IV) nitrate pentahydrate, $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, (Merck 99%), concentrated nitric acid (Merck), perchloric acid (Merck), trifluoromethanesulfonic acid (Aldrich), concentrated aqueous ammonia (25% by weight, Merck), solid sodium hydroxide (Sigma), and solid potassium hydroxide (Aldrich) were used as purchased.

Preparation of Salts. Octaaqua(κ^2 -*O*-perchlorato)thorium(IV) perchlorate monohydrate, $[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4) \cdot \text{H}_2\text{O}$, **1**, was prepared by dissolving weighed amounts of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ in 5 mol·dm⁻³ perchloric acid followed by precipitation of thorium hydroxide with addition of concentrated ammonia.¹⁴ We believe that hydrated thorium hydroxide was formed as it has good solubility in strong acid, whereas thorium dioxide is known to be poorly soluble in strong acid.⁴ The obtained residue, hydrated thorium(IV) hydroxide, was washed with distilled water and dissolved in 11.6 mol·dm⁻³ perchloric acid. The obtained solution was filtered through paper filter and evaporated until a highly viscous concentrated solution, 2.94 mol·dm⁻³, $\rho = 2.35 \text{ g}\cdot\text{cm}^{-3}$, was obtained. After storage in a refrigerator for months, single crystals of suitable quality for crystallographic studies were obtained. Aquaonium hexa-aquatris(κ -*O*-trifluoromethanesulfonato)thorium(IV) hexakis(κ -*O*-trifluoromethanesulfonato)thorate(IV), $(\text{H}_5\text{O}_2)[\text{Th}(\text{H}_2\text{O})_6(\text{OSO}_2\text{CF}_3)_3][\text{Th}(\text{H}_2\text{O})_3(\text{OSO}_2\text{CF}_3)_6]$, **2**, was prepared in the same way as described for **1**, though the hydrated thorium(IV) hydroxide was dissolved in 10 mol·dm⁻³ trifluoromethanesulfonic acid instead.

Preparation of Solutions. A 1.06 mol·dm⁻³ aqueous thorium perchlorate solution was prepared from the concentrated bulk solution by dilution with 1.0 mol·dm⁻³ perchloric acid. It is necessary to keep the pH below 1 at these concentrations to

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Table 1. Concentrations (in mol·dm⁻³) of the Aqueous Thorium(IV) Solutions Used in the LAXS and EXAFS Studies

sample	pH	[Th ⁴⁺]	[ClO ₄ ⁻]	[H ₂ O]	ρ/g·cm ⁻³	μ/cm ⁻¹
Thaq-LAXS	-0.70	1.06	9.240	19.286	1.517	34.445
Th 1-LAXS	0.02	0.54	3.160	48.816	1.320	17.639
Th 2-LAXS	1.23	0.88	3.579	46.278	1.394	27.255
Th 3-LAXS	2.35	0.53	2.120	50.878	1.250	16.898

avoid hydrolysis. An aqueous solution of hydrolyzed thorium(IV) was obtained by addition of 5.0 mol·dm⁻³ sodium hydroxide solution until a pH value of 2.35 (at the limit to precipitation) was reached. The concentration of the final solution was determined to be 0.53 mol·dm⁻³. An aqueous solution of potassium hydroxide, 10 mol·dm⁻³, 2 mL, was added to 10 mL of the 1.06 mol·dm⁻³ aqueous thorium(IV) perchlorate solution to decrease perchlorate concentration. The formed potassium perchlorate was filtered off. This solution was determined to have pH = 1.23, and the thorium(IV) concentration to 0.88 mol·dm⁻³. After a LAXS study of this solution it was acidified by adding portions of 0.037 mL of 11.6 mol·dm⁻³ perchloric acid until a pH value of 0.02 was reached. The final thorium(IV) concentration of this solution was 0.54 mol·dm⁻³.

The thorium(IV) concentration was determined spectrophotometrically using the intensively colored thorium(IV) complex with arsenazo-3 (CAS No. 17306-35-3), λ_{max} = 665 nm.¹⁵ The thorium(IV) solutions were diluted to about 10⁻⁵ mol·dm⁻³ for suitable absorption of the thorium(IV)-arsenazo-3 complex. The composition of the solutions studied by LAXS and EXAFS are summarized in Table 1.

EXAFS - Data collection. EXAFS measurements of the solids 1 and 2, and aqueous solutions thorium(IV) perchlorate at pH values -0.7 (hydrated) and 2.35 (hydrolyzed) were performed at the Th L₃ X-ray absorption edge. The data were collected at the bending magnet beamline 2-3 at the Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, U.S.A., which operated at 3.0 GeV and a maximum current of 100 mA. The EXAFS station was equipped with a Si[220] double crystal monochromator. Higher order harmonics were reduced by detuning the second monochromator crystal to reflect 60% of maximum intensity at the end of the scans. Internal energy calibration was made with a foil of metallic thorium assigned to 16300 eV.¹⁶ All measurements were performed in transmission mode. For each sample 3-4 scans were averaged after energy calibration by means of the EXAFSPAK program package.¹⁷

EXAFS - Data Analysis. The EXAFSPAK and GNXAS program packages were used for the data treatment. The GNXAS code is based on the calculation of the EXAFS signal and a subsequent refinement of the structural parameters.^{18,19} The GNXAS method accounts for multiple scattering (MS) paths by including the configurational average of all the MS signals to allow fitting of correlated distances and bond distance variances described by Debye-Waller factors. A detailed description of the distribution of the ion-solvent distances in a coordination shell should in principle take asymmetry into

account.^{19,20} Therefore the Th-O two-body signals associated with the first coordination shells were modeled with Γ-like distribution functions, which depend on four parameters, the coordination number *N*, the centroid distance *d* (the first moment of the function 4π∫g(r)r² dr), and the mean-square variation in the mean distance σ.

The standard deviations reported for the refined parameters in Table 2 are obtained from *k*³ weighted least-squares refinements of the EXAFS function χ(*k*), and do not include systematic errors of the measurements. These statistical error values allow reasonable comparisons, for example, of the significance when comparing relative shifts in the distances. However, the variations in the refined parameters, including the shift in the *E*₀ value (for which *k* = 0), using different models and data ranges, indicate that the absolute accuracy of the distances given for the separate complexes is within ±0.005 to 0.02 Å for well-defined interactions. The "standard deviations" given in the text have been increased accordingly to include estimated additional effects of systematic errors.

Large Angle X-ray Scattering (LAXS). The scattering of MoK_α X-ray radiation (λ = 0.7107 Å) from the free surface of aqueous solutions of thorium(IV) perchlorate at pH = -0.7, 0.02, 1.23, and 2.35, was measured by means of a large angle θ-θ diffractometer at 450 discrete points in the range 1 < θ < 65°; the scattering angle is 2θ. The solutions were contained in a Teflon cup inside an airtight radiation shield with beryllium windows. The scattered radiation was monochromatized in a focusing LiF crystal monochromator. At each preset angle 100,000 counts were accumulated and the entire angular range was scanned twice, which corresponds to a statistical error of about 0.3%. The divergence of the primary X-ray beam was limited by 1 or 1/4° slits for different θ regions, with partially overlapping data for scaling purposes. The experimental setup and the theory of the data treatment and modeling have been described elsewhere.²¹ The data treatment was carried out by means of the KURVLR program.²² The experimental intensities were normalized to a stoichiometric unit of volume containing one thorium atom, using the scattering factors *f* for neutral atoms, including corrections for anomalous dispersion,²³ Δ*f*' and Δ*f*'' and for Compton scattering.^{24,25} Least squares refinements of the model parameters were carried out by means of the STEPLR program,²⁶ where the expression $U = \sum w(s)[s \cdot i_{\text{exp}}(s) - s \cdot i_{\text{calc}}(s)]^2$ is minimized, where the scattering variable is $s = (4\pi/\lambda) \sin\theta$ and *w*(*s*) a weighting factor. The refinement of the model parameters was made for data in the high *s*-region, 4.0-16.0 Å⁻¹ for which the intensity contribution from the long-range distances can be neglected.^{27,28} A Fourier back-transformation procedure was used to improve the alignment of the experimental structure-dependent intensity function *i*_{exp}(*s*) before the refinements by removing spurious non-physical peaks below 1.2 Å in the radial distribution function (RDF).²⁹

Single Crystal X-ray Diffraction. Data were collected with a Bruker SMART CCD diffractometer and graphite monochromator

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Table 2. Mean Bond Distances, $d/\text{\AA}$, Number of Distances, N , and Temperature Coefficients, $b/\text{\AA}^2$, the Half-Height Full Width, $l/\text{\AA}$, in the LAXS (L) and EXAFS (E) Studies of the Hydrated and Hydrolyzed Thorium(IV) Complexes in Aqueous Solution at Room Temperature

species	interaction	N	d	b/σ^2	l	method
Solid $[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4)_3$ (1)						
$\text{Th}(\text{OH}_2)_9^{4+}$	Th–O _I	9	2.450(3)	0.0115(3)	0.214(3)	E
	Th–Cl	1	3.29(3)	0.025(5)	0.32(4)	
	MS1	16	3.76(3)	0.007(3)		
	MS2	16	3.97(2)	0.005(2)		
Solid $(\text{H}_5\text{O}_2)[\text{Th}(\text{H}_2\text{O})_6(\text{OSO}_2\text{CF}_3)_3][\text{Th}(\text{H}_2\text{O})_3(\text{OSO}_2\text{CF}_3)_6]$ (2)						
$\text{Th}(\text{OH}_2)_9^{4+}$	Th–O	9	2.448(2)	0.0105(2)	0.205(2)	E
	Th–S	4.5	3.851(5)	0.0210(7)	0.289(4)	
Thorium(IV) Perchlorate in Water, $1.06 \text{ mol}\cdot\text{dm}^{-3}$, pH = –0.70						
$\text{Th}(\text{OH}_2)_9^{4+}$	Th–O _I	9	2.454(6)	0.0059(9)	0.108(8)	L
	Th··O _{II}	12	4.547(8)	0.023(1)	0.21(1)	
	Th··O _{III}	10	6.85(-)	0.090(-)	0.42(-)	
ClO_4^- (aq)	Cl–O	4	1.454(3)	0.0025(2)	0.071(3)	
	(Cl)–O···O	4	2.940(5)	0.0317(12)	0.252(5)	
	Cl(O)···O	4	3.70(-)	0.0250(-)	0.022(-)	
water bulk	O _I ···O _{II}	2	2.773(8)	0.0055(9)	0.104(9)	
Thorium(IV) Perchlorate in Water, $0.54 \text{ mol}\cdot\text{dm}^{-3}$, pH = 0.02						
$\text{Th}(\text{OH}_2)_9^{4+}$	Th–O _I	9	2.462(4)	0.0039(3)	0.088(3)	L
	Th··O _{II}	18	4.657(8)	0.039(3)	0.28(1)	
	Th··O _{III}	12	6.85(-)	0.090(-)	0.42(-)	
	O _I ···O _{II}	2	2.715(8)	0.0034(4)	0.082(5)	
ClO_4^- (aq)	Cl–O	4	1.453(3)	0.0021(2)	0.065(3)	
	(Cl)–O···O	4	3.04(-)	0.0075(-)	0.122(-)	
	Cl(O)···O	4	3.70(-)	0.0250(-)	0.22(-)	
water bulk	O _w ···O _w	2	2.880(6)	0.0230(6)	0.214(3)	
Thorium(IV) Perchlorate in Water, $1.06 \text{ mol}\cdot\text{dm}^{-3}$, pH = –0.70						
$\text{Th}(\text{OH}_2)_9^{4+}$	Th–O _I	9	2.451(3)	0.0067(3)	0.164(4)	E
Thorium(IV) Perchlorate in Water, Hydrolyzed, $0.88 \text{ mol}\cdot\text{dm}^{-3}$, pH = 1.23 (Dimer and Tetramer)						
$50\% [(\text{H}_2\text{O})_6\text{Th}(\text{OH})_2\text{Th}(\text{H}_2\text{O})_6]^{8+} + 50\% [\text{Th}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$						
$\text{Th}(\text{OH}_2)_9^{4+}$	Th–O _{OH}	3	2.370(5)	0.0041(6)	0.091(7)	L
	Th··O _I	5	2.473(3)	0.0095(5)	0.138(4)	
	Th··O _{II}	10	4.667(5)	0.063(5)	0.35(2)	
	Th··Th	0.75	3.975(4)	0.0101(5)	0.142(4)	
	Th····Th	0.13	4.72(-)	0.023(-)	0.21(-)	
	Th····Th	0.13	6.53(-)	0.025(-)	0.26(-)	
	O _I ···O _{II}	2	2.768(8)	0.0110(9)	0.148(6)	
	O _I ···O _{II}	2	2.768(8)	0.0110(9)	0.148(6)	
ClO_4^- (aq)	Cl–O	4	1.453(3)	0.0021(2)	0.065(3)	
	(Cl)–O···O	4	3.04(-)	0.0075(-)	0.122(-)	
	Cl(O)···O	4	3.70(-)	0.0250(-)	0.22(-)	
Na^+ (aq)	Na–O	7	2.409(12)	0.032(3)	0.25(1)	
water bulk	O _w ···O _w	2	2.881(7)	0.0228(7)	0.213(3)	
Thorium(IV) Perchlorate in Water, $0.53 \text{ mol}\cdot\text{dm}^{-3}$, pH = 2.35 (Hexamer)						
$[\text{Th}_6\text{O}_8(\text{H}_2\text{O})_n]^{8+}$	Th–O	8	2.456(5)	0.0087(6)	0.132(3)	L
	Th··O _{II}	8	4.63(4)	0.045(4)	0.14(2)	
	Th··Th	1.33	3.973(2)	0.0085(2)	0.130(2)	
	Th····Th	0.625	4.719(12)	0.020(2)	0.20(1)	
	Th····Th	0.25	6.52(-)	0.024(-)	0.17(-)	
ClO_4^- (aq)	Cl–O	4	1.420(5)	0.0041(3)	0.091(4)	
	(Cl)–O···O	4	3.04(-)	0.018(-)	0.19(-)	
Na^+ (aq)	Na–O	7	2.403(11)	0.032(3)	0.25(1)	
Thorium(IV) Perchlorate in Water, Hydrolyzed, pH = 2.35						
$[\text{Th}_6\text{O}_8(\text{H}_2\text{O})_n]^{8+}$	Th–O _H	4.67	2.405(7)	0.0089(8)	0.187(7)	E
	Th··O _I	3.33	2.499(10)	0.0094(514)	0.194(4)	
	Th··Th	2.67	3.966(6)	0.0171(7)	0.26(1)	

using MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation at $295 \pm 1 \text{ K}$.³⁰ The structures of **1** and **2** were solved by standard direct methods in

the SHELXTL program package.³¹ The data were refined by full matrix least-squares on F^2 . Hydrogen atoms positions were solved geometrically, and refined in anisotropic approximation.

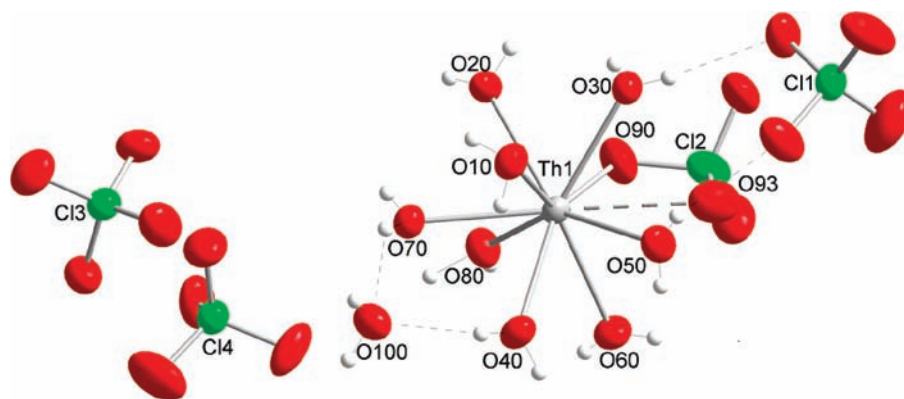
(30) SMART and SAINT, Area Detector Control and Integration Software; Bruker Analytical X-ray Systems: Madison, WI, 1995.

(31) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

Table 3. Crystallographic Measurement Data for $[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Th}(\text{H}_2\text{O})_6(\text{OSO}_2\text{CF}_3)_3]\text{CF}_3\text{SO}_3$ (**2**)^a

identification code	$[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$	$(\text{H}_5\text{O}_2)[\text{Th}(\text{H}_2\text{O})_6(\text{OSO}_2\text{CF}_3)_3][\text{Th}(\text{H}_2\text{O})_3(\text{OSO}_2\text{CF}_3)_6]$
empirical formula	H18 Cl4 O25 Th	H23 C9 F27 S9 O38 Th2
formula weight	791.977 u	2004.867 u
temperature	295(2) K	298(2) K
wavelength	0.71073 Å	0.71073 Å
crystal system	monoclinic	monoclinic
space group	$P2_1/n$ (No.14)	$P2_1/c$ (No.14)
unit cell dimensions		
<i>a</i>	9.9008(8) Å	11.792(5) Å
<i>b</i>	18.7330(15) Å	13.870(5) Å
<i>c</i>	10.9694(9) Å	32.426(14) Å
β	95.151(2)°	92.909(8)°
volume	2026.3(3) Å ³	5296(4) Å ³
<i>Z</i>	4	4
density (calculated)	2.596 Mg/m ³	2.513 Mg/m ³
absorption coefficient	8.002 mm ⁻¹	6.157 mm ⁻¹
<i>F</i> (000)	1504	3788
crystal size	0.48 × 0.32 × 0.10 mm ³	0.10 × 0.05 × 0.03 mm ³
θ range for data collection	2.16–29.01°	1.26–28.32°
absorption correction	Sadabs	Sadabs
reflections collected	12629	16033
independent reflections	4883 [<i>R</i> (int) = 0.0656]	11411
completeness to $\theta = 29.01^\circ$	90.7%	86.4%
max. and min transmission	0.4468 and 0.0144	0.83 and 0.52
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4883/15/339	11411/426/843
Goodness-of-fit on <i>F</i> ²	0.973	0.933
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0411, <i>wR</i> ₂ = 0.0994	<i>R</i> ₁ = 0.0962, <i>wR</i> ₂ = 0.2115
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0515, <i>wR</i> ₂ = 0.1033	<i>R</i> ₁ = 0.2726, <i>wR</i> ₂ = 0.2726
Largest diff. peak and hole	2.167 and -2.618 e.Å ⁻³	4.202 and -4.836 e.Å ⁻³

^a Definition of *R*: SHELX $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

**Figure 1.** Representation of the crystal structure of octaaqua(κ^2 O-perchlorato)thorium(IV) perchlorate, with thermal ellipsoids at 50% probability. Thin dashed lines show hydrogen bonding.

Selected crystal and experimental data are summarized in Table 3.

Results and Discussion

Crystal Structure of $[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (1**).** The crystal structure of octaaqua(κ^2 O-perchlorato)thorium(IV) perchlorate monohydrate, **1**, was solved and refined in the monoclinic space group $P2_1/n$ (No. 14), and consists of octaaqua(κ^2 O-perchlorato)thorium(IV) and perchlorate ions, and one water molecule in the lattice. The configuration around thorium(IV) ion is a severely distorted tricapped trigonal prism (*ttp*) with a Th–O mean bond distance of 2.470(6) Å, and an additionally bound oxygen atom from the perchlorate ion at 2.757(8) Å, Figure 1. Oxygen atoms O10, O20, O30, O40, O50, and O60 lie in the vertices of a trigonal prism. Two capping water oxygen atoms O70 and

O80, and the perchlorate oxygen atom O90 complete the *ttp* configuration. The perchlorate oxygen O93 is bound to thorium at a longer distance which causes the distortion in the *ttp*. This is reflected in the configuration of the coordinated perchlorate anion. Instead of normal tetrahedral angles, O–Cl–O angles range from 98.8 to 115.0° degrees. Coordination numbers larger than nine are not common, and if encountered, those usually involve small bidentate ligands. In **1**, 10 atoms are coordinated to thorium, 9 within common Th–O bond distances, and the 10th oxygen bond distance is rather long and outside the positions of the *ttp*, Figure 1. Considering a *ttp* configuration around thorium three triangles which represent the top plane of trigonal prism with O–Th–O angles of 66.79, 68.69, and 79.9°, a corresponding bottom plane with O–Th–O angles of 66.40, 68.8, and 92.95°, an equatorial capping plane with

O–Th–O angles of 126.94, 111.1, and 141.13° can be drawn. Three perchlorate anions act as counterions and one non-coordinated water molecule is present in the lattice. The hydrogen bonds from the bound water molecules to the lattice water molecule and perchlorate anions stabilize the structure. The mean Th–O bond distance to the capping oxygen atoms is slightly longer, 2.486 Å, than the mean Th–O bond distance to oxygen atoms in the prism, 2.463 Å; the perchlorate anion binds in a capping position, Figure 1.

The EXAFS study of **1** gave a mean Th–O bond distance of 2.450(7) Å and a large Debye–Waller factor coefficient of 0.0115(7) Å², showing a wide bond distance distribution as indeed found crystallographically. The Th–O bond distance determined by EXAFS is somewhat shorter than the mean value obtained from X-ray crystallography. This is most probably because the contribution of a single scattering event to the EXAFS function increases with decreasing Th–O distance and increasing Debye–Waller factor coefficient, and the observed mean value may become somewhat shorter than the real one. The obtained Th···Cl single and Th–O–Cl three-leg scattering paths are in good agreement with the distances observed in **1**. The structure parameters are summarized in Table 2, and the fitting of the EXAFS data are shown in Figure 2.

Crystal structure of (H₅O₂)[Th(H₂O)₆(OSO₂CF₃)₃]-[Th(H₂O)₃(OSO₂CF₃)₆] (2**).** The crystal structure of aquaioxonium hexaaquatris(*κ*O-trifluoromethanesulfonato)thorium(IV) trisquaahexakis(trifluoromethanesulfonato)thorinate(IV), H₅O₂[Th(H₂O)₆(OSO₂CF₃)₃][Th(H₂O)₃(OSO₂CF₃)₆], **2**, was solved and refined in the monoclinic space group *P*2₁/*n* (No. 14). It consists of individual hexaaquatris(*κ*O-trifluoromethanesulfonato)thorium(IV) and trisquaahexakis(*κ*O-trifluoromethanesulfonato)thorinate(IV) ions, and an aquaioxonium ion which bridges these two ions through hydrogen bonding. The hexaaquatris(*κ*O-trifluoromethanesulfonato)thorium(IV) ion binds three trifluoromethanesulfonate ions through one of their oxygen atoms and five water molecules in a square antiprism (*sap*), with an additional water molecule in a capping position. The mean Th–O bond distance to the trifluoromethanesulfonate oxygens is 2.410(16) Å, and the mean Th–O distance of the five water molecules in the *sap* is 2.458(17) Å, while the capping water molecule has a slightly longer distance, 2.538(16) Å. The mean Th–O distance is 2.451(17) Å, Figure 3. The anion has a *ttp* configuration, and binds the six trifluoromethanesulfonate oxygens coordinated via oxygen atoms in the prism with a mean Th–O distance of 2.388(16) Å, and three capping water molecules at a mean distance of 2.497(15) Å, giving a mean Th–O distance of 2.424(16) Å, Figure 3. It is common in nine-coordinate actinoids that the capping water molecules are bound at slightly longer distances. Such a configuration may be explained from a thermodynamic point of view if the formation of two structural units is governed by an enthalpy factor.³

Four hydrogen bonds were found within **2**. The aquaioxonium ion forms two hydrogen bonds to two trifluoromethanesulfonate ions thus, holding the two structural units together, Figure 3. The EXAFS study of **2** gave a mean Th–O bond distance of 2.448(5) Å and a Debye–Waller factor coefficient of 0.0105(5) Å². The large

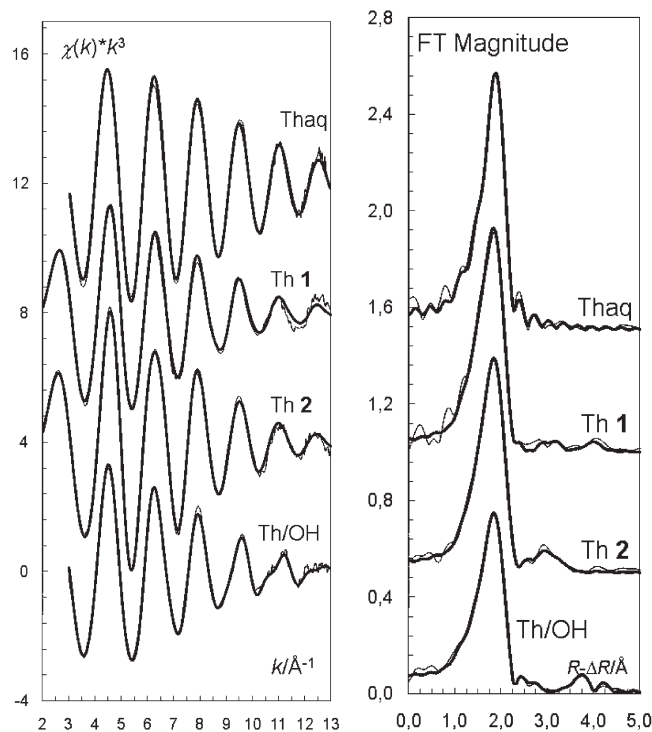


Figure 2. (a) Fit of EXAFS data and (b) their respective Fourier transforms for the solutions Thaq, Th 1, Th 2, Th 3 (as listed in Table 1). The EXAFS data are offset by 4 (cumulative) for each solution, respectively, and the Fourier transforms by 1.5.

Debye–Waller factor coefficient is in agreement with the large bond distance distribution found in **2**, 0.18 Å. The observed Th···S single scattering path, 3.851(12), is in good agreement with the distances observed in **2**. The structure parameters are summarized in Table 2, and the fit of the EXAFS data is given in Figure 2.

Hydrated Thorium(IV) Ion in Aqueous Solution. The EXAFS functions of the acidic aqueous solution of thorium(IV) perchlorate can be fitted using only one Th–O bond distance giving a mean Th–O bond distance of 2.45(1) Å of the hydrated thorium(IV) ion, Table 2 and Figure 2. No multiple scattering was detected in these EXAFS functions indicating a complex with low symmetry. In comparison to the crystal structure of **1**, the thorium(IV) ion appears to be coordinated only by water molecules in aqueous solution, as neither any Th···Cl nor Th–O–Cl scattering paths were detected.

The RDFs from the LAXS experiments of thorium(IV) perchlorate solutions show a distinct peak at 2.45(1) Å for the 1.06 mol·dm⁻³ thorium solution in 5 mol·dm⁻³ HClO₄ and 2.46(1) Å for the 0.54 mol·dm⁻³ thorium solution with pH = 0.02, corresponding to the Th–O distance in the first hydration sphere, Figure 4, and Supporting Information, Figure S3. Large peaks at 4.55(2) Å and 4.66(2) Å originate from the second hydration sphere. In the latter solution the best fit was obtained with a total of 18 water molecules forming the second hydration sphere, whereas in the more concentrated solution, the best fit was obtained with 13 water molecules, which shows a lack of water to form a complete second hydration sphere. The more diluted solution also shows traces of a third hydration shell at 6.85(5) Å, Supporting Information, Figures S3 and S4. The broad

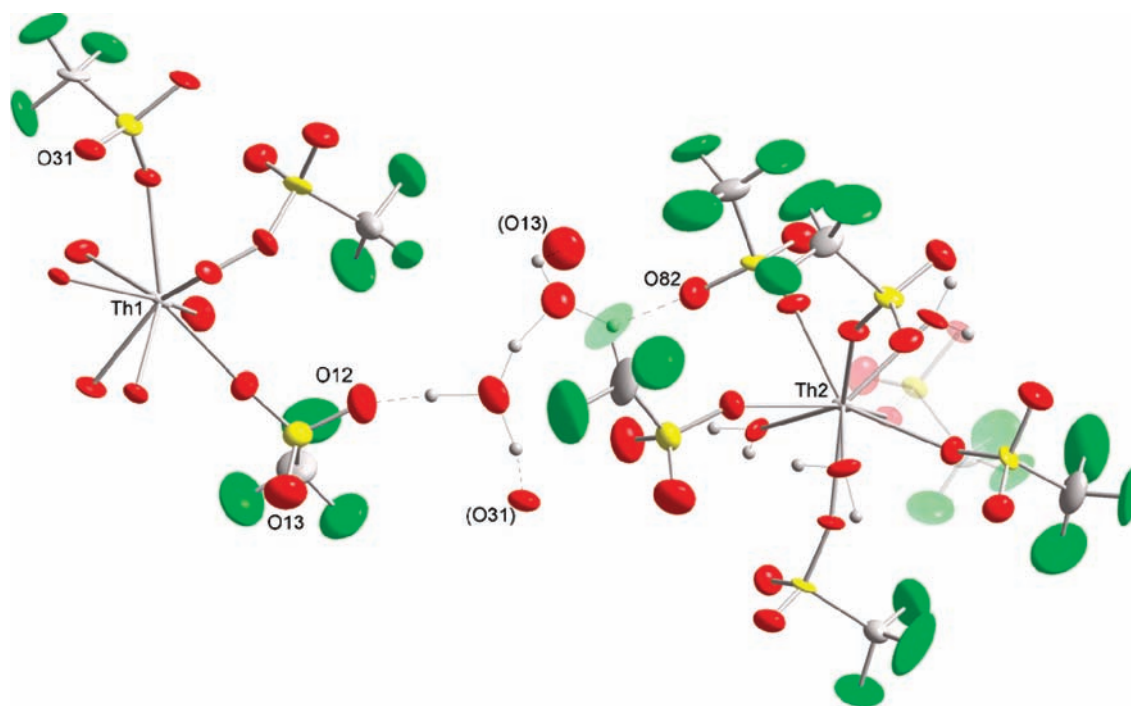


Figure 3. Representation of the crystal structure of hexaaquatrakis(κ O-trifluoromethane-sulfonato)thorium(IV) trifluoromethanesulfonato. The overlapping fluorine atom (F72) has been faded for the purpose of clarity of showing the hydrogen bonding network. One of the trifluoromethanesulfonate ions (No. 9), pointing inward, has also been faded for the purpose of clarity. The connections to the extended crystal structure are marked with the appropriate oxygen atom labels in parentheses.

peaks at 2.79 Å for the more concentrated solution and 2.72 Å for the more diluted one correspond to the $O_I \cdots O_{II}$ distances between the first and second hydration sphere. The hydrogen bond distance is consistent for what is expected for a metal ion with high polarizing power, with a charge to ionic radius ratio, $q/r = 3.7$. In this respect, thorium(IV) can be placed in the same group as rhodium(III), chromium(III), and aluminum(III).³² A small peak at 3.04 Å corresponds to the hydrogen bonds between the water molecules and the perchlorate ions.

The thorium(IV) ion is strongly hydrated with a mean Th–O bond distance of 2.45(1) Å. This Th–O bond distance strongly indicates that the hydrated thorium(IV) ion is nine-coordinated, probably in *ttp* fashion even though monocapped square antiprismatic (*m-sap*) or other nine-coordinated configurations cannot be excluded, in acidic aqueous solution in a similar way as observed in the hydrated thorium(IV) ion in the solid hydrates **1** and **2** but with only water as ligand. This Th–O bond distance was also reported in previous studies, but then associated to higher coordination numbers.^{5–7} The difference in Th–O bond distance between water molecules in the prism and the capping positions is smaller than in the hydrated lanthanoid(III) and actinoid(III) ions.^{33,34} This is probably due to the much higher polarizing effect of the tetravalent

ions and thereby stronger electrostatic bonds to the hydrating water molecules.

Hydrolyzed Thorium(IV) Ion in Aqueous Solution. The distribution of thorium(IV) hydrolysis species depends on the level of pH, the total thorium(IV) concentration, and the $\text{OH}^-/\text{Th}^{4+}$ ratio in the complex, n . The higher the total thorium concentration, the lower the pH value will be at which polynuclear species start to form. At the total thorium(IV) concentrations used in this study, 0.53–1.06 mol·dm⁻³, the hydrolysis starts below pH = 1, and polymeric species are strongly dominating. Dimers are formed when $n = 1$ and tetramers when $n = 2$. The structure of the dimer is assumed to be similar to those described crystallographically,^{9–12} while the structures of the higher hydrolysis species are not yet described. The LAXS measurement on the solution with a pH value of 1.23 showed that the number of Th···Th distances at about 4.0 Å is about 50% larger than a contribution from only dimeric species. Furthermore, there are small though still significant contributions in the RDF at 4.7 and 6.6 Å which correspond to Th···Th distances in, for example, a tetramer. The observed Th···Th distances fit very well with a diamond shaped tetramer with Th···Th···Th angles of about 70 and 110°. The $\text{Th}(\text{OH})_2\text{Th}$ units with double $\mu^2\text{O}$ -hydroxo bridges, as in the dimer, see Figure 5, are expected to be the main building blocks also in the tetramer. Cyclic tetrameric hydrolysis species of the tetravalent zirconium and hafnium ions with the composition $[\text{M}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ have a square planar configuration with double hydroxo bridges between the metal ions and with four terminally bound water molecules to every metal ion in a distorted *sap*.³⁵ The corresponding

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(33) (a) Persson, I.; D'Angelo, P.; De Panfilis, S.; Sandström, M.; Eriksson, L. *Chem.—Eur. J.* **2007**, *14*, 3056–3066. (b) Abbasi, A.; Lindqvist-Reis, P.; Eriksson, L.; Sandström, D.; Lidin, S.; Persson, I.; Sandström, M. *Chem.—Eur. J.* **2005**, *11*, 4066–4077.

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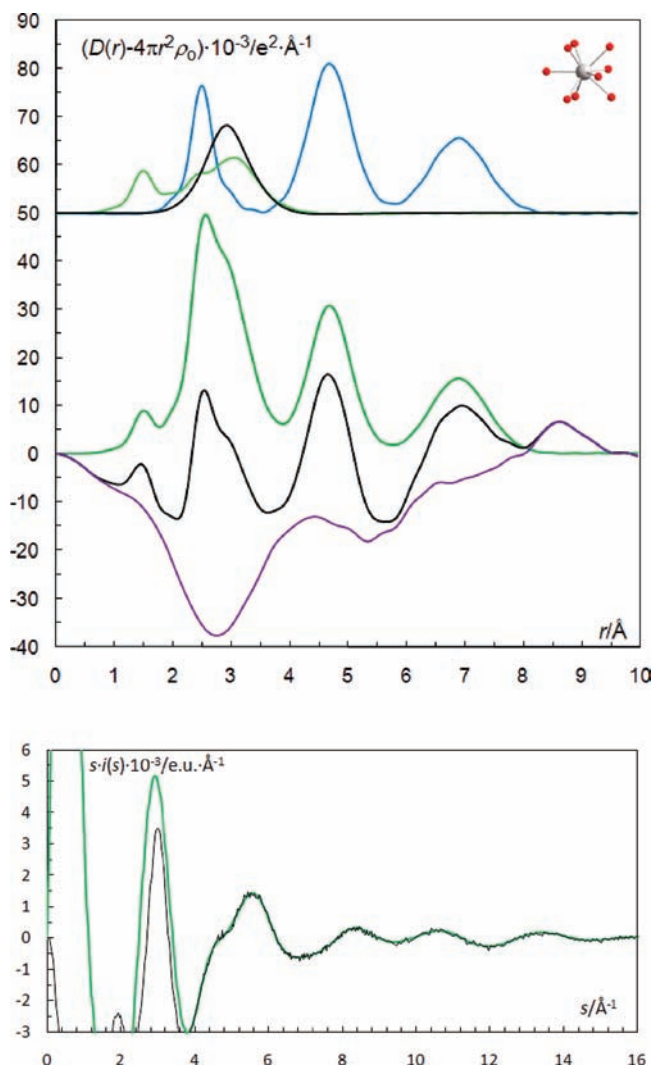


Figure 4. (Top) LAXS radial distribution curves for a $0.54 \text{ mol} \cdot \text{dm}^{-3}$ acidified aqueous solution of thorium(IV) perchlorate. Upper part: Separate model contributions (offset: 50) of the hydrated thorium(IV) ion (blue line), the perchlorate ion (green line), and bulk water (black line). (Middle) Experimental RDF: $D(r) - 4\pi r^2 \rho_0$ (black line), sum of model contributions (dark green line); difference (purple line). (Bottom) Reduced LAXS intensity functions $s \cdot i(s)$ (thin black line); model $s \cdot i_{\text{calc}}(s)$ (dark green line).

tetrameric thorium(IV) hydrolysis complex seems to have the same composition, but the angles around the metal ions are less strained as the angles around the thorium(IV) ions are close to the ideal ones of a square antiprism. The reason for the observed difference between thorium(IV) on one hand, and zirconium(IV) and hafnium(IV) on the other, is probably the higher charge density on the metal ions causing a significant repulsion between the metal ions in the latter, while in the thorium complex the repulsion is smaller and the ideal geometry for *sap* fashion is obtained.

Refinement of the LAXS data on the solution with pH 1.23 showed that the number of $\text{Th} \cdots \text{Th}$ distances at 4.0 \AA is about 0.75 per thorium, and at 4.7 and 6.5 \AA there are about 0.13 $\text{Th} \cdots \text{Th}$ distances per thorium; the error in the number of $\text{Th} \cdots \text{Th}$ distances per thorium is estimated to 20%. This gives a composition of about 50% of the thorium present as dimers and about 50% as tetramers. The mean $\text{Th}-\text{O}$ bond distance to the bridging

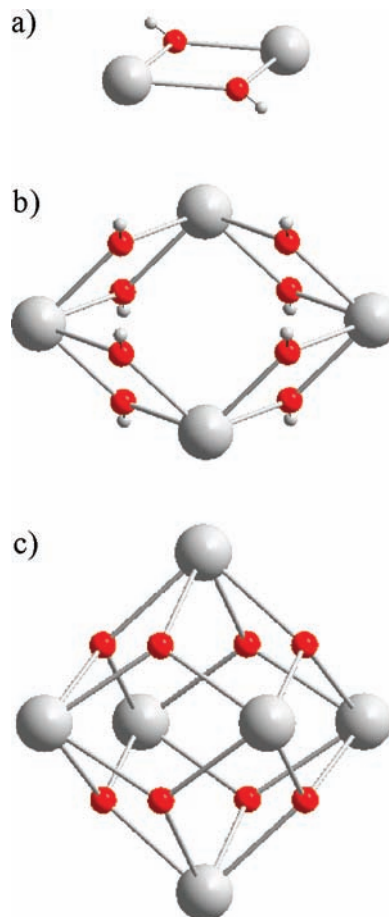


Figure 5. Schematic structures of the (a) dimeric, (b) tetrameric, and (c) hexameric hydrolysis complexes of thorium(IV).

hydroxo group was refined to $2.37(1) \text{ \AA}$, and the $\text{Th}-\text{O}$ bond distances to the terminal water molecules was refined to $2.47(1) \text{ \AA}$, Table 2. The mean $\text{Th} \cdots \text{Th}$ bond distance in the dimer ($0.25 \text{ Th} \cdots \text{Th}$ (fixed)) and the tetramer ($0.50 \text{ Th} \cdots \text{Th}$ (fixed)) was refined to $3.97(1) \text{ \AA}$. It can be expected that the $\text{Th} \cdots \text{Th}$ distance in the dimer and tetramer is similar as the surrounding of thorium in these two complexes is almost the same. The longer diagonal $\text{Th} \cdots \text{Th}$ distances in the diamond shaped tetramer were not refined, instead these distances were varied to the best possible fit in the RDF. The oxygen atoms of the water molecules in the second hydration sphere, O_{II} , are most probably hydrogen bound to the terminal water molecules, and were refined to $4.67(2) \text{ \AA}$. The refined structure parameters of the mean $\text{Th}-\text{O}$, $\text{Th} \cdots \text{Th}$, and $\text{Th} \cdots \text{O}_{\text{II}}$ distances and the hydrated perchlorate ion are summarized in Table 2, and the fit of the intensity function and the RDF are given in Figure 6.

Refinement of the LAXS data on the solution with pH = 2.35 showed that the number of $\text{Th} \cdots \text{Th}$ distances at 4.0 \AA is about 1.33 per thorium, and at 4.7 and 6.5 \AA there are about 0.83 and 0.33 $\text{Th} \cdots \text{Th}$ distances per thorium, respectively; the error in the number of $\text{Th} \cdots \text{Th}$ distances per thorium is estimated to 10, 10, and 20%, respectively. This set of distances strongly indicates predomination of a hexamer with the same diamond shaped tetramer in one plane and another diamond perpendicular

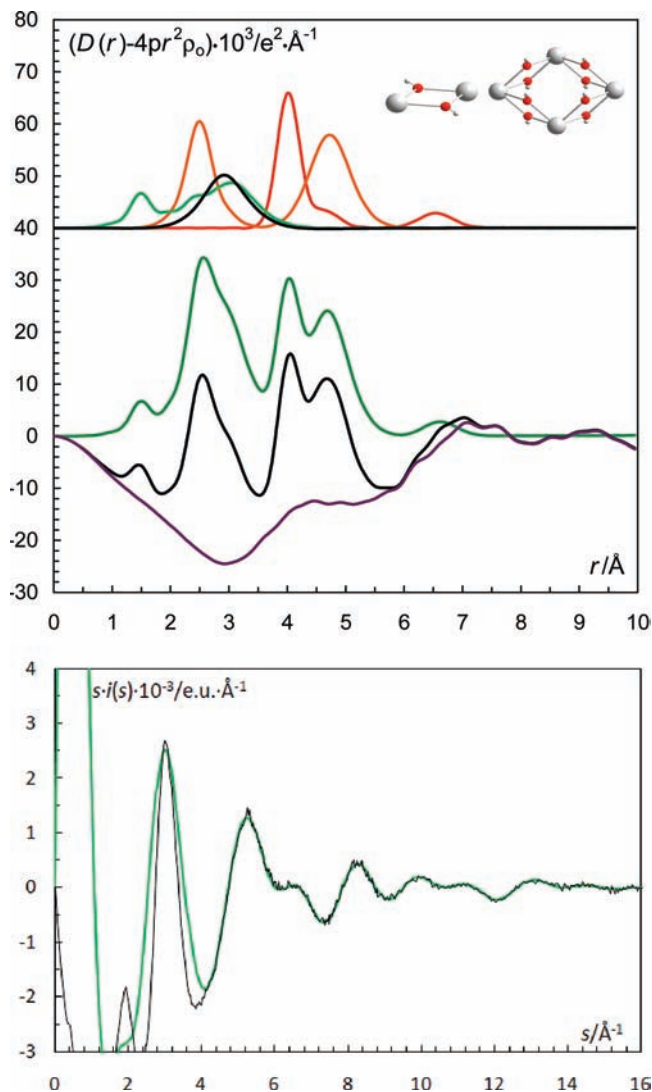


Figure 6. (Top) LAXS radial distribution curves for a dimer/tetramer hydrolyzed aqueous solution of thorium(IV) perchlorate, pH = 1.23. Upper part: Separate model contributions (offset: 40) of the hydrolyzed thorium(IV) dimer (red line), tetramer (orange line), the perchlorate ion (green line), and bulk water (black line). (Middle) Experimental RDF: $D(r) - 4\pi r^2 \rho_0$ (black line); sum of model contributions (thin gray line); difference (thin blue line). (Bottom) Reduced LAXS intensity functions $si(s)$ (thin black line); model $si_{\text{calc}}(s)$ (dark green line).

to the first diamond plane forming a rhomboctahedral configuration, Figure 5. To form a stable and rigid hexamer with three well-defined Th···Th distances it is very likely that all Th···Th distances are separated by double μ^2O -hydroxo bridges giving a core composition of $[\text{Th}_6(\text{OH})_{16}]^{8+}$. However, a model of such a complex shows that the oxygens of the hydroxide groups from the perpendicular Th_4 planes coincide, Supporting Information, Figure S1, making the $[\text{Th}_6(\text{OH})_{16}]^{8+}$ composition structurally impossible. Instead, the hexameric structure must be described as where the two additional thorium(IV) ions bind to oxygens above and below the Th_4 plane in the tetrameric structure and that the protons on these oxygens are released forming a $[\text{Th}_6\text{O}_8]^{8+}$ oxo complex. This complex is equivalent to a $[\text{Th}_6(\text{OH})_{16}]^{8+}$ complex from a proton activity point-of-view, and therefore impossible to distinguish from each other in methods measuring proton activity. The hexameric complexes

proposed from potentiometric measurements, $[\text{Th}_6(\text{OH})_{14}]^{10+}$ and $[\text{Th}_6(\text{OH})_{15}]^{9+}$, most certainly have the compositions $[\text{Th}_6\text{O}_6(\text{OH})_2]^{10+}$ and $[\text{Th}_6\text{O}_7(\text{OH})]^{9+}$, respectively. These complexes will have a lower symmetry than a $[\text{Th}_6\text{O}_8]^{8+}$ complex and should therefore be less stable. It therefore seems likely that the $[\text{Th}_6\text{O}_8]^{8+}$ complex is the dominating hydrolyzed thorium(IV) species in aqueous solution very close to the conditions for precipitation of hydrated thorium(IV) hydroxide. The refined Th–O_{oxo} distance is slightly longer, 2.405 Å, than observed in the dimer and the tetramer, 2.37 Å. This is expected as the oxygens in O^{2-} and OH^- have different ionic radii, 1.40 and 1.37 Å, respectively.² The Th–O_{H₂O} and Th···Th distances of the hexamer are in very good agreement with those obtained for the dimer and tetramer indicating a similar structural build-up, but with oxo groups bridging three thorium(IV) ions. An EXAFS study of the hexamer supports the structure parameters obtained by LAXS, but with better resolution between the Th–O_{oxo} and Th–O_{H₂O} bond distances and a significant contribution from the shortest Th···Th distance, whereas the contribution from the longer Th···Th distances are negligible, Table 2. Refinement of the short diagonal Th···Th distance from the LAXS data was refined to 4.72(4) Å, whereas the long diagonal Th···Th distance in the rhomboctahedron was varied to obtain the possible fit in the RDF, 6.50 Å. The water molecules in the second hydration sphere, O_{II}, which most probably are hydrogen bound to the terminal water molecules, were refined to 4.63(4) Å. The refined structure parameters of the hexamer are summarized in Table 2, the fit of the intensity function and the RDF are given in Figure 7, and the fit of the EXAFS data is given in Figure 2. The mechanism of the formation of the hexamer is unknown and can be subject for further investigation. We assume that when a hexamer is formed, water molecules on the incoming thorium(IV) species and protons on the μ^2O -hydroxide groups on the tetramer are released.

For uranium(IV) a similar structure with an $\text{U}_6\text{O}_8^{8+}$ core in rhomboctahedral configuration has been reported.³⁶ All other hexameric uranium compounds show an octahedral configuration of the uranium atoms, but here the mean oxidation number is higher than four causing a higher repulsion between them and, thereby higher symmetry.³⁷

Overview of the Structures of the Hydrated Actinoid(IV)

Ions. One of the features of the actinoids is the presence of 5f electrons, and in comparison to lanthanoid series with 4f electrons, the 5f orbital is more shielded from the nuclear charge and thereby able to participate in the bond formation up to neptunium.¹ The oxidized forms of actinoids have often high charge and large ionic radii making them hard Lewis acids, which easily release protons in aqueous solution and therefore are very prone to hydrolysis. Within the same oxidation state, for example, +IV, and for a given coordination number there is steady decrease in the ionic radii of the actinoids because of the actinoid contraction.² A survey of

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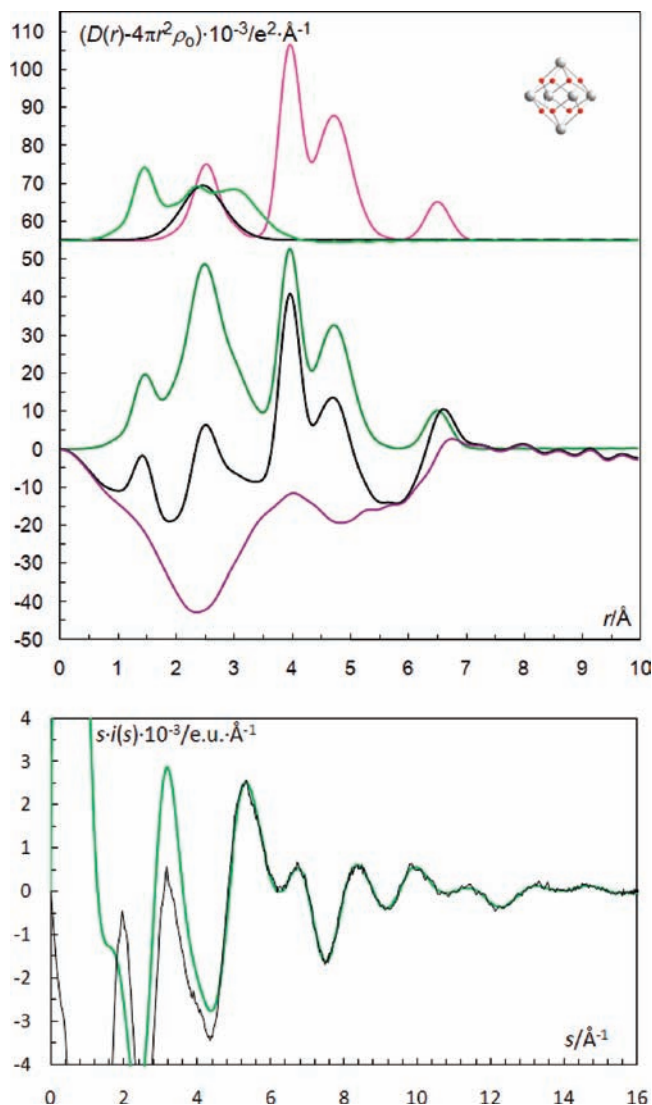


Figure 7. (Top) LAXS radial distribution curves for a hexamer hydrolyzed aqueous solution of thorium(IV) perchlorate, pH = 2.35. Upper part: Separate model contributions (offset: 55) of the hydrolyzed thorium(IV) hexamer (pink line), the perchlorate ion (green line) and bulk water (black line). (Middle) Experimental RDF: $D(r) - 4\pi r^2 \rho_0$ (black line); sum of model contributions (thin gray line); difference (thin blue line). (Bottom) Reduced LAXS intensity functions $si(s)$ (thin black line); model $si_{\text{calc}}(s)$ (dark green line).

thorium(IV) containing crystal structures gives a mean Th–O bond distance of 2.571 Å when the coordination number is 12 (CN = 12) {12 structures}; 2.537 Å for CN = 11 {3}; 2.501 Å for CN = 10 {21}; 2.451 Å for CN = 9 {21}; 2.408 Å for CN = 8 {25}; 2.357 Å for CN = 7 {1} and 2.301 Å for CN = 6 {2}, Table 4. This survey shows that the mean Th–O bond distance is significantly different for every coordination number, and that the variation in bond distance at a given coordination number is small, and indeed smaller than the difference between two neighboring coordination numbers, Table 4. The An–O bond distances in the crystal structures of thorium(IV), uranium(IV), neptunium(IV), and plutonium(IV) complexes and salts with mono- and bidentate neutral and anionic oxygen donor ligands are summarized in Table 4, Supporting Information, Tables S4–S7, and Figure 8. The expected trend is independent of

Table 4. Mean Actinoid(IV)/Oxygen Bond Distances, in Å, As Function of the Coordination Number^a

coordination number	Th–O	U–O	Np–O	Pu–O
6	2.301 {2}	2.277 {2}	n/a	n/a
7	2.357 {1}	n/a	n/a	n/a
8	2.408 {25}	2.363 {16}	2.343 {6}	2.329 {7}
9	2.451 {20}	2.409 {3}	2.403 {2}	2.386 {1}
10	2.501 {21}	2.456 {6}	2.454 {1}	2.429 {1}
11	2.537 {3}	n/a	n/a	n/a
12	2.571 {12}	2.510 {3}	2.504 {2}	2.484 {1}

^aThe number of structures obtained from the literature for each actinoid and coordination number is given within the {} brackets. Full references are listed for each element in Tables S4–S7.

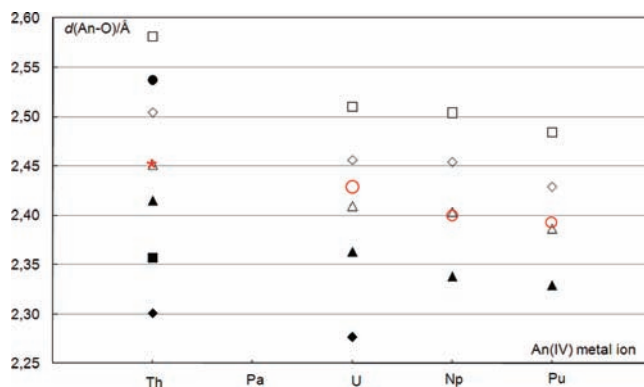


Figure 8. Overview of the actinoid(IV)/oxygen bond distances and their corresponding coordination numbers from crystallographic data of oxygen donor ligands, Supporting Information, Tables S4–S7 (♦ CN = 6, ■ CN = 7, ▲ CN = 8, △ CN = 9, ◇ CN = 10, ● CN = 11, □ CN = 12); asterisks, EXAFS Th–O bond distance in this work; red circles, EXAFS An–O bond distances as reported in refs 7 (U–O); 35,36 (Np–O); and 37,38 (Pu–O).

coordination number, and the mean An–O bond distance is well-defined *within* each coordination number. The hydrated uranium(IV) ion in aqueous solution is reported to have a mean U–O bond distance of 2.43 Å and a coordination number of 10.8 ± 0.5 .⁷ However, the reported U–O bond distance corresponds to the coordination number 9, Figure 8; the U–O bond distance for CN = 9, 2.409 Å, based on only three crystal structures, seems to be too short in comparison with the values for thorium(IV) with CN = 8 and 10, and the other lanthanoid(IV) ions with CN = 9, Table 5, and a more reasonable value is 2.42–2.43 Å. A repeated study shows that EXAFS data of an aqueous uranium(IV) solution with the same composition as reported by Moll et al.⁷ is equally well-fitted with CN = 9 giving the same U–O bond distance, 2.423(3) Å, and an almost identical Debye–Waller coefficient, 0.0092 Å², see Supporting Information, Figure S2 for fit of EXAFS data in this study.

Two EXAFS studies of the hydrated neptunium(IV) ion in acidic aqueous solution have reported a mean Np–O bond distance of 2.40 Å and CN = 10 and 11.^{38,39} On the basis of the crystallographic data, Table 5, and Figure 8, it is obvious that with a Np–O bond distance of

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Table 5. Summary of Ionic Radii of Actinoid(IV) Ions^a

	CN = 6		CN = 7		CN = 8		CN = 9		CN = 10		CN = 11		CN = 12	
	$r_{\text{Sh}}/\text{\AA}$	$r/\text{\AA}$	$r_{\text{Sh}}/\text{\AA}$	$r/\text{\AA}$	$r_{\text{Sh}}/\text{\AA}$	$r/\text{\AA}$	$r_{\text{Sh}}/\text{\AA}$	$r/\text{\AA}$	$r_{\text{Sh}}/\text{\AA}$	$r/\text{\AA}$	$r_{\text{Sh}}/\text{\AA}$	$r/\text{\AA}$	$r_{\text{Sh}}/\text{\AA}$	$r/\text{\AA}$
Th ^{IV}	0.94	0.961	n/a	1.017	1.067	1.075	1.09	1.110	1.13	1.160	1.18	1.198	1.21	1.229
Pa ^{IV}	0.90	0.95	n/a	n/a	1.01	1.05 ^b	n/a	1.09 ^b	n/a	1.14 ^b	n/a	n/a	n/a	1.21 ^b
U ^{IV}	0.89	0.937	0.95	n/a	1.00	1.026	1.05	1.076	n/a	1.121	n/a	n/a	1.17	1.182
Np ^{IV}	0.87	n/a	n/a	n/a	0.98	1.005	n/a	1.059	n/a	1.102	n/a	n/a	n/a	1.158
Pu ^{IV}	0.86	n/a	n/a	n/a	0.96	0.985	n/a	1.041	n/a	1.082	n/a	n/a	n/a	1.135

^aListed by Shannon for six-, seven-, eight-, nine-, ten-, eleven-, and twelve-coordination, r_{Sh} (ref 2.) whenever available, and the corresponding calculated ionic radii for six-, seven-, eight-, nine-, ten-, eleven-, and twelve-coordination based upon the reported actinoid(IV) complexes and compounds by neutral, monodentate oxygen donor ligands, Supporting Information, Tables S4–S7, assuming an atomic radius of 1.34 Å for oxygen (refs 39. and 40). CN = coordination number. ^bNo values determined experimentally, but estimated through interpolation.

2.40 Å the coordination number has been overestimated and CN = 9 seems much more reasonable. An EXAFS study of plutonium(IV) in 1 mol·dm⁻³ perchloric acid reported 8–10 aqua ligands at 2.39 Å, whereas the Pu–O bond distance in the hydrated plutonium(III) ion is 2.48 Å with the same number of aqua ligands in acidic solution.^{40,41} A Pu–O distance of 2.39 Å for the hydrated plutonium(IV) ion correlates very well with CN = 9, Table 4 and Figure 8. Thus, the result of thorium(IV) in this study, and the reported U–O, Np–O and Pu–O bond distances of the hydrated uranium(IV), neptunium(IV) and plutonium(IV) ions in acidic aqueous solution, strongly indicate that they all display the same coordination number, namely, 9. It is not possible from the present data or other data reported in the literature to determine the absolute configuration of these ions in aqueous solution. However, in complexes with mainly electrostatic interactions with ligands without space-demanding properties, nature strives toward the highest possible symmetry, where a tricapped trigonal prismatic configuration seems to be the most likely one. This configuration maximizes hydrogen bonding as has been found in the structurally similar lanthanoids.^{33,34}

The fairly large number of reported crystal structures of actinoid(IV) complexes and compounds with monodentate oxygen donor ligands makes it possible to propose more accurate ionic radii than those proposed by Shannon,² which were based on very limited statistics, estimates, and calculated values. We have, in a separate study on the lanthanoid(III) ions,⁴² shown that the size of the oxygen atom in coordinated water and neutral monodentate oxygen donor ligands, except tetrahydrofuran and other ethers, have the same atomic radius, 1.34 Å, the value suggested by Beattie et al.⁴³ A noticeable difference was seen in the lanthanoid(III) study between neutral and non-neutral O-donor ligands.⁴² Nevertheless, for statistical purposes, we found that an inclusion of anionic O-donors was necessary to reach a suitable number of tetravalent actinoid structures. The underlying

reason for this alternation is the higher charge density on the actinoid(IV) ions, and should be kept in mind when comparing An–O distances with different oxygens.

By subtracting the radius of the oxygen from the mean An–O bond distances in Supporting Information, Tables S4–S7, summarized in Figure 8, improved ionic radii for the actinoid(IV) ions (Th–Pu) for the coordination numbers 6–12 can be obtained, Table 5 and Supporting Information, Figure S4. Furthermore, the regular pattern in ionic radii for the actinoid(IV) ions makes it possible to safely predict the ionic radii of protactinium(IV) for CN = 8, 9, 10, and 12 and neptunium(IV) for CN = 10, Supporting Information, Figure S4. The predictions have been limited to those CNs where sufficient data is available. The actinoid contraction, with steadily decreasing ionic radii over the series, can be seen for all coordination numbers.

Conclusions

- In the solid thorium(IV) hydrates of perchlorate and trifluoromethanesulfonate thorium binds to the anion and no pure homoleptic hydrates are formed. The prevailing coordination number of these complexes is nine but with two different configurations, tricapped trigonal prism and monocapped square antiprism.
- The hydrated thorium(IV) has a mean bond distance of 2.45(1) Å in aqueous solution which is in full accordance with previous studies.^{5–7} This Th–O bond distance strongly indicates that the hydrated thorium(IV) ion is nine-coordinated in acidic aqueous solution. The presence of a second hydration sphere of about 18 water molecules and traces of a third hydration have been shown by LAXS.
- The hydrated thorium(IV), uranium(IV), neptunium(IV), and plutonium(IV) ions seem to be nine-coordinated in acidic aqueous solution.
- Three types of hydrolysis species of thorium(IV) were identified in aqueous solution, a dimer, [Th₂(OH)₂(H₂O)₁₂]⁶⁺, with double μ^2 O-hydroxo bridges between the thorium(IV) ions, a tetramer, [Th₄(OH)₈(H₂O)₁₆]⁸⁺, with the thorium(IV) ions forming a diamond and with double μ^2 O-hydroxo bridges between the thorium(IV) ions as in the dimer, and a hexamer, [Th₆O₈(H₂O)_n]⁸⁺, where each μ^3 O-oxo group binds to three thorium(IV) ions and the six thoriums form a rhomboctahedron with Th···Th···Th angles of 70 and 110 °,

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Figure 5. At the formation of the hexamer the protons in the μ^2O -hydroxo bridges in the tetramer are replaced by two thorium(IV) ions, as there is no space for 16 bridging μ^2O -hydroxo groups with the Th...Th distances experimentally observed.

- On the basis of the summary of all actinoid(IV) (Th–Pu) complexes with oxygen donor ligands reported in the solid state, improved ionic radii for these ions with CN = 6–12 have been proposed, Table 5.

Acknowledgment. The financial support from the Swedish Research Council and the Visby Program through the Swedish Institute is gratefully acknowledged, as well as the technical support to the crystallographic

studies from Mrs. Ann-Sofi Ullström. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. The SSRL Structural Molecular Biology Program is supported by the Department of Energy, Office of Biological and Environmental Research, and by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program.

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