

Linking Solution Structures and Energetics: Thorium Nitrate Complexes

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Crystallographic Structure Refinement.

Table S1. Crystal Data and Structure Refinements for $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_4$ and $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_3 \cdot (\text{H}_2\text{O})_2$.^a

	$\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_4$	$\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_3 \cdot (\text{H}_2\text{O})_2$
Fw	552.14	570.16
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Fdd2$
<i>Z</i>	4	8
<i>a</i> , Å	7.354(1)	11.1411(6)
<i>b</i> , Å	17.441(3)	22.732(1)
<i>c</i> , Å	9.149(2)	10.5378(6)
β , °	99.852(2)	/
<i>V</i> , Å ³	1156.2(3)	2668.8(3)
ρ_c , g/cm ³	3.172	2.838
μ , cm ^{−1}	130.1	112.8
<i>R(F)</i> ^b	0.0234	0.0181
<i>R_w(F_o²)</i> ^c	0.0491	0.0435

^aFor both structures, $T = 100(2)$ K, $\lambda = 0.71073$ Å. ^b $R(F) = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.
^c $R_w(F_o^2) = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w F_o^4\}^{1/2}$ for all data.

Table S2a. Selected Th-ligand distances and coordination numbers obtained from the Th(NO₃)₄(H₂O)₄ single-crystal structural refinement.

	Coord. No.	Distance (Å)	Average (Å)
Total (O)	12		
- O water	4	2.461(2) – 2.585(2)	2.52(5)
- O nitrate	8	2.555(2) – 2.638(2)	2.60(3)
Other Th correlations			
- H water	8	2.95(4) – 3.13(4)	3.04(6)
- N nitrate	4	3.024(3) – 3.063(3)	3.04(2)
- Th	12	6.8583(7) - 8.722(1)	7.5(9)

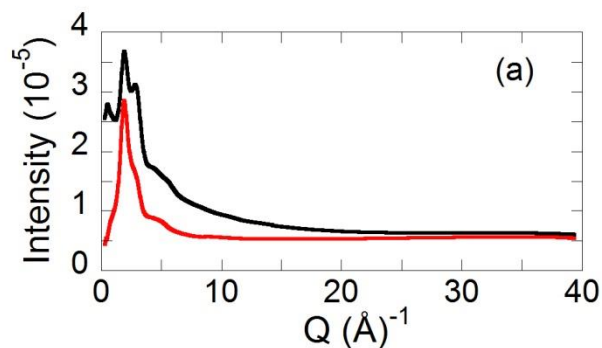
Table S2b. Selected Th-ligand distances and coordination numbers obtained from the Th(NO₃)₄(H₂O)₃·(H₂O)₂ single-crystal structural refinement.

	Coord. No.	Distance (Å)	Average (Å)
Total (O)	11		
- O water	3	2.408(6) – 2.457(4)	2.44(2)
- O nitrate	8	2.525(3) – 2.626(3)	2.58(4)
Other Th correlations			
- H water	6	2.96(6) – 3.01(6)	2.99 (2)
- N nitrate	4	3.017(4) – 3.022(4)	3.020(3)
- Th	8	6.8553(3) – 7.6676(3)	7.3(9)

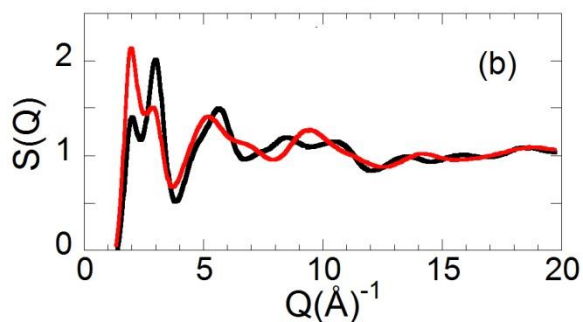
Description of Hydrogen Bonding in Solid Phases. Th(NO₃)₄(H₂O)₄ crystallizes in the monoclinic space group $P2_1/n$ with one crystallographically unique Th, four N, and sixteen O positions (twelve for nitrate anions and four for water molecules). All these atoms sit on the general position, $4e$ with the site symmetry of 1. Th(NO₃)₄(H₂O)₃·(H₂O)₂ crystallizes in the higher symmetry orthorhombic space group $Fdd2$ with one crystallographically unique Th, two N, and nine O positions (six for nitrate anions and three for water molecules). Th and OW1 sit on the special position, $8a$ with the site symmetry of $.2$, whereas the other atoms occupy the general position $16b$ with the site symmetry of 1. Besides the variation in the metal coordination environments in the tetrahydrate and trihydrate, the hydrogen bonding that stitches the metal nitrate complexes together is drastically different in the two structures. The tetrahydrate is

formed by relatively weak intermolecular water-nitrate hydrogen bonds between $[\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_4]$ complexes. More specifically, eight hydrogen atoms in each $[\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_4]$ complex involve fifteen hydrogen bonds with nitrate anions from neighboring units. They include $\text{Ow}(2)-\text{H}(4)\cdots\text{O}(9)$ (2.796(3) Å), $\text{Ow}(4)-\text{H}(8)\cdots\text{O}(13)$ (2.805(3) Å), $\text{Ow}(4)-\text{H}(7)\cdots\text{O}(7)$ (2.855(3) Å), $\text{Ow}(1)-\text{H}(2)\cdots\text{O}(10)$ (2.942(3) Å), $\text{Ow}(2)-\text{H}(3)\cdots\text{O}(14)$ (2.990 (3) Å), $\text{Ow}(3)-\text{H}(6)\cdots\text{O}(6)$ (3.025(3) Å), $\text{Ow}(2)-\text{H}(3)\cdots\text{O}(7)$ (3.063 (3) Å), $\text{Ow}(3)-\text{H}(5)\cdots\text{O}(5)$ (3.073(3) Å), $\text{Ow}(2)-\text{H}(3)\cdots\text{O}(16)$ (3.130(3) Å), $\text{Ow}(3)-\text{H}(5)\cdots\text{O}(13)$ (3.153(3) Å), $\text{Ow}(1)-\text{H}(2)\cdots\text{O}(11)$ (3.172(3) Å), $\text{Ow}(3)-\text{H}(6)\cdots\text{O}(7)$ (3.193(3) Å), $\text{Ow}(1)-\text{H}(1)\cdots\text{O}(16)$ (3.203(3) Å), and $\text{Ow}(4)-\text{H}(7)\cdots\text{O}(16)$ (3.343(3) Å), in the order of increasing interatomic distances between the hydrogen bond donor and acceptor. In contrast, $[\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_3]$ complexes in the structure of trihydrate are mostly connected by solvent water molecules through stronger intermolecular water-water and weak water-nitrate hydrogen bonds. The hydrogen bonding scheme in the trihydrate structure is much simpler than that in the structure of tetrahydrate, which includes two water-water bonds ($\text{Ow}(1)-\text{H}(1)\cdots\text{Ow}(3)$ (2.696(5) Å) and $\text{Ow}(2)-\text{H}(2)\cdots\text{Ow}(3)$ (2.683(5) Å) and three water-nitrate bonds ($\text{Ow}(3)-\text{H}(4)\cdots\text{O}(9)$ (2.862(5) Å), $\text{Ow}(3)-\text{H}(5)\cdots\text{O}(6)$ (2.909(5) Å), and $\text{Ow}(2)-\text{H}(3)\cdots\text{O}(8)$ (2.918(5) Å)).

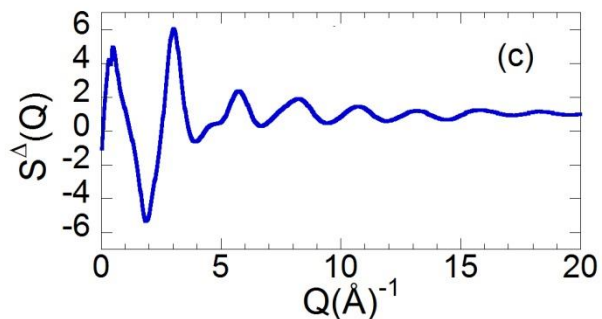
Figure S1. The HEXS data reduction process, exemplified for the 0.4 m Th in 2 m HNO₃/2 m HClO₄ sample, applied to all spectra before fitting the Th-based correlations in real space.



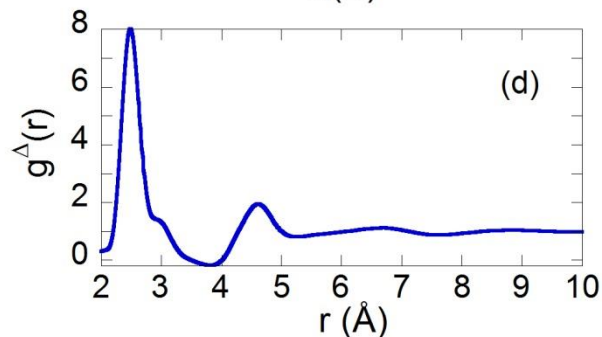
(a) Raw intensity data after rendering from 2-D area detector using FIT2D¹ software. Data are obtained from the sample (black) and also a background solution (red) consisting of 2 m HNO₃ and 2 m HClO₄.



(b) The sample and background scattering functions $S(Q)$ are reduced independently following standard protocols.²⁻⁵



(c) The background subtracted scattering functions are directly subtracted from sample data to produce a difference scattering pattern. Ideally, these data include only scattering that includes a Th component.



(d) The scattering pattern is Fourier transformed to yield a difference pair (dPDF). Peaks in the pattern correspond to Th-L correlations, where L = solvent (O,H), nitrate (N,O), perchlorate (Cl, O) or other Th.

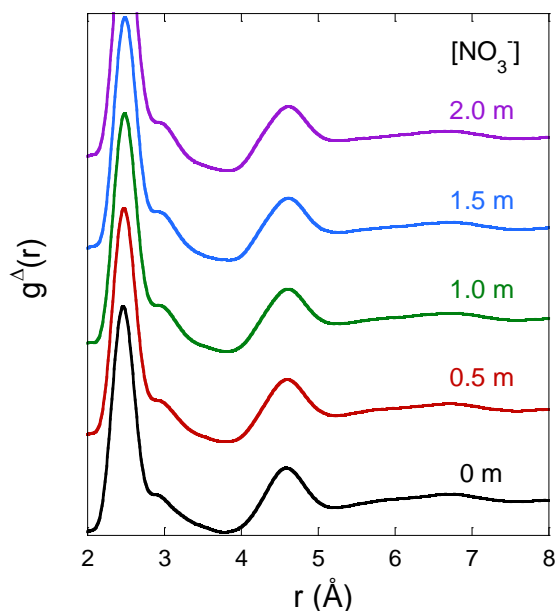
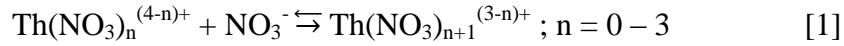


Figure S2. Extended range plot of the dPDFs obtained from background-subtracted, Fourier transformed HEXS data from 0.4 m Th solutions. In this series perchlorate is replaced by nitrate under the constraint of maintaining solutions at a constant ionic strength of 4 m. All correlations, represented as peaks in the plot, involve Th as the central ion.

Th speciation in perchlorate solution. Of general interest is the end-member of the solution series, which contains no nitrate but instead is composed of 0.4 m Th in 4 m perchlorate. As expected, and confirming a previously published study,⁶ there is no evidence of perchlorate entering into the Th^{IV} first coordination sphere. Fitting the $g^A(r)$ vs r data required two Gaussians yields, centered at 2.46(1) and 2.93(3) Å, which were assigned to correlations involving Th-O_{water} and Th-H_{water} respectively. The observation of a correlation peak in the dPDF pattern attributable to proton correlation is not without precedent,^{7,8} and not unexpected because 25% of the water electron count comes from its protons. The combined electron count from the two peaks is 97(3), the same within error as the 99(3) electrons obtained by integrating the intensity of the $g^A(r)$ vs r data over the r range of 2.0-3.6 Å. The Th coordination number is the same, within error, as was previously obtained from HEXS experiments for Th in an acidic bromide solution, where 10 waters were assigned to Th in the first coordination shell.⁹ This latter interpretation was supported by a solid-state X-ray refinement from a single-crystal of [Th(H₂O)₁₀]Br₄, the only previously published Th-water homoleptic structure, in which a bicapped square-antiprismatic geometry is reported, with an average Th-O distance of 2.498(4) Å, slightly longer than the distances observed in solution. Whereas recent theoretical modeling

efforts are able to well reproduce the Th-O bond distances, they continue to underestimate the coordination number based on these findings,¹⁰⁻¹⁸ even when the anions bromide or perchlorate are explicitly included in the calculations.^{19,20}

Determination of stability constants. As described, the fits of the dPDF patterns provide quantitative information on the average number of nitrate ions bound to Th as a function of nitrate concentration, which can be used to directly estimate stability constants, β_N . Assuming the solution equilibria:



with the equilibrium constants, K_n , for the addition of each nitrate dependent on complex concentrations according to:

$$K_n = \frac{[\text{Th}(\text{NO}_3)_{n+1}]}{[\text{Th}(\text{NO}_3)_n][\text{NO}_3]}.$$

Equilibrium constants are directly related to stability constants through:

$$\beta_n = \prod_0^n K_n \quad [2]$$

The quantitative analyses of the dPDFs detailed in Table 3 are compared in Figure S3 following the relation:²¹

$$\bar{n} = \frac{A - a}{B} \quad [3]$$

where \bar{n} is average number of nitrate bound to Th, A is the total nitrate in a given solution and B is the concentration of Th, in this case fixed at 0.4 m.

The relation in equation 3 is used to determine a , the free, unbound nitrate in solution. Once a is known for each sample, β can be determined by:²¹

$$\bar{n} = \frac{\sum_0^N n \beta_n a^n}{\sum_0^N \beta_n a^n}$$

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