



The crystal chemistry of four thorium sulfates

Amanda J. Albrecht, Ginger E. Sigmon, Laura Moore-Shay, Rebecca Wei, Colleen Dawes, Jennifer Szymanowski, Peter C. Burns*

Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, IN 46556, USA

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ABSTRACT

Four thorium sulfate compounds have been synthesized and characterized. $[\text{Th}(\text{SO}_4)_2(\text{H}_2\text{O})_7] \cdot 2\text{H}_2\text{O}$ (**ThS1**) crystallizes in space group $P2_1/m$, $a=7.2488(4)$, $b=12.1798(7)$, $c=8.0625(5)$ Å, $\beta=98.245(1)^\circ$; $\text{Na}_{10}[\text{Th}_2(\text{SO}_4)_9(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**ThS2**), $Pna2_1$, $a=17.842(2)$, $b=6.9317(8)$, $c=27.550(3)$ Å; $\text{Na}_2[\text{Th}_2(\text{SO}_4)_5(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (**ThS3**), $C2/c$, $a=16.639(2)$, $b=9.081(1)$, $c=25.078(3)$ Å, $\beta=95.322(2)^\circ$; $[\text{Th}_4(\text{SO}_4)_7(\text{OH})_2(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ (**ThS4**), $Pnma$, $a=18.2127(9)$, $b=11.1669(5)$, $c=14.4705(7)$ Å. In all cases the Th cations are coordinated by nine O atoms corresponding to SO_4 tetrahedra, OH groups, and H_2O groups. The structural unit of **ThS1** is an isolated cluster consisting of a single Th polyhedron with two monodentate SO_4 tetrahedra and seven H_2O groups. A double-wide Th sulfate chain is the basis of **ThS2**. The structures of **ThS3** and **ThS4** are frameworks of Th polyhedra and sulfate tetrahedra, and each contains channels that extend through the framework. One of the Th cations in **ThS3** is coordinated by a bidentate SO_4 tetrahedron, and **ThS4** is unusual in the presence of a pair of Th cations that share a polyhedral face.

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1. Introduction

Thorium and uranium are the only actinides that occur in nature in appreciable quantities, and both can be the fuel of nuclear energy. Thorium-232 has a half-life of 1.4×10^{10} years and can be used to breed ^{233}U that is subsequently fissioned in a reactor. It is unlike most of the early actinides in that it is only stable in the tetravalent oxidation state. It is therefore a useful analog for the behavior of Np(IV) and Pu(IV) in the solid state.

Thorium is coordinated by 6–15 ligands in reported crystal structures. It has a strong tendency to form complexes with anions, and its crystal chemistry is relatively complex [1]. The interaction of Th with sulfate has been studied in solution [2] and the solid state [3–10], in part because Th sulfate complexes may be important for understanding the fate of Th in environments impacted by mining. To date there are seven strictly inorganic Th sulfate structures, and in each Th cations are coordinated by sulfate. These are dominated by the sharing of polyhedral elements between Th polyhedra and sulfate tetrahedra. Structural units are formed where Th and sulfate polyhedra are linked into finite clusters [3,4], chains [5,6], sheets [7,8], and frameworks [9,10]. An unusual Th sulfate has an extended framework structure that resembles zeolite-like materials [9] with channels that

are 11.5 Å in diameter. Two organically templated Th sulfates have also been reported with Th sulfate sheet structural units [8].

Here, we report the synthesis and characterization of four Th sulfate compounds. These exhibit considerable structural diversity, with structural units consisting of a cluster, a chain, and two frameworks of polyhedra.

2. Experimental

2.1. Syntheses

Caution! Thorium-232 is radioactive. Appropriate facilities and trained personnel are required for working with radioactive materials.

$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (International Bio-Analytical Industries, Inc.), H_2SO_4 (LabChem, Inc.), Na_2SO_4 (Aldrich), and NaOH (Fisher) were used as received. Water was distilled and Millipore-filtered, 18.2 MΩ cm.

In a Teflon-lined 125-mL Parr acid digestion vessel, 0.7500 g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ and 20.6 mL H_2O were combined and the pH was adjusted to 4.0 by adding 1 M NaOH. The solution was heated to 65 °C for 24 h in a mechanical convection oven. The result was a clear colorless solution hereafter designated *solution-1*. In a glass beaker 13.8049 g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ was dissolved in 50.0 mL H_2O at room temperature, giving a clear solution hereafter referred to as *solution-2*.

* Corresponding author.

E-mail addresses: pburns@nd.edu, Peter.Burns.50@nd.edu (P.C. Burns).

Table 1
Crystallographic data for **ThS1**, **ThS2**, **ThS3**, and **ThS4**.

	ThS1 [Th(SO ₄) ₂ (H ₂ O) ₇] · 2H ₂ O	ThS2 Na ₁₀ [Th ₂ (SO ₄) ₉ (H ₂ O) ₂] · 3H ₂ O	ThS3 Na ₂ [Th ₂ (SO ₄) ₅ (H ₂ O) ₃] · H ₂ O	ThS4 [Th ₄ (SO ₄) ₇ (OH) ₂ (H ₂ O) ₆] · 2H ₂ O
<i>a</i> (Å)	7.2488(4)	17.842(2)	16.639(2)	18.2127(9)
<i>b</i> (Å)	12.1798(7)	6.9317(8)	9.081(1)	11.1669(5)
<i>c</i> (Å)	8.0625(5)	27.550(3)	25.078(3)	14.4705(7)
β (deg)	98.245(1)	90	95.322(2)	90
Volume (Å ³)	704.47(7)	3405.3(4)	3772.8(8)	2943.0(2)
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>Pna</i> 2 ₁	<i>C</i> 2/ <i>c</i>	<i>Pnma</i>
<i>Z</i>	2	4	4	4
<i>F</i> (000)	552	3048	3792	3104
μ (mm ⁻¹)	10.966	9.542	16.47	20.79
<i>D</i> _{calc} (g/cm ³)	2.764	3.194	3.712	3.974
Crystal size (mm)	0.12 × 0.11 × 0.090	0.090 × 0.085 × 0.075	0.15 × 0.13 × 0.10	0.16 × 0.12 × 0.10
Radiation	MoK α	MoK α	MoK α	MoK α
<i>T</i> (K)	298(2)	298(2)	298(2)	298(2)
Frame width (deg)	0.3	0.3	0.3	0.3
Count time per frame (s)	10	120	10	10
θ range (deg)	2.55–28.68	2.28–31.96	2.46–27.89	2.56–34.52
Reflections collected	8430	44,074	25,726	57,974
Independent reflections	1807	11,722	4494	6405
Unique <i>F</i> _o > 4 σ _{<i>F</i>}	1746	8247	3875	5278
<i>R</i> ₁	0.0133	0.0518	0.0322	0.0306
<i>wR</i> ₂	0.0309	0.1017	0.0722	0.0648
<i>S</i>	1.05	1.02	1.04	1.03

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o| \quad R_w2(F_o^2) = \left[\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4 \right]^{1/2}$$

Table 2
Selected interatomic distances in the structure of **ThS1**.*

Bond	Length (Å)	Bond	Length (Å)
Th(1)–O(3)	2.3645(18)	S(1)–O(2)	1.464(2)
Th(1)–O(3) ^a	2.3646(18)	S(1)–O(8) ^d	1.4659(19)
Th(1)–O(5) ^b	2.4474(19)	S(1)–O(4)	1.4664(18)
Th(1)–O(5) ^c	2.4474(19)	S(1)–O(3)	1.4854(18)
Th(1)–O(7)	2.4775(19)	<S(1)–O>	1.470
Th(1)–O(7) ^a	2.4775(19)		
Th(1)–O(10)	2.483(3)		
Th(1)–O(6)	2.492(3)		
Th(1)–O(1)	2.509(3)		
<Th(1)–O>	2.451		

* Symmetry transformations: (a) *x*, $-y+1/2$, *z*, (b) $-x+2$, $-y$, $-z$, (c) $-x+2$, $y+1/2$, $-z$, and (d) $-x+2$, $-y$, $-z+1$.

[Th(SO₄)₂(H₂O)₇] · 2H₂O, **ThS1**: Thorium nitrate tetrahydrate (0.4419 g) was dissolved in 2 mL of 1.5 M H₂SO₄. The solution was covered by parafilm with a small hole to allow slow evaporation. After 2 weeks blocky crystals formed and were recovered for analysis.

Na₁₀[Th₂(SO₄)₉(H₂O)₂] · 3H₂O, **ThS2**: *Solution-1* (0.250 mL) and Na₂SO₄ (0.146 g) were combined and heated in a 5 mL polypropylene vial contained inside a 125 mL Teflon-lined Parr acid digestion vessel that was heated at 100 °C for 24 h. Twenty-five milliliters of H₂O was placed in the outer liner of the vessel to provide counter pressure. The resulting crystal-free solution was transferred to a glass vial that was capped. After several months, bladed crystals appeared in solution and were recovered for analysis.

Na₂[Th₂(SO₄)₅(H₂O)₃] · H₂O, **ThS3**: *Solution-1* (0.250 mL) and H₂SO₄ (0.100 mL concentration) were combined and heated at 100 °C for 24 h in a 5 mL polypropylene vial that was placed inside a 125 mL Teflon-lined Parr acid digestion vessel. Twenty-five milliliters of H₂O was placed in the outer liner of the vessel to provide counter pressure during heating. After heating the

resulting crystal-free solution was transferred to a glass vial that was capped. After several months bladed crystals appeared in solution and were harvested for analysis.

[Th₄(SO₄)₇(OH)₂(H₂O)₆] · 2H₂O, **ThS4**: *Solution-2* (1.000 mL) was combined with 1.000 mL of 0.200 M H₂SO₄. The resulting solution was heated in a 23 mL Parr acid digestion vessel at 180 °C for 5 days. The crystal-free solution was then transferred to a glass vial that was capped. After several weeks blocky crystals appeared in solution and were recovered for analysis.

2.2. Crystallographic studies

A suitable single crystal of each compound without evident twinning or inclusions was selected using a polarized-light microscope and was glued to a tapered glass fiber. Spheres of X-ray diffraction data were collected using an APEX (**ThS2** and **ThS4**) or APEX II (**ThS1** and **ThS3**) detector mounted on a three-circle goniometer using graphite-monochromated MoK α radiation. The data were collected with frame widths of 0.3° in ω and 10 (or 120) s spent counting per step. Data were integrated and corrected for Lorentz, background, and polarization effects for each crystal using the APEX II software [11]. Data were corrected for absorption using SADABS [12], and the structures were solved and refined using the Bruker SHELXTL v6.12 [13] software. The final model for **ThS1** included H atoms. These were located in difference-Fourier maps and were refined with the constraint that O–H bond lengths be ~ 0.96 Å. The displacement parameters of all non-H atoms were refined anisotropically for all compounds. H atoms were not located for the structures of **ThS2**, **ThS3**, or **ThS4**; O atoms in these structures were assigned as O²⁻, OH⁻, or H₂O on the basis of the bond-valence sums incident upon these positions. Structures were examined in search of higher symmetry using PLATON as implemented in WinGX [14]. Crystallographic data for all four compounds is shown in Table 1, and selected interatomic distances are in Tables 2–5. Full details of the crystal structures are given in the supporting information.

Table 3
Selected interatomic distances in the structure of **ThS2**.*

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Th(1)–O(14)	2.353(10)	S(1)–O(17)	1.444(10)	S(6)–O(12)	1.429(9)
Th(1)–O(23)	2.355(10)	S(1)–O(35)	1.458(11)	S(6)–O(11)	1.461(9)
Th(1)–O(35)	2.371(11)	S(1)–O(2)	1.461(12)	S(6)–O(31)	1.474(11)
Th(1)–O(21)	2.463(11)	S(1)–O(36)	1.502(11)	S(6)–O(14)	1.504(11)
Th(1)–O(34)	2.486(10)	<S(1)–O>	1.466	<S(1)–O>	1.467
Th(1)–O(19)	2.491(11)				
Th(1)–O(26)	2.507(11)	S(2)–O(6)	1.387(10)	S(7)–O(10)	1.435(12)
Th(1)–O(18)	2.539(10)	S(2)–O(4)	1.471(11)	S(7)–O(8)	1.438(11)
Th(1)–O(30)	2.582(11)	S(2)–O(30)	1.499(10)	S(7)–O(13)	1.446(11)
<Th(1)–O>	2.460	S(2)–O(21)	1.533(11)	S(7)–O(15)	1.499(12)
		<S(1)–O>	1.473	<S(1)–O>	1.454
Th(2)–O(15)	2.324(12)				
Th(2)–O(36)	2.359(10)	S(3)–O(24)	1.424(11)	S(8)–O(5)	1.452(9)
Th(2)–O(29)	2.369(9)	S(3)–O(28)	1.447(12)	S(8)–O(7)	1.470(8)
Th(2)–O(37)	2.453(10)	S(3)–O(18)	1.494(12)	S(8)–O(37) ^a	1.478(10)
Th(2)–O(25)	2.459(10)	S(3)–O(19)	1.508(11)	S(8)–O(29)	1.485(10)
Th(2)–O(20)	2.492(11)	<S(1)–O>	1.468	<S(1)–O>	1.471
Th(2)–O(16)	2.532(10)				
Th(2)–O(32)	2.532(11)	S(4)–O(22)	1.449(11)	S(9)–O(34) ^a	1.464(10)
Th(2)–O(33)	2.537(10)	S(4)–O(27)	1.459(11)	S(9)–O(23)	1.486(10)
<Th(2)–O>	2.451	S(4)–O(20)	1.481(10)	S(9)–O(9)	1.492(10)
		S(4)–O(16)	1.491(11)	S(9)–O(3)	1.504(14)
		<S(1)–O>	1.47	<S(1)–O>	1.487
		S(5)–O(1)	1.411(11)		
		S(5)–O(41)	1.459(11)		
		S(5)–O(25)	1.483(11)		
		S(5)–O(33)	1.499(11)		
		<S(1)–O>	1.463		

* Symmetry transformations (a) $x, y+1, z$, (b) $x-1/2, -y-5/2, z$, (c) $-x-1/2, y+1/2, z+1/2$, (d) $x+1/2, -y-5/2, z$, (e) $x-1/2, -y-3/2, z$, (f) $-x, -y-2, z+1/2$, (g) $-x-1/2, y-1/2, z+1/2$, (h) $x+1/2, -y-3/2, z$, (i) $-x-1, -y-2, z+1/2$, (j) $x, y-1, z$, (k) $-x, -y-2, z-1/2$, (l) $-x-1/2, y-1/2, z-1/2$, (m) $-x-1/2, y+1/2, z-1/2$, and (n) $-x-1, -y-2, z-1/2$.

2.3. Infrared spectroscopy

A SensIR technology IlluminIR FT-IR Microspectrometer with a ContactIR diamond attenuated total reflectance (ATR) IR objective was used to collect data ranging from 650 to 4000 cm^{-1} for each compound. In each case a crystal was placed on a glass side and was contacted by the ATR objective. The spectra are in the supporting information.

2.4. Chemical analysis

Crystals of **ThS3** were dissolved in 5% HNO_3 and the resulting solution was analyzed using a Perkin-Elmer Optima 2000DV inductively coupled-plasma optical-emission-spectrometer. The analysis provided a Th:S:Na ratio of 2:5.06:2.09, respectively.

3. Results

The cation coordination polyhedra in the four compounds under study are similar. Each Th cation is coordinated by nine O atoms that belong to OH^- , H_2O , or $(\text{SO}_4)^{2-}$ groups. Polyhedral geometries range from monocapped square antiprisms (**ThS3** and **ThS4**) to tricapped trigonal prisms (**ThS1**, **ThS2**, **ThS3**, and **ThS4**). The Th–O bond lengths range from 2.313(6) to 2.720(6) Å, and the averages for individual polyhedra range from 2.438 to 2.460 Å. Each of the S^{6+} cations are tetrahedrally coordinated by four O atoms, with bond lengths ranging from 1.411(11) to 1.508(11) Å across the structures, and individual tetrahedral averages ranging from 1.447 to 1.487 Å.

Whereas the local cation coordination environments are similar in the compounds under study, their extended structures reveal considerable diversity. **ThS1** is the simplest of these

structures, and it contains only single crystallographically distinct Th and S cations. Two monodentate SO_4 tetrahedra, as well as seven H_2O groups, coordinate each Th cation. The result is a small electroneutral cluster of composition $[\text{Th}(\text{H}_2\text{O})_7(\text{SO}_4)_2]$ (Fig. 1). A single crystallographically unique H_2O group is located between the thorium sulfate clusters, where it is held in place by H bonding. An extensive network of H bonds extend from the H_2O groups of the Th polyhedra to O atoms of SO_4 tetrahedra in other clusters, as well as to the interstitial H_2O group. Each of the terminal O atoms of the SO_4 tetrahedra are H bond acceptors with $\text{H}\cdots\text{O}$ bond lengths in the range 1.8–2.0 Å. The O(8) anion accepts bonds from H(1) and H(9), O(4) accepts bonds from H(2) and H(4), and O(2) accepts bonds from H(5) and H(6). Note that these H bonds, together with the S–O bonds, result in bond-valence sums of ~ 2.0 valence units at the O position in each case, consistent with their assignment as O^{2-} anions.

There are two crystallographically distinct Th cations in **ThS2**, as well as nine sulfate tetrahedra. One H_2O group, four O atoms of two bidentate SO_4 tetrahedra, and four O atoms of monodentate SO_4 tetrahedra coordinate each Th cation. Each of the S(1), S(8), and S(9) sulfate tetrahedra bridge between two ThO_9 polyhedra by sharing a vertex with each of them. The S(2), S(3), S(4), and S(5) tetrahedra are bidentate to Th cations. The remaining tetrahedra, S(6) and S(7), share only a single vertex with a ThO_9 polyhedron. Thorium sulfate chains extending along [010] result from the extensive vertex-sharing between the SO_4 tetrahedra and Th polyhedra (Fig. 2). These chains are linked into an extended structure through ten symmetrically distinct Na cations. There are also three H_2O groups that bond only to Na.

ThS3 contains two crystallographically distinct ThO_9 polyhedra. Th(1) is coordinated by one bidentate S(1) O_4 tetrahedron, by six monodentate SO_4 tetrahedra, and by one H_2O group. The Th(2) cation is coordinated by seven monodentate SO_4 tetrahedra

Table 4
Selected interatomic distances in the structure of **ThS3**.*

Bond	Length (Å)	Bond	Length (Å)
Th(1)–O(16) ^a	2.359(6)	S(1)–O(21)	1.444(7)
Th(1)–O(4)	2.371(6)	S(1)–O(6)	1.462(6)
Th(1)–O(2) ^a	2.381(5)	S(1)–O(9) ^c	1.480(6)
Th(1)–O(24) ^b	2.398(6)	S(1)–O(11) ^c	1.490(6)
Th(1)–O(6)	2.402(6)	<S(1)–O>	1.469
Th(1)–O(8)	2.408(6)		
Th(1)–O(11)	2.482(6)	S(2)–O(24)	1.437(7)
Th(1)–O(13)	2.554(6)	S(2)–O(8)	1.456(6)
Th(1)–O(9)	2.720(6)	S(2)–O(22)	1.458(8)
<Th(1)–O>	2.441	S(2)–O(3) ^a	1.472(6)
		<S(2)–O>	1.456
Th(2)–O(10)	2.313(6)	S(2A)–O(24)	1.295(10)
Th(2)–O(7)	2.365(6)	S(2A)–O(22A) ^a	1.45(2)
Th(2)–O(14) ^a	2.391(6)	S(2A)–O(8)	1.516(9)
Th(2)–O(15) ^a	2.440(6)	S(2A)–O(3) ^a	1.525(9)
Th(2)–O(12) ^a	2.442(6)	<S(2A)–O>	1.447
Th(2)–O(3)	2.463(6)		
Th(2)–O(19)	2.488(6)		
Th(2)–O(17)	2.510(5)	S(3)–O(1)	1.454(6)
Th(2)–O(20)	2.560(6)	S(3)–O(14)	1.462(6)
<Th(2)–O>	2.453	S(3)–O(2)	1.470(6)
		S(3)–O(17)	1.478(5)
		<S(3)–O>	1.466
		S(4)–O(5)	1.436(6)
		S(4)–O(16)	1.468(6)
		S(4)–O(12)	1.474(6)
		S(4)–O(10)	1.489(6)
		<S(4)–O>	1.467
		S(5)–O(18)	1.436(6)
		S(5)–O(15)	1.459(6)
		S(5)–O(7)	1.466(6)
		S(5)–O(4)	1.482(6)
		<S(5)–O>	1.461

* Symmetry transformations (a) $x, y-1, z$, (b) $-x, -y+1, -z$, (c) $-x+1/2, y-1/2, z$, (d) $-x, y, -z+1/2$, (e) $x, y+1, z$, (f) $-x+1/2, y+1/2, z$, (g) $x, -y+1, z-1/2$, (h) $x, -y+1, z+1/2$, (i) $x, -y+2, z+1/2$, (j) $-x+1/2, -y+3/2, z+1/2$, (k) $x, -y+2, z-1/2$, and (l) $-x+1/2, -y+3/2, z-1/2$.

and two H₂O groups. There are five crystallographically distinct sulfate tetrahedra. The S(1)O₄ tetrahedron shares an edge with the Th(1) polyhedron, and a single vertex with another Th(1) polyhedron. Each of the S(2) through S(5) tetrahedra share three of their vertices with three different Th polyhedra. The S(2) position is split over two sites, each of which are tetrahedrally coordinated and only one of which can be occupied locally.

The linkages between sulfate tetrahedra and Th polyhedra in **ThS3** result in a complex framework structure (Fig. 3). Within this, layers parallel to (101) are connected through S(1)O₄ tetrahedra. Elongated channels extend through the structure between these layers, and contain disordered Na cations. Additional channels extend along [001], and are bounded by non-bridging O atoms of SO₄ tetrahedra. The framework has the composition Th₂(SO₄)₅(H₂O)₃ and requires four Na cations on general positions to provide charge-balance. Three of these Na cations are sufficiently localized in the channels to be included in the structure refinement. ICP-OES analysis of dissolved crystals of **ThS3** gave atomic ratios of Th:S:Na of 2:5.06:2.09, consistent with the assigned composition Na₂Th₂(SO₄)₅(H₂O)₃ and charge-balance requirements.

There are three crystallographically distinct ThO₉ polyhedra in **ThS4**, of which Th(1)O₉ is a distorted monocapped square antiprism and Th(2)O₉ and Th(3)O₉ are tricapped trigonal prisms. The Th(1)O₉ polyhedra are unusual because a pair of them share a face defined by the O(15), O(19), and O(20) hydroxyl groups. The Th(1)–Th(1) separation is 3.8969(3) Å, indicating no metal–metal

Table 5
Selected interatomic distances in the structure of **ThS4**.*

Bond	Length (Å)	Bond	Length (Å)
Th(1)–O(19)	2.354(4)	S(1)–O(21)	1.455(4)
Th(1)–O(15)	2.393(3)	S(1)–O(23) ^b	1.456(4)
Th(1)–O(3)	2.398(3)	S(1)–O(13)	1.460(4)
Th(1)–O(23)	2.417(4)	S(1)–O(8)	1.469(4)
Th(1)–O(12)	2.432(3)	<S(1)–O>	1.460
Th(1)–O(5)	2.455(3)		
Th(1)–O(18)	2.468(4)	S(2)–O(10)	1.454(4)
Th(1)–O(4)	2.481(3)	S(2)–O(12)	1.465(4)
Th(1)–O(20)	2.694(5)	S(2)–O(14) ^c	1.471(4)
<Th(1)–O>	2.455	S(2)–O(11)	1.478(4)
		<S(2)–O>	1.466
Th(2)–O(17) ^a	2.376(4)	S(3)–O(17) ^c	1.458(4)
Th(2)–O(17)	2.376(4)	S(3)–O(22) ^d	1.459(4)
Th(2)–O(6)	2.382(5)	S(3)–O(3)	1.461(4)
Th(2)–O(13)	2.405(4)	S(3)–O(4) ^e	1.468(3)
Th(2)–O(13) ^a	2.405(4)	<S(3)–O>	1.467
Th(2)–O(11)	2.440(3)		
Th(2)–O(11) ^a	2.440(3)	S(4)–O(5)	1.471(4)
Th(2)–O(9)	2.526(5)	S(4)–O(5) ^f	1.471(4)
Th(2)–O(16)	2.596(5)	S(4)–O(2) ^f	1.477(5)
<Th(2)–O>	2.438	S(4)–O(6) ^f	1.483(5)
		<S(4)–O>	1.476
Th(3)–O(21)	2.362(4)		
Th(3)–O(21) ^a	2.362(4)		
Th(3)–O(22)	2.395(4)		
Th(3)–O(22) ^a	2.395(4)		
Th(3)–O(14)	2.419(4)		
Th(3)–O(14) ^a	2.419(4)		
Th(3)–O(2)	2.463(5)		
Th(3)–O(7)	2.592(6)		
Th(3)–O(1)	2.594(5)		
<Th(3)–O>	2.445		

* Symmetry transformations (a) $x, -y+1/2, z$, (b) $-x+1/2, -y, z-1/2$, (c) $-x+1/2, -y, z+1/2$, (d) $x, y, z+1$, (e) $-x, -y, -z+1$ (f) $x, -y-1/2, z$, and (g) $x, y, z-1$.

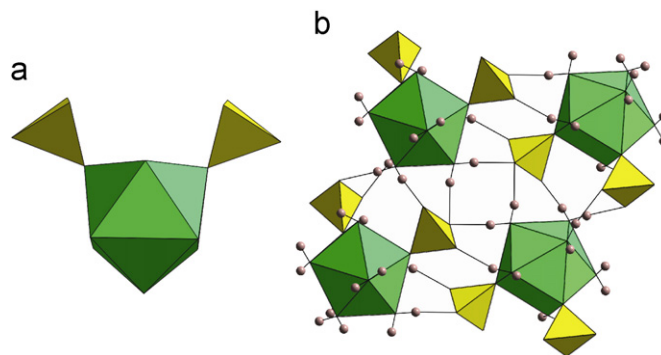


Fig. 1. Representations of the structure of **ThS1**. Thorium and sulfate polyhedra are shown in green and yellow, respectively. H atoms are shown as pink spheres: (a) the thorium sulfate cluster and (b) locations of H atoms that link the thorium sulfate clusters together (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

bonding interaction is present. In addition, each Th(1) cation is coordinated by five monodentate SO₄ tetrahedra and a single H₂O group. Both the Th(2) and Th(3) cations are coordinated by seven monodentate SO₄ tetrahedra and two H₂O groups. There are four crystallographically distinct SO₄ tetrahedra, two of which share three of their vertices with different ThO₉ polyhedra. The remaining two SO₄ tetrahedra [S(3), S(4)] each share all four of their vertices with four different ThO₉ polyhedra.

The direct linkage between pairs of Th(1)O₉ polyhedra, as well as linkages through SO₄ tetrahedra, result in an electroneutral framework (Fig. 4). Elongated channels extend along [010] and contain H₂O.

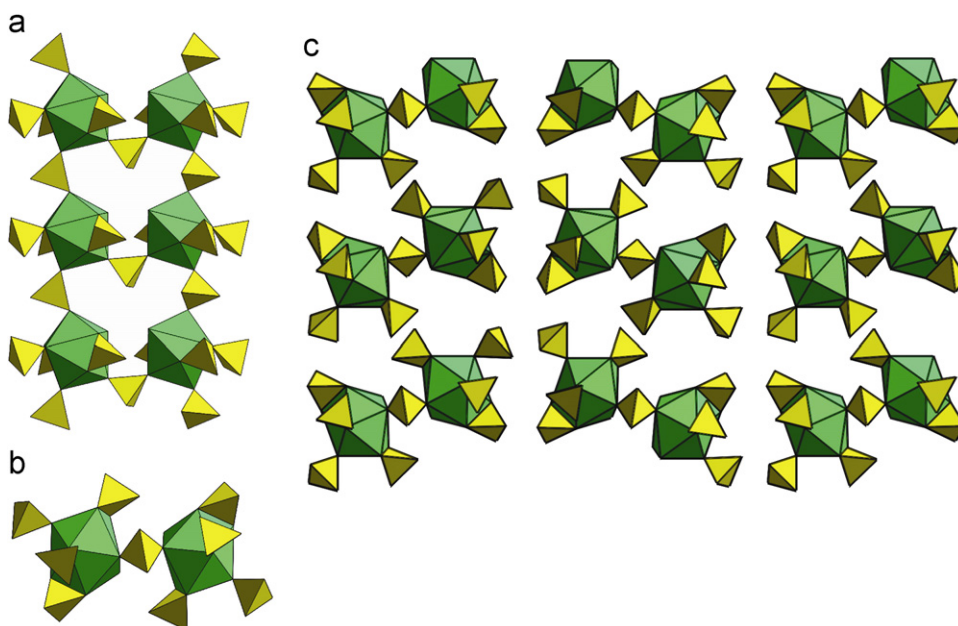


Fig. 2. Polyhedral representations of the structure of **ThS2**: (a) The double chain of Th polyhedra and sulfate tetrahedra that extends along the [010] direction and (b) projection of the chain along [010], and (c) the extended structure projected along [010]. Legend as in Fig. 1.

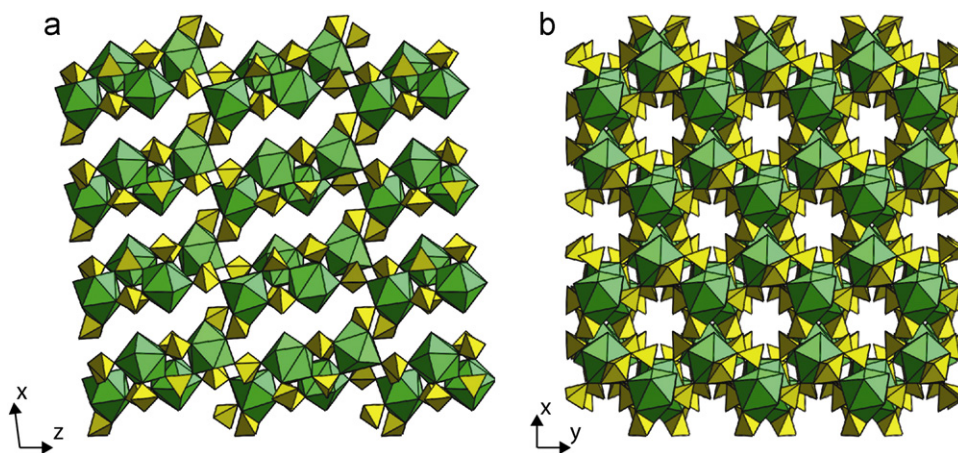


Fig. 3. Polyhedral representations of the structure of **ThS3**: (a) Projection along [010] showing the channels and (b) projection along [001] showing the second set of channels. Na cations are omitted for clarity. Legend as in Fig. 1.

4. Discussion

The structural topologies of the four hydrous Th sulfates reported herein, and those reported by other researchers, are impacted most by the details of the sharing of polyhedral elements between the sulfate and Th polyhedra. In all of these structures Th cations are coordinated by sulfate tetrahedra. Furthermore, all of the sulfate tetrahedra coordinate between one and four Th polyhedra; none are isolated. The details of the structures are therefore dependent on both the Th:S ratio and the amount of H₂O that is incorporated into the coordination polyhedra about the Th cations.

The cluster structure unit in **ThS1** is unique in tetravalent actinide (*An*) materials. More than 25 *An*(IV) compounds have structures that consist of finite clusters, and several contain tetrahedrally coordinated hexavalent cations. The structure of Th(SO₄)₂(H₂O)₈ contains Th cations that are coordinated by two bidentate SO₄ tetrahedra and six H₂O groups, resulting in a coordination number of 10 [3]. In K₈Th(MoO₄)₆, the Th coordination number is seven and the cation is coordinated by one

bidentate and five monodentate MoO₄ tetrahedra [15]. In K_{5.5}(H₅O₂)_{0.5}Np(SO₄)₅(H₂O), the Np(IV) cation is coordinated by five bidentate SO₄ tetrahedra, giving a coordination number of 10 [16].

There are at least a dozen *An*(IV) compounds that have structural units that consist of chains, as in **ThS2**. Several of these contain tetrahedrally coordinated hexavalent cations. For example, the chain in K₂Th(MoO₄)₃ is denser than that in **ThS2**, each ThO₇ polyhedron shares two of its edges with adjacent ThO₇ polyhedra, and each MoO₄ tetrahedron is two-connected to the chain [17]. In K₄Th(SO₄)₄(H₂O)₂, the coordination number of the Th cations is nine (as in **ThS2**), and each Th cation is coordinated by one bidentate and five monodentate SO₄ tetrahedra, as well as two H₂O groups [18]. This chain differs from that in **ThS2** most notably in that two sulfate tetrahedra bridge between each pair of ThO₉ polyhedra in K₄Th(SO₄)₄(H₂O)₂, whereas in **ThS2** ThO₉ polyhedra are bridged by only a single sulfate tetrahedron. In Na₂(SO₄)₃Th(H₂O)₃(H₂O)₃, in contrast, three sulfate tetrahedra bridge between each Th polyhedron along the chain length [5]. The structure of Na₁₀Np₂(SO₄)₉(H₂O)₄ [19] contains one less H₂O group than **ThS2**, but otherwise is identical to **ThS2**, providing an

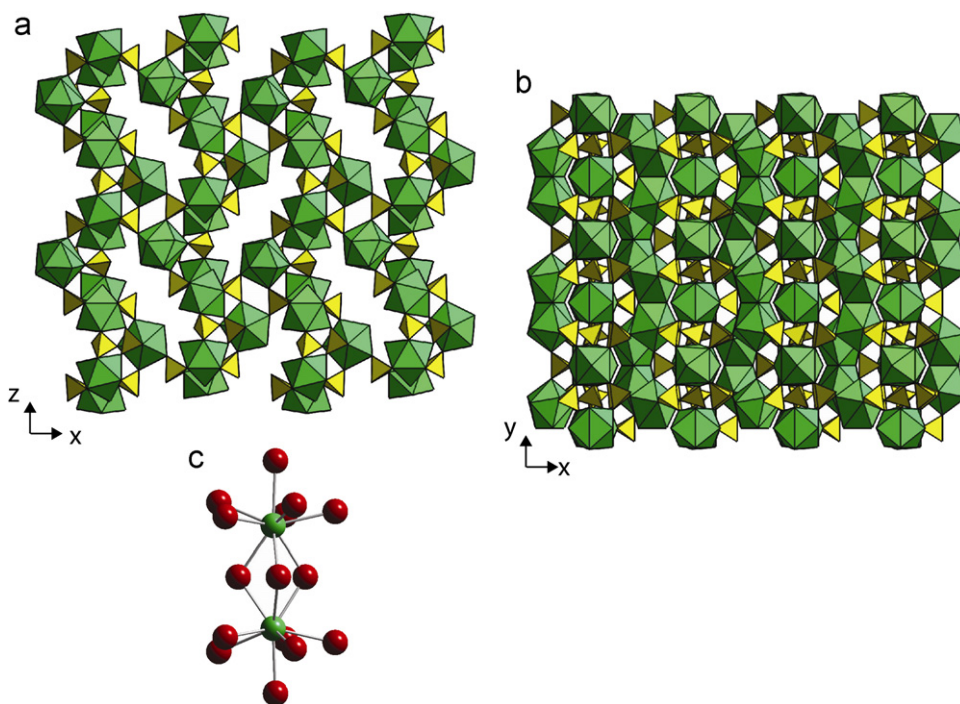


Fig. 4. Representations of the structure of **ThS4**: (a) projection along [010], (b) projection along [100], and (c) face sharing between two Th polyhedra. Legend as in Fig. 1 except O and Th atoms are shown as red and green balls, respectively (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

example of complex Th and Np(IV) compounds that are isostructural.

Compounds **ThS3** and **ThS4** join a family of more than 80 framework structures that contain *An*(IV) cations. Here we focus discussion on the most closely related structures that contain tetrahedrally coordinated hexavalent cations. Whereas **ThS3** and **ThS4** contain channels that extend through the framework, they are small in comparison to those in $\text{Th}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}$, which are 11.5 Å in two directions [10]. In this porous structure each of the Th cations are coordinated by seven monodentate SO_4 tetrahedra and two H_2O groups, and the SO_4 tetrahedra are connected to either three of four Th cations. The compound $\text{Th}(\text{OH})_2(\text{SO}_4)$ has a close-knit framework that contains chains of edge-sharing ThO_8 polyhedra [9]. The Th cations are coordinated by four monodentate SO_4 tetrahedra and four OH groups.

Several Th and U(IV) molybdates with framework structures have been reported. Three of these, $\text{CdTh}(\text{MoO}_4)_3$, $\text{CuU}(\text{MoO}_4)_3$, and $\text{Th}(\text{MoO}_4)_2$ have similar frameworks with channels extending along the [001] direction [20,21,22]. In $\text{CdTh}(\text{MoO}_4)_3$ and $\text{CuU}(\text{MoO}_4)_3$, the Cd and Cu cations are located within these channels, where they are octahedrally coordinated by six monodentate MoO_4 tetrahedra. In $\text{Th}(\text{MoO}_4)_2$, half of the channel sites (relative to the other two compounds) are occupied by Th in a usual octahedral coordination. The non-channel Th cations in the structures are coordinated by nine monodentate MoO_4 tetrahedra.

ThMo_2O_8 and UMo_2O_8 have dense frameworks in which each *An*(IV) cation is coordinated by eight monodentate MoO_4 tetrahedra, and each tetrahedron shares all four of its vertices with *An*(IV) polyhedra [23,24]. The compound $\text{K}_4\text{Th}(\text{MoO}_4)_4$ has a framework structure with relatively small channels that extend along [010] [25]. Each Th cation is coordinated by eight monodentate MoO_4 tetrahedra, and each tetrahedron shares vertices with two Th polyhedra. $\text{Cu}_2\text{Th}_4(\text{MoO}_4)_9$ has a close-knit framework in which each Th cation is coordinated by nine monodentate MoO_4 tetrahedra, and each tetrahedron shares all four of its vertices with different Th polyhedra [26]. In $\text{Th}(\text{CrO}_4)(\text{IO}_3)_2$, the

dense framework contains Th cations that are coordinated by three monodentate CrO_4 tetrahedra and six IO_3 pyramids, and each tetrahedron is connected to four Th polyhedra [27].

Relative to other framework structures containing *An*(IV) cations, **ThS3** is unusual in that one of the Th polyhedra has a bidentate SO_4 group. In the case of **ThS4**, the presence of a pair of face-sharing ThO_9 polyhedra is novel, and leads to a denser framework than would otherwise be achieved.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.04.024.

References

- [1] G.T. Seaborg, J.J. Katz, *The Actinide Elements*, First Edition, McGraw-Hill Books, USA, 1954.
- [2] C. Hennig, K. Schmeide, V. Brendler, H. Moll, S. Tsushima, *Inorg. Chem.* 46 (2007) 5882–5892.
- [3] J. Habash, A.J. Smith, *Acta Crystallogr.* C39 (1983) 413–415.
- [4] J. Habash, R.L. Beddoes, *Acta Crystallogr.* C47 (1991) 1595–1597.
- [5] J. Habash, A.J. Smith, *Acta Crystallogr.* C46 (1990) 957–960.
- [6] E.G. Arutyunyan, M.A. Poraj-Koshits, A.K. Molodkin, *Zh. Strukt. Khim.* 7 (1966) 733–737.
- [7] J. Habash, A.J. Smith, *J. Crystallogr. Spectrosc. Res.* 22 (1992) 21–24.
- [8] J.N. Behera, C.N.R. Rao, *Z. Anorg. Allg. Chem.* 631 (2005) 3030–3036.
- [9] G. Lundgren, *Arkiv Kemi* 2 (1950) 535–549.
- [10] R.E. Wilson, S. Skanthakumar, K.E. Knope, C.L. Cahill, L. Soderholm, *Inorg. Chem.* 47 (2008) 9321–9326.

- [11] A.X.S. Bruker, APEX2v2010.11-3, Bruker AXS, Inc., Madison, WI, 2010.
- [12] (a) G.M. Sheldrick, SADABS 2001, Program for absorption correction using SMART CCD based on the method of Blessing; (b) R.H. Blessing, *Acta Crystallogr. A* 51 (1995) 33.
- [13] G.M. Sheldrick, SHELXTL PC, Version 6.12; An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 2001.
- [14] L.J. Farrugia, *J. Appl. Cryst.* 32 (1999) 837–838.
- [15] M. Huyghe, M.R. Lee, S. Jaulmes, M. Quarton, *Acta Crystallogr. C* 49 (1993) 950–954.
- [16] I.A. Charushnikova, N.N. Krot, Z.A. Starikova, *Radiokhim.* 41 (1999) 104–108 (transl.).
- [17] M. Huyghe, M.R. Lee, M. Quarton, F. Robert, *Acta Crystallogr. C* 47 (1991) 244–246.
- [18] E.G. Arutyunyan, M.A. Poral-Koshits, *Z. Struk. Khim.* 4 (1963) 276–277 (transl.).
- [19] I.A. Charushnikova, N.N. Krot, Z.A. Starikova, *Radiokhim.* 42 (2000) 36–39 (transl.).
- [20] S. Launay, A. Rimsky, *Acta Crystallogr. B* 36 (1980) 910–912.
- [21] O. Sedello, H. Muller-Buschbaum, *Z. Naturforsch. B* 51 (1996) 450–452.
- [22] E.M. Larson, P.G. Eller, T.L. Creemers, R.A. Penneman, C.C. Herrick, *Acta Crystallogr. C* 45 (1989) 1669–1672.
- [23] T.L. Creemers, P.G. Eller, R.A. Penneman, *Acta Crystallogr. C* 39 (1983) 1165–1167.
- [24] T.L. Creemers, P.G. Eller, R.A. Penneman, C.C. Herrick, *Acta Crystallogr. C* 39 (1983) 1163–1165.
- [25] M. Huyghe, M.R. Lee, M. Quarton, F. Robert, *Acta Crystallogr. C* 47 (1991) 1797–1799.
- [26] S. Launay, S. Jaulmes, F. Lucas, M. Quarton, *J. Solid State Chem.* 136 (1998) 199–205.
- [27] T.A. Sullens, P.M. Almond, J.A. Byrd, J.V. Beitz, T.H. Bray, T.E. Albrecht-Schmitt, *J. Solid State Chem.* 179 (2006) 1192–1201.