

An Open-Framework Thorium Sulfate Hydrate with 11.5 Å Voids

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We report the synthesis of a thorium sulfate hydrate with 11.5 Å open channels that propagate through the structure. The compound crystallizes in the tetragonal space group $P4_2/nmc$, $a = b = 25.890(4)$ Å, $c = 9.080(2)$ Å, $Z = 8$, $V = 6086.3(2)$ Å³. The thermal stability of the compound was investigated using thermogravimetric analysis and high-energy X-ray scattering (HEXS) revealing that the compound begins to undergo decomposition near 200 °C with an accompanied loss in crystallinity. The immediate coordination environment about the thorium atoms remains intact through heating to 500 °C as demonstrated by HEXS. Further heating reveals the formation of at least two crystalline phases, $\text{Th}(\text{SO}_4)_2$ and ThO_2 , which ultimately decompose to ThO_2 .

Introduction

Inspired by the properties of zeolites and zeotype materials, microporous and open-framework materials of the transition-metal phosphates and silicates have been of interest as designer catalysts, ion-exchange materials, and molecular sieves.¹ Of newer interest are microporous structures involving sulfate and selenate tetrahedra.² Most of the reported syntheses of these materials employ an organic agent, usually an amine or organic surfactant, as a template or structure-directing agent. Porous and open-framework materials synthesized without the use of such agents are rare and present interesting questions regarding their formation and assembly.

Among the actinide elements several open-framework materials have been reported. Most numerous are the open-framework materials of uranium. Structures employing both inorganic and organic ligands have been reported. Most notable are the large nanotubes reported by Krivovichev^{3,4}

prepared both in the presence and absence of templating agents. Recently, a uranyl sulfate templated using a crown-ether was reported by Krivovichev with a similar channel dimension to the compound here.⁵ Additional materials isolated as the metal hydrolysis products⁶ or as molybdate,^{7,8} silicate,⁹ or phosphate¹⁰ have all been reported with varying channel dimensions. Open-framework compounds have also been synthesized using organic ligands as the linkages between the metal centers in f-element compounds.¹¹ Notably, the bulk of the structures reported for actinide compounds of this type have been based on hexavalent uranium, which for the most part (excluding cation–cation¹² containing structures and cis-dioxo compounds^{13,14}) limits the coordination environment to the equatorial plane of the

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- (1) Auerbach, S. M.; Carrado, K. A.; Dutta, P. K. *Handbook of Zeolite Science and Technology*; Marcel Dekker Inc.: New York, 2003; p 1172.
- (2) Rao, C. N. R.; Behera, J. N.; Dan, M. *Chem. Soc. Rev.* **2006**, 35 (4), 375–387.
- (3) Krivovichev, S. V.; Kahlenberg, V.; Tananaev, I. G.; Kaindl, R.; Mersdorf, E.; Myasoedov, B. F. *J. Am. Chem. Soc.* **2005**, 127 (4), 1072–1073.
- (4) Krivovichev, S. V.; Kahlenberg, V.; Kaindl, R.; Mersdorf, E.; Tananaev, I. G.; Myasoedov, B. F. *Angew. Chem., Int. Ed.* **2005**, 44 (7), 1134–1136.

- (5) Alekseev, E. V.; Krivovichev, S. V.; Depmeier, W. *Angew. Chem., Int. Ed.* **2008**, 47, 549–551.
- (6) Li, Y. P.; Cahill, C. L.; Burns, P. C. *Chem. Mater.* **2001**, 13 (11), 4026–4031.
- (7) Krivovichev, S. V.; Cahill, C. L.; Nazarchuk, E. V.; Burns, P. C.; Armbruster, T.; Depmeier, W. *Microporous Mesoporous Mater.* **2005**, 78 (2–3), 209–215.
- (8) Krivovichev, S. V.; Cahill, C. L.; Burns, P. C. *Inorg. Chem.* **2003**, 42 (7), 2459–2464.
- (9) Li, Y. P.; Krivovichev, S. V.; Burns, P. C. *Am. Mineral.* **2000**, 85 (10), 1521–1525.
- (10) Doran, M. B.; Stuart, C. L.; Norquist, A. J.; O'Hare, D. *Chem. Mater.* **2004**, 16 (4), 565–566.
- (11) Cahill, C. L.; de Lill, D. T.; Frisch, M. *CrystEngComm* **2007**, 9 (1), 15–26.
- (12) Sullens, T. A.; Jensen, R. A.; Shvareva, T. Y.; Albrecht-Schmitt, T. E. *J. Am. Chem. Soc.* **2004**, 126 (9), 2676–2677.
- (13) Vaughn, A. E.; Barnes, C. L.; Duval, P. B. *Angew. Chem., Int. Ed.* **2007**, 46 (35), 6622–6625.
- (14) Villiers, C.; Thuery, P.; Ephritikhine, M. *Angew. Chem., Int. Ed.* **2008**, 47 (32), 5892–5893.

rigid linear dioxo uranyl cation. However, one might expect a greater variety of coordination modes and structure types from the spherical non -yl cations of the trivalent and tetravalent actinides, which accommodate much larger coordination numbers and are not geometrically constrained by an inherent molecular structure. Such diversity is already widely demonstrated for the trivalent lanthanide elements.

Additionally, sulfate may produce widely varying structures and stoichiometries. For instance, in the alkali metal containing thorium sulfate complexes alone there are at least five different structures. Within these complexes, the occurrence of bidentate sulfate, monodentate sulfate, and sulfate anions linking across metal centers to form sheets, chains, and molecular dimers is seen. Such diversity in the coordination modes of the sulfate tetrahedra are not uncommon and have been described in detail for uranyl sulfates by Burns.¹⁵

Among the open-framework and microporous structures reported for tetravalent thorium are the series of TOF complexes reported by O'Hare and co-workers.^{16,17} These organically linked thorium open-framework and microporous compounds contain voids and accessible pore vacancies of up to 11 Å when accounting for the van der Waals radius of water. In the complex TFO-2, a thorium fluoride benzenetricarboxylate, reported by O'Hare, hexagonal 11 Å vacant pores propagate down the *c*-axis of their material which were shown to be accessible to CO₂ but not N₂. Additionally the authors showed that the compound maintains its structure to about 410 °C, ultimately decomposing to ThOF₂.

Inorganic complexes of thorium that demonstrate open-framework and microporous structures include sulfates, silicates, and mixed iodate/selenate phases. In the sulfate complexes reported by Rao, organic templating agents were used to produce layered sheets of thorium sulfate materials with open-framework structures.¹⁸ The thorium-sulfate linkages are a mixture of monodentate and bidentate coordination in these complexes. In these structures, [Th₂(SO₄)₆(H₂O)₂]⁴⁺ and [Th₃(SO₄)₇(H₂O)₄]²⁺, the residual charge is balanced by the presence of an amine templating agent residing in the interlayers, not the pore vacancies. There was no demonstration of the porosity or thermal properties of these complexes.

We report here a variety of synthetic approaches to a thorium sulfate material and the crystal structure of the resulting compound, which is an example of a growing family of actinide open-framework materials.^{3–12,19–22} Compared with similar actinide inorganic materials, its voids are

larger than the untemplated, uranyl-selenate nanotubes of Krivovichev and similar in size to the uranyl sulfates also prepared by Krivovichev,^{3–5} but smaller than the 11 Å vacancies in the thorium complex TFO-2 reported by O'Hare. The compound reported here forms rapidly from thorium-sulfuric acid solutions at elevated temperature. Interestingly, while the structure of the reported compound contains large open-framework voids, complementary characterization methods indicate that these voids are vacant.

Experimental Methods

Caution! ²³²Th is an alpha-emitting radionuclide and should be handled using proper radiochemical techniques. In the quantities reported here, the material should be handled in a fume hood.

Synthesis of Th₃(SO₄)₆(H₂O)₆·H₂O (I). Synthesis 1. Starting with 300 mg of Th(NO₃)₄·4H₂O in 5 mL of water, we added NH₄OH to precipitate Th(OH)₄. This slurry was washed and centrifuged until the pH of the supernatant was neutral as determined by pH paper. The precipitate was then resuspended in 10 g of H₂O and transferred to a 40 mL Pyrex cone and placed in a waterbath at 100 °C where 1 mL of 18 M H₂SO₄ was added forming a clear solution. One milliliter of a LiOH solution (1.2 g/10 mL H₂O) was added instantaneously forming needles of **I**. Alternatively, LiOH was replaced with CsOH (1.5 g/10 mL H₂O) producing the same needle crystals with the same structure.

Synthesis 2. A 500 mg quantity of Th(NO₃)₄·4H₂O was dissolved in distilled water and precipitated, washed, and resuspended as above. To this was added 0.5 mL of 18 M H₂SO₄ and 0.200 mL of 9 M H₂SO₄; after approximately 1 h a white precipitate formed that upon study by X-ray diffraction was determined to be compound **I**. In the syntheses employing the alkali hydroxides the compound redissolved on standing after 24 h. However, in the vessel where LiOH had been added the compound recrystallized after a few days in nearly quantitative yield. In the vessel where CsOH had been added the compound recrystallized along with the well-known thorium sulfate salt Cs₂Th(SO₄)₃·2H₂O.²³

The compound may be separated from the mother liquor by filtration and washing with methanol, it is stable, and may be stored indefinitely in air once dried.

Single Crystal X-ray Diffraction. X-ray Crystallography. Diffraction data were collected at room temperature on a Bruker AXS diffractometer equipped with an APEX II CCD camera. Absorption corrections were applied using the program SADABS. The structure solution and refinement were carried out using direct methods and subsequent full matrix least-squares refinements on *F*² using the suite of software SHELXTL.²⁴ All atoms were refined anisotropically.²⁵

High-Energy X-ray Scattering. High-energy X-ray scattering data were collected at the Advanced Photon Source, Argonne

- (15) Hawthorne, F. C.; Krivovichev, S. V.; Burns, P. C. The Crystal Chemistry of Sulfate Mineral. In *Reviews in Mineralogy and Geochemistry: Sulfate Mineral, Crystallography, Geochemistry, and Environmental Significance*; Alpers, C. N., Jambor, J. L., Nordstrom, D. K. Eds.; The Mineralogical Society of America: Washington, D.C., 2000; Vol. 40.
- (16) Kim, J. Y.; Norquist, A. J.; O'Hare, D. *J. Am. Chem. Soc.* **2003**, *125* (42), 7707–7709.
- (17) Ok, K. M.; Sung, J.; Hu, G.; Jacobs, R. M. J.; O'Hare, D. *J. Am. Chem. Soc.* **2008**, *130* (12), 3762–3763.
- (18) Behera, J. N.; Rao, C. N. R. *Z. Anorg. Allg. Chem.* **2005**, *631* (15), 3030–3036.
- (19) Norquist, A. J.; Doran, M. B.; Thomas, P. M.; O'Hare, D. *Inorg. Chem.* **2003**, *42* (19), 5949–5953.
- (20) Kim, J. Y.; Norquist, A. J.; O'Hare, D. *Chem. Commun.* **2002**, (19), 2198–2199.

- (21) Halasyamani, P. S.; Walker, S. M.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121* (32), 7415–7416.
- (22) Doran, M.; Norquist, A. J.; O'Hare, D. *Chem. Commun.* **2002**, (24), 2946–2947.
- (23) Habash, J.; Smith, A. J. *J. Cryst. Spec. Res.* **1992**, *22* (1), 21–24.
- (24) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.
- (25) Crystal data: M.W. 1384.48, space group *P42/nmc*, tetragonal (No. 137), *a* = *b* = 25.890(4) Å, *c* = 9.080(2) Å, *Z* = 8, *V* = 6086.3(2) Å³, ρ_{diff} = 3.022 Å³, crystal dimensions, 0.350 × 0.040 × 0.040 mm, μ(Mo, K) = 15.142 mm⁻¹, *T* = 295 K. Total reflections/independent reflections 69106/4245, *R*₁ = 0.0341, *wR*₂ 0.0853 (*I* > 2σ). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247–808–666; e-mail: crysdata@fiz-karlsruhe.de) on quoting deposition number CSD-418749.

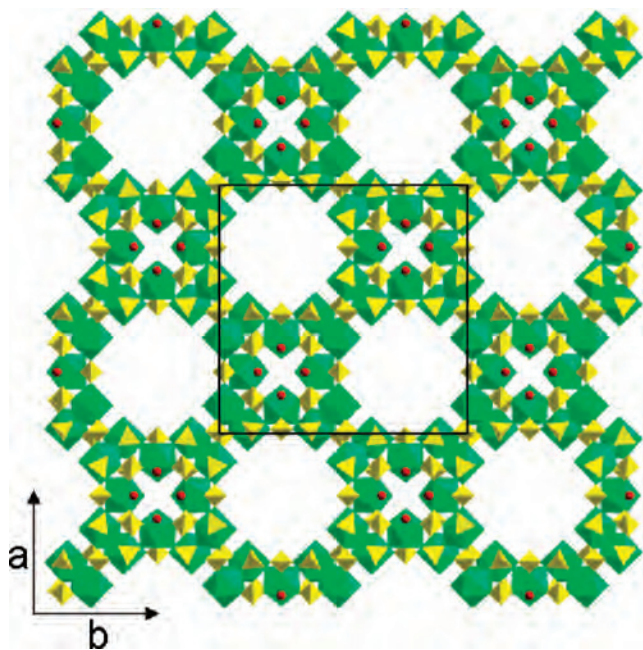


Figure 1. Projection of **I** with the *c*-axis pointed into the page to highlight the open vacancies of the framework. In green are the thorium atoms, the sulfate tetrahedra are in yellow, and the unbound water molecules are shown by red spheres.

National Laboratory on the undulator beamline 11-ID-B. Data were collected using an amorphous silicon flat panel detector (GE Healthcare), at a detector distance corresponding to $Q_{\max} = 35 \text{ \AA}^{-1}$. Data reduction methods were described previously.²⁶

Results and Discussion

Our newly synthesized compound is based on the formula $\text{Th}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}$ (**I**) determined from single crystal diffraction data. It precipitates from acidic thorium sulfate solution at elevated temperature or upon the introduction of alkali hydroxides. The compound was originally synthesized from acidic aqueous solution by the addition of LiOH or CsOH whereupon rapid formation of the compound resulted. Further studies into the synthesis of **I** showed that the compound may be produced directly from sulfuric acid solution without the aid of any additional reagents beyond that of Th^{4+} . Results from X-ray powder and single-crystal diffraction indicate that all three syntheses produce the same material.

$\text{Th}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}$ crystallizes in the tetragonal space group $P4_2/nmc$ (No. 137), $a = b = 25.890(4) \text{ \AA}$, $c = 9.080(2) \text{ \AA}$. Presented in Figure 1 is a projection of the structure down the *c*-axis. Orthogonally intersecting chains of thorium cations stack together with corner-sharing sulfate tetrahedra to form neutral networks of 11.5 \AA square channels (oxygen-to-oxygen) or 8.8 \AA accounting for water's van der Waals radius of 1.35 \AA . Similar to the compounds reported by Rao, the monodentate sulfate linkages between the compounds form the basis for the formation of the framework voids. In the structure of the compound $[\text{HN}(\text{CH}_2)_6\text{NH}]_2[\text{Th}_2(\text{SO}_4)_6(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, the sinusoidal chains of thorium sulfate are

linked together by a $\text{Th}_2(\text{SO}_4)_4$ unit to form sheet structures.¹⁸ The spacing between these linkages across the chains are what creates the framework voids in that structure. In our compound this similar structural motif is demonstrated as a $\text{Th}_2(\text{SO}_4)_3$ unit as demonstrated in Figure 2, and creates the open-framework voids that propagate down the *c*-axis of the crystal.

We are unable to assign any solvent water to these framework voids. Solutions to the X-ray structures in which Cs^+ was substituted for Li^+ , in an attempt to identify the presence of an alkali cation, were not successful. Taking guidance from the synthetic procedures used to prepare the compound (both with and without alkali metal) it is worth considering that cations probably do not reside in the channels of the compound and are certainly not a prerequisite for its formation. Furthermore, the framework as it is written is neutral suggesting that any cations trapped in the voids would have to be charge balanced by residual sulfate anions.

There are two crystallographically unique thorium positions in the complex, Table 1, both of which are nine coordinate $\text{Th}(\text{SO}_4)_7(\text{H}_2\text{O})_2$, Figure 2. Th(1), the thorium atom resides on a special position, a mirror plane. The two coordinated water molecules have $\text{Th}(1)-\text{O}(\text{w})$ bond distances of $2.479(1)$ and $2.542(1) \text{ \AA}$ consistent with $\text{Th}-\text{OH}_2$ distances of $2.492(3) \text{ \AA}$ and $2.520(5) \text{ \AA}$ known from $[\text{Th}(\text{H}_2\text{O})_{10}]\text{Br}_4$.²⁷ The remaining $\text{Th}(1)-\text{OSO}_3$ bond distances are $2.349(6)$ and $2.408(2) \text{ \AA}$ to the S(1) and S(3) sulfate anions, and $2.439(6)$, $2.476(6) \text{ \AA}$ for $\text{Th}-\text{O}$ bonds to S(2) sulfate anions. The Th(2) atom resides on the general position with $\text{Th}(2)-\text{OSO}_3$ bond distances of $2.381(6)$, $2.402(6) \text{ \AA}$ for coordination to the S(4) sulfate anions, $2.355(7)$ and $2.422(7) \text{ \AA}$ for S(2), $2.411(7)$ and $2.487(7) \text{ \AA}$ for S(1) anions, and $2.393(6) \text{ \AA}$ for S(3). The remaining $\text{Th}(2)-\text{O}(\text{w})$ bond distances are $2.486(7)$, and $2.597(7) \text{ \AA}$. All of the $\text{Th}-\text{OSO}_3$ linkages are monodentate, unlike the bidentate linkages found in the compound $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$.²⁸ The distribution of $\text{Th}-\text{OSO}_4$ bond distances in **I** is in good agreement for those reported for other thorium sulfate compounds containing monodentate sulfate linkages such as $\text{K}_4\text{Th}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, a compound which contains only monodentate sulfate coordination.²⁹

Among the sulfate anions, the $\text{S}(2)\text{O}_4^{2-}$ and $\text{S}(4)\text{O}_4^{2-}$ are fully coordinated through monodentate corner-sharing linkages to thorium cations. The S(1) and S(3) sulfate anions are coordinatively unsaturated with the non-bonded oxygen atom of the sulfate tetrahedron pointed inward to the void cavity. The mean $\text{Th}-\text{S}$ bond distance in **I** is 3.789 \AA consistent with the bond distances reported in other Th-sulfate compounds containing sulfate in monodentate coordination. This distance would be considerably shorter if the sulfate were present as a bidentate ligand. For example, in

(27) Wilson, R. E.; Skanthakumar, S.; Burns, P. C.; Soderholm, L. *Angew. Chem. Int. Ed.* **2007**, *26*, 8043–8045.

(28) Habash, J.; Smith, A. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *39* (APR), 413–415.

(29) Arutyunyan, E. G.; Porai-Koshits, M. A.; Molodkin, A. K. *Zh. Struk. Khim.* **1966**, *7*, 733–737.

(26) Skanthakumar, S.; Soderholm, L. *Mater. Res. Soc. Symp. Proc.* **2006**, *893*, 411–416.

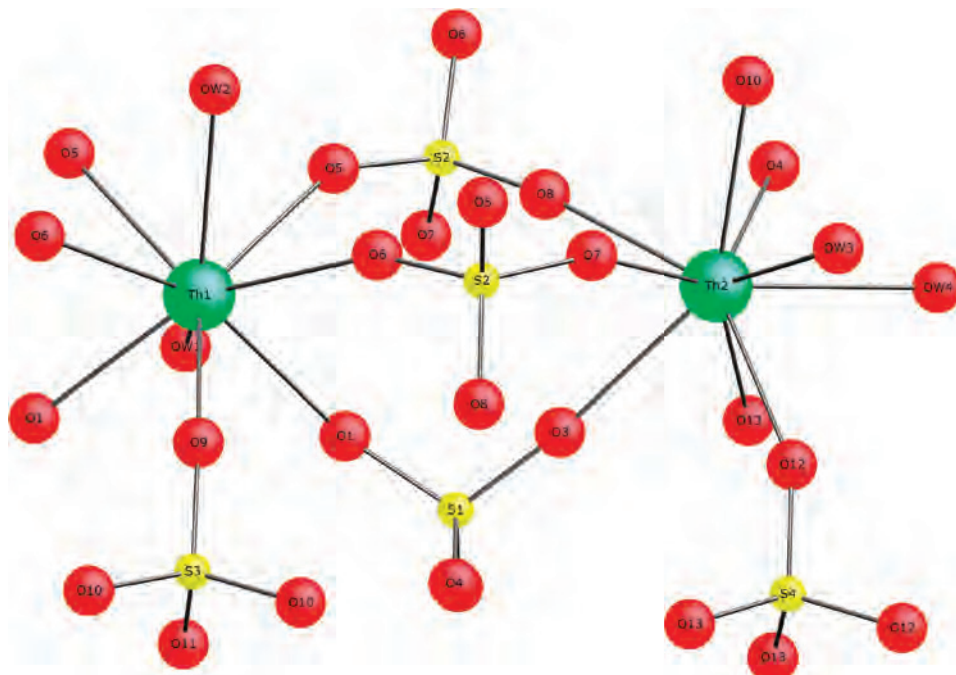


Figure 2. Model demonstrating the local coordination environments about the thorium positions in I.

Table 1. Bond Lengths about the Thorium Atoms^a

Th(1)–O(1)	2.349(6) ¹	Th(2)–O(3)	2.411(7)
Th(1)–O(5)	2.439(6) ¹	Th(2)–O(4)	2.487(7) ²
Th(1)–O(6)	2.476(6) ¹	Th(2)–O(7)	2.422(7) ³
Th(1)–O(9)	2.408(1)	Th(2)–O(8)	2.355(7) ¹
Th(1)–O(w1)	2.542(1)	Th(2)–O(10)	2.393(6) ³
Th(1)–O(w2)	2.479(1)	Th(2)–O(12)	2.402(6)
Th(1)–S(1)	3.782(3)	Th(2)–O(13)	2.381(6)
Th(1)–S(2)	3.764(3), 3.855(3)	Th(2)–O(w3)	2.597(7)
Th(1)–S(3)	3.727(3)	Th(2)–O(w4)	2.486(7)
		Th(2)–S(1)	3.809(3), 3.860(3)
		Th(2)–S(2)	3.778(3), 3.779(3)
		Th(2)–S(3)	3.739(3)
		Th(2)–S(4)	3.763(3), 3.787(3)

^a Symmetry for equivalent positions 1, (x, 1/2 - y, z); 2, (y, x, 1/2 + z); 3, (1/2 - y, x, -1/2 + z). All distances reported in Å.

the compound $\text{Cs}_2\text{Th}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$, which co-crystallizes with I on standing in the mother liquor, the Th–S distance averages 3.170 Å.

X-ray diffraction data collected on powders of I indicate phase purity from all the reported syntheses. Heating the compound in air at 110° causes the material to turn from bright white to a gray color without loss of crystallinity as supported by the X-ray diffraction data (Supporting Information) and high-energy X-ray scattering (HEXS) data taken.

Raman spectra taken of the complex as synthesized show bands indicative of bound sulfate anions with an intense grouping of bands near 1060 cm^{-1} , and two weaker groupings of bands at 650 and 450 cm^{-1} . The presence of coordinated water to the Th cation is confirmed by FT-ATR-IR. A multiplet of bands characteristic of ionic sulfate are present in the spectra between 1000 and 1200 cm^{-1} as well as a band near 1650 cm^{-1} attributable to the coordinated water of hydration.³⁰ There is limited spectroscopic evidence of free water in the spectrum consistent with the results from a thermogravimetric analysis (TGA) of the compound, which shows that the complex loses its water of hydration upon heating to about 175 °C, Figure 3. The mass loss at this

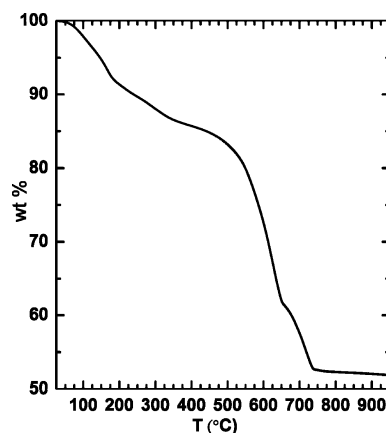


Figure 3. Thermogravimetric analysis of I conducted with a ramp of 10 °C · min⁻¹ under flowing N₂.

temperature corresponds to 7.4%, in comparison to the 9.0% expected based on the water of hydration in the structural formula. If the channels of the complex were occupied by water we would expect a much larger discrepancy between the calculated and the observed mass changes indicating that the channels are most likely vacant.

Over the course of heating, X-ray powder diffraction lines from the sample at 400 °C are consistent with $\text{Th}(\text{SO}_4)_2$ as a secondary phase resulting from thermal decomposition.³¹ Unfortunately, the structural report of this anhydrous sulfate includes only the peak positions and their intensities. Heating to 500 °C shows X-ray evidence of some phase decomposition and by 600 °C the data are consistent with a mixture of at least three phases including ThO_2 , $\text{Th}(\text{SO}_4)_2$, and minor contributions from an unknown phase. Further heating of the compound to 950 °C results in a total mass loss of 49.1%,

(30) Nyquist, R. A.; Kagel, R. O. *The Handbook of Infrared and Raman Spectra of Inorganic Compounds and Organic Salts*; Academic Press Inc.: San Diego, 1997; Vol. 4, p 495.

in excellent agreement with the expected decomposition of the complex to thoria. An X-ray powder pattern after TGA treatment confirms thoria as the sole remaining decomposition product.

The thermal stability of the structure was further probed using HEXS data,^{26,32} the Fourier transform of which reveals atomic correlations in the sample without the requirement of long-range order.³³ The data, in the form of pair-distribution functions (PDFs), are shown for selected temperatures in Figure 4. The correlations observed in the room-temperature data are consistent with the refined crystal structure and show no additional peaks that would indicate a non-crystalline component to the sample. Specifically, there is no evidence of correlations resulting from additional ions residing within the framework voids, a result consistent with all the other available data. Although the data obtained at 110 °C appear very similar to those obtained at room temperature, the PDF from the 200 °C sample reveals a marked decrease in crystallinity, as measured by the lack of significant correlations at distances longer than about 8 Å. Evidence of longer range correlations return at 400 °C, as expected from the diffraction peaks in the powder patterns. The maintenance of the peak position at 3.8 Å along with the absence of a new peak at about 3.2 Å suggests that the sulfate remains as monodentate through the structural rearrangement.²⁸ These data include contributions from the previously reported hexagonal phase, $\text{Th}(\text{SO}_4)_2$,³¹ suggesting that the anhydrous $\text{Th}(\text{SO}_4)_2$ is most likely a structure with monodentate sulfate coordination. The PDF obtained at 500 °C has broadened, less intense peaks consistent with the powder pattern that shows evidence of further decomposition of the Th-sulfate phase.

Although the long-range correlations have disappeared upon heating to 200 °C, the short-range correlations present out to about 5 Å remain largely unchanged, as shown in the bottom panel of Figure 4. The most prominent changes in the patterns occur in two regions. The decreasing intensity with increasing temperature in the 2.6 to 3.2 Å region corresponds to loss of O–O correlations. Both bound and unbound O(w5) water–water correlations contribute significantly to this distance range. The second region of change occurs with the broad peak centered at about 4.6 Å. In the single crystal this distance has contributions from the distant, bridging, sulfate oxygen and from the Th-bound waters. The latter interaction is the correlation between the water bound to one Th interacting with the Th on the other crystallographic site. Taken together, these data show that the basic Th-sulfate correlations remain intact and that the loss of bound water is responsible for the collapse of long-range interactions by 200 °C. This result is somewhat surprising because there does not appear to be a sufficient change in the number of ions in the Th first coordination sphere, at 2.5 Å, that should occur with the loss of two water molecules.

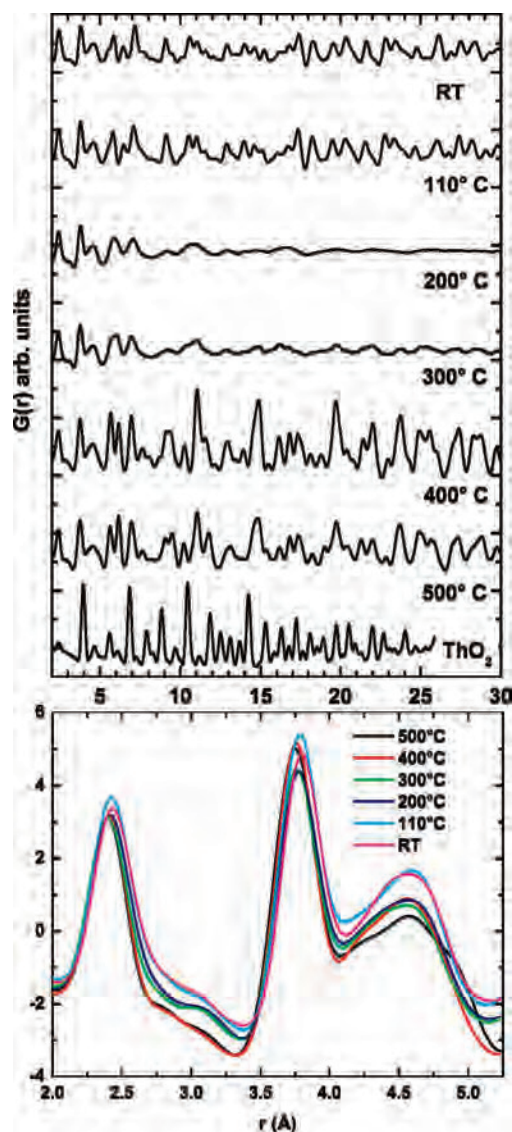


Figure 4. (top) Pair distribution functions (PDF) from HEXS collected on **I** as synthesized and after heating for 24 h at the indicated temperatures. Comparison with a PDF of ThO_2 indicates that the sulfate coordination in **I** is present until at least 500°. (bottom) Enlargement and overlay of the 2.0 Å to 5.5 Å region comparing the coordination environment about the thorium positions throughout the heating process. Systematic changes in the 2.6 to 3.4 Å and 4.0 to 5.0 Å are attributed to changes in O–O and Th–O correlations, respectively.

Lack of an accurate knowledge of the sample stoichiometry at 200 °C prohibits a detailed analysis of changing coordination number.²⁶

Comparing the most intense correlations reappearing in the PDF at higher temperatures to those of a thoria sample indicates that until the onset of the sulfate decomposition above 500 °C as shown by the TGA, the bulk of the sample remains a sulfate phase as indicated by the persistence of the 1.5 Å peak from the S–O correlations in the sulfate tetrahedra, and the 3.8 Å peak arising from Th–S correlations. Above 500 °C, the TGA data indicate a significant mass loss with the appearance of anhydrous thorium sulfate.

- (31) Mudher, K. D. S.; Keskar, M.; Venugopa, V. *J. Nucl. Mater.* **1999**, *265*, 146–153.
 (32) Soderholm, L.; Skanthakumar, S.; Neufeind, J. *Anal. Bioanal. Chem.* **2005**, *381*, 44–55.
 (33) Egami, T.; Billinge, S. J. L. *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*; Pergamon: Amsterdam, 2003.

Conclusions

The compound reported here is a new addition to the growing number of porous and open-framework actinide materials. Whereas the reported results indicate limited to no porosity of this compound, its channel size is comparable to the largest of the microporous and open-framework actinide materials reported to date. The thermal stability is limited with respect to the long-range order and crystallinity of the compound; however, HEXS data indicate that the local coordination environment about the thorium cations with respect to the sulfate anion remains relatively intact. Further work, including the synthesis and characterization of the corresponding Th-selenate phase, would help to characterize the behavior of these zeotype materials.

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Supporting Information Available: Indexed X-ray powder diffraction data, FT-IR and Raman data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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