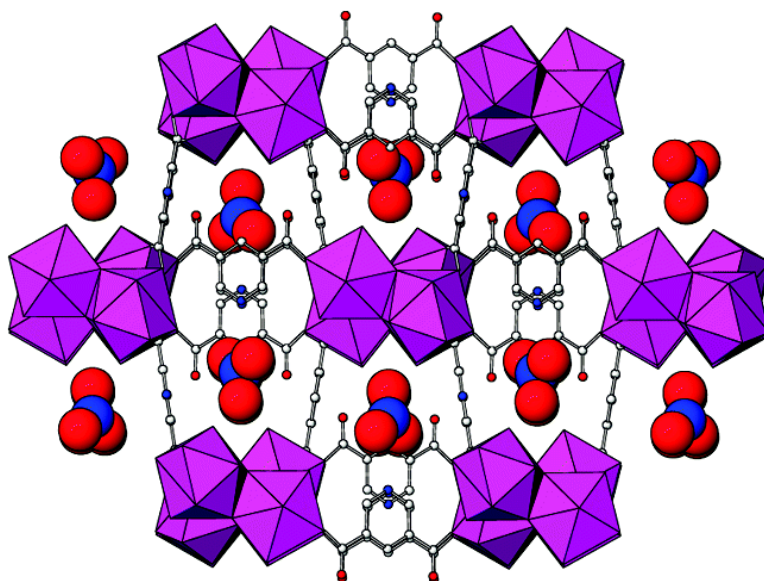


[(ThF)(NCHO)(HO)][NO]: An Actinide–Organic Open Framework

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[(Th₂F₅)(NC₇H₅O₄)₂(H₂O)][NO₃]: An Actinide–Organic Open Framework

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There has been intense effort to synthesize zeolite-like materials with an open-framework structure because such frameworks could be suitable for applications in sorption,^{1a,b} separation,^{1c} and heterogeneous catalysis.^{1d} Recently, a number of 3D organic,² metal–organic,³ and inorganic⁴ framework materials have been reported. One of the approaches to synthesize such compounds is the construction of frameworks from molecular building units using metal–ligand coordination. Many metal–organic frameworks exhibit guest exchange,^{3c,e,5} gas adsorption,^{1a,b} microporosity, or selective catalytic activity.⁶ However, the metal components have been mainly limited to the main group or transition metal elements having either tetrahedral, square pyramidal, or octahedral geometries. There are currently few examples of metal–organic framework solids incorporating actinide elements.⁷ These actinide elements are likely to exhibit coordination numbers of seven, eight, or nine. Thus, frameworks built from MX₇, MX₈, and MX₉ units, where M is actinide element, would create a completely distinct class of materials. Furthermore, actinide-containing materials can be very important for applications such as catalysis.⁸ We have recently synthesized a series of new organically templated actinide materials such as uranium fluorides,⁹ phosphites,^{10a} phosphate,^{10b} sulfates,¹¹ and thorium fluorides¹² by hydrothermal reaction. In this work, we report the phase-pure synthesis, structure, and characterization of a new three-dimensionally connected, actinide–organic framework solid, thorium fluoride pyridinedicarboxylate (I), [(Th₂F₅)(NC₇H₅O₄)₂(H₂O)][NO₃] (Figure 1).

I is synthesized in a one-step process by the reaction of thorium nitrate with 3,5-pyridinedicarboxylic acid under hydrothermal conditions in the presence of HF and DMF (*N,N*-dimethylformamide). The starting materials, Th(NO₃)₄·5H₂O (0.570 g, 1.0 mmol), HF (40% aq., 0.120 g), H₂O (5.00 g), NC₇H₅O₄ (0.279 g, 1.67 mmol), and DMF (0.049 g, 0.67 mmol), were placed in a Teflon-lined stainless steel autoclave at room temperature. The mixture was heated to 120 °C for 24 h and cooled to room temperature at 3 °C h⁻¹. The material is isolated as rod-shaped, pale-yellow crystals. A monophasic crystalline product was recovered in ~90% yield based on thorium.^{13,14}

I is composed of thorium oxyfluoride chain running along the [010] direction with cross-linking pyridinedicarboxylate (PDC) groups (Figure 2). The chain is made up of corner-sharing thorium oxyfluoride polyhedra containing 9-coordinate thorium. Each thorium is coordinated to four oxides and five fluorides in a tricapped prismatic environment. A similar coordination geometry has been observed in condensed uranium and thorium fluorides such as UFO-*n* (Uranium Fluorides from Oxford; *n* = 1–3),^{9a,b} TFO-*n* (Thorium Fluorides from Oxford; *n* = 1,2),¹² β-NH₄UF₅,¹⁵ LiUF₅,¹⁶ and K₂U₂F₉.¹⁷ The observed Th–F bond distances, ranging from 2.307(2) to 2.374(6) Å, are somewhat shorter than Th–O distances

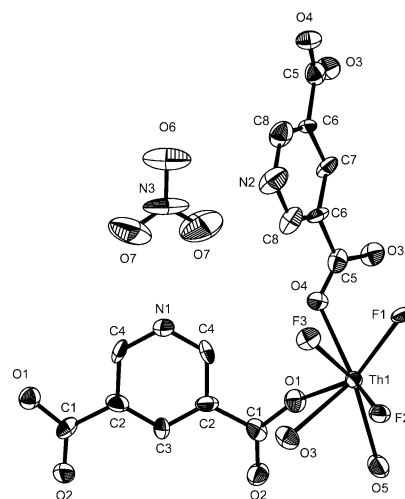


Figure 1. View of the asymmetric unit of I, showing non-hydrogen atoms represented by thermal ellipsoids with 80% probability. Hydrogen atoms have been omitted for clarity.

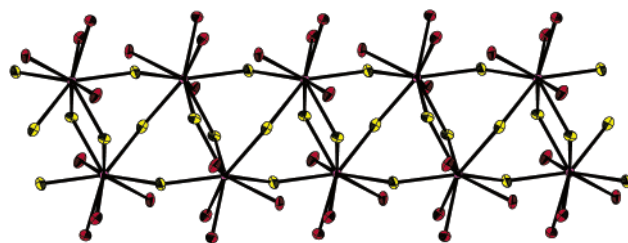


Figure 2. Thermal ellipsoidal representation of thorium backbone chain running along the [010] direction (50% probability ellipsoid). Magenta, red, and yellow colors represent thorium, oxygen, and fluorine atoms, respectively.

(2.426(7)–2.502(7) Å). Three oxides from a PDC and one water molecule (Th–O(5): 2.502(7) Å) are bound to each thorium center.

Each thorium center shares an edge with a neighboring thorium through two fluorides (F(1) × 2), creating dimers. These dimers are linked to one another through shared corners (F(2) × 2 and F(3) × 2), forming chains that run along the [010] direction. See Figure 2. The Th(1)–F(2)–Th(1) and Th(1)–F(3)–Th(1) bond angles are 152.5(4)° and 147.1(3)°, respectively, while the angles involving the edge-sharing fluorides (Th(1)–F(1)–Th(1)) are 115.9(2)°. Three Th–Th nearest neighbor distances are 3.99, 4.48, and 4.49 Å. The example of inorganic chains combining with organic linkers to form 3D-networks is found in lanthanide materials such as Nd–glutarate.¹⁸ This contains single-polyhedron width chains composed of edge-sharing NdO₈(H₂O) polyhedra, unlike the present double-polyhedron width thorium chains.

Adjacent thorium fluoride chains are connected to one another in a three-dimensional fashion by PDC linkers, which can adopt one of two bonding motifs. Each carboxylate group on the first type of PDC linker is bound to one thorium center through a single

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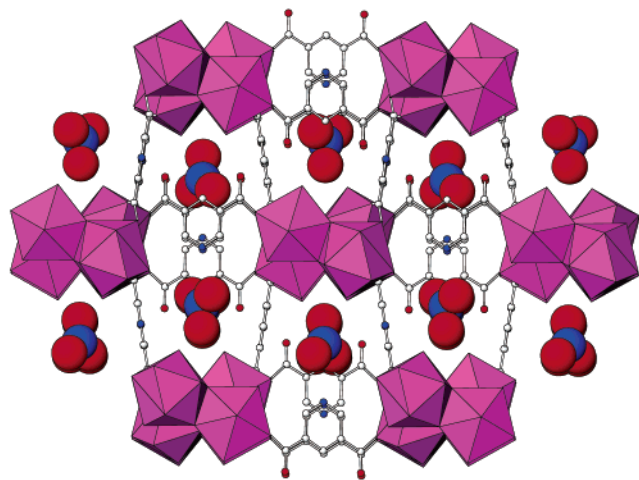


Figure 3. Polyhedral view of the thorium–PDC framework in **I** along the [010] direction with nitrate anions (large spheres) within the framework cavity. White, red, and blue colors represent carbon, oxygen, and nitrogen atoms, respectively.

oxide, O(1). O(2) is bound only to C(1). This forms chains that run along the [100] direction. The C(1)–O distances reflect the differences in coordination of the respective oxide ligands; the C(1)–O(1) distance is 1.295(11) Å, while the C(1)–O(2) distance is 1.218(11) Å. The second type of PDC contains carboxylate groups that are bound to two adjacent thorium centers each, as opposed to one thorium center per carboxylate in the first type of PDC. The thorium fluoride chains are linked along the [001] direction by this second type of PDC. Differences in carboxylate coordination are also reflected in the Th(1)–O bond lengths. The Th(1)–O(1) bond length is 2.426(7) Å, while the Th(1)–O(3) and Th(1)–O(4) bond lengths are 2.501(7) and 2.472(7) Å, respectively.

The connectivity creates a cavity between the chains and pyridine rings, in which nitrate anions reside. The cavity has a width of 3.3 Å × 3.8 Å, (shortest atom–atom contact distance considering van der Waals radii). The nitrate anions form weak hydrogen bonds with the protonated pyridine moiety (N(1)–H(5)–O(7): 2.90 Å). A hydrogen bond is also observed between bound water and nitrate (O(6)–H(8)–O(5): 2.81 Å) (Figure 3).

Preliminary studies indicate that **I** undergoes anion exchange with halides and other pseudohalides. Further studies on the anion binding affinities and the kinetics of ion exchange are currently in progress.

This work demonstrates the feasibility of constructing 3D metal–organic open-framework networks, in which actinide elements with large coordination numbers such as nine-coordinated thorium are incorporated as metal centers. In this initial example the structure consists of a cationic actinide–organic framework, which contains nitrate anions as guests.

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Supporting Information Available: A crystallographic information file (CIF) containing complete tables of crystallographic details, atomic coordinates, thermal parameters, and bond lengths and angles; thermogravimetric analysis data for **I**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Elemental analyses **I**: obsd (calcd) C 19.43 (17.31), H 1.33 (1.04), N 4.61 (4.33), Th 42.86 (48.99).
- (14) Single crystals of dimension 0.04 mm × 0.04 mm × 0.08 mm were used for structural determination. Data were collected using an Enraf Nonius FR 590 Kappa CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystals were mounted on a glass fiber using N-Paratone oil and cooled in situ using Oxford Cryostream 600 Series to 120 K for data collection. Frames were collected, indexed, and processed using Denzo SMN and the files scaled together using HKL GUI within Denzo SMN.¹⁹ The heavy atom positions were determined using SIR97.²⁰ All other non-hydrogen atoms were located from Fourier difference maps and refined with anisotropic thermal parameters using full matrix least-squares procedures on F_o^2 . Hydrogen atoms were placed in geometrically idealized positions. All calculations were performed using CRYSTALS²¹ and CAMERON²² software packages. For **I**: orthorhombic, space group *Pnmb* (No. 52), $a = 13.6590(6)$ Å, $b = 8.4270(3)$ Å, $c = 18.6420(9)$ Å, $V = 2145.78(16)$ Å³, $Z = 4$, $D_c = 3.062$ g cm⁻³, 7917 reflections collected of which 2447 were independent and 1455 were observed [$I > 2\sigma(I)$]. Refinement converged with $R = 0.0282$, $wR = 0.0500$.
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