ChemComm
www.rsc.org/chemcomm

The first organically templated thorium compounds, $[C_4N_2H_{12}]_{0.5}[ThF_5]$ and $[C_5N_2H_{14}][ThF_6]\cdot0.5H_2O$

Jong-Young Kim, Alexander J. Norquist and Dermot O'Hare*
Inorganic Chemistry Laboratory, South Parks Road, University of Oxford, Oxford, UK OX1 3QR.
E-mail: dermot.ohare@chem.ox.ac.uk; Fax: +44 1865 272690; Tel: + 44 1865 272658

Received (in Cambridge, UK) 11th July 2002, Accepted 14th August 2002
First published as an Advance Article on the web 30th August 2002

Organically templated thorium compounds were synthesized for the first time under hydrothermal conditions; the piperazine containing compound consists of 2-D layers, while the 2-methylpiperazine phase contains unprecedented 1-D chains of face-sharing ThF_9 polyhedra.

Hydrothermal synthesis[1] is a powerful technique for the preparation of new inorganic–organic hybrid materials with structural architectures ranging from molecular to three-dimensional. Much attention has been paid to the synthesis of zeolite-analogues owing to their practical application in shape-selective catalysis,[2] ion exchange,[3] molecular sieving,[4] and gas separation.[5] In the past several years, a host of new metal–organic coordination compounds incorporating main group or transition metals have been synthesized using hydrothermal techniques. These two- and three-dimensional inorganic networks have the potential to exhibit desirable host–guest chemistry, which can be tailored by tuning the building blocks from which the network is assembled.

We have recently synthesized a series of new organically templated uranium fluorides,[6] phosphites,[7] and molybdates[8] under hydrothermal conditions. These compounds range from molecular zero-dimensional materials to three-dimensional open-framework compounds. Actinide elements such as uranium exhibit interesting topologies and coordination chemistry because of the accessibility of higher coordination numbers, which are not possible with main group elements. The structural diversity of the inorganic framework is dependent upon the detailed reaction condition and the structure-directing agent. However, the structural diversity of uranium(VI) compounds is rather constrained because of strongly favoured uranyl ($O{=}U{=}O^{2+}$) group which tends to induce 2D-layered structures. In this respect, we extended our research to new actinide compounds incorporating thorium, which does not contain a strongly favoured unit such as the uranyl group, in an attempt to discover new structural topologies. In this work, the synthesis, structure, and characterization of two new organically templated thorium phases are reported for the first time. $[C_4N_2H_{12}]_{0.5}[ThF_5]$ and $[C_5N_2H_{14}][ThF_6]\cdot0.5H_2O$ are denoted TFO-1 and TFO-2, respectively (Thorium Fluoride from Oxford).

TFO-1 and TFO-2 are synthesized in a one-step process by the reaction of $Th(NO_3)_4\cdot3H_2O$ under autogeneous hydrothermal conditions at 180 °C in the presence of HF and either piperazine or 2-methylpiperazine. The materials are isolated in phase pure form as platelet crystals in high yield.†

The crystal structure of TFO-1‡ is closely related to the layered UFO-*n* (*n* = 1–3) compounds[6ab] which contain U^{IV} cations. TFO-1 consists of negatively charged thorium fluoride layers, $[ThF_5]^-$, separated by charge-balancing $[C_4N_2H_{12}]^{2+}$. The thorium fluoride layers and templates of TFO-1 are shown in Fig. 1. The structure is stabilized by hydrogen bonding between the $[C_4N_2H_{12}]^{2+}$ cations and the negatively charged $[Th_2F_{10}]^{2-}$layers (N–H···F(5): 2.66 Å, N–H···F(3): 2.81 Å, N–H···F(2): 2.94 Å).

The structure of the individual thorium fluoride layers is analogous to those of UFO-*n* (*n* = 1–3; see Fig. 2). Each thorium atom is bound to nine fluoride ligands in a tricapped prismatic coordination environment.

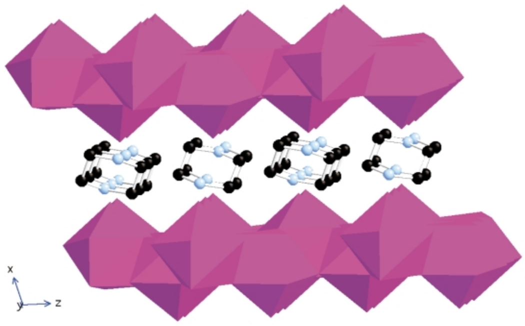

Fig. 1 The structure of TFO-1 viewed along [010] direction, showing the thorium fluoride layers and occluded template molecules.

A similar coordination geometry has been observed in condensed uranium fluorides such as UFO-*n* (*n* = 1–3),[6ab] β-NH_4UF_5,[9] $LiUF_5$,[10] and $K_2U_2F_9$.[11] Equivalent ThF_9 polyhedra share three edges with three adjacent polyhedra and share two corners with two additional polyhedra to form thorium fluoride sheets. The ninth terminal fluoride of each polyhedra points toward the interlayer region, and forms strong hydrogen bonds to the interlamellar organic cation (N–H···F(5): 2.66 Å). Each polyhedron may be described as $[ThF_{8/2}F_{1/1}]^-$, with eight bridging and one terminal fluorides. The Th–F bond for a terminal fluoride (2.278(5) Å) is shorter than the bridging Th–F bonds (mean distance: 2.39 Å; ranging between 2.360 Å and 2.464 Å) as expected.

The structure and topology of TFO-2 are completely unprecedented in the field of thorium and uranium chemistry. TFO-2 consists of one-dimensional thorium fluoride chains which are formed from the unprecedented face sharing ThF_9

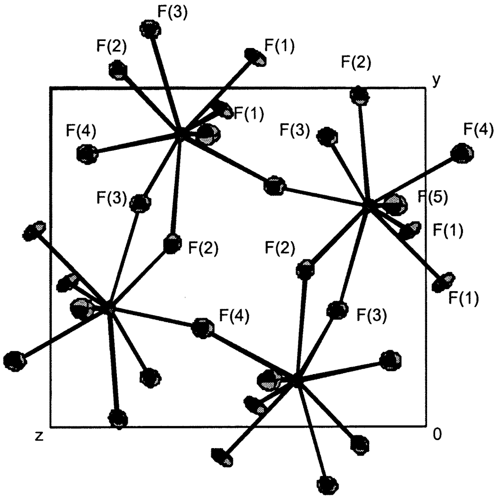

Fig. 2 Thermal ellipsoidal representation of a single thorium fluoride layer in TFO-1 viewed perpendicular to the layers (along [100] direction), showing the construction of thorium fluoride layers from corner- and edge-sharing $[ThF_9]$ tricapped trigonal prisms.

DOI: 10.1039/b206749h

polyhedra (see Fig. 3 and 4). Within the thorium fluoride chains, each thorium is coordinated by nine fluorine atoms in a tricapped trigonal prismatic arrangement. Each thorium fluoride polyhedron shares a face with adjacent polyhedra to form chains. Thus, around each thorium cation there are six bridging and three terminal fluorine atoms, and the local coordination can be described as $[ThF_{6/2}F_{3/1}]^{2-}$.

The Th–Th distance is 3.8032(2) Å in TFO-2, which is shorter than in TFO-1(3.9460(6) Å). The thorium fluoride chains run along the [100] direction and are separated by charge-balancing 2-methylpiperazine cations. Strong ionic and hydrogen bonding interactions between thorium fluoride chains and the disordered 2-methylpiperazine cations ($N(2)–H\cdots F(1)$: 2.63 Å, 2.72 Å) stabilize the structure and create an extended hydrogen bonded network. In this network, there is a channel of approximate dimensions 2.0 Å × 2.8 Å along the [100] direction, which is occupied by solvent water molecules.

In summary, we have reported the phase-pure syntheses and crystal structures of the first examples of organically templated thorium-containing solids. Using organic templates as the structure directing agents, we demonstrate that new actinide–organic hybrid materials having novel structural features and physicochemical properties can be exploited by hydrothermal synthesis. Importantly, an unprecedented face-sharing ThF_9 chain has been found in 2-methylpiperazine templated compound. Extension of this work to the other systems will be reported shortly.

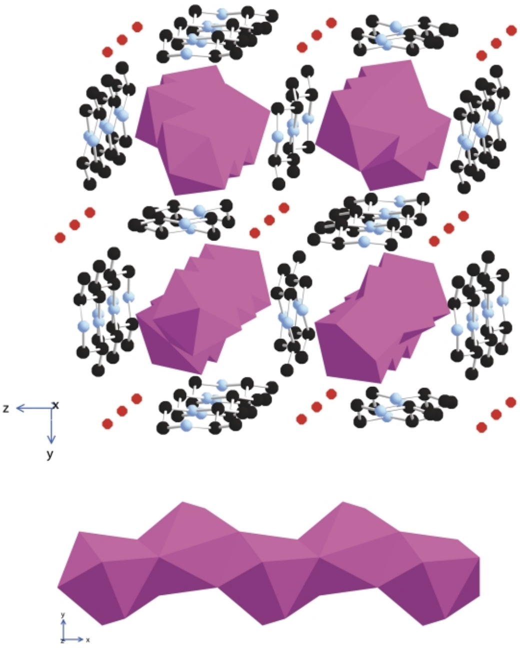

Fig. 3 Polyhedral and ball-and-stick representation of TFO-2 viewed along thorium fluoride chain ([100] direction), which is separated by 2-methylpiperazine cations (white balls) and occluded water (larger circles: oxygen of water). **(b)** Polyhedral view of $[ThF_9]$ chain running along [100] direction.

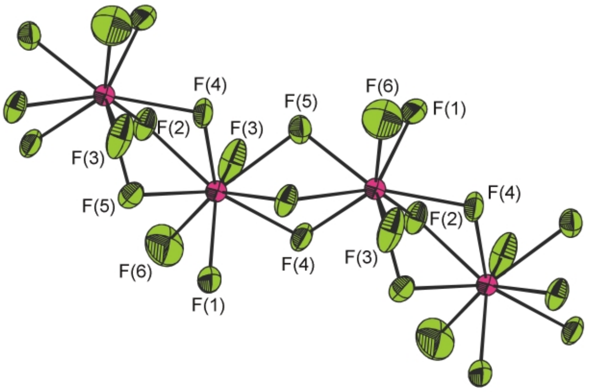

Fig. 4 Local coordination around thorium in the chain of face-sharing $[ThF_9]$ polyhedra of TFO-2.

Notes and references

† TFO-1 and TFO-2 were synthesized by combining $Th(NO_3)_4\cdot 3H_2O$ (0.570 g), HF (0.800 g), H_2O (1.00 g), $C_4N_2H_{10}$ (0.689 g) or $C_5N_2H_{12}$ (0.796 g) at room temperature. The respective mixtures were heated to 180 °C for 1 day and cooled to room temperature at 3 °C h^{-1}. Monophasic samples were recovered for TFO-1 and TFO-2 in $\geq$ 90% yield based on thorium.

Elemental analyses: TFO-1: obsd (calcd): C 6.48 (6.47), H 1.70 (1.63), N 3.90 (3.77), Th 61.87 (62.53)%; TFO-2: obsd (calcd): C 10.97 (13.14), H 2.84 (3.31), N 5.71 (6.13), Th 48.60 (50.75)%.

‡ *Crystallographic data:* Single crystals of dimension 0.04 × 0.04 × 0.06 mm for TFO-1 and 0.02 × 0.08 × 0.14 mm for TFO-2 were used for structural determination. Data were collected using an Enraf Nonius FR 590 Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Frames were collected, indexed and processed using Denzo SMN and the files scaled together using HKL GUI within Denzo SMN.[12] The heavy atom positions were determined using SIR97[13] and other non-hydrogen atoms refined using Crystals.[14] All non-hydrogen atom were located from Fourier difference maps and refined with anisotropic thermal parameters using full matrix least squares procedures on F_o^2 with $I > 3\sigma(I)$. All calculations were performed using Crystals[14] and Cameron.[15]

For TFO-1: monoclinic, space group $P2_1/c$ (No. 14), a = 8.9255(3) Å, b = 7.2633(3) Å, c = 8.9504(4) Å, β = 105.054(2)°, V = 560.3(4) Å^3, Z = 4, D_c = 4.40 g cm^{-3}, 2356 reflections collected of which 1265 were independent and 1031 were observed [$I > 3\sigma(I)$]. Refinement converged with R = 0.026, Rw = 0.061.

For TFO-2: orthorhombic, space group $Pcnb$ (No. 60), a = 6.8048(2) Å, b = 17.6478(6) Å, c = 17.7611(7) Å, V = 2132.9(4) Å^3, Z = 8, D_c = 2.835 g cm^{-3}, 4797 reflections collected of which 2423 were independent and 1683 were observed [$I > 3\sigma(I)$]. Refinement converged with R = 0.030, Rw = 0.074.

CCDC 189998 and 189999. See http://www.rsc.org/suppdata/cc/b2/b206749h/ for crystallographic data in CIF or other electronic format.

1 (*a*) T. E. Gier and G. D. Stucky, *Nature*, 1991, **349**, 508; (*b*) G. Ferey, *J. Fluorine Chem.*, 1995, **72**, 187.
2 P. B. Venuto, *Microporous Mater.*, 1994, **2**, 297.
3 A. Clearfield, *Chem. Rev.*, 1988, **88**, 125.
4 (*a*) D. W. Breck, *Zeolite Molecule Sieves: Structure, Chemistry, and Use*, Wiley and Sons, London, 1974; (*b*) R. Szostak, *Molecule Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinold, New York, 1989.
5 T. R. Gaffney, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 69.
6 (*a*) R. J. Francis, P. S. Halasyamani and D. O'Hare, *Angew. Chem., Int. Ed.*, 1998, **37**, 2214; (*b*) R. J. Francis, P. S. Halasyamani and D. O'Hare, *Chem. Mater.*, 1998, **10**, 3131; (*c*) A. Simon, S. Barlow, P. S. Halasyamani, J. F. W. Mosselmans, D. O'Hare, S. M. Walker and R. I. Walton, *Inorg. Chem.*, 2000, **39**, 3791; (*d*) S. M. Walker, P. S. Halasyamani, A. Simon and D. O'Hare, *J. Am. Chem. Soc.*, 1999, **121**, 10513; (*e*) R. J. Francis, P. S. Halasyamani, J. S. Bee and D. O'Hare, *J. Am. Chem. Soc.*, 1999, **121**, 1609; (*f*) P. S. Halasyamani, S. M. Walker and D. O'Hare, *J. Am. Chem. Soc.*, 1999, **121**, 7415.
7 M. Doran, S. M. Walker and D. O'Hare, *Chem. Commun.*, 2001, 1988.
8 P. S. Halasyamani, R. J. Francis, S. M. Walker and D. O'Hare, *Inorg. Chem.*, 1999, **38**, 271.
9 R. A. Penneman and R. R. Ryan, *Acta Crystallogr.*, 1974, **B30**, 1966.
10 G. Brunton, *Acta Crystallogr.*, 1966, **21**, 814.
11 G. Brunton, *Acta Crystallogr.*, 1968, **B25**, 1919.
12 Z. Otwinowski, *Data Collection and Processing*, Daresbury Laboratory, Warrington, 1993.
13 G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
14 D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, *CRYSTALS Issue 11*, Chemical Crystallography Laboratory, Oxford, UK, 2001.
15 D. J. Watkin, C. K Prout and L. J. Pearce, *CAMERON*, Chemical Crystallography Laboratory, Oxford, UK, 1996.