

The First Open Framework Actinide Material (C₄N₂H₁₂)U₂O₄F₆ (MUF-1)

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Zeolites (microporous aluminosilicates) and other open framework materials (metal phosphates) are of current interest, owing to their industrially important properties such as catalysis and ion-exchange.^{1–4} A defining characteristic of these materials is the occurrence of large channels, or pores, within the structural architecture. The pore sizes are defined by the number of tetrahedral atoms (T-atoms) that form the ring, and pores as large as 20-T atoms have been observed.⁵ Zeolites are strictly limited to aluminosilicates, whereas microporous metal phosphates include transition (Co,⁶ Mo,⁷ and Fe⁸) and main group (Ga,⁹ In,¹⁰ and Sn¹¹) metals, whose structures contain not only tetrahedrally coordinated atoms but also square pyramidal and octahedral moieties. However, no zeolite-type materials have been observed that incorporate lanthanide or actinide elements. These large metal cations are observed commonly in seven, eight, or higher coordinate environments. A zeolite-type material built from MX₇, MX₈, or even MX₉ units, where M is a lanthanide or actinide, would create a completely new and distinct class of microporous material. Here we report the phase-pure synthesis and crystal structure of the first open framework actinide material, (C₄N₂H₁₂)-U₂O₄F₆; the structure contains three intersecting one-dimensional channels of 10-, 8-, and 6-pentagonal bipyramidal UO₂F₅ units.

Our new material, (C₄N₂H₁₂)U₂O₄F₆, which we denote MUF-1 (microporous uranium fluoride number 1) was synthesized by using piperazine (C₄N₂H₁₀) as the structure-directing agent. MUF-1 was synthesized hydrothermally by combining UO₂(CH₃-COO)₂·2H₂O (0.406 g, 1.0 × 10⁻³ mol), HF_(aq) (BDH, 40% solution) (1.15 g, 2.3 × 10⁻² mol), and C₄N₂H₁₀ (Aldrich, 95%) (0.086 g, 1.0 × 10⁻³ mol) in a Teflon-lined, 23 mL stainless steel autoclave. UO₂(CH₃COO)₂·2H₂O was synthesized as previously described.¹² The autoclave was sealed, heated for 1d at 180 °C, and cooled at 6 °C hr⁻¹ to room temperature over an additional day. The only product recovered, a yellow polycrystalline material, was obtained in 75% yield based on uranium (Exp. (Calcd) %C 6.54 (6.47), %N 3.77 (3.77), %H 1.79 (1.63), %F 15.36 (16.08)). Powder X-ray diffraction on the product is in excellent agreement with the generated pattern from the single-crystal data (see Supporting Information).¹³

MUF-1 is a three-dimensional material consisting of corner and edge-shared uranium pentagonal bipyramids (PBs). Each U^{VI} is axially bonded to two oxygens, forming a uranyl unit (U=O,

1.773(4) Å and 1.779(4) Å) with an O=U=O bond angle of 178.37(2)°. Equatorially, each U^{VI} is bonded to five fluorines, four of which bridge to an adjacent uranium, with U–F bonds ranging from 2.274(1) Å to 2.353(4) Å, whereas the fifth fluorine is singly bonded (U–F, 2.196(8)). Thus, in connectivity terms, each uranium PB can be described as an [UO₂F_{4/2}F_{1/1}]⁻ anion, with charge balance maintained by a piperazinium cation.

Each uranium PB shares an edge to form dimers, that are corner linked along the [110], [010], and [001] directions, thus creating a three-dimensional network. This network contains three intersecting one-dimensional channels consisting of 10-PB, 8-PB, and 6-PB-atom membered-rings (10-MRs, 8-MRs, and 6-MRs). The 10-MR channels run along the [110] direction (Figure 1a); perpendicular to, and intersecting, these channels are the 8-MR pores that run along the [001] direction (Figure 1b). The 8-MR pores intersect and are perpendicular to both the 10-MR and 6-MR channels, whereas the 6-MR channels (running along the [010]) (Figure 1c) intersect the 10-MR channels at a 45° angle. The pore sizes for the three channels are 5.5 Å × 12.2 Å (10-MR), 2.6 Å × 6.0 Å (8-MR), and 2.7 Å × 4.1 Å (6-MR). The pore sizes are the distances between “opposite” fluorine or oxygen atoms, taking into account their atomic radii.¹⁷ The piperazinium cations are found in both the 10-MR and 8-MR channels. Orientational disorder is observed in N(2), with two equivalent sites each given 50% occupancy during the crystal structure refinement. Hydrogen bonding is observed for both nitrogens with the terminal, F(3), and bridging, F(4), fluorine atoms (D···A, Å; N(1)···F(3), 2.793(6) Å, N(2)···F(3), 2.787(6) Å, N(2)···F(4), 2.821(6) Å).

Infrared and Raman spectroscopy on MUF-1 revealed bands consistent with uranyl as well as U–F bonds. In addition, bands at 1590 cm⁻¹ and 1620 cm⁻¹ as well as a broad stretch centered at 3120 cm⁻¹ were observed, consistent with piperazine vibrations. Thermogravimetric measurements in static air and N₂ revealed similar behavior: MUF-1 is stable up to 350 °C, at which point the template is removed resulting in a weight loss of 11.5% (calcd 11.8%). A broad weight loss is then observed between 400 to 700 °C, with the calcined material shown to be U₃O₈ by powder X-ray diffraction (total weight loss observed 23.4%, calcd 24.4%).

It is apparent that similar to zeolites the organic template, in our case piperazine, profoundly influences the anion framework. As with both zeolites and microporous metal phosphates, the ability of the organic template to direct the structure is a well-established concept,^{18–20} although the exact nature of this process is unclear. However, the most striking feature of MUF-1 is its *direct structural analogy to zeolites*. All zeolite materials are built from one fundamental structural unit, TO₄ tetrahedra, that are linked by T–O–T bonds. Similarly, MUF-1 is built from one

(13) A small yellow prismatic crystal (0.12 mm × 0.12 mm × 0.15 mm) was selected from the polycrystalline powder and mounted on a glass fiber. Single-crystal data were acquired on an Enraf-Nonius DIP 2000 image-plate diffractometer at 150.0(2)K. Each frame was collected, indexed, and processed by using DENZO,¹⁴ and scaled by using SCALEPACK.¹⁴ The structure was solved by direct-methods using SIR92¹⁵ and refined using SHELXL-93.¹⁵ An XABS absorption correction was applied to the data.¹⁶ Crystal data for (MUF-1) (C₄N₂H₁₂)U₂O₄F₆: monoclinic, C2/c, a = 9.108(1) Å, b = 10.059(1) Å, c = 13.633(1) Å, β = 97.023(1)°, V = 1239.62(3) Å³, Z = 4, R(F) = 0.040, GOF = 1.103.

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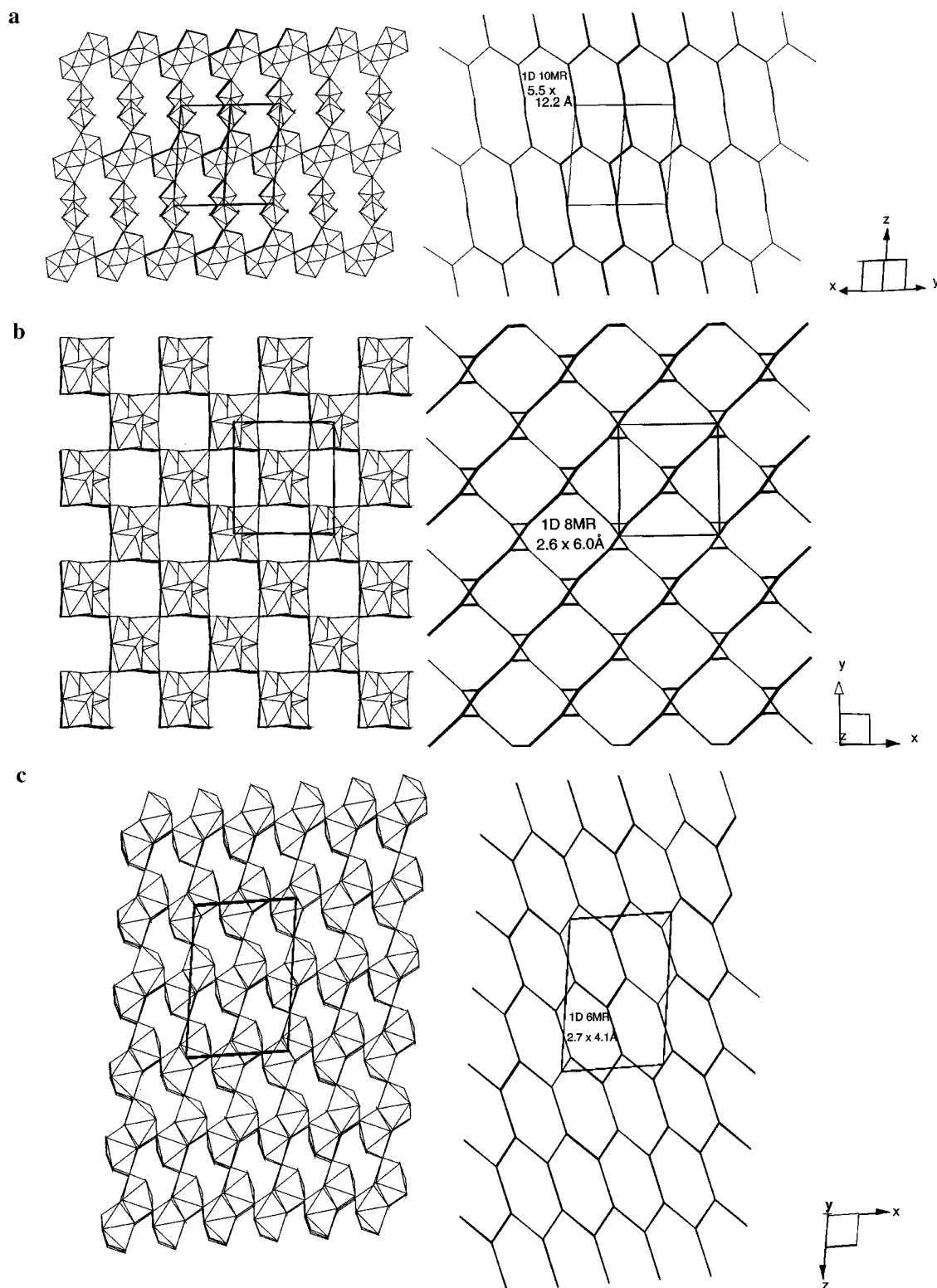


Figure 1. Polyhedral and wire representation of MUF-1 showing the (a) 10-MR channels, (b) 8-MR channels, and (c) 6-MR channels. The piperazinium cations have been removed for clarity.

fundamental unit, UO_2F_5 pentagonal bipyramids, that are connected by U–F–U bonds. Thus, as with zeolites, the topological range of open framework materials based on this one unit is potentially limitless. Experiments are currently underway to synthesize a variety of open framework uranium compounds, with different templates, and to study their physical properties.²¹

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Supporting Information Available: ORTEP diagram, X-ray powder diffraction pattern (PDF) and complete crystallographic data in CIF format for MUF-1 are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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