

Variable Dimensionality in the Uranium Fluoride/2-Methyl-Piperazine System: Syntheses and Structures of UFO-5, -6, and -7; Zero-, One-, and Two-Dimensional Materials with Unprecedented Topologies

R. J. Francis, P. S. Halasyamani, J. S. Bee, and D. O'Hare*

*Inorganic Chemistry Laboratory, University of Oxford
South Parks Road, Oxford, UK OX1 3QR*

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Recently, low temperature ($T < 300$ °C) hydrothermal reactions of inorganic precursors in the presence of organic cations have proven highly productive for the synthesis of novel solid-state materials.^{1–3} Interest in these materials is driven by the astonishingly diverse range of structures produced,^{4–10} as well as by their many potential materials chemistry applications.^{11–13} Our work has focused on exploiting the hydrothermal technique to synthesize novel hybrid inorganic/organic uranium-based phases, a relatively unexplored area despite their potential as catalysts and ion-exchange agents,¹⁴ and recently we reported the first examples of organically templated uranium phosphate and uranium fluoride materials.^{15,16} Despite the impressive range of synthetic materials, there is often a lack of understanding of the relationships between the reaction conditions employed and the product obtained. Thus, these syntheses are frequently characterized by an absence of control over the structures and stoichiometries of the products formed and often result in a complex mixture of many different, and frequently unidentified, phases. For almost all of the many applications envisioned, phase purity is an essential prerequisite, and a degree of rational control over the framework architecture would be very desirable. Our approach has been to identify key reaction variables and systematically explore their influence, to experimentally determine stability regions where particular compounds can be synthesized in phase-pure form. One manner in which these stability regions may be determined is through the use of composition space diagrams (see Figure 1a).^{17–19} We have extended this concept to include the quantity of solvent, in our case H₂O, as a fourth variable and in doing so have altered the two-dimensional composition space (Figures 1a and b) to a three-

dimensional compositional prism (Figure 1c). The prism axis is the amount of H₂O added to each reaction. We have used such an approach to study one particular system, specifically the UO₂/2-methyl-piperazine/HF_(aq)/H₂O system, and have succeeded in determining reaction conditions in which three uranium fluoride phases of unprecedented structure types, **UFO-5** (C₅N₂H₁₄)₂(H₃O)U₂F₁₃, **UFO-6** (C₅N₂H₁₄)₂U₂F₁₂·H₂O, and **UFO-7** (C₅N₂H₁₄)(H₃O)U₂F₁₁, can be synthesized in phase-pure form. Not only do these materials comprise a new family of inorganic–organic uranium compounds synthesized using *the same template molecule*, but they also represent the structural evolution of molecular **UFO-5**, to linear **UFO-6**, to layered **UFO-7** uranium frameworks achieved via systematic control of the reaction conditions.²⁰

The title compounds were synthesized by combining the following in separate 23-mL Teflon-lined autoclaves. For **UFO-5**, a clear green liquid was recovered (pH 4.5). After the liquid stood for several days, light green crystals of **UFO-5** were observed. For **UFO-6**, green needlelike crystals were recovered in 85% yield based on uranium, together with a mother liquor of pH 2.5. For **UFO-7** green rod-shaped crystals were recovered along with a green powder in 40% yield based on uranium and a mother liquor of pH 1.5.²¹ Powder X-ray diffraction on the mixture of powder and crystals indicated a single-phase product, consistent with the crystal structure.

UFO-5 is a molecular, or “zero-dimensional”, phase consisting of dimeric [U₂F₁₃]⁵⁻ units separated by 2-methyl-piperazine and hydronium cations. These dimeric units have never previously been observed in uranium-based materials. Within each dimer the uranium cation is bonded to eight fluorine atoms in a distorted bicapped trigonal prismatic coordination. These trigonal prisms share faces, with a U(1)–U(2) distance of 3.832(1) Å. In connectivity terms each uranium can be described as [UF_{3/2}F_{5/1}]^{2.5-} with five terminal and three bridging fluorines.

UFO-6 displays a structure type which is completely unprecedented in the field of uranium chemistry. **UFO-6** has a one-dimensional structure and contains uranium fluoride chains formed from edge-sharing polyhedra. The uranium fluoride chains run along the [001] direction and are separated by charge-balancing 2-methyl-piperazine cations. Strong ionic and hydrogen bonds between the uranium fluoride chains and the 2-methyl-piperazine cations bind the structure together and create a tightly bound diamond shaped network structure. Within the uranium fluoride chains, each uranium cation is coordinated by eight fluorine atoms in a distorted bicapped trigonal prismatic arrangement. Each uranium fluoride polyhedron shares an edge with two adjacent polyhedra to form the chains. Thus, around each uranium cation there are four bridging and four terminal fluorine atoms, and the

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(20) **UFO-5** (C₅N₂H₁₄)₂(H₃O)U₂F₁₃: 0.270 g (1.0 × 10⁻³ mol) UO₂ (Supplied by British Nuclear Fuels Limited), 0.60 g (6.0 × 10⁻³ mol) 2-methyl-piperazine (95%, Aldrich), 0.90 g (1.8 × 10⁻² mol) HF_(aq) (40% solution, BDH), and 5 g H₂O. **UFO-6** (C₅N₂H₁₄)₂U₂F₁₂·H₂O: 0.270 g (1.0 × 10⁻³ mol) UO₂, 0.70 g (7.0 × 10⁻³ mol) 2-methyl-piperazine, 1.27 g (2.5 × 10⁻² mol) HF_(aq), and 5 g H₂O. **UFO-7** (C₅N₂H₁₄)(H₃O)U₂F₁₁: 0.270 g (1.0 × 10⁻³ mol) UO₂, 0.099 g (9.9 × 10⁻⁴ mol) 2-methyl-piperazine, 2.40 g (4.8 × 10⁻² mol) HF_(aq), and 5 g H₂O. The autoclaves were heated at 180 °C for 24 h and slowly cooled at 6 °C hr⁻¹ to room temperature.

(21) Single-crystal X-ray analyses were performed on an Enraf-Nonius DIP 2000 image plate diffractometer. In all cases monochromated Mo K α radiation was used, with the phase problem solved by direct methods.²² Anisotropic thermal parameters were used for U, F, C, N, and O,²³ and an XABS absorption correction was applied.²⁴ Hydrogen atoms were placed in idealized positions (not refined) and given isotropic thermal parameters 1.2 times that of the attached atom. Crystal data for (**UFO-5**) (C₅N₂H₁₄)₂(H₃O)U₂F₁₃: monoclinic, $P2_1/c$, $a = 15.385(3)$ Å, $b = 12.688(3)$ Å, $c = 17.532(3)$ Å, $\beta = 107.48(1)^\circ$, $V = 3264.30(9)$ Å³, $Z = 4$, $R = 0.074$, $GOF = 0.937$. Crystal data for (**UFO-6**) (C₅N₂H₁₄)₂U₂F₁₂·H₂O: monoclinic, $C2/m$, $a = 13.702(1)$ Å, $b = 12.555(1)$ Å, $c = 6.607(1)$ Å, $\beta = 107.08(4)^\circ$, $V = 1086.5(3)$ Å³, $Z = 2$, $R = 0.031$, $GOF = 1.107$. Crystal data for (**UFO-7**) (C₅N₂H₁₄)(H₃O)U₂F₁₁: monoclinic, $C2/c$, $a = 19.366(1)$ Å, $b = 8.599(1)$ Å, $c = 14.249(1)$ Å, $\beta = 99.165(3)^\circ$, $V = 2342.60(3)$ Å³, $Z = 8$, $R = 0.054$, $GOF = 1.072$. Satisfactory elemental analyses (C, H, N, and U) were found for **UFO-6** and **UFO-7**.

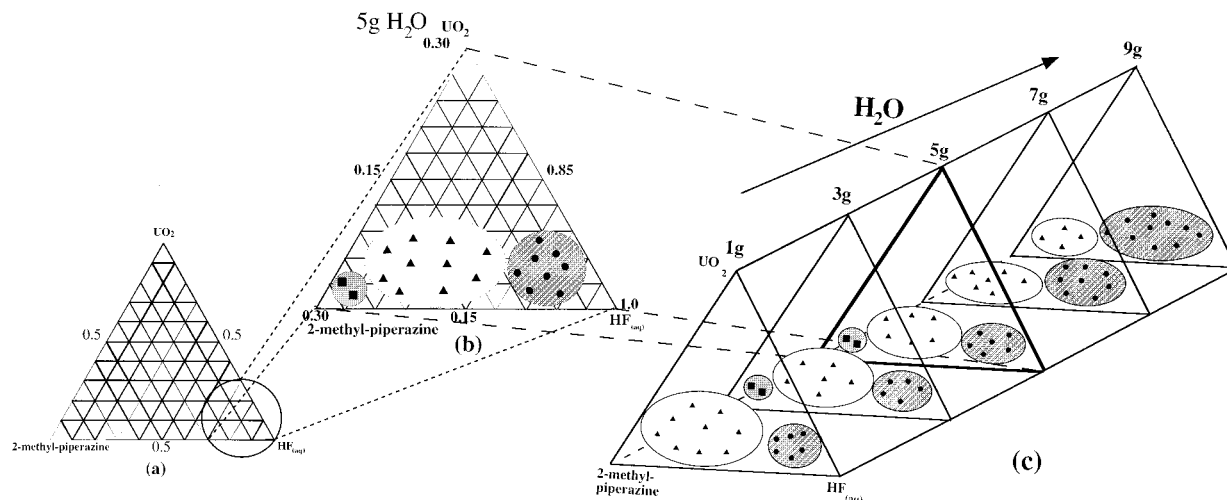


Figure 1. (a) Composition space of the UO_2 /2-methyl-piperazine/ $\text{HF}_{(\text{aq})}$ system. The circled area is expanded in (b). (b) Composition space with 5 g of H_2O added to each reaction. Stability regions are delineated wherein single phase, crystalline products are recovered. **UFO-5** ■ $(\text{C}_5\text{N}_2\text{H}_{14})_2(\text{H}_3\text{O})\text{U}_2\text{F}_{13}$, **UFO-6** ▲ $(\text{C}_5\text{N}_2\text{H}_{14})_2\text{U}_2\text{F}_{12}\cdot\text{H}_2\text{O}$, and **UFO-7** ● $(\text{C}_5\text{N}_2\text{H}_{14})(\text{H}_3\text{O})\text{U}_2\text{F}_{11}$. Reactions with molar reagent concentrations outside delineated areas (i.e., above stability regions) produces mixtures of phases that included polycrystalline UO_2 . For all reactions the molar amount of $\text{HF}_{(\text{aq})}$ was normalized to a 100% solution. (c) Composition prism, with each triangle indicating the amount of H_2O (in grams) added to each reaction.

local coordination can be described as $[\text{UF}_{4/2}\text{F}_{4/1}]^{2-}$. Between the uranium fluoride/2-methyl-piperazine network there is a cavity of approximate dimensions $7 \text{ \AA} \times 8 \text{ \AA}$ that is occupied by solvent water molecules. We have shown through thermogravimetric and powder XRD experiments that upon dehydration **UFO-6** retains crystallinity. Additionally, rehydration and conversion back to **UFO-6** occurs at room temperature over several hours. Thus **UFO-6** may be considered to be a porous uranium material.

UFO-7 consists of anionic sheets of nine coordinate uranium cations that are separated by protonated 2-methyl-piperazine and occluded hydronium cations. In contrast to the previously synthesized two-dimensional uranium fluoride compounds **UFO-1–4**¹⁶ the sheet topology in **UFO-7** is wholly unprecedented. Within the layers, each uranium cation is coordinated by nine fluorines in a tricapped trigonal prismatic environment. In connectivity terms, each uranium may be described as $[\text{UF}_{7/2}\text{F}_{2/1}]^{1.5-}$, with seven bridging and two terminal fluorines. Upon heating to $180 \text{ }^\circ\text{C}$ in air, **UFO-7** also retains crystallinity; however, unlike **UFO-6** rehydration back to the parent phase does not occur upon standing in air over several hours.

The three-dimensional composition prism for the UO_2 /2-methyl-piperazine/ $\text{HF}_{(\text{aq})}$ / H_2O system is shown in Figure 1b. In addition, the stability regions for **UFO-5**, **-6**, and **-7** are delineated. Although a variety of factors are involved in determining the final product, a controlling factor is the ratio of 2-methyl-piperazine to $\text{HF}_{(\text{aq})}$, at a constant amount of UO_2 . At high molar ratios of 2-methyl-piperazine (greater than 25%), after the hydrothermal reaction, no solid product is recovered from the autoclave with only a clear green solution observed. Upon standing in air for several days this solution produces light green crystals, **UFO-5**. Raman experiments on the green solution resulted in identifiable stretches corresponding to U–F vibrations. At somewhat lower 2-methyl-piperazine molar ratios (and consequently higher HF molar ratios), **UFO-6**, the one-dimensional phase, is observed as a solid product, together with a clear yellow/green supernatant. As the molar ratio of 2-methyl-piperazine is decreased still further to less than 9%, **UFO-7**, the layered two-dimensional phase, is formed. The above observations are consistent with regard to the pH of the mother liquors of the products. *We observe a direct*

relationship between the acidity and dimensionality of the final product. As the acidity is increased, the dimensionality of the recovered material evolves from molecular **UFO-5**, to one-dimensional **UFO-6**, to finally two-dimensional **UFO-7**. An interesting possibility is that the dimeric $[\text{U}_2\text{F}_{13}]^{5-}$ anions found in **UFO-5** are also the direct solution-phase precursors to the higher dimensionality materials **UFO-6** and **-7**, and that, under the correct conditions of pH and template:uranium ratio, **UFO-6** and **-7** are formed via condensation and polymerization reactions of those dimeric units. The observed dependence of the product formed on the pH of solution is consistent with such a possibility since, as the pH is lowered, anions such as $[\text{U}_2\text{F}_{13}]^{5-}$ would be expected to be increasingly protonated, facilitating their condensation into higher dimensionality materials. Support for this hypothesis is provided by experiments in which the clear green **UFO-5** solution was acidified, by adding $\text{HF}_{(\text{aq})}$, to the pH level found in the mother liquors of **UFO-6** and **-7**. These solutions were heated again under identical hydrothermal conditions as previously. The products, as shown by powder X-ray diffraction, were pure **UFO-6** and **-7** respectively. However, it must be emphasized that the identity of the solution-phase species in the mother liquors of **UFO-6** and **-7** and their relationships to the final products have not yet been unambiguously determined.

In summary, we have described the high yield, phase pure hydrothermal syntheses of three new uranium fluoride phases with unprecedented structure types. Through the systematic control of the synthesis conditions we have successfully controlled the architecture and dimensionality of the phase formed and selectively synthesized novel zero-, one-, and two-dimensional materials. We have extended this work to other systems and will be reporting on them shortly.

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Supporting Information Available: Ball-and-stick, polyhedral, and ORTEP diagrams of **UFO-5**, **-6**, and **-7**, X-ray powder diffraction patterns, and data for **UFO-6** and **-7**, and complete crystallographic data in CIF format for **UFO-5**, **-6**, and **-7** are available (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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