Building Unit and Topological Evolution in the Hydrothermal DABCO−U−F System

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Compounds NDUF-1 ($[C_6H_{14}N_2](UO_2)_2F_6$; $P2_1/c$, $a = 6.9797(15)$ Å, $b = 8.3767(15)$ Å, $c = 23.760(5)$ Å, $\beta = 91.068(4)°$, $V = 1388.9(5)$ Å^3, $Z = 4$), NDUF-2 ($[C_6H_{14}N_2]_2(UO_2)_2F_5UF_7{\cdot}H_2O$), NDUF-3 ($(NH_4)_7U_6F_{31}$; $R\bar{3}$, $a = 15.4106(8)$ Å, $c = 10.8142(8)$ Å, $V = 2224.1(2)$ Å^3, $Z = 3$), and NDUF-4 ($[NH_4]U_3F_{13}$) have been synthesized hydrothermally from fixed composition reactant mixtures over variable time periods [DABCO ($C_6H_{12}N_2$), $UO_2(NO_3)_2{\cdot}6H_2O$, HF, and H_2O; 2−14 days]. Observed is a systematic evolution of the structural building units within these materials from the UO_2F_5 pentagonal bipyramid in NDUF-1 and -2 to the UF_8 trigonal prism in NDUF-2 and finally to the UF_9 polyhedron in NDUF-3 and -4 as a function of reaction time. Coupled to this coordination change is a reduction of U^{VI} to U^{IV} as well as a breakdown of the organic structure-directing agent from DABCO to NH_4^+. These processes contribute to a structural transition from layered topologies (NDUF-1) to chain (NDUF-2), back to layered (NDUF-3), and ultimately to framework (NDUF-4) connectivities. The synthesis conditions, crystal structures, and possible transformation mechanisms within this system are presented.

Introduction

Open-structured (or framework) materials are currently of great interest considering their applicability and potential in such areas as catalysis, separations, electronics, gas storage, and radioactive waste immobilization.[1] Many such compounds are based on Al−Si−O chemistry, zeolites being well-known examples.[2] Several investigators have explored departures from these compositions, however, and have synthesized (among others) open-structured borates,[3] phosphates,[4,5] sulfides,[6−9] and actinides.[10−13] Our interest in the latter is 2-fold. First, a fundamental knowledge of actinide crystal chemistry is of great relevance to understanding the behavior of spent nuclear fuel under geologic repository conditions (i.e., oxic, likely hydrothermal).[14] Second, as has been recently demonstrated,[10−13,15−17] the organic−U−F system gives rise to a number of new and interesting topologies. As such, this system provides an excellent forum in which to address some key issues surrounding the directed syntheses of microporous materials in general, namely, the role(s) of the organic structure-directing agent ("template")[18] and also the formation and polymerization of variable building units within a given system.[19] The speciation of building units is of unique interest to non-oxide families of open-structured materials as opposed to aluminosilicates (for example), in which structural moieties are invariably TO_4 tetrahedra (T = Al, Si).

The current synthetic investigation of the DABCO−U−F (DABCO = 1,4-diazabicyclo[2.2.2]octane) system examines these issues of template role and building unit speciation. This effort has resulted in the formation of a novel uranium oxyfluoride material, NDUF-1 ($[C_6H_{12}N_2](UO_2)F_6$). Subsequent aging of the NDUF-1 reaction mixture at constant temperature leads to the formation of NDUF-2 ($[C_6H_{12}N_2]_2(UO_2)_2F_5UF_7{\cdot}H_2O$), as well as the hydrothermal formation of NDUF-3 ($[NH_4]_7U_6F_{31}$) and NDUF-4 ($[NH_4]U_3F_{13}$), two previously reported compounds synthesized at high temperature. Thus, reported herein are the reaction conditions for the syntheses of these compounds, the crystal structures of NDUF-1 and -3, and a discussion of the relationship between such phases in terms of structural building unit evolution and assembly, both as a function of reaction mixture oxidation state and structure-directing-agent decomposition.

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Table 1. Crystal Data and Structure Refinement for NDUF-1 and -3

	NDUF-1	NDUF-3
chemical formula	$[C_6H_{14}N_2](UO_2)_2F_6$	$[NH_4]_7U_6F_{31}$
fw	768.22	2143.50
space group	$P2_1/c$	$R\bar{3}$
a, Å	6.9797(15)	15.4106(8)
b, Å	8.3767(15)	15.4106(8)
c, Å	23.760(5)	10.8142(8)
β, deg	91.068(4)	90.000
V, Å^3	1388.9(5)	2224.1(2)
Z	4	3
ρ_{calcd}, Mg/m^3	3.675	4.803
λ (Mo Kα), mm^{-1}	23.370	32.850
temp, K	293(2)	293(2)
λ, Å	0.710 73	0.710 73
final R indices [$I > 2\sigma(I)$]	R1 ^{a} = 0.0528, wR2 ^{b} = 0.1101	R1 ^{a} = 0.0185, wR2 ^{b} = 0.0432

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Experimental Section

All syntheses were carried out in Teflon lined, stainless steel Parr reaction vessels held at constant temperature in Isotemp ovens. For the formation of the phases discussed below, a typical reaction mixture consisted of 0.15 g of uranium oxynitrate (Alfa, $UO_2(NO_3)_2{\cdot}6H_2O$), 2.4 g of H_2O, 100 μL of HF(49%), and 0.56 g of DABCO(aq) (Aldrich, $C_6H_{12}N_2$; 27% w/w), combined in that order (pH = 4.5). Reaction mixtures were held at 180 °C for 2 days (NDUF-1), 7−10 days (NDUF-2), or 14 days (NDUF-3). NDUF-4 was formed as an impurity phase in longer (>6 days) duration runs. Reactions were terminated by removing the reaction vessels and allowing them to cool to room temperature (∼2.5 h). End-products were collected and washed with deionized H_2O and ethanol and dried in air. Crystals suitable for single-crystal X-ray diffraction were isolated from these batches: NDUF-1 as pale-yellow needles, NDUF-2 as green blades, NDUF-3 as green rhombohedra, and NDUF-4 as green plates.

It was not uncommon for reaction products to consist of two phases (see Discussion and Figure 5). Pure phases, however, could easily be isolated by adjustment of temperature and duration. For example, single-phase NDUF-2 could be obtained after 7 days at 200 °C and NDUF-3 after 2.5 days at 220 °C, both in approximately 75% yield. NDUF-4, however, has resisted formation as a single phase (typical yield: ∼50% of end-products). Bulk characterization of reaction products was done with powder XRD (Rigaku Miniflex, Cu Kα radiation, 0.02° step scans, 1.0 s/step) in conjunction with diffraction spectra calculated using CrystalDiffract.[20]

Subsequent thermogravimetric analyses were carried out on a TA Instruments SDT 2960 Simultaneous DTA/TGA under flowing nitrogen, whereas IR studies used a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analysis of NDUF-3 by combustion was done by Galbraith Laboratories (Knoxville, TN).

Single-Crystal X-ray Diffraction. All single-crystal analyses were performed on a Bruker 1K CCD based SMART diffractometer at room temperature using Mo Kα radiation. For each material (NDUF-1, -2, -3, -4), a hemisphere of three-dimensional data was collected at a crystal-to-detector distance of 5.0 cm using 0.3° frame widths in ω. The data were reduced and corrected for Lorentz polarization and background effects with the Bruker program SAINT,[21] while semiempirical absorption corrections were done in XPREP[22] by modeling the crystals as plates (NDUF-1,2) or as an ellipsoid (NDUF-3) or using SADABS (NDUF-4). Final unit cell dimensions (Table 1) were refined using least-squares techniques on strong reflections harvested from the final data set.

Structures were solved with SHELXS[23] and refined with SHELXL[24] within the SHELXTL[25] suite of programs. Graphical representation utilized Crystalmaker[26] and WINGX.[27] Selected details of the structural analyses can be found in Table 1, whereas a complete listing of atomic positions, bond lengths, angles, and displacement parameters for NDUF-1 and -3 can be found in the Supporting Information. The locations of hydrogen atoms on intact DABCO molecules (NDUF-1) were calculated at idealized positions and allowed to refine by "riding" on their parent carbon atoms at a fixed distance. Anisotropic displacement parameters of non-hydrogen atoms were refined where possible.

Results

NDUF-1. The structure of NDUF-1 ($[C_6H_{14}N_2](UO_2)_2F_6$) is shown in Figure 1. The primary building units of this structure are $(U^{(VI)}O_2)F_5$ pentagonal bipyramids (Figure 1, inset). The equatorial positions of these polyhedra are occupied by F atoms, whereas apical O atoms (also referred to as "uranyl" oxygens) cap the bipyramid. These pentagonal bipyramids polymerize by sharing edges to form tetramers, which in turn are linked by sharing corners to form sheets that are stacked along [100]. The uranyl oxygen atoms remain singly coordinated to the central U atom only, although it is possible that they accept hydrogen bonds. Bond lengths within each U^{6+} polyhedron average 1.79 Å for U−O and 2.31 Å for U−F and are consistent with those in other structures containing this building unit.[10,17,28,29] Bond valence summations[30,31] for the U(1) and U(2) sites are 5.6 and 5.8 vu, respectively.

Linking of the uranyl fluoride tetramer units to form sheets results in pores measuring approximately 5.1 Å × 11.7 Å (as determined from shortest F atom center to F atom center distances). The pores are aligned in subsequent layers; such a unidimensional topology has been observed in several other materials with porous sheets, or three-dimensional frameworks.[32−35] Protonated DABCO molecules (Figure 1) reside in the interlayer region at distances as short as 2.62 Å (N−F), suggesting a weak hydrogen-bonding interaction. The protons were not located in the X-ray analysis of NDUF-1; however, an IR investigation confirmed their presence. These are presumably the result of the HF in the starting mixture. A cursory examination of the disposition of the DABCO molecules (Figure 1) suggests they play a templating role in the formation of NDUF-1. The molecules, however, are above and below the plane of the layers and not entirely within the pores. Further, the formation of other structure types with this structure-

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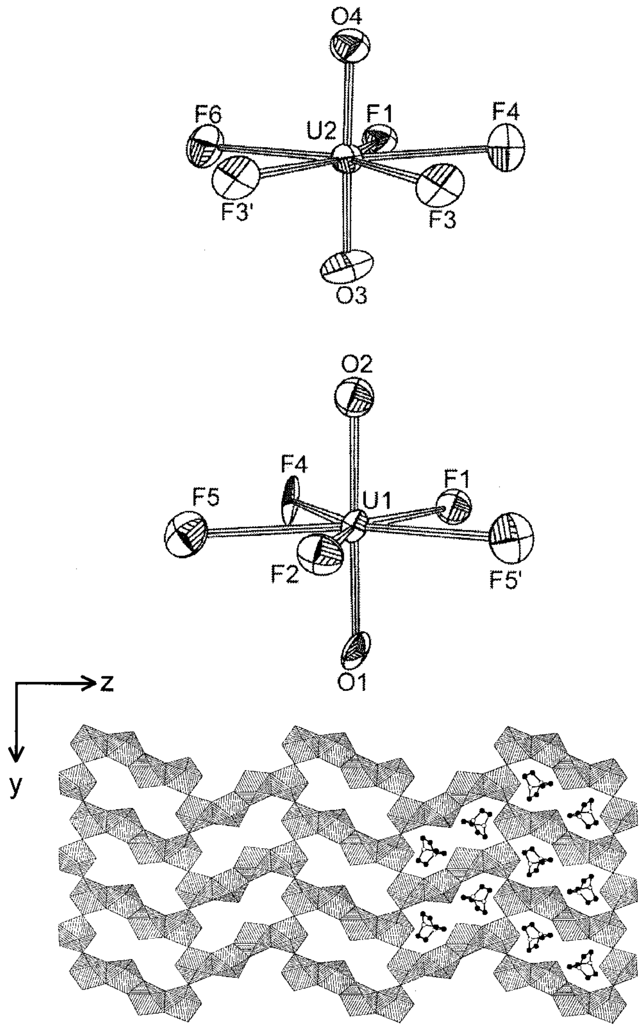

Figure 1. Top: ORTEP diagram (probability ellipsoids 50%) of the U1 and U2 local environments. Bottom: structure of a single layer of NDUF-1 shown down [100]. Edge-shared $(UO_2)F_5$ pentagonal bipyramids form tetramers that link by sharing corners to form sheets. For clarity, only a few of the occluded DABCO molecules are shown. Dark circles are carbon, whereas open circles are nitrogen. Hydrogen atoms are not shown.

directing agent (below, NDUF-2) rather supports a space-filling role.[18] No other interlayer species (e.g., H_2O groups) were observed in the X-ray analysis. TGA supports this observation with a single weight loss event of approximately 20% beginning around 275 °C.

NDUF-2. The structure of NDUF-2 ($[C_6H_{14}N_2]_2(UO_2)_2F_5$-$UF_7$·$H_2O$; Figure 2) was recently reported by O'Hare and coworkers[11] (UFO-17 in their study). Briefly, this material contains two distinct cation polyhedra: the $(U^{(VI)}O_2)F_5$ pentagonal bipyramid as found in NDUF-1 (Figure 1) and also the $U^{(IV)}F_8$ trigonal prisms. This building unit has been described previously in several other compounds.[10,13,16] The pentagonal bipyramids share edges through four equatorial F anions to form chains along [001]. The UF_8 trigonal prisms form a second chain type parallel to the bipyramid chains. Each UF_8 unit is edge-shared to another within the chain direction and also to a $(UO_2)F_5$ bipyramid perpendicular to the chain direction. The (UO_2) ions in the $(UO_2)F_5$ units are rotated 90° with respect to those in the chain of pentagonal bipyramids. For both chain types, the connectivity within the chain is strictly edge-sharing with no coordination between chains or to vertexes other than equatorial. The two chain types thus form a "sheet" of chains that stacks along [100]; subsequent layers are staggered. Further structural details as well as an EXAFS study and magnetic properties can be found in the original report.[11]

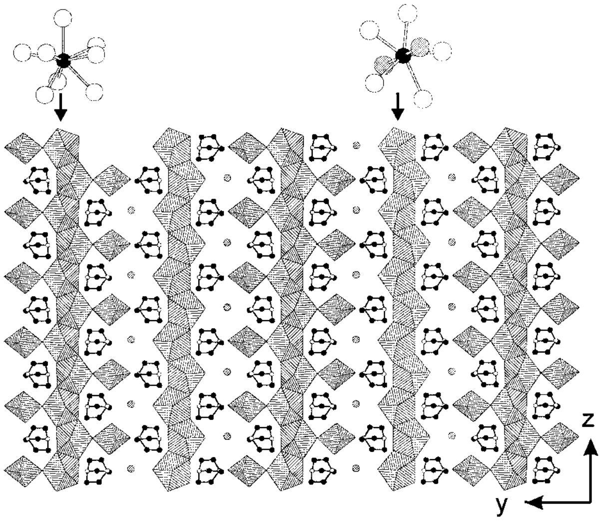

Figure 2. Chain structure of NDUF-2 shown down [100]. Polyhedra are $(UO_2)F_5$ pentagonal bipyramids and UF_8 trigonal prisms. Ball and stick models of the $(UO_2)F_5$ and UF_8 polyhedra are shown above the chains in which they are found. Protonated DABCO molecules are shown in the void spaces (same scheme as Figure 1). The gray circle is an H_2O molecule.

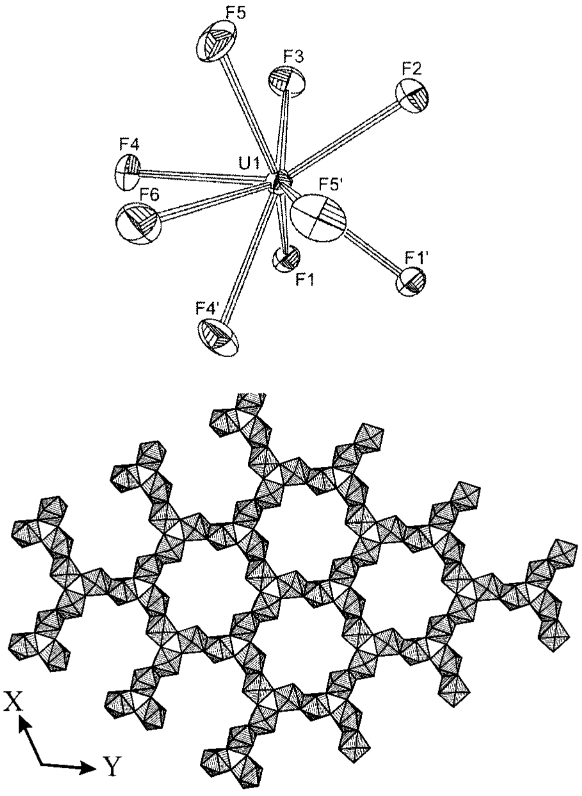

Figure 3. Top: ORTEP diagram (probability ellipsoids 50%) of the uranium environment (UF_9) in NDUF-3. Bottom: a single layer of the structure shown down [001]. UF_9 polyhedra share corners and edges to form 12-membered rings within each layer. For clarity, the NH_4^+ cations in the pore spaces are not shown.

NDUF-3. The structure of NDUF-3 ($(NH_4)_7U_6F_{31}$; Figure 3) contains a single unique U site coordinated to nine F anions. These $U^{(IV)}F_9$ polyhedra alternatively link by sharing corners and edges to form zigzag chains that are approximately parallel to [110]. Each corner-linked site on the chain is bridged by a

U_2F_{16} dimer that connects adjacent chains to form planar sheets. This type of connectivity gives rise to 12-membered rings within the sheets, resulting in large pores (approximately 10.7 Å in diameter, as determined from shortest F atom center to F atom center distances). Subsequent layers are linked through F atoms and are staggered (unlike NDUF-1) along [001] such that the pores defined by the 12-rings are not aligned. Bond lengths within the UF_9 polyhedra range from 2.19 to 2.61 Å, and average 2.34 Å, and are consistent with those found in O'Hare's UFO-1, -2, and -3 materials.[13] Differences arise, however, in the number of terminal U−F bonds. NDUF-3 has three terminal F anions per polyhedron with two short (2.19, 2.21 Å) and one long (2.61 Å) bond lengths, whereas the UFO series all contain a single terminal F anion ranging from 2.13 to 2.18 Å with a mean distance of 2.16 Å. Bond valence summations[30] are in agreement with the 4+ charge assignment (4.15 vu).

The interlayer region of NDUF-3 hosts two unique NH_4^+ cation sites. These positions were originally thought to be portions of disordered DABCO molecules. Elemental analysis, however, failed to detect any carbon (wt % by combustion: <0.5 C; 1.31 H; 4.58 N). It was thus concluded that the DABCO molecules had broken down to form NH_4^+ cations under the hydrothermal conditions of these longer duration (vs NDUF-1 and -2) experiments. Reasonable occupancy factors and displacement parameters for N atoms in these sites were obtained during refinement of the X-ray data, whereas IR and elemental analyses confirmed the assignment. Such breakdown of structure-directing agents has recently been observed in uranium oxyfluoride[15,16] and other systems.[6,19,36]

The formation of the material α-$NH_4\cdot UF_4$ has been reported from the reaction of UF_4 and NH_4F.[37] The cell parameters of this compound are identical to that of NDUF-3, yet the structure was not reported until this study. Further, this structure type has been described previously in the compounds $Na_7Zr_6F_{31}$[38] and $Tl_7U_6F_{31}$, the latter having been grown via flux methods.[39] In the current study, however, this structure type results from hydrothermal treatment of oxidized U starting materials followed by reduction and fluorination to form identical building units and topology. It is plausible that the Tl in $Tl_7U_6F_{31}$ and the NH_4^+ in NDUF-3 play similar roles in directing the formation of their respective host structures.

NDUF-4. The structure of NDUF-4 ($[NH_4]U_3F_{13}$) has been reported previously to result from high-temperature reactions in the NH_4F-UF_4 system[40] and also in low yields in the hydrothermal pyridine and pyrazole uranium fluoride systems.[15] The relevance to the current study and the fact that this compound has been synthesized hydrothermally warrant a brief description here.

The structure of NDUF-4 contains two unique $U^{(IV)}$ sites, both of which are in 9-coordination with F anions. Polymerization of these building units gives rise to the extended three-dimensional structure shown in Figure 4. The structure may be described as consisting of (010) sheets of corner- and edge-linked UF_9 (all U(2)) polyhedra (Figure 4). Parallel layers are linked together through corner-shared chains of U(1) polyhedra along [001]. This polymerization of the sheets ultimately gives rise to 6-ring channels along [001]. The channels are continuous throughout the structure and measure approximately 6 Å × 6 Å (as measured from the shortest F−F distance). Further structural details are given in the original report.[40]

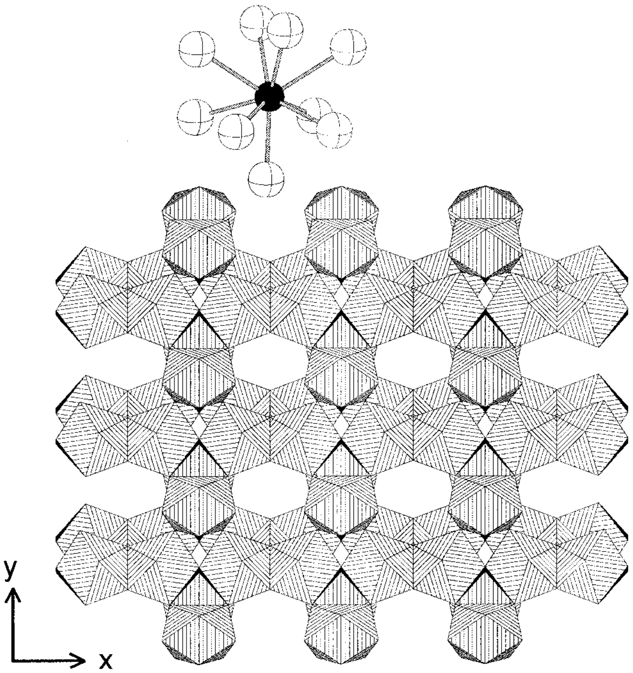

Figure 4. Structure of NDUF-4 shown down [001]. UF_9 polyhedra (ball and stick; inset) are linked by sharing corners and edges to form a three-dimensional framework. The space-filling NH_4^+ cations have been omitted for clarity.

Discussion

A summary of the structures reported herein and the conditions under which they were synthesized is given in Figure 5. Recall from the synthesis section (above) that the starting mixture for the formation of each compound is identical; therefore, the only variable in these experiments has been time. Within the hydrothermal DABCO−U−F−H_2O system, we observe an evolution of structural building units from the UO_2F_5 pentagonal bipyramid to the UF_8 trigonal prism and finally to the UF_9 polyhedron. Coupled to this building unit transition is an oxidation state change on the U from 6+ to 4+. Not unexpectedly, there is no evidence of any $U^{(V)}$ compounds because these are typically less common species.[41] Further, as the duration of the syntheses was extended, a breakdown of the organic structure-directing agent was observed (DABCO to NH_4^+). It is conceivable that there is an evolution of the structure-directing agent as well; DABCO can direct formation of NDUF-1 and -2, (but not -3 and -4), whereas NH_4^+ is necessary for the formation of NDUF-3 and -4. Thus, there are a number of simultaneous and perhaps complementary processes at work in this system.

It is difficult to describe adequately the overall redox activity in this system. Clearly the U species are reduced from U^{6+} to U^{4+}, yet the simultaneous oxidation process remains ambiguous. It is conceivable that the decomposition of the DABCO molecules to NH_4^+ cations under these oxic hydrothermal conditions involves an oxidative process, but because the decomposition products (other than NH_4^+) are not ordered in the final crystal structure, one can only speculate on their

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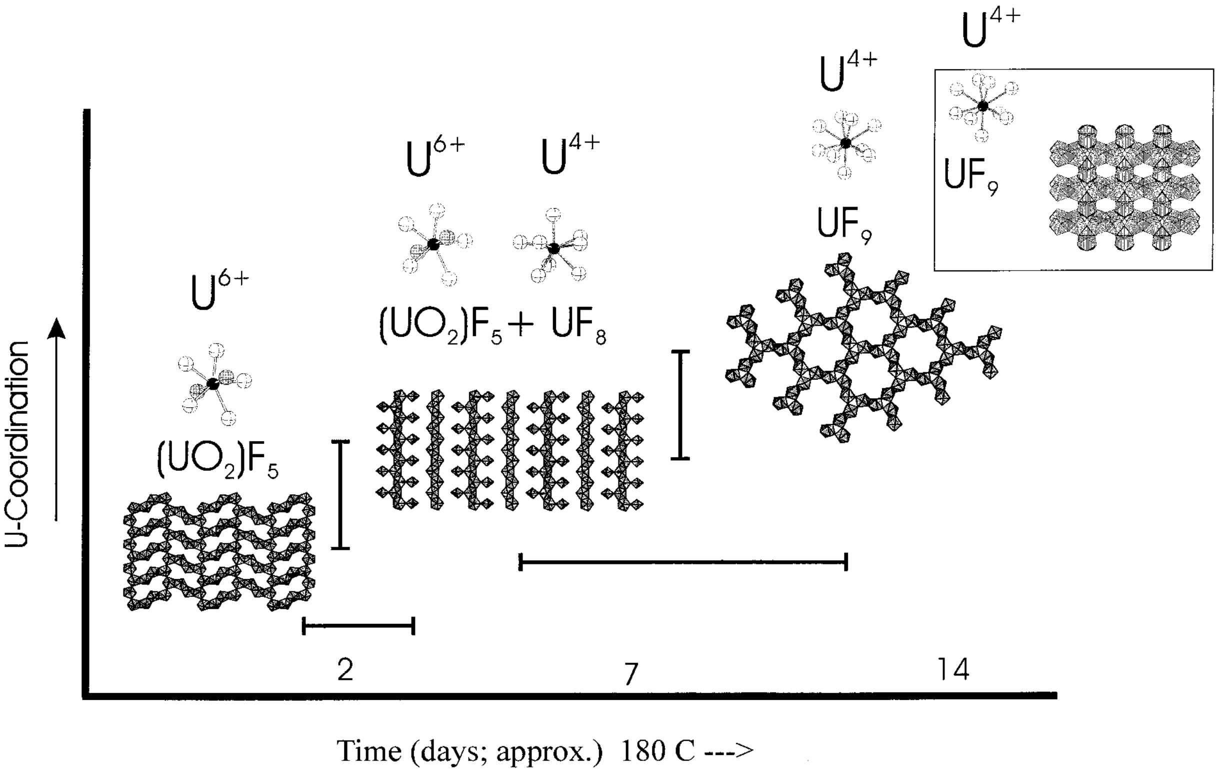

Figure 5. Schematic representation of U coordination and structure type vs reaction duration. Structure types and polyhedra are represented as in previous figures. For a system at constant (starting) composition at 180 °C, shorter duration runs produce structures containing $(UO_2)F_5$ polyhedra. Longer duration runs result in a progressive fluorination of the U atoms to form UF_8 and finally UF_9 polyhedra. Bars are included to show regions of overlap. NDUF-4 is shown as an inset because the phase boundaries of this material remain unclear.

identity. A thorough examination of the end-product liquid phase with mass spectrometry or chromatography would perhaps offer some insight.

Comments on the transformation mechanism of the solid-phase compounds at this stage of the investigation are somewhat speculative. Evidence for a solid-state transformation is limited, considering that there is little structural resemblance between members of the series. Further, the increased coordination of the U atoms and their simultaneous reduction suggest an interaction with the solution phase. Although there is considerable phase overlap with respect to time (Figure 5), no zoning or reaction rinds were observed by optical inspection of the end products. Rather, reaction products generally consisted of discrete crystals of each phase, readily discernible by shape. A more thorough examination would of course require SEM/TEM techniques; however, preliminary observations suggest that this is not necessary. Plans to examine the stability of each compound are in place, including seeding of reaction mixtures with pure phases and monitoring of their reactivity.

Conclusions

Open-structured U−O−F and U−F materials consisting of both novel and known structure types have been synthesized under hydrothermal conditions in the presence of the organic structure-directing agent DABCO. A fixed starting composition and temperature with variable reaction duration has resulted in the evolution of structural building units from UO_2F_5 pentagonal bipyramids in NDUF-1 to UF_8 trigonal prisms in NDUF-2 to UF_9 polyhedra in NDUF-3 and -4. This transition is coupled to a reduction of U species from U^{VI} to U^{IV} and a simultaneous decomposition of the DABCO to form NH_4^+ cations. The exact mechanism for the redox changes within this system is thought to be complex and requires further study. Interestingly, however, the hydrothermal syntheses described herein have resulted in the formation of two previously reported structure types obtained from high-temperature investigations (NDUF-3 and -4). Such a finding suggests potential for the syntheses of a number of related materials under these “softer” conditions.

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Supporting Information Available: A file of X-ray crystallographic data in CIF format for NDUF-1 and -3. This material is available free of charge via the Internet at http://pubs.acs.org.

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