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# The effects of hydrofluoric acid addition on the hydrothermal synthesis of templated uranium sulfates†

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The effect of employing hydrofluoric acid as a mineraliser in the formation of organically templated uranium sulfate materials has been studied. Variable amounts of HF<sub>(aq)</sub> were added to a series of reaction gels in which all other reactant concentrations were invariant, resulting in the formation of three different phases, depending upon the fluoride concentration. Two of these phases are novel; [N<sub>2</sub>C<sub>4</sub>H<sub>14</sub>][UO<sub>2</sub>(H<sub>2</sub>O)(SO<sub>4</sub>)<sub>2</sub>] is a new templated uranium sulfate, containing anionic [UO<sub>2</sub>(H<sub>2</sub>O)(SO<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> chains that hydrogen bond to one-another forming *pseudo*-layers, and [N<sub>2</sub>C<sub>4</sub>H<sub>14</sub>][UO<sub>2</sub>F(SO<sub>4</sub>)<sub>2</sub>] is the first example of a templated uranium sulfate fluoride, which consists of uranium fluoride chains linked by sulfate groups to form [UO<sub>2</sub>F(SO<sub>4</sub>)]<sup>-</sup> layers. The role of F<sup>-</sup> in these reactions is two-fold; it acts as a mineraliser when present in small concentrations, while it is incorporated into the reaction product when present in larger mole fractions. Both of the new materials have been characterised using a range of physical techniques including single crystal X-ray structure analysis.

## Introduction

Hydrothermal synthesis is a well established method for the formation of *N*-dimensional solids, with examples incorporating a range of elements displaying a great variety of structure types.<sup>1-9</sup> Typical components of these hydrothermal reactions include a metal source, an aqueous acid, a 'structure directing agent' (usually an amine) and water. A mineraliser, which may or may not be incorporated into the product framework, can be employed to aid the formation of soluble species. The fluoride and hydroxide anions are good examples of such mineralisers.

An example of the utility of fluoride anions in hydrothermal reactions can be found in the synthesis of ITQ-4, a large pore pure silica zeolite.<sup>10</sup> This compound cannot be formed in the absence of F<sup>-</sup>, however, fluoride anions are not incorporated into the framework, and instead are occluded in the pores within the material. They are removed upon calcination at 500 °C. Fluoride ions do have a unique structure-directing effect, leading to crystallisation in a polar non-centrosymmetric spacegroup.<sup>11</sup> Nevertheless, the materials SSZ-42<sup>12</sup> and MCM-58<sup>13</sup> are isostructural with ITQ-4 and are obtained in the absence of fluoride. Another role for F<sup>-</sup> was demonstrated by Férey *et al.* through the incorporation of F<sup>-</sup> into the framework in a series of oxyfluorinated microporous compounds, with product composition depending upon the nature of the fluorinating agent, HF<sub>(aq)</sub> or NH<sub>4</sub>F.<sup>14</sup> In the synthesis of Cloverite,<sup>15</sup> and ITQ-21<sup>16</sup> the fluoride ions acted as templates, encapsulated within the double-4-ring cage building units.

In this study, we report an investigation into the systematic addition of HF<sub>(aq)</sub> to the reaction gel for a previously synthesised templated uranium sulfate, USO-12 (USO = Uranium Sulfate from Oxford),<sup>17</sup> in order to explore the effects of HF<sub>(aq)</sub> addition on the formation of the reaction product. USO-12 is a member of the family of organically templated metal sulfates, which have begun to receive considerable attention in the past three years.<sup>17-43</sup> The amount of 40% HF<sub>(aq)</sub> added to the reaction mixture was varied from 0 to 2.5 mmol per reaction. We were interested in the effects of variation of the F<sup>-</sup> concentrations within a series

of experiments designed to probe the hydrothermal synthesis of uranium sulfates. Any decrease in pH, owing to the addition of HF<sub>(aq)</sub> to the reaction mixture, will be negligible owing to the relatively high concentration of sulfuric acid in the reaction mixture, therefore any change in the reaction product will be a direct result of the presence of fluoride. Three compounds are observed, two of which are novel. The synthesis, structure and characterisation of two new compounds is reported. USO-26, is a uranium sulfate that contains no fluoride, while USFO-1 (USFO = Uranium Sulfate Fluoride from Oxford) incorporates both fluoride and sulfate into the inorganic framework.

## Experimental

**CAUTION:** Although all uranium materials used in these experiments were depleted, extra care and good laboratory practice should be ensured when handling uranium-containing materials.

## Materials

1,4-Diaminobutane (99%, Aldrich), sulfuric acid (98%, Aldrich) and HF<sub>(aq)</sub> (40%, BDH) were used as received. Deionised water was used in these syntheses. UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O was prepared<sup>44</sup> from UO<sub>3</sub> (99.8%, Strem).

## Synthesis

All reactions were conducted in poly(fluoro-ethylene-propylene) lined 23 ml stainless steel autoclaves. Reactions were heated to 180 °C at 10 °C min<sup>-1</sup>, where the temperature was held constant for 24 h. The reactions were cooled to room temperature at 6 °C h<sup>-1</sup>, and the autoclaves opened. Solid products were recovered using filtration, and washed with deionised water and acetone, and allowed to dry in air.

**[N<sub>2</sub>C<sub>4</sub>H<sub>14</sub>][UO<sub>2</sub>(H<sub>2</sub>O)(SO<sub>4</sub>)<sub>2</sub>], (USO-26).** USO-26 was synthesised through the reaction of 0.2364 g (5.58 × 10<sup>-4</sup> mol) of UO<sub>2</sub>OAc<sub>2</sub>·2H<sub>2</sub>O, 0.2791 g (2.85 × 10<sup>-3</sup> mol) of H<sub>2</sub>SO<sub>4</sub>, 0.1602 g (1.77 × 10<sup>-3</sup> mol) of 1,4-diaminobutane, 1.010 g (5.55 × 10<sup>-2</sup> mol) of deionised water and 0.0242 g (4.80 × 10<sup>-4</sup> mol) of HF<sub>(aq)</sub> (40%). Yellow blocks were isolated after reaction in a yield of 22%. Elemental microanalysis for USO-26 obsd. (calc.);

† Electronic supplementary information (ESI) available: Powder X-ray diffraction patterns of USFO-1 and USO-26. See <http://www.rsc.org/suppdata/dt/b4/b413062f/>

N, 5.05 (4.91); C, 8.65 (8.42); H, 2.95 (2.83); S, 10.19 (11.24); U, 40.94% (41.73%).

**[N<sub>2</sub>C<sub>4</sub>H<sub>14</sub>][UO<sub>2</sub>F(SO<sub>4</sub>)<sub>2</sub>], (USFO-1).** USFO-1 was synthesized through the reaction of 0.2364 g ( $5.56 \times 10^{-4}$  mol) of UO<sub>2</sub>OAc<sub>2</sub>·2H<sub>2</sub>O, 0.2792 g ( $2.85 \times 10^{-3}$  mol) of H<sub>2</sub>SO<sub>4</sub>, 0.1592 g ( $1.77 \times 10^{-3}$  mol) of 1,4-diaminobutane, 0.9945 g ( $5.53 \times 10^{-2}$  mol) of deionised water and 0.1232 g ( $2.46 \times 10^{-3}$  mol) of HF<sub>(aq)</sub> (40%). Yellow rods were isolated after reaction in a yield of 42%. Elemental microanalysis for USFO-1 obsd. (calc.); N, 3.30 (3.26); C, 5.60 (5.58); H, 1.71 (1.64); S, 7.30 (7.45); U, 53.43% (55.33%).

Although yields appear relatively low, a significant amount of U<sup>6+</sup> remains soluble after reaction. Slow evaporation of the post cooling supernatant solution resulted in the formation of each respective reaction product in a phase pure fashion, increasing the overall yield.

Powder X-ray diffraction patterns of each bulk sample (see ESI†) match the pattern generated from the respective single crystal X-ray structure data.

### Single crystal X-ray diffraction

Single crystals of each compound were used for structure determination. Data were collected using an Enraf Nonius FR 590 Kappa CCD diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystals were mounted on a glass fibre using N-Paratone oil and cooled *in-situ* using an Oxford Cryostream 600 Series to 150 K for data collection. Frames were collected, indexed and processed using Denzo SMN and the files scaled together using HKL GUI within Denzo SMN.<sup>45</sup> The heavy atom positions were determined using SIR92.<sup>46</sup> All other non-hydrogen sites were located from Fourier difference maps. All non-hydrogen sites were refined using anisotropic thermal parameters using full matrix least squares procedures on  $F_o^2$  with  $I > 3\sigma(I)$ . Hydrogen atoms were placed in geometrically idealized positions. All calculations were performed using Crystals<sup>47</sup> and Cameron.<sup>48</sup> Relevant crystallographic data are listed in Table 1.

CCDC reference numbers 248605 and 248606.

See <http://www.rsc.org/suppdata/dt/b4/b413062f/> for crystallographic data in CIF or other electronic format.

### Powder X-ray diffraction

Powder X-ray diffraction patterns were recorded on a PANalytical X'pert Pro powder diffractometer. Samples were mounted on stainless steel plates. Calculated powder patterns were generated

from the single crystal data using the computer program, ATOMS v. 6.0.<sup>49</sup>

### Infrared spectroscopy

All infrared measurements were obtained using a Perkin Elmer 1600 FT spectrometer. Samples were diluted with spectroscopic grade KBr and pressed into a pellet. Scans were run over the range 400–4000 cm<sup>-1</sup>.

### Elemental analysis

C, H and N analyses were conducted using an Elementar Vario EL analyzer. S and U compositions were determined by ICP using a Thermo Jarrell Ash Scan 16 instrument.

### Thermogravimetric analysis

TGA measurements were performed using a Rheometric Scientific STA 1500H thermal analyzer. The samples were loaded into an alumina crucible and heated at 10 °C min<sup>-1</sup> under flowing argon.

## Results

### [N<sub>2</sub>C<sub>4</sub>H<sub>14</sub>]<sub>2</sub>[UO<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>]·2H<sub>2</sub>O, USO-12

This compound was reported previously.<sup>17</sup> USO-12 contains zero-dimensional [UO<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>]<sup>4-</sup> anions, with doubly protonated 1,4-diaminobutane templates. The structure of the inorganic molecular units and the three-dimensional packing are shown in Fig. 1.

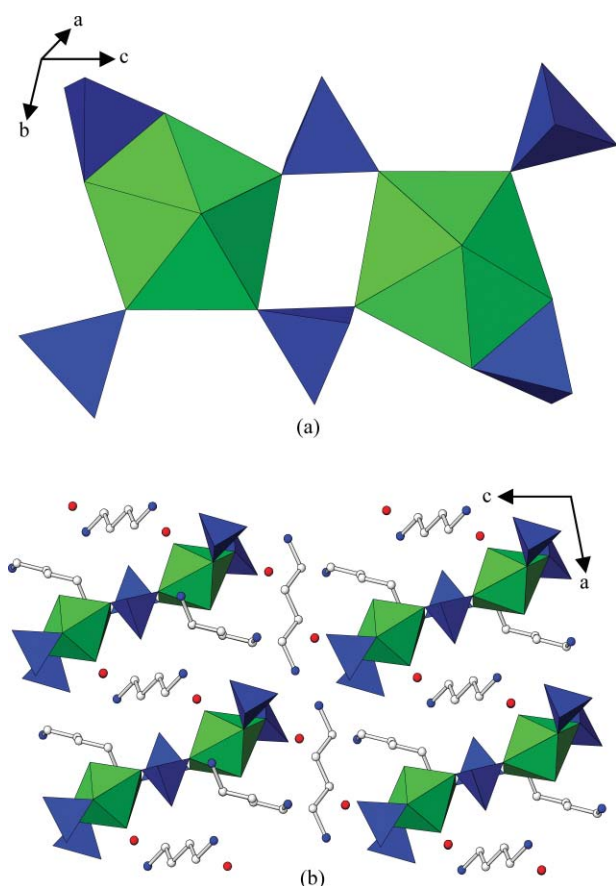
### [N<sub>2</sub>C<sub>4</sub>H<sub>14</sub>][UO<sub>2</sub>(H<sub>2</sub>O)(SO<sub>4</sub>)<sub>2</sub>], USO-26

A single uranium environment exists in USO-26. The uranium centre is co-ordinated to two axial oxide ligands, forming a uranyl group, UO<sub>2</sub><sup>2+</sup>. The U=O bond lengths are 1.769(5) and 1.772(5) Å, with an O=U=O angle of 179.1(2)°. These values are in good agreement with the average values reported by Burns *et al.*<sup>50</sup> U(1) is co-ordinated to five oxide ligands in the equatorial plane, forming a pentagonal bipyramid. Four of the five equatorial coordination sites are occupied by oxide ligands which bridge to sulfur centres, with the last being occupied by a bound water molecule. U–O<sub>sulfate</sub> distances range between 2.342(4) and 2.390(5) Å, with a U–O<sub>water</sub> distance of 2.492(5) Å. Each UO<sub>7</sub> polyhedron shares vertices with four sulfate tetrahedra forming chains, which are aligned along the [0 0 1] direction (see Fig. 2 (a)). This chain topology has been observed

**Table 1** Crystallographic data

Compound	USO-26	USFO-1
Formula	[N <sub>2</sub> C <sub>4</sub> H <sub>14</sub> ][UO <sub>2</sub> (H <sub>2</sub> O)(SO <sub>4</sub> ) <sub>2</sub> ]	[N <sub>2</sub> C <sub>4</sub> H <sub>14</sub> ][UO <sub>2</sub> F(SO <sub>4</sub> ) <sub>2</sub> ]
<i>M</i>	570.34	860.35
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)
<i>a</i> /Å	7.4199(2)	6.7754(5)
<i>b</i> /Å	7.8380(2)	8.4094(8)
<i>c</i> /Å	12.0319(3)	14.1492(14)
$\alpha$ /°	79.1237(9)	90
$\beta$ /°	79.9015(9)	93.245(3)
$\gamma$ /°	83.1098(9)	90
<i>V</i> /Å <sup>3</sup>	673.79(3)	804.89(13)
<i>Z</i>	2	2
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	2.811	3.550
$\mu$ /mm <sup>-1</sup>	12.412	20.438
$\lambda$ /Å	0.71073	0.71073
Reflections collected	5767	3189
Independent reflections	3056	1803
<i>R</i> ( <i>F<sub>o</sub></i> ) <sup>a</sup>	0.0290	0.0328
<i>R<sub>w</sub></i> ( <i>F<sub>o</sub></i> <sup>2</sup> ) <sup>b</sup>	0.0670	0.0751

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .



**Fig. 1** (a)  $[(\text{UO}_2)_2(\text{SO}_4)_6]^{8-}$  molecular dimers in USO-12. Green and blue polyhedra represent  $[\text{UO}_7]$  and  $[\text{SO}_4]$  respectively. (b) Three-dimensional packing in USO-12. Red, white and blue spheres represent oxygen, carbon and nitrogen atoms respectively. Hydrogen atoms are omitted for clarity.

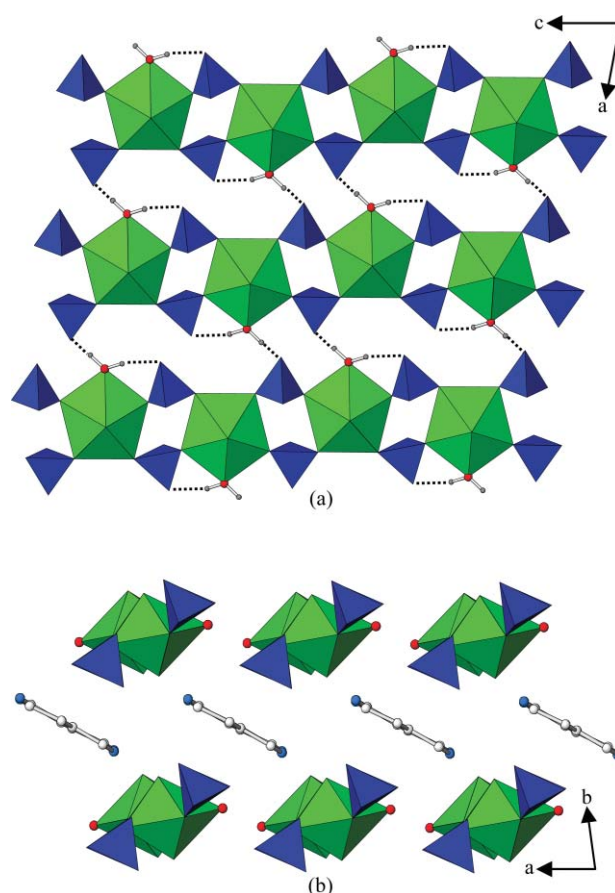
previously in the inorganic phases  $\text{Mn}(\text{UO}_2)(\text{SO}_4)_2(\text{H}_2\text{O}) \cdot 4\text{H}_2\text{O}$ <sup>51</sup> and  $[(\text{UO}_2)(\text{H}_2\text{PO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_2$ ,<sup>52</sup> and in USO-1,<sup>29</sup> USO-3,<sup>31</sup> USO-9,<sup>32</sup> USO-11,<sup>17</sup> USO-18<sup>24,28</sup> and USO-22.<sup>24</sup> However, differences in the hydrogen bonding are observed. Both inter- and intra-chain hydrogen bonding are observed in USO-26, between the oxygen centre of the bound water molecules and adjacent sulfate groups. The inter-chain hydrogen bonds serve to connect adjacent chains, along the  $[1\ 0\ 0]$  direction to form hydrogen bonded *pseudo*-layers. Protonated 1,4-diaminobutane molecules,  $[\text{dabH}_2]^{2+}$ , reside between these *pseudo*-layers (see Fig. 2 (b)). These serve to stabilise the structure, both through balancing the negative charge of the inorganic structure, and donating hydrogen bonds.

The presence of the template is further confirmed using infrared spectroscopy. N–H bending and stretching modes are observed at 1626 and 3200  $\text{cm}^{-1}$ . The C–H stretch is observed at 2960  $\text{cm}^{-1}$ . Absorptions at 926 and 1100  $\text{cm}^{-1}$  emanate from the asymmetric uranyl stretch and S–O and S=O stretches respectively.

The loss of the bound water molecule between 170 and 200 °C is observed using thermogravimetric analysis. A further weight loss of 16.1%, between 330 and 400 °C, owing to template decomposition (calc. 15.8%) is observed. On further heating to 900 °C, the structure collapses to  $\text{UO}_2$ , as confirmed by powder X-ray diffraction, with a total weight loss of 51.8% (calc. 53.0%).

#### $[\text{N}_2\text{C}_4\text{H}_{14}][\text{UO}_2\text{F}(\text{SO}_4)_2]$ , USFO-1

There is one crystallographically distinct uranium centre in USFO-1. It is co-ordinated by two oxide ligands in the axial direction, forming a uranyl group,  $\text{UO}_2^{2+}$ . U=O distances are each 1.786(8) Å. The O=U=O angle is 179.2(4)°, in good



**Fig. 2** (a)  $[\text{UO}_2(\text{H}_2\text{O})(\text{SO}_4)_2]^{2-}$  chains in USO-26. Green and blue polyhedra represent  $[\text{UO}_7]$  and  $[\text{SO}_4]$  respectively. Red and grey spheres represent oxygen and hydrogen atoms respectively. Broken lines represent hydrogen bonds. (b) Three-dimensional packing in USO-26. Red, white and blue spheres represent oxygen, carbon and nitrogen atoms respectively. Hydrogen atoms are omitted for clarity.

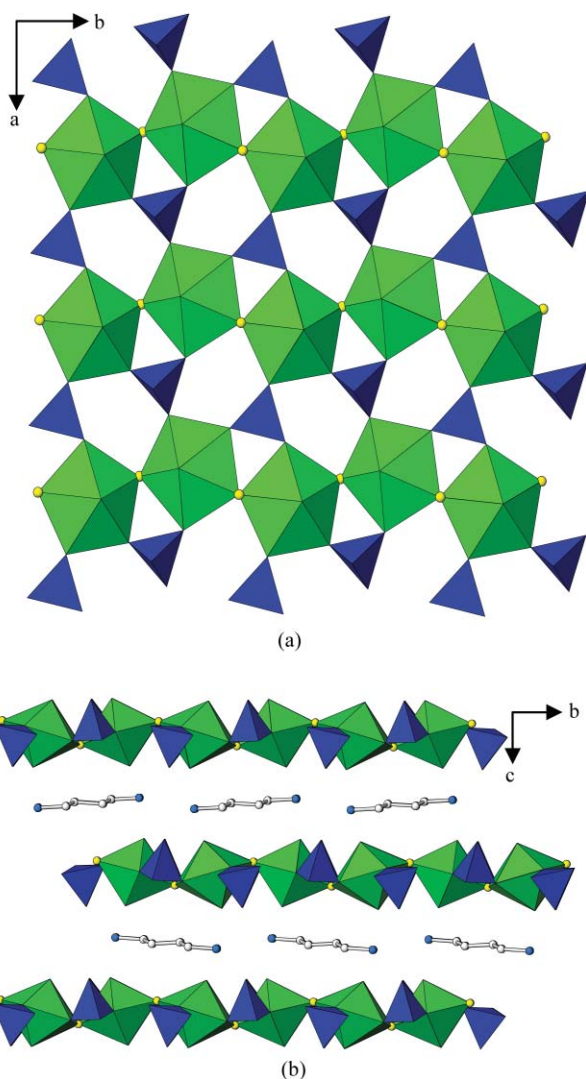
agreement with the reported average value. In the equatorial plane, the uranyl group is co-ordinated to three sulfate oxide ligands and two fluoride ligands. The average U–O bond length is 2.375(13) Å, with shorter U–F bonds, at 2.288(7) and 2.315(7) Å. Adjacent uranium polyhedra are connected through U–F–U linkages, forming chains along the  $[0\ 1\ 0]$  direction. These chains are linked together in the  $[1\ 0\ 0]$  direction through bridging sulfate groups, forming layers in the *ab* plane (see Fig. 3 (a)). This layer topology has been observed previously in the piperazine templated uranyl phosphonate, UPNO-1.<sup>53</sup> The layers stack along the  $[0\ 0\ 1]$  direction, with protonated 1,4-diaminobutane molecules,  $[\text{dabH}_2]^{2+}$ , in the inter-layer space (see Fig. 3 (b)). These balance the negative charge of the layers, and donate hydrogen bonds to the layers.

Bending and stretching modes resulting from N–H bonds are observed at 1614 and 3100  $\text{cm}^{-1}$  in the infrared spectrum of USFO-1. The C–H bend is observed at 1450  $\text{cm}^{-1}$  and the C–H stretch at 2940  $\text{cm}^{-1}$ . U–F and U=O stretches appear at 493 and 920  $\text{cm}^{-1}$ . The absorption at 1100  $\text{cm}^{-1}$  results from S–O stretching modes.

An observed weight loss of 5%, using thermogravimetric analysis, between 340 and 375 °C indicates the start of template decomposition (total 10.5%). A rapid mass loss follows, between 375 and 450 °C, with slower decomposition up to 900 °C. The total mass loss is 36%, corresponding with decomposition to  $\text{UO}_2$  (calc. 37%), confirmed using powder X-ray diffraction.

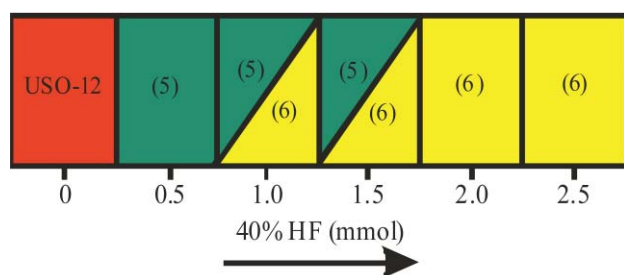
## Discussion

The products from a series of experiments, in which the reaction gel compositions were identical with the exception of the



**Fig. 3** (a)  $[\text{UO}_2\text{F}(\text{SO}_4)]^-$  layers in USFO-1. Green and blue polyhedra represent  $[\text{UO}_2\text{F}_2]$  and  $[\text{SO}_4]$  respectively. Yellow spheres represent fluorine atoms. (b) Three-dimensional packing in USFO-1. Yellow, white and blue spheres represent fluorine, carbon and nitrogen atoms respectively. Hydrogen atoms are omitted for clarity.

amount of  $\text{HF}_{(\text{aq})}$  added, are displayed in Fig. 4. The experiment with no added  $\text{HF}_{(\text{aq})}$  results in the formation of USO-12, which has the formula  $[\text{N}_2\text{C}_4\text{H}_{14}]_2[(\text{UO}_2)(\text{SO}_4)_3]\cdot 2\text{H}_2\text{O}$ . The introduction of only 0.5 mmol of  $\text{HF}_{(\text{aq})}$  (to 5 mmol of reactants) results in the formation of a completely different product,  $[\text{N}_2\text{C}_4\text{H}_{14}]_2[\text{UO}_2(\text{H}_2\text{O})(\text{SO}_4)_2]$  (USO-26). As the fluoride concentration is increased further, a new phase is observed,  $[\text{N}_2\text{C}_4\text{H}_{14}][\text{UO}_2\text{F}(\text{SO}_4)]_2$  (USFO-1), in which fluoride anions have been incorporated into the inorganic structure. USFO-1 co-crystallizes with USO-26 when either 1.0 or 1.5 mmol of  $\text{HF}_{(\text{aq})}$  were used, and is formed phase pure when the fluoride concentration is increased to 2.0 mmol.



**Fig. 4** Plot of product composition as a function of the amount of  $\text{HF}_{(\text{aq})}$  added to the reaction gel.

Marked differences are observed between the structures of the three products in this series of reactions, USO-12, USO-26 and USFO-1. The inorganic architecture present in USO-12 is constructed solely of  $[\text{UO}_2]^{2+}$  and  $[\text{SO}_4]^{2-}$ . USO-26 contains  $[\text{UO}_2]^{2+}$ ,  $[\text{SO}_4]^{2-}$  and  $(\text{H}_2\text{O})$  within the inorganic component. However, fluoride anions have been incorporated into the  $[\text{UO}_2\text{F}(\text{SO}_4)]^-$  layers of USFO-1. No  $\text{HF}_{(\text{aq})}$  was present in the synthesis of USO-12, therefore none could be incorporated into the reaction product. In USO-26, the effect of adding 0.5 mmol  $\text{HF}_{(\text{aq})}$  to the reaction mixture is marked, with the formation of a completely different uranium sulfate framework. Although no fluoride ions have been incorporated into USO-26, their presence is responsible for the differences between USO-12 and USO-26, as the reaction gel is otherwise unchanged. The role of fluoride in the synthesis of USO-26 is that of a mineraliser, where it promotes the solvation of  $[\text{UO}_2]^{2+}$ , but is not necessarily incorporated into the structure. The effect of adding larger amounts of  $\text{HF}_{(\text{aq})}$  to the same reaction mixture results in the formation of USFO-1, in which the incorporation of  $\text{F}^-$  into the product is observed. The role of the fluoride anions is dependent upon its initial concentration. It can act not just as a mineraliser, as in the synthesis of USO-26, but also as a reactant.

Understanding of the change in reaction product upon the addition of  $\text{HF}_{(\text{aq})}$  to the reaction mixture can be approached by considering the role of the fluoride anions in solution. Férey reported a series of compounds containing ULM-3, ULM-4 and ULM-5, with a proposed mechanism of formation where the structure of the templated inorganic solid is dependent on the charge density of the amine and the oligomeric inorganic building unit (SBU).<sup>14</sup> These two species form neutral amine-SBU pairs that allow for the precipitation of a neutral extended solid. First, we consider the formation of USO-12 from the species in solution. USO-12 contains zero-dimensional dimers,  $[(\text{UO}_2)_2(\text{SO}_4)_6]^{8-}$ . These dimers are also present in USO-13 and USO-14, where they coalesce to form two- and one-dimensional structures respectively. Using Férey's proposed mechanism, the SBU, which precedes the formation of the solid products, would closely resemble the zero-dimensional dimer in USO-12.

The introduction of small concentrations of  $\text{F}^-$  produces conditions under which the fluoride acts as a mineraliser. The nature of the soluble uranium species will be affected. The  $[(\text{UO}_2)_2(\text{SO}_4)_6]^{8-}$  dimers are prevented from crystallising and a different reaction product is observed. The fluoride ion concentration is still relatively low, and is therefore not incorporated into the product.

As the fluoride ion concentration is further increased, its importance in solution increases. Displacement of the  $\text{F}^-$  anions from the uranium coordination sphere upon crystallisation is far less likely as the fluoride concentration increases. Retention of  $\text{F}^-$  allows for the formation of U-X-U linkages, previously unseen in the many templated uranium sulfates that have been reported.<sup>17,23-32</sup> This leads to the formation of U-F-U chains, and ultimately, the layered material, USFO-1.

## Conclusion

The role of fluoride ions in hydrothermal synthesis is dependent upon their concentration within the reaction gel. In relatively low concentrations they act as a mineraliser, modifying the solubility characteristics of the reaction. This results in a new product upon crystallisation,  $[\text{N}_2\text{C}_4\text{H}_{14}][\text{UO}_2(\text{H}_2\text{O})(\text{SO}_4)]$ , with respect to their absence from the reaction,  $[\text{N}_2\text{C}_4\text{H}_{14}]_2[(\text{UO}_2)(\text{SO}_4)_3]$ , although they are not incorporated into the reaction product. A relatively high concentration of fluoride within the reaction results in a far greater change in the reaction product. The fluoride anions are incorporated into the reaction product owing to their greater concentration in solution, resulting in the formation of the first example of a uranium sulfate fluoride material,  $[\text{N}_2\text{C}_4\text{H}_{14}][\text{UO}_2\text{F}(\text{SO}_4)]_2$ .

## Acknowledgements

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