PF_6^- Hydrolysis as a route to unique uranium phosphate materials†

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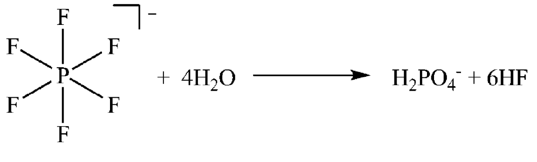
An uranium phosphate fluoride with a unique pentameric secondary building unit is prepared under hydrothermal conditions with $UO_2(NO_3)_2{\cdot}6H_2O$, PF_6^- and 4,4′-bipyridine; the single-crystal structure is determined.

Metal phosphate chemistry has been explored extensively as related to areas such as materials chemistry[1] and mineralogy.[2] In particular, uranyl (UO_2^{2+}) phosphate phases have been studied owing to their ubiquity in actinide-bearing minerals,[3,4] structural diversity,[5,6] and potential applications and relevance in areas such as the long-term stewardship of spent nuclear fuel.[7,8] The insolubility of uranium phosphates, and indeed uranium phosphate fluorides, makes the synthesis of new crystalline products difficult as amorphous or microcrystalline products often result when phosphate is immediately available to uranium.[9] As a result, there is a limited catalogue of synthetic uranium phosphate compounds. Traditional hydrothermal synthesis of these materials generally involves phosphate anions that are introduced via *preformed* alkali metal phosphates or phosphoric acid. We report herein an alternative route, namely the hydrolysis of the hexafluorophosphate anion (PF_6^-) to yield phosphate bearing phases. Inspired by intriguing results from *in situ* ligand synthesis,[10–13] wherein framework components are produced gradually over time, we began an investigation of hydrolysis of the PF_6^-. *In situ* methods applied to solid state chemistry have typically involved organic species. Now, we have intentionally used *in situ* generation of phosphate building units *via* hydrolysis of an inorganic precursor, to create a new uranium phosphate fluoride with an unprecedented pentameric secondary building unit. Hydrolysis of the PF_6^- anion (Scheme 1) as a route to tetrahedral phosphate building units may be significant and useful in realizing the potential structural diversity of other synthetic systems, thus broadening our catalogue of solid state materials.

The new material, $[(UO_2)_5(HPO_4)_3(PO_4)F_4](H_9C_{10}N_2)_3$ (**1**)†‡ contains a layered, anionic uranium fluoride phosphate sheet with protonated 4,4′ bipyridine providing charge balance in the interlayer (Fig. 1). The layer is composed of both pentagonal and hexagonal uranyl bipyramids which fulfill their equatorial coordination through fluoride ions and phosphate oxygen atoms from edge and corner sharing phosphates. There are four crystallographically unique phosphate tetrahedra in **1**, three of which must be protonated for charge balance. Analysis of bond lengths and valence suggest that these are randomly distributed. A secondary building unit within this sheet is realized in the pentameric cluster of four pentagonal uranyl bipyramids flanking a single hexagonal uranyl bipyramid. The central hexagonal bipyramid is composed of a linear uranyl cation (with the uranium at a center of inversion) coordinated equatorially to two μ_3-fluorides and four oxygen atoms from edge shared phosphate tetrahedra. It is flanked on each side by two pentagonal bipyramids that are each composed of linear uranyl cations coordinated to three equatorial oxygens, the aforementioned μ_3-fluoride, and one additional equatorial μ_2-fluoride. A dimer of these results from edge sharing of the μ_3- and μ_2-fluoride sites and links through two equatorial edges of the central hexagonal uranyl hub. This pentameric cluster is connected to the greater sheet through four corner sharing and two edge sharing phosphate tetrahedra.

Infrared spectroscopy on **1** revealed a broad stretch centered at 3415 cm^{-1} consistent with protonated bpy or a hydroxyl group of a phosphate tetrahedra, and a strong stretch at 1115 cm^{-1} consistent with the P=O bonds of the phosphates. Thermogravimetric measurements in flowing N_2 show **1** to be stable up to 400 °C at which point much of the bpy is removed resulting in a weight loss of 17% (calc. 20.8%). A broad weight loss is then seen between 500 and 900 °C (total weight loss observed 27.5%). The X-ray powder diffraction of the calcined material is consistent with mixed uranium phosphate phases.

To date, only six synthetic uranium phosphate fluorides, all synthesized with phosphoric acid and HF as the phosphate and fluorine sources, respectively, have been reported[14–17] and of these, five contain the uranyl cation[15–17] while one contains tetravalent uranium.[14] The five previously synthesized uranyl phosphate fluorides have secondary building units previously seen in uranyl literature, primarily uranyl dimers and monomers. The most striking structural feature of **1** is its distinct



Scheme 1 Hydrolysis of PF_6^-.

$$PF_6^- + 4H_2O \longrightarrow H_2PO_4^- + 6HF$$

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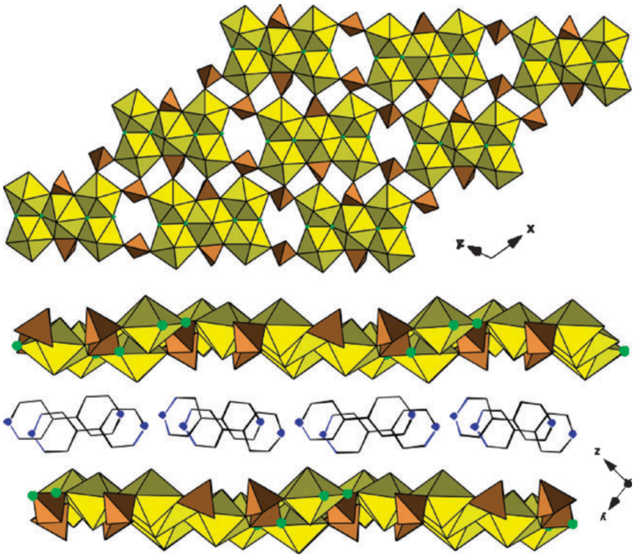

Fig. 1 The top figure is a polyhedral representation of **1** viewed down the [0 1 −1] direction illustrating the anionic sheet topology. The lower figure illustrates the stacking of the two-dimensional sheets with the singly protonated bpy molecules in the interlayer. Yellow polyhedra are uranium(VI) atoms in pentagonal and hexagonal bipyramid geometry. Brown polyhedra represent phosphate tetrahedra while green and blue spheres represent fluoride ions and nitrogen atoms, respectively.

pentameric secondary building unit. Though uranium phosphate minerals of the phosphuranylite group[18] are known to have chains formed with hexagonal bipyramids and pentagonal uranyl bipyramids, this isolated pentamer motif is unknown in previous uranium phosphate literature and moreover, is unique to all previously reported uranium chemistry. Efforts to recreate **1** utilizing identical reaction conditions and stoichiometric equivalents of all reactants substituting *preformed* phosphate sources and HF for PF_6^- instead forms a structure with the known autunite type sheet[19] charge balanced by protonated bpy, namely $[(UO_2)(PO_4)]\cdot 2H_2O\cdot C_{10}H_{10}N_2$. This supports the notion that the unique structural motif seen in **1** is a result of all reactants not being immediately available. While the partial hydrolysis of PF_6^- to form monofluorophospate (FPO_3^{2-}) has been reported in the past,[20,21] ^{19}F NMR analysis of **1** dissolved in D_2O/DCl suggest this is not present in our material. Further study of this system will include *in situ* NMR studies to examine the speciation of hydrolysis products as a function of time.

The *in situ* generation of phosphate anions *via* hydrolysis of hexafluorophosphate anions provides a previously unexplored route to novel uranium phosphate materials. Additionally, we have successfully demonstrated the generality of PF_6^- hydrolysis by creating two transition metal phosphates, namely giniite ($Fe^{2+}Fe^{3+}{}_4(PO_4)_4(OH)_2\cdot 2H_2O$) and libethenite ($Cu_2(PO_4)(OH)$). More generally, this type of hydrolysis could be applied to other metal phosphate systems and perhaps to form other building units such as borates and silicates through hydrolysis of their respective fluoro-anions.

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Notes and references

‡ *Synthesis*: Compound **1**, was synthesized hydrothermally by combining $UO_2(NO_3)_2\cdot 6H_2O$ (0.264 g, 5.26×10^{-4} mol), tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (0.180 g, 4.65×10^{-4} mol), 4,4′-bipyridine (bpy) (0.158 g, 1.01×10^{-3} mol), and distilled water (4.507 g, 0.250 mol) in a Teflon-lined, 23 mL stainless steel Parr bomb. The Parr bomb was sealed, heated statically at 180 °C for 8 days and then cooled to room temperature. Two products, a brown powder and a yellow crystalline solid, were obtained. Separation of the yellow crystals from the brown phase was achieved as the latter is easily dispersed in water and decanted. The yield of the resulting yellow, crystaline product based on uranium is 44.1%. Elemental analysis: (wt%, calc./found): **1**, C 15.80/15.61, H 1.33/1.30, N 3.68/3.70, F 3.33/3.79. Powder X-ray diffraction on the product is in agreement with the calculated pattern from the single-crystal data.[22] Prior to 8 days $[(UO_2)_2(OH)_5](H_9C_{10}N_2)$ can be obtained at a low yield. This *hydroxide* phase will be described in a future publication.
Crystallography: A yellow plate-like crystal (0.12 mm × 0.08 mm × 0.03 mm) was selected and mounted on a glass fiber with epoxy gel. Single crystal data were acquired on a Bruker SMART diffractometer equipped with an APEX II CCD detector. Data processing was performed using Bruker software and the structure was solved using direct methods. Refinements were carried out with SHELXL-97[23] within the WINGX[24] software suite. *Crystal data* for $[(UO_2)_5(HPO_4)_3(PO_4)_1F_4](H_9C_{10}N_2)_3$: $M = 2280.63$, triclinic, $P\bar{1}$, $a = 13.274(3)$, $b = 14.179(3)$, $c = 14.437(3)$ Å, $\alpha = 94.727(3)$, $\beta = 99.36(3)$, $\gamma = 114.01(3)$, $V = 2415.5(9)$ Å^3, $Z = 2$, 13 100 reflections measured, 10 669 unique ($R_{int} = 0.0520$; $I > 2\sigma(I)$), $R1 = 0.0352$, $wR2 = 0.0659$, GOF = 1.016. The crystal studied is a two component twin, and the final model was refined against HKLF5 data. A bpy molecule was disordered about an inversion center and is modeled in the final refinement.

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