Organically templated layered uranium(VI) phosphates: hydrothermal syntheses and structures of $[NHEt_3][(UO_2)_2(PO_4)(HPO_4)]$ and $[NPr_4][(UO_2)_3(PO_4)(HPO_4)_2]$

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Two organically templated layered uranium(VI) phosphates have been prepared under hydrothermal conditions from U_3O_8 and H_3PO_4 using either NPr_4^+ or $NHEt_3^+$ ions as structure directing agents; both compounds have layered structures which contain infinite chains of edge-sharing $[UO_7]$ pentagonal bipyramids cross linked by bridging $[PO_4]$ tetrahedra to form two dimensional sheets of $[(UO_2)_n(HPO_4)_{n-1}(PO_4)]_m^{m-}$ anions.

Crystalline layered and microporous phosphates have attracted great attention owing to their rich chemistry based on the intercalation, ion-exchange, or absorption of guest molecules into the host framework.[1,2] This has led to interest in the synthesis of new metal phosphates with novel layered and open-framework structures. Recently a wide variety of new compounds have been synthesized in which metals such as Be,[3] Ga,[4] In,[5] Zn,[6] V,[7] Fe,[8] Co,[9] and Mo[10] have been incorporated into the phosphate framework. When the syntheses are performed under hydrothermal conditions in the presence of organic templates both layered and microporous phases are formed, which often display unusual framework topologies. To date, however, we are not aware of any organically templated hydrothermal syntheses of new phosphate materials incorporating actinide elements. It is expected that the incorporation of bulky organic templates in an actinide phosphate framework could result in new and unusual framework topologies. Clearfield and co-workers have synthesised a number of uranyl phosphonates in which the presence of the bulky organic substituents on the phosphonate groups leads to the formation of novel structure types.[11,12] We have been exploring the hydrothermal synthesis of uranium phosphate based materials in the presence of organic templates. We report here the synthesis and structural characterization of the first examples of organically templated layered uranium(VI) phosphates to be isolated, namely $[NHEt_3][(UO_2)_2(PO_4)(HPO_4)]$ **1** and $[NPr_4][(UO_2)_3(PO_4)(HPO_4)_2]$ **2**.

Single crystals of **1** were grown by heating mixtures of composition $U_3O_8 : 9H_3PO_4 : 3NEt_3 : 240H_2O$ under autogenous hydrothermal conditions in Teflon lined autoclaves at 180 °C for 3 d.‡ The crystals formed as flat plates together with a small amount of microcrystalline impurity. Single crystals of **2** were grown by heating mixtures of composition $U_3O_8 : 6H_3PO_4 : 3NPr_4OH : 240H_2O$ at 180 °C for 3 d.‡ The crystals formed as thin needles together with a small amount of a microcrystalline impurity.

Compound **1** adopts a layered structure§ in which the two unique U atoms are both coordinated in a slightly distorted pentagonal bipyramidal arrangement by seven O atoms, a common coordination environment for U. The axial O and the U atoms form almost linear [angles of 178.8(4)° and 169.1(3)°] uranyl UO_2^{2+} units with a mean U–O distance of 1.77 Å with the five equatorial O at a larger mean distance of 2.40 Å. These values are typical for U^{VI} in this coordination environment.[13] Valence sum calculations are consistent with this assignment.[14] Zigzag $PaCl_5$ type chains are formed along the (101) direction by UO_2O_5 pentagonal bipyramidal units sharing opposite edges. $(UO_2O_5)_n$ chains such as these are a common structural unit found in other uranium oxides and phosphates such as α-U_3O_8, UVO_5,[15] $U_2V_2O_{11}$,[15] and $U(UO_2)(PO_4)_2$.[16] Individual chains are cross-linked through O atoms of bridging tetrahedral phosphate units to form a corrugated layer structure in the [010] plane. Each phosphate group bonds to a U atom in one chain *via* two O atoms and also bonds to a second U atom in an adjacent chain *via* a third O atom (Fig. 1). The fourth O of the phosphate group does not bridge but instead projects above and below the phosphate layers. These layers are stacked along the (010) direction and are separated from adjacent layers by charge balancing $NHEt_3^+$ cations to form a structure consisting of alternating inorganic and organic layers. The separation between adjacent phosphate layers is 9.2 Å. To maintain charge balance, one of the phosphate groups must be protonated, giving the indicated formula $[NHEt_3][(UO_2)_2(PO_4)(HPO_4)]$. The IR spectrum of **1** also revealed broad weak bands at 2750 and 1620 cm^{-1} that are consistent with P–OH vibrations. The location of the OH proton could not be determined from the X-ray analysis, and a consideration of the P–O distances did not reveal any obviously longer bonds indicative of a P–OH group. The P–O distances range from 1.50(1) to 1.56(1) Å with an average of 1.54 Å. However, valence sum calculations indicate that the terminal O atoms projecting above and below the layers have unsatisfied valence and these calculations are consistent with the assumption that the proton is likely to be located on these atoms. However, it is not possible to determine which of the two unique phosphate groups contains the OH group. It seems likely that the H is disordered over both sites.

Compound **2** also forms as a layered structure.§ As in **1** the layers consist of $PaCl_5$ type $(UO_2O_5)_n$ chains formed from edge sharing pentagonal bipyramidal (UO_2O_5) units which are then further cross-linked by phosphate groups to form uranium

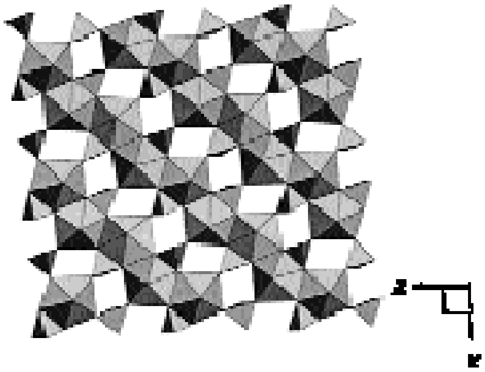

Fig. 1 A view of the structure of the layers in $[NHEt_3][(UO_2)_2(PO_4)(HPO_4)]$ **1** parallel to the *b* axis, showing the chains of edge-sharing $[UO_7]$ pentagonal bipyramids and bridging $[PO_4]$ tetrahedra

phosphate layers similar to those in **1** in the [01$\bar{1}$] plane. There are three unique U atoms in the asymmetric unit. The coordination around all three is again typical for a U^{VI} atom in this environment, with a mean uranyl U–O distance of 1.75 Å and a mean equatorial U–O distance of 2.40 Å. Valence sum calculations are consistent with this assignment.[14] Each tetrahedral phosphate group bonds to one U atom *via* two O atoms and another U atom in the next $(UO_2O_5)_n$ chain *via* a third O atom. The fourth O atom projects above and below the phosphate layers. Each phosphate layer is separated from the next by intercalated NPr_4^+ cations forming alternating inorganic–organic layers along the (01$\bar{1}$) direction. The separation between adjacent phosphate layers is 12.2 Å. As in **1**, to maintain charge balance the existence of protonated P–OH groups must be inferred.

Although the coordination of the uranium and phosphate species in both **1** and **2** are the same, subtle differences in the geometry of the bridging phosphate groups leads to differences in the structures of the layers. In **1** chains of bridging phosphate groups running along the (100) direction [*ca.* 45° to the $(UO_2O_5)_n$ chains] have terminal P–O bonds that either stick 'up' or 'down' from the layers in a strictly alternating [all-up : all-down : all-up] manner along the (001) direction. However, in **2** the same chains of bridging phosphates alternate in the sequence [all-up : both up and down : all-down] along (011). This has the effect that in **1** the layers are corrugated in an approximately sinusoidal manner, whereas in **2** the layers consist of approximately flat sections connected by 'steps' (Fig. 2).

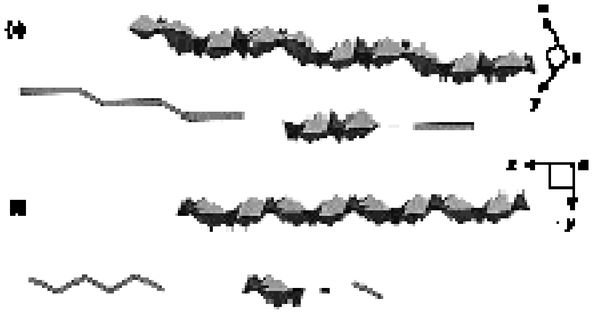

Fig. 2 View of a single layer of $[(UO_2)_n(HPO_4)_{n-1}(PO_4)]^-$ in **1** (*a*) and **2** (*b*) along the (100) direction; also shown is a schematic representation of the layer structure

The charged framework and large interlayer spacing found in these materials suggested that they may be capable of undergoing ion-exchange reactions with other charged species. Preliminary experiments indicate that the template molecules can indeed be exchanged for a variety of alkali metal, transition metal and other quaternary ammonium cations, such as Na^+, Co^{2+} and NMe_4^+, whilst still retaining the integrity of the uranium phosphate layers.

The isolation and characterization of **1** and **2** demonstrate that organic templates can be used to hydrothermally synthesize new hybrid inorganic–organic uranium phosphate materials in which the structure directing organic species is incorporated into the U/P/O framework. Furthermore, these materials show that the detailed structure of the inorganic layers can be influenced by the precise nature of the organic template used. Given the variety of coordination modes and framework topologies[13] displayed by uranium minerals and inorganic phases, there appears to be much scope for synthesizing new materials displaying novel structural features and properties using this methodology. We are currently investigating further the absorption, catalytic, and ion-exchange properties of **1** and **2**.

We would like to thank British Nuclear Fuels Limited for support, and the Leverhulme Fund (P. S. H.), the Commonwealth Scholarship Commission (C. R.) and EPSRC (R. J. F., M. J. D.) for financial support.

Footnotes and References

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† D. O'Hare is the Royal Society of Chemistry Sir Edward Frankland Fellow.

‡ *Synthesis* **1**: a mixture of U_3O_8, H_3PO_4 NEt_3, and H_2O in mol ratio 1 : 9 : 3 : 240 was placed in a 23 ml capacity Teflon lined autoclave and heated to 180 °C at autogenous pressure for 3 d. After cooling to room temp., light green plates of **1** and a small amount of powder impurity were filtered, washed with water, and allowed to dry in air. The crystals could be easily separated by sieving. IR (Nujol mull, ν/cm^{-1}): 2750w (br), 1623m (br), 1096s, 1062s, 1030s, 959s, 919s, 850m, 800w, 721w, 612m, 538m.

2: a mixture of U_3O_8, H_3PO_4, NPr_4OH and H_2O in the mol ratio 1 : 6 : 3 : 240 was placed in a 23 ml capacity Teflon lined autoclave and heated to 180 °C at autogenous pressure for 3 d. After cooling to room temp., light green needles of **2** and a small amount of powder impurity were filtered, washed with water and allowed to dry in air. Due to the small size of the crystals it was difficult to obtain a sample suitable for analysis.

‡ *Crystal data*: $C_6H_{17}NO_{12}P_2U_2$ **1**: monoclinic, space group $P2_1/c$, $a = 9.336(4)$, $b = 18.325(5)$, $c = 9.864(4)$ Å, $\beta = 93.075(5)°$, $U = 1685.1(2)$ Å^3, $Z = 4$, $D_c = 3.281$ g cm^{-3}. 13 372 reflections collected (Enraf-Nonius DIP2000 diffractometer, Mo-Kα, 150 K), of which 3272 were independent and 2346 were observed [$I > 5\sigma(I)$]. Refinement converged with $R = 0.0570$, $wR = 0.0650$, $S = 1.101$.

$C_{12}H_{30}NO_{18}P_3U_3$ **2**: triclinic, space group $P\bar{1}$, $a = 9.401(2)$, $b = 13.048(3)$, $c = 13.447(1)$ Å, $\alpha = 108.021(3)$, $\beta = 103.164(2)$, $\gamma = 100.978(4)°$, $U = 1465.4(3)$ Å^3, $Z = 2$, $D_c = 2.904$ g cm^{-3}. 10 394 reflections collected [Siemens SMART CCD diffractometer on the single-crystal diffraction station (9.8) at the Daresbury Laboratory Synchrotron Radiation Source, UK, $\lambda = 0.6956$ Å, 160 K], of which 8120 were independent and 5244 were observed [$I > 5\sigma(I)$]. Refinement converged with $R = 0.0564$, $wR = 0.0661$, $S = 0.733$. CCDC 182/660.

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Received in Cambridge, UK, 23rd September 1997; 7/06873E