

Reactant-Mediated Diversity in Uranyl Phosphonates

Michael B. Doran, Alexander J. Norquist, and Dermot O'Hare*

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

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Four organically templated uranyl phosphonates, $[C_4N_2H_{12}]_2[UO_2F(PO_3CH_3)]_2$ (UPNO-1), $[C_4N_2H_{12}]_2[UO_2(PO_3CH_3)(PO_2(OH)CH_3)]_2$ (UPNO-2), $[C_4N_2H_{12}]_2[(U_2O_4F_3)(UO_2F(H_2O))(PO_3C_6H_5)_2] \cdot 2H_2O$ (UPNO-3), and $[C_4N_2H_{12}]_2[(UO_2)_5(PO_3CH_2C_6H_5)_6(PO_2(OH)CH_2C_6H_5)_2]$ (UPNO-4) have been synthesized under hydrothermal conditions. UPNO-1 contains doubly protonated piperazine templates, $[C_4N_2H_{12}]^{2+}$, residing between $[UO_2F(PO_3CH_3)]^{1-}$ anionic layers. Distinct hydrophobic and hydrophilic regions are present between $[UO_2(PO_3CH_3)(PO_2(OH)CH_3)]^{1-}$ layers in UPNO-2. The template is found in the hydrophilic interlayer space only, completely segregated from the methyl groups of the uranyl methylphosphonate layer, which protrude into the hydrophobic interlayer space. UPNO-3 contains $[(U_2O_4F_3)(UO_2F(H_2O))(PO_3C_6H_5)_2]^{2-}$ layers separated by both piperazine templates, $[C_4N_2H_{12}]^{2+}$, and phosphonate phenyl groups, which exist in the same interlayer region. In UPNO-4 the region between $[(UO_2)_5(PO_3CH_2C_6H_5)_6(PO_2(OH)CH_2C_6H_5)_2]^{4-}$ layers is completely hydrophobic as a result of the large number of benzyl groups occupying the interlayer space. The template is found in voids within each layer. The structures of these compounds are dependent upon the reactant concentrations. Crystal data for the compounds are as follows: UPNO-1, $a = 6.9288(3)$ Å, $b = 8.1174(4)$ Å, $c = 14.8505(9)$ Å, $\beta = 91.7173(19)^\circ$, monoclinic $P2_1/n$ (no. 14), $Z = 2$; for UPNO-2, $a = 10.0682(4)$ Å, $b = 8.9121(3)$ Å, $c = 12.9631(7)$ Å, $\beta = 90.4901(15)^\circ$, monoclinic $P2_1/a$ (no. 14), $Z = 2$; for UPNO-3, $a = 6.7796(1)$, $b = 17.2821(4)$ Å, $c = 24.6754(6)$ Å, orthorhombic $Pbcm$ (no. 57), $Z = 4$; and for UPNO-4, $a = 11.4732(2)$ Å, $b = 14.9097(2)$ Å, $c = 15.4480(3)$ Å, $\alpha = 64.2307(6)^\circ$, $\beta = 70.2105(7)^\circ$, $\gamma = 84.136(1)^\circ$, triclinic $P\bar{1}$ (no. 2), $Z = 2$.

Introduction

The area of metal phosphonate chemistry has been the focus of intense research in recent years, owing to potential applications in ion exchange, sensors, and catalysis.¹ Early work focused on the synthesis of crystalline zirconium phenyl and alkylphosphonates in the late 1970s.² This early work has led to a vast range of metal phosphonate compounds, displaying wide structural variation.³ The three strategies that are commonly employed in the search for new compounds and novel topologies are the introduction of variation in the R-group of the phosphonate, utilization of metal centers that exhibit diverse coordination geometries, and the use of organic templates.

Phosphonates, $[H_2PO_3R]$, have great potential for structural variation through changing the R-substituent. The majority of the compounds are layered, with the organic R-groups pointing into the interlayer region; however, a number of metal diphosphonates have been synthesized in which the alkyl chain acts as a tether between two layers.⁴

* To whom correspondence should be addressed. E-mail: dermot.ohare@chem.ox.ac.uk.

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Several different metals have been employed in the synthesis of metal phosphonates with novel structure types. Group II metals incorporated into such structures include Mg,^{4(c)} Ca,⁵ Sr,⁶ and Ba.⁷ Interest has been shown in transition metal phosphonates, with metals including Mn,⁸ Co,⁹ Cu,¹⁰ and Zn.^{9,10} Recently, two mixed-metal phosphonates were synthesized containing Mg/Zn and Ni/Zn.¹¹ Clearfield et al. have reported several uranium containing phosphonates. The actinides are attractive candidates for use in the synthesis of materials with novel topologies owing to the accessibility of high coordination numbers. These compounds display a range of interesting properties, and exhibit a wide variety of structures and dimensionality. $[UO_2(HO_3-$

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$\text{PC}_6\text{H}_5)_2(\text{H}_2\text{O})_2 \cdot 8\text{H}_2\text{O}$ and $\text{UO}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ adopt linear chain structures,¹² $\text{UO}_2(\text{O}_3\text{PCH}_3)$ ¹³ and $\text{UO}_2(\text{O}_3\text{PCH}_2\text{Cl})$ ¹⁴ are layered, and $\text{UO}_2(\text{O}_3\text{PC}_6\text{H}_5) \cdot 0.7\text{H}_2\text{O}$ ¹⁵ and $(\text{UO}_2)_3(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{O}_3\text{PC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}$ ¹⁶ have tubular structures with hydrophobic exteriors and hydrophilic interiors.

The use of organic structure-directors has been exploited using Fe,¹⁷ Ni,¹⁸ Cu,¹⁹ and Zn²⁰ diphosphonates. Typical templates are organic diamines, such as ethylenediamine, 1,4-diaminobutane, 1,5-diaminoheptane, and 1,6-diaminohexane. The combination of these three approaches holds great promise in the search for new materials with novel structures. We have utilized all three approaches in an attempt to synthesize novel templated uranium phosphonates.

The reaction of a series of different phosphonates (methyl-, phenyl-, and benzyl) with uranyl acetate and piperazine resulted in the formation of four new uranium phosphonates, which are designated UPNO-1, UPNO-2, UPNO-3, and UPNO-4 (using an acronym for uranium phosphonate from Oxford), which are reported here. UPNO-1 and UPNO-2 are uranyl methylphosphonates. UPNO-3 and UPNO-4 are uranyl phenyl- and benzylphosphonates, respectively.

Experimental Section

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

Materials and Methods. All chemicals were used as obtained without further purification. Piperazine (95%) and phenylphosphonic acid (98%) were from Aldrich. Benzylphosphonic acid (97%) and methylphosphonic acid (98%) were from Lancaster. (40%) $\text{HF}_{(\text{aq})}$ was from BDH. Uranyl acetate dihydrate, $\text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O}$ (AC = CH_3CO_2), was synthesized as previously reported.²¹

All reactions were conducted in poly(fluoro-ethylene-propylene)-lined 23-mL stainless steel autoclaves. These were heated to 180 °C at 10 °C min⁻¹ and held at this temperature for 24 h. The reactions were cooled to room temperature at 6 °C h⁻¹ and the autoclaves were opened in air. Solid products were recovered using filtration, washed with deionized water and acetone, and dried in air.

Synthesis of $[\text{C}_4\text{N}_2\text{H}_{12}][\text{UO}_2\text{F}(\text{PO}_3\text{Me})_2]$ (UPNO-1). UPNO-1 was synthesized through the reaction of 0.212 g (5.00 × 10⁻⁴ mol) of $\text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O}$, 0.076 g (8.82 × 10⁻⁴ mol) of piperazine, 0.274 g (2.90 × 10⁻³ mol) of methylphosphonic acid, 5.023 g of deionized water, and 1 drop of $\text{HF}_{(\text{aq})}$. Yellow rods were obtained in an 88% yield, based on uranium. Elemental

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microanalysis for UPNO-1: obsd (calcd) C, 8.39 (8.44); N, 3.18 (3.28); H, 2.09 (2.12); P, 7.16 (7.25); U, 55.09 (55.73).

Synthesis of $[\text{C}_4\text{N}_2\text{H}_{12}][\text{UO}_2(\text{PO}_3\text{Me})(\text{PO}_2(\text{OH})\text{Me})_2]$ (UPNO-2). UPNO-2 was synthesized through the reaction of 0.424 g (1.0 × 10⁻³ mol) of $\text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O}$, 0.065 g (7.55 × 10⁻⁴ mol) of piperazine, 0.432 g (4.50 × 10⁻³ mol) of methylphosphonic acid, and 3.051 g of deionized water. A yellow powder was obtained in an 80% yield, based on uranium. Elemental microanalysis for UPNO-2: obsd (calcd) C, 9.74 (9.55); N, 2.84 (2.78); H, 2.68 (2.60); P, 12.04 (12.31); U, 46.35 (47.31). Crystals suitable for single-crystal X-ray diffraction were synthesized through the reaction of 0.212 g (5.00 × 10⁻⁴ mol) of $\text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O}$, 0.129 g (1.50 × 10⁻³ mol) of piperazine, 1.008 g (1.05 × 10⁻² mol) of methylphosphonic acid, 5.104 g of deionized water, and 1 drop of $\text{HF}_{(\text{aq})}$. A mixture of phases containing UPNO-1 and UPNO-2 was formed in this reaction, with a yield of approximately 75%.

Synthesis of $[\text{C}_4\text{N}_2\text{H}_{12}][(\text{U}_2\text{O}_4\text{F}_3)(\text{UO}_2\text{F}(\text{H}_2\text{O}))(\text{PO}_3\text{C}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ (UPNO-3). UPNO-3 was synthesized through the reaction of 0.424 g (1.00 × 10⁻³ mol) of $\text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O}$, 1.054 g (6.67 × 10⁻³ mol) of phenylphosphonic acid, 0.057 g (6.62 × 10⁻⁴ mol) of piperazine, 3.093 g of deionized water, and 10 drops of $\text{HF}_{(\text{aq})}$. Two different morphologies of the same product, yellow blocks and needles, were obtained in a 90% yield. Elemental microanalysis for UPNO-3: obsd (calcd) C, 14.80 (14.34); N, 2.13 (2.09); H, 2.36 (2.11); P, 4.54 (4.62); U, 52.79 (53.27).

Synthesis of $[\text{C}_4\text{N}_2\text{H}_{12}][(\text{UO}_2)_5(\text{PO}_3\text{Bz})_6(\text{PO}_2(\text{OH})\text{Bz})_2]$ (UPNO-4). UPNO-4 was synthesized through the reaction of 0.324 g (7.64 × 10⁻⁴ mol) of $\text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O}$, 0.582 g (3.38 × 10⁻³ mol) of benzylphosphonic acid, 0.054 g (6.27 × 10⁻⁴ mol) of piperazine, 5.142 g of deionized water, and 2 drops of $\text{HF}_{(\text{aq})}$. UPNO-4 was not obtainable phase-pure, and crystals had to be manually separated from the noncrystalline impurity phase. The yield is approximately 40%, based upon a 1:1 ratio of UPNO-4/impurity, with some uranium remaining in solution. Elemental analysis for UPNO-4: obsd (calcd) C, 26.39 (26.61); N, 1.91 (1.94); H, 3.14 (2.86).

X-ray Crystallographic Analysis. Data were collected using an Enraf Nonius Kappa CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Single crystals were mounted on a glass fiber 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 were scaled together using HKL GUI within Denzo SMN.²² The heavy atom positions were determined using SIR97 and other non-hydrogen atoms were refined using Crystals.²³ All non-hydrogen atom sites were refined using anisotropic thermal parameters using full matrix least-squares procedures on F_0^2 with $I > 3\sigma(I)$. Disordered atomic sites in UPNO-4 were refined using isotropic thermal parameters. Hydrogen atoms attached to bound water molecules were located from Fourier difference maps. All others were placed in geometrically idealized positions. All calculations were performed using Crystals²³ and Cameron.²⁴ Relevant crystallographic data are presented in Table 1.

Infrared Spectroscopy. FTIR spectra were collected on a Perkin-Elmer FT 1710 spectrometer. Samples were diluted with spectroscopic KBr and pressed into a pellet. Scans were run over the range 400–4000 cm⁻¹. See Supporting Information for spectra.

Thermogravimetric Analysis. TGA measurements were performed on a Rheometric Scientific STA 1500H thermal analyzer. The samples were loaded into an alumina crucible and heated at 10 °C min⁻¹ under flowing argon. See Supporting Information for TGA traces.

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Table 1. Crystallographic Data

compound	UPNO-1	UPNO-2	UPNO-3	UPNO-4
formula	$[\text{C}_4\text{N}_2\text{H}_{12}]$ $[\text{UO}_2\text{F}(\text{PO}_3\text{Me})]_2$	$[(\text{C}_4\text{N}_2\text{H}_{12})][\text{UO}_2(\text{PO}_3\text{Me})$ $(\text{PO}_2(\text{OH})\text{Me})]_2$	$[\text{C}_4\text{N}_2\text{H}_{12}]$ $[(\text{U}_2\text{O}_4\text{F}_3)$ $(\text{UO}_2\text{F}(\text{H}_2\text{O}))(\text{PO}_3\text{Ph})_2] \cdot 2\text{H}_2\text{O}$	$[\text{C}_4\text{N}_2\text{H}_{12}]_2$ $[(\text{UO}_2)_5$ $(\text{PO}_3\text{Bz})_6(\text{PO}_2(\text{OH})\text{Bz})_2]$
fw	854.22	1006.25	1340.43	2889.29
space group	$P2_1/n$ (no. 14)	$P2_1/a$ (no. 14)	$Pbcm$ (no. 57)	$P\bar{1}$ (no. 2)
a (Å)	6.9288(3)	10.0682(4)	6.7796(1)	11.4732(2)
b (Å)	8.1174(4)	8.9121(3)	17.2821(4)	14.9097(2)
c (Å)	14.8505(9)	12.9631(7)	24.6754(6)	15.4480(3)
α (°)	90	90	90	64.2307(6)
β (°)	91.7173(19)	90.4901(15)	90	70.2105(7)
γ (°)	90	90	90	84.136(1)
V (Å ³)	834.9	1163.1	2891.1	2236.1
Z	2	2	4	2
ρ_{calc} (g cm ⁻³)	3.398	2.873	3.070	2.113
T (K)	150	150	150	150
λ (Å)	0.71073	0.71073	0.71073	0.71073
μ (cm ⁻¹)	19.636	14.256	16.969	9.244
$R(F_0)^a$	0.0396	0.0254	0.0252	0.0368
$Rw(F_0^2)^b$	0.0924	0.0560	0.0589	0.0881

^a $R = \sum |F_0| - |F_c| / \sum |F_0|$. ^b $Rw = [\sum w(|F_0^2| - |F_c^2|)^2 / \sum w(F_0^2)^2]^{1/2}$.

Results

UPNO-1. The U^{6+} cation in UPNO-1 is seven coordinate, in the form of a pentagonal bipyramidal. The uranyl unit, $[\text{UO}_2]^{2+}$, has $\text{U}(1)-\text{O}(1)$ and $\text{U}(1)-\text{O}(2)$ bond lengths of 1.78(1) and 1.79(1) Å, respectively. These values are close to the average reported uranyl bond length in pentagonal bipyramidal coordination, which is 1.758(4) Å.²⁵ The $\text{O}(1)-\text{U}(1)-\text{O}(2)$ bond angle is 178.5(5)°. The five equatorial coordination sites are occupied by two fluoride and three oxide ligands. The average $\text{U}-\text{F}$ bond length is 2.368 Å. The average $\text{U}-\text{O}_{\text{eq}}$ bond length is 2.36 Å. Bond valence calculations,^{26,27} using parameters by Burns et al., give a value of 5.834 for $\text{U}(1)$. Each oxide ligand is part of a $[\text{PO}_3\text{Me}]^{2-}$ unit. There is one phosphorus site in UPNO-1. The phosphorus coordination sites are occupied by three bridging oxide ligands and a methyl group.

One-dimensional chains are formed by fluoride ligands linking adjacent uranium polyhedra. Adjacent chains are linked by $[\text{PO}_3\text{Me}]^{2-}$ tetrahedra, forming $[\text{UO}_2\text{F}(\text{PO}_3\text{Me})]^{1-}$ layers in the *ab* plane (Figure 1). The positively charged $[\text{pipH}_2]^{2+}$ template lies in the interlayer space, and balances the charge of the anionic layers. Hydrogen bonding between the layers and the template imparts stability to the structure (Figure 2).

The template N–H stretching and bending modes are displayed in the IR spectrum as a weak peak at 3028 cm⁻¹ and a strong, sharp peak at 1622 cm⁻¹. The sharp peak at 1460 cm⁻¹ corresponds to the C–H bending mode. The phosphonate methyl group displays asymmetric and symmetric deformations at 1408 and 1314 cm⁻¹, respectively.²⁸ A group of peaks centered around 1000 cm⁻¹ correspond to $-\text{PO}_3$ stretches. The peak at 914 cm⁻¹ corresponds to the uranyl asymmetric stretch.

UPNO-1 is thermally stable up to 350 °C, using thermogravimetric analysis. A rapid weight loss of 15.0% is observed between 350 and 425 °C. This accounts for the decomposition of the template (10.3%)

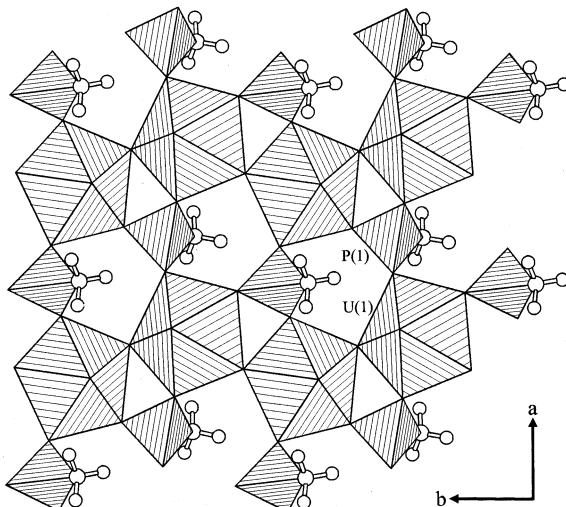


Figure 1. Two-dimensional $[\text{UO}_2\text{F}(\text{PO}_3\text{Me})]^{1-}$ layer in UPNO-1. Tetrahedra and pentagonal bipyramids represent phosphonate and uranium polyhedra, respectively. The central atoms are labeled.

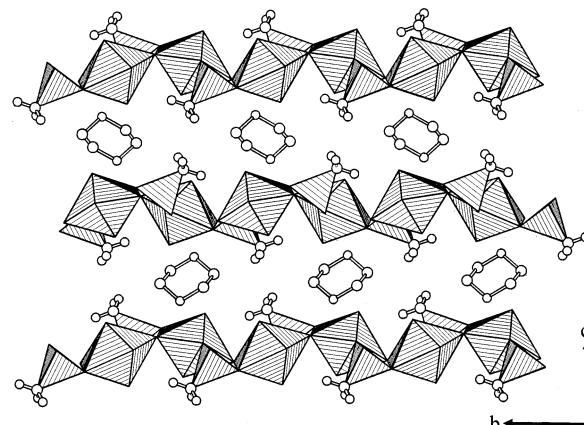


Figure 2. Three-dimensional packing in UPNO-1, showing the $[\text{pipH}_2]^{2+}$ template in the interlayer space. Tetrahedra and pentagonal bipyramids represent phosphonate and uranium polyhedra, respectively. Template hydrogen atoms have been removed for clarity.

and the onset of breakdown of the phosphonate methyl groups. A further weight loss of 3.0% is observed up to 800 °C. The material completely calcines to $\text{U}_2\text{O}(\text{PO}_4)_2$,

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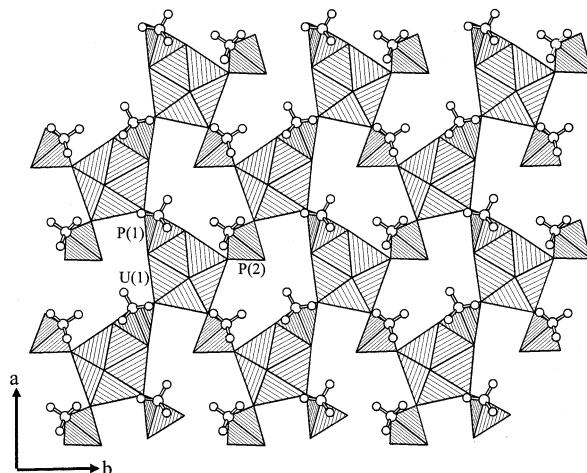


Figure 3. Two-dimensional $[\text{UO}_2(\text{PO}_3\text{Me})(\text{PO}_2(\text{OH})\text{Me})]^{1-}$ layer in UPNO-2. Tetrahedra and pentagonal bipyramids represent phosphonate and uranium polyhedra, respectively. The central atoms are labeled.

as determined using powder X-ray diffraction, with a corresponding weight loss of 18.0% (calc. 20.2%).

UPNO-2. One unique uranium site is observed in UPNO-2. U(1) is seven coordinate, with two uranyl and five equatorial oxide ligands, in a pentagonal bipyramidal geometry. The uranyl bond lengths, $\text{U}(1)-\text{O}(1)$ and $\text{U}(1)-\text{O}(2)$, are 1.782(5) and 1.786(5) Å, respectively, with an $\text{O}-\text{U}-\text{O}$ bond angle of 179.0(2)°. The equatorial oxide ligands are part of phosphonate tetrahedra, three containing P(1) and two containing P(2). The average $\text{U}-\text{O}_{\text{eq}}$ bond length is 2.340 Å. Bond valence calculations give a value of 5.923 for U(1). The three oxide ligands in the $[\text{PO}_3\text{Me}]^{2-}$ tetrahedra, containing P(1), bridge to the uranium, with P(1)-O bond lengths of 1.509(5), 1.536(5), and 1.539(5) Å. This tetrahedron shares an edge with the $[\text{UO}_7]$ pentagonal bipyramidal. Two of the oxide ligands in the $[\text{PO}_2(\text{OH})\text{Me}]^{1-}$ tetrahedra, containing P(2), bridge to the uranium, whereas the third is part of a terminal hydroxide group. The P(2)-O bond lengths are 1.522(5), 1.522(5), and 1.568(5) Å, respectively. The average P-C bond length is 1.775 Å.

Two-dimensional $[\text{UO}_2(\text{PO}_3\text{Me})(\text{PO}_2(\text{OH})\text{Me})]^{1-}$ layers are formed because the $[\text{PO}_3\text{Me}]^{2-}$ tetrahedra share an edge and a corner with two $[\text{UO}_7]$ pentagonal bipyramids, and the $[\text{PO}_2(\text{OH})\text{Me}]^{1-}$ tetrahedra share two corners with $[\text{UO}_7]$ pentagonal bipyramids (Figure 3). Layers form in the *ab* plane. Adjacent layers are related by a 180° rotation about the *a*-axis, resulting in a bilayer type structure that consists of two distinct interlayer regions: one filled by methyl groups and the other filled by $[\text{pipH}_2]^{2+}$ cations. These two different layers alternate along the *c*-axis (Figure 4). The $[\text{pipH}_2]^{2+}$ template participates in hydrogen bonding with the inorganic layer.

The N-H stretch of the piperazine template is displayed as a weak peak at 3020 cm⁻¹, in the infrared spectrum, with the N-H bend as a stronger, sharper peak at 1620 cm⁻¹. The template C-H bend has a frequency of 1484 cm⁻¹. Phosphonate methyl group asymmetric and symmetric deformations are displayed at 1418 and 1314 cm⁻¹. A group of peaks around 100 cm⁻¹ correspond to the stretching of the $-\text{PO}_3$ groups. Peaks at 918 and 866 cm⁻¹ correspond to the uranyl asymmetric and symmetric stretching modes.

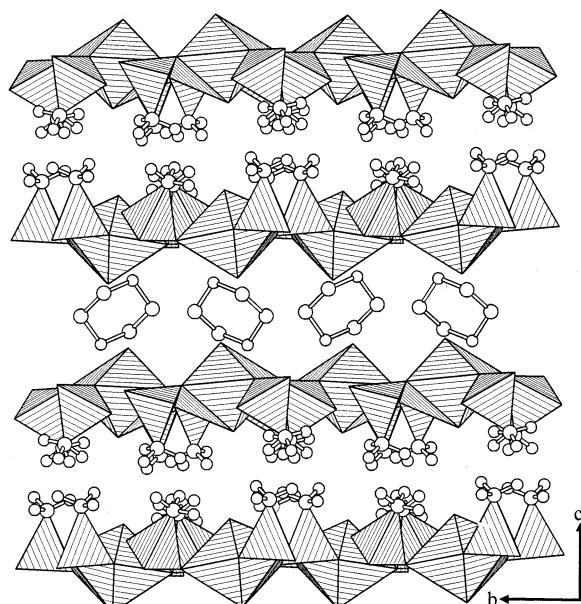


Figure 4. Three-dimensional packing in UPNO-2. Hydrophobic and hydrophilic interlayer spaces are shown, with the $[\text{pipH}_2]^{2+}$ template in the hydrophilic region. Tetrahedra and pentagonal bipyramids represent phosphonate and uranium polyhedra, respectively. Template hydrogen atoms have been removed for clarity.

Thermal stability is observed up to 280 °C, using thermogravimetric analysis. A rapid weight loss of 12.5% occurs between 280 and 550 °C, indicating decomposition of template (9.0%) and most of the phosphonate methyl groups (6.0%). A further weight loss of 2.0% is observed up to 800 °C. The material completely calcines to UP_2O_7 , as determined using powder X-ray diffraction, with a corresponding weight loss of 14.5% (calc. 18.1%).

UPNO-3. Two crystallographically distinct uranium sites are observed in UPNO-3. U(1) and U(2) are both seven coordinate, containing two uranyl oxide ligands, with an average $\text{U}-\text{O}$ bond length of 1.770 Å, and an average $\text{O}-\text{U}-\text{O}$ bond angle of 176.7°. The five equatorial coordination sites around U(1) are occupied by two oxide ligands, which are part of $[\text{PO}_3\text{Ph}]^{2-}$ tetrahedra, and three fluoride ligands. Two of these fluoride ligands, F(2) and F(3), are shared with a second uranium pentagonal bipyramidal, via an edge, resulting in a dimer. The average $\text{U}(1)-\text{F}$ bond length is 2.344 Å. The average $\text{U}(1)-\text{O}_{\text{eq}}$ bond length is 2.303 Å. The five equatorial coordination sites around U(2) are occupied by two fluoride ligands and three oxide ligands. The fluoride ligands are shared with the U(1) polyhedra forming chains. Bond valence calculations give values of 5.949 and 5.989 for U(1) and U(2). Two of the oxide ligands are from $[\text{PO}_3\text{Ph}]^{2-}$ tetrahedra, and the third is from a bound water molecule. The $\text{U}(2)-\text{O}-\text{P}(1)$ distance is 2.356(6) Å. The $\text{U}-\text{O}_{\text{H}_2\text{O}}$ bond length is 2.48(1) Å, in agreement with previously reported $\text{U}-\text{O}_{\text{H}_2\text{O}}$ distances.²⁹

Two-dimensional $[(\text{U}_2\text{O}_4\text{F}_3)(\text{UO}_2\text{F}(\text{H}_2\text{O}))(\text{PO}_3\text{C}_6\text{H}_5)_2]^{2-}$ layers are formed because each $[\text{PO}_3\text{Ph}]^{2-}$ tetrahedra

(29) (a) Norquist, A. J.; Thomas, P. M.; Doran, M. B.; O'Hare, D. *Chem. Mater.* **2002**, *14*, 5179. (b) Thomas, P. M.; Norquist, A. J.; Doran, M. B.; O'Hare, D. *Mater. J. Mater. Chem.* **2003**, *13*, 88. (c) Doran, M. B.; Norquist, A. J.; O'Hare, D. M. *Chem. Commun.* **2002**, 2946.

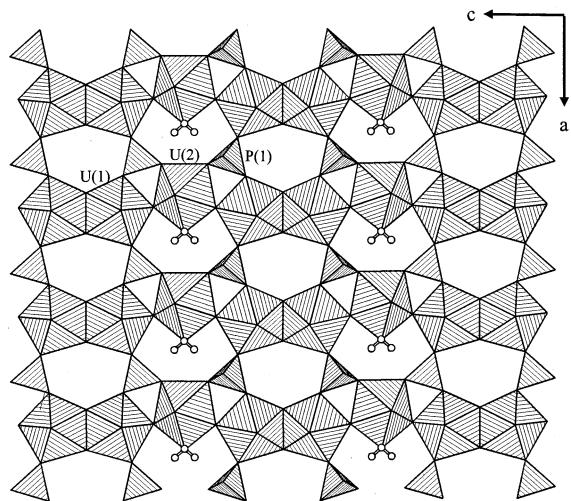


Figure 5. Two-dimensional $[(U_2O_4F_3)(UO_2F(H_2O))(PO_3C_6H_5)_2]^{2-}$ layer in UPNO-3. Tetrahedra and pentagonal bipyramids represent phosphonate and uranium polyhedra, respectively. The central atoms are labeled. Phenyl groups have been removed for clarity.

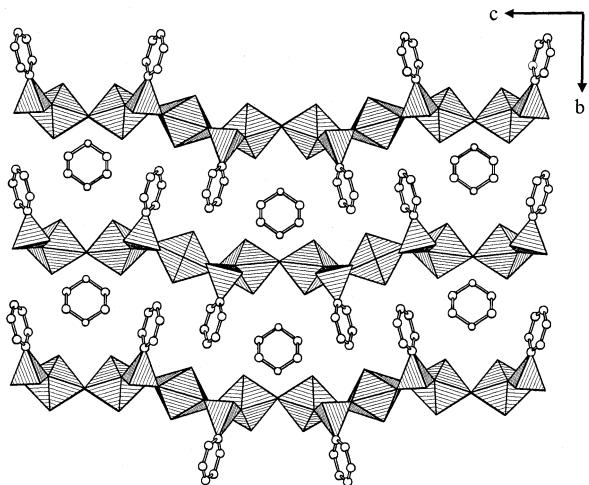


Figure 6. Three-dimensional packing in UPNO-3, showing the pairing of phenyl groups forming hydrophobic regions. The $[pipH_2]^{2+}$ template is shown in the hydrophilic regions. Tetrahedra and pentagonal bipyramids represent phosphonate and uranium polyhedra, respectively. Occluded water molecules and hydrogen atoms have been removed for clarity.

links three adjacent uranium polyhedra (Figure 5). The bound water molecule on U(2) donates hydrogen bonds to adjacent oxide ligands. The O(6)…O(7) distance is 2.915 Å. The anionic layers lie in the *ac* plane. The $[pipH_2]^{2+}$ templates and occluded water reside in the interlayer space, between pairs of phenyl rings, participating in a hydrogen bonding network with the layers (Figure 6).

The N–H stretching and bending modes are displayed in the infrared spectrum as peaks at 3014 and 1618 cm^{-1} . The band at 1438 cm^{-1} is due to skeletal vibration of the phenyl rings, with their out-of-plane vibrations at 758 and 700 cm^{-1} .³⁰ Peaks at 1008, 1064, and 1038 cm^{-1} are due to $-\text{PO}_3$ stretching modes. Peaks at 912 and 826 cm^{-1} are due to the uranyl group's asymmetric and symmetric stretches.

A small weight loss from room temperature to 250 °C, leading into a more rapid weight loss up to 350 °C accounts for 12.4% of the mass, and corresponds to loss of occluded water (4.0%), template (6.6%), and the onset of decomposition of the phosphonate phenyl groups. A further weight loss of 14.9% occurs between 350 °C and 800 °C. The material calcines to $\text{U}_2\text{O}(\text{PO}_4)_2$, as determined using powder X-ray diffraction, with a weight loss of 27.3% (calc. 23.7%).

UPNO-4. Three crystallographically distinct uranium sites are observed in UPNO-4. U(1) and U(2) are each seven coordinate, with two uranyl and five oxide ligands. U(3) is six coordinate, with two uranyl and four oxide ligands. The average uranyl bond length is 1.773 Å, and the average uranyl O–U–O bond angle is 178.8°. Two U(1) pentagonal bipyramids share an edge, forming a dimer. Similarly, two U(2) polyhedra share an edge. Values of 6.192, 6.103, and 5.881 for U(1), U(2), and U(3), respectively, are obtained from bond valence calculations. The equatorial coordination sites around U(1) and U(2) are occupied by oxide ligands that are part of $[\text{PO}_3\text{Bz}]^{2-}$ and $[\text{PO}_2(\text{OH})\text{Bz}]^{1-}$ tetrahedra. The equatorial coordination sites around U(3) are occupied by oxide ligands that are part of $[\text{PO}_3\text{Bz}]^{2-}$ tetrahedra only. The average U–O_{eq} bond lengths are 2.381 Å and 2.351 Å for U(1) and U(2), and 2.289 Å for U(3). Four crystallographically distinct phosphorus sites are observed. P(1) is part of a $[\text{PO}_3\text{Bz}]^{2-}$ tetrahedron that exhibits three bridging oxide ligands, two of which share an edge with U(2) polyhedra. P(2) is part of a $[\text{PO}_3\text{Bz}]^{2-}$ tetrahedron that exhibits three bridging oxide ligands. P(3) is part of a $[\text{PO}_2(\text{OH})\text{Bz}]^{1-}$ tetrahedron that has two bridging oxide ligands and one terminal hydroxide ligand. P(4) is part of a $[\text{PO}_3\text{Bz}]^{2-}$ tetrahedron that has two bridging oxide ligands and one terminal oxide ligand. The two bridging oxide ligands share an edge with U(1) polyhedra. The average P–O bond length for the edge-sharing oxide ligands in UPNO-4 is 1.541 Å. The average P–O bond length for the standard bridging oxide ligands is 1.522 Å. The P–O_{terminal} bond length is 1.507(8) Å. The P–OH distance is 1.559(6) Å.

Two-dimensional $[(\text{UO}_2)_5(\text{PO}_3\text{Bz})_6(\text{PO}_2(\text{OH})\text{Bz})]^{4-}$ sheets are formed as a result of the bridging between the benzylphosphonate tetrahedra and the uranium polyhedra (Figure 7). The benzyl groups point into the interlayer space. The $[pipH_2]^{2+}$ templates also lie between the layers, and hydrogen-bond to the layers. Disorder is observed in the benzyl ring attached to P(4). Also, the $[pipH_2]^{2+}$ template is disordered over two orientations (Figure 7).

Peaks in the infrared spectrum at 3028 and 1316 cm^{-1} correspond to the N–H stretching and bending modes of the piperazine template. The sharp peaks at 1494 and 1452 cm^{-1} correspond to skeletal vibrations in the aromatic rings of the benzyl groups. Peaks at 784 and 696 cm^{-1} correspond to out-of-plane vibrations of the benzyl rings. The group of peaks around 1000 cm^{-1} correspond to $-\text{PO}_3$ vibrations. The uranyl group asymmetric and symmetric stretches are displayed as peaks at 910 and 820 cm^{-1} respectively.

Thermal stability is observed up to 300 °C using thermogravimetric analysis. A weight loss of 9.5% occurs between 300 and 400 °C, corresponding to template

(30) Poojary, D. M.; Cabeza, A.; Aranda, M. A. G.; Bruque, S.; Clearfield, A. *Inorg. Chem.* **1996**, 35, 1468.

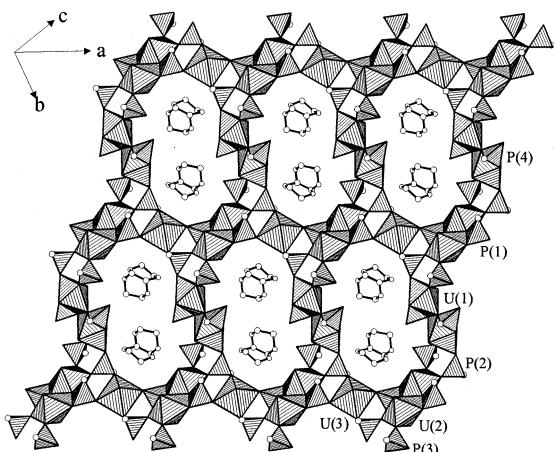


Figure 7. Two-dimensional $[(\text{UO}_2)_5(\text{PO}_3\text{Bz})_6(\text{PO}_2(\text{OH})\text{Bz})_2]^{4-}$ layer in UPNO-4. Tetrahedra represent phosphonate polyhedra. Octahedra and pentagonal bipyramids represent uranium polyhedra. The central atoms are labeled. Benzyl groups have been removed for clarity.

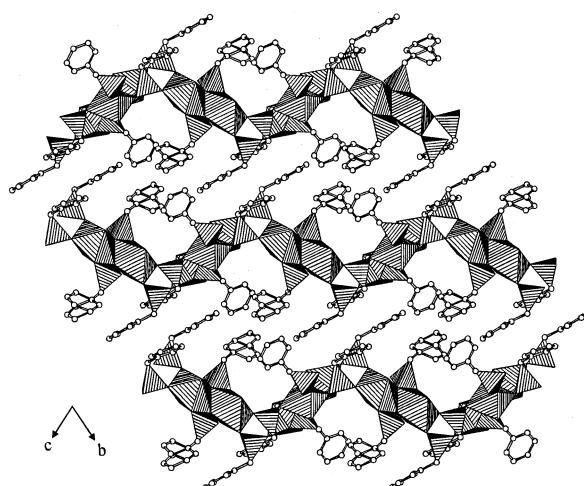


Figure 8. Three-dimensional packing in UPNO-4, showing the occupation of the interlayer space by disordered benzyl groups. The $[\text{pipH}_2]^{2+}$ template and all hydrogen atoms have been removed for clarity.

decomposition (6.1%) and the start of the decomposition of the benzyl groups. A steadier mass loss of 8.0% is observed up to 800 °C, leaving an amorphous product.

Discussion

A great deal of structural diversity is displayed in these piperazine templated uranyl phosphonates. The layer topologies in this family of compounds and their interlayer spaces vary greatly.

The methylphosphonate UPNO-1 was synthesized in the $\text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O}$ /piperazine/ MePO_3H /HF/ H_2O system. UPNO-2 was also produced from this system, although as a mixed phase with UPNO-1. The phase-pure synthesis of UPNO-2 was achieved in the $\text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O}$ /piperazine/ MePO_3H / H_2O system, similar to the first system but without HF. The two main differences between UPNO-1 and UPNO-2 are the absence of fluoride ligands in UPNO-2, and the increased phosphorus/piperazine ratio in UPNO-2 with respect to that of UPNO-1. The effect of varying the amount of $\text{HF}_{(\text{aq})}$ warrants further investigation.

A 3.3:1 ratio of methylphosphonic acid/piperazine was used in the synthesis of UPNO-1. A 6.7:1 ratio of methylphosphonic acid/piperazine was used in the synthesis of UPNO-2. This increase in the methylphosphonic acid concentration with respect to that of piperazine is reflected in the structures obtained, which have phosphorus/piperazine ratios of 2:1 and 4:1, respectively. In UPNO-1 the template lies between each layer, whereas in UPNO-2, where alternate layers are rotated 180° with respect to each other forming hydrophobic and hydrophilic regions, the template is found only in the hydrophilic region, and alternate interlayer spaces contain no template. A number of structures of uranyl phenylphosphonates have been reported in which the orientation of the phenyl groups gives rise to hydrophobic and hydrophilic regions. $(\text{UO}_2)_3(\text{HO}_3\text{P-C}_6\text{H}_5)_2(\text{O}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ and $\text{UO}_2(\text{O}_3\text{PC}_6\text{H}_5) \cdot 0.7\text{H}_2\text{O}$ ¹⁵ both form tubular structures in which the phenyl groups are perpendicular to the unidimensional pores, forming hydrophobic regions. The interior of the pores is hydrophilic. $[\text{UO}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{H}_2\text{O})]_2 \cdot 8\text{H}_2\text{O}$ ¹² forms a quasi one-dimensional structure in which the chains orient their hydrophobic and hydrophilic sides together. The molybdenyl phenylphosphonate, $\text{MoO}_2(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}$,³¹ has a double-layered structure analogous to that of UPNO-2, in which adjacent double chains face each other. Hydrophobic and hydrophilic regions, similar to those found in UPNO-2, are observed.

Contrary to the uranyl phenylphosphonates noted above, UPNO-3 adopts a layered structure in which there is no such distinctive hydrophobic and hydrophilic separation. The phenyl groups are perpendicular to the plane of the layer, as a result of the carbon atom of the P–C bond being aromatic, and point directly into the interlayer space. Within a layer the orientation of the phenyl groups alternates in a two up, two down fashion (Figure 6). Phenyl groups of adjacent layers pair up at a distance of approximately 4 Å. This pairing of the phenyl groups divides the interlayer space into two alternating regions. The region containing the phenyl groups has hydrophobic character, with the void that is created as a result of the pairing of the phenyl groups being hydrophilic. This is analogous to the hydrophobic and hydrophilic interlayer spaces found in UPNO-2, although not as pronounced. The hydrophilic region is occupied by the $[\text{pipH}_2]^{2+}$ template and occluded water molecules. The larger phenyl substituent of the phenylphosphonate group, with respect to the methyl substituent on the methylphosphonate group of UPNO-1, has an effect upon the orientation of the template. The distance between adjacent layers in UPNO-1 is 8.14 Å (measured as the distance between uranium centers), compared with 10.29 Å in UPNO-3. As a result, in UPNO-1 the template lies tilted approximately 45° to the layer in order to adopt the most favorable position to form hydrogen bonds with the layer. The larger interlayer space in UPNO-3 forces the template into a position almost perpendicular to the layer to enable hydrogen bonding.

The structure of UPNO-4 shows marked differences from those of the other uranyl phosphonates reported here. Although fluoride ions were present in the syn-

(31) Poojary, D. M.; Zhang, Y.; Zhang, B.; Clearfield, A. *Chem. Mater.* **1995**, 7, 822.

thesis of UPNO-4 none are present in the product. The $\text{HF}_{(\text{aq})}$ in the reaction gel acts as a mineralizer but is not incorporated into the structure. In the synthesis of UPNO-3 the reaction mixture contained proportionately more $\text{HF}_{(\text{aq})}$ than in UPNO-4. This is reflected in the structure of UPNO-4 as compared with UPNO-3. In UPNO-4, all of the equatorial coordination sites around each uranium center are occupied by oxide ligands. In UPNO-3, the equatorial coordination sites of U(1) are occupied by three fluoride ligands and two oxide ligands. The equatorial coordination sites of U(2) are occupied by two fluoride ligands and three oxide ligands, one of which is from a coordinated water molecule. Each of the oxide ligands in UPNO-3 and UPNO-4, except for the coordinated water molecule in UPNO-3, is part of a phenyl- or benzylphosphonate group. This gives uranium/phosphorus ratios of 3:2 and 5:8 for UPNO-3 and UPNO-4, respectively. The increase in the number of phosphonate groups in UPNO-4 means there are proportionately more benzyl groups in the interlayer space than phenyl groups in UPNO-3. In UPNO-4, almost all of the interlayer space is occupied by benzyl groups. The template resides in the plane of the layer within holes. This is in contrast to UPNO-3, where the template and phenyl groups are found in the interlayer space.

The interlayer space in UPNO-4 is completely hydrophobic owing to its occupancy by benzyl groups. This is analogous to UPNO-2 where methyl groups and template molecules are segregated, with the methyl groups forming a hydrophobic interlayer space and the $[\text{pipH}_2]^{2+}$ template forming a hydrophilic interlayer space. How-

ever, in UPNO-4 the template is not found in an adjacent interlayer space. It is located in hydrophilic voids within the layer.

Conclusion

The structures of these compounds are dependent upon the reactant concentrations. An increase in the amount of methylphosphonic acid in the synthesis of UPNO-2, compared with that in UPNO-1, causes the incorporation into the structure of more methylphosphonate groups. There is a separation of these and the template, creating hydrophobic and hydrophilic interlayer spaces. The incorporation of fluoride into the layer in UPNO-1 and UPNO-3 reduces the number of phosphonate groups in the layer, and the template and phosphonate groups reside in the same interlayer space. In UPNO-4 the bulky nature of the phosphonate substituent results in the benzyl groups occupying all of the interlayer space, while the template resides within voids in the plane of the layer.

Acknowledgment. We thank the EPSRC for support. We also thank Dr. A. R. Cowley for crystallographic assistance.

Supporting Information Available: An X-ray crystallographic file (CIF) containing complete tables of atomic coordinates, thermal parameters, and bond lengths and angles; IR spectra and TGA traces (pdf). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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