

Synthesis, Crystal Structures, and Proton Conductivity of Two Linear-Chain Uranyl Phenylphosphonates

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Received March 27, 1996[⊗]

Two uranyl phenylphosphonates, $[\text{UO}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{H}_2\text{O})]_2 \cdot 8\text{H}_2\text{O}$ (**1**) and $\text{UO}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ (**2**), have been synthesized and their structures solved by single-crystal methods. Both compounds crystallize in the triclinic space group $P\bar{1}$. Unit cell parameters are $a = 11.724(4)$ Å, $b = 16.676(8)$ Å, $c = 11.375(2)$ Å, $\alpha = 101.61(5)^\circ$, $\beta = 106.76(3)^\circ$, $\gamma = 102.57(4)^\circ$, and $Z = 2$ for compound **1** and $a = 9.332(6)$ Å, $b = 11.48(1)$ Å, $c = 5.672(2)$ Å, $\alpha = 98.98(6)^\circ$, $\beta = 92.78(5)^\circ$, $\gamma = 108.54(5)^\circ$, and $Z = 1$ for compound **2**. In both compounds the metal to phosphonate ratio is 1:2, and they both form linear chains. Each metal atom in these structures is surrounded by four oxygens of four different phosphonate groups which take up the metal's equatorial positions. However, in compound **1** an additional oxygen of a water molecule binds to the uranium atom in the equatorial plane. This leads to a distorted pentagonal bipyramidal geometry of uranium in compound **1** and to a distorted octahedral geometry of uranium in compound **2**. Adjacent uranium atoms are bridged by two phosphonates, and every phosphonate group uses only two of its oxygens for this purpose. The third oxygen is not involved in metal coordination, and it is protonated. In compound **1**, all phenyl rings of each uranyl phosphonate chain point into one general direction, perpendicularly to the chain, and the adjacent chains orient their "phenyl sides" almost toward each other to form planes of alternating hydrophobic and hydrophilic regions. The hydrophilic regions are filled with solvent water molecules. In compound **2**, the phenyl rings also point perpendicularly to the chains, but in opposite directions, and the chains are stacked in a "staircase" fashion without forming regions of different natures as in compound **1**. Compound **1** also exhibits a reasonably high proton conductivity $\sigma(25^\circ\text{C}) = 3.25 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 85% humidity due to the Bronsted acidity of its phosphonate OH groups. Both compounds are unstable in air mainly due to the loss of their solvent molecules.

Introduction

Synthesis of crystalline layered zirconium phosphates by Clearfield and Stynes¹ in 1964 and the subsequent crystal structure determination of the α -phase in 1969² led to an understanding of their physical and ion exchange properties on a structural basis. Although earlier these compounds were used mostly as ion exchangers,³ recent studies indicated their usefulness in catalysis and in sorption as well.^{4,5} Research interest in layered compounds further intensified when organophosphates and phosphonates of tetravalent metals were prepared in the 1970's.^{6,7} Since these metal phosphonates were obtained only in the microcrystalline form, their structures were not known with certainty, but they were thought to be structurally closely related to their phosphate analogs. With the use of powder diffraction data, we have recently solved the structure

of $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_5)_2$, which indeed proved to resemble that of a layered α - $\text{Zr}(\text{O}_3\text{POH})_2$.⁸ The only significant difference between the two structures is the interlayer distance, which is larger in the phenylphosphonate due to the projection of the phenyl groups into the interlayer space. $\text{Zr}(\text{O}_3\text{PCH}_2\text{Cl})_2$ ⁹ was also found to adopt this layered structural pattern. In the meanwhile, zirconium phosphonates with other organic moieties were prepared and characterized; some formed new layer arrangements¹⁰ while others formed double chains.¹¹ A variety of other divalent and trivalent metal phosphonates have been synthesized and structurally characterized.¹² Most of these compounds were layered while others exhibited interesting linear¹³ and porous structures.¹⁴

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[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1996.

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Recently, we have synthesized and characterized a number of uranyl phosphonates in an effort to explore the binding capabilities of Nature's heaviest common element in its highest oxidation state VI. So far, several structural patterns have been reported. Uranyl (chloromethyl)phosphonate forms two-dimensional layers by virtue of bridging and chelation of phosphonate oxygens.¹⁵ Interestingly, the uranyl group interacts with phenylphosphonic acid in a variety of ways leading to a number of phases of which we have recently reported two polymorphic phases and their X-ray powder structures.^{16,17} These compounds were found to form unidimensional porous channels with the phenyl rings pointing outside the channels forming hydrophobic regions. Here, we describe the synthesis and structural characterization of two other phases which are neither layered nor porous; instead they have linear chainlike structures. We also present the TGA, IR, and the proton conductivity data of one of the compounds which arises due to the mobility of the phosphonate protons through the lattice water molecules.

Experimental Section

Materials and Methods. Chemicals of reagent grade quality were obtained from commercial companies and they were used without further purification. Thermogravimetric analysis (TGA) was carried out on a DuPont Model No. 951 thermal analysis unit at a rate of 10 °C in air. The solid-state ³¹P MAS NMR spectrum was collected on a Bruker MSL 300 spectrometer. IR spectra were obtained on a BIO-RAD FTS-40 spectrometer by the KBr disk method in the range 4000–400 cm⁻¹ with 64 scans and 4 cm⁻¹ resolution. Proton conductivity measurements were performed on cold pressed pellets (15 000 psi) using gold as a blocking electrode. The pellet was placed between two gold foils, and the sample was spring loaded to ensure good electrode–sample contact. This assembly was placed inside a constant-temperature cell with regulated humidity ranging between 30 and 80%. Impedance measurements were performed in the range 5 Hz–13 MHz using an HP 412A impedance analyzer. The four terminal pair measurement principle was used to estimate impedance (*Z*) and the phase angle (*t*) at each selected frequency. Measurements at elevated temperatures were carried out at 30% humidity in the temperature range 280–340 K.

Synthesis of [UO₂(HO₃PC₆H₅)₂(H₂O)]₂·8H₂O (1). A 2.00 g (4.0 mmol) amount of UO₂(NO₃)₂·6H₂O (Strem Chemicals) was dissolved in 40 mL of deionized water, and the yellow solution was filtered into a plastic beaker. A 1.19 mL (34 mmol) amount of 48% HF (Aldrich) was added to it. Next, 5.056 g (32 mmol) of H₂O₃PC₆H₅ (Aldrich) was dissolved in 60 mL of deionized water and filtered into the uranyl solution while stirring. The total volume was adjusted to approximately 120 mL and seeded with previously grown tiny crystals, and the beaker was covered with a plastic lid. The next day, groups of thin yellow needles appeared, and after 3 more days of growing they were isolated, washed with deionized water, and air-dried (yield 0.65 g or 24.1%). Since the crystals quickly dehydrated and decomposed in dry conditions (as well as in vacuum), a certain degree of humidity must be ensured when handling the crystals in air.

Synthesis of UO₂(HO₃PC₆H₅)₂·2CH₃CH₂OH (2). A 1.00 g amount of UO₂(NO₃)₂·6H₂O (2.0 mmol) was dissolved in 50 mL of absolute ethanol and filtered. Next, 1.4 g (8.9 mmol) of H₂O₃PC₆H₅ was dissolved in 50 mL of 100% ethanol, filtered, and added to the uranyl solution. The solution was covered, and the beaker was set aside at the room temperature. After several hours, tiny cubelike shaped crystals appeared on the walls of the beaker, and they were allowed to grow for 2 days. The crystals were very unstable air, and they were found to decompose even in the mother liquor after 5–6 days.

Table 1. Crystallographic Data for Compounds **1** and **2**

	compd	
	1	2
formula	C ₂₄ H ₄₄ O ₂₆ P ₄ U ₂	C ₁₆ H ₂₄ O ₁₀ P ₂ U
fw	1348.5	676.34
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	11.724(4)	9.332(6)
<i>b</i> (Å)	16.676(8)	11.48(1)
<i>c</i> (Å)	11.375(5)	5.672(2)
α (deg)	101.61(5)	98.98(6)
β (deg)	106.76(3)	92.78(5)
γ (deg)	102.57(4)	108.54(5)
<i>V</i> (Å ³)	1994	565.9
<i>Z</i>	2	1
temp (°C)	–110	–110
λ (Å)	0.710 69	0.710 69
ρ_{calc} (g/cm ³)	2.246	1.984
μ (cm ⁻¹)	79.3	68.7
<i>R</i> (<i>F</i> _o) ^a	0.077	0.077
<i>R</i> _w (<i>F</i> _o) ^b	0.091	0.085

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

X-ray Structure Analysis. [UO₂(HO₃PC₆H₅)₂·H₂O]₂·8H₂O (**1**). The very thin needlelike crystals were found to be twinned. Although several crystals were scanned on the diffractometer, no untwinned crystals could be found. Despite the poor quality of the crystals, reasonable results were obtained. A crystal of dimensions 0.1 × 0.03 × 0.05 mm was separated and mounted on a glass fiber. All crystallographic measurements were carried out on a Rigaku AFC5R diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.710 69$ Å) and a 12 kW rotating anode generator. Indexing was done by twin deconvolution. Cell parameters for data collection were obtained from a least-squares refinement of 24 reflections chosen from the 8–35° 2 θ shell immediately preceding data collection. Intensity data were collected at –110 °C using the ω –2 θ scan mode in shells to a maximum value of 50° in 2 θ . Three intensity standards were measured every 150 reflections to monitor crystal decay. Scans of (1.63 + 0.3 tan θ)° were made at a speed of 16°/min in ω . The weak reflections (*I* < 10.0 σ (*I*)) were rescanned (maximum of 3) for good counting statistics. A total of 4894 reflections were collected of which 4609 were unique (*R*_{int} = 0.083). The total number of observed reflections (*I* > 4.0 σ (*I*)) was 2817. Data were corrected for Lorentz and polarization effects.

The positions of the uranium atoms were located from the Patterson map.¹⁸ Then positions of the atoms within the uranium coordination sphere and the phosphorus and carbon atoms were obtained in difference Fourier maps. Following partial refinement of positional and thermal parameters, a total of eight positions were identified corresponding to the oxygen atoms of the eight lattice water molecules. No hydrogen atoms could be found in the difference maps, so they were placed on the phenyl groups in calculated positions and assigned fixed temperature factors. Except for the carbon and lattice water oxygen atoms all other atoms were refined anisotropically. The final cycle of full-matrix refinement was based on 2817 reflections and 345 variables. An empirical absorption correction based on ψ -plot was applied, and it yielded transmission factors ranging from 0.60 to 1.00. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.85 and –3.46 e/Å³. The highest residual peaks were found near the uranium atom and some minor peaks near the disordered water molecules.

UO₂(HO₃PC₆H₅)₂·2CH₃CH₂OH (2). The crystals were highly air sensitive. A small crystal of dimensions 0.3 × 0.25 × 0.1 mm was mounted on a glass fiber and quickly transferred into the diffractometer steady nitrogen stream at a constant temperature of –110 °C. The crystal was found to be stable in the nitrogen atmosphere for the entire duration of data collection. As in the case of compound **1**, this crystal was also twinned, and it was indexed by the twin deconvolution technique. Data were collected up to 50° in 2 θ , in a manner similar for compound **1**. A total of 2140 reflections were obtained out of which

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Table 2. Atomic Coordinates and $B(\text{eq})$ Values (\AA^2) for Compound 1

atom	x	y	z	$B(\text{eq})^a$
U1	0.1720(1)	-0.1967(1)	-0.2678(1)	1.28(6)
U2	0.0114(1)	-0.1674(1)	0.1949(1)	1.21(6)
P1	0.228(1)	-0.2374(7)	0.0438(9)	1.5(4)
P2	0.221(1)	-0.2484(7)	0.430(1)	1.7(4)
P3	-0.083(1)	-0.1714(7)	-0.137(1)	1.7(4)
P4	-0.082(1)	-0.1716(8)	0.476(1)	2.1(4)
O1	0.119(3)	-0.232(2)	0.085(3)	4(1)
O2	0.250(3)	-0.190(1)	-0.047(2)	2(1)
O3	0.349(2)	-0.189(2)	0.173(2)	2(1)
O4	0.128(3)	-0.231(2)	0.325(2)	3(1)
O5	0.244(3)	-0.190(1)	0.562(2)	3(1)
O6	0.342(2)	-0.225(2)	0.391(2)	2(1)
O7	-0.025(2)	-0.130(2)	0.003(2)	3(1)
O8	0.008(2)	-0.188(2)	-0.191(2)	2(1)
O9	-0.135(2)	-0.104(2)	-0.204(2)	2(1)
O10	0.005(2)	-0.207(2)	0.560(3)	4(1)
O11	-0.030(2)	-0.141(2)	0.386(2)	3(1)
O12	-0.096(3)	-0.093(2)	0.574(2)	3(1)
O13	0.213(2)	-0.084(1)	-0.227(2)	1.6(8)
O14	0.138(2)	-0.307(1)	-0.301(2)	2(1)
O15	-0.120(2)	-0.260(2)	0.125(2)	2(1)
O16	0.144(2)	-0.070(2)	0.265(2)	3(1)
O(W1)	0.397(2)	-0.181(2)	-0.193(3)	3(1)
O(W2)	-0.129(2)	-0.072(2)	0.185(3)	3(1)
O(W3)	0.208(3)	0.004(2)	0.036(3)	3.5(6)
O(W4)	0.444(7)	0.065(5)	0.020(7)	18(2)
O(W5)	0.450(4)	0.170(3)	0.423(4)	9(1)
O(W6)	0.784(5)	-0.001(3)	0.442(5)	11(1)
O(W7)	0.457(6)	0.074(4)	0.846(6)	15(2)
O(W8)	0.435(5)	0.064(4)	0.239(5)	13(2)
O(W9)	0.395(5)	0.019(4)	0.402(5)	12(2)
O(W10)	0.395(8)	0.043(5)	0.627(8)	19(3)
C1	0.221(4)	-0.348(3)	-0.005(4)	2.3(8)
C2	0.290(4)	-0.376(3)	-0.075(4)	2.3(8)
C3	0.290(4)	-0.461(3)	-0.108(4)	2.8(9)
C4	0.229(6)	-0.515(4)	-0.061(5)	6(1)
C5	0.171(4)	-0.484(3)	0.021(4)	3(1)
C6	0.163(3)	-0.406(3)	0.045(3)	1.8(8)
C7	0.186(4)	-0.358(3)	0.423(4)	2.4(9)
C8	0.279(4)	-0.382(3)	0.505(4)	3(1)
C9	0.241(5)	-0.470(3)	0.526(5)	4(1)
C10	0.122(4)	-0.524(3)	0.441(4)	3(1)
C11	0.042(4)	-0.501(3)	0.351(5)	4(1)
C12	0.069(4)	-0.417(3)	0.351(4)	3(1)
C13	-0.209(4)	-0.258(3)	-0.171(4)	2.2(8)
C14	-0.206(5)	-0.341(4)	-0.216(5)	5(1)
C15	-0.305(5)	-0.419(3)	-0.256(5)	4(1)
C16	-0.427(6)	-0.414(4)	-0.235(6)	7(2)
C17	-0.414(5)	-0.323(4)	-0.172(5)	5(1)
C18	-0.321(4)	-0.256(3)	-0.155(4)	4(1)
C19	-0.235(4)	-0.246(3)	0.402(4)	2.1(8)
C20	-0.278(4)	-0.303(3)	0.462(4)	4(1)
C21	-0.395(5)	-0.344(4)	0.423(5)	5(1)
C22	-0.481(4)	-0.357(3)	0.289(4)	3(1)
C23	-0.433(4)	-0.294(3)	0.226(4)	4(1)
C24	-0.315(4)	-0.245(3)	0.288(4)	1.9(8)

$$^a B(\text{eq}) = \frac{4}{3} \sum_i \sum_j \beta_{ij} A_i A_j$$

2008 were unique ($R_{\text{int}} = 0.056$). Data were corrected for Lorenz and polarization effects.

The structure was solved by the Patterson method. The position of the U atom was obtained by deconvolution of the Patterson function. Other atoms were found by difference Fourier methods, and all the atoms were refined anisotropically. The data were corrected for absorption and secondary extinction effects. The weighting scheme was based on counting statistics, and it included a factor ($p = 0.03$) to downweight the intense reflections. The maximum and minimum residual peaks were 4.0 and -6.0 e/\AA^3 , and they were found very close to the uranium atoms.

The relatively high R -values for both compounds **1** and **2** are mainly attributed to the following crystal properties. First, both compounds

Table 3. Atomic Coordinates and $B(\text{eq})$ Values (\AA^2) for Compound 2

atom	x	y	z	$B(\text{eq})^a$
U1	1.0000	0.0	0.0	2.41(5)
P1	0.8784(5)	0.1533(5)	0.5279(7)	2.1(2)
O1	0.881(1)	0.094(1)	0.277(2)	3.3(6)
O2	0.999(2)	0.284(2)	0.562(4)	8(1)
O3	0.911(2)	0.084(2)	0.713(2)	4.3(6)
O4	1.162(2)	0.135(2)	0.064(2)	3.9(6)
O5	0.097(3)	0.394(3)	0.105(4)	10(1)
C1	0.703(2)	0.175(2)	0.563(3)	1.7(6)
C2	0.641(2)	0.231(3)	0.400(3)	4(1)
C3	0.502(3)	0.248(3)	0.427(4)	5(1)
C4	0.414(2)	0.202(2)	0.602(4)	4(1)
C5	0.476(3)	0.142(2)	0.764(4)	4(1)
C6	0.614(2)	0.129(2)	0.740(3)	3.0(8)
C7	0.260(5)	0.448(4)	0.12(1)	11(3)
C8	0.304(6)	0.524(5)	-0.033(8)	12(3)

$$^a B(\text{eq}) = \frac{4}{3} \sum_i \sum_j \beta_{ij} A_i A_j$$

Table 4. Selected Intramolecular Distances (\AA) for Compound 1

U1-O(W1)	2.46(2)	P1-O2	1.46(2)
U1-O2	2.38(2)	P1-O3	1.63(3)
U1-O5	2.34(3)	P1-C1	1.80(4)
U1-O8	2.35(2)	P2-O4	1.49(2)
U1-O10	2.29(2)	P2-O5	1.53(2)
U1-O13	1.76(2)	P2-O6	1.60(2)
U1-O14	1.74(2)	P2-C7	1.76(4)
U2-O1	2.30(2)	P3-O7	1.49(2)
U2-O(W2)	2.52(2)	P3-O8	1.43(2)
U2-O4	2.30(2)	P3-O9	1.61(2)
U2-O7	2.34(2)	P3-C13	1.71(4)
U2-O11	2.35(2)	P4-O10	1.49(3)
U2-O15	1.78(3)	P4-O11	1.45(2)
U2-O16	1.84(2)	P4-O12	1.61(3)
P1-O1	1.49(2)	P4-C19	1.79(4)

Table 5. Selected Intramolecular Bond Angles (deg) for Compound 1

O(W1)-U1-O2	68(1)	O1-P1-O2	117(2)
O(W1)-U1-O5	71.3(9)	O1-P1-O3	105(2)
O(W1)-U1-O13	87(1)	O1-P1-C1	109(2)
O(W1)-U1-O14	91(1)	O2-P1-O3	103(1)
O2-U1-O8	73.9(9)	O2-P1-C1	114(2)
O2-U1-O13	90.2(9)	O3-P1-C1	109(2)
O2-U1-O14	87(1)	O4-P2-O5	113(1)
O5-U1-O10	73.0(9)	O4-P2-O6	100(1)
O5-U1-O13	87(1)	O4-P2-C7	112(2)
O5-U1-O14	94(1)	O5-P2-O6	110(2)
O8-U1-O10	73.7(8)	O5-P2-C7	113(2)
O8-U1-O13	86(1)	O6-P2-C7	107(2)
O8-U1-O14	95(1)	O7-P3-O8	111(2)
O10-U1-O13	91(1)	O7-P3-O9	108(2)
O10-U1-O14	92(1)	O7-P3-C13	111(2)
O13-U1-O14	177(1)	O8-P3-O9	104(1)
O1-U2-O4	71.8(8)	O8-P3-C13	116(2)
O1-U2-O7	73(1)	O9-P3-C13	107(2)
O1-U2-O15	91(1)	O10-P4-O11	111(2)
O1-U2-O16	90(1)	O10-P4-O12	104(2)
O(W2)-U2-O7	70(1)	O10-P4-C19	112(2)
O(W2)-U2-O11	71(1)	O11-P4-O12	110(2)
O(W2)-U2-O15	91(1)	O11-P4-C19	114(2)
O(W2)-U2-O16	88(1)	O12-P4-C19	105(2)
O4-U2-O11	74(1)	U2-O1-P1	156(2)
O4-U2-O15	94(1)	U1-O2-P1	141(2)
O4-U2-O16	88(1)	U2-O4-P2	165(2)
O7-U2-O15	92(1)	U1-O5-P2	137(2)
O7-U2-O16	87(1)	U2-O7-P3	140(2)
O11-U2-O15	91(1)	U1-O8-P3	173(2)
O11-U2-O16	89(1)	U1-O10-P4	154(2)
O15-U2-O16	178(1)	U2-O11-P4	150(2)

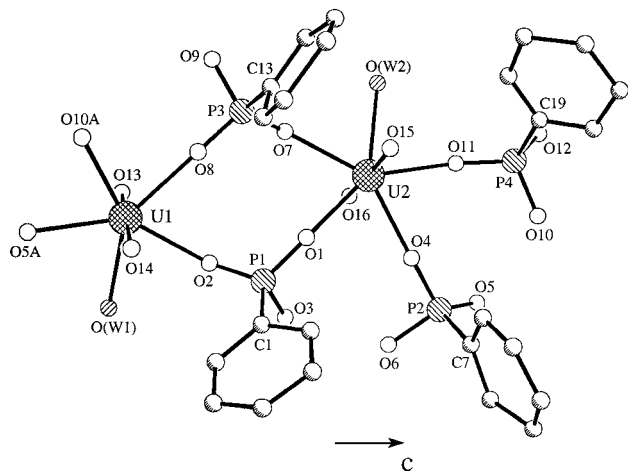
were relatively unstable in air and very easily lost their solvent molecules. Second, we were able to isolate only twinned crystals for the X-ray analysis. Third, the uranium atoms strongly absorbed X-ray

Table 6. Selected Intramolecular Distances (Å) for Compound 2

U1—O1	2.30(1) (2×)	P1—O2	1.54(2)
U1—O3	2.27(1) (2×)	P1—O3	1.48(1)
U1—O4	1.76(2) (2×)	P1—C1	1.75(2)
P1—O1	1.48(1)		

Table 7. Selected Intramolecular Bond Angles (deg) for Compound 2

O1—U1—O1	180.00	O4—U1—O4	180.00
O1—U1—O3	89.4(4) (2×)	O1—P1—O3	114(1)
O1—U1—O3	90.6(4) (2×)	O1—P1—C1	110(1)
O1—U1—O4	89.4(6) (2×)	O2—P1—O3	110(1)
O1—U1—O4	90.6(6) (2×)	O2—P1—C1	107(1)
O3—U1—O3	180.00	O3—P1—C1	109(1)
O3—U1—O4	89.0(6) (2×)	O1—P1—O2	106(1)
O3—U1—O4	91.0(6) (2×)		

**Figure 1.** Molecular drawing of compound 1 showing the coordination of uranium atoms and their bridging by phenylphosphonate groups.

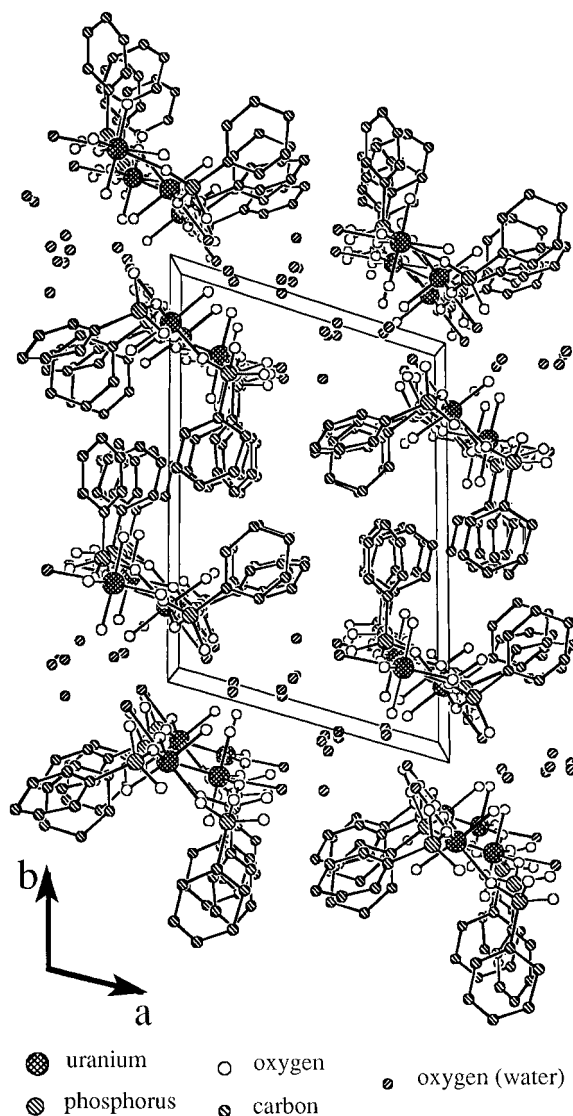
radiation, which was not completely corrected for, and further contributed to the higher *R*-values.

Crystallographic data for both compounds are listed in Table 1. Positional and thermal parameters for compounds 1 and 2 are listed in Tables 2 and 3, respectively, the interatomic distances and the bond angles for 1 in Tables 4 and 5, and the interatomic distances and the bond angles for 2 in Tables 6 and 7.

Results

[UO₂(HO₃PC₆H₅)₂·H₂O]₂·8H₂O (1). Structure. Compound 1 forms a quasi one-dimensional structure with two independent uranyl groups and four independent phenylphosphonate groups (Figure 1). The metal atom U1 adopts a somewhat distorted pentagonal bipyramidal geometry with the uranyl oxygens O13 and O14 in the axial positions. In the equatorial plane, U1 is coordinated by four oxygens O2, O8, O10A, and O5A of four different phosphonate groups and by the oxygen atom O(W1) of a water molecule. The phosphonate group P1 uses its two oxygens O2 and O1 to form a bridge between U1 and another uranium atom U2. The third oxygen O3 does not participate in any coordination, and it is protonated. Similarly, the phosphonate group P3 uses its oxygens O8 and O7 to form another bridge between U1 and U2, and its third oxygen O9 is also protonated. The uranium atom U2 is crystallographically distinct from U1; however, it has a coordination similar to that of U1. Its strongly bonded oxygens O15 and O16 in the axial positions are terminal, as well as the water oxygen atom in the equatorial position. The linear chain is propagated by two other phosphonate groups P2 and P4 which connect the U2 atom to another uranium atom U1A which is translated from U1 by a unit cell dimension *c*.

The U—O_{axial} bond lengths range from 1.74(2) to 1.84(2) Å which is much less than the sum of the atomic covalent radii

**Figure 2.** View of the unit cell along the linear chains in compound 1. The chains orient their hydrophobic sides together and their hydrophilic sides together.

(2.15 Å) suggesting a bond order 2 or higher. On the other hand, the U—O_{equatorial} bond lengths range from 2.29 to 2.52 Å, the longest distance being that involving the water oxygen. These longer bond distances suggest a relatively weak interaction of all oxygen atoms with uranium in its equatorial plane. The O—U—O bond angles in the equatorial plane range between 68 and 74° for U1 and between 70 and 74° for U2, which is fairly close to the ideal 72° for a regular pentagonal arrangement. The angle between the uranyl axes of U1 and U2 atoms derived from the torsion angle O14—U1—U2—O15 is 41.7°.

The values found for P—O_{bridging} bond distances (1.45(2)–1.53(2) Å) are very typical for tetrahedral phosphates and phosphonates.¹⁹ However, the longer P—O_{terminal} distances (1.60–1.63 Å) are indicative of the P—OH bond, with the bonding order about 1. This longer P—O_{terminal} bond thus clearly confirms that the terminal oxygens are protonated.

The linear uranyl phosphonate chains propagate along the *c*-axis (*c* = 11.375 Å) (Figures 2 and 3), with the phenyl rings of each chain forming two rows standing perpendicularly to the chain. The angle between the two rows of the same chain derived from the torsion angle C1—P1—P3—C13 (see Figure

(19) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: Amsterdam, 1974.

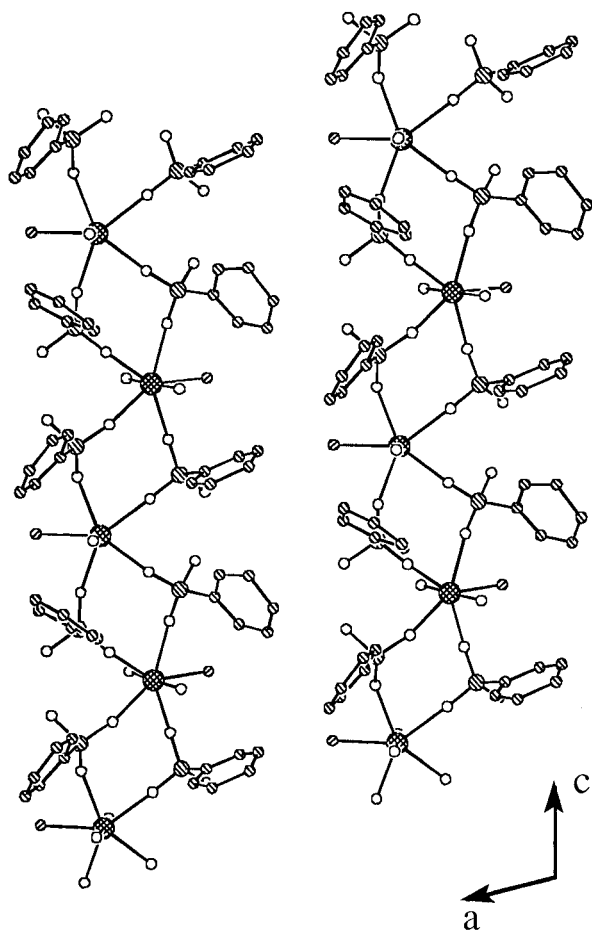


Figure 3. Structure of the linear chains in compound **1** viewed along the *b*-axis. Lattice water molecules are omitted.

1) is approximately 33° . This arrangement makes one side of each chain hydrophobic due to the phenyl rings in adjacent chains facing each other, whereas the other side is hydrophilic. The neighboring chains stack their sides to each other hydrophobic to hydrophobic and hydrophilic to hydrophilic, thus creating two-dimensional, alternating hydrophobic and hydrophilic planes parallel to the *a*-*c* plane.

The rows of phenyl rings of adjacent chains are stacked so they partially overlap each other (Figure 2). This kind of overlapping is not usually seen in layered divalent and tetravalent phenylphosphonates,^{8,9,12} because in the reported layered structures the phenyl rings are more densely packed. The denser packing of the phenyl rings then leaves so little void spaces between them that the rings from the opposite layers do not penetrate or overlap but stack against each other at van der Waals distances.

The hydrophilic region of the structure is located on the opposite side of the linear chains from the phenyl rings. The phosphonate hydroxyl groups, and the coordinated as well as the lattice water molecules, are located in this region. A total of ten positions were identified for water molecules in the structure. Two of them coordinate the two uranium atoms, and eight are lattice molecules. Four of the lattice water molecules are hydrogen bonded to the phosphonate hydroxyl groups. O(W7) is hydrogen bonded to O3, O(W5) to O6, O(W3) to O9, and O(W6) to O12 with distances of 2.72(7), 2.55(5), 2.73(4), and 2.70(6) Å, respectively. The lattice water molecules are involved in extensive hydrogen bonding among themselves, and their positions are disordered with relatively high thermal parameters. The occupancies for most lattice water molecules refined to values lower than one: O(W4), 0.55; O(W5), 0.77;

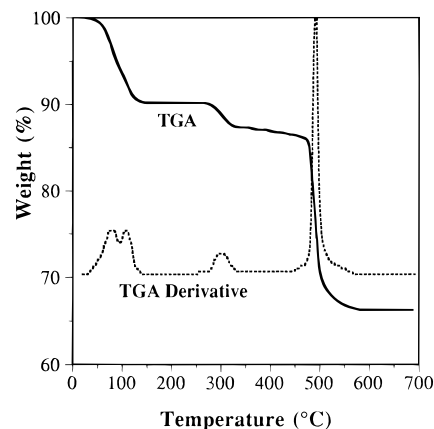


Figure 4. Thermogravimetric analysis (TGA) curve and its first derivative of compound **1**.

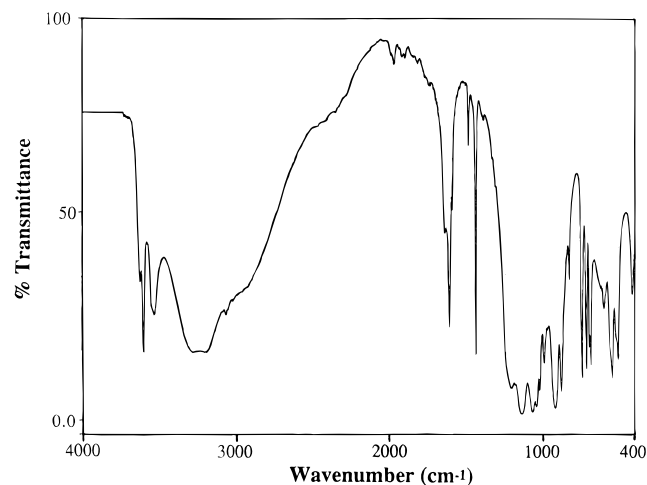


Figure 5. Infrared spectrum of compound **1**.

O(W6), 0.83; O(W7), 0.68; O(W8), 0.60; O(W9), 0.60; O(W10), 0.50. This is in agreement with the TGA observation according to which the crystals indeed lost water when kept in an environment with lower humidity.

Thermogravimetric Analysis. The weight loss occurred in three steps (Figure 4). The first step took place between 50 and 130 °C, and it corresponded to the loss of almost eight lattice water molecules. Several TGA measurements were carried out, and it appeared that the value of the weight loss in this step decreased if the sample was stored at a lower humidity. This also explains the partial occupancies of lattice water oxygens in the X-ray results. The differential thermogravimetric curve actually shows two peaks in the approximate 1:1 ratio attributable to types of lattice water molecules leaving at slightly different temperatures. We presume that the four water molecules (O(W4), O(W8), O(W9), O(W10)) not bonded to the phosphonate OH groups leave in the first step, whereas the four water molecules (O(W3), O(W5), O(W6), O(W7)) bonded to the four phosphonate OH groups leave in the second step. The second weight loss occurs between 260 and 335 °C, and it is attributed to the loss of the two water molecules coordinating the two uranium atoms. The third weight loss occurs between 450 and 600 °C, and is attributed to the decomposition of the four phenyl rings.

IR Spectrum. The high-wavenumber region of the IR spectrum (Figure 5) is dominated by the bands belonging to the O-H and C-H stretches, whereas the low-energy region mostly exhibits peaks indicative of the oxygen-bridged uranyl phosphonate chain. The complete assignment of peaks is given in Table 8. All the important features of the structure documented

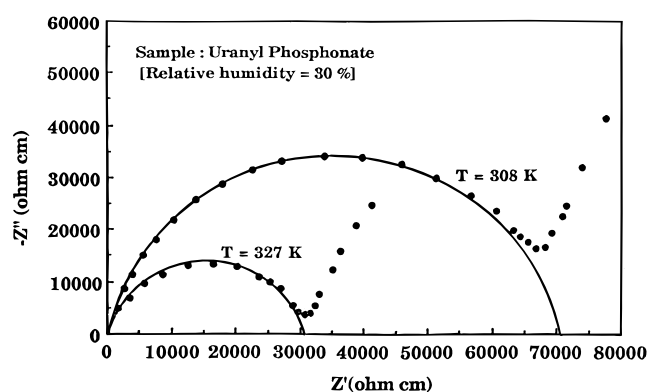
Table 8. Assignment of the Infrared Spectrum of Compound 1

wavenumber (cm ⁻¹) (intensity) ^a	assgnt
3632 (m), 3610 (s)	O—H stretch in H-bonded lattice H ₂ O dimers
3540 (s)	O—H stretch in U-coord H ₂ O
3400–3100 (s, br)	O—H stretch in lattice water
3000–2600 (sh)	O—H stretch in POH
3070 (s)	C _{arom} —H stretch in phenyl rings
1645 (w)	H ₂ O bending
1612 (s), 1482 (w)	phenyl ring stretch
1440 (s)	C _{arom} —H bending in phenyl rings
1210–995 (vs) range of several peaks	P=O and P—O antisym and sym stretching modes of the phosphonate group
925 (vs)	U=O antisym stretch
835 (w)	U=O sym stretch
750 (s), 721 (s), 690 (s)	monosubstituted phenyl ring and P—C stretch
550 (s), 512 (s)	O—P—O bending

^a vs = very strong; s = strong; m = medium; w = weak; br = broad; sh = shoulder.

Table 9. Conductivity of Compound 1 at Room Temperature and Relative Humidity

conductivity (Ω ⁻¹ cm ⁻¹)	rel humidity				
	20% (±3%)	30% (±3%)	50% (±4%)	65% (±4%)	85% (±5%)
	7.43 × 10 ⁻⁷	8.45 × 10 ⁻⁶	3.86 × 10 ⁻⁵	1.25 × 10 ⁻⁴	3.25 × 10 ⁻³

**Figure 6.** Cole–Cole impedance plot of conductivity for compound 1 taken at two different temperatures and 30% humidity.

in the X-ray analysis are confirmed,^{20–22} particularly the network of hydrogen bonds which shows as the sharp “doublet” at 3600 cm⁻¹. Several different frequencies of the P—O stretch are caused by several different P—O bonding distances.

³¹P MAS NMR. The spectrum exhibited a doublet of peaks in a 1:1 ratio at +21.1 and +18.5 ppm which correspond to the two phosphorus atoms P1 and P3 in the two different rows (Figure 2). P2 is found in the same row as P1, and P4 in the same row as P3, so they are assumed to produce signals equivalent to the mentioned atoms.

Proton Conductivity. The main reason for carrying out the proton conductivity measurements was the presence of protons on the phosphonate groups and the network of hydrogen bonded water molecules. Conductivity data were collected at room temperature as a function of relative humidity (Table 9). The conductivity, σ , rapidly decreased from 3.35×10^{-3} to 7.43×10^{-7} on changing the humidity from 85% to 20%. The plot of $\log \sigma$ vs reciprocal temperature in the temperature range 25–80 °C yielded a linear dependence, and from its slope the activation energy of the protons was determined to be $E_a = 0.36$ eV. The Cole–Cole plots representing some of the impedance data are shown in Figure 6.

Dehydration Experiments. The crystals of compound 1 were subjected to dehydration by various means, and the results

were monitored by TGA and by the X-ray powder patterns. Dehydration of unground needlelike crystals in a stream of nitrogen gas at room temperature for 9 h did not affect the two water molecules coordinated to the uranium atoms, but 6 water molecules of the 8 that are uncoordinated were lost. Dehydration under the same conditions for a longer time (7 days) had no effect in the removal of any more water molecules. The powder pattern of the dehydrated product showed a dominant peak at 16.7 Å, while all other peaks either strongly diminished or disappeared. The peaks at $2\theta > 23^\circ$ disappeared completely. This observation indicates that the long-range ordering of the phenylphosphonate chains was disturbed by dehydration. However, the presence of the strong peak at 16.7 Å indicative of the *b*-axis dimension suggests that the structural feature of the alternating hydrophobic and hydrophilic planes remained unaltered (see Figure 2).

This dehydration was reversible. Exposure of the dehydrated powder to water for 4–5 h or to air saturated with water vapor for 2 days led to a complete rehydration (as determined by TGA). The X-ray powder pattern of the rehydrated sample was restored to strongly resemble that of the original compound 1.

Dehydration of a ground sample under the same conditions led to complete removal of all eight water molecules uncoordinated to the uranium atoms while the coordinated molecules remained unaffected. The same result was achieved by exposing the compound to a vacuum. However, in both of the latter cases, the powder patterns revealed that the original structure was severely altered; most original peaks including that at 16.7 Å were lost or significantly diminished, and a number of new peaks appeared.

UO₂(HO₃PC₆H₅)₂·2CH₃CH₂OH (2). Structure. This compound also forms one-dimensional linear chains along the *c*-axis with metal to phosphonate ratio 1:2; however, there are some major differences between compounds 1 and 2. In 2, there is only one crystallographically distinct and hexacoordinate uranium atom that becomes the center of symmetry for the two pairs of adjacent phosphonate groups (Figure 7). The uranium geometry is a tetragonally distorted octahedron (*D_{4h}*) with the two uranyl centrosymmetrically related O4 oxygen atoms in the axial positions at 1.76 Å and with two pairs of centrosymmetrically related oxygen atoms O1 and O3 in the equatorial positions at 2.30 and 2.27 Å, respectively. The O—U—O bond angles in the equatorial plane are close to 90° (within 0.6°), and the equatorial plane is perpendicular to the uranyl axis, within 1°.

(20) Nakanishi, K.; Solomon, P. H. *Infrared Absorption Spectroscopy*; Holden-Day Inc.: San Francisco, 1977.

(21) Pekarek, V.; Vesely, V. J. *Inorg. Nucl. Chem.* **1964**, *27*, 1151.

(22) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons, Inc.: New York, 1986.

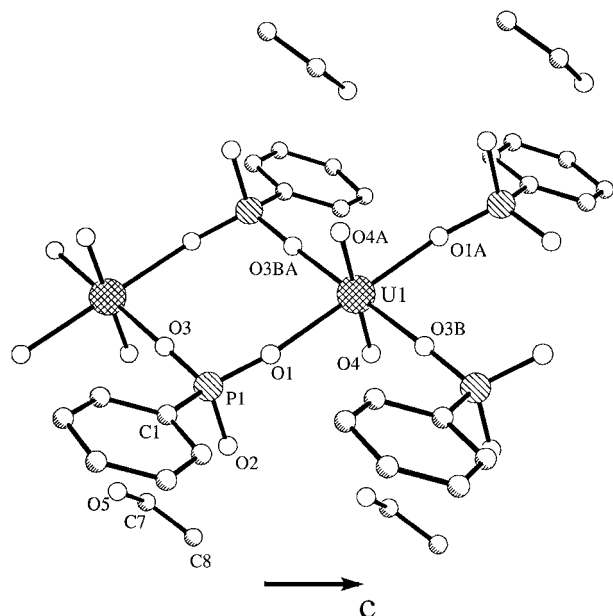


Figure 7. Molecular drawing depicting the structure of the linear chain in compound **2**.

As in **1**, only two oxygen atoms O1 and O3 of each phosphonate group are used for bridging the uranium atoms; the third oxygen atom O2 is terminal, and it is protonated. The P–O_{terminal} bond distance (1.54 Å) is again longer than the P–O_{bridging} bond distance (1.48 Å). The phosphonate hydroxyl oxygen O2 is hydrogen bonded to the ethanol oxygen O5 at a distance of 3.10 Å.

The one-dimensional chains propagate infinitely along the *c*-axis, and the dimension *c* = 5.67 Å is almost exactly half that of compound **1**. The structure of the chains in the two compounds, however, differs in one important aspect. Whereas in **1** the two rows of phenyl rings point into the same general area of the chain creating hydrophobic and hydrophilic regions, in **2** the two phenyl rows point exactly opposite from each other, which gives both sides of the chain the same, hydrophobic nature. Ultimately, this results in a different kind of stacking of the chains. There are no segregated hydrophobic and hydrophilic regions, instead the chains translated along the *a*-axis stack their phenyl groups on each other, so that the phenyl rings of one chain always overlap the phenyl rings of the adjacent chain (Figure 8). This stacking leads to a kind of very loosely held metal phosphonate sheet in the *a*–*c* plane. The distance between the “sheets” is $b \times \sin \gamma = 10.88$ Å, and the space between the sheets is filled with ethanol molecules. There are two symmetrically related ethanol molecules per a uranium atom, and they are located between the uranyl phosphonate pseudo sheets in the *a*–*c* plane. Therefore, in a classical sense, this compound is considered an ethanol intercalate of uranyl phenylphosphonate.

Discussion

The most frequent geometries of the uranyl ion in coordination compounds are polygonal bipyramids²³ with the two uranyl oxygens occupying the axial positions. Due to the size of the uranium atom, more than four substituents can be placed in the equatorial plane. If the ligands are small enough (H₂O, NO₃[−]), hexagonal bipyramidal geometry can be expected. When the anions are larger polydentates such as phenylphosphonate, the pentagonal bipyramidal geometry of uranium (VI) is more likely to result, as indeed occurred in compound **1**. However, in

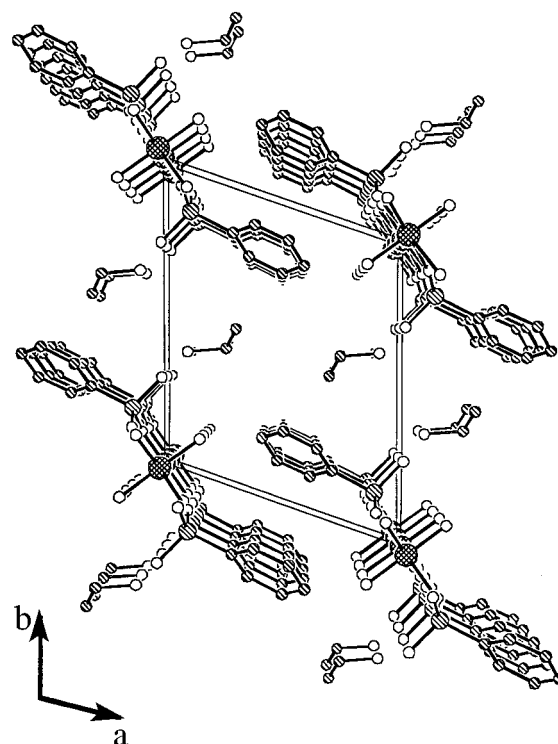


Figure 8. Unit cell of compound **2** with projection of the linear chains along the *c*-axis. The phenyl rings of adjacent chains stack on each other in a “staircase” manner.

compound **2**, the uranium atom adopts a rather rare tetragonally distorted octahedral geometry, which is caused in part by the poor coordination capability of the ethanol molecule.

A number of linear metal phosphonates have been described in the literature. One of the phases of [(VO)(O₃P(CH₂)PO₃)]^{2−} formed puckered linear chains,²⁴ where both phosphonate groups of each diphosphonate unit formed bridges between the adjacent vanadyl ions. As might be expected, the vanadium atom coordination was square pyramidal with the vanadyl oxygen in the apex and with two pairs of phosphonate oxygen atoms in the base.

The structure of UO₂(O₃PCH₂OH)·5H₂O is also linear²⁵ containing pentagonal bipyramidal uranium atoms, but unlike in **1**, the metal to phosphonate ratio is 1:1, and all three phosphonate oxygens participated in bridging of the uranyl ions. The network of hydrogen bonded water molecules also formed channels between the uranyl phosphonate chains, but the extent of hydrophobic–hydrophilic segregation did not occur to such an extent as in compound **1**, because of the absence of the clearly hydrophobic groups.

To the best of our knowledge, only two other linear metal phenylphosphonates have been synthesized and structurally characterized. One of them is an iron compound HFe(HO₃PC₆H₅)₄,^{13a} which crystallizes in the triclinic space group *P1* (*a* = 14.968 Å, *b* = 5.36 Å, *c* = 8.678 Å). The distorted, octahedrally coordinated Fe(III) ions are bridged by two phosphonates as in **2**, but the two axial positions are occupied by pendant HO₃PC₆H₅ groups. The linear chains propagate along the *b*-axis, and it is interesting that the *b*-axis dimension (5.36 Å) is very close to the *c*-axis dimension of **2** (along which its chains propagate) and also to half the *c*-axis dimension of **1**.

The other linear metal phenylphosphonate is MoO₂(O₃PC₆H₅)·H₂O,^{13b} which crystallizes in the orthorhombic space

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(25) Brittel, P. A.; Wozniak, M.; Boivin, J. C.; Nowogrocki, G.; Thomas, D. *Acta Crystallogr.* **1986**, *C42*, 1502.

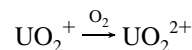
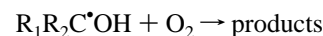
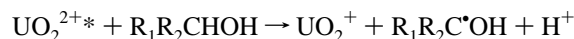
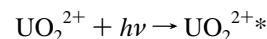
group $P222$ ($a = 6.3610 \text{ \AA}$, $b = 16.0889 \text{ \AA}$, $c = 9.3573 \text{ \AA}$). In this compound, the metal to phosphonate ratio is 1:1, and the linear chains propagate along the a -axis. The phenyl rings point into one direction from each chain, and the adjacent chains stack their hydrophobic and hydrophilic groups together in a way similar to compound **1**.

Recently, we have prepared and characterized other uranyl phenylphosphonate phases. $\text{UO}_2(\text{O}_3\text{PC}_6\text{H}_5)\cdot 0.7\text{H}_2\text{O}^{16}$ and $(\text{UO}_2)_3(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{O}_3\text{PC}_6\text{H}_5)_2\cdot \text{H}_2\text{O}^{17}$ are porous, unlike the structures presented here. These phases were obtained only in microcrystalline form, and their crystal structures were solved by using powder diffraction data. $\text{UO}_2(\text{O}_3\text{PC}_6\text{H}_5)\cdot 0.7\text{H}_2\text{O}$ crystallizes in the hexagonal space group $P6/mcc$ with $a = b = 21.827 \text{ \AA}$ and $c = 7.0796 \text{ \AA}$, and the structure forms unidimensional unattached channels running parallel to the c -axis. The wall of the pore is built up by six uranium and six phosphorus atoms alternating around the ring of the pore and connected by oxygen atoms. The phenyl rings are on the outer periphery, and the diameter of the pore is about 12.1 \AA . The other porous compound $(\text{UO}_2)_3(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{O}_3\text{PC}_6\text{H}_5)_2\cdot \text{H}_2\text{O}$ crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 17.1966 \text{ \AA}$, $b = 7.21 \text{ \AA}$, and $c = 27.8282 \text{ \AA}$. The asymmetric unit cell contains three uranyl, two phosphonate, and two hydrogen phosphonate groups and a lattice water molecule, all crystallographically independent. The pore diameter is $7.0 \times 6.5 \text{ \AA}$, and as in the case of the hexagonal phase, the phenyl rings are arranged on the outer periphery of the pore. Structural studies on other phases are in progress.

A number of observations other than those reported in the Results section were conducted to determine the reasons for the high instability of both reported compounds. Slow dehydration of **1** in approximately 60% humidity over several days lead to a gradual loss of up to three lattice molecules out of eight. During the slow dehydration, apparently the most weakly bound water molecules were lost, and the remaining molecules were able to redistribute themselves over the vacated sites. This resulted in partial occupancies of water molecules, but the structure remained intact. However, fast dehydration, such as passing nitrogen over the crystals of **1**, resulted in the visually detected decomposition within seconds, while TGA of the same sample revealed that only two of the eight water molecules were lost. During this fast dehydration, the weakly bound water molecules were lost, but the remaining molecules did not have enough time to redistribute themselves to the vacated sites, and the structure collapsed, as observed by X-ray powder patterns. If compound **1** lost more than three water molecules, it collapsed regardless of the dehydration rate, as observed by X-ray powder patterns and TGA.

The instability of compound **2** in air at room temperature results from two separate processes. The more immediate decomposition resulted from the loss of ethanol solvent molecules, which hold the uranyl phosphonate pseudo sheets apart. This leads to the subsequent collapse of the structure when sufficient amount of ethanol is removed. A similar collapse of a layered structure due to the loss of solvent was observed in hydrogen uranyl phosphate.²⁶ However, it had been observed that the crystals of **2** decomposed within several days even in its mother liquor or in pure ethanol. The reason for this decomposition is most likely photochemical in nature. Photolysis of primary and secondary alcohols by the uranyl ion in aqueous solutions has been earlier described by Matsushima²⁷ and more recently by Bakac and Espenson.²⁸ The mechanism

involves an electron transfer from the alcohol to the excited uranyl ion, followed by α -hydrogen abstraction, and oxidation of the alcohol by molecular oxygen:



The proton conductivity of compound **1** significantly depends on humidity, and two reasons may have caused this dependence. As the humidity is increased, adsorption of water molecules on the surface may occur, and this adsorbed surface water may have contributed to the overall conductivity increase as was observed for α -zirconium phosphate.²⁹ However, this contribution is probably very low because of the high crystallinity and a resulting low surface area of the sample. The more likely reason for the strong conductivity–humidity dependence is the dehydration observations mentioned above. The reversible loss of a significant portion of the lattice water molecules can certainly account for such a decrease of conductivity at a lower humidity. It is reasonable to suggest that the conductivity of compound **1** with complete water molecule occupancies corresponds to the measurement carried out at 85% humidity ($\sigma = 3.25 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$). Due to the network of the hydrogen-bonded water molecules, a Grotthus mechanism is likely to predominate when the lattice water molecules are fully occupied, while increased proton hopping or ion diffusion can be expected on partial dehydration. For comparison, a layered proton conductor, hydrogen uranyl phosphate, with one proton and four water molecules per a unit cell³⁰ gave $\sigma = 3 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ at $22 \text{ }^\circ\text{C}$, whereas the crystalline α -zirconium phosphate with one proton and one water molecule³¹ gave only $\sigma = 3 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$. The highly hydrated heteropolyacids $\text{H}_3\text{Mo}_{12}\text{PO}_{40}\cdot 29\text{H}_2\text{O}$ and $\text{H}_3\text{W}_{12}\text{PO}_{40}\cdot 29\text{H}_2\text{O}$ containing free H_3O^+ ions have exhibited even a higher proton conductivity $\sigma = 1.8 \times 10^{-1} \Omega^{-1} \text{ cm}^{-1}$ and $\sigma = 1.7 \times 10^{-1} \Omega^{-1} \text{ cm}^{-1}$, respectively.³² On the basis of the above examples, the proton conductivity seems to increase with Bronsted acidity of the conducting protons and with the degree of hydration, and compound **1** apparently abides by these criteria.

Acknowledgment. This work was supported by the Robert A. Welch Foundation (Grant No. A 673) for which grateful acknowledgment is made. D.G. thanks the Welch Foundation for awarding him a Graduate Fellowship for 1995–96.

Supporting Information Available: Tables of atomic coordinates of calculated hydrogen atoms (Tables S1 and S2), anisotropic thermal parameters (Tables S3 and S4), nonessential intramolecular distances (Tables S5 and S6), and nonessential bond angles (Tables S7 and S8) for compounds **1** and **2**, respectively (8 pages). Ordering information is given on any current masthead page.

IC960332Y

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