Structure Determination of a Complex Tubular Uranyl Phenylphosphonate, $(UO_2)_3(HO_3PC_6H_5)_2(O_3PC_6H_5)_2 \cdot H_2O$, from Conventional X-ray Powder Diffraction Data

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The three-dimensional structure of a complex tubular uranyl phosphonate, $(UO_2)_3(HO_3PC_6H_5)_2(O_3PC_6H_5)_2 \cdot H_2O$, was determined *ab initio* from laboratory X-ray powder diffraction data and refined by the Rietveld method. The crystals belong to the space group $P2_12_12_1$, with $a = 17.1966(2)$ Å, $b = 7.2125(2)$ Å, $c = 27.8282(4)$ Å, and $Z = 4$. The structure consists of three independent uranium atoms, among which two are seven-coordinated and the third is eight-coordinated. These metal atoms are connected by four different phosphonate groups to form a one-dimensional channel structure along the *b* axis. The phenyl groups are arranged on the outer periphery of the channels, and their stacking forces keep the channels intact in the lattice. The determination of this structure which contains 50 non-hydrogen atoms in the asymmetric unit, from conventional X-ray powder data, represents significant progress in the application of powder techniques to structure solution of complex inorganic compounds, including organometallic compounds.

Introduction

Material properties of molecular solids have an intrinsic correlation with the interactions occurring at the atomic level. Detailed information concerning the molecular structure and packing into solids is therefore essential to understand the physical properties of the solids. Generally, structural data for the materials are obtained by the use of single-crystal methods, which have become fairly routine. There are however compounds which cannot be obtained in single-crystal form, and structure determination of such polycrystalline materials depends mainly on the use of their powder diffraction data. Substantial progress has been made in the application of powder diffraction techniques to solve unknown structures.[1−4] The most complex structure solved by this method to date is that of $La_3Ti_5Al_{15}O_{37}$, which contains 60 independent atoms in the asymmetric unit.[2] To complete the structure solution and successful refinement, complementary use of synchrotron X-ray and neutron diffraction methods was employed. On the other hand, the largest structure solved by the use of laboratory X-ray data to date contained only 29 non-hydrogen atoms in the asymmetric unit.[3] In this paper, we describe the determination and refinement of $(UO_2)_3(HO_3PC_6H_5)_2(O_3PC_6H_5)_2 \cdot H_2O$, a novel channel structure of a uranyl compound containing 50 non-hydrogen atoms in the asymmetric unit from conventional X-ray powder data.

As a part of our ongoing research on metal phosphonate chemistry, we have prepared a number of uranyl phosphonate compounds. The primary importance of these phosphonate compounds is their potential application in the areas of ion exchange, catalysis, sorption, etc.[5] The uranyl compounds in particular have shown some interesting luminescent properties. The mode of the UO_2^{2+} ion binding with the phosphonates, particularly phenylphosphonate, however, is diverse, and accordingly we have isolated a variety of phases depending upon the preparation conditions. Among them we have been able to structurally characterize four different phases. The compounds with uranyl to phosphonate ratios of 1:2 formed linear chain polymers in which the phosphonates are singly protonated.[4a] Another phase with composition $UO_2(O_3PC_6H_5) \cdot 0.7H_2O$,[4b] on the other hand, formed an entirely different type of structure which was observed for the first time for metal phosphonates. The metal−phosphonate interaction in this case led to a porous one-dimensional structure containing inorganic frameworks similar to that found for zeolites. The novel feature of this structure is that the organic groups are projected on the outer periphery of isolated unidimensional channels. Recently two other metal phosphonates, aluminum[6] and copper[7] methylphosphonates, with porous structures were also reported. While these compounds have inorganic frameworks similar to that mentioned above, their organic moieties are projected toward the center of the channels, contrary to the uranyl phenylphosphonate structure. The compound described here is also porous, but it contains exchangeable protons bonded to phosphonate oxygens. The metal−phosphonate linkages along the walls of the channel as well as the packing of the organic groups in the present case are different from those observed for $UO_2(O_3PC_6H_5) \cdot 0.7H_2O$.[4b]

Experimental Section

Materials and Methods. Chemicals used were of reagent grade quality and were obtained from commercial sources without further purification. Thermogravimetric analysis (TGA) and differential

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thermal analysis (DTA)were carried out with a Rigaku Thermoflex apparatus at a heating rate of 10 K/min. Infrared spectra were recorded on a Perkin-Elmer 883 spectrometer using a dry KBr pellet containing 2% of the sample.

Compound Preparation. A 150 mL portion of a 0.1 M $UO_2(NO_3)_2$ solution was slowly added to 175 mL of 0.5 M phenylphosphonic acid with constant stirring. The resulting yellow suspension was refluxed for 30 days. The yellow crystalline powder was filtered off and washed two times with hot water, and two times with cold water, and finally with acetone. The sample was then air-dried at room temperature.

The uranium content was determined gravimetrically. The sample (80 mg) was dissolved in 16 mL of aqueous nitric acid solution (1:1). The metal was precipitated as uranyl oxinate, which was then calcined at 900 °C to yield U_3O_8. The H and C contents were determined from an elemental analysis using a Perkin-Elmer 240C analyzer. The P content was deduced from the amount of carbon and by the known P/C ratio of 1/6. The water content was determined from the weight loss in TGA. Anal. Calc for $[UO_2]_3[HO_3PC_6H_5]_2[O_3PC_6H_5]_2 \cdot H_2O$: U, 49.11; P, 8.53; C, 19.81; H, 1.65; H_2O, 1.24. Found: U, 49.1; P, 8.4; C, 19.93; H, 1.67; H_2O, 1.48.

X-ray Powder Data Collection. Step-scanned X-ray powder diffraction data for the sample (side-loaded into a flat aluminum sample holder) were collected on the finely ground sample. The X-ray source was a Rigaku rotating-anode generator operating at 50 kV and 180 mA with a copper target and graphite monochromator. A 0.5° divergence and scatter slits together with a 0.15° receiving slit were employed for the data collection. Using a Rigaku computer-controlled diffractometer, the data were collected in the 2θ range 3−85° with a step size of 0.01° and a count time of 10 s/step. The $K\alpha_2$ contribution was mathematically removed from the data and peak selection was conducted as described earlier.[8] The pattern was indexed by Ito methods on the basis of the first 20 observed reflections in the profile.[9] The systematic absences were consistent with the space group $P2_12_12_1$. However, if some very weak reflections were ignored, the absences corresponded to the centric space group *Pnma*.

Crystal Structure Solution. Integrated intensities were extracted from the profile by using the Le Bail method[10] in the program GSAS.[11] Structure factors were extracted for 2972 ($K\alpha_1 + K\alpha_2$) reflections, of which 1486 $K\alpha_1$ reflections were used for structure solution in the TEXSAN series of programs.[12a] Use of direct methods (MITHRIL)[12b] in the space group $P2_12_12_1$ gave no solution. When the space group was switched to *Pnma*, the *E* map showed peaks corresponding to the three uranium atoms, two out of four P atoms, and six oxygen atoms. In the space group *Pnma*, the uranyl groups and the phosphonate groups are located on a mirror plane at $y = {}^1/_4$. It may be noted that even in this symmetry the number of independent atoms in the asymmetric unit is 46. The positions of the uranium atoms were consistent with the vectors in the Patterson map calculated with the same data set, although the interatomic vectors showed the *y* coordinates of the U atoms slightly off from 0.25, indicating the lower symmetry space group. The positions of the remaining two P atoms were derived from the Patterson map on the basis of U−P interatomic vectors. No additional structural information could be derived from the structure factors extracted using the Le Bail method.

Rietveld refinement of the pattern using the partial structural model as obtained above was carried out in the program GSAS. The calculations were carried out in the centric space group *Pnma*. Initial least-squares refinements of the profile included terms for scale factor, background, lattice parameters, zero point, and peak shape. A series of difference Fourier maps, computed at this stage, revealed peaks corresponding to the approximate positions of the remaining atoms in the structure, except that of the lattice water oxygen atom. These positions were associated with large errors, which is expected because the dominant scatterers in the structure are the uranium atoms ($R_{wp} = 0.29$ for three uranium atoms only). Therefore, in addition to the peaks in the difference Fourier maps, it was necessary to utilize modeling techniques to obtain satisfactory geometries for the phenyl groups. The refinement of the positional parameters as well as their thermal parameters at this stage converged with $R_{wp} = 0.20$. In addition, the geometries of the phosphonate and one uranyl group, in particular, were not satisfactory, indicating that the atoms, in fact, are not constrained to the mirror symmetry of the space group *Pnma*. The refinement was then switched to the noncentric space group $P2_12_12_1$, which was consistent with the systematic absences. The mirror constraint on the groups was removed, which resulted in four additional atoms (an oxygen from each phosphonate group) in the asymmetric unit being located. The refinement then progressed smoothly and also allowed the location and refinement of the lattice water molecule. Hydrogen atoms of the phenyl groups were included at calculated positions but were not refined. It should be pointed out, however, that a large number (89) of geometrical observations in the form of soft constraints were needed to stabilize the refinement of the phosphonate groups. These constraints were applied to the phosphonate groups and to the linear uranyl groups. The tetrahedral geometry about the P atoms was constrained by P−O (1.53(1) Å) and P−C (1.80(1) Å) bond distances and by the nonbonded distances between the oxygen and carbon atoms (O---O = 2.55(1) Å; O---C = 2.73(1) Å). The C−C distances in the phenyl groups were constrained to a distance of 1.38(1) Å. To obtain similar constraints on the bond angles, the distances between the two atoms bonded to the carbon atom whose angle was to be constrained were held to a value of 2.39(1) Å. Since the arrangement of phosphonate oxygen atoms perpendicular to the uranyl axis is not regular, no soft constraints were applied to them. During the final cycles of refinement, the weight for the soft constraints was reduced, but could not be lifted without distorting the phosphonate geometry.

Table 1. Crystallographic Data for $(UO_2)_3(HO_3PC_6H_5)_2(O_3PC_6H_5)_2 \cdot H_2O$[a]

pattern range (2θ)	7−85°
step-scan increment (2θ)	0.01°
step-scan time	10 s
radiation source	rotating anode
λ	1.5406, 1.5444 Å
empirical formula	$C_{24}H_{24}O_{19}P_4U_3$
fw	1454
space group	$P2_12_12_1$ (No. 19)
a	17.1966(2) Å
b	7.2125(2) Å
c	27.8282(4) Å
V	3451.6(2) Å^3
Z	4
ρ_{calcd}	2.799 g cm^{-3}
T	23 °C
no. of contributing reflns ($K\alpha_1 + K\alpha_2$)	2694
U−O(uranyl) distance and tolerence	1.73(1) Å
P−O distances and tolerence	1.53(1) Å
C−C distances and tolerence	1.38(1) Å
no. of structural parameters	160
no. of profile parameters	11
statistically expected R_{wp}	0.03
R_{wp}	0.128
R_p	0.089
R_F	0.05

[a] $R_{wp} = [\sum w(I_o - I_c)^2/\sum(wI_o{}^2)]^{1/2}$; $R_p = \sum|I_o - I_c|/\sum I_c$; $R_F = \langle|F_o| - |F_c|\rangle/\langle|F_o|\rangle$; expected $R_{wp} = R_{wp}/(\chi^2)^{1/2}$; $\chi^2 = \sum w(I_o - I_c)^2/(N_{obs} - N_{var})$.

The crystallographic data are given in Table 1, and the final Rietveld difference plot is given in Figure 1. Atomic and thermal parameters are listed in Table 2 while bond parameters are presented in Table 3. Metal coordination along with atom labeling is shown in Figure 4. Figures 5 and 6 show three-dimensional aspects of the structure.

Results

Thermal Analysis and Spectroscopic Studies. TGA and DTA analyses (Figure 2) were carried out between room temperature and 850 °C at 10 K/min using Al_2O_3 as a reference. The DTA curve shows a sharp endotherm peak at 152 °C without an associated weight loss.The endotherms at 250 and

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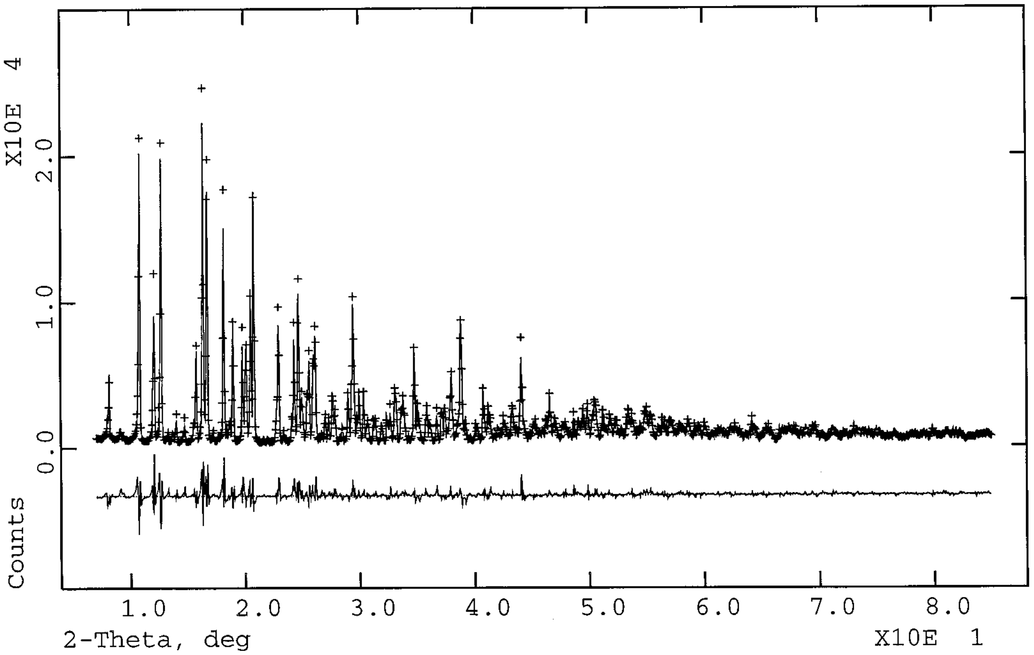

Figure 1. Observed (+) and calculated (—) profiles (X-ray intensity versus 2θ) for the Rietveld refinement. The bottom curve is the difference plot on the same intensity scale. Final Rietveld refinement was carried out between 7 and 85°.

310 °C are partially overlapped with approximate weight losses of 1.2 and 1.4%, respectively. The curve also shows a strong endotherm around 350 °C and very strong exotherms at about 400 and 450 °C. The weight loss corresponding to these exotherms amounts to 21.25%, for a total weight loss of 23.85%. These weight losses may be explained as follows. There are two distinct processes at 250 and 310 °C resulting in a weight loss of 2.64%. The calculated value for the loss of 2 mol of water is 2.48%. One mole of water is present in the tunnels and probably comes out at the lower temperature, and the other arises from the condensation of the two protonated phenylphosphonate groups. These losses are followed by the splitting out of the organic portions of the phosphonate groups, $C_{12}H_{10}$ per two phenylphosphonates. The calculated value for these losses is 21.22%, in close agreement with the observed value. The final thermal decomposition product was a mixture of UP_2O_7 and $U(UO_2)(PO_4)_2$, as identified by their X-ray powder patterns. Thus the total calculated weight loss is 23.75% and the observed value is 23.85%. Rietveld analysis was carried out on the final decomposition product to find out the ratio of these two phases. The refinement showed 0.39(1) molar fraction of UP_2O_7 and 0.61(1) molar fraction of $U(UO_2)(PO_4)_2$. The P/U ratio of 1.31(1) calculated from these data is in good agreement with that derived from the crystal structure analysis of the parent compound (see below).

The IR spectrum was recorded between 4000 and 400 cm^{-1}. The spectrum (Figure 3) shows asymmetric and symmetric stretching vibrations at 3610 and 3540 cm^{-1} corresponding to the P—OH stretching vibrations. The stretching vibration of the —OH group of the water molecule can be seen as a broad band centered at 3225 cm^{-1}. The H—O—H deformation band is seen as a shoulder at 1620 cm^{-1} near the intense band at 1595 cm^{-1} due to the phenyl ring stretching vibration. The bands at 1490 and 1440 cm^{-1} are due to the the skeletal vibrations of the rings. There are several bands around 1000 cm^{-1} corresponding to the stretching of the $-PO_3$ groups. The frequencies due to UO_2 vibrations are seen at 925 (asymmetric) and 850 (symmetric) cm^{-1}.[13] The three bands around 690, 740,

Table 2. Positional and Thermal Parameters

atom	x	y	z	U_{iso},[a] Å^2
U1	0.6140(2)	0.241(1)	0.1362(1)	0.002(2)
U2	0.4994(2)	0.251(1)	0.3785(1)	0.003(3)
U3	0.3166(2)	0.346(1	0.2188(1)	0.006(3)
P1	0.4364(9)	0.239(3)	0.1127(6)	0.002(1)
P2	0.3209(6)	0.250(3)	0.3530(5)	0.002(1)
P3	0.6980(8)	0.335(3)	0.3524(6)	0.002(1)
P4	0.7718(9)	0.311(3)	0.2150(6)	0.002(1)
O1	0.4863(14)	0.060(3)	0.1206(9)	0.002(1)
O2	0.3660(10)	0.244(6)	0.1465(7)	0.003(2)
O3	0.4924(13)	0.404(3)	0.1215(10)	0.003
O4	0.3749(14)	0.414(3)	0.3625(10)	0.003
O5	0.2828(14)	0.261(7)	0.3022(6)	0.003
O6	0.3666(14)	0.066(3)	0.3593(11)	0.003
O7	0.6917(16)	0.187(3)	0.3132(11)	0.003
O8	0.6306(10)	0.298(7)	0.3907(8)	0.003
O9	0.6839(21)	0.531(3)	0.3309(12)	0.003
O10	0.7380(19)	0.127(5)	0.2348(12)	0.003
O11	0.7473(14)	0.322(6)	0.1598(6)	0.003
O12	0.7383(17)	0.492(5)	0.2399(17)	0.003
O13	0.6350(14)	0.241(5)	0.0749(4)	0.003
O14	0.5874(14)	0.222(5)	0.1977(4)	0.003
O15	0.5090(15)	0.222(5)	0.3153(4)	0.003
O16	0.4753(15)	0.229(5)	0.4395(4)	0.003
O17	0.2159(8)	0.334(4)	0.1989(9)	0.003
O18	0.4082(8)	0.341(3)	0.2403(8)	0.003
O(W)	0.5906(17)	0.434(4)	0.2680(10)	0.003
C1	0.3982(19)	0.231(10)	0.0515(6)	0.005(4)
C2	0.3236(22)	0.294(16)	0.0428(8)	0.005
C3	0.2980(17)	0.313(10)	−0.0041(10)	0.005
C4	0.3496(22)	0.292(10)	−0.0417(7)	0.005
C5	0.4272(20)	0.258(9)	−0.0320(8)	0.005
C6	0.4470(22)	0.194(11	0.0133(7)	0.005
C7	0.2410(10)	0.256(6)	0.3959(8)	0.005
C8	0.2499(17)	0.192(17	0.4424(14)	0.005
C9	0.1853(19)	0.165(9)	0.4712(11)	0.005
C10	0.1119(16)	0.192(8)	0.4521(13)	0.005
C11	0.1045(14)	0.294(11)	0.4104(15)	0.005
C12	0.1675(13)	0.302(11)	0.3794(13)	0.005
C13	0.7869(11)	0.325(4)	0.3864(9)	0.005
C14	0.8039(28)	0.476(6)	0.4159(21)	0.005
C15	0.8640(40)	0.464(9)	0.4487(25)	0.005
C16	0.8998(23)	0.296(10)	0.4564(16)	0.005
C17	0.8650(40)	0.136(8)	0.4388(23)	0.005
C18	0.8127(30)	0.152(5)	0.4015(23)	0.005
C19	0.8762(9)	0.304(5)	0.2151(11)	0.005
C20	0.9155(18)	0.436(7)	0.1881(25)	0.005
C21	0.9835(34)	0.392(11)	0.1643(29)	0.005
C22	1.0207(19)	0.227(12)	0.1754(19)	0.005
C23	0.9780(40)	0.086(9)	0.1960(26)	0.005
C24	0.9110(19)	0.131(6)	0.2212(19)	0.005

[a] $U_{iso} = B_{iso}/8\pi^2$.

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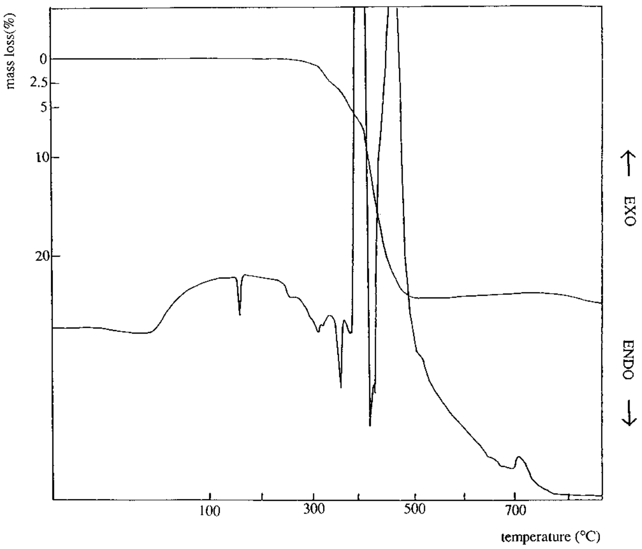

Figure 2. TGA–DTA curves for $(UO_2)_3(HO_3PC_6H_5)_2(O_3PC_6H_5)_2{\cdot}H_2O$.

Table 3. Bond Lengths (Å) for $(UO_2)_3(HO_3PC_6H_5)_2(O_3PC_6H_5)_2{\cdot}H_2O$

U1–O1	2.59(2)	U1–O3	2.44(2)
U1–O4	2.36(2)	U1–O6	2.37(2)
U1–O11	2.46(2)	U1–O13	1.74(1)
U1–O14	1.78(1)	U2–O1	2.24(2)
U2–O3	2.51(2)	U2–O4	2.48(2)
U2–O6	2.70(2)	U2–O8	2.31(2)
U2–O15	1.78(1)	U2–O16	1.76(1)
U3–O2	2.31(2)	U3–O5	2.47(2)
U3–O7	2.62(2)	U3–O9	2.66(2)
U3–O10	2.58(2)	U3–O12	2.96(2)
U3–O17	1.82(1)	U3–O18	1.69(1)
P1–O1	1.57(1)	P1–O2	1.53(1)
P1–O3	1.55(1)	P1–C1	1.82(1)
P2–O4	1.53(1)	P2–O5	1.56(1)
P2–O6	1.55(1)	P2–C7	1.82(1)
P3–O7	1.53(1)	P3–O8	1.60(1)
P3–O9	1.55(1)	P3–C13	1.80(1)
P4–O10	1.55(1)	P4–O11	1.60(1)
P4–O12	1.58(1)	P4–C19	1.80(1)
	phenyl ⟨C–C⟩	1.38(1)	

and 770 cm^{-1} are characteristic of the out-of-plane vibrations of the phenyl rings.[14]

Crystal Structure. The asymmetric unit contains three independent uranyl groups, four phosphonate groups, and a lattice water molecule (Figure 4). The uranium atoms, U1 and U2 are arranged in the form of a zigzag chain along the *b* axis direction with an intermetallic distance of about 4.1 Å (Figure 5). The tunnels run parallel to the short *b* axis. Oxygen atoms O3 and O1 of the P1 phosphonate as well as O4 and O6 of the P2 phosphonate are involved in chelation and bridging these uranium atoms. The arrangement thus creates a kind of double chain, which involves the zigzag chain of metal atoms, along the *b* axis with alternating four-membered rings. One such ring consists of two U atoms (U1, U2) and two O atoms (O1, O4 or O3, O6) and the other involves one U atom (U1, U2) and the chelation group (P1, O1, O3 or P2, O4, O6). This type of connectivity arises because the chelating oxygens also donate an electron pair to adjacent U atoms. This chelation donation bonding is common in metal phosphonate structures.[13] These double chains are connected to each other through O2–U3–O5 atoms aligned in the *a* direction. Thus, adjacent double chains are related to each other by a 2_1 axis and their midpoints are about 7.1 Å apart.

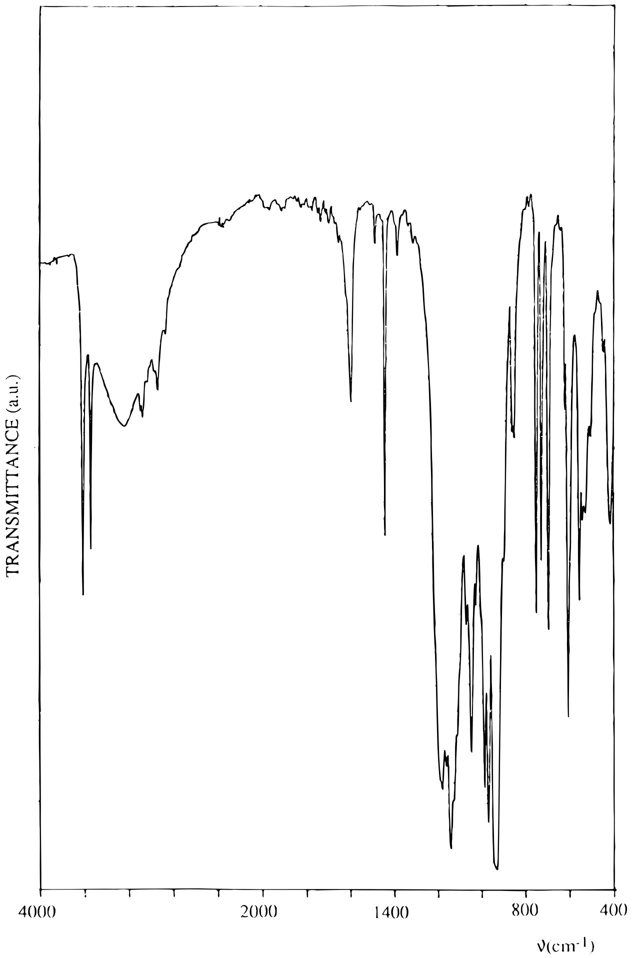

Figure 3. IR spectrum for $(UO_2)_3(HO_3PC_6H_5)_2(O_3PC_6H_5)_2{\cdot}H_2O$.

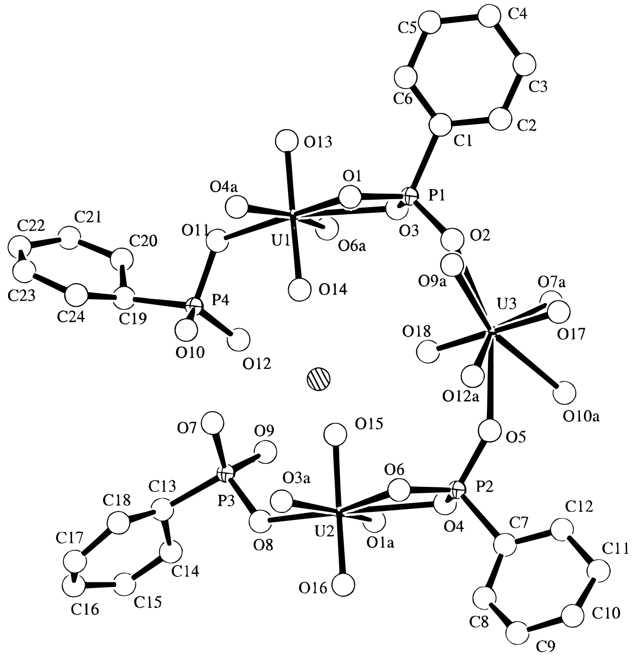

Figure 4. Structure of uranyl phenylphosphonate as viewed down the *b* axis, showing the coordination about the uranium atoms and the numbering scheme. The hatched circle represents the water molecule.

Focusing on the U3 atoms, it is observed in Figure 5 that they form linear chains along the *b* axis direction with intermetallic distances of about 7.2 Å. The U3 atoms are linked by oxygens of P3 (O9, O7) and P4 (O10, O12) phosphonate groups creating eight-membered rings (U3A–O7–P3–O9–U3B–O12–P4–O10). This connectivity also creates a second

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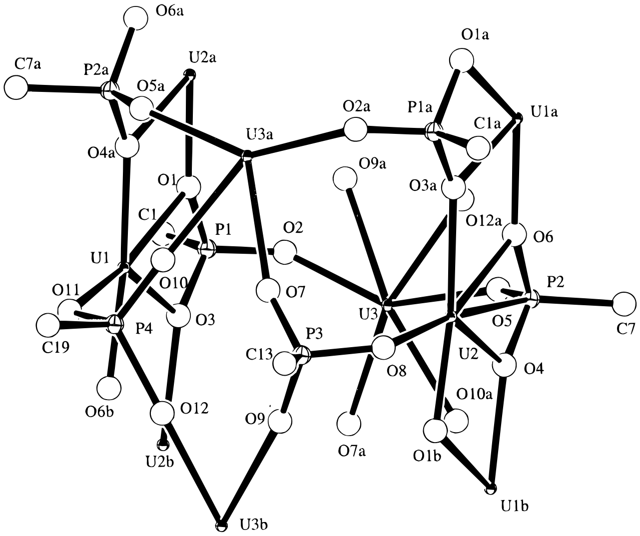

Figure 5. Schematic representation of the linkages between U atoms and phosphonate oxygens along the wall of the channel. Uranyl oxygens and C atoms other than those bonded to P atoms are not included. The *b* axis is vertical.

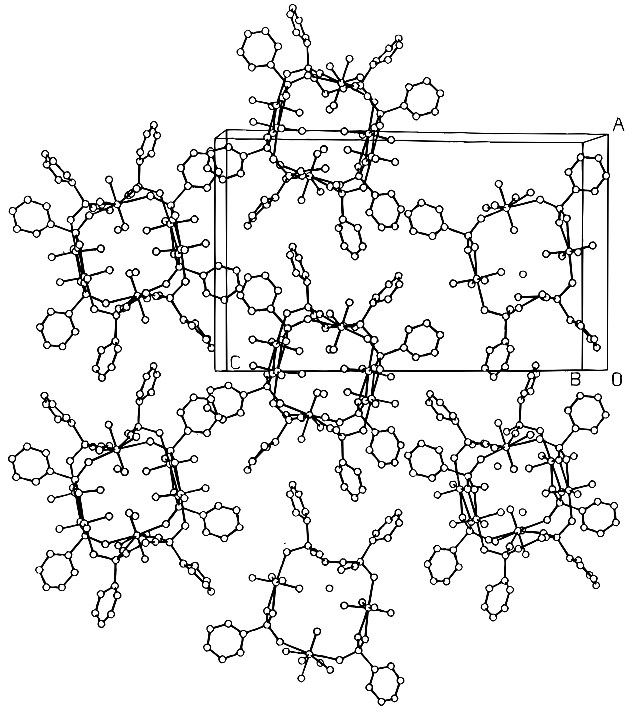

Figure 6. Projection of the structure down the *b* axis, showing unidimensional pores separated by the hydrophobic regions.

linkage between the U1, U2 double chains related by the 2_1 axis, viz. U2−O8−P3−O9−U3−O12−P4−O11−U1. Another eight-membered ring, illustrated by U3A−O2A−P1A−O3A−U2−O8−P3−O7, arises from this connectivity. A second U3 chain about 6.5 Å from the first is created by the 2_1 axis parallel to the *b* axis. These two U3 chains lie on either side of the U1 , U2 double chains, and connecting them creates a tubular structure as shown in Figure 4 and 6. The pore is not quite circular being 7 × 6.5 Å^2. One oxygen of each of the uranyl groups and the lattice water molecule are located within the pore.

The uranium atoms U1 and U2 are seven-coordinated, and their geometries may be described as distorted pentagonal bipyramids with the uranyl oxygens (O13, O14, O15, O16) in the axial positions. On the other hand, U3 is eight-coordinated and has a distorted hexagonal bipyramidal geometry. Among the four phosphonate groups, two are protonated. Since the interaction of P1 and P2 groups in this case is similar to that of the unprotonated phosphonates in $UO_2(O_3PC_6H_5)\cdot 0.7H_2O$, the protons must be on the P3 and P4 phosphonate groups. The oxygens in these phosphonate groups are all two-coordinate whereas two of the oxygens in the P1 and P2 groups are three-coordinate. The U−O bond lengths involving O7 and O9 of P3 as well as O10 and O12 of P4 are longer than those involving other phosphonate oxygens. The two protons thus may be disordered over these four oxygens. The phenyl groups and three uranyl oxygens (one each from the 3 U atoms: O13, O16, O17) are arranged on the outer periphery of the pore. The planes of the phenyl rings of P1 and P2 are almost perpendicular to the *b* axis, while the phenyl rings of the P3 and P4 groups are inclined to the *ac* plane. The stacking interactions between the P1 and P2 phenyl rings as well as those between the P3 and P4 rings hold together the neighboring uranyl−phosphonate tunnels in the lattice (Figure 6).

All the UO_2 groups are nearly linear with O−U−O angles of 174.7(2), 165.3(1), and 174.9(1)° for U1, U2, and U3 atoms, respectively. The average U═O bond length, 1.76(1) Å, is within the error limits of the constrained value (1.73(1) Å). The phosphonate oxygens are located in a plane perpendicular to the O═U═O axes. The average bond angle between the oxygens in this basal plane for U1 and U2 metal atoms is 72°, consistent with a pentagonal arrangement of atoms. In the case of the U3 atom, the arrangement of the phosphonate oxygens is approximately hexagonal, as indicated by the average bond angle of 61°. The polyhedron about the U3 atom however is more distorted compared to those of U1 and U2. Constraining these basal atoms to a regular hexagon using soft constraints resulted in poor *R*-factors, and therefore they were not included in the refinements. The phosphonate groups display regular tetrahedral geometries with expected bond parameters. The phenyl groups are roughly planar with an average C−C bond length of 1.38 Å and an average angle of about 120°. The lattice water molecule is located at the center of the cavity and appears to be held strongly by the surrounding oxygens. The strongest H-bonding interaction is with oxygen atom O9 with an O---O distance of 2.48(3) Å. It is also about 2.5 Å from two uranyl oxygens, O14 and O15, and since uranyl oxygens are weakly polar, they are probably packing contacts rather than regular hydrogen bonds. The location of the water molecule at the center of the unidimensional cavity together with its strong interaction with the sorrounding oxygens is the reason that its loss is seen at a relatively high temperature in the TGA study.

The subject compound of the present study is similar to $UO_2(O_3PC_6H_5)\cdot 0.7H_2O$[4b] in terms of the arrangement of double chains along the wall of the pore and the grouping of phenyl rings although in the latter case all the phenyl rings are perpendicular to the channel axis and the pore consists of six U and six P atoms connected uniformly to form a ring in a plane with a diameter of ∼12.2 Å. It may also be added that the arrangement of the double chains, involving U1 and U2 atoms, in these compounds is similar to that observed in the layered compound $UO_2(O_3PCH_2Cl)$.[15]

Discussion

The uranyl phosphonate compound reported here is the second one recently synthesized to have a tubular tunnel structure. Both compounds have the walls of the tunnels built up through the connectivity of the metal−PO_3 groups. The phenyl rings are located on the outer periphery of the tunnels and serve to space the tunnels in packing arrangements conditioned by van der Waals forces between the phenyl rings of adjacent tunnels. In

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both uranyl compounds, the oxygens of the uranyl groups lie perpendicular to the tunnel wall with one oxygen pointing toward the center of the tunnel and the other pointing outward. The uranyl oxygens pointing away from the tunnels in turn determine the spacing of the phenyl rings since the rings point away from these oxygen atoms. There is thus a hydrophobic–hydrophilic separation of groups. The exterior of the tunnels is essentially hydrophobic and the interior hydrophilic. The separation of polar and nonpolar groups is a feature observable in many metal phosphonate compounds.[14−16] These compounds have shown a remarkable diversity of structures, including layered,[14−16] linear,[17] and tunnel types.[4,6,7] In all cases where both polar and nonpolar groups are present in the structure, they tend to separate as shown here. In the cases of the Al[6] and Cu[7] methylphosphonates, the hydrophobic groups reside inside the tunnels whose walls are made out of the metal phosphate network. These structures are three-dimensional unlike the two uranyl structures described above. In the case of molybdenyl phenylphosphonate, $MoO_2(O_3PC_6H_5)\cdot H_2O$,[16b] the structure consists of double chains with the molybdenyl oxygens of the two chains pointing toward each other while the phenyl rings lie on the opposite sides and point toward phenyl rings of the adjacent double molybdenyl chains.

The solubility of the metal phosphonate compounds increases as the charge on the metal decreases. Zirconium phosphonates are very insoluble, and therefore it is only with the greatest difficulty that single crystals can be prepared.[16h] On the other hand, zinc phosphonates are highly soluble in acid solutions, and therefore by proper adjustments of pH and solution concentrations, it has been possible to obtain single crystals for X-ray studies.[14c] However, by use of powder methods, we have been able to make excellent progress in solving structures of the relatively insoluble phosphonates, thus gaining insight into their chemical behavior. It is therefore appropriate that some discussion of powder methods be introduced here.

Apart from those compounds mentioned in the Introduction,[1−4] a number of simple to fairly complex inorganic compounds have been structurally characterized by X-ray powder methods.[18] Normally conventional heavy-atom methods and direct methods have been employed to derive a structural model which will then be refined using the full pattern. Attempts are also underway in the application of entropy maximization and likelihood ranking to determine unknown crystal structures.[18c] Our recent efforts in this area were focused mainly on *ab initio* structure solution of metal compounds containing organic groups from powder data.[16] Apart from heavier scattering groups like metal and phosphates, these compounds contain large numbers of light atoms such as C and N. In this regard, these compounds are very similar to the organometallic compounds. Although the location and refinement of these light atoms are difficult by using X-ray powder data, we have been successful in arriving at solutions for compounds containing both rigid and flexible organic skeletons. Recently we completed the structure solution of zinc phenyphosphonate intercalated with primary amines containing up to five carbon atoms in the chain.[16g] The nitrogen atom of the amine binds to the metal, while its alkyl chains project into interlayer space. These structures were solved using conventional X-ray powder diffraction data. On the other hand, it was necessary to use a high-intensity synchrotron data set for the structure solution of a mixed-metal phosphonate/phosphate.[16d] In this compound the phosphonate has a large complexant (methylimino)diacetate group that is not bonded to the metal but is projected freely into the interlayer space. These developments show confidence that these powder methods can, in fact, be used for the structure solution of traditional organometallic compounds. The structures of two such compounds have been successfully solved and refined.[19] In most cases, laboratory X-ray sources may be sufficient, but the use of combined synchrotron X-ray and neutron powder data would significantly improve the accuracy of the structural results.[1a]

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