# Syntheses and Crystal Structures of a Linear-Chain Uranyl Phenylphosphinate $UO_2(O_2PHC_6H_5)_2$ and Layered Uranyl Methylphosphonate $UO_2(O_3PCH_3)$

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Two extended uranyl organophosphorus compounds have been synthesized and structurally characterized. Linear-chain uranyl bis(phenylphosphinate), $UO_2(O_2PHC_6H_5)_2$, was synthesized at 60 °C, and its structure was solved by single-crystal methods. $UO_2(O_2PHC_6H_5)_2$ crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 5.648(1)$ Å, $b = 8.115(2)$ Å, $c = 9.171(2)$ Å, $\alpha = 64.97(3)°$, $\beta = 80.59(3)°$, $\gamma = 83.34(3)°$, and $Z = 1$. The geometry of the uranium atom is tetragonal bipyramidal, and the neighboring uranyl ions are bridged by pairs of phenylphosphinate anions. The phenyl groups form two rows pointing in opposite directions of each chain, and neighboring chains arrange in a staircase fashion. Layered uranyl methylphosphonate, $UO_2(O_3PCH_3)$ (UPMe), was synthesized hydrothermally at 200 °C, and its structure was solved by powder pattern X-ray methods and refined by the Rietveld method. UPMe crystallizes in space group $P\bar{1}$ with unit cell parameters $a = 6.4027(3)$ Å, $b = 6.6912(3)$ Å, $c = 7.0983(3)$ Å, $\alpha = 90.473(2)°$, $\beta = 99.684(2)°$, $\gamma = 97.333(2)°$, and $Z = 2$. The uranyl ions, connected by the phosphonate anions, form parallel inorganic layers, and the methyl groups point perpendicularly between the layers.

## Introduction

The area of metal−phosphonate chemistry has expanded significantly in recent years.[1−4] Perhaps the most important factor which has driven this growth has been the ability of metal−phosphonate systems to self-assemble into lattices with functional groups which influence the optical,[5,6] intercalation,[7−11] magnetic,[12,13] electrical,[14] and other properties of these materials, which makes them candidates for potential industrial use. Aside from the applied aspect of metal−phosphonate materials, chemists have prepared a large number of metal−organophosphorus compounds in order to better understand the factors which influence their structure types,[15−24] particularly their dimensionality.[25,26]

Recently, we and others have prepared a number of extended uranyl phosphonates.[27−33] Although the geometry around the uranyl ion changes little in these compounds, extended uranyl phosphonates exhibit a wide variety of structures, linear-chain, tubular, and layered. During the synthesis, sometimes several phases precipitate out, particularly under mild reaction conditions. This multiple phase occurrence results from the relatively

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weak interaction between the uranium atom and the oxygen atoms of the phosphonate moiety in its equatorial plane. Due to this weak metal−ligand interaction, some uranyl phosphonates have shown interesting phase transformations, even under room temperature conditions,[27,28] while other types of phase transformations occur at elevated temperatures.[34] In addition to the rich structural aspect of uranyl phosphonate chemistry, these compounds also exhibit interesting spectroscopic and luminescence properties which are due to the presence of the uranyl ion.[35] In the present work, uranyl methylphosphonate and uranyl phenylphosphinate have been prepared and structurally characterized with the intention to subsequently study their luminescence properties.[36]

## Experimental Section

**Materials.** All reactants were of reagent grade quality, and they were obtained from commercial companies. Uranyl nitrate hexahydrate was recrystallized from water, and other chemicals were used without purification.

**Synthesis of $UO_2(O_2PHC_6H_5)_2$.** A 2.00 g (4.0 mmol) amount of $UO_2(NO_3)_2{\cdot}6H_2O$ (Strem Chemicals) was dissolved in 30 mL of deionized water in a plastic beaker, and 7.5 mL (215 mmol) of 48% HF (Aldrich) was added to it. Next, 2.272 g (16 mmol) of $(HO)(O)PHC_6H_5$ (Aldrich) was dissolved in 30 mL of deionized water and slowly added into the uranyl solution. The U:P:F molar ratio was 1:4:54, and no precipitate appeared. The beaker was covered with a plastic lid and set in an oven at 60 °C. After about 20 h small yellow crystals of irregular shape appeared, and after 3 days they were recovered by filtration, washed, and air-dried.

**Synthesis of $UO_2(O_3PCH_3)$.** A 1.00 g (2.0 mmol) amount of $UO_2(NO_3)_2{\cdot}6H_2O$ was dissolved in about 10 mL of deionized water. Then, 0.288 g (3.0 mmol) of $H_2O_3PCH_3$ (Aldrich) was dissolved in 15 mL of doubly deionized (ddi) $H_2O$ and added to the uranyl solution. No precipitate appeared. The yellow solution was loaded into a 40 mL Teflon-lined steel pressure vessel and placed in an oven at 200 °C. After 5 days, the bomb was taken out, cooled in air, and opened, and the yellow suspension was filtered off, washed, and air-dried.

**Crystal Structure Analysis. $UO_2(O_2PHC_6H_5)_2$.** A yellow crystal of dimensions 0.2 × 0.2 × 0.5 mm was isolated from the solution, mounted on a glass fiber, and then transferred onto the diffractometer under a steady nitrogen stream at a constant temperature of −80 °C. Data collection was carried out on a Siemens P4 diffractometer with the sealed tube X-ray generator operating at 50 kV and 30 mA with Mo Kα radiation ($\lambda = 0.71073$ Å), equipped with a Siemens LT-2 cryostat. Unit cell parameters were calculated from 25 reflections recorded between 15° and 30° in $2\theta$. Intensity data were collected at −80 °C using the $\omega{-}2\theta$ scan mode to a maximum value of $2\theta = 50°$. Three intensity standards were measured every 100 reflections, and their intensities were found to be constant within the entire data collection. A total of 1423 reflections were collected, and the total number of observed unique reflections ($I > 2.0\sigma$) was 1283. An absorption correction was applied, and data were also corrected for Lorenz and polarization effects.

**Table 1.** Crystallographic Data for $UO_2(O_2PHC_6H_5)_2$ and $UO_2(O_3PCH_3)$

| | $UO_2(O_2PHC_6H_5)_2$ | $UO_2(O_3PCH_3)$ |
|---|---|---|
| formula | $C_{12}H_{12}O_6P_2U$ | $CH_3O_5PU$ |
| fw | 552.2 | 364.0 |
| space group | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) |
| $a$ (Å) | 5.648(1) | 6.4027(3) |
| $b$ (Å) | 8.115(2) | 6.6912(3) |
| $c$ (Å) | 9.171(2) | 7.0983(3) |
| α (deg) | 64.97(3) | 90.473(2) |
| $\beta$ (deg) | 80.59(3) | 99.684(2) |
| $\gamma$ (deg) | 83.34(3) | 97.333(2) |
| $V$ (Å$^3$) | 375.2 | 297.2 |
| $Z$ | 1 | 2 |
| temp (°C) | −80 | 20 |
| $\lambda$ (Å) | 0.71073 | 0.730 10 |
| $\rho_{calc}$ (g/cm$^3$) | 2.444 | 4.068 |
| $\mu$ (cm$^{-1}$) | 109 | |
| $R_w$ ($F^2$) [$I > 2\sigma(I)$]$^a$ | 0.062 | |
| $R(F)^a$ | 0.024 | 0.055 |
| $R_p{}^a$ | | 0.079 |
| $R_{wp}{}^a$ | | 0.092 |

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$. $R_w(F^2) = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o)^4]\}^{1/2}$. $R_{wp} = [\sum w(I_o - I_c)^2/\sum w(I_o)^2]^{1/2}$. $R_p = \sum(|I_o - I_c|)/\sum I_c$.

**Table 2.** Atomic Coordinates and $U$(eq) for $UO_2(O_2PHC_6H_5)_2$

| atom | $x$ | $y$ | $z$ | $U$(eq)$^a$ |
|---|---|---|---|---|
| U1 | 0.0000 | 0.0000 | 0.0000 | 0.0152(1) |
| P1 | 0.4156(3) | −0.0414(2) | 0.2762(2) | 0.0184(3) |
| H1 | 0.33(1) | 0.100(9) | 0.305(8) | 0.02(2) |
| O1 | 0.2149(8) | −0.0924(6) | 0.2151(5) | 0.028(1) |
| O2 | 0.3491(8) | 0.0088(7) | −0.1673(5) | 0.031(1) |
| O3 | 0.0262(9) | 0.2301(6) | −0.0371(6) | 0.031(1) |
| C1 | 0.457(1) | −0.2129(8) | 0.4739(7) | 0.019(1) |
| C2 | 0.6742(7) | −0.3141(4) | 0.5035(5) | 0.026(1) |
| C3 | 0.6986(7) | −0.4505(4) | 0.6565(3) | 0.030(1) |
| C4 | 0.5096(5) | −0.4838(4) | 0.7785(4) | 0.032(2) |
| C5 | 0.2927(7) | −0.3815(4) | 0.7511(4) | 0.030(1) |
| C6 | 0.2686(7) | −0.2458(5) | 0.5983(4) | 0.026(1) |

[a] The equivalent isotropic displacement parameter $U$(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table 3.** Selected Bond Distances (Å) and Bond Angles (deg) for $UO_2(O_2PHC_6H_5)_2$

| | | | |
|---|---|---|---|
| U1−O1 | 2.290(4) 2× | P1−O1 | 1.511(4) |
| U1−O2 | 2.280(5) 2× | P1−O2 | 1.503(5) |
| U1−O3 | 1.770(4) 2× | P1−C1 | 1.791(6) |
| | | P1−H1 | 1.31(7) |
| O1−U1−O1 | 180.0 2× | O2−P1−O1 | 115.5(3) |
| O2−U1−O2 | 180.0 2× | O2−P1−C1 | 110.2(3) |
| O3−U1−O3 | 180.0 2× | O1−P1−C1 | 108.9(3) |
| O3−U1−O2 | 90.1(2) 2× | O2−P1−H1 | 112(3) |
| O3−U1−O2 | 89.9(2) 2× | O1−P1−H1 | 106(3) |
| O3−U1−O1 | 89.9(2) 2× | C1−P1−H1 | 103(3) |
| O3−U1−O1 | 90.1(2) 2× | P1−O1−U1 | 143.3(3) |
| O2−U1−O1 | 90.3(2) 2× | P1−O2−U1 | 171.3(3) |
| O2−U1−O1 | 89.7(2) 2× | | |

The structure of $UO_2(O_2PHC_6H_5)_2$ was solved by the Patterson method using the SHELXS-86 program and then refined using the SHELXL-93 program. First, the position of the uranium atom was located in the Patterson map, and the positions of the remaining atoms were obtained in difference Fourier maps. One hydrogen atom was found to be attached to the phosphorus atom, and it remained stable during the refinement. Aromatic hydrogen atoms were placed on the phenyl groups in calculated positions and assigned fixed temperature factors. All non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1283 reflections and 101 parameters. The maximum and minimum residual peaks on the final difference Fourier map corresponded to +1.57 and −1.04 e/Å$^3$. Crystallographic data for $UO_2(O_2PHC_6H_5)_2$ are listed in Table 1, atomic coordinates in Table 2, and the bond distances and bond angles in Table 3.

**$UO_2(O_3PCH_3)$.** X-ray powder data were collected on a Rigaku D/max-B diffractometer mounted on a Rigaku Rotaflex RU200B rotating-anode generator. For a more detailed description of the setup see ref 32. The sample was prepared on a filter paper by using a tubular aerosol suspension chamber[37] to minimize preferred orientation of the crystallites. Data were mathematically stripped of the K$\alpha_2$ contribution, and peak picking was conducted by a modification of the double-

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**Table 4.** Atomic Coordinates and *U*(eq) for $UO_2(O_3PCH_3)$

| atom | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| U | 0.4784(4) | 0.1428(4) | 0.2463(4) | 0.0188(3) |
| P | 0.572(2) | 0.704(2) | 0.258(2) | 0.020(3) |
| O1 | 0.756(3) | 0.189(4) | 0.298(4) | 0.009(3) |
| O2 | 0.199(3) | 0.088(4) | 0.210(5) | 0.009(3) |
| O3 | 0.522(4) | 0.824(3) | 0.077(3) | 0.009(3) |
| O4 | 0.519(4) | 0.827(3) | 0.422(3) | 0.009(3) |
| O5 | 0.458(4) | 0.487(3) | 0.244(4) | 0.009(3) |
| C1 | 0.857(4) | 0.694(6) | 0.0296(6) | 0.02(1) |

[a] The equivalent isotropic displacement parameter *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table 5.** Selected Bond Distances (Å) and Bond Angles (deg) for $UO_2(O_3PCH_3)$

| | | | |
|---|---|---|---|
| U−O1 | 1.74(2) | U−O5 | 2.33(2) |
| U−O2 | 1.76(2) | P−O3 | 1.53(3) |
| U−O3 | 2.51(2) | P−O4 | 1.53(3) |
| U−O3 | 2.31(2) | P−O5 | 1.53(2) |
| U−O4 | 2.49(2) | P−C | 1.81(3) |
| U−O4 | 2.36(2) | | |
| O1−U−O2 | 176(2) | O3−U−O3 | 66(1) |
| O1−U−O3 | 87(2) | O3−U−O4 | 59(1) |
| O1−U−O3 | 92(2) | O3−U−O5 | 84(1) |
| O1−U−O4 | 85(2) | O4−U−O4 | 65(1) |
| O1−U−O4 | 87(2) | O4−U−O5 | 85(1) |
| O1−U−O5 | 90(2) | O3−P−O4 | 107(2) |
| O2−U−O3 | 93(2) | O3−P−O5 | 115(2) |
| O2−U−O3 | 92(2) | O3−P−C | 106(3) |
| O2−U−O4 | 91(2) | O4−P−O5 | 112(2) |
| O2−U−O4 | 89(2) | O4−P−C | 109(3) |
| O−U−O5 | 91(2) | O5−P−C | 108(2) |

derivative method.[38] The pattern was indexed to a triclinic unit cell using Ito and trial and error methods.[39] The cell parameters, as confirmed by profile refinement with the program FULLPROF,[40] were $a = 6.3906(7)$ Å, $b = 6.6776$ (8) Å, $c = 7.0849(8)$ Å, $\alpha = 90.411(4)°$, $\beta = 99.633(4)°$, and $\gamma = 97.329(5)°$. After integrated intensities were extracted, a Patterson map was calculated with the program GSAS,[41] revealing the positions of the U and O atoms. After the structure model was completed by subsequent difference Fourier calculations, the structure was refined in space group $P\bar{1}$. Distance constraints were introduced to fix the geometry of the $UO_2^{2+}$ and the $[H_3CPO_3]^{2-}$ groups, and the thermal displacement parameters of the O atoms were constrained to be equal. For the final structure refinement, high-resolution data were collected at the X7A beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. The sample was loaded into a thin-wall glass capillary (0.3 mm), and data were collected with radiation of wavelength $\lambda = 0.7301$ Å. A silicon (111) double-crystal monochromator was used in combination with a linear position sensitive detector with an active area of 10 × 1 cm. The detector was stepped at intervals of 0.25° over the angular range of 2.5−70° in 2$\theta$ with counting times ranging from 40 s at low angle to 640 s at high angle. The total counting time was 20 h. The data appeared to be affected by preferred orientation (presumably along the capillary wall) that could not be modeled completely. Therefore, the region below 7.5° in 2$\theta$ containing the (100) reflection was excluded; the two largest difference peaks are due to the mismatch of the observed and calculated intensities of the (200) and the (300) reflections. The crystallographic data and agreement factors are listed in Table 1, atomic coordinates in Table 4, and the bond lengths and bond angles in Table 5. The observed and the calculated powder patterns and the difference plot are shown in Figure 1.

**Structure of $UO_2(O_2PHC_6H_5)_2$.** Uranyl phenylphosphinate forms a pseudo-one-dimensional structure with the uranyl-to-phosphinate ratio 1:2 (Figure 2). The uranium atom has a slightly distorted tetragonal bipyramidal coordination geometry, and it is located on an inversion center. The uranyl oxygen atoms form the apexes of the bipyramid, and four oxygen atoms of four different phosphinate groups reside in the equatorial plane. The axial U−O bonds are much shorter (1.77 Å) than the equatorial U−O bonds (2.28−2.29 Å) (Table 3). The uranyl axis is almost perpendicular to the equatorial plane with the $O_{axial}$−U−$O_{equatorial}$ angles (Table 4), and the O−U−O bond angles in the equatorial plane being almost 90°. The neighboring uranyl ions are spaced apart by 5.648 Å, and they are bridged by pairs of phenylphosphinate groups. Unlike the phosphonate group which contains three oxygen atoms capable of metal coordination, the phosphinate group has only two such oxygen atoms, and in $UO_2(O_2PHC_6H_5)_2$, both of them are used to coordinate the neighboring uranyl ions. The phosphorus atom has a tetrahedral geometry which is distorted primarily due to the small size of the coordinating hydrogen atom (Table 4). The P−O bond distances of 1.50−1.51 Å, the P−C bond of 1.791 Å, and the P−H bond of 1.31 Å are in good agreement with corresponding distances found in other phosphonates and phosphinates.[42]

Each uranyl phenylphosphinate chain arranges its phenyl groups into two rows which point in opposite directions, away from the inorganic backbone of the chain (Figure 3). The chains propagate along the *a*-axis, and they stack upon each other in a staircase fashion where the phenyl groups of one chain overlap with the phenyl groups of the neighboring chain. This stacking creates a pseudolayer of weakly held uranyl phosphinate sheets in the ac plane with a distance between the sheets $b \sin \alpha = 7.35$ Å.

**Structure of $UO_2(O_3PCH_3)$ (UPMe).** Unlike in $UO_2(O_2PHC_6H_5)_2$, uranyl methylphosphonate, UPMe, forms layers, in which the uranyl-to-phosphorus ratio is 1:1. The coordination about the uranyl ion is pentagonal bipyramidal with the uranyl oxygens located in the apexes and the phosphonate oxygens coordinating the metal atom in the equatorial plane (Figure 4). As in all uranyl compounds, the U−$O_{axial}$ bonds are much shorter (1.74−1.76 Å) than the U−$O_{equatorial}$ bonds (2.31−2.51 Å). The uranyl axis is almost perpendicular to the equatorial plane. The methylphosphonate anion contains three oxygen atoms; it uses two of them (O3 and O4) for chelation of one uranyl group, and the third oxygen O5 is used for bridging to an adjacent uranyl group. In addition to chelation, oxygen atoms O3 and O4 bond to adjacent U atoms through electron pair donation. The uranyl ions are arranged along the *c*-axis in a zigzag fashion and chelated by the phosphonate groups to form double chains propagating along the *c*-axis. These double chains are linked together by the bridging oxygens O5 to form the inorganic backbone of a UPMe layer. The methyl groups attached to the phosphorus atoms protrude into the interlayer space (Figure 5). No solvent molecules reside between the layers, and the methyl groups thus determine the interlayer distance to be only 6.35 Å.

## Discussion

The structural motif of the new uranyl phenylphosphinate strongly resembles that of the ethanol phase of uranyl phenylphosphonate, $UO_2(HO_3PC_6H_5)_2{\cdot}2CH_3CH_2OH$.[30] In both compounds, the uranium atoms are six-coordinate with pairs of their respective oxophosphorus moieties bridging the neighboring metal centers. In both structures, the phenyl groups are arranged in two rows pointing away from each other, and the uranium atoms represent the centers of symmetry. Actually, there are two differences between the two compounds. The first is the distance between the weakly bound pseudolayers formed by overlapping of neighboring linear chains (Figure 3). In uranyl phosphinate which contains no solvent molecules, the distance is merely 7.35 Å, whereas in uranyl phosphonate the intercalated ethanol molecules expand the distance between the pseudolayers to 10.88 Å. The second difference is the fact that the phospho-

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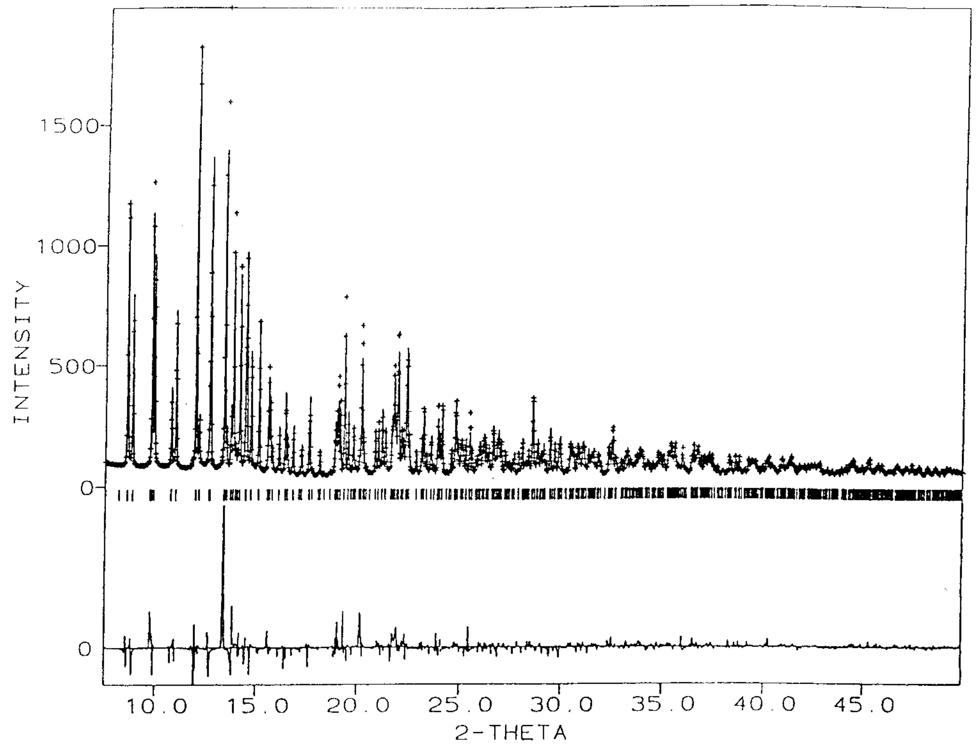

**Figure 1.** Observed (+) and calculated (−) profiles for the Rietveld refinement of $(UO_2)O_3PCH_5$ and the difference plot.

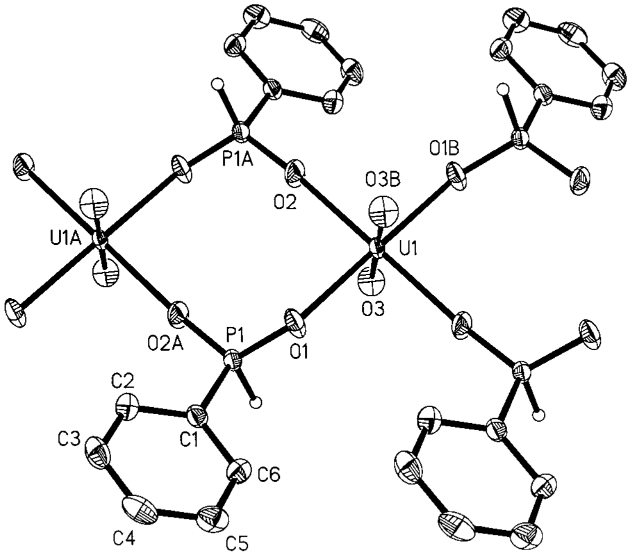

**Figure 2.** Coordination and bonding in uranyl phenylphosphite, $UO_2(O_2PHC_6H_5)_2$, together with the atom-labeling scheme.

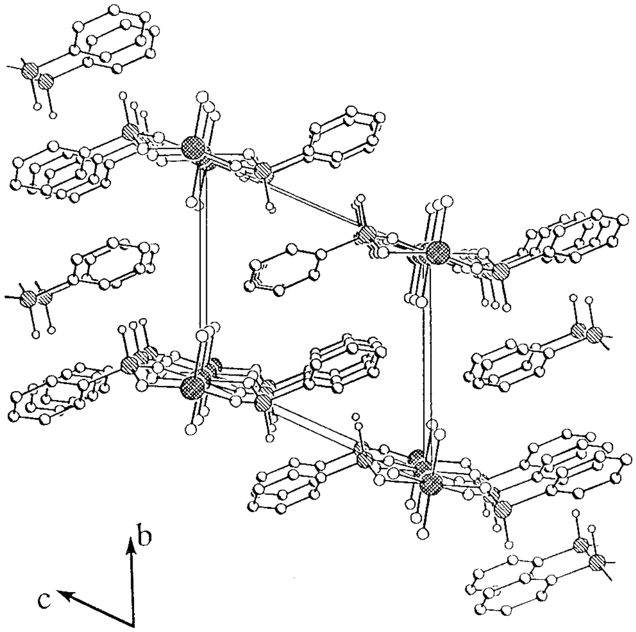

**Figure 3.** Unit cell of $UO_2(O_2PHC_6H_5)_2$ viewed along the propagating linear chains (*a*-axis) illustrating the packing of the linear chains. The cross-hatched atoms at the corners of the unit cell are U atoms, the lined smaller circles are P atoms, and the smallest open circles are H atoms bonded to P.

nate group in the ethanol intercalate contains a pendant OH group instead of the H atom found in the phosphinate. Although the number of oxygen atoms capable of coordinating metal ions generally does influence the structure type and the dimensionality of an extended compound, in this particular case, this factor has little consequence on the structure type. This is given by the low, one-dimensional nature of the linear chains thereby making the protonated oxygen atom in the phosphonate uninvolved in the coordination. Similar bridging of metal centers by pairs of phosphonate anions with a metal-to-phosphorus ratio of 1:2 has been observed in two other uranyl phenylphosphonates, the cis α-UPP ($[UO_2(HO_3PC_6H_5)_2(H_2O)]_2 \cdot 8H_2O$) and the trans *β*-UPP $[UO_2(HO_3PC_6H_5)_2(H_2O) \cdot 2H_2O]$.[28] In these two linear-chain compounds only two oxygen atoms are used for coordination, and the third is protonated. Both of those compounds, however, contain an extra water molecule in the coordination sphere of the uranium atom thereby making its geometry pentagonal bipyramidal.

Several phosphinates of transition metals that have been prepared earlier also show a similar pattern in which neighboring metal cations are bridged by pairs of phenylphosphinate anions to form linear chains. The coordination around the metal ion, however, strongly depends on the nature of the metal cation. Zinc phenylphosphinate, $Zn(O_2PHC_6H_5)_2$, also forms linear zigzag chains where the metal ions are bridged by pairs of

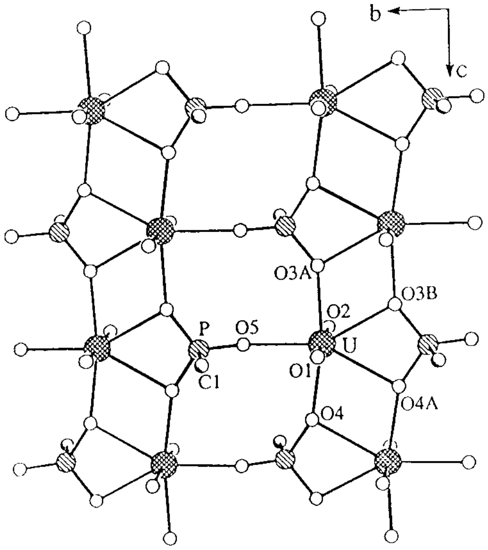

**Figure 4.** Structure of a portion of the uranyl methylphosphonate (UPMe) layer showing the in-plane connectivity and atom-labeling scheme.

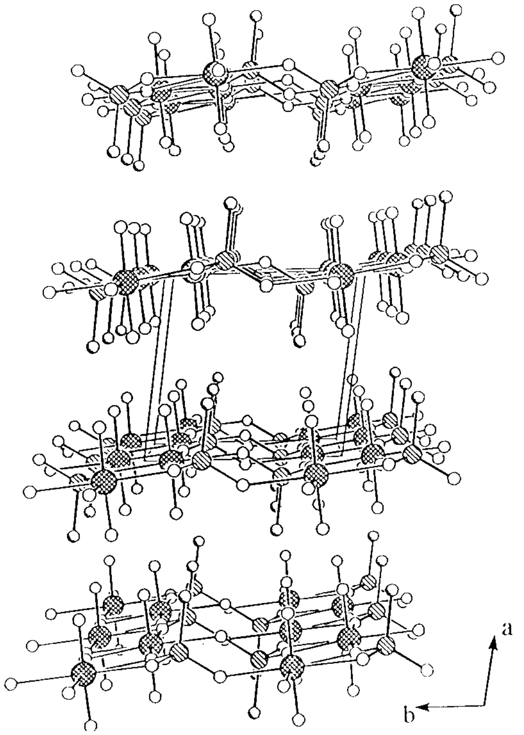

**Figure 5.** Packing diagram for UPMe and the outline of a unit cell. The atom designation is as for Figure 3.

bidentate anions; however, the zinc atom has a tetrahedral coordination.[43] Lead(II) bis(biphenylphosphinate), $Pb(O_2P(C_6H_5)_2)_2$, forms linear chains where the metal cations are bridged by pairs of phosphinate anions.[44] In the lead compound, however, the metal centers are trigonal bipyramidal due to the presence of the electron lone pair on lead(II), and the hydrogen atoms coordinating phosphorus are replaced by extra phenyl groups.

Utilization of three oxygen atoms on the phosphonate allows the uranyl methylphosphonate to expand into two dimensions due to the chelation-bridging connectivity of the uranyl ions. This chelation-bridging pattern has been observed in two other uranyl phosphonates, in layered uranyl chloromethylphosphonate, $UO_2(O_3PCH_2Cl)$,[32] and in tubular uranyl phenylphosphonate $\gamma$-UPP ($UO_2(O_3PC_6H_5)\cdot 0.7H_2O$).[31] In fact, the layered uranyl chloromethylphosphonate and methylphosphonate are isostructural. The only difference between the two compounds is the presence of the chlorine atom in the former phosphonate, which makes its interlayer distance slightly larger (6.50 Å) compared to the interlayer distance of the latter (6.35 Å).

A number of methylphosphonates and chloromethylphosphonates of other metal cations have been prepared. One phase of zinc chloromethylphosphonate monohydrate, $Zn(O_3PCH_2Cl)\cdot H_2O$, forms a layered structure with octahedral metal cation coordination and with a chelation-bridging motif similar to that observed in the title uranyl compound.[45] In this phase, two of the zinc coordination sites are occupied by a single chelating phosphonate group, another three positions are occupied by three bridging phosphonate groups, and the last site is occupied by a solvating water molecule. Copper methylphosphonate monohydrate, $Cu(O_3PCH_3)\cdot H_2O$, forms a layered structure in which the metal cation is pentagonal pyramidal.[46] Four coordination sites of the copper cation are occupied by oxygen atoms of four different phosphonate groups, and the fifth site is occupied by a water molecule. Several hydrogen bond interactions interconnect the atoms within the layer, but no chelation is observed. Another copper methylphosphonate, $\beta$-$Cu(O_3PCH_3)$, forms an interesting tunnel structure in which the walls of the tunnels are linked together by an array of metal−oxygen bonds and the methyl groups point inside the tunnels.[12]

When comparing the two prepared compounds and considering the influence of the organophosphorus moiety on their structures, one realizes that the quality of their organic groups has little consequence on the overall structure and dimensionality. If the organic group is sufficiently small, divalent and tetravalent metal (M = Zr, Cd, Zn, Ni, Co) phosphonates typically form layered structures.[47−53] In these lattices, the layers are formed by the metal−oxygen−phosphorus bonds and the organic groups protrude into the interlayer space. Uranyl methyphosphonate belongs in this family. The number of oxygen atoms available for coordination of the metal ion, however, plays a very important role in determining the maximum dimensionality a prepared compound with an extended structure can have. To the best of our knowledge, two- or three-dimensional metal phosphinates have not been prepared yet, which stems from the fact that only two oxygen atoms are present in the phosphinate group. This does not necessarily mean that a compound cannot have a lower dimensionality than expected, e.g., due to protonation of the phosphonate oxygen atoms, as was observed in α-UPP and $\beta$-UPP, which in turn depends on the p$K_a$ of the starting acid and pH of the solution.

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Layered zirconium phosphinates can be prepared in the presence of orthophosphate ions.[54] The layers have the structure of the $\gamma$-phase of zirconium phosphate,[55] $Zr(PO_4)[(HO)_2PO_2]\cdot 2H_2O$. All four oxygens of the phosphate group but only two oxygens of the dihydrogen phosphate group are bonded to the Zr atoms in octahedral coordination. In the phosphin ate compounds both hydroxyls in the latter group are replaced by organic groups, but the layered nature of the compound arises from the availability of six oxygens from two bonding groups, while the two organic groups extend into the interlayer space.

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**Supporting Information Available:** A table of anisotropic thermal parameters (S1) for $UO_2(O_2PHC_6H_5)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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