

Crystal Structures of Three Framework Alkali Metal Uranyl Phosphate Hydrates

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Three homeotypic hydrated alkali metal uranyl phosphates, $A_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$, $A = \text{Cs}$ (*CsUP*), Rb (*RbUP*), K (*KUP*), were synthesized by hydrothermal methods. Intensity data were collected at room temperature using $\text{MoK}\alpha$ radiation and a CCD-based area detector. Their crystal structures were solved by Patterson (*CsUP*) and direct (*RbUP*, *KUP*) methods and refined by full-matrix least-squares techniques to agreement indices (*CsUP*, *RbUP*, *KUP*) $wR_2 = 0.048, 0.230, 0.072$ for all data, and $R1 = 0.023, 0.078, 0.038$ calculated for 5338, 4738, 4514 unique observed reflections ($|F_o| \geq 4\sigma_F$), respectively. The compound *CsUP* is orthorhombic, space group $\text{Cmc}2_1$, $Z = 4$, $a = 14.854(1)$, $b = 13.879(1)$, $c = 12.987(1)$ Å, $V = 2677.5(3)$ Å³.

Both *RbUP* and *KUP* are monoclinic, space group Cm , but are presented in the unconventional pseudo-orthorhombic space group $\text{Fm}11$ to facilitate comparison with *CsUP* and to allow a model for *RbUP* that includes the effects of pseudo-merohedral twinning. *RbUP* is monoclinic, space group $\text{Fm}11$, $Z = 4$, $a = 15.72(2)$, $b = 13.84(1)$, $c = 13.05(1)$ Å, $\alpha = 90.39^\circ(2)$, $V = 2839(5)$ Å³; *KUP* is monoclinic, space group $\text{Fm}11$, $Z = 4$, $a = 15.257(1)$, $b = 13.831(1)$, $c = 13.007(1)$ Å, $\alpha = 91.760^\circ(1)$, $V = 2743.4(3)$ Å³. The structures consist of sheets of phosphate tetrahedra and uranyl pentagonal bipyramids, with composition $[(\text{UO}_2)(\text{PO}_4)]^-$, that are topologically identical to the uranyl silicate sheets in uranophane-beta. These sheets are connected by a uranyl pentagonal bipyramid in the interlayer that shares corners with two phosphate tetrahedra on each of two adjacent sheets and whose fifth equatorial vertex is an H_2O group, resulting in an open framework with alkali metal cations in the larger cavities of the structures. Where *CsUP* and *RbUP* have two alkali metal positions and a H_2O group in these cavities, *KUP* has four K atoms and two H_2O groups, all of which are partially occupied, in the interstitial sites. © 2002

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Key Words: uranyl phosphate; crystal structure refinement; hydrothermal synthesis.

INTRODUCTION

Uranyl minerals and compounds possess extraordinary chemical and structural complexity (1,2). They are important for understanding the genesis of uranium deposits, and water-rock interactions in such deposits (3). Uranyl phases are also common alteration products of nuclear waste in conditions similar to those expected in the proposed repository at Yucca Mountain (4,5), and may impact significantly upon the release of radionuclides in such systems (6–9). Uranyl phosphates are important for understanding the mobility of uranium in natural systems (10), and have been found in soils contaminated by actinides (11). As part of our ongoing research into the structures of uranyl phosphates (12), we have synthesized three compounds with a novel uranyl phosphate framework.

EXPERIMENT

Crystal Synthesis

Single crystals of $\text{Cs}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$ —*CsUP*, $\text{Rb}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$ —*RbUP*, and $\text{K}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$ —*KUP*, were obtained by hydrothermal reaction. The reactants (proportions listed in the order *CsUP*, *RbUP*, *KUP*) were natural fluorapatite (0.1183, 0.1122, 0.1007 g), ideally $\text{Ca}_5(\text{PO}_4)_3\text{F}$, from the Liscombe Deposit, near Wilberforce, Ontario, Canada, concentrated HNO_3 (0.15, 0.16, and 0.15 g), $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ (0.1160, 0.1231, and 0.1094 g), alkali metal nitrate ($\text{CsNO}_3 = 0.5968$ g, $\text{RbNO}_3 = 0.4439$ g, $\text{KNO}_3 = 0.3040$ g) and ultrapure H_2O (4 mL each). The reactants were weighed into Teflon-lined Parr autoclaves and heated at $200(1)^\circ\text{C}$ in a Fisher Isotemp oven for 7 days. The autoclaves were then removed to air and allowed to cool to room temperature. The products were filtered and washed with ultrapure water, and consisted of bright-yellow translucent crystals up to 150, 500, and $50\ \mu\text{m}$ in

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maximum dimension for *CsUP*, *RbUP*, and *KUP*, respectively. Product purity was confirmed by powder X-ray diffraction; however, incomplete reaction of the starting fluorapatite precluded quantitative determination of reaction yields.

Single-Crystal X-Ray Diffraction

For each of the three compounds, a suitable crystal was mounted on a Bruker PLATFORM three-circle X-ray diffractometer operated at 50 keV and 40 mA and equipped with a 4 K APEX CCD detector with a crystal to detector distance of 4.7 cm. A sphere of three-dimensional data was collected using graphite-monochromatized $\text{MoK}\alpha$ X-radiation and frame widths of 0.3° in ω , with count-times per frame of 20 s for *CsUP*, 10 s for *RbUP*, and 40 s for *KUP*. Data were collected for $4^\circ \leq 2\theta \leq 69^\circ$ in 15, 8 and 30.5 h, respectively; comparison of the intensities of equivalent reflections measured at different times during data collection showed no significant decay for any of the three compounds. The unit cells (Table 1) were refined with 11,755 reflections for *CsUP*, 4327 reflections for *RbUP* and

3061 reflections for *KUP* using least-squares techniques. The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. In each case, a semi-empirical absorption correction was applied by modeling the crystal as a plate and rejecting data within 3° of the primary X-ray beam. For *CsUP*, this procedure lowered R_{INT} of 7480 intense reflections from 0.188 to 0.058; for *RbUP*, R_{INT} of 2638 intense reflections dropped from 0.182 to 0.074; and for *KUP*, R_{INT} of 1676 intense reflections decreased from 0.089 to 0.027.

Systematic absences of reflections for *CsUP* were consistent with space groups *Cmc2*₁, *Cmcm* and *Ama2*; trial solutions were obtained for all three space groups, but reasonable interatomic distances were obtained only in the case of *Cmc2*₁. A total of 24,922 intensities was collected, of which 460 were discarded as being inconsistent with the space group; only one of these intensities was classified as observed, corresponding to a single unique reflection. Of the 24,462 remaining intensities, 5698 were unique ($R_{\text{INT}} = 0.063$), of which 5338 were classified as observed reflections ($|F_o| \geq 4\sigma_F$).

TABLE 1
Crystallographic and Structure Data for $\text{Cs}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$, $\text{Rb}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$
and $\text{K}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$

Compound	<i>CsUP</i>	<i>RbUP</i>	<i>KUP</i>
a (Å)	14.8542(10)	15.72(2)	15.2566(8)
b (Å)	13.8792(10)	13.839(14)	13.8313(12)
c (Å)	12.9873(9)	13.051(11)	13.0069(7)
α	90°	$90.385^\circ(18)$	$91.760^\circ(1)$
V (Å ³)	2677.5(3)	2839(5)	2743.4(3)
Space group	<i>Cmc2</i> ₁	<i>Fm</i> 11 (unconventional)	<i>Fm</i> 11 (unconventional)
Z	4	4	4
Formula	$\text{Cs}_2(\text{UO}_2)_5(\text{PO}_4)_4(\text{H}_2\text{O})_2$	$\text{Rb}_2(\text{UO}_2)_5(\text{PO}_4)_4(\text{H}_2\text{O})_2$	$\text{K}_2(\text{UO}_2)_5(\text{PO}_4)_4(\text{H}_2\text{O})_2$
Formula weight (g/mol)	2031.87	1936.99	1844.25
λ (Å)	0.71073	0.71073	0.71073
$F(000)$	3432	3288	3144
μ (mm ⁻¹)	33.17	32.16	30.06
D_{calc} (g/cm ³)	5.041(1)	4.532(8)	4.465(1)
Crystal size (mm)	$0.14 \times 0.14 \times 0.02$	$0.40 \times 0.08 \times 0.01$	$0.05 \times 0.05 \times 0.005$
θ range of data collection	$2.01\text{--}34.52^\circ$	$2.50\text{--}34.15^\circ$	$2.50\text{--}34.54^\circ$
Data collected	$-23 \leq h \leq 23, -22 \leq k \leq 22,$ $-20 \leq l \leq 20$	$-24 \leq h \leq 24, -21 \leq k \leq 21,$ $-20 \leq l \leq 20$	$-24 \leq h \leq 24, -21 \leq k \leq 21,$ $-20 \leq l \leq 20$
Total reflections	24462	10344	12813
Unique reflections, R_{int}	5698, 0.063	5406, 0.080	5616, 0.044
Unique $ F_o \geq 4\sigma_F$	5338	4738	4514
Completeness $\theta = 34.5^\circ, 34.15^\circ, 34.5^\circ$	98.40%	94.40%	96.70%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Parameters varied	188	116	119
$R1^a$ for $ F_o \geq 4\sigma_F$	0.023	0.078	0.038
$R1^a$ all data, $wR2^b$ all data	0.025, 0.048	0.096, 0.230	0.048, 0.072
Goodness of fit all data	0.994	1.097	0.891
Max. min. peaks ($e/\text{Å}^3$)	3.4, -3.3	10.3, -7.8	3.8, -2.2

^a $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$.

^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$.

In the case of *RbUP*, systematic absences of reflections were consistent with space groups *Cm*, *C2* and *C2/m*, and assigning phases to a set of normalized structure factors gave a mean value of $|E^2 - 1|$ of 0.712, consistent with space groups *Cm* and *C2*. Trial solutions were obtained for both space groups, but reasonable interatomic distances were obtained only in the case of *Cm*. A total of 20,644 intensities was collected, of which 10,300 were discarded as being inconsistent with the space group; three of these intensities were classified as observed, corresponding to three unique reflections. Of the 10,344 remaining intensities, 5406 were unique ($R_{\text{INT}} = 0.080$), of which 4738 were classified as observed reflections ($|F_o| \geq 4\sigma_F$).

Systematic absences of reflections for *KUP* were also consistent with space groups *Cm*, *C2* and *C2/m*, and assigning phases to a set of normalized structure factors gave a mean value of $|E^2 - 1|$ of 0.759, consistent with space groups *Cm* and *C2*. Trial solutions were obtained for both space groups, but reasonable interatomic distances were obtained only in the case of *Cm*. A total of 25,725 intensities was collected, of which 12,912 were discarded as being inconsistent with the space group; none of these intensities were classified as observed. Of the 12,813 remaining intensities, 5616 were unique ($R_{\text{INT}} = 0.044$), of which 4514 were classified as observed reflections ($|F_o| \geq 4\sigma_F$).

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-ray Crystallography, Volume IV* (13). The Bruker SHELXTL Version 5 (14) series of programs was used for the solution and refinement of the crystal structures.

STRUCTURE SOLUTION AND REFINEMENT

The structure of *CsUP* was solved by Patterson methods and was refined successfully based on F^2 for all unique data in space group *Cmc2*₁. A structure model including the racemic twin law $[-100/0-10/00-1]$ and anisotropic displacement parameters for all atoms converged, and gave an agreement index (*R1*) of 0.023, calculated for the 5338 observed unique reflections ($|F_o| \geq 4\sigma_F$). The racemic twin-component scale factor refined to 0.577(5). The final value of wR_2 was 0.048 for all data using the structure-factor weights assigned during least-squares refinement: $a = 0.0136$ and $b = 0$, where $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{0.5}$, $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$, and $P = \frac{1}{3}\max(0, F_o^2) + \frac{2}{3}F_c^2$. In the final cycle of refinement the mean parameter shift/e.s.d. was 0.000, and the maximum peaks in the final difference-Fourier maps were 3.4 and $-3.3 e/\text{\AA}^3$. The atomic positional parameters and displacement parameters are given in Table 2, and selected

TABLE 2
Atomic Coordinates ($\times 10^4$) and Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$

<i>CsUP</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
U(1)	2216(1)	2393(1)	5743(1)	11(1)	16(1)	9(1)	9(1)	0(1)	-1(1)	-1(1)
U(2)	2698(1)	-76(1)	4259(1)	13(1)	19(1)	9(1)	9(1)	0(1)	1(1)	1(1)
U(3)	0	1063(1)	2327(1)	14(1)	13(1)	12(1)	16(1)	-1(1)	0	0
Cs(1)	0	4009(1)	1657(1)	46(1)	40(1)	28(1)	68(1)	10(1)	0	0
Cs(2)	0	1986(1)	-1266(1)	54(1)	63(1)	55(1)	43(1)	8(1)	0	0
P(1)	1897(1)	2405(1)	3329(1)	11(1)	16(1)	8(1)	9(1)	0(1)	-1(1)	-2(1)
P(2)	2356(1)	-154(1)	6658(1)	11(1)	16(1)	9(1)	8(1)	0(1)	0(1)	-1(1)
O(1)	1039(3)	2332(3)	5946(3)	22(1)	20(2)	23(2)	22(2)	-3(2)	0(2)	-6(2)
O(2)	3394(3)	2404(3)	5533(3)	22(1)	25(3)	24(2)	17(2)	-4(2)	-2(2)	-5(2)
O(3)	2614(3)	2555(3)	2493(3)	16(1)	21(2)	19(2)	9(2)	2(1)	2(2)	-1(2)
O(4)	2271(3)	716(3)	5917(3)	20(1)	40(3)	8(2)	11(2)	2(1)	-1(2)	0(2)
O(5)	2787(3)	-915(3)	5935(3)	16(1)	30(3)	9(2)	8(2)	-1(1)	2(2)	4(2)
O(6)	1910(3)	3266(2)	4109(3)	13(1)	23(2)	9(2)	7(2)	-2(1)	0(1)	-3(1)
O(7)	2165(3)	1548(3)	4043(3)	15(1)	26(2)	10(2)	11(2)	1(1)	-4(1)	0(2)
O(8)	1591(3)	-500(3)	4142(3)	20(1)	17(2)	22(2)	22(2)	4(2)	3(2)	2(2)
O(9)	3818(3)	322(3)	4452(3)	26(1)	28(3)	23(2)	28(2)	-2(2)	-1(2)	-3(2)
O(10)	3003(3)	81(3)	7531(3)	20(1)	22(2)	24(2)	12(2)	-2(1)	1(2)	-6(2)
O(11)	0	530(5)	3550(4)	25(1)	25(4)	34(3)	15(3)	9(2)	0	0
O(12)	0	1585(5)	1090(4)	24(1)	27(4)	33(3)	14(3)	3(2)	0	0
O(13)	967(3)	2292(3)	2884(3)	17(1)	18(2)	14(2)	19(2)	-2(1)	-5(2)	-2(2)
O(14)	1449(3)	-459(3)	7060(3)	21(1)	16(2)	22(2)	26(2)	1(2)	3(2)	-1(2)
OW(15)	0	-574(6)	1456(9)	62(3)	47(6)	33(4)	107(8)	-43(5)	0	0
OW(16)	0	6167(7)	2177(12)	112(6)	191(17)	35(5)	108(11)	18(6)	0	0

Note. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement parameter exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for $\text{Cs}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$

U(1)–O(1)	1.769(5)			P(2)–O(14)	1.507(5)	O(14)–P(2)–O(10)	111.5(2)
U(1)–O(2)	1.772(5)	O(1)–U(1)–O(2)	177.7(2)	P(2)–O(10)	1.522(5)	O(14)–P(2)–O(5)	112.8(3)
U(1)–O(3)a	2.287(4)	O(1)–U(1)–O(3)a	87.9(2)	P(2)–O(5)	1.549(4)	O(10)–P(2)–O(5)	109.6(3)
U(1)–O(4)	2.340(4)	O(1)–U(1)–O(4)	88.4(2)	P(2)–O(4)	1.551(4)	O(14)–P(2)–O(4)	111.2(3)
U(1)–O(5)b	2.361(4)	O(1)–U(1)–O(5)b	91.8(2)	$\langle \text{P(2)–O} \rangle$	1.53	O(10)–P(2)–O(4)	110.4(2)
U(1)–O(6)	2.485(3)	O(1)–U(1)–O(6)	88.3(2)			O(5)–P(2)–O(4)	100.9(2)
U(1)–O(7)	2.502(4)	O(1)–U(1)–O(7)	94.5(2)				
$\langle \text{U(1)–O} \rangle$	2.22			Cs(1)–OW(16)	3.070(11)		
				Cs(1)–O(13)e	3.215(5)	OW(16)–Cs(1)–O(13)e	128.0(2)
				Cs(1)–O(13)	3.215(5)	OW(16)–Cs(1)–O(13)	128.0(2)
U(2)–O(8)	1.753(4)			Cs(1)–O(2)g	3.409(6)	OW(16)–Cs(1)–O(2)g	130.9(1)
U(2)–O(9)	1.771(5)	O(8)–U(2)–O(9)	176.6(2)	Cs(1)–O(2)h	3.409(6)	OW(16)–Cs(1)–O(2)h	130.9(1)
U(2)–O(10)c	2.289(4)	O(8)–U(2)–O(10)c	95.7(2)	Cs(1)–O(10)h	3.414(6)	OW(16)–Cs(1)–O(10)h	64.3(1)
U(2)–O(6)d	2.382(3)	O(8)–U(2)–O(6)d	84.1(2)	Cs(1)–O(10)g	3.414(6)	OW(16)–Cs(1)–O(10)g	64.3(1)
U(2)–O(7)	2.405(4)	O(8)–U(2)–O(7)	89.7(2)	Cs(1)–O(12)	3.433(8)	OW(16)–Cs(1)–O(12)	179.6(3)
U(2)–O(5)	2.472(4)	O(8)–U(2)–O(5)	88.3(2)	Cs(1)–O(9)g	3.480(5)	OW(16)–Cs(1)–O(9)g	85.5(3)
U(2)–O(4)	2.496(4)	O(8)–U(2)–O(4)	89.1(2)	Cs(1)–O(9)h	3.480(5)	OW(16)–Cs(1)–O(9)h	85.5(3)
$\langle \text{U(2)–O} \rangle$	2.23			$\langle \text{Cs(1)–O} \rangle$	3.36		
U(3)–O(11)	1.752(6)			Cs(2)–O(12)	3.110(6)		
U(3)–O(12)	1.763(6)	O(11)–U(3)–O(12)	179.3(3)	Cs(2)–O(8)f	3.181(4)	O(12)–Cs(2)–O(8)f	73.7(1)
U(3)–O(13)	2.335(5)	O(11)–U(3)–O(13)	91.6(2)	Cs(2)–O(8)c	3.181(4)	O(12)–Cs(2)–O(8)c	73.7(1)
U(3)–O(13)e	2.335(5)	O(11)–U(3)–O(13)e	91.6(2)	Cs(2)–OW(16)i	3.265(13)	O(12)–Cs(2)–OW(16)i	138.6(3)
U(3)–O(14)c	2.344(4)	O(11)–U(3)–O(14)c	89.0(1)	Cs(2)–O(2)h	3.445(5)	O(12)–Cs(2)–O(2)h	51.4(1)
U(3)–O(14)f	2.344(4)	O(11)–U(3)–O(14)f	89.0(1)	Cs(2)–O(2)g	3.445(5)	O(12)–Cs(2)–O(2)g	51.4(1)
U(3)–OW(15)	2.539(7)	O(11)–U(3)–OW(15)	91.5(4)	Cs(2)–O(11)f	3.501(8)	O(12)–Cs(2)–O(11)f	83.6(2)
$\langle \text{U(3)–O} \rangle$	2.20			Cs(2)–OW(15)f	3.548(12)	O(12)–Cs(2)–OW(15)f	136.2(2)
				$\langle \text{Cs(2)–O} \rangle$	3.33		
P(1)–O(13)	1.505(4)	O(13)–P(1)–O(3)	112.3(2)				
P(1)–O(3)	1.536(5)	O(13)–P(1)–O(7)	112.5(2)				
P(1)–O(7)	1.559(4)	O(3)–P(1)–O(7)	110.3(2)				
P(1)–O(6)	1.566(4)	O(13)–P(1)–O(6)	109.8(2)				
$\langle \text{P(1)–O} \rangle$	1.54	O(3)–P(1)–O(6)	110.2(2)				
		O(7)–P(1)–O(6)	101.2(2)				

Note. Symmetry transformations used to generate equivalent atoms: (a) $-x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (b) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (c) $x, -y, z - \frac{1}{2}$; (d) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (e) $-x, y, z$; (f) $-x, -y, z - \frac{1}{2}$; (g) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (h) $-x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (i) $-x, -y + 1, z - \frac{1}{2}$.

interatomic distances and angles are in Table 3. The locations of the H atoms in the unit cell were not determined.

The structure of *RbUP* was initially solved in space group *Cm* using direct methods and the unit cell $a = 13.05(1)$, $b = 15.72(1)$, $c = 9.479(8)$, $\beta = 133.12(1)^\circ$, and was refined successfully based on F^2 for all unique data. This model refined to an unusually high agreement index (*R1*) of 0.117. In addition, several significant electron-density peaks were present in the difference-Fourier maps at locations incompatible with additional atomic sites. Inspection of the observed and calculated structure factors showed that the most disagreeable reflections all had $F_{\text{obs}} > F_{\text{calc}}$, consistent with the presence of twinning. Re-examination of the raw intensity data showed that the twinning involved essentially complete overlap of the diffraction patterns that corresponded to each twin

component. The transformation matrix $[0-10/-10-2/100]$ was applied to obtain an unconventional face-centered pseudo-orthorhombic cell with $a = 15.72(2)$, $b = 13.84(1)$, $c = 13.05(1)$, $\alpha = 90.39(2)^\circ$, and to allow a model that included the effects of pseudo-merohedral twinning. The structure of *RbUP* was solved in space group *Fm11* using direct methods and refined to an agreement index (*R1*) of 0.214. The twin law $[-100/0-10/001]$ was applied along with the racemic twin law $[-100/0-10/00-1]$ and the structure was refined according to published methods (15, 16), resulting in a significant improvement of the agreement index. The twin-component scale factor refined to 0.45(3) and the racemic twin-component scale factor refined to 0.565(3). The final structure model including anisotropic displacement parameters for U, P and Rb atoms converged, and gave an agreement index (*R1*) of 0.078, calculated for the 4738 observed unique reflections

TABLE 4
Atomic Coordinates ($\times 10^4$) and Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$

<i>RbUP</i>	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	2657(1)	-3478(1)	6526(1)	14(1)	16(1)	18(1)	9(1)	3(1)	0(1)	-2(1)
U(2)	-2268(1)	8984(1)	10029(1)	14(1)	16(1)	16(1)	9(1)	1(1)	-1(1)	1(1)
U(3)	0	-4560(1)	8359(2)	16(1)	13(1)	21(1)	14(1)	-3(1)	0	0
Rb(1)	5000	-2163(6)	6396(8)	42(2)	20(2)	44(4)	61(5)	-19(4)	0	0
Rb(2)	0	-2153(8)	5664(8)	45(2)	25(3)	60(5)	51(6)	14(4)	0	0
P(1)	2811(6)	-3579(8)	4096(7)	17(2)	18(4)	20(4)	12(3)	4(3)	1(3)	-2(3)
P(2)	-1880(6)	9092(8)	12418(7)	15(2)	15(3)	20(4)	9(3)	-6(3)	0(3)	-3(3)
O(1)	1570(19)	-3090(20)	6520(30)	23(5)						
O(2)	3763(19)	-3860(20)	6460(30)	22(5)						
O(3)	2170(17)	-3380(20)	3270(20)	20(5)						
O(4)	-2204(18)	9880(20)	11720(20)	19(5)						
O(5)	-1943(17)	8195(19)	11670(20)	16(5)						
O(6)	2930(20)	-2720(20)	4850(30)	26(6)						
O(7)	2450(20)	-4340(20)	4860(30)	24(6)						
O(8)	-1160(20)	9120(30)	9860(20)	31(7)						
O(9)	-3360(19)	8780(20)	10240(20)	22(5)						
O(10)	-2470(20)	8980(30)	13300(20)	20(4)						
O(11)	0	-5070(30)	9570(40)	24(8)						
O(12)	0	-9060(30)	2130(40)	25(8)						
O(13)	3640(20)	-3870(20)	3630(20)	28(6)						
O(14)	-940(20)	9210(20)	12780(20)	23(5)						
OW(15)	0	-2820(90)	8980(100)	110(40)						
OW(16)	0	-2980(80)	3560(100)	100 ^a						

Note. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement parameter exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

^aFixed during refinement.

($|F_o| \geq 4\sigma_F$). The final value of wR_2 was 0.230 for all data using the structure-factor weights assigned during least-squares refinement: $a = 0.1293$ and $b = 860.0$, where wR_2 , a , and b have the same definitions as above. In the final cycle of refinement the mean parameter shift/e.s.d. was 0.000, and the maximum peaks in the final difference-Fourier maps were 10.3 and -7.8 e/\AA^3 . The atomic positional parameters and displacement parameters are given in Table 4, and selected interatomic distances and angles are in Table 5. The locations of the H atoms in the unit cell were not determined. The final agreement indices are somewhat higher than expected for a well-behaved crystal, and there is a higher-than-normal uncertainty in the atomic positional parameters, which is reflected in the relatively large errors reported for the interatomic distances. The uncertainties in the final refinement of *RbUP* are attributed to the twinning; material from two separate syntheses was examined, but all of the crystals were twinned, and data were collected using the best available crystal.

The structure of *KUP* was solved initially in space group *Cm* using direct methods and the unit cell $a = 13.007(1)$, $b = 15.257(1)$, $c = 9.347(1)$, $\beta = 132.306(1)^\circ$, and was refined successfully based on F^2 for all unique data. A structure model including the racemic twin law $[-100/0-10/00-1]$ and anisotropic displacement parameters for

U and P atoms converged, and gave an agreement index (*R1*) of 0.038, calculated for the 4514 observed unique reflections ($|F_o| \geq 4\sigma_F$). The racemic twin-component scale factor refined to 0.43(1). The final value of wR_2 was 0.072 for all data using the structure-factor weights assigned during least squares refinement: $a = 0.0196$ and $b = 0$, where wR_2 , a , and b have the same definitions as above. In the final cycle of refinement the mean parameter shift/e.s.d. was 0.000, and the maximum peaks in the final difference-Fourier maps were 3.8 and -2.2 e/\AA^3 . To facilitate comparison with *CsUP* and *RbUP*, the transformation matrix $[0-10/-10-2/100]$ was applied to obtain an unconventional face-centered pseudo-orthorhombic cell with $a = 15.257(1)$, $b = 13.831(1)$, $c = 13.007(1)$, $\alpha = 91.760(1)^\circ$. The structure of *KUP* was solved in space group *Fm11* using direct methods and refined (with the same racemic twin law) to the identical agreement indices listed above as no other twinning was involved, and the transformation from *Cm* to *Fm11* is merely a mathematical restatement of the same structure model. The atomic positional parameters and displacement parameters are given in Table 6, and selected interatomic distances and angles are in Table 7. The locations of the H atoms in the unit cell were not determined.

The refined solutions obtained for *CsUP*, *RbUP* and *KUP* were checked with the ADDSYM algorithm in the

TABLE 5
Selected Interatomic Distances (Å) and Angles (°) for $\text{Rb}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$

U(1)–O(1)	1.79(3)			P(2)–O(10)	1.48(3)	O(10)–P(2)–O(4)	109.3(18)
U(1)–O(2)	1.82(3)	O(1)–U(1)–O(2)	176.9(15)	P(2)–O(4)	1.51(3)	O(10)–P(2)–O(14)	111.9(17)
U(1)–O(3)a	2.29(3)	O(1)–U(1)–O(3)a	95.8(13)	P(2)–O(14)	1.55(3)	O(4)–P(2)–O(14)	115.2(17)
U(1)–O(4)b	2.40(3)	O(1)–U(1)–O(4)b	90.3(12)	P(2)–O(5)	1.58(3)	O(10)–P(2)–O(5)	110.8(18)
U(1)–O(5)c	2.41(3)	O(1)–U(1)–O(5)c	87.6(11)	<P(2)–O>	1.53	O(4)–P(2)–O(5)	99.9(15)
U(1)–O(6)	2.47(4)	O(1)–U(1)–O(6)	91.6(14)			O(14)–P(2)–O(5)	109.1(16)
U(1)–O(7)	2.49(3)	O(1)–U(1)–O(7)	90.8(13)				
<U(1)–O>	2.24			Rb(1)–O(14j)	3.00(3)		
				Rb(1)–O(14c)	3.00(3)	O(14j)–Rb(1)–O(14c)	59.2(12)
U(2)–O(8)	1.76(3)			Rb(1)–OW(16)p	3.05(13)	O(14j)–Rb(1)–OW(16)	71.4(18)
U(2)–O(9)	1.76(3)	O(8)–U(2)–O(9)	176.7(15)	Rb(1)–O(2)	3.05(3)	O(14j)–Rb(1)–O(2)	141.6(9)
U(2)–O(10)d	2.30(3)	O(8)–U(2)–O(10)d	93.1(14)	Rb(1)–O(2)k	3.05(3)	O(14j)–Rb(1)–O(2)k	98.9(8)
U(2)–O(7)e	2.35(3)	O(8)–U(2)–O(7)e	89.9(14)	Rb(1)–O(5)j	3.11(3)	O(14j)–Rb(1)–O(5)j	49.2(8)
U(2)–O(6)f	2.39(3)	O(8)–U(2)–O(6)f	88.4(14)	Rb(1)–O(5)c	3.11(3)	O(14j)–Rb(1)–O(5)c	108.4(8)
U(2)–O(5)	2.47(3)	O(8)–U(2)–O(5)	87.3(12)	Rb(1)–O(8)c	3.25(3)	O(14j)–Rb(1)–O(8)c	75.2(8)
U(2)–O(4)	2.52(3)	O(8)–U(2)–O(4)	90.8(13)	Rb(1)–O(8)j	3.25(3)	O(14j)–Rb(1)–O(8)j	107.4(9)
<U(2)–O>	2.22			Rb(1)–OW(15)l	3.28(13)	O(14j)–Rb(1)–OW(15)l	138.4(16)
				<Rb(1)–O>	3.12		
U(3)–O(11)	1.73(5)			Rb(2)–O(9)c	2.94(3)		
U(3)–O(12)g	1.75(5)	O(11)–U(3)–O(12)g	179(2)	Rb(2)–O(9)m	2.94(3)	O(9)c–Rb(2)–O(9)m	122.5(12)
U(3)–O(13)a	2.37(4)	O(11)–U(3)–O(13)a	91.7(10)	Rb(2)–OW(16)	2.97(13)	O(9)c–Rb(2)–OW(16)	89.6(12)
U(3)–O(13)h	2.37(4)	O(11)–U(3)–O(13)h	91.7(10)	Rb(2)–O(1)	3.00(3)	O(9)c–Rb(2)–O(1)	62.7(7)
U(3)–O(14)i	2.38(3)	O(11)–U(3)–O(14)i	89.8(14)	Rb(2)–O(1)n	3.00(3)	O(9)c–Rb(2)–O(1)n	169.1(10)
U(3)–O(14)b	2.38(3)	O(11)–U(3)–O(14)b	89.8(14)	Rb(2)–O(11)o	3.23(5)	O(9)c–Rb(2)–O(11)o	61.3(6)
U(3)–OW(15)	2.53(12)	O(11)–U(3)–OW(15)	96(3)	Rb(2)–O(12)g	3.27(5)	O(9)c–Rb(2)–O(12)g	118.0(6)
<U(3)–O>	2.22			<Rb(2)–O>	3.05		
P(1)–O(13)	1.49(4)	O(13)–P(1)–O(3)	110.1(17)				
P(1)–O(3)	1.51(3)	O(13)–P(1)–O(6)	111(2)				
P(1)–O(6)	1.55(3)	O(3)–P(1)–O(6)	112.9(18)				
P(1)–O(7)	1.56(4)	O(13)–P(1)–O(7)	113.5(19)				
<P(1)–O>	1.53	O(3)–P(1)–O(7)	110.1(18)				
		O(6)–P(1)–O(7)	99.0(17)				

Note. Symmetry transformations used to generate equivalent atoms: (a) $-x + \frac{1}{2}, y, z + \frac{1}{2}$; (b) $-x, y - \frac{3}{2}, z - \frac{1}{2}$; (c) $x + \frac{1}{2}, y - 1, z - \frac{1}{2}$; (d) $-x - \frac{1}{2}, y, z - \frac{1}{2}$; (e) $-x, y + \frac{3}{2}, z + \frac{1}{2}$; (f) $x - \frac{1}{2}, y + 1, z + \frac{1}{2}$; (g) $x, y + \frac{1}{2}, z + \frac{1}{2}$; (h) $x - \frac{1}{2}, y, z + \frac{1}{2}$; (i) $x, y - \frac{3}{2}, z - \frac{1}{2}$; (j) $-x + \frac{1}{2}, y - 1, z - \frac{1}{2}$; (k) $-x + 1, y, z$; (l) $x + \frac{1}{2}, y, z - \frac{1}{2}$; (m) $-x - \frac{1}{2}, y - 1, z - \frac{1}{2}$; (n) $-x, y, z$; (o) $x, y + \frac{1}{2}, z - \frac{1}{2}$; (p) $x + \frac{1}{2}, y, z + \frac{1}{2}$.

program PLATON (17–19); no higher symmetry was found.

RESULTS

Structure Description

In *CsUP*, there are three symmetrically independent U atoms, each of which is part of an approximately linear $(\text{UO}_2)^{2+}$ cation. In each case, the uranyl ions are coordinated by five additional anions arranged at the equatorial positions of pentagonal bipyramids, with the uranyl O atoms at the apices of the bipyramids. The equatorial anions of U(1) and U(2) consist of O atoms, whereas the equatorial anions of U(3) consist of four O atoms and an H_2O group.

The U(1) and U(2) pentagonal bipyramids share an equatorial edge, giving a chain of alternating U(1) and U(2) bipyramids that is one polyhedron wide. Phosphate tetrahedra are attached to either side of the chains by sharing edges with the uranyl polyhedra (Fig. 1). The orientations of the phosphate tetrahedra alternate along the length of any uranyl phosphate chain such that the apical (non-sheet) tetrahedral ligand occurs alternately above and below the sheet. Translationally equivalent uranyl phosphate chains are joined by the sharing of equatorial vertices of uranyl pentagonal bipyramids with phosphate tetrahedra from adjacent chains, resulting in sheets that are parallel to (100). The uranyl phosphate chains are topologically identical to the uranyl silicate chains in uranophane-beta, $\text{Ca}[\text{UO}_2]\text{SiO}_3(\text{OH})_2(\text{H}_2\text{O})_5$ (20).

TABLE 6
Atomic Coordinates ($\times 10^4$) and Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{K}_2(\text{UO}_2)(\text{UO}_2)(\text{PO}_4)_4(\text{H}_2\text{O})_2$

<i>KUP</i>	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	2244(1)	1369(1)	1882(1)	12(1)	20(1)	8(1)	7(1)	0(1)	1(1)	-2(1)
U(2)	2671(1)	3903(1)	3380(1)	17(1)	27(1)	12(1)	12(1)	0(1)	-2(1)	-2(1)
U(3)	5000	2841(1)	220(1)	16(1)	14(1)	15(1)	18(1)	-7(1)	0	0
P(1)	1883(2)	1455(2)	4282(2)	10(1)	17(1)	8(1)	5(1)	0(1)	1(1)	-1(1)
P(2)	2762(2)	3789(2)	951(2)	12(1)	20(2)	6(1)	11(1)	-2(1)	1(1)	0(1)
K(1)	0	259(7)	3311(8)	43(2)						
K(2)	5000	246(9)	2508(10)	55(3)						
K(3)	0	-221(12)	5093(14)	103(5)						
K(4)	5000	1868(9)	3369(10)	73(4)						
O(1)	1110(5)	1489(5)	1702(6)	20(2)						
O(2)	3381(6)	1215(6)	2114(6)	22(2)						
O(3)	2556(5)	1360(5)	5138(6)	11(2)						
O(4)	2909(5)	4681(5)	1702(6)	10(2)						
O(5)	2394(5)	3057(5)	1715(6)	14(2)						
O(6)	2176(5)	2284(5)	3562(5)	11(1)						
O(7)	1926(5)	564(5)	3541(6)	14(2)						
O(8)	1595(6)	4310(5)	3388(6)	18(2)						
O(9)	3798(6)	3521(6)	3302(7)	28(2)						
O(10)	2058(6)	4009(6)	131(7)	23(2)						
O(11)	5000	3308(9)	-989(11)	37(3)						
O(12)	5000	2410(9)	1491(10)	33(3)						
O(13)	3613(6)	3442(6)	466(7)	30(2)						
O(14)	970(5)	1589(5)	4672(6)	19(2)						
OW(15)	5000	4537(13)	979(14)	71(5)						
OW(16)	5000	2730(30)	5260(20)	57(8)						
OW(17)	5000	1020(40)	4430(40)	140(20)						

Note. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement parameter exponent takes the form: $-2\pi^2[h^2a^*{}^2 U_{11} + \dots + 2hka^* b^* U_{12}]$.

The U(3) pentagonal bipyramid is located in the interlayer, between the uranyl phosphate sheets. Four equatorial oxygen atoms of the U(3) pentagonal bipyramid are shared with phosphate tetrahedra, providing linkage of the uranyl phosphate sheets, and resulting in an open uranyl phosphate framework structure (Fig. 2). The coordination polyhedron about U(3) is completed by an H_2O group—OW(15).

The two symmetrically unique Cs atoms occupy the larger cavities of the structure along with an interstitial H_2O group—OW(16)—(Fig. 3); Cs(1) is in ten-fold coordination with a mean Cs(1)—O distance of 3.36 Å, and Cs(2) is in eight-fold coordination with a mean Cs(2)—O distance of 3.33 Å. The Cs atoms are coordinated primarily by the O atoms of the uranyl cations (Table 3).

The structures of *CsUP*, *RbUP* and *KUP* are homeotypic frameworks, following the definition given in (21); *Cm* is a subgroup of *Cmc2₁*, and the connectivity of the uranyl polyhedra and phosphate tetrahedra are identical in all three structures. *RbUP* and *KUP* are lower symmetry derivatives of *CsUP* and differ from it in the positions of the alkali metal atoms and the interstitial H_2O groups, and in the details of the configuration of the uranyl phosphate framework. *RbUP* and *KUP* are isostructural, with the

exception of their alkali metal atomic positions and interstitial H_2O groups.

In *RbUP* the large channels in the framework are occupied by an interstitial H_2O group, OW(16), and two Rb atoms (Fig. 4); the latter are coordinated mainly by oxygen atoms of the uranyl cations (Table 5); Rb(1) is in ten-fold coordination with a mean Rb(1)—O distance of 3.12 Å, and Rb(2) is in seven-fold coordination with a mean Rb(2)—O distance of 3.05 Å.

In *KUP*, the interstitial sites contain four K atoms and two H_2O groups, all of which are partially occupied. K(1) is in nine-fold coordination with a mean K(1)—O of 3.05 Å, K(2) is in seven-fold coordination with a mean K(2)—O of 3.07 Å, K(3) is in seven-fold coordination with a mean K(3)—O of 3.18 Å, and K(4) is in six-fold coordination with a mean K(4)—O of 2.89 Å. Because of the site occupancy disorder present in *KUP*, characterization of the contents of the interstitial sites is difficult; the magnitudes of the displacement parameters are highly correlated with the site occupancy factors during least-squares refinement. In the model presented here, the K and interstitial H_2O sites were constrained during refinement to be half-occupied; K(1) is 2.43(2) Å from K(3), whereas K(2) is 2.48(2) Å from K(4), OW(16) is 2.57(6) Å from OW(17), and OW(17) is 1.84(6) Å from K(4).

TABLE 7
Selected Interatomic Distances (Å) and Angles (°) for $\text{K}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$

U(1)–O(1)	1.755(8)			K(1)–O(14)	2.916(12)		
U(1)–O(2)	1.774(9)	O(1)–U(1)–O(2)	177.4(4)	K(1)–O(14)g	2.916(12)	O(14)–K(1)–O(14)g	61.0(4)
U(1)–O(3)a	2.288(7)	O(1)–U(1)–O(3)a	89.8(3)	K(1)–O(7)	2.982(8)	O(14)–K(1)–O(7)	49.8(2)
U(1)–O(4)b	2.350(7)	O(1)–U(1)–O(4)b	89.2(3)	K(1)–O(7)g	2.982(8)	O(14)–K(1)–O(7)g	110.8(4)
U(1)–O(5)	2.362(7)	O(1)–U(1)–O(5)	89.1(3)	K(1)–O(9)h	3.024(12)	O(14)–K(1)–O(9)h	142.9(4)
U(1)–O(6)	2.495(7)	O(1)–U(1)–O(6)	91.6(3)	K(1)–O(9)b	3.024(12)	O(14)–K(1)–O(9)b	100.4(3)
U(1)–O(7)	2.505(8)	O(1)–U(1)–O(7)	88.3(3)	K(1)–OW(15)h	3.16(2)	O(14)–K(1)–OW(15)h	139.1(3)
$\langle \text{U(1)–O} \rangle$	2.22			K(1)–O(1)g	3.220(11)	O(14)–K(1)–O(1)g	109.0(4)
				K(1)–O(1)	3.220(11)	O(14)–K(1)–O(1)	78.0(3)
				$\langle \text{K(1)–O} \rangle$	3.05		
U(2)–O(8)	1.734(9)						
U(2)–O(9)	1.800(10)	O(8)–U(2)–O(9)	176.5(4)				
U(2)–O(10)c	2.314(9)	O(8)–U(2)–O(10)c	98.8(3)	K(2)–OW(17)	2.69(6)		
U(2)–O(6)	2.381(7)	O(8)–U(2)–O(6)	90.3(3)	K(2)–O(2)e	2.864(11)	OW(17)–K(2)–O(2)e	89.5(7)
U(2)–O(7)d	2.382(7)	O(8)–U(2)–O(7)d	86.1(3)	K(2)–O(2)	2.864(11)	OW(17)–K(2)–O(2)	89.5(7)
U(2)–O(5)	2.467(7)	O(8)–U(2)–O(5)	89.3(3)	K(2)–O(8)b	3.001(11)	OW(17)–K(2)–O(8)b	79.0(7)
U(2)–O(4)	2.490(8)	O(8)–U(2)–O(4)	89.7(3)	K(2)–O(8)I	3.001(11)	OW(17)–K(2)–O(8)i	79.0(7)
$\langle \text{U(2)–O} \rangle$	2.22			K(2)–O(12)	3.308(16)	OW(17)–K(2)–O(12)	92.0(13)
				K(2)–O(11)j	3.366(18)	OW(17)–K(2)–O(11)j	76.1(12)
				$\langle \text{K(2)–O} \rangle$	3.07		
U(3)–O(11)	1.719(14)						
U(3)–O(12)	1.774(13)	O(11)–U(3)–O(12)	177.5(6)	K(3)–OW(16)h	2.85(5)		
U(3)–O(13)e	2.293(9)	O(11)–U(3)–O(13)	89.0(3)	K(3)–O(14)g	2.974(16)	OW(16)h–K(3)–O(14)g	149.2(3)
U(3)–O(13)	2.293(9)	O(11)–U(3)–O(13)e	89.0(3)	K(3)–O(14)	2.974(16)	OW(16)h–K(3)–O(14)	149.2(3)
U(3)–O(14)a	2.371(7)	O(11)–U(3)–O(14)a	90.9(4)	K(3)–O(10)k	3.316(11)	OW(16)h–K(3)–O(10)k	71.2(3)
U(3)–O(14)f	2.371(7)	O(11)–U(3)–O(14)f	90.9(4)	K(3)–O(10)j	3.316(11)	OW(16)h–K(3)–O(10)j	71.2(3)
U(3)–OW(15)	2.518(18)	O(11)–U(3)–OW(15)	89.2(6)	K(3)–O(9)h	3.402(17)	OW(16)h–K(3)–O(9)h	64.1(6)
$\langle \text{U(3)–O} \rangle$	2.19			K(3)–O(9)b	3.402(17)	OW(16)h–K(3)–O(9)b	64.1(6)
				$\langle \text{K(3)–O} \rangle$	3.18		
P(1)–O(14)	1.491(8)	O(14)–P(1)–O(3)	113.2(4)				
P(1)–O(3)	1.523(8)	O(14)–P(1)–O(6)	112.5(4)				
P(1)–O(7)	1.542(8)	O(14)–P(1)–O(7)	110.0(4)	K(4)–O(12)	2.577(18)		
P(1)–O(6)	1.569(7)	O(3)–P(1)–O(6)	108.9(4)	K(4)–OW(16)	2.702(18)	O(12)–K(4)–OW(16)	137.0(11)
$\langle \text{P(1)–O} \rangle$	1.53	O(3)–P(1)–O(7)	110.1(4)	K(4)–O(9)e	2.934(13)	O(12)–K(4)–O(9)e	73.9(4)
		O(7)–P(1)–O(6)	101.5(4)	K(4)–O(9)	2.934(13)	O(12)–K(4)–O(9)	73.9(4)
				K(4)–O(2)	3.081(12)	O(12)–K(4)–O(2)	65.6(3)
				K(4)–O(2)e	3.081(12)	O(12)–K(4)–O(2)e	65.6(3)
				$\langle \text{K(4)–O} \rangle$	2.89		
P(2)–O(13)	1.515(10)	O(10)–P(2)–O(4)	111.2(4)				
P(2)–O(5)	1.546(8)	O(13)–P(2)–O(10)	111.9(5)				
P(2)–O(10)	1.551(10)	O(13)–P(2)–O(4)	111.7(5)				
P(2)–O(4)	1.566(7)	O(13)–P(2)–O(5)	111.9(4)				
$\langle \text{P(2)–O} \rangle$	1.54	O(13)–P(2)–U(2)	117.3(4)				
		O(5)–P(2)–O(10)	109.7(5)				
		O(5)–P(2)–O(4)	99.8(4)				

Note. Symmetry transformations used to generate equivalent atoms: (a) $-x + \frac{1}{2}, y, z - \frac{1}{2}$; (b) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (c) $-x + \frac{1}{2}, y, z + \frac{1}{2}$; (d) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (e) $-x + 1, y, z$; (f) $x + \frac{1}{2}, y, z - \frac{1}{2}$; (g) $-x, y, z$; (h) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (i) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (j) $x, y - \frac{1}{2}, z + \frac{1}{2}$; (k) $-x, y - \frac{1}{2}, z + \frac{1}{2}$.

The presence of potassium in *KUP* was independently confirmed by energy dispersive spectroscopy using an electron microprobe; the K $K\alpha$ peak overlaps that of U $M\beta$, and the resultant anomalously high $M\beta:M\alpha$ ratio corroborates the presence of potassium.

The roles of the interstitial cations are relatively passive and have only a subtle influence upon the crystallization of these extended inorganic structures (22, 23). Whereas the large Cs atoms are accommodated by a higher symmetry structure, the Rb atoms are fully ordered in a derivative structure of identical structural connectivity, and the relatively small K atoms are disordered within an identical derivative framework.

Bond Valence Analysis

Bond valence analysis was performed using the parameters of Burns *et al.* (24) for $^{17}\text{U}^{6+}$, and Brown and Altermatt (25) for P, Cs, Rb, and K. For *CsUP*, the bond valence sums at the U sites are 5.98, 5.96, and 6.14 valence units for U(1), U(2), and U(3), respectively, whereas the sums at the P and Cs sites are 4.91, 5.04, 0.85 and 0.73 valence units for P(1), P(2), Cs(1), and Cs(2), respectively. These results are consistent with formal valences of U^{6+} , P^{5+} and Cs^+ . The bond valence sums for OW(15) and OW(16) are 0.46 and 0.27 valence units, respectively, consistent with their assignment as H_2O groups. The bond

DISCUSSION

Uranyl phosphates are important in natural systems for understanding the mobility of U (10, 26), and are less soluble than most uranyl minerals (27). About 45 uranyl phosphate minerals have been described, although the structures are known for only 16 of these. Parsonsite, $\text{Pb}_2[(\text{UO}_2)(\text{PO}_4)_2]$ (28), is the only uranyl phosphate mineral known to contain chains of polyhedra of higher bond-valence. Others involve sheets of vertex- and edge-sharing uranyl polyhedra and phosphate tetrahedra, and are grouped according to the details of the topological arrangements of the anions within the sheets (1). The autunite and phosphuranylite anion-topologies dominate the structures of uranyl phosphates. Sheets based upon the autunite anion-topology involve the sharing of vertices between uranyl square bipyramids and phosphate tetrahedra. Those based upon the phosphuranylite anion-topology contain uranyl pentagonal and hexagonal bipyramids that share edges to form chains, which are cross-linked by sharing vertices and edges with phosphate tetrahedra. In some cases, sheets in minerals of the phosphuranylite group are linked by bonds to U^{6+} in the interlayer, resulting in framework structures. The only uranyl phosphate sheet known in a mineral that is not based upon the autunite or phosphuranylite anion

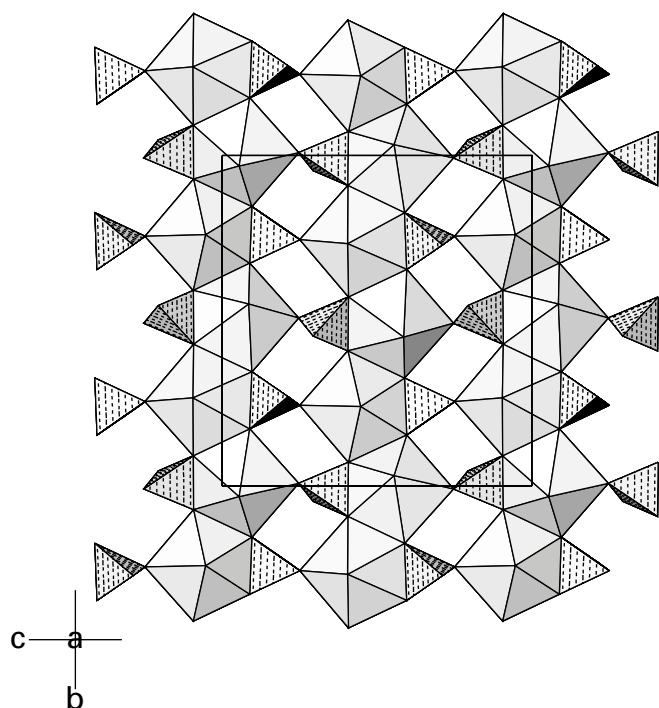


FIG. 1. Polyhedral representation of the uranyl phosphate sheet of $\text{Cs}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)_4(\text{H}_2\text{O})_2]$ projected along [100]. The sheets have the composition $[(\text{UO}_2)(\text{PO}_4)]^{1-}$ and are topologically identical with the uranyl silicate sheets of uranophane-beta. The uranyl polyhedra are shown in shades of gray and the phosphate tetrahedra are stippled.

valence sums for the remaining O atoms range from 1.72 to 2.17 valence units.

For *RbUP*, the bond valence sums at the U sites are 5.65, 5.98, and 6.12 valence units for U(1), U(2), and U(3), respectively, whereas the sums at the P and Rb sites are 5.11, 5.07, 1.03 and 0.88 valence units for P(1), P(2), Rb(1), and Rb(2), respectively. These results are consistent with formal valences of U^{6+} , P^{5+} and Rb^+ . The bond valence sums for OW(15) and OW(16) are 0.45 and 0.27 valence units, respectively, consistent with their assignment as H_2O groups. The bond valence sums for the remaining O atoms range from 1.67 to 2.22 valence units.

For *KUP*, the bond valence sums at the U sites are 5.99, 5.93, and 6.28 valence units for U(1), U(2), and U(3), respectively, whereas the sums at the P and partially occupied K sites are 5.06, 4.87, 0.79, 0.77, 0.50 and 0.90 valence units for P(1), P(2), K(1), K(2), (K3), and K(4), respectively. These results are consistent with formal valences of U^{6+} , P^{5+} and K^+ . The bond valence sums for OW(15), OW(16), and OW(17) are 0.46, 0.36 and 0.22 valence units, respectively, consistent with their assignment as H_2O groups. The bond valence sums for the remaining O atoms range from 1.73 to 2.20 valence units. The bond valence parameters of the K atoms to the O atoms have been scaled for half-occupancy, where necessary.

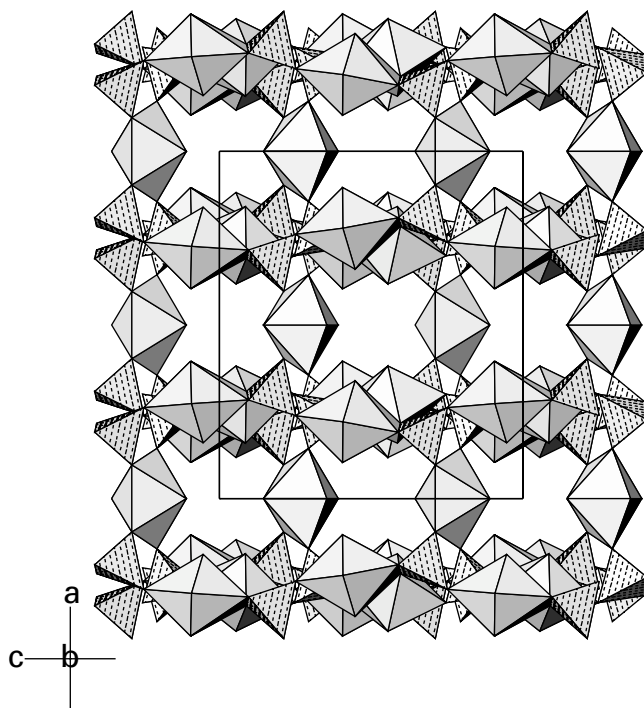


FIG. 2. Polyhedral representation of the structure of $\text{Cs}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)_4(\text{H}_2\text{O})_2]$ projected along [010]. The uranyl polyhedra are shown in shades of gray and the phosphate tetrahedra are stippled.

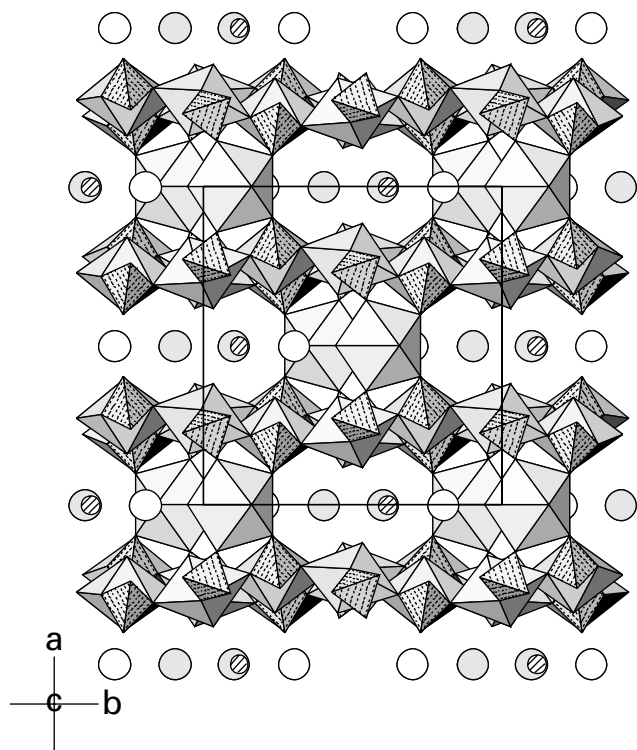


FIG. 3. Polyhedral representation of the structure of $\text{Cs}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)_4(\text{H}_2\text{O})_2$ projected along [001]. The uranyl polyhedra are shown in shades of gray and the phosphate tetrahedra are stippled. Cs(1) is shown as unfilled circles, Cs(2) as filled circles, and the OW(16) H_2O group is shown as striped small circles.

topologies is in ulrichite, $\text{Cu}[\text{Ca}(\text{UO}_2)(\text{PO}_4)_2](\text{H}_2\text{O})_4$ (29, 30), which is based upon the uranophane anion topology that involves triangles, pentagons and squares (2). In addition to uranyl pentagonal bipyramids and phosphate tetrahedra, the sheet in ulrichite contains Ca polyhedra.

The uranyl phosphate sheet in the structures of *CsUP*, *RbUP* and *KUP* is based upon the uranophane anion topology, and is topologically identical to the uranyl silicate sheet in the structure of uranophane-beta. Limiting consideration to minerals, the sheets in *CsUP*, *RbUP* and *KUP* are most similar to those in ulrichite from a topological perspective, although the composition of the sheets is substantially different. Additional uranyl phosphate sheets based upon the uranophane anion topology occur in $(\text{UO}_2)_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$ (12), as well as in the mixed organic-inorganic compounds $[\text{NH}_4][(\text{UO}_2)_2(\text{PO}_4)(\text{HPO}_4)]$, $[\text{NPr}_4][(\text{UO}_2)_3(\text{PO}_4)(\text{HPO}_4)_2]$ and $\{(\text{C}_2\text{H}_5)_2\text{NH}_2\}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)_4]$ (31, 32). In the cases of *CsUP*, *RbUP*, *KUP* and $(\text{UO}_2)_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$, the uranyl phosphate sheets are linked to uranyl pentagonal bipyramids in the interlayers of the structures, while in $\{(\text{C}_2\text{H}_5)_2\text{NH}_2\}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)_4]$ the sheets are linked via uranyl square bipyramids, resulting in relatively open uranyl phosphate frameworks. In *CsUP*, *RbUP* and *KUP*, the uranyl

pentagonal bipyramid in the interlayer is linked to four phosphate polyhedra by sharing its equatorial ligands, whereas the fifth ligand corresponds to an H_2O group. In the interlayer of $(\text{UO}_2)_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$ the uranyl pentagonal bipyramids are only linked to two phosphate tetrahedra, one from the sheet on either side, with three of the equatorial ligands corresponding to H_2O groups. In $\{(\text{C}_2\text{H}_5)_2\text{NH}_2\}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)_4]$, all four equatorial ligands of the uranyl square bipyramid in the interlayer are linked to phosphate tetrahedra.

It is relatively rare for frameworks to form in uranyl solids, although open-structured uranium frameworks are of interest because of potential applications in areas such as separations, catalysis, and nuclear waste immobilization (33). Owing to the polarized distribution of bond strengths within uranyl polyhedra, polymerization with other polyhedra of higher bond valence tends to be through the equatorial ligands only, and most often results in sheets of polyhedra that are seldom linked in the third dimension. The sharing of apices of uranyl polyhedra, which correspond to the oxygen atoms of the uranyl ion, with

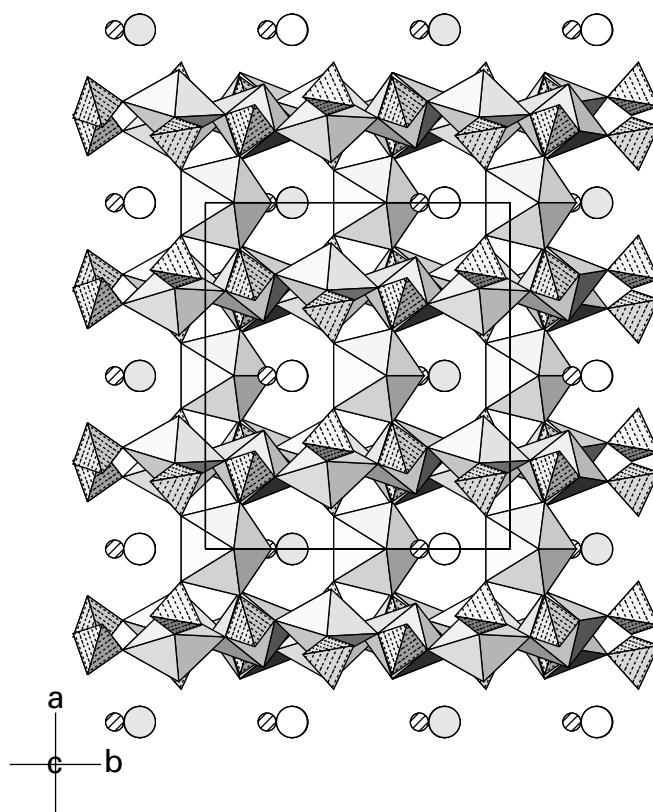


FIG. 4. Polyhedral representation of the structure of $\text{Rb}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)_4(\text{H}_2\text{O})_2$ projected along [001]. The uranyl polyhedra are shown in shades of gray and the phosphate tetrahedra are stippled. Rb(2) is shown as unfilled circles, Rb(1) as filled circles and the OW(16) H_2O group is shown as striped small circles.

other polyhedra of higher bond valence is very unusual because of the strong U—O bond within the uranyl ion. Frameworks containing only uranyl polyhedra have recently been discovered (34, 35), although these each involve some U^{6+} in distorted octahedral coordination with no uranyl ion present. This facilitates three-dimensional linkages because of the more even distribution of bond valences within the octahedron. Uranyl compounds containing additional polyhedra of higher bond-valence show more of a tendency towards framework structures; for example, those found in the uranyl silicates soddyite, $(UO_2)_2(SiO_4)(H_2O)_2$ (36), weeksite, $(K,Ba,Ca)_2[(UO_2)_2(Si_5O_{13})]H_2O$ (37), and $Na_4(UO_2)_2(Si_4O_{10})_2(H_2O)_4$ (38), and the uranyl molybdates α - $Cs_2(UO_2)_2(MoO_4)_3$ (39), $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ ($M = Cs, NH_4$) (40). In these structures, as in the uranyl phosphate frameworks of $\{(C_2H_5)_2NH_2\}_2(UO_2)[(UO_2)(PO_4)]_4$, *CsUP*, *RbUP* and *KUP*, linkages in the third dimension are facilitated by the non-uranyl polyhedra.

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