Structures and synthesis of framework Rb and Cs uranyl arsenates and their relationships with their phosphate analogues

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Abstract

Two hydrated uranyl arsenates, $Cs_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_2$ (*CsUAs*) and $Rb_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_{4.5}$ (*RbUAs*), were synthesized by hydrothermal methods. Intensity data were collected at room temperature using Mo$K\alpha$ radiation and a CCD-based area detector. The crystal structure of *RbUAs* was solved by direct methods, whereas the structure model of the phosphate $Cs_2(UO_2)[(UO_2)(PO_4)]_4(H_2O)_2$ was used for *CsUAs*; both were refined by full-matrix least-squares techniques on the basis of F^2 to agreement indices (*CsUAs*, *RbUAs*) w$R_2 = 0.061, 0.041$, for all data, and $R_1 = 0.032, 0.021$, calculated for 5098, 4991 unique observed reflections ($|F_o| > 4\sigma_F$), respectively. The compound *CsUAs* is orthorhombic, space group $Cmc2_1$, $Z = 4$, $a = 15.157(2)$, $b = 14.079(2)$, $c = 13.439(2)$ Å, $V = 2867.9(1)$ Å^3. *RbUAs* is monoclinic, space group $C2/m$, $Z = 4$, $a = 13.4619(4)$, $b = 15.8463(5)$, $c = 14.0068(4)$ Å, $\beta = 92.311(1)°$, $V = 2985.52(2)$ Å^3. The structures consist of sheets of arsenate tetrahedra and uranyl pentagonal bipyramids, with composition $[(UO_2)(AsO_4)]^-$, 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 arsenate 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. *CsUAs* is isostructural with its phosphate analogue, and has two Cs atoms and a H_2O group in its structural cavities. *RbUAs* is not isostructural with its phosphate analogue, although it has a homeotypic framework. Its structural cavities are occupied by three Rb atoms and four H_2O groups; one Rb position and three of the interstitial H_2O groups are half-occupied. The partial occupancies of these positions probably result from the accommodation of the larger As atoms (relative to P) in the framework and resultant larger cavities.

1. Introduction

Framework uranyl structures are relatively rare, despite the extraordinary diversity of U^{6+} crystal chemistry [1]. The polarized distribution of bond strengths within uranyl bipyramidal polyhedra is generally consistent with polymerization only through equatorial ligands, resulting in chains or sheets. Formation of framework structures by linkages in the third dimension usually involves non-uranyl polyhedra in uranyl compounds that contain additional polyhedra of higher bond valence, such as silicate [2–4], molybdate [5,6], vanadate [7], or phosphate [8–10].

Uranyl arsenates are often structurally identical with their chemically corresponding uranyl phosphates because of the similar crystal-chemical roles played by arsenate and phosphate tetrahedra. For example, the isostructural minerals abernathyite, $K[(UO_2)(AsO_4)](H_2O)_3$, and meta-ankoleite, $K[(UO_2)(PO_4)](H_2O)_3$, contain autunite-type sheets of vertex-sharing tetrahedra and uranyl square bipyramids [11,12]. It can therefore be expected that uranyl arsenate frameworks will be structurally similar to their phosphate counterparts. As part of our ongoing research into the structures of uranyl phosphates and uranyl arsenates, we have synthesized Rb and Cs uranyl arsenate hydrates, and determined their structures.

2. Experiment

2.1. Crystal synthesis

Single crystals of $Cs_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_2$ (*CsUAs*), and $Rb_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_{4.5}$

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(*RbUAs*) were obtained by hydrothermal reaction. The reactants (proportions listed in the order *CsUAs*, *RbUAs*) were $H_5As_3O_{10}$ (0.1625 g, 0.0796 g), UO_2 $(NO_3)_2(H_2O)_6$ (0.1172 g, 0.1030 g), alkali metal nitrate ($CsNO_3$ 0.5935 g, $RbNO_3$ 0.4466 g,) and ultrapure H_2O (4 mL each). The reactants were weighed into Teflon-lined Parr autoclaves and heated at 180(1)°C in a Fisher Isotemp oven for 12.5 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 of *CsUAs* and *RbUAs*, overgrown by square plates of $A[(UO_2)(AsO_4)](H_2O)_3$, *A* = Cs, Rb, respectively. Crystals of the compounds of interest were removed physically from their coatings of abernathyite-structure [11] materials; synthesis yields were not determined.

2.2. Single-crystal X-ray diffraction

For both 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 4K APEX CCD detector and a crystal-to-

detector distance of ~4.7 cm. A sphere of three-dimensional data was collected at room temperature for each crystal using graphite-monochromatized Mo$K\alpha$ X-radiation and frame widths of 0.3° in ω, with count-times per frame of 10 s for *CsUAs* and 60 s for *RbUAs*. Comparison of the intensities of equivalent reflections measured at different times during data collection showed no significant decay for either of the compounds. The unit cells (Table 1) were refined with 5976 reflections for *CsUAs* and 8644 reflections for *RbUAs* using least-squares techniques. The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. For *CsUAs*, a semi-empirical absorption correction was applied by modeling the crystal as an ellipsoid; this procedure lowered R_{INT} of 2963 intense reflections from 0.180 to 0.057. For *RbUAs*, an empirical correction for absorption was applied using the program SADABS (G. Sheldrick, unpublished) on the basis of the intensities of equivalent reflections; this lowered R_{INT} of 14,895 intense reflections from 0.099 to 0.028.

Systematic absences of reflections for *CsUAs* were consistent with space groups $Cmc2_1$, $Cmcm$ and

Table 1
Crystallographic data and details of the structure refinements for $Cs_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_2$ (*CsUAs*) and $Rb_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_{4.5}$ (*RbUAs*)

Compound	*CsUAs*	*RbUAs*
a (Å)	15.157(2)	13.4619(4)
b (Å)	14.079(2)	15.8463(5)
c (Å)	13.439(2)	14.0068(4)
β (°)	90	92.311(1)
V (Å^3)	2867.9(1)	2985.52(2)
Space group	$Cmc2_1$	$C2/m$
Analysis temperature (K)	293(2)	293(2)
Formula ($Z=4$)	$Cs_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_2$	$Rb_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_{4.5}$
Formula weight (g/mol)	2207.7	2157.8
Wavelength (Å)	0.71073	0.71073
F (000)	3720	3676
μ (mm^{-1})	35.32	34.78
D_{calc} (g/mL)	5.11	4.80
Crystal size (mm)	$0.18 \times 0.10 \times 0.06$	$0.10 \times 0.06 \times 0.04$
θ range of data collection	1.97–34.55°	2.43–34.50°
Data collected	$-23 \leqslant h \leqslant 24, -22 \leqslant k \leqslant 22, -21 \leqslant l \leqslant 21$	$-21 \leqslant h \leqslant 21, -24 \leqslant k \leqslant 24, -22 \leqslant l \leqslant 22$
Total reflections	29183	30541
Unique reflections	6188	6348
R_{int}	0.074	0.034
Unique $|F_o| \geqslant 4\sigma_F$	5098	4991
Completeness	99.6% ($\theta = 34.55°$)	97.1% ($\theta = 34.50°$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Parameters varied	188	199
$R_1{}^a$ for $|F_o| \geqslant 4\sigma_F$	0.032	0.021
w$R_2{}^b$ all data	0.061	0.041
Weighting factor a	0.0165	0.0119
Goodness of fit all data	0.90	0.92
Max. min. peaks (e/Å^3)	4.1, −3.0	1.8, −2.4

[a] $R_1 = [\sum||F_o| - |F_c||]/\sum|F_o|$.
[b] w$R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$, w $= 1/(\sigma^2(F_o^2) + (aP)^2)$, $P = 1/3 \max(0, F_o^2) + 2/3F_c^2$.

Table 2
Atomic coordinates ($\times 10^4$) and displacement parameters ($\text{Å}^2 \times 10^3$) for $Cs_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_2$

CsUAs	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	2206(1)	2399(1)	5699(1)	11(1)	17(1)	7(1)	10(1)	0(1)	−1(1)	−1(1)
U(2)	2736(1)	−66(1)	4310(1)	13(1)	21(1)	8(1)	10(1)	0(1)	0(1)	1(1)
U(3)	0	1052(1)	2323(1)	14(1)	13(1)	14(1)	16(1)	−2(1)	0	0
Cs(1)	0	4029(1)	1637(1)	60(1)	40(1)	45(1)	94(1)	29(1)	0	0
Cs(2)	0	1853(1)	−1168(1)	57(1)	70(1)	55(1)	44(1)	4(1)	0	0
As(1)	1913(1)	2412(1)	3276(1)	11(1)	16(1)	8(1)	8(1)	0(1)	−1(1)	−1(1)
As(2)	2392(1)	−148(1)	6708(1)	11(1)	16(1)	8(1)	9(1)	0(1)	0(1)	−1(1)
O(1)	1056(4)	2292(4)	5850(5)	22(1)	24(3)	18(3)	24(4)	−4(3)	−1(3)	−8(3)
O(2)	3381(5)	2464(5)	5517(5)	31(2)	33(4)	38(4)	22(4)	−3(3)	0(3)	−7(3)
O(3)	2680(4)	2584(4)	2395(5)	21(1)	26(4)	26(3)	10(3)	3(3)	6(3)	−3(3)
O(4)	2321(5)	750(4)	5889(4)	25(2)	59(5)	4(3)	13(3)	−3(2)	−3(3)	3(3)
O(5)	2857(4)	−935(4)	5916(4)	19(1)	30(4)	11(3)	14(3)	0(2)	1(2)	6(3)
O(6)	1916(4)	3306(4)	4143(4)	16(1)	28(3)	7(3)	14(3)	−5(2)	2(2)	−3(2)
O(7)	2213(4)	1518(4)	4063(4)	19(1)	37(4)	8(3)	11(3)	−1(2)	2(2)	7(3)
O(8)	1635(4)	−479(4)	4177(5)	23(1)	33(4)	16(3)	20(3)	1(3)	−2(3)	−5(3)
O(9)	3829(4)	323(5)	4509(5)	25(2)	19(4)	28(4)	29(4)	4(3)	−6(3)	−7(3)
O(10)	3079(4)	104(4)	7634(4)	19(1)	20(3)	27(3)	9(3)	−3(2)	2(2)	1(3)
O(11)	0	583(7)	3518(6)	22(2)	19(5)	27(5)	19(5)	6(4)	0	0
O(12)	0	1491(7)	1102(7)	24(2)	23(5)	31(5)	18(5)	2(4)	0	0
O(13)	916(4)	2312(4)	2806(5)	20(1)	20(4)	15(3)	25(4)	2(3)	−6(3)	−1(2)
O(14)	1425(4)	−492(6)	7143(6)	33(2)	14(3)	48(5)	36(4)	−9(4)	4(3)	−12(3)
OW(15)	0	−636(8)	1589(11)	51(3)	44(7)	31(6)	78(9)	−34(7)	0	0
OW(16)	0	3745(14)	7320(20)	129(8)	130(18)	77(12)	180(20)	14(16)	0	0

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

$Ama2 = C2cm$; the space group $Cmc2_1$ was assigned in accord with the structure refinement of $Cs_2(UO_2)$ $[(UO_2)(PO_4)]_4(H_2O)_2$ [10]. In the case of $RbUAs$, 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 1.038, consistent with space group $C2/m$. Trial solutions were obtained for all three space groups, but the best solution was obtained in $C2/m$, in contrast to the non-centrosymmetric structure (space group Cm) of the analogous phosphate, $Rb_2(UO_2)$ $[(UO_2)(PO_4)]_4(H_2O)_2$ [10]. Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-ray Crystallography*, *Volume IV* [13]. The SHELXTL Version 5 series of programs was used for the solution and refinement of the crystal structures.

3. Structure solution and refinement

The crystal structure of $CsUAs$ was refined in space group $Cmc2_1$ using the atomic positions of $Cs_2(UO_2)$ $[(UO_2)(PO_4)]_4(H_2O)_2$ [10] as a starting point. A structure model including the racemic twin law $[-100/$ $0-10/00-1]$ and anisotropic displacement parameters for all non-H atoms converged, and gave an agreement index (R_1) of 0.032, calculated for the 5098 observed

unique reflections ($|F_o| \geqslant 4\sigma_F$). The racemic twin-component scale factor refined to 0.480(6). The final value of wR_2 was 0.061 for all data using the structure-factor weights assigned during least-squares refinement. In the final cycle of refinement the mean parameter shift/e.s.d. was 0.000. The atomic positional parameters and displacement parameters are given in Table 2, and selected interatomic distances and angles are in Table 3. The locations of the H atoms in the unit cell were not determined. The refined solution obtained for $CsUAs$ was checked with the ADDSYM algorithm in the program PLATON [14–16]; no higher symmetry was found.

The structure of $RbUAs$ was solved in space group $C2/m$ using direct methods, and was refined based on F^2 for all unique data. A structure model including anisotropic displacement parameters for U, Rb, As and non-interstitial O atoms converged, and gave an agreement index (R_1) of 0.021, calculated for the 4991 observed unique reflections ($|F_o| \geqslant 4\sigma_F$). The final value of wR_2 was 0.041 for all data using the structure-factor weights assigned during least-squares refinement. In the final cycle of refinement the mean parameter shift/e.s.d. was 0.000. The atomic positional parameters and displacement parameters are given in Table 4 and selected interatomic distances and angles in Table 5. The locations of the H atoms in the unit cell were not determined.

Table 3

Selected interatomic distances (Å) and angles (°) for $Cs_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_2$

U(1)–O(1)	1.762(7)		
U(1)–O(2)	1.801(7)	O(1)–U(1)–O(2)	177.7(3)
U(1)–O(3)a	2.286(6)	O(1)–U(1)–O(3)a	87.8(3)
U(1)–O(4)	2.341(6)	O(1)–U(1)–O(4)	88.7(3)
U(1)–O(5)b	2.366(6)	O(1)–U(1)–O(5)b	91.7(2)
U(1)–O(6)	2.490(6)	O(1)–U(1)–O(6)	88.0(3)
U(1)–O(7)	2.524(6)	O(1)–U(1)–O(7)	93.6(3)
$\langle U(1)–O_{ap}\rangle$	1.78		
$\langle U(1)–O_{eq}\rangle$	2.40		
U(2)–O(9)	1.766(6)		
U(2)–O(8)	1.775(7)	O(9)–U(2)–O(8)	176.9(3)
U(2)–O(10)c	2.312(6)	O(9)–U(2)–O(10)c	86.8(3)
U(2)–O(6)d	2.362(5)	O(9)–U(2)–O(6)d	96.1(3)
U(2)–O(7)	2.390(6)	O(9)–U(2)–O(7)	92.4(3)
U(2)–O(5)	2.488(6)	O(9)–U(2)–O(5)	87.2(3)
U(2)–O(4)	2.495(6)	O(9)–U(2)–O(4)	87.9(3)
$\langle U(2)–O_{ap}\rangle$	1.77		
$\langle U(2)–O_{eq}\rangle$	2.41		
U(3)–O(11)	1.737(8)		
U(3)–O(12)	1.753(9)	O(11)–U(3)–O(12)	178.3(5)
U(3)–O(14)e	2.311(7)	O(11)–U(3)–O(14)e	88.1(2)
U(3)–O(14)c	2.311(7)	O(11)–U(3)–O(14)c	88.1(2)
U(3)–O(13)	2.344(6)	O(11)–U(3)–O(13)	91.8(3)
U(3)–O(13)f	2.344(6)	O(11)–U(3)–O(13)f	91.8(3)
U(3)–OW(15)	2.572(10)	O(11)–U(3)–OW(15)	90.1(5)
$\langle U(3)–O_{ap}\rangle$	1.75		
$\langle U(3)–O_{eq}\rangle$	2.38		
As(1)–O(13)	1.644(6)	O(13)–As(1)–O(3)	112.2(3)
As(1)–O(3)	1.677(6)	O(13)–As(1)–O(6)	109.1(3)
As(1)–O(7)	1.706(6)	O(13)–As(1)–O(7)	114.9(3)
As(1)–O(6)	1.715(5)	O(3)–As(1)–O(6)	111.8(3)
$\langle As(1)–O\rangle$	1.69	O(3)–As(1)–O(7)	111.1(3)
		O(7)–As(1)–O(6)	96.9(3)
As(2)–O(14)	1.652(7)	O(10)–As(2)–O(4)	111.7(3)
As(2)–O(10)	1.662(6)	O(10)–As(2)–O(5)	110.5(3)
As(2)–O(4)	1.679(6)	O(14)–As(2)–O(10)	110.7(3)
As(2)–O(5)	1.691(6)	O(14)–As(2)–O(4)	113.4(4)
$\langle As(2)–O\rangle$	1.67	O(14)–As(2)–O(5)	113.6(3)
		O(4)–As(2)–O(5)	96.2(3)
Cs(1)–O(13)f	3.199(6)		
Cs(1)–O(13)	3.199(6)	O(13)f–Cs(1)–O(13)	51.4(2)
Cs(1)–OW(16)g	3.267(19)	O(13)f–Cs(1)–OW(16)g	125.9(4)
Cs(1)–O(10)h	3.430(6)	O(13)f–Cs(1)–O(10)h	116.45(16)
Cs(1)–O(10)i	3.430(6)	O(13)f–Cs(1)–O(10)i	73.07(15)
Cs(1)–O(9)i	3.487(7)	O(13)f–Cs(1)–O(9)i	112.30(16)
Cs(1)–O(9)h	3.487(7)	O(13)f–Cs(1)–O(9)h	145.20(17)
Cs(1)–O(2)i	3.564(8)	O(13)f–Cs(1)–O(2)i	57.53(17)
Cs(1)–O(2)h	3.564(8)	O(13)f–Cs(1)–O(2)h	93.46(16)
Cs(1)–O(12)	3.645(10)	O(13)f–Cs(1)–O(12)	49.93(16)
$\langle Cs(1)–O\rangle$	3.43		
Cs(2)–O(12)	3.094(9)		
Cs(2)–O(8)e	3.178(6)	O(12)–Cs(2)–O(8)e	75.85(16)
Cs(2)–O(8)c	3.178(6)	O(12)–Cs(2)–O(8)c	75.85(16)
Cs(2)–OW(16)j	3.35(2)	O(12)–Cs(2)–OW(16)j	136.8(5)
Cs(2)–O(11)e	3.455(9)	O(12)–Cs(2)–O(11)e	87.5(2)
Cs(2)–OW(15)e	3.467(15)	O(12)–Cs(2)–OW(15)e	140.9(3)
Cs(2)–O(2)h	3.475(7)	O(12)–Cs(2)–O(2)h	53.31(15)
Cs(2)–O(2)i	3.475(7)	O(12)–Cs(2)–O(2)i	53.31(15)
$\langle Cs(2)–O\rangle$	3.33		

Symmetry transformations used to generate equivalent atoms: a: $-x+1/2, -y+1/2, z+1/2$; b: $x+1/2, y+1/2, z$; c: $x, -y, z-1/2$; d: $-x+1/2, y-1/2, z$; e: $-x, -y, z-1/2$; f: $-x, y, z$; g: $-x, -y+1, z-1/2$; h: $-x+1/2, -y+1/2, z-1/2$; i: $-1/2, -y+1/2, z-1/2$; j: $x, y, z-1$.

4. Results

4.1. Structure description

CsUAs is isostructural with its phosphate analogue, $Cs_2(UO_2)[(UO_2)(PO_4)]_4(H_2O)_2$ [10]. In these compounds, there are three symmetrically independent U atoms, each of which is part of an approximately linear $(UO_2)^{2+}$ cation. In each case, the uranyl ions are coordinated by five additional ligands arranged at the equatorial positions of pentagonal bipyramids, with the uranyl O atoms at the apices of the bipyramids. The equatorial ligands of U(1) and U(2) consist of O atoms, whereas the equatorial ligands 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 rise to a chain of alternating U(1) and U(2) bipyramids that is one polyhedron wide. In *CsUAs*, arsenate tetrahedra are attached to either side of the chains by sharing edges with the uranyl polyhedra (Fig. 1). The orientations of the arsenate tetrahedra alternate along the length of any uranyl arsenate chain such that the apical (non-sheet) tetrahedral ligand occurs alternately above and below the sheet. Translationally equivalent uranyl arsenate chains are joined by the sharing of equatorial vertices of uranyl pentagonal bipyramids with arsenate tetrahedra from adjacent chains, resulting in sheets that are parallel to (100). The uranyl arsenate sheets are topologically identical to the uranyl silicate sheets in uranophane-beta, $Ca[(UO_2)SiO_3(OH)]_2(H_2O)_5$ [17].

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

The two symmetrically independent Cs atoms occupy the larger cavities of the structure along with an interstitial H_2O group—OW(16)—(Fig. 2); Cs(1) is in ten-fold coordination with a mean Cs(1)–O distance of 3.43 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 coordination geometries and polyhedral connectivity of the uranyl polyhedra and arsenate tetrahedra in *RbUAs* are identical with those of *CsUAs*; both structures are frameworks that consist of uranyl arsenate sheets linked by uranyl pentagonal bipyramids. These two structures are homeotypic frameworks, following the definition given in Ref. [18]; $C2/m$ and $Cmc2_1$ are both subgroups of $Cmcm$. *RbUAs* has lower symmetry than *CsUAs* and differs from it in the

Table 4
Atomic coordinates ($\times 10^4$) and displacement parameters ($\mathring{A}^2 \times 10^3$) for $Rb_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_{4.5}$

$RbUAs$	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	752(1)	2711(1)	3789(1)	11(1)	8(1)	18(1)	8(1)	0(1)	0(1)	0(1)
U(2)	−676(1)	2296(1)	1251(1)	11(1)	8(1)	17(1)	9(1)	−2(1)	0(1)	1(1)
U(3)	2466(1)	0	2696(1)	14(1)	12(1)	14(1)	15(1)	0	−1(1)	0
As(1)	1707(1)	1914(1)	1349(1)	10(1)	7(1)	15(1)	8(1)	0(1)	0(1)	1(1)
As(2)	−1699(1)	2819(1)	3651(1)	11(1)	7(1)	16(1)	9(1)	1(1)	0(1)	1(1)
Rb(1)	5662(1)	0	1696(1)	38(1)	32(1)	40(1)	42(1)	0	13(1)	0
Rb(2)	0	0	5000	37(1)	34(1)	26(1)	51(1)	0	6(1)	0
Rb(3)[a]	258(1)	0	137(1)	34(1)	57(2)	19(1)	28(1)	0	12(1)	0
O(1)	−895(2)	3076(2)	4574(2)	15(1)	11(1)	26(2)	8(1)	−2(1)	−1(1)	−2(1)
O(2)	890(2)	2090(2)	404(2)	16(1)	11(1)	30(2)	8(1)	3(1)	−2(1)	1(1)
O(3)	931(2)	2240(2)	2203(2)	17(1)	9(1)	30(2)	12(1)	−2(1)	1(1)	3(1)
O(4)	−781(2)	1185(2)	1375(2)	20(1)	24(2)	18(2)	18(2)	0(1)	3(1)	1(1)
O(5)	−2540(2)	2085(2)	3918(2)	18(1)	9(1)	19(2)	25(2)	3(1)	4(1)	−1(1)
O(6)	−836(2)	2427(2)	2919(2)	18(1)	8(1)	34(2)	12(1)	−7(1)	1(1)	0(1)
O(7)	704(2)	3769(2)	3387(2)	20(1)	21(2)	21(2)	19(2)	4(1)	1(1)	1(1)
O(8)	759(2)	1662(2)	4207(2)	19(1)	22(2)	18(2)	19(2)	2(1)	5(1)	−1(1)
O(9)	2663(2)	2577(2)	1293(2)	19(1)	8(1)	25(2)	24(2)	2(1)	−1(1)	−5(1)
O(10)	1977(2)	895(2)	1371(2)	20(1)	30(2)	15(2)	14(1)	−1(1)	−2(1)	6(1)
O(11)	−2320(2)	3608(2)	3158(2)	25(1)	23(2)	23(2)	28(2)	10(1)	−8(1)	6(1)
O(12)	−531(2)	3400(2)	1120(2)	23(1)	25(2)	17(2)	27(2)	−2(1)	−1(1)	−2(1)
O(13)	3706(3)	0	2332(3)	29(1)	17(2)	28(3)	42(3)	0	3(2)	0
O(14)	1255(3)	0	3103(3)	24(1)	20(2)	23(2)	28(2)	0	6(2)	0
OW(15)	3090(4)	0	4385(3)	47(2)	66(4)	47(4)	26(3)	0	−15(3)	0
OW(16)[a]	5035(19)	0	5217(13)	90(5)						
OW(17)[a]	1953(5)	417(4)	5823(5)	39(2)						
OW(18)[a]	−2334(7)	495(6)	2560(6)	65(3)						
OW(19)	3324(7)	0	2(7)	122(3)						

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

[a] Site is half-occupied.

positions of the alkali metal atoms and the interstitial H_2O groups, and in the details of the configuration of the uranyl arsenate framework (Fig. 3). In $RbUAs$, the interstitial sites contain three Rb atoms and four H_2O groups, and the Rb atoms are coordinated mainly by the oxygen atoms of the uranyl cations (Table 5). Rb(1) is in seven-fold coordination with mean Rb(1)–O of 2.99 Å, and Rb(2) is in eight-fold coordination with mean Rb(2)–O of 3.05 Å. The Rb(3) position is half-occupied and separated from its symmetry equivalent position by 0.781(4) Å, and is effectively in eight-fold coordination with mean Rb(3)–O of 3.12 Å. Similarly, OW(16), OW(17) and OW(18) are distributed over split positions, with separation distances from their symmetry equivalent positions of 0.61(4), 1.32(1) and 1.57(2) Å, respectively.

4.2. Symmetry of RbUAs

$RbUAs$, space group $C2/m$, differs from its phosphate analogue, $Rb_2(UO_2)[(UO_2)(PO_4)]_4(H_2O)_2$, RbUP, space group Cm, both in symmetry and hydration [10]. The effective ionic radius of $^{[4]}As^{5+}$ is essentially double that of $^{[4]}P^{5+}$ [19]. Accommodation of the larger As atoms in

$RbUAs$ evidently results in a different configuration of the coordination geometry of the interlayer U position (Fig. 3), and the interstitial positions in comparison to RbUP. In the case of the Rb(3) position in $RbUAs$, Rb is too small to occupy the center of the interstitial cavity at atomic coordinates 0, 0, 0, as this would result in 12-fold coordination with mean Rb–O distances of ~3.33 Å, and unreasonable anisotropic displacement parameters. Rather, the Rb(3) position is best described by a split-site model, with strongly asymmetric coordination (Fig. 4).

For comparison, the structure of $RbUAs$ was also solved and refined in space group Cm. In this model, there are four symmetrically independent Rb atoms. Despite the ordered nature of the Rb positions, the Cm model is not an improvement over the disordered $C2/m$ model. The Cm model yields unusual interatomic distances and geometry for the Rb(4) position, gives considerably higher estimated standard deviations for all interatomic distances, shows very high correlation and slow convergence, does not permit the use of anisotropic displacement parameters for O atoms, gives a higher agreement index (R_1) of 0.025, and still requires that four interstitial OW atoms occupy disordered

Table 5
Selected interatomic distances (Å) and angles (°) for $Rb_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_{4.5}$

U(1)–O(8)	1.762(3)		
U(1)–O(7)	1.769(3)	O(8)–U(1)–O(7)	177.96(13)
U(1)–O(5)a	2.321(3)	O(8)–U(1)–O(5)a	96.55(12)
U(1)–O(3)	2.364(3)	O(8)–U(1)–O(3)	90.88(12)
U(1)–O(1)b	2.366(3)	O(8)–U(1)–O(1)b	84.79(11)
U(1)–O(6)	2.459(3)	O(8)–U(1)–O(6)	89.11(12)
U(1)–O(1)	2.581(3)	O(8)–U(1)–O(1)	93.58(11)
⟨U(1)–O$_{ap}$⟩	1.77		
⟨U(1)–O$_{eq}$⟩	2.42		
U(2)–O(12)	1.770(3)		
U(2)–O(4)	1.775(3)	O(12)–U(2)–O(4)	178.21(14)
U(2)–O(9)e	2.249(3)	O(12)–U(2)–O(9)e	91.62(13)
U(2)–O(2)f	2.347(2)	O(12)–U(2)–O(2)f	92.62(12)
U(2)–O(6)	2.364(3)	O(12)–U(2)–O(6)	91.74(12)
U(2)–O(2)	2.482(3)	O(12)–U(2)–O(2)	88.95(12)
U(2)–O(3)	2.497(3)	O(12)–U(2)–O(3)	89.62(12)
⟨U(2)–O$_{ap}$⟩	1.77		
⟨U(2)–O$_{eq}$⟩	2.39		
U(3)–O(14)	1.749(4)		
U(3)–O(13)	1.764(4)	O(14)–U(3)–O(13)	177.8(2)
U(3)–O(11)a	2.313(3)	O(14)–U(3)–O(11)a	90.91(9)
U(3)–O(11)c	2.313(3)	O(14)–U(3)–O(11)c	90.91(9)
U(3)–O(10)d	2.406(3)	O(14)–U(3)–O(10)d	91.25(14)
U(3)–O(10)	2.406(3)	O(14)–U(3)–O(10)	91.25(14)
U(3)–OW(15)	2.479(5)	O(14)–U(3)–OW(15)	88.46(19)
⟨U(3)–O$_{ap}$⟩	1.76		
⟨U(3)–O$_{eq}$⟩	2.38		
As(1)–O(10)	1.655(3)	O(10)–As(1)–O(2)	107.91(14)
As(1)–O(9)	1.665(3)	O(10)–As(1)–O(3)	115.11(14)
As(1)–O(3)	1.700(3)	O(10)–As(1)–O(9)	116.49(15)
As(1)–O(2)	1.709(3)	O(3)–As(1)–O(2)	95.83(13)
⟨As(1)–O⟩	1.68	O(9)–As(1)–O(2)	109.60(14)
		O(9)–As(1)–O(3)	109.81(14)
As(2)–O(11)	1.642(3)	O(11)–As(2)–O(5)	106.58(15)
As(2)–O(5)	1.677(3)	O(11)–As(2)–O(6)	111.93(15)
As(2)–O(6)	1.698(3)	O(5)–As(2)–O(6)	111.46(14)
As(2)–O(1)	1.701(3)	O(11)–As(2)–O(1)	115.78(15)
⟨As(2)–O⟩	1.68	O(5)–As(2)–O(1)	114.29(14)
		O(6)–As(2)–O(1)	96.73(13)
Rb(1)–OW(19)g	2.790(9)		
Rb(1)–O(13)	2.813(4)	OW(19)g–Rb(1)–O(13)	140.0(2)
Rb(1)–OW(18)h	3.016(9)	OW(19)g–Rb(1)–OW(18)h	83.2(2)
Rb(1)–O(7)a	3.066(3)	OW(19)g–Rb(1)–O(7)a	131.61(12)
Rb(1)–O(7)c	3.066(3)	OW(19)g–Rb(1)–O(7)c	131.61(12)
Rb(1)–O(12)c	3.090(3)	OW(19)g–Rb(1)–O(12)c	92.53(12)
Rb(1)–O(12)a	3.090(3)	OW(19)g–Rb(1)–O(12)a	92.53(12)
⟨Rb(1)–O⟩	2.99		
Rb(2)–OW(17)i	2.904(7)		
Rb(2)–OW(17)d	2.904(7)	OW(17)i–Rb(2)–OW(17)d	153.7(3)
Rb(2)–O(8)b	3.051(3)	OW(17)i–Rb(2)–O(8)b	91.73(15)
Rb(2)–O(8)	3.051(3)	OW(17)i–Rb(2)–O(8)	111.27(15)
Rb(2)–O(8)i	3.051(3)	OW(17)i–Rb(2)–O(8)i	68.73(15)
Rb(2)–O(8)d	3.051(3)	OW(17)i–Rb(2)–O(8)d	88.27(15)
Rb(2)–O(14)i	3.205(4)	OW(17)i–Rb(2)–O(14)i	80.22(15)
Rb(2)–O(14)	3.205(4)	OW(17)i–Rb(2)–O(14)	99.78(15)
⟨Rb(2)–O⟩	3.05		

Table 5 (continued)

Rb(3)–O(4)j	2.938(3)		
Rb(3)–O(4)f	2.938(3)	O(4)j–Rb(3)–O(4)f	79.49(12)
Rb(3)–O(4)d	2.947(3)	O(4)j–Rb(3)–O(4)d	98.61(11)
Rb(3)–O(4)	2.947(3)	O(4)j–Rb(3)–O(4)	164.74(6)
Rb(3)–O(10)	3.167(3)	O(4)j–Rb(3)–O(10)	119.26(10)
Rb(3)–O(10)d	3.167(3)	O(4)j–Rb(3)–O(10)d	85.17(8)
Rb(3)–O(2)d	3.435(3)	O(4)j–Rb(3)–O(2)d	52.89(7)
Rb(3)–O(2)	3.435(3)	O(4)j–Rb(3)–O(2)	128.99(9)
⟨Rb(3)–O⟩	3.12		

Symmetry transformations used to generate equivalent atoms: a: $x + 1/2, -y + 1/2, z$; b: $-x, y, -z + 1$; c: $x + 1/2, y - 1/2, z$; d: $x, -y, z$; e: $x - 1/2, -y + 1/2, z$; f: $-x, y, -z$; g: $-x + 1, -y, -z$; h: $x + 1, y, z$; i: $-x, -y, -z + 1$; j: $-x, -y, -z$.

Note: Duplicate interatomic distances from split sites are not shown. The following sites are half-occupied: Rb(3), OW(16), OW(17), OW(18).
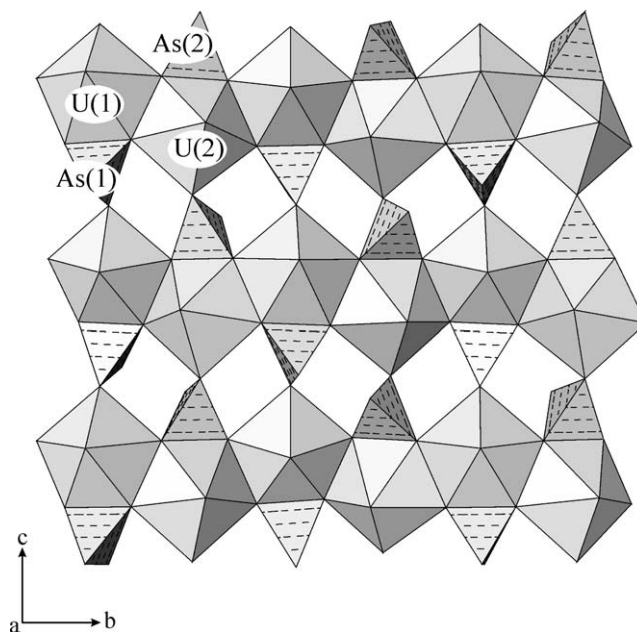

Fig. 1. Polyhedral representation of the uranyl arsenate sheet of $Cs_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_2$ projected along [100]. The sheets have the composition $[(UO_2)(AsO_4)]^{1-}$ and are topologically identical with the uranyl silicate sheets of uranophane-beta. The uranyl polyhedra are shown in shades of gray and the arsenate tetrahedra are stippled.

positions. In agreement with the conclusions of Marsh [20,21], a centrosymmetric description is preferred for *RbUAs*.

4.3. Bond valence analysis

Bond valence analyses were performed using the parameters of Burns et al. [22] for $^{[7]}U^{6+}$, and that of Brown and Altermatt [23] for As, Cs, and Rb; where
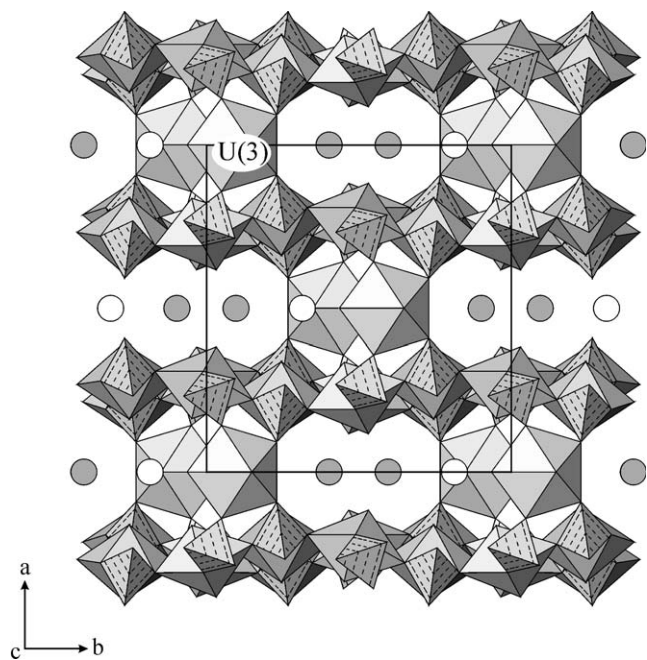
Fig. 2. Polyhedral representation of the structure of $Cs_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_2$ projected along [001]. The uranyl polyhedra are shown in shades of gray and the arsenate tetrahedra are stippled. Cs(1) is shown as filled circles and Cs(2) as unfilled circles. For clarity, interstitial H_2O groups are not shown.
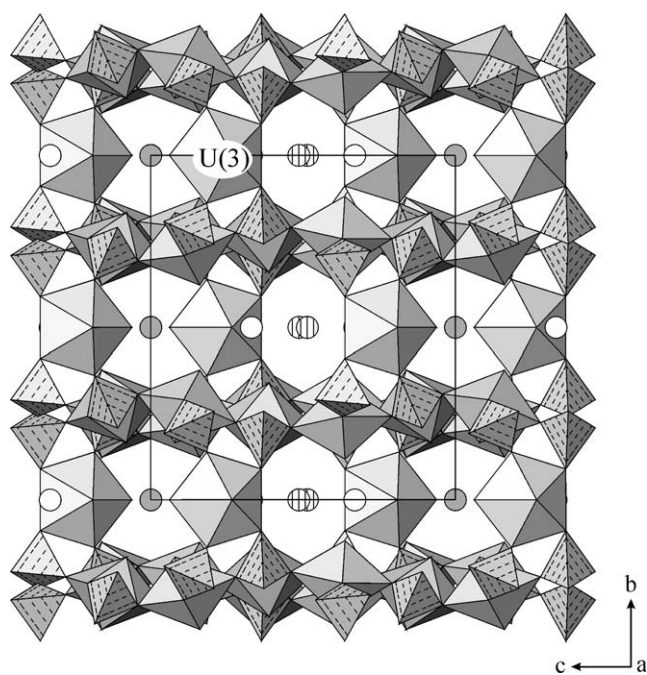

Fig. 4. Polyhedral representation of part of the structure of $Rb_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_{4.5}$ projected along [−407], showing Rb–O interatomic distances in Å. Uranyl polyhedra are shown in shades of gray, arsenate tetrahedra are stippled, and the Rb(3) position and its symmetry equivalent are shown as filled and unfilled spheres, respectively.

Fig. 3. Polyhedral representation of the structure of $Rb_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_{4.5}$ projected along [100]. The uranyl polyhedra are shown in shades of gray and the arsenate tetrahedra are stippled. Rb(1) is shown as unfilled circles, Rb(2) as filled circles, and Rb(3) as striped circles. For clarity, interstitial H_2O groups are not shown.

necessary bond valences were scaled for partial occupancies. For *CsUAs*, the bond valence sums at the U sites are 5.88, 5.90, and 6.26 valence units for U(1), U(2), and U(3), respectively, whereas the sums at the As and Cs sites are 5.00, 5.19, 0.71, and 0.73 valence units for As(1), As(2), Cs(1), and Cs(2), respectively. These results are consistent with formal valences of U^{6+}, As^{5+}, and Cs^+. The bond valence sums for OW(15) and OW(16) are 0.41 and 0.18 valence units, respectively, consistent with their assignment as H_2O groups. The bond valence sums for the remaining O atoms range from 1.72 to 2.24 valence units.

For *RbUAs*, the bond valence sums at the U sites are 5.90, 6.01, and 6.11 valence units for U(1), U(2), and U(3), respectively, whereas the sums at the As and Rb sites are 5.04, 5.08, 1.04, 0.99, and 0.90 valence units for As(1), As(2), Rb(1), Rb(2), and Rb(3), respectively. These results are consistent with formal valences of U^{6+}, As^{5+} and Rb^+. The bond valence sums for OW(15) to OW(19) range from 0 to 0.43 valence units, consistent with their assignment as H_2O groups. The bond valence sums for the remaining O atoms range from 1.73 to 2.18 valence units.

5. Discussion

5.1. Roles of interstitial cations and As

Because *CsUAs* is isostructural with its phosphate analogue, CsUP, one might expect that, as in the sheet

structures of uranyl phosphates and uranyl arsenates, all of the chemically corresponding frameworks are isostructural. However, *RbUAs* is not isostructural with RbUP, but rather shows a homeotypic framework with identical coordination geometries and polyhedral connectivity.

The presence of As expands the framework relative to P; *CsUAs* has a unit-cell volume $\sim 7\%$ greater than CsUP, but the very large Cs atom is still easily accommodated; the mean Cs–O interatomic distances in these compounds are very similar: *CsUAs* $\langle$Cs(1)–O$\rangle$ 3.43 Å, $\langle$Cs(2)–O$\rangle$ 3.33 Å; CsUP $\langle$Cs(1)–O$\rangle$ 3.36 Å, $\langle$Cs(2)–O$\rangle$ 3.33 Å [10]. Generally, the roles of the interstitial cations in uranyl structures are relatively passive and have only a subtle influence upon the crystallization of these extended inorganic structures, with cations of similar size and the same charge yielding identical structures [24]. However, in *RbUAs*, there appears to be a cooperative effect between As and Rb in the formation of the structure. The unit-cell volume of *RbUAs* is only $\sim 5\%$ greater than that of RbUP (in the unconventional pseudo-orthorhombic *Fm*11 setting, $\alpha = 90.39°$), yet the structure changes to a different configuration of the coordination geometry of the interlayer U position and differing interstitial positions than in RbUP. The structural changes take place presumably to maintain mean Rb–O interatomic distances at reasonable values (~ 3.0–3.1 Å).

As in the uranyl phosphate framework structures, Cs is accommodated by a higher symmetry structure, and Rb crystallizes in a derivative structure of identical structural connectivity. Efforts to synthesize the equivalent potassium uranyl arsenate framework did not succeed, and this may be a function of the smaller size of K: effective ionic radii ^{VIII}K 1.51 Å, ^{VIII}Rb 1.61 Å [19]. In the phosphate $K_2(UO_2)[(UO_2)(PO_4)]_4(H_2O)_2$ (KUP), the K atoms are disordered in a structure that is otherwise identical with RbUP [10]. The cavities of an equivalent uranyl arsenate framework would be expected to be even larger, and thus the small K cations might not be accommodated at all.

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