



Rubidium uranyl phosphates and arsenates with polymeric tetrahedral anions: Syntheses and structures of $\text{Rb}_4[(\text{UO}_2)_6(\text{P}_2\text{O}_7)_4(\text{H}_2\text{O})]$, $\text{Rb}_2[(\text{UO}_2)_3(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{12})]$ and $\text{Rb}[(\text{UO}_2)_2(\text{As}_3\text{O}_{10})]$

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ABSTRACT

The three new framework Rb uranyl phosphates and arsenates with anionic parts based on different type of polymeric anions have been prepared by high-temperature solid-state reactions: $\text{Rb}_4[(\text{UO}_2)_6(\text{P}_2\text{O}_7)_4(\text{H}_2\text{O})]$ (**1**), $\text{Rb}_2[(\text{UO}_2)_3(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{12})]$ (**2**), $\text{Rb}[(\text{UO}_2)_2(\text{As}_3\text{O}_{10})]$ (**3**). The crystal structures of the synthesized compounds have been solved by direct methods: **1**—monoclinic $P2_1/c$, $a = 9.672(1)\text{Å}$, $b = 12.951(1)\text{Å}$, $c = 32.231(3)\text{Å}$, $\beta = 90.116(4)^\circ$, $V = 4037.3(6)\text{Å}^3$, $Z = 4$, $R_1 = 0.0926$ for 6351 unique reflections with $|F_0| \geq 4\sigma_F$; **2**—monoclinic, $P2_1/c$, $a = 6.791(1)\text{Å}$, $b = 16.155(3)\text{Å}$, $c = 19.856(4)\text{Å}$, $\beta = 97.48(5)^\circ$, $V = 2159.8(7)\text{Å}^3$, $Z = 4$, $R_1 = 0.0286$ for 3617 unique reflections with $|F_0| \geq 4\sigma_F$; **3**—orthorhombic, $Pbcn$, $a = 10.558(1)\text{Å}$, $b = 11.037(1)\text{Å}$, $c = 11.464(1)\text{Å}$, $V = 1335.9(2)\text{Å}^3$, $Z = 4$, $R_1 = 0.0489$ for 1384 unique reflections with $|F_0| \geq 4\sigma_F$. The structures of title are compounds based on 3D negatively charged frameworks with chemical compositions $[(\text{UO}_2)_6(\text{P}_2\text{O}_7)_4(\text{H}_2\text{O})]^{4-}$ in **1**, $[(\text{UO}_2)_3(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{12})]^{2-}$ in **2** and $[(\text{UO}_2)_2(\text{As}_3\text{O}_{10})]^-$ in **3**. These negative charges are compensated by rubidium cations which are in the channels of **1** and closed cages in structures of **2** and **3**. The channels in **1** are directed along the a direction and have minimum dimensions $\sim 5\text{Å} \times 6\text{Å}$. This is the first example of porosity generation through solid state synthesis in uranyl compounds. For the first time in uranium chemistry polymeric anionic groups P_4O_{12} and As_3O_{10} were observed in structure of **2** and **3**.

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1. Introduction

The research in the field of the synthetic and structural chemistry of uranium (VI) is currently very active due to its importance for a number of industrial and environmental problems, including migration of actinides, safe disposal of radioactive waste, and remediation of contaminated sites. Of special interest are mineral and synthetic phases that form in the $A^1 - \text{UO}_2^{2+} - \text{P}(\text{As})_2\text{O}_5$ systems (where A^1 is an alkali metal or Ag) [1–9]. The hydrated phases occurring in these systems have been under thorough investigations recently [10]. Anhydrous systems have received less attention, though phase formation was studied for Li, Na, K, Cs and Ag uranyl phosphate and arsenates [11–21]. As a rule, anhydrous phases display different structures with complex topology, which involves structural units based on single TO_4 tetrahedra, T_2O_7 dimers, T_3O_{10} trimers, T_4O_{13} tetramers

and polymeric TO_3 chains ($T = \text{P, As}$). In this work, we report three new phases in $\text{Rb} - \text{UO}_2^{2+} - \text{P}(\text{As})_2\text{O}_5$ system: $\text{Rb}_4[(\text{UO}_2)_6(\text{P}_2\text{O}_7)_4(\text{H}_2\text{O})]$ (**1**), $\text{Rb}_2[(\text{UO}_2)_3(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{12})]$ (**2**), and $\text{Rb}[(\text{UO}_2)_2(\text{As}_3\text{O}_{10})]$ (**3**). These compounds possess structural features previously that have not been observed in uranyl phosphate and arsenates such as cyclic P_4O_{12} anions and linear As_3O_{10} groups.

2. Experimental

2.1. Synthesis

Crystals of the title compounds were obtained by high-temperature solid-state reactions. Mixtures of RbNO_3 , UO_2 , $(\text{NO}_3)_2(\text{H}_2\text{O})_6$ and P_2O_5 or As_2O_5 taken in molar ratios of 2:3:5 for **1**, 2:3:8 for **2**, and 1:2:4 for **3** were heated in platinum crucibles to 820°C and then cooled to 50°C with a cooling rate of 7°C/h . The products consisted of greenish transparent crystals of **1** and **2**, and greenish-yellow crystals of **3**. These crystals formed in an amorphous matrix of non-reacted oxides.

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Table 1
Crystallographic data and refinement parameters for **1**, **2** and **3**.

Parameters	1	2	3
<i>a</i> (Å)	9.672(1)	6.791(1)	10.558(1)
<i>b</i> (Å)	12.951(1)	16.155(3)	11.037(1)
<i>c</i> (Å)	32.231(3)	19.856(4)	11.464(1)
α (deg)	–	–	–
β (deg)	90.116(4)	97.48(5)	–
γ (deg)	–	–	–
<i>V</i> (Å ³)	4037.3(6)	2159.8(7)	1335.9(2)
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>Pbcn</i>
Ref. for cell refinement	All	118	All
<i>F</i> ₀₀₀	4592	2560	1728
μ (cm ⁻¹)	292.09	274.79	352.77
<i>Z</i>	4	4	4
<i>D</i> _{calc} (g/cm ³)	4.399	4.523	5.023
Crystal size (mm ³)	0.18 × 0.15 × 0.1	0.35 × 0.15 × 0.12	0.23 × 0.18 × 0.06
Radiation	MoK α	MoK α	MoK α
<i>R</i> _{int}	0.0919	0.0450	0.0489
Total ref.	18784	11550	10162
Unique ref.	6750	5338	1604
Unique ref. <i>F</i> ₀ ≥ 4 σ _{<i>F</i>}	6351	3617	1384
<i>R</i> ₁	0.0926	0.0286	0.0489
<i>wR</i> ₂	0.2349	0.0455	0.1208
<i>GOOF</i>	1.073	0.966	1.049

2.2. Crystal-structure analysis

The crystals selected for data collection were mounted on a Mar345 Image Plate (**1** and **3**) and Stoe Stadi-4 (**2**) diffractometers. All data were collected using monochromatic MoK α X-radiation. The unit-cell dimensions for all compounds (Table 1) were refined using least-squares techniques. More than a hemisphere of data was collected for each crystal and the three-dimensional data were reduced and filtered for statistical outliers using the supporting programs for diffractometers. Data were corrected for Lorentz, polarization, absorption and background effects. Additional information pertinent to the data collection is given in Table 1. The SHELXL 97 program was used for the determination and refinement of the structures. The structures were solved by direct methods and refined to *R*₁ = 0.0926 for **1**, 0.0286 for **2**, and 0.0489 for **3**. The structure of **1** has been solved from a pseudomerohedrally twinned crystal, which is the reason for the relatively high *R*₁ value. The final models included anisotropic displacement parameters for all atoms and weighting schemes of the structure factors. The final atomic positional and displacement parameters, and selected interatomic distances are given in Tables 2 and 5 for **1**, **3** and 6 for **2**, **4** and 7 for **3**. Tables of observed and calculated structure factors for each structure are available from the authors upon request.

3. Results and discussions

3.1. Cation coordination

In all compounds under consideration, U⁶⁺ cations form almost linear UO₂²⁺ uranyl groups with the U=O bond lengths ranging from 1.71 to 1.86 Å. In the equatorial plane, uranyl groups are coordinated by either four or five O atoms that results in the formation of square and pentagonal bipyramids, respectively. The equatorial U–O bond lengths are in the range of 2.18–2.69 Å.

The P and As atoms in the title compounds are tetrahedrally coordinated by four O atoms each. In the structure of **1**, PO₄ tetrahedra are linked via a bridging O atom (O_{br}) to form P₂O₇ dimers. The P–O_{br} bond lengths are in the range of 1.50–1.64 Å, whereas P–O bond lengths to terminal O atoms (O_{term}) vary from

Table 2
Atomic coordinates and displacement parameters (Å²) for **1**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U _{eq}
U(1)	0.0335(1)	0.29699(7)	0.53264(3)	0.0370(3)
U(2)	–0.0347(1)	0.51440(7)	0.73537(3)	0.0385(3)
U(3)	–0.4512(1)	0.49363(7)	0.76890(3)	0.0381(3)
U(4)	–0.0246(1)	0.42767(7)	0.89142(3)	0.0371(2)
U(5)	0.4457(1)	0.20985(7)	0.54294(3)	0.0377(3)
U(6)	–0.4948(1)	0.56935(7)	0.61467(3)	0.0374(3)
P(1)	0.2639(9)	0.4639(5)	0.5381(2)	0.0399(2)
P(2)	–0.3058(9)	0.4301(5)	0.5428(2)	0.038(2)
P(3)	0.2212(8)	0.0425(5)	0.5245(2)	0.037(2)
P(4)	–0.2394(9)	0.3399(5)	0.8078(2)	0.039(2)
P(5)	–0.2463(9)	0.6624(5)	0.6930(2)	0.038(2)
P(6)	–0.706(1)	0.6249(5)	0.7021(2)	0.043(2)
P(7)	0.2149(9)	0.3877(5)	0.7990(2)	0.037(2)
P(8)	–0.2109(9)	0.0909(5)	0.5520(2)	0.035(2)
Rb(1)	–0.4372(3)	0.9057(2)	0.60039(6)	0.0294(5)
Rb(2)	0.0091(3)	0.0939(2)	0.89444(7)	0.0390(7)
Rb(3)	0.2211(4)	0.2756(3)	0.67446(9)	0.063(1)
Rb(4)	–0.7098(6)	0.7287(3)	0.8348(2)	0.089(2)
O(1)	–0.247(3)	0.241(2)	0.7833(7)	0.065(7)
O(2)	–0.091(3)	0.658(2)	0.6891(7)	0.056(6)
O(3)	0.364(3)	0.032(1)	0.5421(7)	0.056(7)
O(4)	0.279(2)	0.275(1)	0.7918(7)	0.042(5)
O(5)	0.118(2)	0.394(2)	0.7625(6)	0.040(5)
O(6)	–0.227(2)	0.992(1)	0.5231(6)	0.041(5)
O(7)	0.079(2)	0.328(2)	0.9176(6)	0.041(5)
O(8)	0.117(2)	–0.018(2)	0.5454(5)	0.036(4)
O(9)	–0.438(3)	0.594(2)	0.8043(7)	0.050(6)
O(10)	–0.389(3)	0.368(2)	0.8206(5)	0.050(6)
O(11)	0.149(3)	0.395(2)	0.8417(6)	0.048(6)
O(12)	–0.833(2)	0.559(1)	0.7013(6)	0.039(4)
O(13)	–0.509(2)	0.691(2)	0.5873(8)	0.059(6)
O(14)	–0.661(3)	0.637(2)	0.6574(6)	0.048(5)
O(15)	0.334(2)	0.537(2)	0.5037(6)	0.038(5)
O(16)	0.052(3)	0.284(2)	0.5876(7)	0.051(6)
O(17)	–0.331(2)	0.530(2)	0.5676(6)	0.040(4)
O(18)	–0.469(2)	0.393(2)	0.7328(6)	0.050(6)
O(19)	0.199(2)	0.159(1)	0.5219(7)	0.044(5)
O(20)	0.297(2)	0.352(1)	0.5287(6)	0.045(5)
O(21)	0.340(2)	0.459(2)	0.7980(7)	0.044(5)
O(22)	0.407(3)	0.218(1)	0.5955(6)	0.056(7)
O(23)	0.000(3)	0.604(1)	0.7742(7)	0.048(6)
O(24)	–0.139(2)	0.049(2)	0.5898(6)	0.041(5)
O(25)	0.007(2)	0.314(1)	0.4766(7)	0.052(6)
O(26)	0.329(3)	0.493(2)	0.5774(6)	0.048(6)
O(27)	–0.407(2)	0.353(2)	0.5509(7)	0.048(6)
O(28)	–0.282(2)	0.592(2)	0.7274(7)	0.043(5)
O(29)	–0.473(3)	0.455(2)	0.6436(7)	0.050(6)
O(30)	–0.128(3)	0.531(2)	0.8654(7)	0.063(8)
O(31)	–0.586(3)	0.594(2)	0.7324(8)	0.082(9)
O(32)	0.113(2)	0.474(2)	0.5388(7)	0.048(6)
O(33)	0.505(2)	0.196(2)	0.4931(7)	0.043(5)
O(34)	–0.133(2)	0.171(2)	0.5271(7)	0.042(5)
O(35)	–0.358(2)	0.128(1)	0.5626(6)	0.038(5)
O(36)	–0.149(2)	0.321(2)	0.8405(7)	0.044(5)
O(37)	–0.206(2)	0.421(2)	0.7757(5)	0.038(5)
O(38)	–0.324(2)	0.649(2)	0.6532(5)	0.042(5)
O(39)	–0.068(3)	0.430(2)	0.6944(7)	0.052(6)
O(40)	–0.158(2)	0.390(1)	0.5456(6)	0.040(5)
H ₂ O(41)	–0.229(3)	0.310(2)	0.923(1)	0.080(10)

1.40 to 1.57 Å. The structure of **2** contains two types of phosphate anions. The P1O₄, P2O₄, P3O₄, and P4O₄ tetrahedra are linked via bridging O2, O6, O22, and O23 atoms into a cyclic P₄O₁₂ anion (the respective P–O_{br} and P–O_{term} bond lengths are in the ranges of 1.576–1.612 and 1.463–1.489 Å, respectively). The P5O₄ and P6O₄ tetrahedra form a P₂O₇ dimer (P–O_{br} = 1.608–1.622 Å; P–O_{term} = 1.484–1.517 Å). In the structure of **3**, AsO₄ tetrahedra form a linear As₃O₁₀ trimer (As–O_{br} = 1.72–1.75 Å; As–O_{term} = 1.64–1.67 Å).

The coordination of Rb⁺ cations in the title compounds is variable with Rb–O bond lengths ranging from 2.88 to 3.64 Å.

Table 3
Atomic coordinates and displacement parameters (\AA^2) for **2**.

Atom	x	y	z	U_{eq}
U(1)	0.20404(3)	0.66567(1)	0.24810(1)	0.01114(4)
U(2)	−0.61497(3)	0.38380(1)	0.402768(9)	0.01070(4)
U(3)	0.21481(3)	0.39202(1)	0.100757(9)	0.01011(4)
P(1)	0.6939(2)	0.36068(9)	0.04037(7)	0.0100(3)
P(2)	0.3371(2)	0.67969(9)	0.43058(7)	0.0107(3)
P(3)	0.0518(2)	0.67572(9)	0.05995(7)	0.0128(3)
P(4)	−0.0761(2)	0.3579(1)	0.46963(7)	0.0128(3)
P(5)	−0.9633(2)	0.44558(9)	0.25911(6)	0.0101(3)
P(6)	−0.3817(2)	0.38498(9)	0.24528(6)	0.0104(3)
Rb(1)	−0.24055(9)	0.57690(5)	0.36841(3)	0.0330(2)
Rb(2)	0.65291(8)	0.56898(4)	0.12131(3)	0.0252(2)
O(1)	0.5089(5)	0.6627(3)	0.4816(2)	0.0148(9)
O(2)	0.2647(5)	0.6627(3)	0.352(2)	0.0150(9)
O(3)	0.8989(5)	0.6220(3)	0.0212(2)	0.021(1)
O(4)	0.8547(5)	0.4133(2)	0.0744(2)	0.0150(9)
O(5)	−0.4942(5)	0.3988(3)	0.1751(2)	0.018(1)
O(6)	−0.1377(5)	0.3563(3)	0.5453(2)	0.0184(9)
O(7)	0.4888(5)	0.3939(3)	0.0326(2)	0.020(1)
O(8)	−0.2017(5)	0.4516(2)	0.2500(2)	0.0150(8)
O(9)	−0.0253(6)	0.6935(3)	0.2729(2)	0.025(1)
O(10)	−0.4983(5)	0.4107(3)	0.3015(2)	0.020(1)
O(11)	0.3450(6)	0.6483(3)	0.3606(2)	0.0154(9)
O(12)	0.2279(5)	0.5009(3)	0.0955(2)	0.0168(9)
O(13)	−0.9058(5)	0.3943(3)	0.2028(2)	0.0179(9)
O(14)	0.4377(6)	0.6309(3)	0.2264(2)	0.022(1)
O(15)	−0.6435(6)	0.2775(3)	0.3843(2)	0.024(1)
O(16)	0.2075(6)	0.2838(3)	0.1037(2)	0.023(1)
O(17)	−0.8955(5)	0.4097(3)	0.4725(2)	0.0171(9)
O(18)	0.0760(6)	0.6679(3)	0.1350(2)	0.020(1)
O(19)	−0.2923(6)	0.2991(3)	0.2545(2)	0.024(1)
O(20)	−0.5741(6)	0.4889(3)	0.4231(2)	0.022(1)
O(21)	−0.8998(5)	0.4122(3)	0.3285(2)	0.020(1)
O(22)	0.7102(6)	0.2748(3)	0.0787(2)	0.022(1)
O(23)	0.9937(6)	0.7661(3)	0.0376(2)	0.030(1)
O(24)	−0.9086(6)	0.5348(3)	0.2538(2)	0.027(1)
O(25)	−0.2537(5)	0.3750(3)	0.4217(2)	0.030(1)

Table 4
Atomic coordinates and displacement parameters (\AA^2) for **3**.

Atom	x	y	z	U_{eq}
U	0.19152(4)	0.67556(4)	0.09679(4)	0.0218(2)
As(1)	0.1903(1)	0.9276(1)	−0.1125(1)	0.0232(3)
As(2)	0	0.9124(2)	1/4	0.0234(4)
Rb	0	0.3918(2)	1/4	0.0467(6)
O(1)	0.035(2)	0.618(1)	0.0945(9)	0.038(2)
O(2)	0.1259(9)	0.8367(8)	0.2072(9)	0.032(2)
O(3)	0.154(1)	0.7878(9)	−0.0691(8)	0.033(2)
O(4)	0.347(1)	0.733(1)	0.1044(8)	0.033(2)
O(5)	0.274(1)	0.9320(8)	−0.2351(9)	0.033(2)
O(6)	0.041(1)	0.991(1)	−0.139(1)	0.049(3)
O(7)	0.254(1)	0.013(1)	−0.011(1)	0.048(3)

3.2. Structure descriptions

$\text{Rb}_4[(\text{UO}_2)_6(\text{P}_2\text{O}_7)_4(\text{H}_2\text{O})]$. The crystal structure of **1** is based upon an open 3D-framework (Fig. 1a) consisting of U_2O_{12} dimers of two edge-sharing UO_7 bipyramids, UO_6 square bipyramids and $\text{UO}_6(\text{H}_2\text{O})$ pentagonal bipyramids and P_2O_7 dimers. The short P–O distances in structure of **1** in our opinion can be a result of “late hydration” and simultaneous strong structure deformation (including twinning). The framework has the composition $[(\text{UO}_2)_6(\text{P}_2\text{O}_7)_4(\text{H}_2\text{O})]^{4-}$. The negative charge of the framework is compensated by extra-framework Rb^+ cations located in the structure channels. The channels are outlined by five U and six P atoms (see skeletal representation in Fig. 1b). The structure can be subdivided into two types of alternating layers (Fig. 2a) linked by

Table 5
Selected interatomic distances (\AA) in the structure of **1**.

U(1)–O(16)	1.79(2)
U(1)–O(25)	1.84(2)
U(1)–O(40)	2.25(2)
U(1)–O(34)	2.30(2)
U(1)–O(19)	2.42(2)
U(1)–O(32)	2.42(2)
U(1)–O(20)	2.65(2)
U(2)–O(23)	1.74(2)
U(2)–O(39)	1.74(2)
U(2)–O(5)	2.32(2)
U(2)–O(12)	2.32(2)
U(2)–O(37)	2.43(2)
U(2)–O(2)	2.44(2)
U(2)–O(28)	2.60(2)
U(3)–O(9)	1.73(2)
U(3)–O(18)	1.76(2)
U(3)–O(31)	2.18(2)
U(3)–O(21)	2.27(2)
U(3)–O(10)	2.41(2)
U(3)–O(28)	2.47(2)
U(3)–O(37)	2.56(2)
U(4)–O(7)	1.84(2)
U(4)–O(30)	1.86(3)
U(4)–O(24)	2.31(2)
U(4)–O(8)	2.33(2)
U(4)–O(11)	2.36(2)
U(4)–O(36)	2.46(2)
U(4)–H ₂ O(41)	2.69(3)
U(5)–O(33)	1.71(2)
U(5)–O(22)	1.74(2)
U(5)–O(35)	2.26(2)
U(5)–O(27)	2.35(2)
U(5)–O(20)	2.38(2)
U(5)–O(3)	2.43(2)
U(5)–O(19)	2.57(2)
U(6)–O(29)	1.76(2)
U(6)–O(13)	1.81(2)
U(6)–O(17)	2.25(2)
U(6)–O(14)	2.29(2)
U(6)–O(38)	2.31(2)
U(6)–O(26)	2.31(2)
P(1)–O(26)	1.46(2)
P(1)–O(32)	1.47(2)
P(1)–O(20)	1.52(2)
P(1)–O(15)	1.61(2)
P(2)–O(27)	1.42(2)
P(2)–O(40)	1.52(2)
P(2)–O(17)	1.54(2)
P(2)–O(15)	1.58(2)
P(3)–O(8)	1.44(2)
P(3)–O(3)	1.50(3)
P(3)–O(19)	1.53(2)
P(3)–O(6)	1.60(2)
P(4)–O(36)	1.40(2)
P(4)–O(1)	1.50(3)
P(4)–O(37)	1.51(2)
P(4)–O(10)	1.54(3)
P(5)–O(28)	1.48(2)
P(5)–O(38)	1.49(2)
P(5)–O(2)	1.51(3)
P(5)–O(4)	1.57(2)
P(6)–O(14)	1.51(2)
P(6)–O(12)	1.50(2)
P(6)–O(31)	1.57(3)
P(6)–O(1)	1.64(2)
P(7)–O(5)	1.50(2)
P(7)–O(11)	1.52(2)
P(7)–O(21)	1.52(2)
P(7)–O(4)	1.60(2)
P(8)–O(24)	1.50(2)

Table 5. (continued)

P(8)–O(34)	1.51(2)
P(8)–O(35)	1.54(2)
P(8)–O(6)	1.59(2)
Rb(1)–O(13)	2.90(2)
Rb(1)–O(10)	3.10(2)
Rb(1)–O(3)	3.14(2)
Rb(1)–O(35)	3.22(2)
Rb(1)–O(33)	3.36(2)
Rb(1)–O(11)	3.36(2)
Rb(1)–O(6)	3.41(2)
Rb(1)–O(24)	3.45(2)
Rb(1)–O(21)	3.48(2)
Rb(1)–O(41)	3.54(3)
Rb(2)–O(25)	2.90(2)
Rb(2)–O(32)	2.91(2)
Rb(2)–O(2)	2.93(2)
Rb(2)–O(7)	3.19(2)
Rb(2)–O(17)	3.45(2)
Rb(2)–O(38)	3.48(2)
Rb(2)–O(12)	3.55(2)
Rb(2)–O(40)	3.57(2)
Rb(2)–O(39)	3.61(2)
Rb(2)–O(26)	3.64(3)
Rb(3)–O(22)	3.21(2)
Rb(3)–O(16)	3.24(2)
Rb(3)–O(9)	3.22(2)
Rb(3)–O(5)	3.38(2)
Rb(3)–O(39)	3.50(3)
Rb(3)–O(23)	3.51(2)
Rb(3)–O(30)	3.55(2)
Rb(4)–O(9)	3.31(3)
Rb(4)–O(29)	3.49(2)
Rb(4)–O(39)	3.50(3)
Rb(4)–O(18)	3.50(2)
Rb(4)–O(35)	3.62(2)

uranyl groups (schematically shown by red dotted lines on Fig. 2a). Both layers are corrugated and consist of U_2O_{12} dimers interlinked by P_2O_7 anionic groups (Fig. 2a and b). Topologically, the layers are identical and the principal difference is their conformation as can be seen in Fig. 2. The framework has a framework density (FD) of ~ 13.8 cations per 1 nm^3 , which is quite low for uranyl phases, and especially for those obtained in solid state reactions. As a consequence of its low density, the framework possess a open channels with dimensions $\sim 5\text{ \AA} \times 6\text{ \AA}$. The channels accommodate the Rb(3) and Rb(4) atoms which have relatively large displacement parameters. One of most interesting points in structure of **1** is an $H_2O(41)$ water molecule coordinated to U(4). The U(4)– $H_2O(41)$ bond length is 2.69 \AA . The $H_2O(41)$ site has a neighboring O(13) site located at 2.91 \AA and belonging to the $U(6)O_2^{2+}$ uranyl ion, which indicates possible formation of a hydrogen bond. Two new uranyl phosphates with the same U:P ratio as in **1** have recently been synthesized, $Li_2[(UO_2)_3(P_2O_7)_2]$ and $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4] \cdot H_2O$. It is noteworthy that their structures also contain U_2O_{12} dimers [20,22]. The $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4] \cdot H_2O$ phase is also microporous but with larger channels compared to **1**, owing to the templating role of the $[H_2bipy]^{2+}$ cation.

$Rb_2[(UO_2)_3(P_2O_7)(P_4O_{12})]$. The structure of **2** is based upon a dense 3D framework built from four different elements: UO_6 square bipyramids, UO_7 pentagonal bipyramids, P_2O_7 linear dimers and P_4O_{12} cyclic tetramers (Fig. 3). Rb^+ cations are in framework cages. In order to provide a clear explanation for the structure topology, the framework can be subdivided into modulated quasi-2D layers (shown by dark dotted lines in Fig. 3). Linkage of the layers is through P_2O_7 dimers. In turn, each layer can be separated into two equivalent sublayers shown in Fig. 4a.

Table 6

Selected interatomic distances (Å) in the structure of **2**.

U(1)–O(9)	1.753(4)
U(1)–O(14)	1.788(4)
U(1)–O(19)	2.239(4)
U(1)–O(24)	2.256(4)
U(1)–O(18)	2.301(4)
U(1)–O(11)	2.330(4)
U(2)–O(20)	1.759(5)
U(2)–O(15)	1.762(5)
U(2)–O(10)	2.296(4)
U(2)–O(21)	2.320(4)
U(2)–O(1)	2.434(4)
U(2)–O(25)	2.437(4)
U(2)–O(17)	2.531(4)
U(3)–O(16)	1.750(5)
U(3)–O(12)	1.765(4)
U(3)–O(13)	2.282(4)
U(3)–O(5)	2.310(4)
U(3)–O(7)	2.439(4)
U(3)–O(3)	2.454(4)
U(3)–O(4)	2.458(4)
P(1)–O(4)	1.476(4)
P(1)–O(7)	1.482(4)
P(1)–O(22)	1.580(4)
P(1)–O(2)	1.607(4)
P(2)–O(1)	1.468(4)
P(2)–O(11)	1.487(4)
P(2)–O(22)	1.576(4)
P(2)–O(6)	1.603(4)
P(3)–O(18)	1.482(4)
P(3)–O(3)	1.489(4)
P(3)–O(23)	1.561(5)
P(3)–O(2)	1.601(4)
P(4)–O(25)	1.463(4)
P(4)–O(17)	1.480(4)
P(4)–O(23)	1.598(5)
P(4)–O(6)	1.612(4)
P(5)–O(13)	1.484(4)
P(5)–O(21)	1.491(4)
P(5)–O(24)	1.496(5)
P(5)–O(8)	1.608(4)
P(6)–O(10)	1.510(4)
P(6)–O(19)	1.516(5)
P(6)–O(5)	1.517(4)
P(6)–O(8)	1.622(4)
Rb(1)–O(20)	2.995(4)
Rb(1)–O(11)	3.027(4)
Rb(1)–O(6)	3.091(4)
Rb(1)–O(8)	3.141(4)
Rb(1)–O(9)	3.163(4)
Rb(1)–O(17)	3.182(4)
Rb(1)–O(1)	3.296(4)
Rb(1)–O(10)	3.380(4)
Rb(1)–O(16)	3.391(5)
Rb(1)–O(25)	3.434(5)
Rb(1)–O(14)	3.447(4)
Rb(1)–O(24)	3.473(4)
Rb(2)–O(14)	2.878(4)
Rb(2)–O(3)	2.888(4)
Rb(2)–O(4)	3.067(4)
Rb(2)–O(12)	3.069(4)
Rb(2)–O(7)	3.141(4)
Rb(2)–O(5)	3.158(4)
Rb(2)–O(8)	3.231(4)
Rb(2)–O(18)	3.268(4)
Rb(2)–O(2)	3.315(4)
Rb(2)–O(15)	3.371(5)
Rb(2)–O(7)	3.440(4)

The sublayer (Fig. 4b) is formed by UO_6 and UO_7 polyhedra interlinked by P_2O_7 groups, which are either dimers or halves of the P_4O_{12} tetramers. It is interesting that all coordination polyhedra of high-valent cations in the structure of **2** link by corner sharing. A topological description of the sublayers is shown in Fig. 4c. This topology is new for uranyl phosphates, though some similarities to the known structures can still be seen. In $\text{Li}_2[(\text{UO}_2)_3(\text{P}_2\text{O}_7)_2]$ [20], a similar motif has been observed: layers of UO_7 polyhedra and P_2O_7 groups are linked in the third dimension by UO_6 square bipyramids. The $A^I\text{:U:P(As)} = 2\text{:}3\text{:}6$ ratio found in **2** is observed in uranyl phosphates and arsenates for the first time. It should be noted that the ratio $\text{U:P} = 1\text{:}2$ is quite widespread in these phases, but with different numbers of the A^I and A^{II} cations [10]. The majority of these phases contains either T_2O_7 groups or single TO_4 tetrahedra, though two phases with mixed anionic parts have also been reported [19]. The P_4O_{12} cyclic tetramer is observed in uranium compounds for the first time. We note that linear tetramers, P_4O_{13} and As_4O_{13} , have been described

previously in $\text{Li}_6[(\text{UO}_2)_{12}(\text{PO}_4)_8(\text{P}_4\text{O}_{13})]$ [21] and $\text{Ag}_6[(\text{UO}_2)_2(\text{As}_2\text{O}_7)(\text{As}_4\text{O}_{13})]$ [19], respectively.

$\text{Rb}[(\text{UO}_2)_2(\text{As}_3\text{O}_{10})]$. Compound **3** is the first example of a uranium phase with As_3O_{10} linear trimer and is isotopic with $\text{K}[(\text{UO}_2)_2(\text{P}_3\text{O}_{10})]$ [18]. The structure of **3** is a 3D framework consisting of UO_6 square bipyramids and As_3O_{10} groups, which can be described as based upon 2D layers, shown in Fig. 5a by the dotted line. Each layer includes AsO_4 tetrahedra from As_3O_{10} groups. The layer topology can be viewed as a simple 2D net based on single AsO_4 tetrahedra and UO_6 octahedra. This topology is characteristic for variscite-type framework structures described for Fe, Al and Ga phosphates and arsenates with general chemical formula $M(\text{TO}_4)(\text{H}_2\text{O})_2$ [23,24]. The Rb^+ cations are located in the framework channels.

Table 7
Selected interatomic distances (Å) in the structure of **3**.

U–O(4)	1.77(1)
U–O(1)	1.77(1)
U–O(7)	2.25(1)
U–O(5)	2.29(1)
U–O(2)	2.291(9)
U–O(3)	2.30(1)
As(1)–O(7)	1.64(1)
As(1)–O(5)	1.66(1)
As(1)–O(3)	1.67(1)
As(1)–O(6)	1.75(1)
As(2)–O(2)	1.644(9) 2 ×
As(2)–O(6)	1.72(1) 2 ×
Rb–O(4)	2.91(1) 2 ×
Rb–O(5)	3.08(1) 2 ×
Rb–O(1)	3.09(1) 2 ×
Rb–O(3)	3.30(1) 2 ×

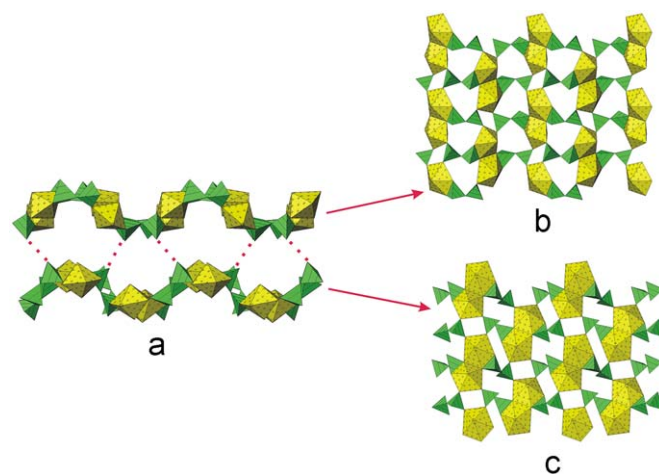


Fig. 2. The quasi-layers in the structure of **1** (for detail see text). Legend: U polyhedra = yellow, PO_4 tetrahedra = green. [For interpretation of the references to color in this figure legend, the reader is referred to the webversion of this article.]

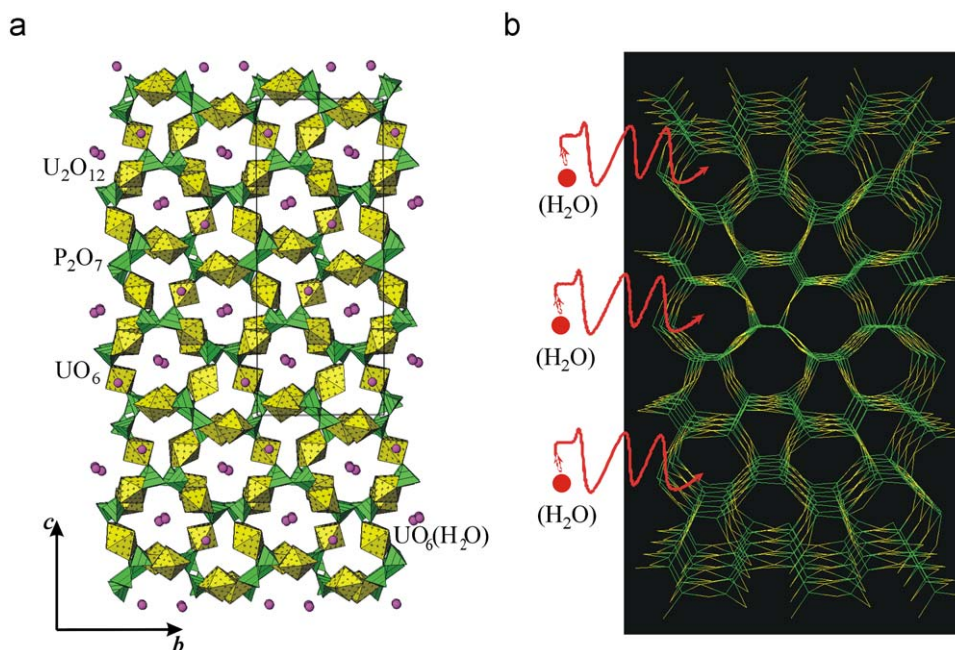


Fig. 1. Fragments of crystal structure of **1** (a) and its 3D framework topology (b). Legend: U polyhedra = yellow, PO_4 tetrahedra = green, Rb^+ —violet circles. [For interpretation of the references to color in this figure legend, the reader is referred to the webversion of this article.]

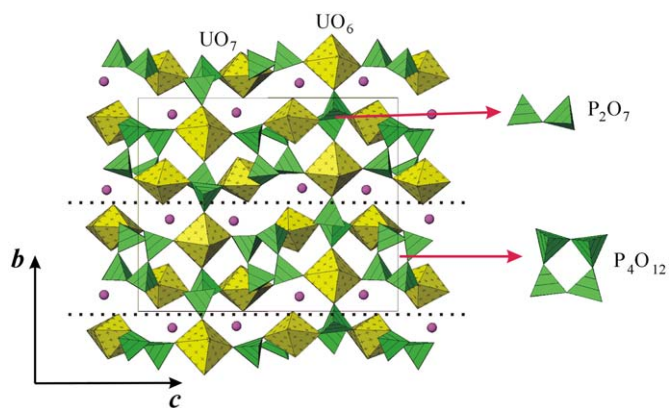


Fig. 3. The fragments of crystal structures of **2**. Legend: U polyhedra = yellow, PO₄ tetrahedra = green, Rb—violet circles. [For interpretation of the references to color in this figure legend, the reader is referred to the webversion of this article.]

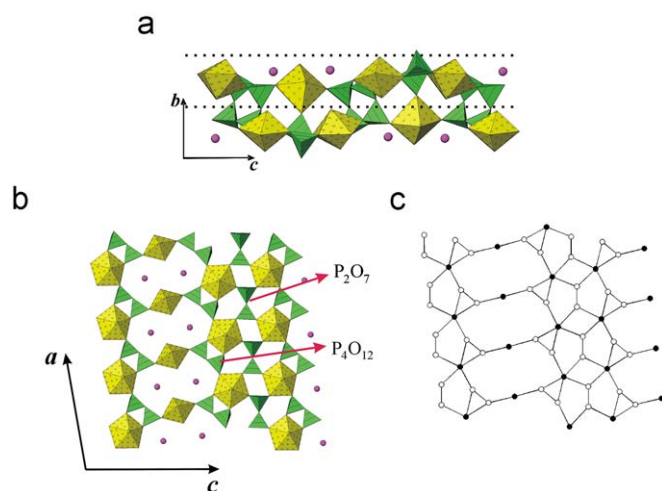


Fig. 4. The quasi-layers in the structure of **2** and their fragments (for detail see text). Legend: U polyhedra = yellow, PO₄ tetrahedra = green, Rb—violet circles. [For interpretation of the references to color in this figure legend, the reader is referred to the webversion of this article.]

The anionic units in uranyl phosphates and arsenates. In the structures of the title compounds, three different types of condensed tetrahedral anions are observed. It is noteworthy that the As₃O₁₀ trimers and P₄O₁₂ cyclic tetramers are observed in uranyl chemistry for the first time. These groups supplement the structural diversity of the large group of compounds—uranyl phosphates and arsenates. Occurrence of polyarsenate species is especially interesting, because of the opinion on the instability of the polymeric chains based upon AsO₄ tetrahedra. During the last two years, development of new methods of solid-state preparative chemistry allowed for the synthesis of uranyl mono-, di-, tetra- and now triarsenates [17,19,21]. These varieties of arsenic based polymeric chains (di-, tri- and tetra) have been found in uranium compounds only. On the basis of these results, one may conclude that such a structural diversity is due to the high coordination capacity of the uranyl ion and its unique electronic properties. It should also be mentioned that structural diversity of uranyl polyphosphates is also remarkable and is generally larger than of polyarsenates because of the higher stability of polymeric phosphate chains [16,18,20,21]. In general, one may qualify uranium arsenates and phosphates as one of the structurally richest groups in polyanionic phosphate and arsenate chemistry.

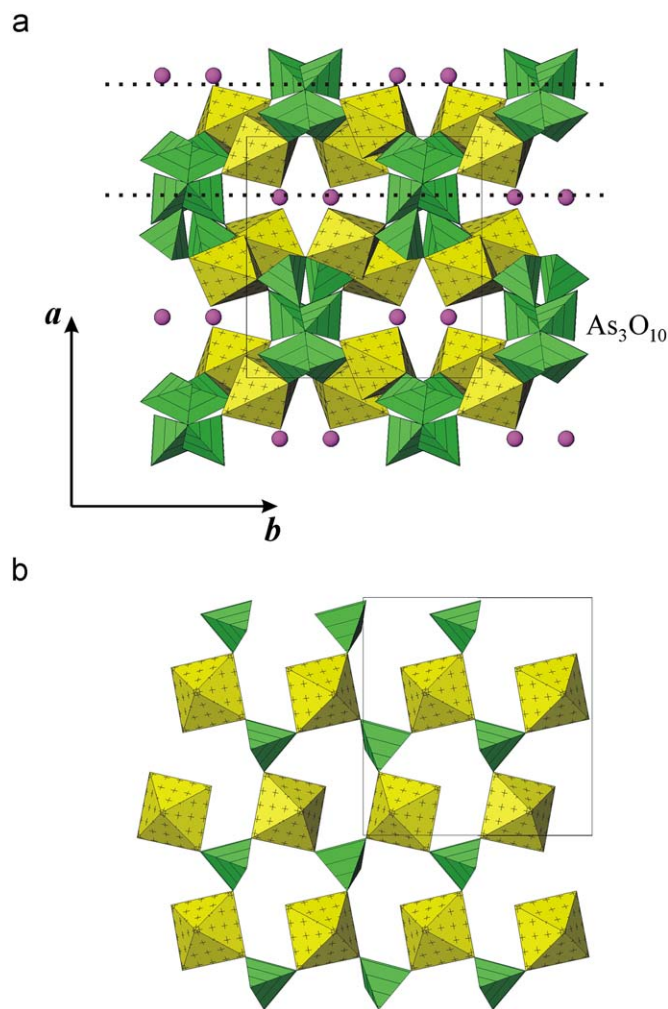


Fig. 5. The structure of **3** and topology of quasi-layers in this structure (for detail see text). Legend: U polyhedra = yellow, AsO₄ tetrahedra = green, Rb—violet circles. [For interpretation of the references to color in this figure legend, the reader is referred to the webversion of this article.]

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.05.022.

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