



Crystal chemistry of anhydrous Li uranyl phosphates and arsenates. II. Tubular fragments and cation–cation interactions in the 3D framework structures of $\text{Li}_6[(\text{UO}_2)_{12}(\text{PO}_4)_8(\text{P}_4\text{O}_{13})]$, $\text{Li}_5[(\text{UO}_2)_{13}(\text{AsO}_4)_9(\text{As}_2\text{O}_7)]$, $\text{Li}[(\text{UO}_2)_4(\text{AsO}_4)_3]$ and $\text{Li}_3[(\text{UO}_2)_7(\text{AsO}_4)_5\text{O}]$

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ABSTRACT

Single crystals of the new compounds $\text{Li}_6[(\text{UO}_2)_{12}(\text{PO}_4)_8(\text{P}_4\text{O}_{13})]$ (**1**), $\text{Li}_5[(\text{UO}_2)_{13}(\text{AsO}_4)_9(\text{As}_2\text{O}_7)]$ (**2**), $\text{Li}[(\text{UO}_2)_4(\text{AsO}_4)_3]$ (**3**) and $\text{Li}_3[(\text{UO}_2)_7(\text{AsO}_4)_5\text{O}]$ (**4**) have been prepared using high-temperature solid state reactions. The crystal structures have been solved by direct methods: **1**—monoclinic, $C2/m$, $a = 26.963(3)\text{Å}$, $b = 7.063(1)\text{Å}$, $c = 19.639(1)\text{Å}$, $\beta = 126.890(4)^\circ$, $V = 2991.2(6)\text{Å}^3$, $Z = 2$, $R_1 = 0.0357$ for 3248 unique reflections with $|F_0| \geq 4\sigma_F$; **2**—triclinic, $P\bar{1}$, $a = 7.1410(8)\text{Å}$, $b = 13.959(1)\text{Å}$, $c = 31.925(1)\text{Å}$, $\alpha = 82.850(2)^\circ$, $\beta = 88.691(2)^\circ$, $\gamma = 79.774(3)^\circ$, $V = 3107.4(4)\text{Å}^3$, $Z = 2$, $R_1 = 0.0722$ for 9161 unique reflections with $|F_0| \geq 4\sigma_F$; **3**—tetragonal, $I4_1/amd$, $a = 7.160(3)\text{Å}$, $c = 33.775(9)\text{Å}$, $V = 1732(1)\text{Å}^3$, $Z = 4$, $R_1 = 0.0356$ for 318 unique reflections with $|F_0| \geq 4\sigma_F$; **4**—tetragonal, $P\bar{4}$, $a = 7.2160(5)\text{Å}$, $c = 14.6540(7)\text{Å}$, $V = 763.04(8)\text{Å}^3$, $Z = 1$, $R_1 = 0.0423$ for 1600 unique reflections with $|F_0| \geq 4\sigma_F$. Structures of all the phases under consideration are based on complex 3D frameworks consisting of different types of uranium polyhedra (UO_6 and UO_7) and different types of tetrahedral TO_4 anions ($T = \text{P}$ or As): PO_4 and P_4O_{13} in **1**, AsO_4 and As_2O_7 in **2**, and single AsO_4 tetrahedra in **3** and **4**. In the structures of **1** and **2**, UO_7 pentagonal bipyramids share edges to form $(\text{UO}_5)_\infty$ chains extended along the b axis in **1** and along the a axis in **2**. The chains are linked via single TO_4 tetrahedra into tubular units with external diameters of 11 Å in **1** and 11.5 Å in **2**, and internal diameters of 4.1 Å in **1** and 4.5 Å in **2**. The channels accommodate Li^+ cations. The tubular units are linked into 3D frameworks by intertubular complexes. Structures of **3** and **4** are based on 3D frameworks composed on layers united by $(\text{UO}_5)_\infty$ infinite chains. Cation–cation interactions are observed in **2**, **3**, and **4**. In **2**, the structure contains a trimeric unit with composition $[\text{O}=\text{U}(1)=\text{O}]-\text{U}(13)-[\text{O}=\text{U}(2)=\text{O}]$. In the structures of **3** and **4**, T-shaped dimers are observed. In all the structures, Li^+ cations are located in different types of cages and channels and compensate negative charges of anionic 3D frameworks.

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1. Introduction

The synthetic and structural chemistry of uranium is remarkable in its unique and unprecedented diversity. One of the main points of current research in this field is focused on syntheses of new phases with interesting properties and structure. Inorganic uranium compounds with curved structural elements are of special interest since the discoveries of uranyl peroxide nanospheres [1,2], and uranyl selenate nanotubes [3–5]. These

intriguing phases have been obtained from aqueous solutions under ambient conditions, whereas materials obtained as a result of high-temperature solid state reactions usually lack significant curvature effects. A series of uranyl phosphonates with tubular units have been reported by Clearfield and co-workers back in 1990s [6–8], indicating the possibility of formation of curved architectures in inorganic uranyl phosphates and arsenates. However, no such structures have been found [9].

Recently, we have systematically investigated phases in the $\text{A}^1-\text{UO}_2^{2+}-\text{P}_2\text{O}_5(\text{As}_2\text{O}_5)$ systems with A^1 being a monovalent cation (such as Li, alkali metals or Ag) [10–13]. In the first part of this series devoted to the study of Li phases, we have reported on syntheses, crystal structures and crystal chemistry of four new lithium uranyl phosphates and arsenates [14]. In this paper, we

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describe four new lithium uranyl compounds: $\text{Li}_6[(\text{UO}_2)_{12}(\text{PO}_4)_8(\text{P}_4\text{O}_{13})]$ (**1**), $\text{Li}_5[(\text{UO}_2)_{13}(\text{AsO}_4)_9(\text{As}_2\text{O}_7)]$ (**2**), $\text{Li}[(\text{UO}_2)_4(\text{AsO}_4)_3]$ (**3**) and $\text{Li}_3[(\text{UO}_2)_7(\text{AsO}_4)_5\text{O}]$ (**4**). The first two compounds are based upon remarkable tubular units similar to those found in uranyl phosphonates [6–8], but connected into 3D framework by intertubular fragments stabilized by cation–cation interactions, which are rather rare in uranyl compounds and have been found in relatively few structure types [15–20]. It should be noted that several new Li framework uranyl phosphates have been reported recently by Obbade et al. [21].

2. Experimental

2.1. Synthesis

The compounds reported here were obtained by high-temperature solid-state reactions in Li-poor systems. Mixtures of Li_2CO_3 , $\text{UO}_2(\text{NO}_3)_2$, P_2O_5 or As_2O_5 taken in molar ratios of 1:2:3 for **1** and **2**, and 1:4:4 and 1:2:2 for **3** and **4** were heated in a Pt crucible to 820 °C and then cooled to 50 °C with a cooling rate of 5 °C/h. The products consisted of dark-orange transparent crystals of the title compounds immersed in amorphous yellow mass.

2.2. Crystal-structure analysis

Crystals selected for data collection were mounted on Mar345 Image Plate diffractometer (**1**, **2** and **4**), or on Stoe Stadi-4 four-circle diffractometer (for **3**). The data were collected using monochromatic $\text{MoK}\alpha$ X-radiation. The unit-cell parameters for all compounds (Table 1) were refined using least-squares techniques. More than a hemisphere of data was collected for each compound and 3D data were reduced and filtered for statistical outliers. The 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 structure determination and refinement. The structures were solved by direct methods and refined to $R_1 = 0.0357$ for **1**, 0.0722 for **2**, 0.0358 for **3** and 0.0415 for **4**. The final models included anisotropic displacement parameters for all atoms (except lithium) and weighting

schemes for the structure factors. The final atomic positional and displacement parameters, and selected interatomic distances are given in Tables 2 and 6 for **1**, **3** and 7 for **2**, **4** and 8 for **3**, **5** and 9 for **4**. Tables of observed and calculated structure factors and anisotropic displacement parameters for each structure are available from the authors upon request.

3. Results

3.1. Cation coordination

In the title compounds, uranium atoms invariably form linear uranyl cations UO_2^{2+} ($\text{U}=\text{O}$ in the range of 1.72–1.86 Å) coordinated by either four or five O atoms to form UO_6 square pyramids or UO_7 pentagonal bipyramids, respectively ($\text{U}-\text{O}$ bonds in the range of 2.19–2.75 Å).

The P and As atoms are tetrahedrally coordinated by four O atoms each. In compound **1**, P(1) O_4 , P(2) O_4 , P(3) O_4 and P(5) O_4 are isolated from each other and demonstrate P–O bond lengths typical for phosphates [22]. The P(4) O_4 and P(6) O_4 tetrahedra form disordered P_4O_{13} linear tetramers with structure described in detail in Discussion. The tetramer is disordered over two independent positions with P6 site-occupation factor equal to 0.5. As a consequence, the P(6) O_4 configuration is apparently distorted with the bond lengths varying from 1.38 to 1.58 Å. This apparent non-typical distortion can be attributed to the effects of short-range ordering induced by the presence of disorder. The O(24) and O(27) sites are bridging between PO_4 tetrahedra in the tetramer and are characterized by elongated P–O bonds (1.573–1.584 Å). In the structure of **2**, there are eleven independent As sites, from which two (As(9) and As(10)) share the common O(48) atom to form an As_2O_7 dimer, whereas other AsO_4 tetrahedra are isolated from each other. There are two and three symmetrically independent single AsO_4 tetrahedra in the structures of **3** and **4**, respectively.

The Li^+ cations in the structures under consideration show remarkable diversity of coordination. In most cases, the coordination can be described as distorted tetrahedral with Li–O bond lengths in the range of 1.82–2.45 Å. In the structure of **4**, Li atoms have fivefold coordination ($\text{Li}-\text{O} = 1.86\text{--}2.36$ Å). The Li(4) and

Table 1
Crystallographic data and refinement parameters for **1**, **2**, **3** and **4**.

Parameters	1	2	3	4
<i>a</i> (Å)	26.963(3)	7.1410(8)	7.160(3)	7.2160(5)
<i>b</i> (Å)	7.063(1)	13.959(1)	7.160(3)	7.2160(5)
<i>c</i> (Å)	19.639(1)	31.925(1)	33.775(9)	14.6540(7)
α (deg)	–	82.850(2)	90	90
β (deg)	126.890(4)	88.691(2)	90	90
γ (deg)	–	79.774(3)	90	90
<i>V</i> (Å ³)	2991.2(6)	3107.4(4)	1732(1)	763.04(8)
Space group	<i>C2/m</i>	$P\bar{1}$	<i>I4₁/amd</i>	$P\bar{4}$
Ref. for cell refinement	All	All	78	All
<i>F</i> ₀₀₀	3708	4252	2520	1018
μ (cm ^{−1})	32.814	39.684	43.087	42.464
<i>Z</i>	2	2	4	1
<i>D</i> _{calc} (g/cm ³)	4.856	5.405	5.769	5.357
Crystal size (mm ³)	0.3 × 0.05 × 0.05	0.2 × 0.02 × 0.02	0.8 × 0.01 × 0.01	0.6 × 0.04 × 0.04
Radiation	$\text{MoK}\alpha$	$\text{MoK}\alpha$	$\text{MoK}\alpha$	$\text{MoK}\alpha$
<i>R</i> _{int}	0.0415	0.0566	0.089	0.0328
Total ref.	11960	25918	1890	5436
Unique ref.	3639	13423	611	1831
Unique ref. $ F_0 \geq 4\sigma_F$	3248	9161	318	1600
<i>R</i> ₁	0.0357	0.0722	0.0356	0.0415
<i>wR</i> ₂	0.0870	0.1902	0.0441	0.1088
<i>S</i>	1.158	1.071	0.943	1.098

Table 2
Atomic coordinates and displacement parameters (\AA^2) for **1**.

Atom	x	y	z	U_{eq}
U(1)	0.41018(2)	0	0.09083(2)	0.01423(8)
U(2)	0.84192(1)	1/2	0.48070(2)	0.01269(8)
U(3)	0.34731(2)	1/2	−0.03225(2)	0.01312(8)
U(4)	0.59134(1)	1/2	0.24543(2)	0.01294(8)
U(5)	0.65867(1)	0	0.23599(2)	0.01310(8)
U(6)	0.65175(1)	1/2	0.73919(2)	0.01501(8)
P(1)	0.7116(1)	1/2	0.24926(1)	0.0120(5)
P(2)	0.5636(1)	0	0.2800(1)	0.0128(5)
P(3)	0.4354(1)	1/2	0.1684(1)	0.0122(5)
P(4)	0.8634(1)	0	0.4614(1)	0.0148(6)
P(5)	0.2934(1)	0	−0.1030(1)	0.0147(6)
P(6) ^a	0.9978(2)	−0.1064(6)	0.5731(2)	0.0179(9)
O(1)	0.4152(2)	−0.6671(7)	0.1056(3)	0.0221
O(2)	0.8415(2)	−0.1715(7)	0.4841(3)	0.020(1)
O(3)	0.5869(2)	−0.1684(6)	0.2555(3)	0.014(1)
O(4)	0.3354(2)	0.1687(7)	−0.0491(3)	0.024(2)
O(5)	0.5932(3)	0	0.3744(4)	0.020(2)
O(6)	0.4122(3)	1/2	−0.0366(5)	0.031(2)
O(7)	0.6711(2)	−0.3323(7)	0.2396(3)	0.017(1)
O(8)	0.4932(3)	0	0.2303(4)	0.017(2)
O(9)	0.4005(3)	1/2	0.2051(4)	0.031(2)
O(10)	0.7197(3)	1/2	0.1787(4)	0.016(2)
O(11)	0.5988(3)	0	0.1265(5)	0.026(2)
O(12)	0.2819(3)	1/2	−0.0331(5)	0.029(2)
O(13)	0.8411(3)	0	0.3704(4)	0.027(2)
O(14)	0.7782(3)	1/2	0.4870(4)	0.020(2)
O(15)	0.9020(3)	1/2	0.4700(5)	0.027(2)
O(16)	0.7747(3)	1/2	0.3351(4)	0.022(2)
O(17)	0.5058(3)	1/2	0.2390(4)	0.018(2)
O(18)	0.5418(3)	1/2	0.1319(5)	0.024(2)
O(19)	0.4633(3)	0	0.0662(5)	0.027(2)
O(20)	0.6416(3)	1/2	0.3570(5)	0.021(2)
O(21)	0.3581(4)	0	0.1155(5)	0.032(2)
O(22)	0.2752(3)	0	−0.1947(4)	0.015(2)
O(23)	0.7169(3)	0	0.3485(5)	0.024(2)
O(24)	0.9363(3)	0	0.5239(5)	0.029(2)
O(25)	0.6537(3)	−0.2453(9)	0.7397(4)	0.035(1)
O(26)	0.2335(3)	0	−0.1144(4)	0.032(2)
O(27) ^a	0	−0.189(2)	1/2	0.024(4)
O(28)	0.0488(4)	0	0.6208(6)	0.052(3)
O(29) ^a	0.9934(5)	−0.265(2)	0.6186(7)	0.031(3)
Li(1)	0.708(1)	1/2	0.492(1)	0.041(6)
Li(2)	1/2	1/2	0	0.08(1)
Li(3) ^b	0.687(1)	0	0.807(2)	0.043(8)
Li(4) ^b	0.997(2)	1/2	0.654(2)	0.051(9)

^a Occupancies of the P(6), O(27) and O(29) sites are 0.5.^b Occupancies of the Li(3) and Li(4) sites are 0.75.**Table 3**
Atomic coordinates and displacement parameters (\AA^2) for **2**.

Atom	x	y	z	U_{eq}
U(1)	0.5490(1)	0.80301(5)	0.26154(2)	0.0168(2)
U(2)	0.9650(1)	0.20755(5)	0.23974(2)	0.0175(2)
U(3)	0.7625(1)	0.45001(6)	0.64360(2)	0.0251(2)
U(4)	0.2837(1)	0.44493(7)	0.13676(2)	0.0291(2)
U(5)	0.4770(1)	0.07139(6)	0.11853(2)	0.0206(2)
U(6)	0.4094(1)	0.28259(6)	0.51553(2)	0.0197(2)
U(7)	0.1108(1)	0.72487(6)	−0.01412(2)	0.0198(2)
U(8)	0.4759(1)	0.07367(6)	0.37732(2)	0.0190(2)
U(9)	0.6022(1)	0.72697(6)	0.04420(2)	0.0217(2)
U(10)	0.0240(1)	0.93467(6)	0.12586(2)	0.0200(2)
U(11)	0.0203(1)	0.94060(6)	0.38497(2)	0.0193(2)
U(12)	0.9175(1)	0.28393(6)	0.45826(2)	0.0198(2)
U(13)	0.6572(1)	0.48422(6)	0.26173(2)	0.0211(2)
U(14)	0.5570(3)	0.8366(2)	0.37786(6)	0.0183(4)
AS(2)	0.9420(3)	0.1785(2)	0.35973(6)	0.0188(4)
AS(3)	0.0979(3)	0.6986(2)	0.08862(6)	0.0207(4)
AS(4)	0.4234(3)	0.3102(2)	0.41237(6)	0.0179(4)
AS(5)	0.4678(3)	0.2746(2)	0.22973(6)	0.0214(4)
AS(6)	0.8965(3)	0.3075(2)	0.55932(6)	0.0198(4)
AS(7)	0.5556(3)	0.8323(2)	0.14229(6)	0.0192(4)
AS(8)	−0.0564(3)	0.1737(2)	0.12357(6)	0.0190(4)

Table 3 (continued)

Atom	x	y	z	U_{eq}
AS(9)	0.9478(3)	0.2541(2)	0.72748(6)	0.0220(4)
AS(10)	0.1489(3)	0.5484(2)	0.24303(6)	0.0234(5)
AS(11)	0.3666(3)	0.3058(2)	0.05474(6)	0.0225(4)
O(1)	0.143(2)	0.173(1)	0.7404(5)	0.027(3)
O(2)	0.278(2)	0.219(1)	0.2425(5)	0.025(3)
O(3)	0.078(2)	0.297(1)	0.5237(4)	0.032(4)
O(4)	0.475(2)	0.082(1)	0.3209(5)	0.035(4)
O(5)	0.655(2)	0.181(1)	0.2394(5)	0.025(3)
O(6)	0.550(2)	0.790(1)	0.1934(5)	0.033(4)
O(7)	0.220(2)	0.262(1)	0.0235(4)	0.025(3)
O(8)	0.354(2)	0.913(1)	0.1268(5)	0.034(4)
O(9)	0.483(2)	0.066(1)	0.4335(5)	0.028(4)
O(10)	0.554(2)	0.301(1)	0.0219(5)	0.033(4)
O(11)	0.926(2)	0.227(1)	0.6012(5)	0.035(4)
O(12)	−0.107(2)	0.269(1)	0.0861(4)	0.025(3)
O(13)	0.940(2)	0.217(1)	0.3095(4)	0.025(3)
O(14)	0.413(2)	0.238(1)	0.1010(4)	0.026(3)
O(15)	0.145(2)	0.010(1)	0.3744(4)	0.024(3)
O(16)	0.903(2)	0.274(1)	0.3863(4)	0.030(4)
O(17)	0.012(2)	0.946(1)	0.0704(5)	0.029(4)
O(18)	0.029(2)	0.936(1)	0.3298(5)	0.034(4)
O(19)	0.734(2)	0.287(1)	0.5251(4)	0.028(4)
O(20)	0.142(2)	0.092(1)	0.1150(5)	0.030(3)
O(21)	0.601(2)	0.740(1)	0.1149(4)	0.021(3)
O(22)	0.447(2)	0.4232(9)	0.3903(4)	0.018(3)
O(23)	0.354(2)	0.916(1)	0.3845(5)	0.027(3)
O(24)	0.614(2)	0.668(1)	0.2691(4)	0.026(3)
O(25)	0.569(2)	0.805(1)	0.3297(4)	0.033(4)
O(26)	0.493(2)	0.933(1)	0.2525(4)	0.026(3)
O(27)	−0.042(2)	0.508(1)	0.2625(5)	0.029(3)
O(28)	0.644(2)	0.522(1)	0.2067(4)	0.033(4)
O(29)	0.875(2)	0.338(1)	0.2340(5)	0.025(3)
O(30)	0.074(3)	0.399(1)	0.1444(6)	0.051(5)
O(31)	0.093(2)	0.768(1)	0.1268(4)	0.033(4)
O(32)	0.033(2)	0.931(1)	0.1820(5)	0.028(3)
O(33)	0.679(2)	0.452(1)	0.3175(6)	0.040(4)
O(34)	−0.052(2)	0.214(1)	0.1704(4)	0.030(4)
O(35)	0.595(2)	0.273(1)	0.4491(4)	0.025(3)
O(36)	0.233(2)	0.305(1)	0.4446(5)	0.028(4)
O(37)	0.848(3)	0.414(1)	0.5774(6)	0.045(5)
O(38)	−0.2061(19)	0.093(1)	0.1234(5)	0.024(3)
O(39)	0.986(2)	0.156(1)	0.4687(4)	0.028(4)
O(40)	0.465(3)	0.322(1)	0.1791(5)	0.036(4)
O(41)	0.7654(19)	0.192(1)	0.7333(4)	0.032(4)
O(42)	0.848(2)	0.410(1)	0.4426(4)	0.026(3)
O(43)	0.708(2)	0.912(1)	0.1326(5)	0.030(4)
O(44)	0.680(2)	0.601(1)	0.0538(5)	0.033(4)
O(45)	0.7045(19)	0.918(1)	0.3827(4)	0.021(3)
O(46)	0.013(2)	0.950(1)	0.4396(5)	0.036(4)
O(47)	0.593(2)	0.738(1)	0.4133(4)	0.024(3)
O(48)	0.076(2)	0.675(1)	0.2320(4)	0.029(4)
O(49)	−0.079(2)	0.738(1)	0.0522(4)	0.025(3)
O(50)	0.585(2)	0.380(1)	0.6452(5)	0.030(4)
O(51)	0.282(2)	0.708(2)	0.0553(5)	0.046(5)
O(52)	0.045(2)	0.0770(9)	0.2465(4)	0.022(3)
O(53)	0.788(2)	0.101(1)	0.3744(4)	0.022(3)
O(54)	0.960(2)	0.327(1)	0.6822(4)	0.022(3)
O(55)	0.495(2)	0.063(1)	0.0645(5)	0.034(4)
O(56)	0.529(3)	0.855(1)	0.0335(5)	0.041(5)
O(57)	0.282(3)	0.421(1)	0.0656(5)	0.042(5)
O(58)	0.941(3)	0.523(1)	0.6416(6)	0.053(5)
O(59)	0.487(2)	0.359(1)	0.2607(4)	0.028(3)
O(60)	0.376(2)	0.408(1)	0.5128(5)	0.035(4)
O(61)	0.097(2)	0.854(1)	−0.0182(5)	0.038(4)
O(62)	0.231(3)	0.512(1)	0.1991(5)	0.040(4)
O(63)	0.453(2)	0.080(1)	0.1743(5)	0.034(4)
O(64)	0.440(2)	0.154(1)	0.5180(4)	0.031(4)
O(65)	0.323(2)	0.538(1)	0.2804(4)	0.030(4)
O(66)	0.089(3)	0.585(1)	0.1073(6)	0.064(6)
O(67)	0.118(3)	0.595(1)	−0.0084(5)	0.038(4)
O(68)	0.424(2)	0.237(1)	0.3757(4)	0.031(4)
O(69)	0.485(4)	0.496(2)	0.1257(6)	0.086(8)
Li(1)	0.250(9)	0.001(5)	−0.001(2)	0.06(1)
Li(2)	0.800(7)	0.421(4)	0.376(2)	0.05(1)
Li(3)	0.035(7)	0.938(4)	0.249(1)	0.04(1)
Li(4)	0.487(6)	0.074(3)	0.253(1)	0.04(1)
Li(5)	0.276(6)	0.000(3)	0.499(1)	0.036(9)

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

Atom	x	y	z	U_{eq}
U(1)	0	1/4	0.09550(2)	0.0107(1)
U(2)	0	1/4	0.22141(2)	0.0148(2)
As(1)	0	1/4	0.31838(5)	0.0110(4)
As(2)	0	3/4	0.1250	0.0162(6)
O(1)	0	0.437(1)	0.3458(3)	0.036(3)
O(2)	0	1/4	0.0415(4)	0.025(3)
O(3)	0	1/4	0.1503(4)	0.022(3)
O(4)	0	0.563(1)	0.0954(3)	0.035(3)
O(5)	-0.180(1)	1/4	0.2856(3)	0.038(3)
O(6)	0	0.009(1)	0.2209(4)	0.040(3)
Li(1)	0	3/4	0.201(2)	0.02(1)

Table 5
Atomic coordinates and displacement parameters (\AA^2) for **4**.

Atom	x	y	z	U_{eq}
U(1)	1/2	0	0.43103(3)	0.0135(1)
U(2)	0	0	0	0.0207(2)
U(3)	0	1/2	0.27861(4)	0.0201(1)
U(4)	1/2	1/2	0.14372(3)	0.0147(1)
AS(1)	1/2	1/2	0.36977(9)	0.0139(3)
AS(2)	0	1/2	0.05558(9)	0.0157(3)
AS(3)	0	0	1/2	0.0264(5)
O(1)	1/2	1/2	0	0.032(4)
O(2)	1/2	0	0.5576(9)	0.038(4)
O(3)	0.500(1)	0.693(1)	0.4314(6)	0.025(2)
O(4)	0.002(1)	0.6874(1)	-0.0102(6)	0.022(2)
O(5)	0	0	0.1211(9)	0.038(4)
O(6)	-0.001(2)	-0.193(1)	0.5690(9)	0.040(3)
O(7)	-0.177(1)	0.498(1)	0.1348(5)	0.026(2)
O(8)	0.681(1)	0.499(1)	0.2939(6)	0.027(2)
O(9)	-0.000(1)	0.744(1)	0.2807(6)	0.028(2)
O(10)	0.500(1)	0.749(1)	0.1499(6)	0.024(2)
O(11)	1/2	0	0.3081(8)	0.030(3)
Li(1)	0	0	0.293(2)	0.007(5)
Li(2)	1/2	0	0.139(2)	0.009(6)

Li(5) sites in the structure of **2** deserve special attention. Both sites have sixfold coordination with the Li–O bond lengths in the range of 2.66–2.89 Å. These bonds are significantly longer than those observed for other Li atoms. The value of bond valence sums for Li(4) and Li(5) sites in the structure of **2** is 0.12 b.v.u. which confirm unusual Li-coordination. The BVS sums for other Li-sites in obtained compounds are in the range of 0.74–0.93 b.v.u. However, refinement of site-occupation factors and detailed inspection of difference Fourier maps do not reveal any additional electron density that can be ascribed to either Li or O atoms. On the other hand, such a ‘relaxed’ coordination of Li⁺ cations is usually observed in Li-intercalated layered compounds and compounds with high ion conductivity, e.g., in LiCa₂(Ta₃O₁₀) [23], fast ion conductor LiZr₂(PO₄)₃ [24], and LiUO₃ [25]. It is very likely that the Li(4) and Li(5) sites correspond either to highly mobile Li⁺ ions or represent average positions of Li⁺ cations located within tubular units of As coordination polyhedra.

3.2. Structure description

Structures of all the phases under consideration are based on complicated 3D frameworks (Figs. 1 and 2) consisting of different types of uranium polyhedra (UO₆ and UO₇) and different types of tetrahedral TO₄ anions (T = P or As): PO₄ and P₄O₁₃ in **1**, AsO₄ and As₂O₇ in **2**, and single AsO₄ tetrahedra in **3** and **4**.

Table 6
Selected interatomic distances (\AA) in the structure of **1**.

U(1)–O(21)	1.74(1)	P(1)–O(16)	1.515(6)
U(1)–O(19)	1.766(9)	P(1)–O(10)	1.527(8)
U(1)–O(8)	2.271(6)	P(1)–O(7)	1.544(5) 2 ×
U(1)–O(1)	2.363(5)		
U(1)–O(1)	2.363(5)	P(2)–O(5)	1.516(7)
U(1)–O(4)	2.527(5) 2 ×	P(2)–O(8)	1.526(7)
		P(2)–O(3)	1.551(5) 2 ×
U(2)–O(15)	1.755(9)		
U(2)–O(14)	1.797(8)	P(3)–O(9)	1.489(9)
U(2)–O(5)	2.276(6)	P(3)–O(17)	1.538(6)
U(2)–O(16)	2.288(6)	P(3)–O(1)	1.551(5) 2 ×
U(2)–O(2)	2.321(5) 2 ×		
		P(4)–O(13)	1.506(7)
U(3)–O(12)	1.754(9)	P(4)–O(2)	1.525(6) 2 ×
U(3)–O(6)	1.802(9)	P(4)–O(24)	1.573(7)
U(3)–O(10)	2.302(6)		
U(3)–O(4)	2.358(5) 2 ×	P(5)–O(26)	1.492(9)
U(3)–O(1)	2.474(5) 2 ×	P(5)–O(4)	1.544(5) 2 ×
		P(5)–O(22)	1.557(7)
U(4)–O(20)	1.753(7)		
U(4)–O(18)	1.783(7)	P(6)–O(28)	1.337(8)
U(4)–O(17)	2.234(8)	P(6)–O(29)	1.48(1)
U(4)–O(3)	2.360(5) 2 ×	P(6)–O(24)	1.525(7)
U(4)–O(7)	2.517(5) 2 ×	P(6)–O(27)	1.584(7)
U(5)–O(11)	1.749(7)	Li(1)–O(14)	1.94(3)
U(5)–O(23)	1.784(7)	Li(1)–O(2)	2.06(2) 2 ×
U(5)–O(22)	2.361(8)	Li(1)–O(20)	2.12(2)
U(5)–O(7)	2.366(5) 2 ×	Li(1)–O(23)	2.51(3)
U(5)–O(3)	2.488(5) 2 ×		
		Li(2)–O(6)	2.019(8) 2 ×
U(6)–O(25)	1.799(7)	Li(2)–O(18)	2.116(7) 2 ×
U(6)–O(25)	1.799(7)		
U(6)–O(9)	2.243(9)	Li(3)–O(25)	2.03(2) 2 ×
U(6)–O(13)	2.273(8)	Li(3)–O(10)	2.37(4)
U(6)–O(28)	2.315(8)	Li(3)–O(21)	2.44(4)
U(6)–O(26)	2.349(6)	Li(3)–O(12)	2.60(3)
U(6)–O(22)	2.753(7)		
		Li(4)–O(29)	1.78(2) 2 ×
		Li(4)–O(8)	2.11(4)
		Li(4)–O(5)	2.13(4)

In the structures of **1** and **2**, UO₇ pentagonal bipyramids share edges to form (UO₅)_∞ chains extended along the *b* axis in **1** and along the *a* axis in **2**. The chains are linked via single TO₄ tetrahedra into tubular units (Fig. 3a). External diameters of the tubes are 11 Å in **1** and 11.5 Å in **2**, internal diameters of channels inside the tubes are 4.1 Å in **1** and 4.5 Å in **2**. The channels accommodate Li⁺ cations. The tubular units are linked into 3D frameworks by intertubular complexes, which have different structures in the reported phases (Fig. 3b). In **1**, the intertubular fragment consists of linear P₄O₁₃ zigzag-like tetramers connected to each other and to tubular units by uranyl groups (Fig. 6a). The intertubular complex in the structure of **2** has a more complicated configuration. It consists of single AsO₄ tetrahedra and As₂O₇ dimers and two different uranium polyhedra (Fig. 6d).

The structures of **3** and **4** are based on 3D frameworks composed of layers united by (UO₅)_∞ infinite chains. The basic difference between the structures is in the layer topology. In **3**, layers have a double structure (consisting of two sublayers) as shown in Figs. 2a and 4a (in Fig. 2a layers are indicated by a red dotted line). Within the layer all U atoms are in sixfold coordination and are connected by single AsO₄ tetrahedra. As a consequence, the layers belong to the autunite topology [9,22]. In the structure of **4**, the autunite layers are also present, but alternate with single layers shown in Fig. 4b. We note that the same type of layers has been described previously in the structure of K₄[(UO₂)(PO₄)₂] [26]. The layers are linked into a 3D framework by UO₇ pentagonal bipyramids located in the interlayer.

Table 7Selected interatomic distances (Å) in the structure of **2**.

U(1)–O(26)	1.77(1)	U(13)–O(28)	1.77(1)
U(1)–O(24)	1.85(2)	U(13)–O(33)	1.79(2)
U(1)–O(25)	2.19(1)	U(13)–O(27)	2.23(2)
U(1)–O(6)	2.21(2)	U(13)–O(59)	2.31(2)
U(1)–O(41)	2.24(1)	U(13)–O(65)	2.46(2)
U(1)–O(1)	2.28(2)	U(13)–O(24)	2.57(2)
		U(13)–O(29)	2.58(2)
U(2)–O(52)	1.80(1)		
U(2)–O(29)	1.80(2)	As(1)–O(25)	1.65(2)
U(2)–O(34)	2.21(1)	As(1)–O(47)	1.65(2)
U(2)–O(13)	2.25(1)	As(1)–O(23)	1.69(2)
U(2)–O(2)	2.28(1)	As(1)–O(45)	1.70(1)
U(2)–O(5)	2.31(1)		
		As(2)–O(13)	1.63(1)
U(3)–O(50)	1.73(2)	As(2)–O(16)	1.67(2)
U(3)–O(58)	1.76(2)	As(2)–O(15)	1.69(2)
U(3)–O(54)	2.27(1)	As(2)–O(53)	1.70(1)
U(3)–O(37)	2.28(2)		
U(3)–O(22)	2.28(1)	As(3)–O(66)	1.64(2)
U(3)–O(65)	2.51(1)	As(3)–O(31)	1.64(2)
		As(3)–O(51)	1.68(2)
U(4)–O(69)	1.72(2)	As(3)–O(49)	1.71(1)
U(4)–O(30)	1.73(2)		
U(4)–O(40)	2.27(2)	As(4)–O(68)	1.65(2)
U(4)–O(66)	2.29(2)	As(4)–O(35)	1.68(1)
U(4)–O(62)	2.30(2)	As(4)–O(22)	1.68(1)
U(4)–O(57)	2.34(1)	As(4)–O(36)	1.69(1)
		As(5)–O(59)	1.65(2)
U(5)–O(55)	1.74(2)	As(5)–O(40)	1.67(2)
U(5)–O(63)	1.80(2)	As(5)–O(2)	1.70(1)
U(5)–O(14)	2.29(2)	As(5)–O(5)	1.70(2)
U(5)–O(38)	2.35(1)		
U(5)–O(20)	2.36(2)	As(6)–O(11)	1.63(2)
U(5)–O(8)	2.51(2)	As(6)–O(37)	1.64(2)
U(5)–O(43)	2.52(2)	As(6)–O(19)	1.69(2)
		As(6)–O(3)	1.70(2)
U(6)–O(60)	1.72(2)		
U(6)–O(64)	1.76(2)	As(7)–O(21)	1.63(1)
U(6)–O(47)	2.26(1)	As(7)–O(6)	1.67(2)
U(6)–O(3)	2.35(2)	As(7)–O(43)	1.69(1)
U(6)–O(19)	2.36(2)	As(7)–O(8)	1.70(2)
U(6)–O(35)	2.48(2)		
U(6)–O(36)	2.58(2)	As(8)–O(34)	1.67(1)
		As(8)–O(12)	1.67(1)
U(7)–O(61)	1.78(2)	As(8)–O(38)	1.69(1)
U(7)–O(67)	1.79(2)	As(8)–O(20)	1.70(2)
U(7)–O(12)	2.29(1)		
U(7)–O(7)	2.36(1)	As(9)–O(1)	1.66(2)
U(7)–O(10)	2.37(2)	As(9)–O(54)	1.67(1)
U(7)–O(49)	2.50(1)	As(9)–O(41)	1.68(2)
U(7)–O(51)	2.52(2)	As(9)–O(48)	1.72(1)
U(8)–O(9)	1.78(2)	As(10)–O(62)	1.61(2)
U(8)–O(4)	1.79(2)	As(10)–O(27)	1.65(2)
U(8)–O(68)	2.24(2)	As(10)–O(65)	1.72(1)
U(8)–O(53)	2.32(1)	As(10)–O(48)	1.74(1)
U(8)–O(15)	2.33(1)		
U(8)–O(45)	2.47(1)	As(11)–O(14)	1.66(1)
U(8)–O(23)	2.48(2)	As(11)–O(10)	1.68(2)
		As(11)–O(57)	1.69(2)
U(9)–O(44)	1.74(2)	As(11)–O(7)	1.70(1)
U(9)–O(56)	1.76(2)		
U(9)–O(21)	2.29(1)	Li(1)–O(26)	1.97(5)
U(9)–O(49)	2.33(1)	Li(1)–O(5)	2.07(5)
U(9)–O(51)	2.37(2)	Li(1)–O(4)	2.18(5)
U(9)–O(7)	2.49(1)	Li(1)–O(2)	2.28(5)
U(9)–O(10)	2.51(2)	Li(1)–O(63)	2.52(5)
U(10)–O(17)	1.76(2)	Li(2)–O(33)	2.03(5)
U(10)–O(32)	1.79(2)	Li(2)–O(16)	2.03(6)
U(10)–O(31)	2.29(2)	Li(2)–O(42)	2.15(5)
U(10)–O(8)	2.32(2)	Li(2)–O(58)	2.17(6)
U(10)–O(43)	2.33(2)	Li(2)–O(22)	2.54(5)
U(10)–O(20)	2.47(2)		
U(10)–O(38)	2.50(2)	Li(3)–O(52)	1.95(5)
U(11)–O(46)	1.77(2)	Li(3)–O(41)	2.12(5)
U(11)–O(18)	1.77(2)		

Table 7. (continued)

U(11)–O(11)	2.29(2)	Li(3)–O(1)	2.17(5)
U(11)–O(45)	2.34(1)	Li(3)–O(32)	2.17(5)
U(11)–O(23)	2.35(1)	Li(3)–O(18)	2.57(5)
U(11)–O(15)	2.52(1)		
U(11)–O(53)	2.53(1)	Li(4)–O(9)	2.72(5)
		Li(4)–O(9)	2.75(5)
U(12)–O(42)	1.75(2)	Li(4)–O(64)	2.76(5)
U(12)–O(39)	1.76(1)	Li(4)–O(64)	2.79(5)
U(12)–O(16)	2.32(1)	Li(4)–O(39)	2.81(5)
U(12)–O(36)	2.35(1)	Li(4)–O(46)	2.84(5)
U(12)–O(35)	2.36(1)		
U(12)–O(3)	2.45(1)	Li(5)–O(61)	2.66(5)
U(12)–O(19)	2.47(1)	Li(5)–O(17)	2.80(5)
		Li(5)–O(17)	2.83(5)
		Li(5)–O(61)	2.83(5)
		Li(5)–O(56)	2.87(5)
		Li(5)–O(56)	2.89(5)

Table 8Selected interatomic distances (Å) in the structure of **3**.

U(1)–O(2)	1.82(1)	As(3)–O(1)	1.628(9) 2 ×
U(1)–O(3)	1.85(1)	As(3)–O(5)	1.70(1) 2 ×
U(1)–O(1)	2.244(9) 2 ×		
U(1)–O(4)	2.241(8) 2 ×	As(4)–O(4)	1.672(9) 4 ×
U(2)–O(6)	1.725(9) 2 ×	Li(1)–O(6)	1.98(2) 2 ×
U(2)–O(5)	2.305(9) 2 ×	Li(1)–O(4)	2.06(4) 2 ×
U(2)–O(3)	2.40(1)		
U(2)–O(5)	2.52(1) 2 ×		

Table 9Selected interatomic distances (Å) in the structure of **4**.

U(1)–O(11)	1.80(1)	As(1)–O(3)	1.660(9) 2 ×
U(1)–O(2)	1.86(1)	As(1)–O(8)	1.713(8) 2 ×
U(1)–O(3)	2.216(9) 2 ×		
U(1)–O(6)	2.22(1) 2 ×	As(2)–O(4)	1.661(8) 2 ×
		As(2)–O(7)	1.724(8) 2 ×
U(2)–O(5)	1.77(1) 2 ×		
U(2)–O(4)	2.261(7) 4 ×	As(3)–O(6)	1.72(1) 4 ×
U(3)–O(9)	1.763(8) 2 ×	Li(1)–O(9)	1.855(9) 2 ×
U(3)–O(8)	2.316(8) 2 ×	Li(1)–O(6)	2.45(2) 2 ×
U(3)–O(2)	2.40(1)		
U(3)–O(7)	2.465(8) 2 ×	Li(2)–O(10)	1.816(8) 2 ×
		Li(2)–O(4)	2.31(2) 2 ×
U(4)–O(10)	1.802(8) 2 ×		
U(4)–O(1)	2.1061(5)		
U(4)–O(7)	2.336(8) 2 ×		
U(4)–O(8)	2.558(8) 2 ×		

In all the structures, Li⁺ cations are located in different types of cages and channels and compensate negative charge of anionic 3D frameworks.

4. Discussion

Li₆[(UO₂)₁₂(PO₄)₈(P₄O₁₃)] and Li₅[(UO₂)₁₃(AsO₄)₉(As₂O₇)]: The structures of Li₆[(UO₂)₁₂(PO₄)₈(P₄O₁₃)] and Li₅[(UO₂)₁₃(AsO₄)₉(As₂O₇)] are unprecedented in the actinide solid state chemistry, since they are the first phases with well-defined tubular units in a 3D framework obtained by high-temperature solid state reaction. One of the most interesting aspects here is the topology of the tubular units. Fig. 5a shows layer with an uranophane topology [27]. As it has been noted in [22], TO₄ tetrahedra in these layers have one non-shared corner that may be oriented either up (U) or

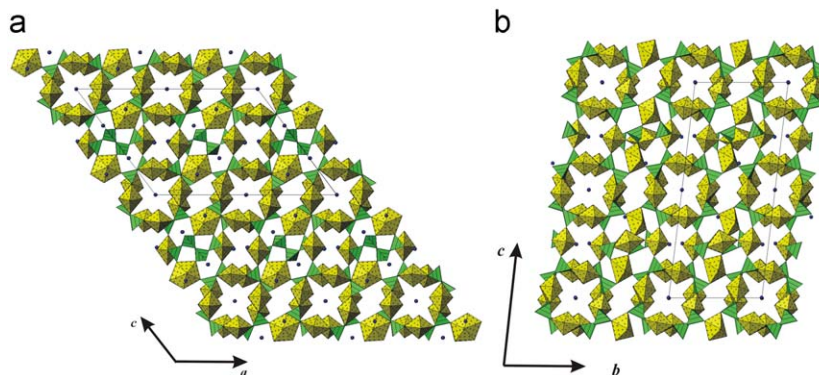


Fig. 1. Crystal structures of $\text{Li}_6[(\text{UO}_2)_{12}(\text{PO}_4)_8(\text{P}_4\text{O}_{13})]$ (**1**) (a) and $\text{Li}_5[(\text{UO}_2)_{13}(\text{AsO}_4)_9(\text{As}_2\text{O}_7)]$ (**2**) (b) (U polyhedra = cross-hatched; P (As) polyhedra = lined; Li atoms shown as dark spheres).

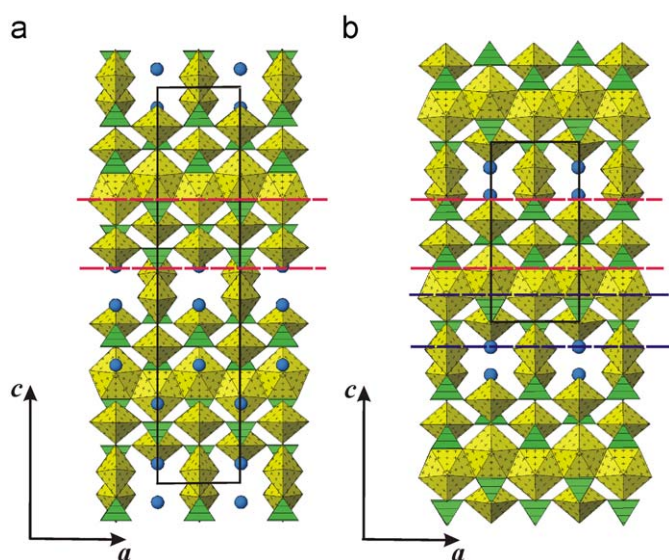


Fig. 2. Crystal structures of $\text{Li}[(\text{UO}_2)_4(\text{AsO}_4)_3]$ (**3**) (a) and $\text{Li}_3[(\text{UO}_2)_7(\text{AsO}_4)_5\text{O}]$ (**2**) (b) (U polyhedra = cross-hatched; As polyhedra = lined; Li atoms shown as dark spheres). Red dotted line show the positions of double layers (Fig. 4a), by dark blue dotted line showed positions of single layers (Fig. 4b). (For interpretation of the references to color in this figure legend, the reader is referred to the webversion of this article.)

down (D) relative to the plane of the layer. This leads to a number of geometrical isomers observed in this kind of structures. In all layered uranyl phases reported to date, the numbers of tetrahedra oriented up and down are equal, i.e. the U:D ratio is 1:1. When the tubular units in the structures of **1** and **2** are unfolded onto a 2D plane, the resulting layer will have all its tetrahedra in the same orientation, namely 'up' relative to the interior of the tube (Fig. 5b). A similar procedure has been proposed to explain the topology of nanoscale tubes in uranyl selenates [3–5].

The comparison of intertubular complexes is also of interest. In the structure of **1**, the complex consists of a linear P_4O_{13} tetramer and two types of U polyhedra. The polyphosphate anion has two possible configurations (related by a mirror plane shown in Fig. 6b by red dotted line) that occur with 50% probability each (site-occupation factors for the P(6), O(27) and O(29) sites are 0.5). Configuration of the single P_4O_{13} tetramer is shown in Fig. 6c. The intertubular complex in **2** consists of a As_2O_7 dimer and single AsO_4 tetrahedra and UO_7 pentagonal bipyramid in between (Fig. 6d,e). As a result, the chemical formula of **2** is equal to the chemical formula of **1** minus one As and plus one U atoms.

Another interesting point in the structure of **2** is the occurrence of cation–cation interactions. It is observed in the intertubular space (Fig. 6f) between uranyl ions of the U(1), U(13) and U(2) atoms. The O(24) atom of the U(1) O_2 group is bonded to the U(13) atom, whereas the latter also forms a bond to the O(29) atom that belongs to the U(2) O_2 group. The resulting trimer has a structure $[\text{O}=\text{U}(1)=\text{O}]-\text{U}(13)-[\text{O}=\text{U}(2)=\text{O}]$, which previously was observed in $\text{Li}_2[(\text{UO}_2)_4(\text{WO}_4)_4\text{O}]$ [18]. The U=O bond lengths participating in cation–cation interactions are 1.80 and 1.85 Å.

It should be noted that tubular-like fragments were observed also in non-P(As) uranyl based compounds such as vanadyl-periodates [28]. But all these phases were obtained from the water solutions and tubular-like fragments wall-by-wall fused.

$\text{Li}[(\text{UO}_2)_4(\text{AsO}_4)_3]$ and $\text{Li}_3[(\text{UO}_2)_7(\text{AsO}_4)_5\text{O}]$: These two compounds are isostructural with the recently reported $\text{A}_3(\text{UO}_2)_7(\text{VO}_4)_5\text{O}$ ($\text{A} = \text{Li}, \text{Ag}$) [20] and $\text{A}(\text{UO}_2)_4(\text{VO}_4)_3$ ($\text{A} = \text{Li}, \text{Ag}$) [19], respectively. This is probably the first time when isotope between uranyl arsenates and uranyl vanadates has been observed. It is well-known that, in general, the crystal chemistry of As(V) and V(V) oxysalts is similar, especially when these atoms occur in tetrahedral coordination to oxygen. However, the U:As ratios in the previously reported uranyl arsenates is 1:1 or lower [9]. In the chemically similar V(V) compounds (with the ratios U:V = 1:1 or lower), vanadium forms V_2O_8 groups with V(V) atoms in tetragonal pyramidal coordination. This type of coordination has not been observed for As(V) and, as a consequence, arsenate and vanadate uranyl phases with similar formulas have different structures. The V atoms have tetrahedral oxygen environment in alkali metal uranyl vanadates, where the U:V ratios are usually higher than 1:1 [29].

Cation–cation interactions are also present in **3** and **4**. However, they are different from the trimers observed in **2**, since, in their structures, uranyl groups form dimers: $[\text{O}=\text{U}(1)=\text{O}]-\text{U}(2)$ in **3** and $[\text{O}=\text{U}(1)=\text{O}]-\text{U}(3)$ in **4**. Similar dimers were first described in [28].

Chemical composition–structure correlations: The U:As ratios in the reported compounds are 1:1 for **1**, 13:11~1.2:1 in **2**, 4:3~1.3:1 in **3** and 7:5~1.4:1 in **4**. These ratios were previously observed in one uranyl tungstate [18] (as in **1**) and uranyl vanadates (as in **3** and **4**) [19,20]. The decrease in the number of Li atoms relative to the composition $\text{Li}[(\text{UO}_2)(\text{P(As)O}_4)]$ (with Li:P(As):U = 1:1:1 [14]) is associated with the decrease in the number of oxygen atoms. As result, the structures of the obtained compounds contain condensed polymeric chains $(\text{UO}_5)_{\infty}$. On the other hand, the increase of the U:P(As) ratio along the line **1**→**2**→**3**→**4** favors generation of cation–cation interactions. The same situation can be observed almost in all known uranyl compounds with cation–cation interactions. The increase of the U:B ratio

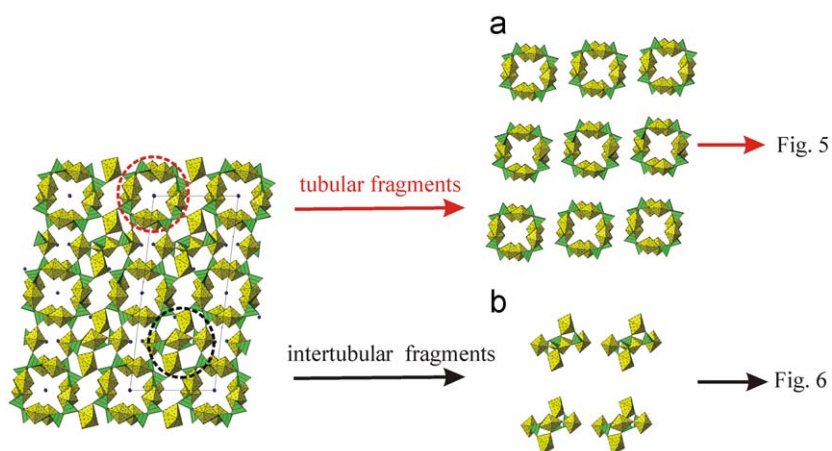


Fig. 3. The crystal structures of **1** and **2** separated into tubular units and intertubular complexes (U polyhedra = cross-hatched; P(As) polyhedra = lined).

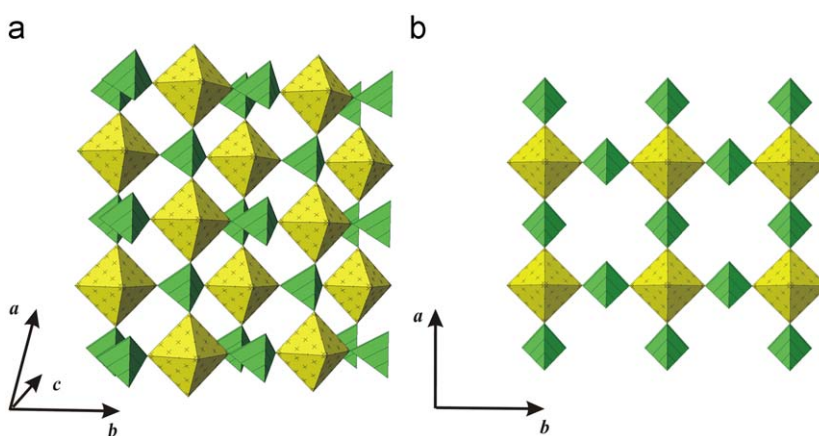


Fig. 4. Structure of layers in **3** and **4** (U polyhedra = cross-hatched; As polyhedra = lined): (a) double layers and (b) single layers.

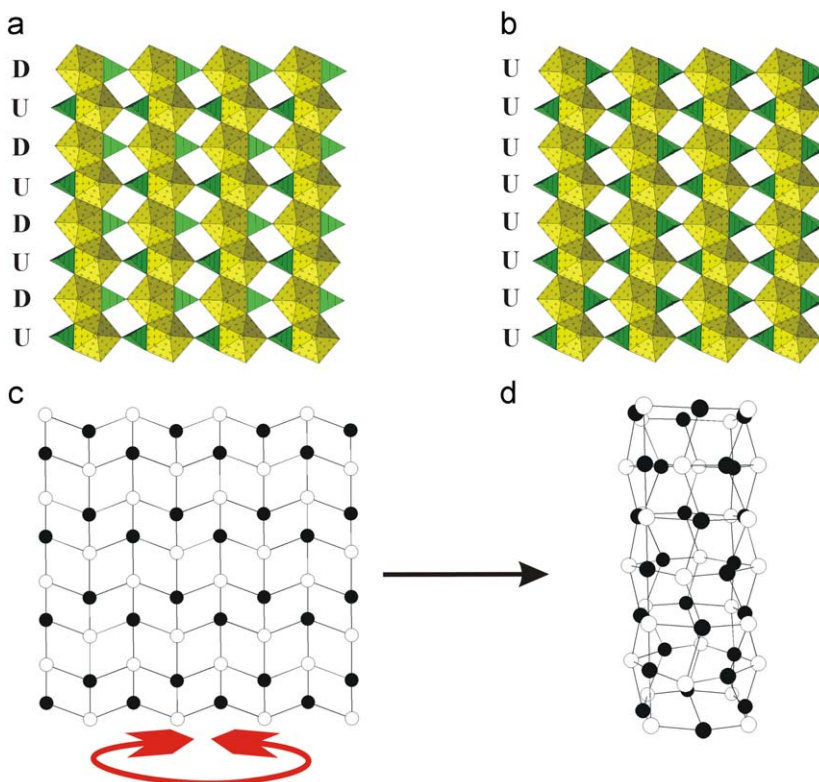


Fig. 5. Topology of tubular units in the structures of **1** and **2** as derivatives of 2D prototype layer structures. See text for details.

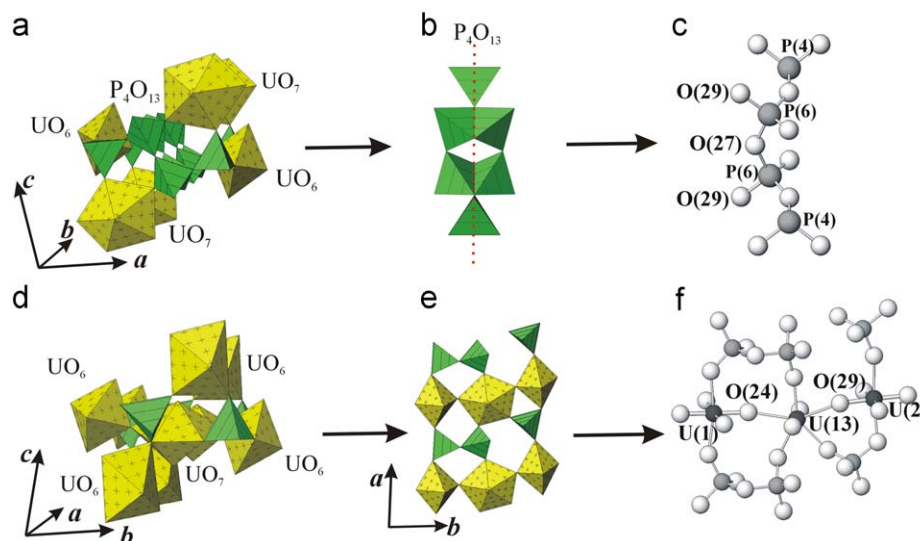


Fig. 6. Intertubular complexes in the structures of **1** and **2**. See text for details. Legend as in Fig. 1.

($B = \text{As, V, S, Mo, W, I}$) favors formation of structural architectures with cation–cation interactions of uranyl groups.

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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.2009.08.003.

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