



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 11Å in **1** and 11.5Å in **2**, and internal diameters of 4.1Å in **1** and 4.5Å 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 $\text{A}^I-\text{UO}_2^{2+}-\text{P}_2\text{O}_5(\text{As}_2\text{O}_5)$ systems with A^I 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

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