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Crystal chemistry of anhydrous Li uranyl phosphates and arsenates. I. Polymorphism and structure topology: Synthesis and crystal structures of α-Li[$(UO_2)(PO_4)$], α-Li[$(UO_2)(AsO_4)$], β-Li[$(UO_2)(AsO_4)$] and $Li_2[(UO_2)_3(P_2O_7)_2]$

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ABSTRACT

Four new Li uranyl phosphates and arsenates have been prepared by high-temperature solid-state reactions: α-Li[$(UO_2)(PO_4)$] (**1**), α-Li[$(UO_2)(AsO_4)$] (**2**), β-Li[$(UO_2)(AsO_4)$] (**3**) and $Li_2[(UO_2)_3(P_2O_7)_2]$ (**4**). The structures of the compounds have been solved by direct methods: **1**—triclinic, $P\bar{1}$, $a = 5.0271(1)$ Å, $b = 9.8799(2)$ Å, $c = 10.8920(2)$ Å, $\alpha = 108.282(9)^\circ$, $\beta = 102.993(8)^\circ$, $\gamma = 104.13(1)^\circ$, $V = 470.69(2)$ Å^3, $Z = 4$, $R_1 = 0.0415$ for 2786 unique reflections with $|F_0| \geqslant 4\sigma_F$; **2**—triclinic, $P\bar{1}$, $a = 5.129(2)$ Å, $b = 10.105(3)$ Å, $c = 11.080(3)$ Å, $\alpha = 107.70(2)^\circ$, $\beta = 102.53(3)^\circ$, $\gamma = 104.74(3)^\circ$, $V = 501.4(3)$ Å^3, $Z = 4$, $R_1 = 0.055$ for 1431 unique reflections with $|F_0| \geqslant 4\sigma_F$; **3**—triclinic, $P\bar{1}$, $a = 5.051(1)$ Å, $b = 5.303(1)$ Å, $c = 10.101(1)$ Å, $\alpha = 90.31(1)^\circ$, $\beta = 97.49(1)^\circ$, $\gamma = 105.08(1)^\circ$, $V = 258.80(8)$ Å^3, $Z = 2$, $R_1 = 0.0339$ for 2055 unique reflections with $|F_0| \geqslant 4\sigma_F$; **4**—triclinic, $P\bar{1}$, $a = 5.312(1)$ Å, $b = 6.696(1)$ Å, $c = 12.542(1)$ Å, $\alpha = 94.532(9)^\circ$, $\beta = 99.059(8)^\circ$, $\gamma = 110.189(7)^\circ$, $V = 409.17(10)$ Å^3, $Z = 2$, $R_1 = 0.0565$ for 1355 unique reflections with $|F_0| \geqslant 4\sigma_F$. The structures of all four compounds are based upon 3-D frameworks of U and *T* polyhedra (T = P, As). Phases **1** and **2** are isostructural and consist of U_2O_{12} dimers and UO_6 square bipyramids linked by single TO_4 tetrahedra. The structure of **3** consists of 3-D framework of corner-sharing UO_6 bipyramids and AsO_4 tetrahedra. In the structure of **4**, the framework is composed of U_2O_{12} dimers, UO_6 bipyramids and P_2O_7 dimers. In all the compounds, Li^+ cations reside in framework cavities. The topologies of the 3-D frameworks can be described as derivatives of the PtS (cooperite) network.

1. Introduction

The structural chemistry of uranium compounds is developing quickly, owing to the challenges related with nuclear energy, material and environmental applications [1–4]. Uranyl phosphates and arsenates are the most common uranium minerals. In nature, these phases usually contain water and most of them belong to the autunite and phosphuranylite mineral groups [5]. Although anhydrous uranyl phosphates and arsenates have also received certain attention [6–11], systematic structural studies of these phases are only beginning [12]. Recently, we have investigated a series of K uranyl arsenates and phosphates, including the layered structure of K[$(UO_2)(As_2O_7)$] [13] with melilite-related topology, and framework structures of α,β-K[$(UO_2)(P_3O_9)$] and K[$(UO_2)_2(P_3O_{10})$] [14]. Applications of symbolic descriptions of the uranyl phosphate and arsenate networks using graph theory provided unique insight into their structural architectures and allowed comparison of their structures with related compounds.

In continuation of our studies, we present here results on four new phases with the compositions α-Li[$(UO_2)(PO_4)$] (**1**), α-Li[$(UO_2)(AsO_4)$] (**2**), β-Li[$(UO_2)(AsO_4)$] (**3**) and $Li_2[(UO_2)_3(P_2O_7)_2]$ (**4**). Again, graphical description of the uranyl arsenate and phosphate structural units allows to analyze topological relations between the different phases and to trace genealogies of the structural topologies. Here we shall demonstrate that the networks of U–*T* linkages (T = P, As) in these compounds under consideration can be treated as modifications of the PtS (cooperite) net.

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2. Experimental

2.1. Synthesis

Crystals of the title compounds were obtained by high-temperature solid-state reactions. Mixtures of Li_2CO_3, $UO_2(NO_3)_2$, P_2O_5 or As_2O_5 taken in molar ratios of 1:1:2 for **1**, **2**, and **3** and 2:3:6 for **4**, were heated in a platinum crucible to 820 °C and then cooled to 50 °C with a cooling rate of 5 °C/h. The products consisted of greenish-yellow transparent crystals of **1**, **2**, **3** and **4**.

2.2. Crystal-structure analysis

The crystals selected for data collection were mounted on an Enraf-Nonius Kappa CCD (**1**), Stoe Stadi-4 (**2** and **3**) and on Mar345 Image Plate (**4**) diffractometers. All data were collected using monochromatic Mo$K\alpha$ 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 $R_1 = 0.045$ for **1**, 0.055 for **2**, 0.0339 for **3** and 0.0565 for **4**. The final models included anisotropic displacement parameters for all atoms (except Li) and weighting schemes of 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 for each structure are available from the authors upon request.

3. Results

3.1. Cation coordination

The uranium atoms in **1**, **2** and **4** have two types of coordination geometries: square bipyramidal and pentagonal

Table 2
Atomic coordinates and displacement parameters (Å^2) for **1**

Atom	x	y	z	U_{eq}
U(1)	0.03259(9)	0.79585(5)	0.02086(4)	0.00628(9)
U(2)	−0.02230(9)	0.72020(5)	0.48380(4)	0.00678(9)
P(1)	0.2758(6)	0.5840(3)	0.2205(3)	0.0060(5)
P(2)	0.3397(7)	1.1093(3)	0.2655(3)	0.0063(5)
Li(1)	0.736(6)	0.905(3)	0.303(3)	0.022(6)
Li(2)	0.677(6)	0.380(3)	0.228(3)	0.022(6)
O(1)	−0.210(2)	0.811(1)	0.1184(9)	0.011(2)
O(2)	0.622(2)	1.248(1)	0.338(1)	0.011(2)
O(3)	0.130(2)	1.119(1)	0.350(1)	0.014(2)
O(4)	0.045(2)	0.563(1)	0.2933(9)	0.012(2)
O(5)	0.566(2)	0.703(1)	0.3258(9)	0.012(2)
O(6)	0.269(2)	0.778(1)	−0.076(1)	0.018(2)
O(7)	0.185(2)	1.096(1)	0.121(1)	0.012(2)
O(8)	0.321(2)	0.431(1)	0.1584(1)	0.010(2)
O(9)	0.177(2)	0.641(1)	0.1108(9)	0.010(2)
O(10)	0.168(2)	0.887(1)	0.468(1)	0.015(2)
O(11)	−0.226(2)	0.556(1)	0.496(1)	0.015(2)
O(12)	0.401(2)	0.960(1)	0.2370(9)	0.009(2)

Table 3
Atomic coordinates and displacement parameters (Å^2) for **2**

Atom	x	y	z	U_{eq}
U(1)	0.0382(1)	0.80059(6)	0.01894(6)	0.0130(2)
U(2)	−0.0194(1)	0.71824(6)	0.47998(6)	0.0135(2)
As(1)	0.2785(3)	0.5817(2)	0.2159(2)	0.0133(4)
As(2)	0.3383(3)	1.1083(2)	0.2716(2)	0.0133(4)
Li(1)	0.747(6)	0.906(3)	0.303(3)	0.014(6)
Li(2)	0.678(7)	0.381(3)	0.231(3)	0.024(7)
O(1)	−0.196(2)	0.816(1)	0.118(1)	0.014(2)
O(2)	0.637(2)	1.259(1)	0.351(1)	0.016(3)
O(3)	0.105(2)	1.110(1)	0.359(1)	0.018(3)
O(4)	0.031(2)	0.558(1)	0.292(1)	0.020(3)
O(5)	0.593(2)	0.709(1)	0.323(1)	0.016(2)
O(6)	0.269(2)	0.783(1)	−0.084(1)	0.015(2)
O(7)	0.177(2)	1.092(1)	0.115(1)	0.021(3)
O(8)	0.325(2)	0.417(1)	0.151(1)	0.017(3)
O(9)	0.173(3)	0.638(1)	0.093(1)	0.026(3)
O(10)	0.185(3)	0.877(1)	0.459(1)	0.030(3)
O(11)	−0.232(3)	0.561(1)	0.497(1)	0.027(3)
O(12)	0.408(2)	0.948(1)	0.236(1)	0.018(3)

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

Parameters	**1**	**2**	**3**	**4**
a (Å)	5.0271(1)	5.129(2)	5.051(1)	5.312(1)
b (Å)	9.8799(2)	10.105(3)	5.303(1)	6.696(1)
c (Å)	10.8920(2)	11.080(3)	10.101(1)	12.542(1)
α (deg)	108.282(9)	107.70(2)	90.31(1)	94.532(9)
β (deg)	102.993(8)	102.53(3)	97.49(1)	99.059(8)
γ (deg)	104.13(1)	104.74(3)	105.08(1)	110.189(7)
V (Å^3)	470.69(2)	501.4(3)	258.80(8)	409.17(10)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Ref. for cell refinement	All	125	125	All
F_{000}	632	704	352	502
μ (cm^{-1})	347.64	388.68	376.48	301.08
Z	4	4	2	1
D_{calc}(g cm^{-3})	5.249	5.510	5.337	4.756
Crystal size (mm^3)	0.24 × 0.18 × 0.12	0.27 × 0.25 × 0.2	0.35 × 0.32 × 0.2	0.18 × 0.10 × 0.03
Radiation	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
R_{int}	0.0415	0.11	0.0349	0.0296
Total ref.	17982	4989	5444	2359
Unique ref.	3018	2392	2722	1425
Unique ref. $\|F_0\| \geqslant 4\sigma_F$	2768	1431	2055	1355
R_1	0.0450	0.0550	0.0339	0.0565
wR_2	0.1271	0.1011	0.0726	0.1631
GOOF	1.286	0.990	1.025	1.111
Largest diff. peak/hole	4.362/−2.739	3.993/−2.716	3.907/−1.755	3.555/−3.104