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High-Temperature, High-Pressure Hydrothermal Synthesis, Characterization, and Structural Relationships of Layered Uranyl Arsenates

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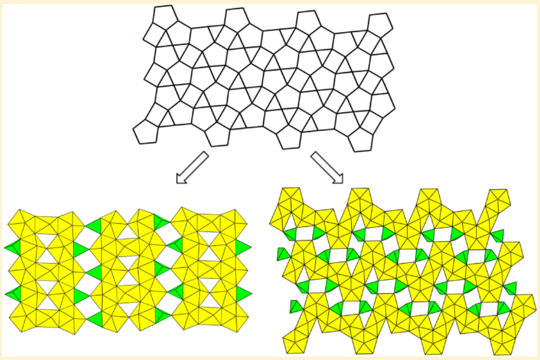
S *Supporting Information*

ABSTRACT: Five new uranyl arsenates, $Na_{14}[(UO_2)_5(AsO_4)_8]\cdot 2H_2O$ (**1**), $K_6[(UO_2)_5O_5(AsO_4)_2]$ (**2a**), $K_4[(UO_2)_3O_2(AsO_4)_2]$ (**2b**), $Rb_4[(UO_2)_3O_2(AsO_4)_2]$ (**3**), and $Cs_6[(UO_2)_5O_2(AsO_4)_4]$ (**4**), were synthesized by high-temperature, high-pressure hydrothermal reactions at about 560 °C and 1440 bar and were characterized by single-crystal X-ray diffraction, thermogravimetric analysis, and photoluminescence spectroscopy. Crystal data for compound **1**: triclinic, $P\bar{1}$, $a = 7.0005(3)$ Å, $b = 12.1324(4)$ Å, $c = 13.7428(5)$ Å, $\alpha = 64.175(2)°$, $\beta = 89.092(2)°$, $\gamma = 85.548(2)°$, $V = 1047.26(7)$ Å^3, $Z = 1$, $R1 = 0.0185$; compound **2a**: monoclinic, $P2_1/c$, $a = 6.8615(3)$ Å, $b = 24.702(1)$ Å, $c = 7.1269(3)$ Å, $\beta = 98.749(2)°$, $V = 1193.89(9)$ Å^3, $Z = 2$, $R1 = 0.0225$; compound **2b**: monoclinic, $P2_1/c$, $a = 6.7852(3)$ Å, $b = 17.3640(8)$ Å, $c = 7.1151(3)$ Å, $\beta = 98.801(3)°$, $V = 828.42(6)$ Å^3, $Z = 2$, $R1 = 0.0269$; compound **3**: monoclinic, $P2_1/m$, $a = 6.9783(3)$ Å, $b = 17.4513(8)$ Å, $c = 7.0867(3)$ Å, $\beta = 90.808(3)°$, $V = 862.94(7)$ Å^3, $Z = 2$, $R1 = 0.0269$; compound **4**: triclinic, $P\bar{1}$, $a = 7.7628(3)$ Å, $b = 9.3324(4)$ Å, $c = 11.9336(4)$ Å, $\alpha = 75.611(2)°$, $\beta = 73.136(2)°$, $\gamma = 86.329(2)°$, $V = 801.37(5)$ Å^3, $Z = 1$, $R1 = 0.0336$. The five compounds have layer structures consisting of uranyl square, pentagonal, and hexagonal bipyramids as well as AsO_4 tetrahedra. Compound **1** contains chains of discrete uranyl square and pentagonal bipyramids, **2a** contains three-polyhedron-wide ribbons of edge- and corner-sharing uranyl square and pentagonal bipyramids, **2b** and **3** contain dimers of edge-shairing pentagonal bipyramids that share edges with hexagonal bipyramids to form chains, and **4** contains one-polyhedron-wide zigzag chains of edge-sharing uranyl polyhedra. The double sheet structure of **1** is new, but the chain topology has been observed in an organically templated uranyl sulfate. Compound **2b** is a new geometrical isomer of the phosphuranylite group. The sheet anion topologies of **2a** and **4** can be obtained by splitting the β-U_3O_8-type sheet into complex chains and connecting the chains by arsenates.



■ INTRODUCTION

Most uranium minerals can be put into two groups: oxidized species that contain U as U^{6+} and reduced species that contain most U as U^{4+}.[1] The U^{6+} cation is almost always present as part of a uranyl ion, UO_2^{2+}, that is linear or nearly so. Dissolved UO_2^{2+}, which is derived from the oxidative dissolution of U-bearing minerals, reacts with oxyanions to form relatively insoluble uranyl oxysalt minerals such as uranyl silicates, phosphates, arsenates, vanadates, and molybdates.[2] Dissolved phosphate anion is a common constituent of many groundwaters, and uranyl phosphates are widely distributed in nature because of their low solubilities and, therefore, are among the most abundant uranium mineral species. Uranyl arsenates are also quite insoluble in water, and they precipitate where dissolved arsenate is available. These minerals are of environmental importance because they largely control the concentration of uranium in groundwaters. The stability and low solubility of uranyl phosphates have prompted research into immobilization of actinides and several phosphates such as monazite, Th-phosphate-diphosphate and kosnarite as potential actinide host phases.[3] Arsenates do not appear to have been considered as practical phases for actinide waste forms probably because of the toxicity of arsenic compounds. A thorough knowledge of the structures and behavior of uranium phosphates and arsenates may form a basis from which to predict the long-term behavior of actinide phosphate phases.

Uranium phosphates and arsenates belong to one of the most important chemical groups of uranium minerals and have been the subjects of intensive studies.[4] Uranyl phosphate and arsenate minerals have been divided into three structurally and chemically related groups, namely, the autunite and meta-autunite groups with U/P(or As) ratio of 1:1, the phosphuranylite group with U/P(or As) = 3:2, and the walpurgite group with U/P(or As) = 1:2.[2] Some uranyl phosphates and arsenates are not readily categorized, having

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Table 1. Reaction Conditions for $Na_{14}[(UO_2)_5(AsO_4)_8]\cdot 2H_2O$ (1), $K_6[(UO_2)_5O_5(AsO_4)_2]$ (2a), $K_4[(UO_2)_3O_2(AsO_4)_2]$ (2b), $Rb_4[(UO_2)_3O_2(AsO_4)_2]$ (3), and $Cs_6[(UO_2)_5O_2(AsO_4)_4]$ (4)

compound	reactants length of gold ampule	*T* (°C) and *P* (bar)	products
1	$Na_2HAsO_4\cdot 7H_2O/UO_3/H_2O$ (55.2 mg/8.7 mg/159 μL; molar ratio: Na/U/As = 11.6/1/5.8), 2.6 cm	560 and 1440	greenish yellow bladed crystals of **1** (major), unknown dark solid (minor), yield of **1**: 75%
2a and **2b**	10 M $KOH/KH_2AsO_4/UO_3/H_2O$ (40.2 μL/37 mg/20.1 mg/242 μL; molar ratio: K/U/As = 9/1/3), 3.3 cm	555 and 1400	yellowish orange needle crystals of **2a** (major), yellow plate crystals of **2b** (minor), yield of **2a**: 81%
3	50 wt % $RbOH/RbH_2AsO_4/UO_3/H_2O$ (49 μL/94.8 mg/20.7 mg/374 μL; molar ratio: Rb/U/As = 11.5/1/5.8), 5.8 cm	560 and 1440	yellow plate crystals of **3** yield: 68%
4	50 wt % $CsOH/CsH_2AsO_4/UO_3/H_2O$ (35 μL/57.5 mg/20 mg/320 μL; molar ratio: Cs/U/As = 6/1/3), 3.7 cm	555 and 1400	greenish yellow plate crystals of **4** yield: 65%

Table 2. Crystallographic Data for $Na_{14}[(UO_2)_5(AsO_4)_8]\cdot 2H_2O$ (1), $K_6[(UO_2)_5O_5(AsO_4)_2]$ (2a), $K_4[(UO_2)_3O_2(AsO_4)_2]$ (2b), $Rb_4[(UO_2)_3O_2(AsO_4)_2]$ (3), and $Cs_6[(UO_2)_5O_2(AsO_4)_4]$ (4)

compound	1	2a	2b	3	4
chemical formula	$As_8H_4Na_{14}O_{44}U_5$	$As_2K_6O_{23}U_5$	$As_2K_4O_{16}U_3$	$As_2O_{16}Rb_4U_3$	$As_4Cs_6O_{28}U_5$
formula weight	2819.40	1942.59	1276.33	1461.81	2735.29
crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/m$ (No. 11)	$P\bar{1}$ (No. 2)
a/Å	7.0005(3)	6.8615(3)	6.7852(3)	6.9783(3)	7.7628(3)
b/Å	12.1324(4)	24.702(1)	17.3640(8)	17.4513(8)	9.3324(4)
c/Å	13.7428(5)	7.1269(3)	7.1151(3)	7.0867(3)	11.9336(4)
α/deg	64.175(2)	90	90	90	75.611(2)
β/deg	89.092(2)	98.749(2)	98.801(2)	90.808(3)	73.136(2)
γ/deg	85.548(2)	90	90	90	86.329(2)
V/Å^3	1047.26(7)	1193.89(9)	828.42(6)	862.94(7)	801.37(5)
Z	1	2	2	2	1
T, °C	23	23	23	23	23
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
D_{calc}, g·cm^{-3}	4.470	5.404	5.117	5.626	5.668
μ(Mo Kα), mm^{-1}	25.81	37.69	34.30	43.17	36.08
R_1[a]	0.0185	0.0225	0.0269	0.0269	0.0336
wR_2[b]	0.0351	0.0502	0.0689	0.0508	0.0989

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\mathrm{Max}(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0033$ and $b = 4.60$ for **1**, $a = 0.0253$ and $b = 2.26$ for **2a**, $a = 0.0399$ and $b = 0.00$ for **2b**, $a = 0.0181$ and $b = 0.00$ for **3**, and $a = 0.0669$ and $b = 2.46$ for **4**.

compositions and structures distinct from the three major groups. Uranyl arsenate minerals are structurally related to the phosphates, and many of them show substantial substitution of As and P in structural sites. In addition to these minerals, there are a number of synthetic uranium arsenates. For examples, Natarajan and co-workers reported several two- and three-dimensional (3D) uranium(IV) and uranium(VI) arsenates that are templated by organic ammonium cations.[5] Locock and Burns synthesized two hydrated uranyl arsenates under mild hydrothermal conditions.[6] A complex mercury(II) uranyl arsenate with a pseudolayered structure consisting uranyl arsenate layers and mercury oxide/hydroxide layers were synthesized under mild hydrothermal conditions by Albrecht-Schmitt and co-workers.[7] Alekseev and co-workers synthesized a number of uranyl arsenates by high-temperature solid-state reactions, and some of them contain interesting polymeric arsenate anions.[8] Recently, we extended the exploratory synthetic and structural studies from uranium silicates and germanates to the phosphates and obtained a new uranium(IV) phosphate, $Na_{10}U_2P_6O_{24}$, and the isotypic cerium(IV) phosphate.[9] They adopt a 3D framework structure with intersecting 12-sided circular and rectangular channels. In this Paper we report five new layered uranyl arsenates, $Na_{14}[(UO_2)_5(AsO_4)_8]\cdot 2H_2O$ (further denoted as **1**), $K_6[(UO_2)_5O_5(AsO_4)_2]$ (**2a**), $K_4[(UO_2)_3O_2(AsO_4)_2]$ (**2b**), $Rb_4[(UO_2)_3O_2(AsO_4)_2]$ (**3**), and $Cs_6[(UO_2)_5O_2(AsO_4)_4]$ (**4**). All of them have been synthesized under high-temperature, high-pressure hydrothermal conditions and structurally characterized by single-crystal X-ray diffraction. Their structural relationships with known compounds will also be discussed.

■ EXPERIMENTAL SECTION

Synthesis and Initial Characterization. High-temperature, high-pressure hydrothermal syntheses were performed using a Tem-Pres autoclave where the pressure was provided by water. Reaction mixtures including alkali metal hydroxide solution, UO_3, alkali metal hydrogen arsenate, and water were sealed in gold ampules (inner diameter = 0.48 cm), which were placed in the autoclave and counterpressured with water at a fill level of 55%. $Na_2HAsO_4\cdot 7H_2O$ (Sigma, ≥ 98%), KH_2AsO_4 (Sigma), RbOH(aq) (Aldrich, 50 wt %) and CsOH(aq) (Aldrich, 50 wt %) were purchased and used as received. RbH_2AsO_4 and CsH_2AsO_4 were prepared from a solution of As_2O_3 dissolved in H_2O_2 with RbOH and CsOH, respectively. The autoclave was heated at about 560 °C for 2 d, cooled to 350 °C at 5 °C/h, and then rapidly cooled to room temperature (r.t.) by removal from the furnace. The pressure at the reaction temperature was estimated according to the P−T phase diagram of pure water. The products were filtered, washed with water, rinsed with ethanol and dried at ambient conditions. Suitable crystals were selected for single-crystal X-ray diffraction, from which the chemical formulas were determined. Reactions for **1** and **2**

Table 3. Selected Bond Lengths (Å) for $Na_{14}[(UO_2)_5(AsO_4)_8]\cdot 2H_2O$ (1), $K_6[(UO_2)_5O_5(AsO_4)_2]$ (2a), $K_4[(UO_2)_3O_2(AsO_4)_2]$ (2b), $Rb_4[(UO_2)_3O_2(AsO_4)_2]$ (3), and $Cs_6[(UO_2)_5O_2(AsO_4)_4]$ (4)

	compound 1[a]		
U(1)−O(17)	1.782(3)	U(1)−O(18)	1.802(3)
U(1)−O(10)	2.279(3)	U(1)−O(11)	2.304(3)
U(1)−O(15)	2.349(3)	U(1)−O(3)	2.412(3)
U(1)−O(2)	2.492(3)	U(2)−O(19)	1.785(3)
U(2)−O(20)	1.805(3)	U(2)−O(16)	2.229(3)
U(2)−O(14)	2.299(3)	U(2)−O(12)	2.324(3)
U(2)−O(7)	2.453(3)	U(2)−O(6)	2.464(3)
U(3)−O(21)	1.801(3) (2×)	U(3)−O(4)	2.252(3) (2×)
U(3)−O(8)	2.263(3) (2×)	As(1)−O(1)	1.654(3)
As(1)−O(2)	1.682(3)	As(1)−O(3)	1.685(3)
As(1)−O(4)	1.712(3)	As(2)−O(5)	1.651(3)
As(2)−O(6)	1.690(3)	As(2)−O(7)	1.695(3)
As(2)−O(8)	1.700(3)	As(3)−O(9)	1.656(3)
As(3)−O(10)	1.679(3)	As(3)−O(11)	1.679(3)
As(3)−O(12)	1.691(3)	As(4)−O(13)	1.634(4)
As(4)−O(14)	1.688(3)	As(4)−O(15)	1.688(3)
As(4)−O(16)	1.670(4)		
	compound 2a[a]		
U(1)−O(5)	1.833(4)	U(1)−O(6)	1.852(4)
U(1)−O(7)	2.105(2)	U(1)−O(8)	2.262(4)
U(1)−O(9)	2.267(4)	U(1)−O(3)	2.513(4)
U(1)−O(4)	2.516(4)	U(2)−O(10)	1.811(4)
U(2)−O(11)	1.814(4)	U(2)−O(9)	2.276(4)
U(2)−O(8)	2.300(4)	U(2)−O(2)	2.317(4)
U(2)−O(3)	2.362(4)	U(2)−O(4)	2.388(4)
U(3)−O(12)	1.835(4) (2×)	U(3)−O(8)	2.266(4) (2×)
U(3)−O(9)	2.272(4) (2×)	As(1)−O(1)	1.641(4)
As(1)−O(2)	1.657(4)	As(1)−O(3)	1.710(4)
As(1)−O(4)	1.716(4)		
	compound 2b[a]		
U(1)−O(6)	1.816(5)	U(1)−O(5)	1.822(5)
U(1)−O(7)	2.251(4)	U(1)−O(7)	2.276(4)
U(1)−O(2)	2.293(5)	U(1)−O(3)	2.365(4)
U(1)−O(4)	2.388(4)	U(2)−O(8)	1.807(5) (2×)
U(2)−O(7)	2.260(4) (2×)	U(2)−O(3)	2.578(4) (2×)
U(2)−O(4)	2.624(4) (2×)	As(1)−O(1)	1.645(5)
As(1)−O(2)	1.659(5)	As(1)−O(3)	1.705(4)
As(1)−O(4)	1.695(4)		
	compound 3[a]		
U(1)−O(5)	1.814(7)	U(1)−O(6)	1.816(7)
U(1)−O(7)	2.251(8)	U(1)−O(8)	2.259(7)
U(1)−O(4)	2.574(5) (2×)	U(1)−O(3)	2.655(6) (2×)
U(2)−O(9)	1.806(5)	U(2)−O(10)	1.815(5)
U(2)−O(7)	2.252(4)	U(2)−O(8)	2.273(4)
U(2)−O(3)	2.358(5)	U(2)−O(2)	2.364(5)
U(2)−O(4)	2.421(5)	As(1)−O(1)	1.642(5)
As(1)−O(2)	1.686(5)	As(1)−O(3)	1.695(5)
As(1)−O(4)	1.706(5)		
	compound 4[a]		
U(1)−O(9)	1.803(6)	U(1)−O(10)	1.807(6)
U(1)−O(7)	2.252(6)	U(1)−O(14)	2.280(5)
U(1)−O(3)	2.319(6)	U(1)−O(4)	2.428(6)
U(1)−O(3)	2.548(6)	U(2)−O(11)	1.786(6)
U(2)−O(12)	1.797(6)	U(2)−O(6)	2.303(6)
U(2)−O(2)	2.334(5)	U(2)−O(14)	2.359(5)
U(2)−O(4)	2.362(6)	U(2)−O(8)	2.482(6)
U(3)−O(13)	1.812(6) (2×)	U(3)−O(14)	2.196(5) (2×)
U(3)−O(8)	2.379(5) (2×)	As(1)−O(1)	1.626(7)
As(1)−O(2)	1.652(6)	As(1)−O(3)	1.714(6)
As(1)−O(4)	1.714(6)	As(2)−O(5)	1.651(6)
As(2)−O(6)	1.672(6)	As(2)−O(7)	1.699(6)
As(2)−O(8)	1.725(6)		

[a] Note: the alkali metal−oxygen distances are available from the Supporting Information.

produced mixtures, whereas those for **3** and **4** gave pure products. Crystals of **1** and **2a** could be manually separated from the side products, giving pure samples, as indicated by powder X-ray diffraction. The yields were calculated based on uranium. The reaction conditions are summarized in Table 1, crystallographic data are given in Table 2, and selected bond lengths are given in Table 3.

Powder diffraction data were collected at r.t. in the range of $5° \leq 2\theta \leq 50°$ on a Shimadzu XRD-6000 powder diffractometer. The powder patterns are given in Figures S1 to S4 in the Supporting Information. Energy dispersive X-ray spectrometry (EDS) analysis on several crystals of each compound using a JEOL JSM-7000F FESEM confirmed the presence of the elements in each compound. EDS spectra can be found in Supporting Information, Figure S5.

Thermal Gravimetric Analysis. A thermogravimetric analysis (TGA) measurement was conducted using a PerkinElmer Pyris 1 TGA thermal analyzer on a powdered sample of **1** in a platinum crucible that was heated from 40 to 900 °C at a rate of 2 °C/min under flowing nitrogen gas. The TGA curve is shown in Supporting Information, Figure S6.

Luminescence Spectroscopy. Photoluminescence data were measured on a powder sample of **1** at r.t. using a Hitachi F-4500 Fluorescence Spectrophotometer. Excitation was achieved using 360 nm light from a xenon lamp.

Single-Crystal X-ray Diffraction. *$Na_{14}[(UO_2)_5(AsO_4)_8]\cdot 2H_2O$ (**1**).* A greenish-yellow bladed crystal of **1** with dimensions of 0.04 × 0.04 × 0.15 mm was selected for indexing and intensity data collection on a Bruker Kappa Apex II CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source. Intensity data were collected at 296 K over 1319 frames with φ and ω scans (width 0.5°/frame) and an exposure time of 30 s/frame. Determination of integrated intensities and unit cell refinement were performed using SAINT program.[10] The SADABS program was used for absorption correction (T_{min}/T_{max} = 0.434/0.746).[11] On the basis of statistical analysis of intensity distribution and successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (No. 2). The structure was solved by direct methods and successive difference Fourier synthesis. The locations of H atoms were not determined. The hydrogen positions for the water molecule were placed geometrically and refined using a riding mode. The final cycles of least-squares refinement including atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms converged at $R1 = 0.0185$, $wR2 = 0.0351$ for 4793 reflections with $I > 2\sigma(I)$, GOF = 1.061, $\rho_{max,min}$ = 0.83 and −0.94 e·Å^{-3}. All calculations were performed using the *SHELXTL* version 6.14 software package.[12]

*$K_6[(UO_2)_5O_5(AsO_4)_2]$ (**2a**).* Yellowish-orange needle crystal, 0.02 × 0.03 × 0.13 mm, T_{min}/T_{max} = 0.460/0.746, space group $P2_1/c$ (No. 14), $R1 = 0.0225$, $wR2 = 0.0502$ for 2623 reflections with $I > 2\sigma(I)$, GOF = 1.046, $\rho_{max,min}$ = 2.41 and −3.24 e·Å^{-3}.

*$K_4[(UO_2)_3O_2(AsO_4)_2]$ (**2b**).* Yellow plate crystal, 0.01 × 0.10 × 0.11 mm, T_{min}/T_{max} = 0.462/0.746, space group $P2_1/c$ (No. 14), $R1$ = 0.0269, $wR2$ = 0.0689 for 1866 reflections with $I > 2\sigma(I)$, GOF = 1.108, $\rho_{max,min}$ = 2.00 and −2.57 e·Å^{-3}.

*$Rb_4[(UO_2)_3O_2(AsO_4)_2]$ (**3**).* Yellow plate crystal, 0.015 × 0.015 × 0.03 mm, T_{min}/T_{max} = 0.505/0.746, space group $P2_1/m$ (No. 11), $R1$ = 0.0269, $wR2$ = 0.0508 for 1738 reflections with $I > 2\sigma(I)$, GOF = 1.006, $\rho_{max,min}$ = 1.31 and −1.64 e·Å^{-3}.

*$Cs_6[(UO_2)_5O_2(AsO_4)_4]$ (**4**).* Greenish-yellow plate crystal, 0.02 × 0.15 × 0.17 mm, T_{min}/T_{max} = 0.273/0.746, space group $P\bar{1}$ (No. 2), $R1$ =

0.0336, $wR2 = 0.0989$ for 3790 reflections with $I > 2\sigma(I)$, GOF = 1.048, $\rho_{\max,\min} = 4.18$ and -2.94 e·Å^{-3}.

RESULTS AND DISCUSSION

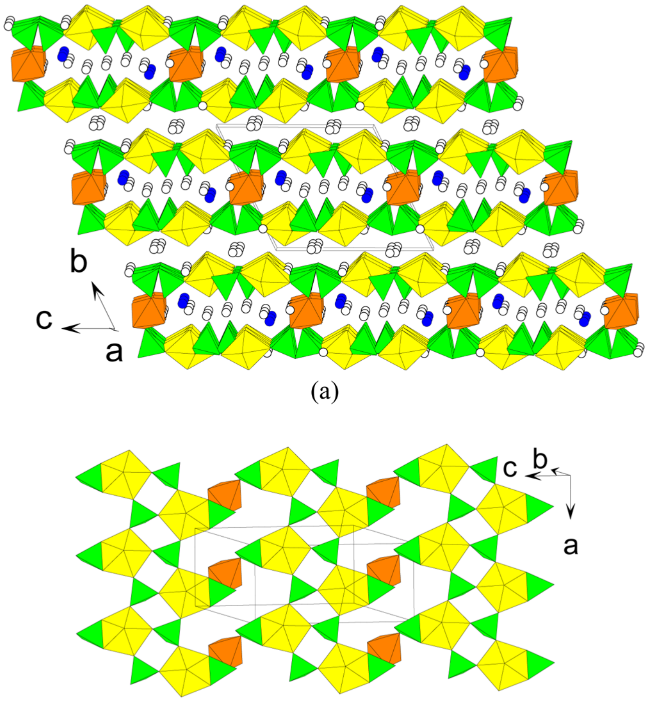


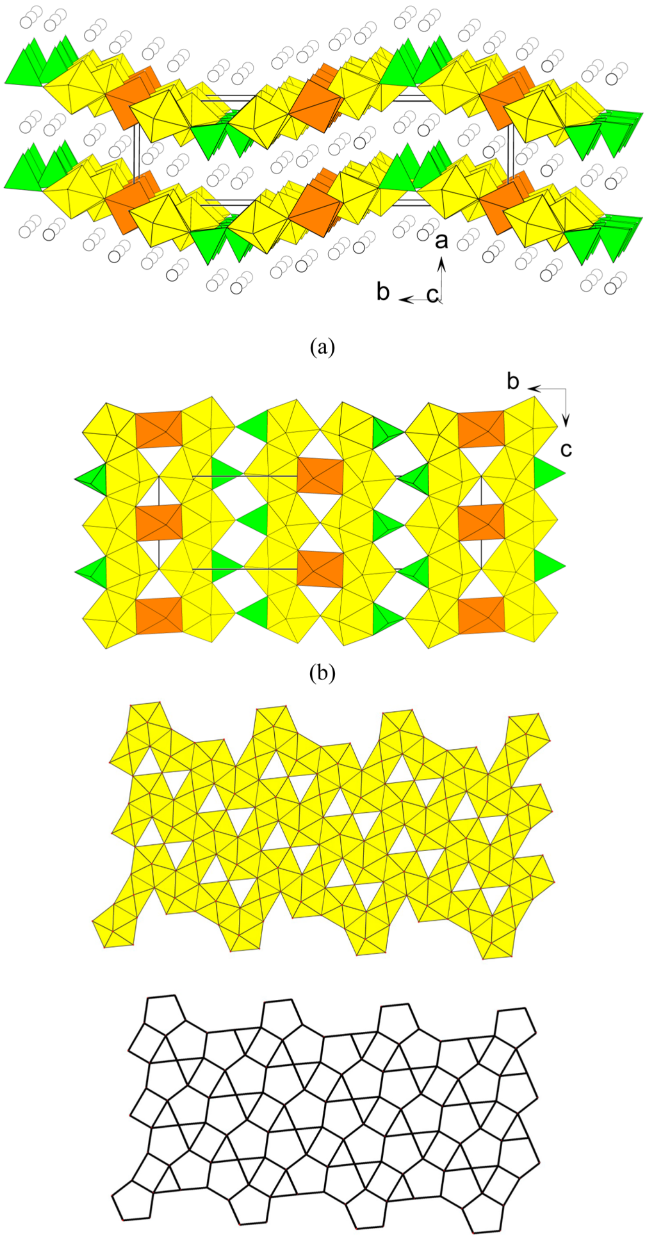
Figure 1. (a) Polyhedral representation of the structure of **1** in a direction approximately parallel to the *a* axis. Key: yellow pentagonal bipyramids, UO_7; orange tetragonal bipyramids, UO_6; green tetrahedra, AsO_4; open circles, Na atoms; blue circles, H_2O molecules. (b) Section of a sheet in the structure of **1**.

$Na_{14}[(UO_2)_5(AsO_4)_8]\cdot 2H_2O$ (1). As shown in Figure 1a, the overall structure of **1** is layered with slabs of uranyl arsenate, separated by Na^+ cations. The intralayer region also contains Na^+ cations and water molecules. The structure is formed from the following structural elements: eight sodium sites, two UO_7 pentagonal bipyramids, one UO_6 tetragonal bipyramid, four AsO_4 tetrahedra, and one water molecule. All Na sites except Na(8) are ordered and fully occupied. Na(8) is disordered over two sites each with a half occupancy. Two Na atoms and the six-coordinate uranium atom, U(3), are at inversion centers and all other atoms are in general positions. All of the three U–O polyhedra have two short U═O bonds (U(1)═O, 1.782 and 1.802 Å; U(2)═O, 1.785 and 1.805 Å; U(3)═O, 1.801 Å (2 ×)), forming a linear or approximately linear $[O{=}U{=}O]^{2+}$ cations, as is typical for U^{6+} in crystal structures, and five or four longer U–O bonds (U(1)–O, 2.279–2.492 Å; U(2)–O, 2.229–2.464 Å; U(3)–O, 2.252–2.263 Å) in the plane normal to this UO_2 axis. Uranyl ions occur in three coordination polyhedra in crystal structures: tetragonal bipyramidal, pentagonal bipyramidal, and hexagonal bipyramidal, with uranyl pentagonal bipyramids being the most common.[13] The bond-valence sums at the U(1), U(2), and U(3) sites, calculated using the coordination-independent bond-valence parameters $R_{ij} = 2.051$ Å and $b = 0.519$ Å reported by Burns et al., were 6.04, 6.11, and 5.92 valence units (vu), respectively.[14] The four symmetrically distinct As atoms are tetrahedrally coordinated by O atoms, with As–O bond lengths ranging from 1.634 to 1.712 Å. The sums of bond valences at the As sites are 5.01–5.20 vu.[15] The valence sum for O1w is 0.50 vu, consistent with its assignment as H_2O group. The values for the remaining O atoms range from 1.84 to 2.17.[15] The Na atoms are coordinated by five, six, or seven O atoms when the limiting value for the Na–O bond length, 3.19 Å, of Donnay and Allmann is considered.[16] The valence sum at the Na(8) site is 0.77 vu and the values for all the other Na sites are from 0.93 to 1.14 vu. Na(8) is located in the intralayer region and has a relatively large thermal parameter, indicating that it is loosely bound. These results are consistent with the formal valences of U^{6+}, As^{5+}, and Na^+. As shown in Supporting Information, Figure S5, the TGA curve shows weight losses in several overlapping steps. The first step (50 to ~150 °C) corresponds to the loss of two water molecules (observedd 1.1%, calculated 1.28%). The second continuous broad weight loss of 1.8% in the range 150–600 °C can be ascribed to partial reduction of As(V) to As(III) with concomitant loss of oxygen. The final decomposition product was not characterized.

The structure of **1** contains $U(1)O_7$ and $U(2)O_7$ pentagonal bipyramids that are connected by sharing their equatorial corners with $As(3)O_4$ and $As(4)O_4$ tetrahedra to form infinite chains along the *a* axis (Figure 1b). Within a chain the AsO_4 tetrahedra share three vertices with uranyl pentagonal bipyramids and the apical oxygen atoms are in the same orientation relative to the plane of the chain. $As(1)O_4$ and $As(2)O_4$ tetrahedra are attached to either side of the chains by sharing edges with the UO_7 pentagonal bipyramids. This chain structure that is based upon the **c1/1b** chain topology has been observed in an organically templated uranyl sulfate, $(C_7H_{20}N_2)$-$[(UO_2)_2(SO_4)_3(H_2O)]$.[17] Translational equivalent uranyl arsenate chains are joined by sharing of equatorial vertices of $U(3)O_6$ tetrgonal bipyramids with $As(1)O_4$ and $As(2)O_4$ tetrahedra from adjacent chains, resulting in sheets that are parallel to the *ac* plane. $U(3)O_6$ are located between two sheets and share two vertices with AsO_4 tetrahedra from each adjacent sheets to form double layers of a new structure type. The intralayer region contains Na^+ ions and water molecules. The water molecule is not only bonded to Na^+ ions but also H-bonded to an arsenate oxygen atom. Adjacent double layers are linked through bonds from the uranyl and arsenate oxygen atoms to the interlayer Na^+ ions.

Supporting Information, Figure S7 shows the photoluminescence spectrum of **1** at r.t. It exhibits several characteristic five-peak emission bands positioned at 502, 519, 540, 562, and 588 nm. This broad structured band is typical of uranyl and is interpreted as a pure electronic luminescence transition at 502 nm followed by a coupling of the O═U═O vibrations resulting in the other peaks in the spectrum.[18]

$K_6[(UO_2)_5O_5(AsO_4)_2]$ (2a). As shown in Figure 2a, the structure of **2a** contains corrugated layers of uranyl arsenate, separated by K^+ cations. The structure is formed from the following structural elements: three potassium sites, two UO_7 pentagonal bipyramids, one UO_6 tetragonal bipyramid, and one AsO_4 tetrahedron. The six-coordinate uranium atom, U(3), and the bridging oxygen atom, O(7), between two U(1) atoms have a center of symmetry and all other atoms are in general positions. All of the three U–O polyhedra have two short U═O bonds (U(1)═O, 1.833 and 1.852 Å; U(2)═O, 1.811 and 1.814 Å; U(3)═O, 1.835 Å (2×)), forming a linear or approximately linear $[O{=}U{=}O]^{2+}$ cations, as is typical for U^{6+} in crystal structures, and five or four longer U–O bonds



(a)

(b)

(c)

Figure 2. (a) Structure of **2a** viewed in a direction approximately parallel to the *c* axis. Key: yellow pentagonal bipyramids, UO_7; orange tetragonal bipyramids, UO_6; green tetrahedra, AsO_4; open circles, K atoms. (b) Section of a corrugated layer in the structure of **2a**. (c) The β-U_3O_8-type sheet and its anion topology.

(U(1)−O, 2.105–2.516 Å; U(2)−O, 2.276–2.388 Å; U(3)−O, 2.266–2.272 Å) in the plane normal to this UO_2 axis. The bond-valence sums at the U(1), U(2), and U(3) sites, calculated using the coordination-independent bond-valence parameters R_{ij} = 2.051 Å and b = 0.519 Å reported by Burns et al., were 6.04, 6.12, and 5.66 valence units (vu), respectively.[14] The value for U(3) differ significantly from the formal valence of 6 vu. However, the parameters for uranyl square bipyramid R_{ij} = 2.074 Å and b = 0.554 Å provide bond-valence sum of 5.83 vu for U(3), which is close to the formal valence. The As atom is tetrahedrally coordinated by O atoms, with As−O bond lengths ranging from 1.641 to 1.716 Å. The sum of bond valences at the As(1) site is 5.05 vu.[15] The values for the remaining O atoms range from 1.80 to 2.18.[15] The K atoms are coordinated by seven or eight O atoms when the limiting value for the K−O bond length, 3.35 Å of Donnay and Allmann is considered.[16] The valence sums at the K(1), K(2), and K(3) sites are 1.14, 0.96, and 0.72 vu, respectively. K(3) showed relatively large thermal parameters, indicative of partial occupancy or positional disorder. The multiplicities of all K atoms were allowed to refine. The K(1), K(2), and K(3) positions, respectively, refined to a multiplicity of 1.000(6), indicating that all K positions are fully occupied. Therefore, we ascribe the large thermal parameters for K(3) to positional disorder. These results are consistent with the formal valences of U^{6+}, As^{5+}, and K^+.

UO_7 pentagonal bipyramids share equatorial edges to form zigzag infinite chains along the *c* axis. Two parallel chains related by an inversion center are connected together by O(7) and UO_6 tetragonal bipyramids to form three-polyhedron-wide ribbons of uranyl square and pentagonal bipyramids (Figure 2b). The equatorial oxygen atoms of UO_6 are common to three uranyl polyhedra. Two ribbons of uranyl polyhedra related by 2_1-screw axis are connected by sharing of equatorial vertices and edges of UO_7 pentagonal bipyramids with AsO_4 tetrahedra, resulting in corrugated sheets in the *bc* plane, which are separated by K^+ cations. Adjacent sheets are linked through bonds from the uranyl and arsenate oxygen atoms to the K^+ cations.

The structure of **2a** is related to that of β-U_3O_8.[19] The anion-topology of β-U_3O_8 is similar to the uranophane anion-topology in that both contain chains of edge-sharing pentagons that are separated by chains of edge-sharing triangles and squares (Figure 2c). The distinction is that pentagons of adjacent chains share vertices only in β-U_3O_8, which also contains more triangles. In the β-U_3O_8-type sheet all pentagons and squares are occupied by uranium. β-U_3O_8 actually has a 3D framework structure, in which adjacent sheets are connected by sharing corners of UO_6 and UO_7 polyhedra such that nearly linear configuration of square- and pentagonal-coordinate uranium atoms is formed. The structure of **2a** contains three-polyhedron-wide chains, identical to those found in the β-U_3O_8-type sheet. Compound **2a** is isostructural with the uranyl vanadate $K_6(UO_2)_5(VO_4)_2O_5$, which was synthesized by solid-state reaction.[20]

$K_4[(UO_2)_3O_2(AsO_4)_2]$ (2b). As shown in Figure 3a, the structure of **2b** contains sheets of uranyl arsenates that are separated by K^+ cations. The structure is formed from the following structural elements: two potassium sites, one UO_7 pentagonal bipyramid, one UO_8 hexagonal bipyramid, and one AsO_4 tetrahedron. Both K^+ ion sites are ordered and fully occupied. The eight-coordinate uranium atom, U(2), has a center of symmetry and all other atoms are in general positions. Both U−O polyhedra have two short U═O bonds (U(1)═O, 1.816 and 1.822 Å; U(2)═O, 1.807 Å (2×)), forming a linear or approximately linear $[O{=}U{=}O]^{2+}$ cations, as is typical for U^{6+} in crystal structures, and five or six longer U−O bonds (U(1)−O, 2.251−2.388 Å; U(2)−O, 2.260−2.624 Å) in the plane normal to this UO_2 axis. The bond-valence sums at the U(1) and U(2) sites, calculated using the coordination-independent bond-valence parameters R_{ij} = 2.051 Å and b = 0.519 Å reported by Burns et al., were 6.15 and 5.92 vu, respectively.[14] The As atom is tetrahedrally coordinated by O atoms, with As−O bond lengths ranging from 1.645 to 1.705 Å. The sum of bond valences at the As(1) site is 5.13 vu.[15] The values for the O atoms range from 1.83 to 2.17 vu.[15] Both K

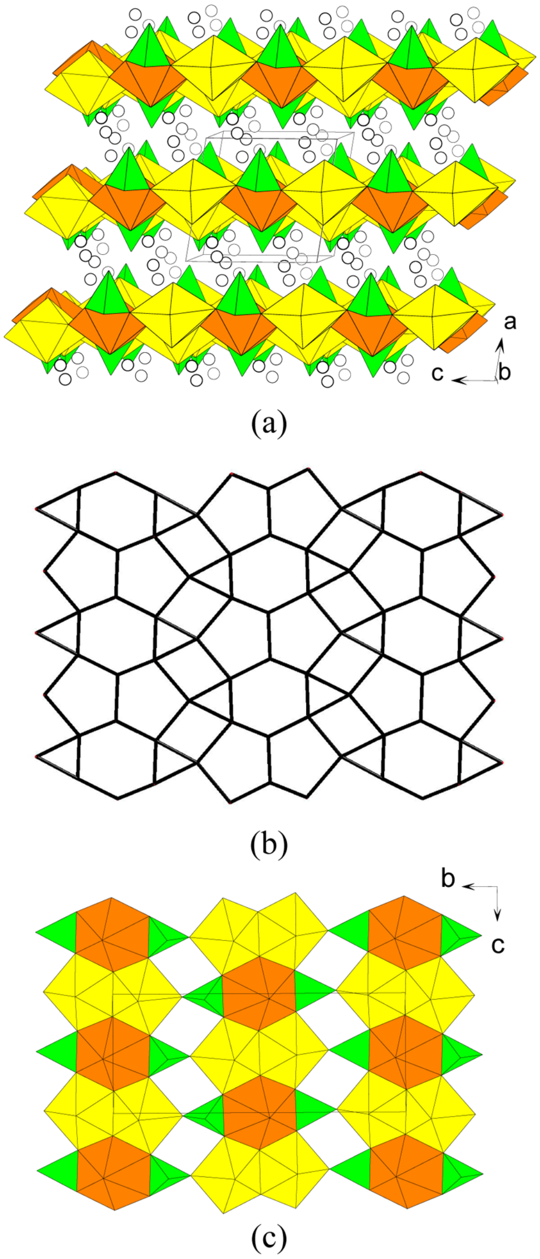


Figure 3. (a) Structure of **2b** viewed in a direction approximately parallel to the *b* axis. Key: yellow pentagonal bipyramids, UO_7; orange hexagonal bipyramids, UO_8; green tetrahedra, AsO_4; open circles, K atoms. (b) The phosphuranylite anion-topology. (c) Section of a uranyl arsenate sheet in the structure of **2b**.

atoms are coordinated by eight O atoms when the limiting value for the K−O bond length, 3.35 Å, of Donnay and Allmann is considered.[16] The valence sums at the K(1) and K(2) sites are 1.10 and 0.75 vu, respectively. The equivalent isotropic thermal parameter for K(2) is about twice of that for K(1), indicating that K(2) is loosely bound in the structure. These results are consistent with the formal valences of U^{6+} and K^+.

The structure of **2b** contains sheets based on an anion topology with triangles, squares, pentagons, and hexagons (Figure 3b). The anion topologies are developed by joining anions by lines if they are separated by less than 3.5 Å according to the method proposed by Burns et al.[4a,13a] The pentagons share edges to form dimers that are connected into chains by sharing edges with hexagons. These chains are linked through chains of alternating edge-sharing triangles and squares, resulting in a phosphuranylite anion-topology.[21] As shown in Figure 3c, in the structure of **2b** the pentagons and hexagons are populated by uranyl ions, and the triangles by arsenate tetrahedra, with the squares being unoccupied. Actually, none with the phosphuranylite anion-topology involves the occupancy of the squares. One of the oxygen atoms, O(7), is common to three uranyl polyhedra. The apical oxygen atoms of arsenate tetrahedra between the uranyl chains are in the same orientation, whereas each pair of tetrahedra attached to a given uranyl hexagonal bipyramid have opposite orientations. The phosphuranylite-type sheet is commonly observed in the structures of actinyl orthophosphates and orthoarsenates that have layer structures. Four different geometrical isomers of the sheets in the minerals of the phosphuranylite group are known; they differ in the orientation of the apical atoms of the tetrahedra.[22] The orientation of arsenate tetrahedra in **2b** is different from the four isomers, yielding a novel geometrical isomer. The interlayers of the structure contain K^+ cations. Adjacent layers are linked through bonds from the uranyl and arsenate oxygen atoms to the K^+ cations.

$Rb_4[(UO_2)_3O_2(AsO_4)_2]$ (3). The structure of **3** is similar to that of **2b** and contains phosphuranylite-type sheets separated by Rb^+ cations. In an asymmetric unit there are three rubidium sites, one UO_7 pentagonal bipyramid, one UO_8 hexagonal bipyramid, and one AsO_4 tetrahedron. All three Rb^+ ion sites are fully occupied. The eight-coordinate uranium atom, U(1), Rb(2), O(5), O(6), O(7) and O(8) lie in mirror planes, Rb(3) has a center of symmetry, and the other atoms are in general positions. Both U−O polyhedra have two short U═O bonds, forming approximately linear $[O{=}U{=}O]^{2+}$ cations, and five or six longer U−O bonds in the plane normal to this UO_2 axis. The O(5)═U(1)═O(6) unit lies in a mirror plane. The bond-valence sums at the U(1) and U(2) sites, calculated using the coordination-independent bond-valence parameters R_{ij} = 2.051 Å and *b* = 0.519 Å reported by Burns et al., were 5.86 and 6.10 vu, respectively.[14] The sum of bond valences at the As(1) site is 5.04 vu, and the values for the O atoms range from 1.88 to 2.19 vu.[15] The valence sums at the Rb(1), Rb(2), and Rb(3) sites are 1.20, 1.32, and 0.80 vu, respectively. The equivalent isotropic thermal parameter for Rb(3) is considerably larger than those for Rb(1) and Rb(2), indicating that Rb(3) is loosely bound in the structure. As shown in Figure 4, in the phosphuranylite-type sheet of **3** the arsenate tetrahedra between uranyl chains alternate orientations in an up−down up−down up−down pattern, and each pair of tetrahedra attached to a given uranyl hexagonal bipyramid has the same orientation. The orientation of tetrahedra in **3** is the same as those in the uranyl phosphate and arsenate minerals vanmeersscheite, dumontite, and hügelite.[23]

$Cs_6[(UO_2)_5O_2(AsO_4)_4]$ (4). As shown in Figure 5a, the structure of **4** consists of planar sheets of uranyl arsenate, separated by Cs^+ cations. The structure is formed from the following structural elements: three cesium sites, two UO_7 pentagonal bipyramids, one UO_6 tetragonal bipyramid, and two AsO_4 tetrahedra. All Cs^+ ion sites are ordered and fully occupied. The six-coordinate uranium atom, U(3), has a center of symmetry, and all other atoms are in general positions. All of the three U−O polyhedra have two short U═O bonds (U(1)═O, 1.803 and 1.807 Å; U(2)═O, 1.786 and 1.797 Å; U(3)═O, 1.812 Å (2×)), forming linear or approximately

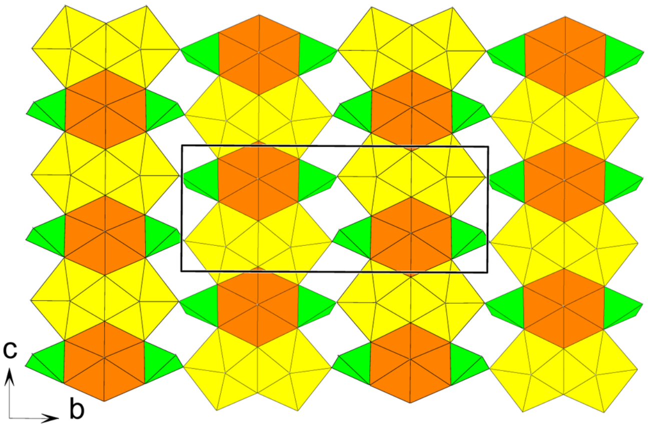


Figure 4. Section of a uranyl arsenate sheet in the structure of **3**. Key: yellow pentagonal bipyramids, UO_7; orange hexagonal bipyramids, UO_8; green tetrahedra, AsO_4.

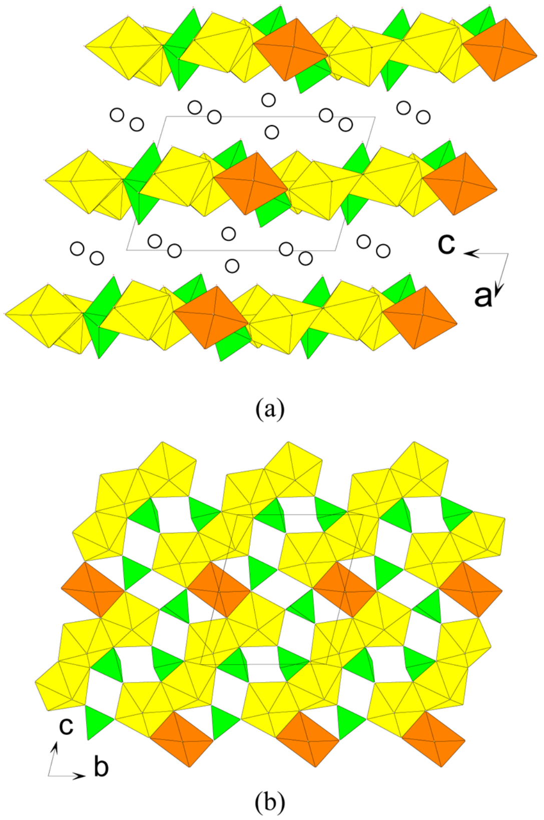


Figure 5. (a) Polyhedral representation of the structure of **4** viewed along the *b* axis. Key: yellow pentagonal bipyramids, UO_7; orange square bipyramids, UO_6; green tetrahedra, AsO_4; open circles, Cs atoms. (b) Section of a uranyl arsenate sheet in the structure of **4**.

linear $[O{=}U{=}O]^{2+}$ cations, as is typical for U^{6+} in crystal structures, and five or four longer U–O bonds (U(1)–O, 2.252–2.548 Å; U(2)–O, 2.303–2.482 Å; U(3)–O, 2.196–2.379 Å) in the plane normal to this UO_2 axis. The bond-valence sums at the U(1), U(2), and U(3) sites, calculated using the coordination-independent bond-valence parameters R_{ij} = 2.051 Å and b = 0.519 Å reported by Burns et al., were 6.00, 6.03, and 5.75 valence units (vu), respectively.[14] However, the parameters for uranyl square bipyramid R_{ij} = 2.074 Å and b = 0.554 Å provide bond-valence sum of 5.97 vu for U(3), which is in good agreement with the formal valence. The two symmetrically distinct As atoms are tetrahedrally coordinated by O atoms, with As–O bond lengths ranging from 1.626 to 1.725 Å. The sums of bond valences at the As(1) and As(2) sites are 5.13 and 4.98 vu, respectively.[15] The values for the O atoms range from 1.88 to 2.19 vu.[15] The Cs atoms are coordinated by seven or eight O atoms when the limiting value for the Cs–O bond length, 3.70 Å, of Donnay and Allmann is considered.[16] The valence sums at the Cs(1), Cs(2), and Cs(3) sites are 1.09, 1.00, and 1.14 vu, respectively. These results are consistent with the formal valences of U^{6+}, As^{5+}, and Cs^{+}.

The structure of **4** contains linear tetramers of edge-sharing UO_7 pentagonal bipyramids that are connected by sharing trans edges of UO_6 tetragonal bipyramids to form zigzag infinite chains along the *c* axis (Figure 5b). One of the oxygen atoms, O(14), is common to three uranyl polyhedra. Translational equivalent uranyl arsenate chains are connected by sharing of equatorial vertices and edges of uranyl polyhedra with AsO_4 tetrahedra, resulting in planar sheets in the *bc* plane, which are separated by Cs^+ cations. Adjacent sheets are linked through bonds from the uranyl and arsenate oxygen atoms to the Cs^+ cations. The structure of **4** is also related to that of β-U_3O_8. The anion topology of the sheet in **4** can be obtained by splitting the β-U_3O_8-type sheet into complex chains and replacing a half of the squares, which are shown in blue in Figure 6, with triangles. Population of the triangles of by arsenate tetrahedra results in the uranyl arsenate sheets of **4**.

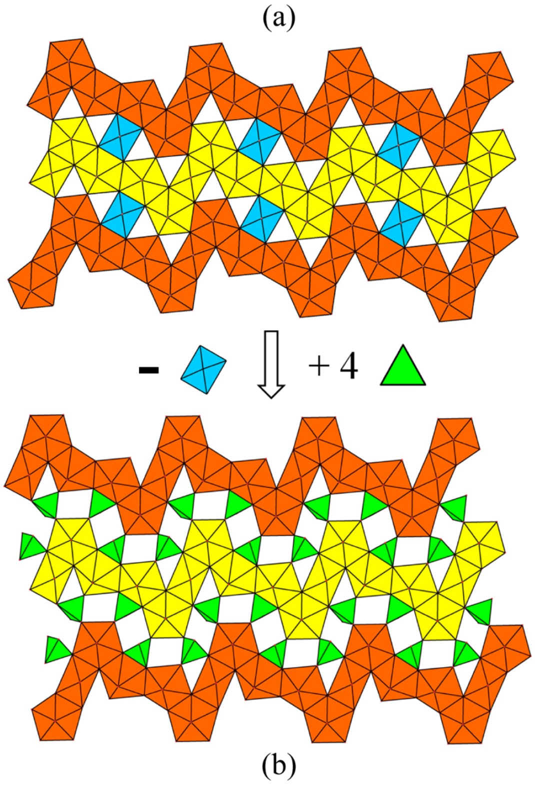


Figure 6. (a) The β-U_3O_8-type sheet. Adjacent zigzag chains are shown in yellow and orange colors. The uranyl arsenate sheet in **4**, which is shown in (b), can be generated from that in β-U_3O_8 by replacing one UO_6 square bipyramid (in blue) with four AsO_4 tetrahedra (in green).

■ CONCLUSION

In summary, this work reports five new uranyl arsenates with two-dimensional layer structures. They are the first examples of high-temperature, high-pressure hydrothermal synthesis of uranyl arsenates. The colors of these compounds and photoluminescence measurement results indicate the presence of hexavalent uranium. Four of the five compounds are anhydrous, although they were synthesized in water. It has been reported that hydrothermal reaction under vigorous conditions prefers the formation of the anhydrous phase as compared with mild conditions.[24] The Rb and Cs uranyl arsenates, which were synthesized under mild hydrothermal conditions, are hydrated.[6] Compounds **1** and **4** adopt new structures, whereas **2a** is isostructural with the corresponding uranyl vanadates, and **2b** and **3** contain the phosphuranylite-type sheet. The molar ratio of arsenate to uranyl unit is the largest for **1** and the smallest for **2a**. Accordingly, the structure of **1** contains chains of discrete uranyl square and pentagonal bipyramids surrounded by arsenate tetrahedra. In contrast, the structure of **2a** contains three-polyhedron-wide ribbons of edge- and corner-sharing uranyl square and pentagonal bipyramids. The structures of **2b** and **3** contain dimers of pentagonal bipyramids that are linked into chains by sharing edges of hexagonal bipyramids, and **4** contains one-polyhedron-wide zigzag chains of edge-sharing uranyl polyhedra. The chain topology in the structure of **1** has been observed in an organically templated uranyl sulfate. The uranyl arsenate sheet in **2b** is a new geometrical isomer of the phosphuranylite group, but the phosphuranylite-type sheet in **3** is the same as those in several uranyl phosphate and arsenate minerals. The structures of **2a** and **4** are related to that of β-U_3O_8 and their sheet anion topologies can be obtained by splitting the β-U_3O_8-type sheet into complex chains and connecting the chains by arsenates.

Uraninite is by far the most important uranium mineral in terms of abundance, widespread occurrence, and economic value. Uranyl oxide hydrates form during the oxidation and corrosion of uraninite-bearing ore deposits, most commonly at or near the surface of corroded uraninite.[1] The structures of two uranyl oxide hydrate minerals, namely, ianthinite and spriggite contain β-U_3O_8-type sheet.[25,26] In the paragenesis of uranium minerals, uranyl phosphates and arsenates are last groups to form. This work reports two interesting layered uranyl arsenates whose anion topologies can be related to the β-U_3O_8-type sheet. A thorough knowledge of the crystal chemistry of urayl phosphates and arsenates can form a basis from which to predict the fate and transport in the environment of uranium.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The X-ray crystallographic data in CIF format, PXRD patterns, TGA curve, EDS spectra, and photoluminescence spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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