

One-dimensional chains in uranyl tungstates: Syntheses and structures of $A_8[(\text{UO}_2)_4(\text{WO}_4)_4(\text{WO}_5)_2]$ ($A = \text{Rb}, \text{Cs}$) and $\text{Rb}_6[(\text{UO}_2)_2\text{O}(\text{WO}_4)_4]$

Evgeny V. Alekseev^{a,b}, Sergey V. Krivovichev^{c,*}, W. Depmeier^b, T. Armbruster^d, H. Katzke^b, Evgeny V. Suleimanov^a, Evgeny V. Chuprunov^a

^aNizhny Novgorod State University, 603095 Nizhny Novgorod, Russia

^bInstitut für Geowissenschaften, Universität Kiel, D-24118 Kiel, Germany

^cDepartment of Crystallography, Federal Agency of Science and Education, St. Petersburg State University, RU-199034, St. Petersburg, Russia

^dLaboratory of Chemical and Mineralogical Crystallography, University of Bern, CH-3012 Bern, Switzerland

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Abstract

Three new uranyl tungstates, $A_8[(\text{UO}_2)_4(\text{WO}_4)_4(\text{WO}_5)_2]$ ($A = \text{Rb}$ (**1**), Cs (**2**)), and $\text{Rb}_6[(\text{UO}_2)_2\text{O}(\text{WO}_4)_4]$ (**3**), were prepared by high-temperature solid-state reactions and their structures were solved by direct methods on twinned crystals, refined to $R_1 = 0.050, 0.042,$ and 0.052 for **1**, **2**, and **3**, respectively. Compounds **1** and **2** are isostructural, monoclinic $P2_1/n$, (**1**): $a = 11.100(7), b = 13.161(9), c = 25.018(17) \text{ \AA}, \beta = 90.033(13)^\circ, V = 3654(4) \text{ \AA}^3, Z = 8$ and (**2**): $a = 11.252(2) \text{ \AA}, b = 13.815(3) \text{ \AA}, c = 25.736(6) \text{ \AA}, \beta = 89.988(2)^\circ, V = 4000.2(16) \text{ \AA}^3, Z = 8$. There are four symmetrically independent U^{6+} sites that form linear uranyl $[\text{O} = \text{U} = \text{O}]^{2+}$ cations with rather distorted coordination in their equatorial planes. There are six W positions: W(1) and W(2) have square-pyramidal coordination (WO_5), whereas W(3), W(4), W(5), and W(6) are tetrahedrally coordinated. The structures are based upon a novel type of one-dimensional (1D) $[(\text{UO}_2)_4(\text{WO}_4)_4(\text{WO}_5)_2]^{4-}$ chains, consisting of WU_4O_{25} pentamers linked by WO_4 tetrahedra and WO_5 square pyramids. The chains run parallel to the a -axis and are arranged in modulated pseudo-2D-layers parallel to (0 1 0). The A^+ cations are in the interlayer space between adjacent pseudo-layers and provide a 3D integrity of the structures. Compounds **1** and **2** are the first uranyl tungstates with $2/3$ of W atoms in tetrahedral coordination. Such a high concentration of low-coordinated W^{6+} cations is probably responsible for the 1D character of the uranyl tungstate units. The compound **3** is triclinic, $P\bar{1}$ $a = 10.188(2), b = 13.110(2), c = 18.822(3) \text{ \AA}, \alpha = 97.853(3), \beta = 96.573(3), \gamma = 103.894(3)^\circ, V = 2388.7(6) \text{ \AA}^3, Z = 4$. There are four U positions in the structure with a typical coordination of a pentagonal bipyramid that contain uranyl ions, UO_2^{2+} , as apical axes. Among eight W sites, the W(1), W(2), W(3), W(4), W(5), and W(6) atoms are tetrahedrally coordinated, whereas the W(7) and W(8) cations have distorted fivefold coordination. The structure contains chains of composition $[(\text{UO}_2)_2\text{O}(\text{WO}_4)_4]^{6-}$ composed of UO_7 pentagonal bipyramids and W polyhedra. The chains involve dimers of UO_7 pentagonal bipyramids that share common O atoms. The dimers are linked into chains by sharing corners with WO_4 tetrahedra. The chains are parallel to $[-101]$ and are arranged in layers that are parallel to (1 1 1). The Rb^+ cations provide linkage of the chains into a 3D structure. The compound **1** has many structural and chemical similarities to its molybdate analog, $\text{Rb}_6[(\text{UO}_2)_2\text{O}(\text{MoO}_4)_4]$. However, the compounds are not isostructural. Due to the tendency of the W^{6+} cations to have higher-than-fourfold coordination, part of the W sites adopt distorted fivefold coordination, whereas all Mo atoms in the Mo compound are tetrahedrally coordinated. Distribution of the WO_5 configurations along the chain extension does not conform to its 'typical' periodicity. As a result, both the chain identity period and the unit-cell volume are doubled in comparison to the Mo analog, which leads to a new structure type.

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1. Introduction

Uranyl tungstates represent an interesting group of inorganic compounds with structures showing many

*Corresponding author. Fax: +219 631 9236.

E-mail address: skrivovi@mail.ru (S.V. Krivovichev).

similarities to uranyl molybdates [1–5]. However, the slightly larger ionic radius of the W^{6+} cation and, most important, the influence of *f*-electrons favors its higher coordination compared to Mo^{6+} . In particular, W^{6+} rarely occurs in tetrahedral coordination, whereas the latter is typical of Mo^{6+} [6–11]. The most common coordinations for W^{6+} are octahedral (as realized in $K_2[(UO_2)(W_2O_8)]$ [3], $Na_2[(UO_2)(W_2O_8)]$ [4], α - and β - $Ag_2[(UO_2)W_2O_8]$ [4], $Na_{10}[(UO_2)_8(W_5O_{20})O_8]$ [3], $Cs_6[(UO_2)_4(W_5O_{21})(OH)_2(H_2O)_2]$ [5], $Li_2[(UO_2)(WO_4)_2]$ and $Li_2[(UO_2)_4(WO_4)_4O]$ [12]) and square pyramidal (as observed in $K_2[(UO_2)_2(WO_5)O]$ [3], $Rb_2[(UO_2)_2(WO_5)O]$ [3], $Cs_2[(UO_2)_2(WO_5)O]$ [13], $Cs_6[(UO_2)_4(W_5O_{21})(OH)_2(H_2O)_2]$ [5]). The only structurally characterized uranyl tungstate with tetrahedral coordination of W^{6+} is $Na_{10}[(UO_2)_8(W_5O_{20})O_8]$ [3], where a $W^{6+}O_4$ tetrahedron is linked to four adjacent $W^{6+}O_6$ octahedra to form a W_5O_{20} unit which has some analogs in uranyl molybdates as well [14]. The tendency of W^{6+} to possess higher coordination numbers causes uranyl tungstates to form high-dimensional topologies. So far, the uranyl tungstate units have been found to be either two-dimensional (2D) [3–5] or three-dimensional [12]. In comparison, uranyl molybdate 1D chains and 0D finite clusters are common and are usually associated with tetrahedral coordination of Mo^{6+} [15,16]. Recently, we have been able to obtain three new uranyl tungstates with 1D topologies. The purpose of this study is to report synthesis and crystal structures of $A_8[(UO_2)_4(WO_4)_4(WO_5)_2]$ ($A = Rb$ (**1**), Cs (**2**)) and $Rb_6[(UO_2)_2O(WO_4)_4]$ (**3**).

2. Experimental

2.1. Synthesis

Crystals of the title compounds were synthesized by high-temperature solid-state reactions. For the synthesis of **1** and **2**, mixtures of $UO_2(CH_3COO)_2$, WO_3 , and A_2CO_3 ($A = Rb, Cs$) taken in molar ratio of 4:2:3 were heated in a platinum crucible to 920 °C and then cooled to 250 °C with a cooling rate of 7 °C/h. The products consisted of crystals of $A_8[(UO_2)_4(WO_4)_4(WO_5)_2]$ and $A_2[(UO_2)_2(WO_5)O]$. The latter phases have been described earlier [3,13]. Crystals of **3** were synthesized by high-temperature solid-state reactions. Mixture of $UO_2(CH_3COO)_2$, WO_3 , and Rb_2CO_3 taken in molar ratio of 6:2:4 were heated in a platinum crucible to 920 °C and subsequently cooled to 250 °C with a cooling rate of 7 °C/h. The products consisted of yellow transparent needles of **3**.

2.2. Crystal-structure analysis

The crystals selected for data collection were mounted on a Bruker three-circle diffractometer equipped with a SMART 1 K charge-coupled device (CCD) detector with a crystal-to-detector distance of 5 cm. Data were collected using monochromatic $MoK\alpha$ X-radiation and frame

widths of 0.3° in ω . The unit-cell dimensions for each compound (Table 1) were refined using least-squares techniques. More than a hemisphere of data was collected for each crystal and the 3D data were reduced and filtered for statistical outliers using the Bruker program SAINT. Data were corrected for Lorentz, polarization and background effects. A psi-scan semi-empirical absorption correction was done by modeling the crystals as ellipsoids. Additional information pertinent to the data collections is given in Table 1.

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the structure. First, the structures of **1** and **2** were solved in the orthorhombic space group $Pmn2_1$. However, the refinement converged to $R_1 \sim 0.08$, some of the U atoms had unreasonably large displacement parameters. In addition, there were some high peaks close to the positions of the heavy atoms in corresponding difference Fourier maps. In order to resolve the problems, several structure models were tested. The best refinements were achieved in monoclinic space group $P2_1/n$ with the β angle close to 90°. Introduction of a twin model with the $[-100/010/001]$ twinning matrix provided significant improvement of the refinement and reduced R_1 values from about 0.080–0.090 to 0.050 and 0.042 for **1** and **2**, respectively. The refined ratios of the twin components were 1:9 and 1:1 for **1** and **2**, respectively. Thus, the crystals studied are monoclinic pseudo-orthorhombic and pseudo-merohedrally twinned. The strong pseudosymmetry resulted in serious correlation problems during refinement, which did not allow to refine the O atoms anisotropically. The final models included

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

Compound	1	2	3
<i>a</i> (Å)	11.098(8)	11.252(2)	10.188(2)
<i>b</i> (Å)	13.161(9)	13.815(3)	13.110(2)
<i>c</i> (Å)	25.017(17)	25.736(6)	18.822(3)
α (deg)	90	90	97.853(3)
β (deg)	90.033(13)	89.998(2)	96.573(3)
γ (deg)	90	90	103.894(3)
<i>V</i> (Å ³)	3654(4)	4000(2)	2388.7(6)
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Ref. for cell refinement	877	966	947
<i>F</i> ₀₀₀	5520	6096	3480
μ (cm ⁻¹)	471.5	405.72	449.3
<i>Z</i>	8	8	4
<i>D</i> _{calc} (g/cm ³)	5.967	6.081	5.729
Crystal size (mm ³)	0.06 × 0.04 × 0.03	0.40 × 0.06 × 0.02	0.14 × 0.04 × 0.04
Radiation	$MoK\alpha$	$MoK\alpha$	$MoK\alpha$
<i>R</i> _{int}	0.066	0.0817	0.0628
Total ref.	21183	21090	13744
Unique ref.	8128	8683	10075
Unique ref. $ F_0 \geq 4\sigma_F$	5923	5204	4252
<i>R</i> ₁	0.050	0.0418	0.052
w <i>R</i> ₂	0.091	0.0843	0.0992
<i>S</i>	1.154	0.776	0.689

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
U(1)	0.60043(6)	0.18147(5)	0.15330(3)	0.0114(2)
U(2)	0.60029(6)	0.12479(5)	0.32743(3)	0.0101(2)
U(3)	0.16187(6)	0.17934(5)	0.15379(3)	0.0125(2)
U(4)	0.15808(6)	0.12722(5)	0.32929(3)	0.0116(2)
W(1)	0.38014(7)	0.23285(5)	0.24885(3)	0.0106(2)
W(2)	0.88085(7)	0.21082(6)	0.24687(3)	0.0118(2)
W(3)	0.87362(7)	0.06099(6)	0.42632(3)	0.0157(2)
W(4)	0.38192(7)	0.06519(6)	0.05345(3)	0.0178(2)
W(5)	0.87757(7)	0.08492(6)	0.06397(3)	0.0157(2)
W(6)	0.38107(7)	0.06945(6)	0.45085(3)	0.0168(2)
Rb(1)	0.6344(2)	−0.1393(2)	0.11304(8)	0.0292(5)
Rb(2)	0.1203(2)	0.2313(2)	−0.01465(8)	0.0251(5)
Rb(3)	0.1361(2)	0.2590(2)	0.48534(8)	0.0263(5)
Rb(4)	0.3787(2)	−0.0721(2)	0.22851(9)	0.0332(5)
Rb(5)	0.8865(2)	0.1291(2)	−0.11491(8)	0.0278(5)
Rb(6)	0.1289(2)	−0.1202(1)	0.42444(8)	0.0237(4)
Rb(7)	0.8909(2)	0.3561(1)	0.10979(8)	0.0241(5)
Rb(8)	0.8527(2)	−0.0711(2)	0.26029(8)	0.2603(7)
O(1)	0.547(1)	0.2015(9)	0.2460(5)	0.017(3)
O(2)	0.753(1)	0.160(1)	0.0884(5)	0.021(3)
O(3)	0.626(1)	0.2484(9)	0.3553(5)	0.023(3)
O(4)	0.608(1)	0.049(1)	0.1680(6)	0.029(4)
O(5)	0.508(1)	0.1424(9)	0.0728(5)	0.016(3)
O(6)	0.253(1)	0.140(1)	0.0731(6)	0.025(3)
O(7)	0.133(1)	0.2521(9)	0.3538(5)	0.021(3)
O(8)	0.381(1)	0.1681(9)	0.3145(5)	0.018(3)
O(9)	0.375(1)	−0.0510(9)	0.4810(5)	0.026(3)
O(10)	0.379(1)	0.1965(9)	0.1754(5)	0.015(3)
O(11)	0.213(1)	0.2050(9)	0.2459(5)	0.015(3)
O(12)	0.872(1)	−0.040(1)	0.0885(5)	0.029(3)
O(13)	0.744(1)	0.0475(9)	0.3832(5)	0.015(3)
O(14)	0.197(1)	0.005(1)	0.3086(5)	0.028(4)
O(15)	0.880(1)	−0.039(1)	0.4706(5)	0.027(3)
O(16)	0.168(1)	0.308(1)	0.1346(5)	0.021(3)
O(17)	0.011(1)	0.146(1)	0.0864(5)	0.020(3)
O(18)	0.168(1)	0.048(1)	0.1709(6)	0.029(4)
O(19)	0.763(1)	0.232(1)	0.1939(5)	0.023(3)
O(20)	0.247(1)	0.092(1)	0.4115(5)	0.023(3)
O(21)	0.388(1)	0.360(1)	0.2630(5)	0.025(3)
O(22)	0.381(1)	−0.049(1)	0.089(6)	0.036(4)
O(23)	0.508(1)	0.081(1)	0.4070(6)	0.034(4)
O(24)	0.009(1)	0.061(1)	0.3868(5)	0.018(3)
O(25)	0.586(1)	0.3121(9)	0.1360(5)	0.017(3)
O(26)	0.380(1)	0.0489(9)	−0.0146(5)	0.026(3)
O(27)	0.382(1)	0.1657(9)	0.4972(5)	0.023(3)
O(28)	0.878(1)	0.0892(9)	−0.0064(5)	0.024(3)
O(29)	0.764(1)	0.129(1)	0.2813(5)	0.023(3)
O(30)	0.865(1)	0.1755(9)	0.4622(5)	0.026(3)
O(31)	0.992(19)	0.128(1)	0.2822(5)	0.024(3)
O(32)	0.887(1)	0.327(1)	0.2790(6)	0.031(4)
O(33)	0.992(1)	0.220(1)	0.1923(6)	0.031(4)
O(34)	0.567(1)	0.002(1)	0.3021(5)	0.022(3)

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
U(1)	0.0096(4)	0.0148(4)	0.0097(4)	0.0000(3)	−0.0009(3)	0.0002(3)
U(2)	0.0080(3)	0.0129(4)	0.0094(4)	0.0006(3)	−0.0012(3)	−0.0001(3)
U(3)	0.0082(3)	0.0182(4)	0.0109(4)	0.0013(3)	−0.0005(3)	−0.0006(3)
U(4)	0.0094(3)	0.0150(4)	0.0102(4)	0.0010(3)	0.0001(3)	0.0007(3)
W(1)	0.0071(3)	0.0157(4)	0.0091(4)	0.0013(3)	−0.0011(3)	0.0010(3)
W(2)	0.0084(3)	0.0194(4)	0.0075(4)	0.0011(3)	−0.0010(3)	−0.0017(3)
W(3)	0.0120(4)	0.0195(4)	0.0155(4)	0.0038(3)	−0.0014(3)	−0.0001(3)
W(4)	0.0145(4)	0.0240(5)	0.0148(4)	0.0004(3)	−0.0029(4)	−0.0006(4)

Table 2 (continued)

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
W(5)	0.0118(4)	0.0208(4)	0.0146(4)	0.0002(3)	−0.0001(3)	0.0002(4)
W(6)	0.0141(4)	0.0227(4)	0.0134(4)	0.0018(3)	−0.0005(4)	0.0013(4)
Rb(1)	0.041(1)	0.029(1)	0.018(1)	0.0002(9)	0.002(1)	0.003(1)
Rb(2)	0.020(1)	0.032(1)	0.024(1)	0.0016(9)	−0.0027(9)	0.0002(9)
Rb(3)	0.024(1)	0.034(1)	0.021(1)	−0.0058(9)	0.0015(9)	0.006(1)
Rb(4)	0.020(1)	0.027(1)	0.053(2)	−0.015(1)	−0.002(1)	−0.001(1)
Rb(5)	0.034(1)	0.031(1)	0.019(1)	0.0038(9)	−0.003(1)	−0.004(1)
Rb(6)	0.020(1)	0.024(1)	0.027(1)	0.0014(9)	−0.0006(9)	0.0023(9)
Rb(7)	0.032(1)	0.018(1)	0.022(1)	−0.003(8)	−0.002(1)	0.0014(9)
Rb(8)	0.039(1)	0.020(1)	0.082(2)	0.008(1)	0.009(1)	0.005(1)

Table 3

Atomic coordinates and displacement parameters (\AA^2) for 2

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
U(1)	0.59879(9)	0.17408(7)	0.15876(4)	0.0163(3)
U(2)	0.6000(1)	0.13181(7)	0.32885(4)	0.0158(3)
U(3)	0.15452(9)	0.17374(7)	0.15973(4)	0.0162(3)
U(4)	0.15450(8)	0.1338(7)	0.33072(4)	0.0136(3)
W(1)	0.3768(2)	0.22540(6)	0.24993(4)	0.0127(2)
W(2)	0.8752(2)	0.21592(7)	0.24880(4)	0.0155(2)
W(3)	0.8733(2)	0.06966(7)	0.42690(4)	0.0170(2)
W(4)	0.3768(3)	0.06721(7)	0.05964(4)	0.0181(2)
W(5)	0.8743(3)	0.08529(6)	0.07080(4)	0.0166(2)
W(6)	0.3803(2)	0.07019(7)	0.44677(4)	0.0176(2)
Cs(1)	0.6277(5)	−0.1415(1)	0.11418(7)	0.0305(4)
Cs(2)	0.1204(4)	0.2283(1)	−0.01088(7)	0.0293(4)
Cs(3)	0.1299(4)	0.2614(1)	0.48931(7)	0.0296(4)
Cs(4)	0.3776(3)	−0.0714(1)	0.23534(7)	0.0360(5)
Cs(5)	0.8811(4)	0.1284(1)	−0.11209(7)	0.0270(4)
Cs(6)	0.1275(3)	−0.1186(1)	0.41803(7)	0.0295(4)
Cs(7)	0.8801(3)	0.3610(1)	0.10933(7)	0.0307(4)
Cs(8)	0.8693(4)	−0.0619(1)	0.2537(1)	0.067(1)
O(1)	0.543(1)	0.200(1)	0.2479(9)	0.020(4)
O(2)	0.747(1)	0.156(1)	0.0904(7)	0.009(5)
O(3)	0.626(3)	0.254(1)	0.3557(7)	0.036(5)
O(4)	0.601(2)	0.048(1)	0.1754(7)	0.024(5)
O(5)	0.505(2)	0.127(2)	0.086(1)	0.035(7)
O(6)	0.250(2)	0.141(1)	0.0821(8)	0.017(5)
O(7)	0.151(2)	0.253(1)	0.3569(6)	0.013(4)
O(8)	0.378(2)	0.1631(9)	0.3127(6)	0.023(4)
O(9)	0.381(3)	−0.048(1)	0.4760(7)	0.036(5)
O(10)	0.375(2)	0.1855(9)	0.1802(5)	0.018(3)
O(11)	0.213(1)	0.204(1)	0.2473(9)	0.022(4)
O(12)	0.877(3)	−0.036(1)	0.0932(7)	0.035(4)
O(13)	0.749(2)	0.074(2)	0.3851(8)	0.022(6)
O(14)	0.170(2)	0.011(2)	0.3052(9)	0.039(6)
O(15)	0.878(2)	−0.0365(9)	0.4640(5)	0.017(3)
O(16)	0.163(2)	0.300(1)	0.1409(8)	0.030(6)
O(17)	0.010(2)	0.136(2)	0.098(1)	0.044(8)
O(18)	0.150(2)	0.047(1)	0.1785(8)	0.032(6)
O(19)	0.764(2)	0.222(2)	0.1958(9)	0.049(7)
O(20)	0.252(2)	0.091(2)	0.4052(8)	0.018(5)
O(21)	0.381(2)	0.352(1)	0.2606(6)	0.021(4)
O(22)	0.384(3)	−0.048(1)	0.0883(7)	0.033(5)
O(23)	0.505(2)	0.078(2)	0.404(1)	0.039(7)
O(24)	0.008(2)	0.069(2)	0.388(1)	0.040(7)
O(25)	0.587(2)	0.300(1)	0.1405(8)	0.032(6)
O(26)	0.374(3)	0.067(1)	−0.0066(7)	0.035(4)
O(27)	0.377(2)	0.1617(9)	0.4956(6)	0.021(4)
O(28)	0.879(3)	0.094(1)	0.0036(7)	0.043(5)

Table 3 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>		
O(29)	0.767(2)	0.146(1)	0.2885(8)	0.030(5)		
O(30)	0.868(2)	0.174(1)	0.4665(6)	0.027(4)		
O(31)	0.990(2)	0.154(2)	0.292(1)	0.058(7)		
O(32)	0.871(3)	0.332(1)	0.2742(7)	0.046(5)		
O(33)	0.988(2)	0.213(2)	0.1969(8)	0.034(5)		
O(34)	0.577(2)	0.014(2)	0.3045(8)	0.031(6)		
Atom	<i>U₁₁</i>	<i>U₂₂</i>	<i>U₃₃</i>	<i>U₂₃</i>	<i>U₁₃</i>	<i>U₁₂</i>
U(1)	0.0178(9)	0.0165(5)	0.0148(6)	−0.0015(5)	−0.0003(5)	0.0006(4)
U(2)	0.0209(9)	0.0129(5)	0.0136(6)	0.0001(5)	−0.0006(5)	−0.0004(4)
U(3)	0.0184(9)	0.0179(5)	0.0124(6)	0.0000(5)	−0.0005(4)	−0.0009(4)
U(4)	0.0119(8)	0.0160(5)	0.0130(6)	0.0012(5)	−0.0001(4)	0.0006(4)
W(1)	0.0111(4)	0.0151(5)	0.0121(5)	0.0002(4)	−0.001(2)	0.001(1)
W(2)	0.0136(4)	0.0207(5)	0.0121(5)	0.0004(5)	−0.002(2)	−0.001(1)
W(3)	0.0128(5)	0.0181(5)	0.020(5)	0.0047(4)	−0.000(1)	−0.0002(7)
W(4)	0.0139(5)	0.0232(5)	0.0171(5)	0.0030(4)	0.0004(9)	−0.0014(9)
W(5)	0.0126(5)	0.0193(5)	0.0178(6)	0.0015(4)	0.001(1)	−0.0003(9)
W(6)	0.0141(6)	0.0210(5)	0.0177(5)	0.0030(4)	−0.0006(9)	−0.0002(7)
Cs(1)	0.039(1)	0.0294(9)	0.024(1)	−0.0021(8)	0.001(2)	0.004(2)
Cs(2)	0.023(1)	0.039(1)	0.026(1)	0.0045(8)	−0.001(2)	−0.002(2)
Cs(3)	0.027(1)	0.036(1)	0.026(1)	−0.0064(8)	−0.001(2)	0.002(2)
Cs(4)	0.0211(8)	0.029(1)	0.058(1)	−0.0084(9)	0.004(1)	−0.003(1)
Cs(5)	0.026(1)	0.029(9)	0.025(9)	0.0015(8)	−0.003(2)	0.002(2)
Cs(6)	0.0263(9)	0.0217(8)	0.040(1)	0.0039(8)	0.001(2)	0.001(1)
Cs(7)	0.040(1)	0.0170(8)	0.035(1)	−0.0057(7)	−0.002(2)	0.001(1)
Cs(8)	0.052(1)	0.025(1)	0.125(2)	0.003(1)	0.002(3)	0.006(2)

anisotropic displacement parameters for heavy atoms and weighting schemes of the structure factors. The final atomic positional and displacement parameters, and selected interatomic distances are given for **1** in Tables 2 and 4 for **2** in Tables 3 and 5, respectively. The structure of **3** was solved by direct methods and refined to $R_1 = 0.052$ on the basis of 4252 unique observed reflections (Table 2–5). The final models included anisotropic displacement parameters for heavy atoms and weighting schemes of the structure factors. The final atomic positional and displacement parameters, and selected interatomic distances are given in Tables 6 and 7, respectively. Tables of observed and calculated structure factors for each structure are available from the authors upon request.

3. Results

3.1. Cation coordination

The compounds **1** and **2** are isostructural and contain four symmetrically independent U^{6+} positions that form linear uranyl $[O = U = O]^{2+}$ cations, typical of structures of hexavalent uranium oxocompounds [17]. The uranyl cations are coordinated in their equatorial planes by five O_{eq} atoms each (O_{eq} = equatorial O atom), thus forming UO_7 pentagonal bipyramids. It is of interest that all the UO_7 polyhedra are rather distorted with one U–O bond length in the range of 2.12–2.19 Å, three U–O bond lengths

Table 4

Selected interatomic distances (Å) in the structure of **1**

U(1)–O(4)	1.78(1)	Rb(2)–O(6)	2.90(1)
U(1)–O(25)	1.78(1)	Rb(2)–O(27) <i>f</i>	2.99(1)
U(1)–O(19) <i>a</i>	2.17(1)	Rb(2)–O(9) <i>g</i>	2.99(1)
U(1)–O(5)	2.32(1)	Rb(2)–O(17)	3.02(1)
U(1)–O(2) <i>a</i>	2.36(1)	Rb(2)–O(30) <i>f</i>	3.04(1)
U(1)–O(1)	2.41(1)	Rb(2)–O(12) <i>h</i>	3.13(1)
U(1)–O(10)	2.53(1)	Rb(2)–O(3) <i>f</i>	3.27(1)
		Rb(2)–O(28)	3.28 (1)
		Rb(2)–O(23) <i>f</i>	3.39 (2)
U(2)–O(34)	1.78 (1)		
U(2)–O(3)	1.79(1)		
U(2)–O(29) <i>a</i>	2.15(1)	Rb(3)–O(5) <i>i</i>	2.92(1)
U(2)–O(23)	2.31(2)	Rb(3)–O(27)	3.01(1)
U(2)–O(13)	2.35(1)	Rb(3)–O(2) <i>j</i>	3.08(1)
U(2)–O(1)	2.35(1)	Rb(3)–O(15) <i>k</i>	3.11(1)
U(2)–O(8)	2.52(1)	Rb(3)–O(20)	3.13(1)
		Rb(3)–O(22) <i>g</i>	3.14(1)
U(3)–O(16)	1.76(1)	Rb(3)–O(30) <i>b</i>	3.25 (1)
U(3)–O(18)	1.78(1)	Rb(3)–O(7)	3.29 (1)
U(3)–O(33)	2.18(1)	Rb(3)–O(28) <i>j</i>	3.35 (1)
U(3)–O(6)	2.32(1)		
U(3)–O(11)	2.40(1)	Rb(4)–O(32) <i>d</i>	2.93(1)
U(3)–O(17)	2.42(1)	Rb(4)–O(34)	2.95(1)
U(3)–O(10)	2.48(1)	Rb(4)–O(14)	3.02(1)
		Rb(4)–O(21) <i>d</i>	3.10(1)
U(4)–O(14)	1.75(1)	Rb(4)–O(7) <i>d</i>	3.10(1)
U(4)–O(7)	1.78(1)	Rb(4)–O(11) <i>d</i>	3.17(1)
U(4)–O(31)	2.19(1)	Rb(4)–O(18)	3.17(1)
U(4)–O(20)	2.33(1)	Rb(4)–O(4)	3.37(1)
U(4)–O(24) <i>b</i>	2.36(1)	Rb(4)–O(22)	3.51(2)
U(4)–O(11)	2.40(1)		
U(4)–O(8)	2.56(1)	Rb(5)–O(28)	2.77(1)
		Rb(5)–O(18) <i>h</i>	2.79(1)
W(1)–O(21)	1.72(1)	Rb(5)–O(12) <i>h</i>	3.01(1)
W(1)–O(8)	1.85(1)	Rb(5)–O(21) <i>f</i>	3.06(1)
W(1)–O(11)	1.89(1)	Rb(5)–O(3) <i>f</i>	3.20(1)
W(1)–O(1)	1.90(1)	Rb(5)–O(8) <i>f</i>	3.20(1)
W(1)–O(10)	1.90(1)	Rb(5)–O(22) <i>h</i>	3.22(2)
		Rb(5)–O(7) <i>f</i>	3.31(1)
W(2)–O(32)	1.73 (1)		
W(2)–O(33)	1.85(1)	Rb(6)–O(16) <i>d</i>	2.85(1)
W(2)–O(31)	1.87(1)	Rb(6)–O(24) <i>b</i>	2.89(1)
W(2)–O(19)	1.88(1)	Rb(6)–O(30) <i>k</i>	2.93(1)
W(2)–O(29)	1.90(1)	Rb(6)–O(25) <i>d</i>	2.96(1)
		Rb(6)–O(20)	3.10(1)
W(3)–O(15)	1.72(1)	Rb(6)–O(15) <i>b</i>	3.18(1)
W(3)–O(30)	1.76(1)	Rb(6)–O(9)	3.21(1)
W(3)–O(24)	1.80(1)	Rb(6)–O(15) <i>k</i>	3.36(1)
W(3)–O(13)	1.81(1)	Rb(6)–O(14)	3.41(1)
		Rb(6)–O(6) <i>d</i>	3.43(1)
W(4)–O(26)	1.72(1)	Rb(6)–O(10) <i>d</i>	3.47(1)
W(4)–O(22)	1.74(1)	Rb(6)–O(5) <i>d</i>	3.48(1)
W(4)–O(5)	1.79(1)		
W(4)–O(6)	1.81(1)	Rb(7)–O(27) <i>f</i>	2.83(1)
		Rb(7)–O(13) <i>g</i>	2.93(1)
W(5)–O(12)	1.76(1)	Rb(7)–O(34) <i>g</i>	2.96(1)
W(5)–O(28)	1.76(1)	Rb(7)–O(33)	2.96(1)
W(5)–O(17)	1.78(1)	Rb(7)–O(19)	3.02(1)
W(5)–O(2)	1.81(1)	Rb(7)–O(2)	3.06(1)
		Rb(7)–O(17)	3.12(1)
W(6)–O(27)	1.72(1)	Rb(7)–O(23) <i>g</i>	3.19(2)
W(6)–O(9)	1.76(1)	Rb(7)–O(16)	3.21(1)
W(6)–O(23)	1.80(2)	Rb(7)–O(25) <i>b</i>	3.49(1)
W(6)–O(20)	1.81(1)		
Rb(1)–O(26) <i>c</i>	2.74(1)	Rb(8)–O(29)	2.87(1)
		Rb(8)–O(21) <i>d</i>	3.07(1)

Table 4 (continued)

Rb(1)–O(32) <i>d</i>	2.75(1)	Rb(8)–O(31)	3.09(1)
Rb(1)–O(4)	2.85(1)	Rb(8)–O(25) <i>d</i>	3.09(1)
Rb(1)–O(12) <i>a</i>	3.00(2)	Rb(8)–O(19) <i>l</i>	3.11(1)
Rb(1)–O(30) <i>e</i>	3.08(1)	Rb(8)–O(32) <i>l</i>	3.13(1)
Rb(1)–O(22)	3.11(2)	Rb(8)–O(1) <i>d</i>	3.20(1)
Rb(1)–O(3) <i>e</i>	3.14(1)	Rb(8)–O(34) <i>b</i>	3.48(1)
Rb(1)–O(7) <i>d</i>	3.39(1)		

Note: $a = x + 1, y, z$; $b = x - 1, y, z$; $c = -x + 3, -y, -z$; $d = -x + 5/2, y - 1/2, -z + 1/2$; $e = -x + 7/2, y - 1/2, -z + 1/2$; $f = x - 1/2, -y + 1/2, z - 1/2$; $g = -x + 5/2, y + 1/2, -z + 1/2$; $h = -x + 2, -y, -z$; $i = x - 1/2, -y + 1/2, z + 1/2$; $j = x + 1/2, -y + 1/2, z + 1/2$; $k = -x + 3, -y, -z + 1$; $l = -x + 3/2, y - 1/2, -z + 1/2$.

Table 5

Selected interatomic distances (Å) in crystal structure of **2**

U(1)–O(4)	1.79(2)	Cs(3)–O(27)	3.11(2)
U(1)–O(25)	1.80(2)	Cs(3)–O(2) <i>i</i>	3.13(2)
U(1)–O(19) <i>a</i>	2.19(2)	Cs(3)–O(5) <i>j</i>	3.24(2)
U(1)–O(5)	2.26(2)	Cs(3)–O(30) <i>b</i>	3.24(2)
U(1)–O(1)	2.41(2)	Cs(3)–O(22) <i>g</i>	3.31(1)
U(1)–O(2) <i>a</i>	2.44(2)	Cs(3)–O(15) <i>i</i>	3.33(1)
U(1)–O(10)	2.59(2)	Cs(3)–O(7)	3.42(2)
		Cs(3)–O(28) <i>i</i>	3.46(3)
U(2)–O(34)	1.76(2)	Cs(3)–O(20)	3.48(2)
U(2)–O(3)	1.84(2)	Cs(3)–O(26) <i>j</i>	3.74(2)
U(2)–O(29) <i>a</i>	2.15(2)		
U(2)–O(23)	2.33(2)	Cs(4)–O(21) <i>d</i>	3.10(2)
U(2)–O(1)	2.37(2)	Cs(4)–O(34)	3.10(2)
U(2)–O(13)	2.37(2)	Cs(4)–O(32) <i>d</i>	3.13(3)
U(2)–O(8)	2.57(2)	Cs(4)–O(14)	3.16(2)
		Cs(4)–O(11) <i>d</i>	3.30(2)
U(3)–O(18)	1.81(2)	Cs(4)–O(18)	3.37(2)
U(3)–O(16)	1.81(2)	Cs(4)–O(7) <i>d</i>	3.41(2)
U(3)–O(33)	2.17(2)	Cs(4)–O(4)	3.38(2)
U(3)–O(17)	2.33(2)	Cs(4)–O(16) <i>d</i>	3.68(2)
U(3)–O(6)	2.31(2)	Cs(4)–O(33) <i>d</i>	3.77(2)
U(3)–O(11)	2.38(2)	Cs(4)–O(8)	3.80(1)
U(3)–O(10)	2.54(2)	Cs(4)–O(22)	3.80(2)
U(4)–O(7)	1.78(1)	Cs(5)–O(28)	3.02(2)
U(4)–O(14)	1.83(2)	Cs(5)–O(18) <i>h</i>	2.99(2)
U(4)–O(31)	2.12(2)	Cs(5)–O(12) <i>h</i>	3.04(4)
U(4)–O(20)	2.29(2)	Cs(5)–O(7) <i>f</i>	3.17(2)
U(4)–O(24) <i>b</i>	2.38(2)	Cs(5)–O(22) <i>h</i>	3.25(3)
U(4)–O(11)	2.44(2)	Cs(5)–O(21) <i>f</i>	3.29(1)
U(4)–O(8)	2.59(2)	Cs(5)–O(3) <i>f</i>	3.30(3)
		Cs(5)–O(8) <i>f</i>	3.47(1)
W(1)–O(21)	1.77 (1)		
W(1)–O(8)	1.83(1)	Cs(6)–O(24) <i>b</i>	3.03(2)
W(1)–O(11)	1.87(2)	Cs(6)–O(16) <i>d</i>	3.02(2)
W(1)–O(10)	1.88(1)	Cs(6)–O(30) <i>k</i>	3.07(2)
W(1)–O(1)	1.90 (2)	Cs(6)–O(25) <i>d</i>	3.06(2)
		Cs(6)–O(20)	3.23(2)
W(2)–O(32)	1.74(2)	Cs(6)–O(15) <i>b</i>	3.25(2)
W(2)–O(29)	1.86(2)	Cs(6)–O(9)	3.36(3)
W(2)–O(19)	1.85(2)	Cs(6)–O(14)	3.45(2)
W(2)–O(33)	1.84(2)	Cs(6)–O(6) <i>d</i>	3.59(2)
W(2)–O(31)	1.90(2)	Cs(6)–O(10) <i>d</i>	3.70(1)
	1.75(1)		
W(3)–O(30)	1.76(1)	Cs(7)–O(27) <i>f</i>	2.94(1)
W(3)–O(13)	1.76(2)	Cs(7)–O(34) <i>g</i>	3.10(2)
W(3)–O(24)	1.82(2)	Cs(7)–O(19)	3.22(2)

Table 5 (continued)

W(4)–O(26)	1.71(2)	Cs(7)–O(2)	3.25(2)
W(4)–O(5)	1.79(2)	Cs(7)–O(13) <i>g</i>	3.26(2)
W(4)–O(22)	1.76(2)	Cs(7)–O(33)	3.28(2)
W(4)–O(6)	1.85(2)	Cs(7)–O(23) <i>g</i>	3.28(2)
		Cs(7)–O(16)	3.39(2)
W(5)–O(12)	1.78(2)	Cs(7)–O(17)	3.45(2)
W(5)–O(28)	1.73(2)	Cs(7)–O(25) <i>b</i>	3.50(2)
W(5)–O(2)	1.80(2)	Cs(7)–O(15) <i>g</i>	3.74(2)
W(5)–O(17)	1.82(2)	Cs(7)–O(9) <i>g</i>	3.70(3)
W(6)–O(23)	1.78(2)	Cs(8)–O(21) <i>d</i>	3.07(2)
W(6)–O(27)	1.78(1)	Cs(8)–O(32) <i>l</i>	3.16(3)
W(6)–O(9)	1.80(2)	Cs(8)–O(29)	3.23(2)
W(6)–O(20)	1.82(2)	Cs(8)–O(25) <i>d</i>	3.37(2)
		Cs(8)–O(1) <i>d</i>	3.44(2)
		Cs(8)–O(31)	3.43(2)
Cs(1)–O(26) <i>c</i>	2.96(2)	Cs(8)–O(19) <i>l</i>	3.58(2)
Cs(1)–O(32) <i>d</i>	2.90(2)	Cs(8)–O(34) <i>b</i>	3.69(2)
Cs(1)–O(4)	3.08(2)	Cs(8)–O(14)	3.77 (2)
Cs(1)–O(22)	3.10(3)	Cs(8)–O(3) <i>d</i>	3.80(2)
Cs(1)–O(12) <i>a</i>	3.20(4)		
Cs(1)–O(3) <i>e</i>	3.22(3)		
Cs(1)–O(30) <i>e</i>	3.29(2)		
Cs(1)–O(7) <i>d</i>	3.53(2)		
Cs(2)–O(6)	3.05(2)		
Cs(2)–O(30) <i>f</i>	3.15(2)		
Cs(2)–O(27) <i>f</i>	3.13(2)		
Cs(2)–O(9) <i>g</i>	3.22(2)		
Cs(2)–O(17)	3.32(2)		
Cs(2)–O(28)	3.32(3)		
Cs(2)–O(12) <i>h</i>	3.39(2)		
Cs(2)–O(3) <i>f</i>	3.44(2)		
Cs(2)–O(26)	3.62(3)		
Cs(2)–O(23) <i>f</i>	3.69(2)		

Note: $a = x + 1, y, z$; $b = x - 1, y, z$; $c = -x + 3, -y, -z$; $d = -x + 5/2, y - 1/2, -z + 1/2$; $e = -x + 7/2, y - 1/2, -z + 1/2$; $f = x - 1/2, -y + 1/2, z - 1/2$; $g = -x + 5/2, y + 1/2, -z + 1/2$; $h = -x + 2, -y, -z$; $i = x + 1/2, -y + 1/2, z + 1/2$; $j = x - 1/2, -y + 1/2, z + 1/2$; $k = -x + 3, -y, -z + 1$; $l = -x + 3/2, y - 1/2, -z + 1/2$.

in the range of 2.31–2.44 Å, and one U–O bond length in the range of 2.48–2.59 Å. There are six W positions in each structure. The W(1) and W(2) atoms have square pyramidal WO₅ coordination with a short bond to an apical O atom (1.72–1.77 Å) and four longer bonds to equatorial O atoms (1.83–1.90 Å). The W(3), W(4), W(5), and W(6) atoms are tetrahedrally coordinated (W–O = 1.71–1.85 Å). The structures possess eight alkali metal *A* sites each, coordinated by O atoms with coordination numbers varying from 8 to 10. Average *A*⁺–O bond lengths are given in Tables 4 and 5.

There are four symmetrically independent U positions in the structure of **3**. They have a typical coordination of a pentagonal bipyramid that contain uranyl ions, UO₂²⁺, as apical axes. In the equatorial plane, the uranyl ions are coordinated by five O atoms each. The structure of **3** contains also eight W sites. The W(1), W(2), W(3), W(4), W(5), and W(6) atoms are tetrahedrally coordinated (WO₄). The W–O bond lengths within the tungstate tetrahedra are

Table 6
Atomic coordinates and displacement parameters (\AA^2) for **3**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
U(1)	0.4422(1)	0.72153(9)	0.09089(6)	0.0156(3)
U(2)	0.2232(1)	0.72419(9)	0.29751(6)	0.0154(3)
U(3)	0.7418(1)	0.73150(9)	−0.20727(6)	0.0160(3)
U(4)	0.9426(1)	0.73278(9)	−0.39836(6)	0.0154(3)
W(1)	0.7226(1)	0.1313(1)	0.48831(6)	0.0153(3)
W(2)	0.3895(1)	0.6210(1)	−0.12571(6)	0.0180(3)
W(3)	−0.1330(1)	0.6222(1)	0.38336(6)	0.0173(3)
W(4)	0.5520(1)	0.5966(1)	−0.40581(6)	0.0190(3)
W(5)	0.5661(1)	0.9024(1)	0.27317(6)	0.0173(3)
W(6)	0.7756(1)	0.8633(1)	0.00773(6)	0.0166(3)
W(7)	0.1093(1)	0.6237(1)	0.11590(6)	0.0175(3)
W(8)	0.0544(1)	0.9037(1)	−0.22981(6)	0.0192(3)
Rb(1)	0.2990(3)	0.0644(3)	0.3486(2)	0.0269(8)
Rb(2)	0.1958(3)	0.9374(3)	0.1447(2)	0.0267(8)
Rb(3)	0.7336(4)	0.5719(2)	−0.0047(2)	0.0353(9)
Rb(4)	−0.0448(3)	0.9315(3)	0.4004(2)	0.0334(9)
Rb(5)	0.3534(3)	0.7649(3)	−0.3068(2)	0.0314(9)
Rb(6)	−0.0469(3)	0.4340(3)	0.2333(2)	0.0270(8)
Rb(7)	0.5236(3)	0.5748(2)	0.2641(2)	0.0267(8)
Rb(8)	0.1989(4)	0.5728(3)	0.4722(2)	0.0351(9)
Rb(9)	0.5934(3)	0.7894(3)	0.4563(2)	0.0315(8)
Rb(10)	0.5598(3)	0.0623(3)	0.1009(2)	0.0319(9)
Rb(11)	0.8549(3)	0.7690(3)	0.1942(2)	0.0329(9)
Rb(12)	0.0911(4)	0.7666(3)	−0.0471 (2)	0.043(1)
O(1)	0.664(2)	0.845(1)	−0.2131(9)	0.017(5)
O(2)	0.786(2)	0.018(2)	0.509(1)	0.025(5)
O(3)	0.173(2)	0.844(2)	0.2844(9)	0.021(5)
O(4)	0.707(2)	0.971(2)	−0.013(1)	0.029(5)
O(5)	0.898 (2)	0.847(2)	−0.4335(9)	0.020(5)
O(6)	0.403(2)	0.843(2)	0.067(1)	0.025(5)
O(7)	0.274(2)	0.607(2)	0.312(1)	0.030(5)
O(8)	0.228 (2)	0.636(1)	0.0453(9)	0.017(4)
O(9)	0.979(2)	0.616(2)	−0.3736(9)	0.026(5)
O(10)	0.842(2)	0.217(1)	0.4447(9)	0.018(5)
O(11)	0.111(2)	0.831(2)	−0.3014(9)	0.023(5)
O(12)	0.579(2)	0.638(2)	−0.3098(9)	0.020(5)
O(13)	0.059 (2)	0.639(2)	0.2093(9)	0.018(4)
O(14)	0.714(2)	0.209(2)	0.5716(9)	0.022(5)
O(15)	0.590(2)	0.816(2)	0.200 (1)	0.028(5)
O(16)	0.556(2)	0.092(2)	0.436(1)	0.032(5)
O(17)	−0.227(2)	0.495(2)	0.341(1)	0.024(5)
O(18)	0.986(2)	0.005(2)	−0.256 (1)	0.037(6)
O(19)	0.718(2)	0.954(2)	0.330(1)	0.034(6)
O(20)	0.449(2)	0.822(2)	0.319 (1)	0.038(6)
O(21)	0.852(2)	0.773(1)	−0.3004(9)	0.025(5)
O(22)	0.956(2)	0.838(17)	−0.165(1)	0.038(6)
O(23)	0.027(2)	0.652 (1)	0.3508(9)	0.023(5)
O(24)	−0.228(2)	0.712(1)	0.3610(9)	0.022(5)
O(25)	0.297(2)	0.712(2)	−0.147(1)	0.027(5)
O(26)	−0.091(2)	0.631(2)	0.479(1)	0.029(5)
O(27)	0.943(2)	0.908(2)	0.054(1)	0.031(5)
O(28)	0.283(2)	0.495(2)	−0.156(1)	0.031(6)
O(29)	0.535(2)	0.635(1)	−0.1700(9)	0.021(5)
O(30)	0.445(2)	0.643(2)	−0.0315(9)	0.024(5)
O(31)	0.287 (2)	0.710 (1)	0.1779(9)	0.023(4)
O(32)	−0.010(2)	0.689 (2)	0.075(1)	0.032(5)
O(33)	0.476(2)	0.457 (2)	−0.428(1)	0.032(5)
O(34)	0.714(2)	0.637 (2)	−0.434 (1)	0.033(5)
O(35)	0.479(2)	0.604(2)	0.112(1)	0.031(5)
O(36)	0.210(2)	0.972(2)	−0.177(1)	0.043(6)
O(37)	0.668(2)	0.784(2)	0.060(1)	0.026(5)
O(38)	0.036(2)	0.483(2)	0.094(1)	0.031(5)
O(39)	0.441(2)	0.668(2)	−0.438(1)	0.044(6)

Table 6 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}		
O(40)	0.802(2)	0.615(2)	−0.200(1)	0.034(5)		
O(41)	0.774(2)	0.781(2)	−0.075(1)	0.029(5)		
O(42)	0.492(2)	0.001(2)	0.244(1)	0.043(6)		
Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
U(1)	0.0169(6)	0.0148(6)	0.0152(6)	0.0033(5)	0.0001(5)	0.0053(5)
U(2)	0.0163(6)	0.0152(6)	0.0156(6)	0.0031(5)	0.0008(5)	0.0062(5)
U(3)	0.0168(6)	0.0171(7)	0.0153(6)	0.0033(5)	0.0019(5)	0.0070(5)
U(4)	0.0182(6)	0.0143(6)	0.0147(6)	0.0036(5)	0.0010(5)	0.0061(5)
W(1)	0.0171(7)	0.0167(7)	0.0133(6)	0.0047(5)	0.0007(6)	0.0064(6)
W(2)	0.0191(7)	0.0179(7)	0.0150(6)	0.0010(5)	0.0009(5)	0.0029(6)
W(3)	0.0170(7)	0.0174(7)	0.0164(6)	0.0028(5)	0.0010(5)	0.0030(6)
W(4)	0.0193(7)	0.0170(7)	0.0199(6)	0.0020(5)	0.0032(5)	0.0038(5)
W(5)	0.0167(7)	0.0209(8)	0.0155(6)	0.0032(6)	0.0016(6)	0.0073(6)
W(6)	0.0214(7)	0.0174(7)	0.0156(6)	0.0043(5)	0.0040(5)	0.0075(5)
W(7)	0.0214(7)	0.0174(7)	0.0156(6)	0.0043(5)	0.0040(5)	0.0075(5)
W(8)	0.0205(7)	0.0226(8)	0.0169(6)	0.0039(6)	0.0040(6)	0.0093(6)
Rb(1)	0.025(2)	0.028(2)	0.026(2)	0.005(1)	−0.004(2)	0.009(2)
Rb(2)	0.029(2)	0.026(2)	0.025(2)	0.005(1)	0.001(2)	0.008(2)
Rb(3)	0.039(2)	0.018(2)	0.046(2)	0.000(2)	0.004(2)	0.005(2)
Rb(4)	0.026(2)	0.025(2)	0.044(2)	0.006(2)	−0.009(2)	0.002(2)
Rb(5)	0.027(2)	0.040(2)	0.029(2)	0.005(2)	0.004(2)	0.015(2)
Rb(6)	0.026(2)	0.031(2)	0.024(2)	0.005(1)	0.001(1)	0.010(1)
Rb(7)	0.035(2)	0.023(2)	0.024(2)	0.004(1)	0.006(2)	0.011(2)
Rb(8)	0.040(2)	0.017(2)	0.045(2)	0.004(2)	−0.004(2)	0.007(2)
Rb(9)	0.028(2)	0.042(2)	0.026(2)	0.004(2)	0.005(2)	0.012(2)
Rb(10)	0.028 (2)	0.021(2)	0.041(2)	0.004(2)	−0.009(2)	0.003(2)
Rb(11)	0.024(2)	0.048(2)	0.029(2)	0.004(2)	−0.002(2)	0.017(2)
Rb(12)	0.044(2)	0.070(3)	0.028(2)	0.021(2)	0.008(2)	0.033(2)

in the range of 1.71–1.82 Å. The coordinational configurations of W(7) and W(8) deserve special attention (Fig. 1a, b). The W(7) site is coordinated by four O atoms at 1.78–1.90 Å and one additional O(31) atom at 2.03 Å. From a geometrical point of view, the W(7)O₅ polyhedron can be described as a trigonal bipyramid with one of the equatorial W(7)–O bonds elongated in comparison to the other two (Fig. 1a). The W(8) site has fivefold coordination as well. It forms four shorter W(8)–O bonds (1.74–1.83 Å) and one long W(8)–O(21) bond of 2.45 Å. The W(8)O₅ polyhedron can again be described as a trigonal bipyramid but with one apical W(8)–O being strongly elongated (Fig. 1a). There are twelve symmetrically independent Rb⁺ cations in the structure of **3**. The Rb atoms are coordinated by eight to ten O atoms.

3.2. Bond-valence analysis

Bond-valence sums incident upon atom sites have been calculated using bond-valence parameters provided by Burns et al. [17] for the U⁶⁺–O bonds and by Brese and O’Keeffe [18] for other bonds. The bond-valence sums for the U sites are in the range of 5.87–6.23 v.u. (valence units), whereas variations of the W bond-valence sums are larger and are from 5.63 to 6.41 v.u. The bond-valence sums for

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

U(1)–O(35)	1.76(2)	Rb(3)–O(32) <i>f</i>	2.82(2)
U(1)–O(6)	1.84(2)	Rb(3)–O(8) <i>g</i>	2.86(2)
U(1)–O(8)	2.21(2)	Rb(3)–O(35) <i>g</i>	3.06(2)
U(1)–O(31)	2.40(2)	Rb(3)–O(37)	3.13(2)
U(1)–O(30)	2.40(2)	Rb(3)–O(41)	3.16(2)
U(1)–O(15)	2.40(2)	Rb(3)–O(30) <i>g</i>	3.17(2)
U(1)–O(37)	2.41(2)	Rb(3)–O(38) <i>g</i>	3.20(2)
		Rb(3)–O(28) <i>g</i>	3.27(2)
U(2)–O(7)	1.78(2)	Rb(3)–O(30)	3.30(2)
U(2)–O(3)	1.80(2)		
U(2)–O(13)	2.18(2)	Rb(4)–O(19) <i>e</i>	2.72(2)
U(2)–O(20)	2.31(2)	Rb(4)–O(2) <i>a</i>	2.85(2)
U(2)–O(23)	2.39(2)	Rb(4)–O(5) <i>d</i>	2.87(2)
U(2)–O(31)	2.41(2)	Rb(4)–O(24)	2.98(2)
U(2)–O(14) <i>a</i>	2.45(2)	Rb(4)–O(18) <i>d</i>	3.03(2)
		Rb(4)–O(2) <i>e</i>	3.09(2)
U(3)–O(40)	1.79(2)	Rb(4)–O(5) <i>h</i>	3.52(2)
U(3)–O(1)	1.85(2)	Rb(4)–O(3)	3.56(2)
U(3)–O(21)	2.25(2)		
U(3)–O(22)	2.28(2)	Rb(5)–O(11) <i>e</i>	2.81(2)
U(3)–O(12)	2.37(2)	Rb(5)–O(39)	2.96(2)
U(3)–O(29)	2.42(2)	Rb(5)–O(42) <i>d</i>	3.09(2)
U(3)–O(41)	2.45(2)	Rb(5)–O(12)	3.15(2)
		Rb(5)–O(10) <i>d</i>	3.15(5)
U(4)–O(9)	1.77(2)	Rb(5)–O(25)	3.26(2)
U(4)–O(5)	1.85(2)	Rb(5)–O(17) <i>i</i>	3.29(2)
U(4)–O(21)	2.21(2)	Rb(5)–O(1)	3.30(2)
U(4)–O(34)	2.34(2)	Rb(5)–O(16) <i>d</i>	3.35(2)
U(4)–O(11)	2.35(2)		
U(4)–O(10) <i>b</i>	2.43(2)	Rb(6)–O(13)	2.76(2)
U(4)–O(26) <i>c</i>	2.45(2)	Rb(6)–O(40) <i>g</i>	2.84(2)
		Rb(6)–O(9) <i>g</i>	2.85(2)
W(1)–O(14)	1.77(2)	Rb(6)–O(25) <i>i</i>	2.94(2)
W(1)–O(16)	1.78(2)	Rb(6)–O(38)	2.95(2)
W(1)–O(10)	1.80(2)	Rb(6)–O(17)	3.04(2)
W(1)–O(2)	1.82(2)	Rb(6)–O(28) <i>i</i>	3.08(2)
		Rb(6)–O(23)	3.24(2)
W(2)–O(28)	1.72(2)	Rb(6)–O(7)	3.53(2)
W(2)–O(25)	1.74(2)		
W(2)–O(30)	1.76(2)	Rb(7)–O(7)	2.90(2)
W(2)–O(29)	1.77(2)	Rb(7)–O(35)	2.94(2)
		Rb(7)–O(29) <i>g</i>	2.95(2)
W(3)–O(17)	1.74(2)	Rb(7)–O(24) <i>f</i>	2.97(2)
W(3)–O(24)	1.75(2)	Rb(7)–O(12) <i>g</i>	3.01(2)
W(3)–O(26)	1.78(2)	Rb(7)–O(33) <i>g</i>	3.17(1)
W(3)–O(23)	1.78(2)	Rb(7)–O(28) <i>g</i>	3.18(2)
		Rb(7)–O(17) <i>f</i>	3.24(2)
W(4)–O(39)	1.74(2)	Rb(7)–O(15)	3.48(2)
W(4)–O(34)	1.77(2)	Rb(7)–O(20)	3.54(2)
W(4)–O(33)	1.78(2)	Rb(7)–O(40) <i>g</i>	3.60(2)
W(4)–O(12)	1.78(2)		
		Rb(8)–O(39) <i>j</i>	2.73(2)
W(5)–O(19)	1.71(2)	Rb(8)–O(9) <i>g</i>	2.94(2)
W(5)–O(15)	1.74(2)	Rb(8)–O(26) <i>k</i>	2.95(2)
W(5)–O(42)	1.76(2)	Rb(8)–O(14) <i>a</i>	3.04(2)
W(5)–O(20)	1.78(2)	Rb(8)–O(34) <i>g</i>	3.11(2)
		Rb(8)–O(10) <i>a</i>	3.11(2)
W(6)–O(27)	1.75(2)	Rb(8)–O(23)	3.16(2)
W(6)–O(41)	1.77(2)	Rb(8)–O(26)	3.24(2)
W(6)–O(4)	1.79(2)	Rb(8)–O(7)	3.25(2)
W(6)–O(37)	1.80(2)	Rb(8)–O(33) <i>g</i>	3.60(2)
W(7)–O(38)	1.79(2)	Rb(9)–O(24) <i>f</i>	2.95(2)
W(7)–O(32)	1.81(2)	Rb(9)–O(20)	2.96(2)
W(7)–O(13)	1.88(2)	Rb(9)–O(39) <i>j</i>	3.04(2)

Table 7 (continued)

W(7)–O(8)	1.90(2)	Rb(9)–O(33) <i>g</i>	3.09(2)
W(7)–O(31)	2.03(2)	Rb(9)–O(14) <i>a</i>	3.12(2)
		Rb(9)–O(2)	3.12(2)
W(8)–O(36)	1.74(2)	Rb(9)–O(16) <i>a</i>	3.13(2)
W(8)–O(18)	1.75(2)	Rb(9)–O(34) <i>j</i>	3.38(2)
W(8)–O(11)	1.78(2)	Rb(9)–O(5) <i>j</i>	3.39(2)
W(8)–O(22)	1.83(2)	Rb(9)–O(19)	3.57(2)
W(8)–O(21)	2.45(2)		
		Rb(10)–O(36) <i>b</i>	2.77(2)
Rb(1)–O(16)	2.84(2)	Rb(10)–O(6)	2.88(2)
Rb(1)–O(3)	2.89(2)	Rb(10)–O(4) <i>d</i>	2.92(2)
Rb(1)–O(1) <i>d</i>	2.98(2)	Rb(10)–O(25) <i>d</i>	2.93(2)
Rb(1)–O(5) <i>d</i>	3.05(2)	Rb(10)–O(42)	3.02(2)
Rb(1)–O(18) <i>d</i>	3.07(2)	Rb(10)–O(4)	3.03(2)
Rb(1)–O(21) <i>d</i>	3.09(2)	Rb(10)–O(6) <i>d</i>	3.57(7)
Rb(1)–O(42)	3.11(2)	Rb(10)–O(1) <i>d</i>	3.59(4)
Rb(1)–O(2) <i>a</i>	3.16(2)		
		Rb(11)–O(15)	2.92(2)
Rb(2)–O(27) <i>e</i>	2.83(2)	Rb(11)–O(32) <i>f</i>	2.97(2)
Rb(2)–O(1) <i>d</i>	2.91(2)	Rb(11)–O(13) <i>f</i>	3.01(2)
Rb(2)–O(4) <i>d</i>	3.06(2)	Rb(11)–O(18) <i>b</i>	3.01(2)
Rb(2)–O(3)	3.06(2)	Rb(11)–O(37)	3.04(2)
Rb(2)–O(18) <i>d</i>	3.08(2)	Rb(11)–O(3) <i>f</i>	3.33(2)
Rb(2)–O(6)	3.10(2)	Rb(11)–O(28) <i>g</i>	3.35(2)
Rb(2)–O(42)	3.23(2)	Rb(11)–O(24) <i>f</i>	3.48(2)
Rb(2)–O(32)	3.41(2)	Rb(11)–O(27)	3.49(2)
Rb(2)–O(31)	3.44(2)		
Rb(2)–O(22) <i>d</i>	3.63(2)	Rb(12)–O(32)	2.83(2)
		Rb(12)–O(22) <i>e</i>	2.87(2)
		Rb(12)–O(8)	3.05(2)
		Rb(12)–O(25)	3.12(2)
		Rb(12)–O(38) <i>i</i>	3.18(2)
		Rb(12)–O(27) <i>e</i>	3.22(2)
		Rb(12)–O(41) <i>e</i>	3.27(2)
		Rb(12)–O(6)	3.46(2)
		Rb(12)–O(4) <i>d</i>	3.51(2)

Note: $a = -x + 1, -y + 2, -z + 1, b = -x + 2, -y + 2, -z, c = x + 1, y, z - 1, d = -x + 1, -y + 2, -z, e = x - 1, y, z, f = x + 1, y, z, g = -x + 1, -y + 1, -z, h = x - 1, y, z + 1, i = -x, -y + 1, -z, j = x, y, z + 1, k = -x, -y + 1, -z + 1.$

the alkali metal sites and all except one of the O atoms are in the range of 0.75–1.23 and 1.75–2.21 v.u., respectively. One of the terminal O atoms of the WO₄ tetrahedra in the structure of **2** has rather low bond-valence sum of 1.58 v.u., which we ascribe to the errors in bond lengths due to the effects of twinning and pseudosymmetry that cause serious correlation problems.

3.3. Structure descriptions

The structures of **1** and **2** are based upon 1D chains of U and W coordination polyhedra shown in Fig. 2. The chains can be considered as consisting of the WU₄O₂₅ pentamers formed by a central W(1)O₅ square pyramid surrounded by four UO₇ pentagonal bipyramids. On the sides, the pentamers are incrustated by the W(4)O₄ and W(6)O₄ tetrahedra that provide linkage of the uranyl pentagonal bipyramids centered by U(1) and U(3), and U(2) and U(4), respectively. The resulting [(WO₅)(UO₂)₄(WO₄)₂O₈]

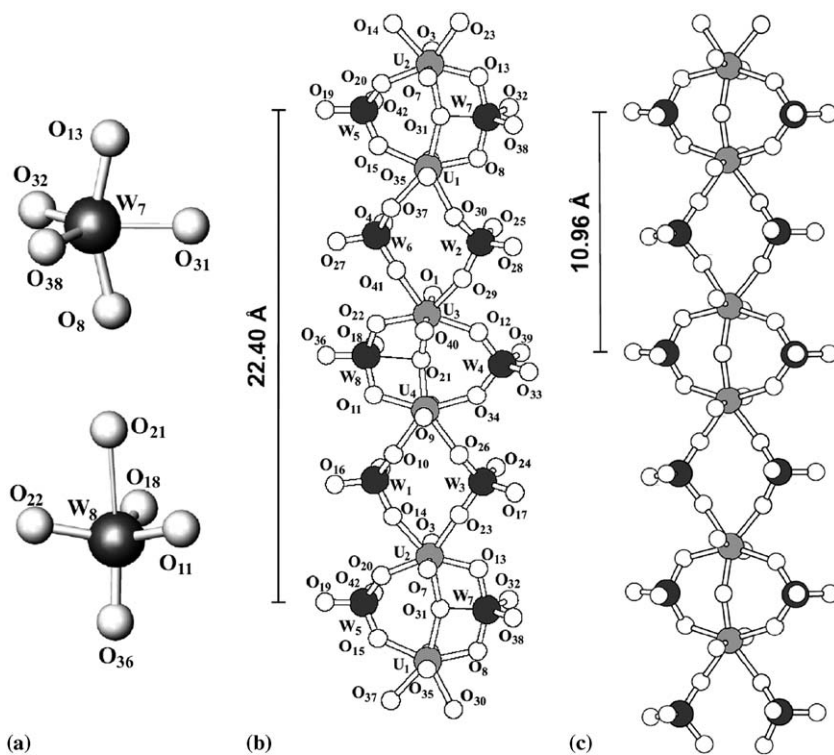


Fig. 1. Coordination of the W(7) and W(8) atoms in the structure of **3** (a), ball-and-stick representations of the $[(UO_2)_2O(MO_4)_4]^{6-}$ chains ($M = W, Mo$) in the structures of **3** (b) and its molybdate analog (c).

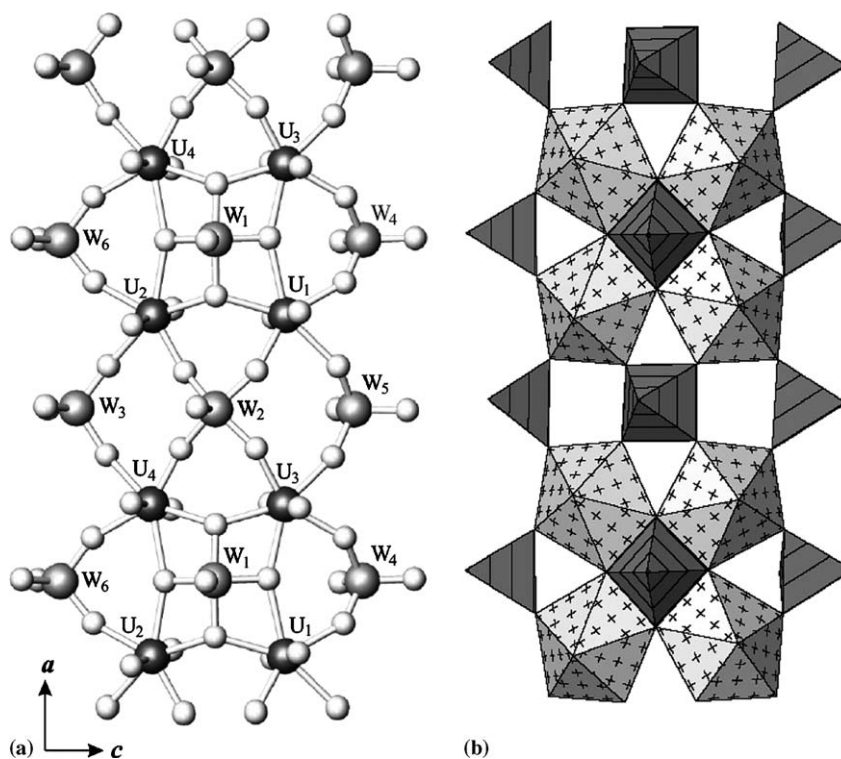


Fig. 2. Ball-and-stick (a) and polyhedral (b) representations of the uranyl tungstate chain in the structure of **2** (U polyhedra = cross-hatched; Mo polyhedra = lined.)

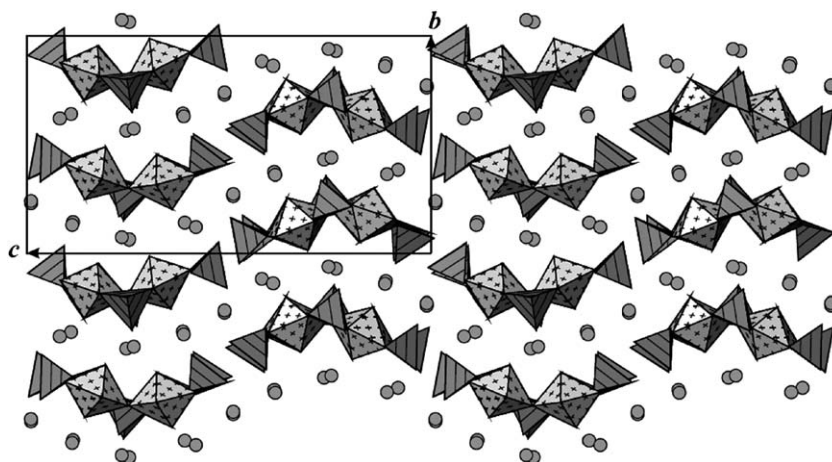


Fig. 3. The structure of **2** projected along the *a*-axis (U polyhedra = cross-hatched; Mo polyhedra = lined.)

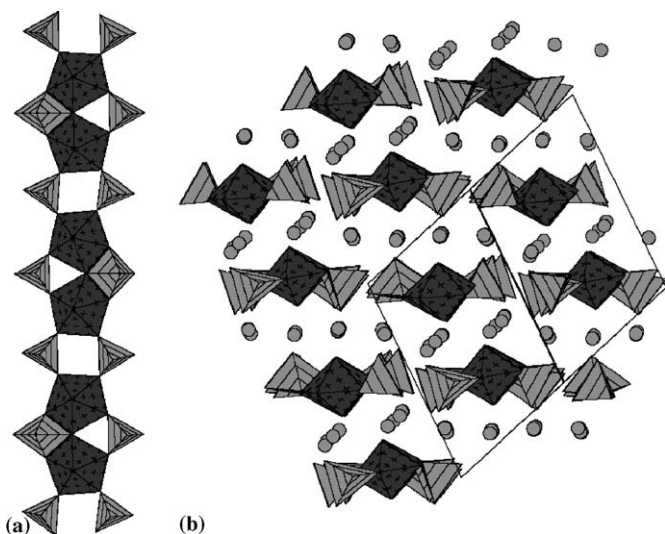


Fig. 4. The uranyl tungstate chain (a) and the structure of **3** projected along [110] (b). (U polyhedra = cross-hatched; W polyhedra = lined; Rb atoms shown as circles.)

units are linked into 1D chains by $W(2)O_5$ square pyramids and $W(3)O_4$ and $W(5)O_4$ tetrahedra (Fig. 2). The $[(UO_2)_4(WO_4)_4(WO_5)_2]^{4-}$ chains run parallel to the *a* axis and are arranged in pseudo-2D-layers parallel to (010) (Fig. 3). The layers are rather modulated along the *b*-axis. The modulation waves have a periodicity identical to the *c* parameter (i.e. 25.017 Å for **1** and 25.736 Å for **2**) with amplitudes of about 5 Å in both compounds. It is noteworthy that the chains themselves are non-centrosymmetric with the apical $W=O$ bonds of the WO_5 square bipyramids oriented in the same direction relative to the planes of the chains. However, within the pseudo-layers, the up- and down-orientations of the chains alternate with each other. The A^+ cations are in the interlayer space between adjacent pseudo-layers and provide a 3D integrity of the structures.

The structure of **3** contains chains of composition $[(UO_2)_2O(WO_4)_4]^{6-}$ composed of UO_7 pentagonal bipy-

ramids and W polyhedra (Fig. 1c). The chains involve dimers of UO_7 pentagonal bipyramids that share the common O atoms. The dimers are linked into chains by sharing corners with WO_4 tetrahedra (Fig. 4a). The chains are parallel to $[-101]$ and are arranged in layers that are parallel to (111) (Fig. 4b). The Rb^+ cations provide linkage of the chains into a 3D structure.

4. Discussion

The compounds **1** and **2** reported here are the first examples of uranyl tungstates that contain 1D chains of U and W polyhedra. Moreover, the chains observed are novel and have not been reported previously for any inorganic uranyl compound [19,20]. In addition, they are the first uranyl tungstates with 2/3 of the W atoms in tetrahedral coordinations. Such a high portion of low-coordinated W^{6+} cations is probably responsible for the 1D character of the uranyl tungstate units. As it can be seen from Fig. 1, the WO_4 tetrahedra are on both sides of the chains with two vertices of each tetrahedron not bonded to U. The O atoms located at the terminal vertices of the WO_4 tetrahedra receive about 1.5 v.u. due to the $W^{6+}-O$ bonds. Therefore, their bond-valence requirements are satisfied and the rest is provided by weaker A^+-O bonds to the alkali metal A^+ cations. Thus, it is the tetrahedral coordination of the W^{6+} cations and the topological function of the WO_4 tetrahedra that are most likely responsible for the 1D character of structures **1** and **2**.

It is of interest that the WU_4O_{25} pentamers that serve as fundamental building units for the uranyl tungstate chains reported here have been previously observed in the structures of uranyl tungstates and uranyl molybdates. For instance, they have been found in $K_8[(UO_2)_8(MoO_5)_3O_6]$ [2] (Fig. 5a and b), and $Cs_6[(UO_2)_4(W_5O_{21})(OH)_2(H_2O)_2]$ [5] (Fig. 5c and d). In both structures, pentamers are further linked into dense 2D

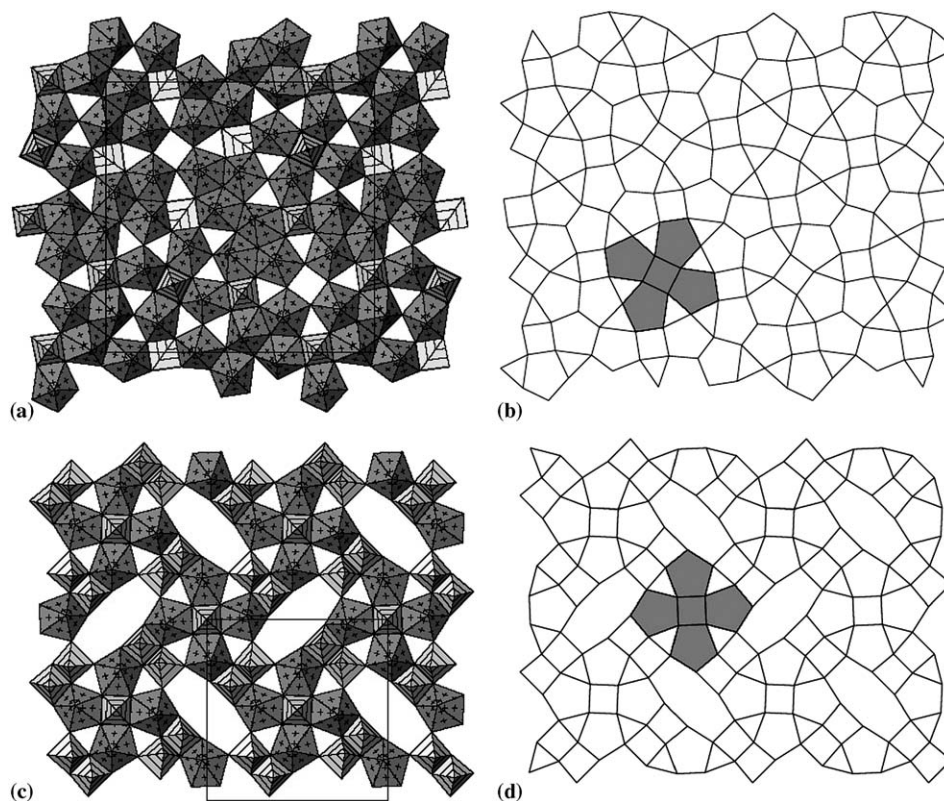


Fig. 5. The sheets of MO_5 square pyramids (lined; $M = \text{Mo}, \text{W}$) and UO_7 pentagonal bipyramids (cross-hatched) in the structures of $\text{K}_8[(\text{UO}_2)_8(\text{MoO}_5)_3\text{O}_6]$ (a), and $\text{Cs}_6[(\text{UO}_2)_4(\text{W}_5\text{O}_{21})(\text{OH})_2(\text{H}_2\text{O})_2]$ (c) and their anion topologies (b and d, respectively) produced according to the method proposed by Burns et al. [19,20]. The space occupied by pentamers are highlighted in the respective anion topologies (b) and (d).

units via additional U and W polyhedra. Thus, the structures reported here are the only examples of 1D arrangements of the pentamers.

The studied compound $\text{Rb}_6[(\text{UO}_2)_2\text{O}(\text{WO}_4)_4]$ (**3**) has many structural and chemical similarities to its molybdate analog, $\text{Rb}_6[(\text{UO}_2)_2\text{O}(\text{MoO}_4)_4]$ [15]. However, the compounds are not isostructural. The W compound has approximately doubled unit-cell volume relative to its Mo analog. However, the close relationship between the two structures becomes obvious if the unit-cell dimensions of the W compound are transformed according to the matrix $[1 \ 0 \ 0/0.5 \ 0 \ 0.5/0 \ -1 \ 0]$. The resulting subcell has the following parameters $[a-b-c-\alpha-\beta-\gamma]$: 10.188–10.175–13.110–75.72–76.11–66.75. These parameters are very close to those of the Mo phase that has the unit cell with dimensions 10.157–10.182–13.113–76.92–76.55–65.24. The subcell volume of the W phase (1194.4 \AA^3) is very close to the unit-cell volume of the Mo compound (1184.8 \AA^3). However, the real unit cell of the W compound is doubled relative to the Mo phase. The reasons for the unit-cell doubling can be inferred from a more closer look at the structure of the $[(\text{UO}_2)_2\text{O}(\text{WO}_4)_4]^{6-}$ chains.

Figs. 1b and c provide structural diagrams of the $[(\text{UO}_2)_2\text{O}(\text{WO}_4)_4]^{6-}$ chain in **3** and of the $[(\text{UO}_2)_2\text{O}(\text{MoO}_4)_4]^{6-}$ chain in its molybdate analog. As can be seen, all Mo^{6+}

cations in the structure of the Mo compound are tetrahedrally coordinated, whereas two out of eight W sites in the structure of **3** have fivefold coordinations. The fivefold coordination of the W atoms is realized by formation of the long W–O bonds to the O_{br} atoms bridging between two U centers in the $[\text{O}_6(\text{UO}_2)\text{O}(\text{UO}_2)\text{O}_6]$ dimers (Fig. 1b). It is noteworthy that the arrangement of the longer W–O bonds is asymmetrical relative to the chain extension.

The dimer formed by the U(1) and U(2) centers bridged by the O(31) atom is associated with the W(7)–O(31) bond of 2.03 Å. As a consequence, the U(1)–O(31) and U(2)–O(31) bonds are rather long (2.40 and 2.41 Å, respectively). In contrast, the dimer formed by the U(3) and U(4) atoms with its bridge at the O(21) atom is linked to the W(8)–O(21) bond of 2.45 Å. The U(3)–O(21) and U(4)–O(21) bonds are short, 2.25 and 2.21 Å, respectively. As can be seen from Fig. 1b, the direction of the W(8)–O(21) bond is antiparallel to the direction of the W(7)–O(31) bond, i.e. the fivefold coordinated W atoms are located on different sides of the dimers relative to the chain extension. As a consequence, the identity period of the chain in the W compound is doubled compared to the chain in the Mo compound. In the latter, the O_{br} atoms do not form bonds to Mo^{6+} and chains are not deformed by long $\text{M}^{6+}\text{--O}_{\text{br}}$ bonds.

In general, the structure of **3** is an excellent example of the evolution of the structure type when a *d*-element is replaced by an *f*-element with almost the same ionic radius. Due to the tendency of the W^{6+} cations to have higher-than-fourfold coordination, part of the W sites adopt distorted fivefold coordination. Distribution of the WO_5 configurations along the chain extension does not conform with its ‘typical’ periodicity, which is known, for instance, from the structure of $Rb_6[(UO_2)_2O(MoO_4)_4]$ [15]. As a result, both the chain identity period and the unit-cell volume are doubled in comparison with the Mo analog, thus leading to a new structure type.

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