Original paper

The role of potassium atoms in the formation of uranyl selenates: the crystal structure and synthesis of two novel compounds

Vladislav V. GURZHIY[1,*], Olga S. TYUMENTSEVA[1], Ilya V. KORNYAKOV[1], Sergey V. KRIVOVICHEV[1], Ivan G. TANANAEV[2]

[1] *Department of Crystallography, Geological Faculty, St. Petersburg State University, University Emb. 7/9, St. Petersburg, 199034, Russian Federation; vladgeo17@mail.ru*

[2] *Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Leninskiy pr. 31, Block 4, Moscow, 119991, Russian Federation*

[*] *Corresponding author*

Single crystals of two new uranyl selenates $K_3(H_3O)[(UO_2)_4(SeO_4)_6(H_2O)_4] \cdot 5H_2O$ (**I**) and $K_{2.5}(NO_3)_{0.5}[(UO_2)_2(SeO_4)_3 (H_2O)] \cdot 4H_2O$ (**II**) have been prepared by room-temperature evaporation from aqueous solution of uranyl nitrate, selenic acid, potassium carbonate and (for the compound **I**) carbamide. The crystal structure of **I** has been solved by direct methods [monoclinic, $P2_1/m$, $a = 12.001(3)$, $b = 13.613(3)$, $c = 13.753(3)$ Å, $\beta = 109.187(4)°$, $V = 2122.0(8)$ Å^3 and $Z = 2$] and refined to $R_1 = 0.029$ ($wR_2 = 0.084$) for 4865 reflections with $|Fo| \geq 4\sigma F$ using least-square methods. The crystal structure of **II** has been solved by direct methods [monoclinic, $C2/c$, $a = 20.290(4)$, $b = 10.380(2)$, $c = 21.436(4)$ Å, $\beta = 103.446(3)°$, $V = 4391.0(13)$ Å^3 and $Z = 4$] and refined to $R_1 = 0.027$ ($wR_2 = 0.066$) for 7944 reflections with $|F_o| \geq 4\sigma F$ using least-square techniques. The structures of **I** and **II** are based upon the $[(UO_2)_2(SeO_4)_3(H_2O)_2]^{2-}$ and $[(UO_2)_2(SeO_4)_3(H_2O)]^{2-}$ layers, respectively, consisting of UO_7 pentagonal bipyramids sharing corners with SeO_4 tetrahedra. Potassium cations induce curvature of the uranyl selenate layers, which is mediated by the interlayer water molecules, hydronium ions and nitrate groups. The topology of the 2D units in the structure of **I** is novel for the structural chemistry of uranyl selenates.

1. Introduction

The problem of safe disposal of spent nuclear fuel is responsible for the increasing interest in the study of secondary uranium-bearing compounds. Understanding the formation of natural and synthetic uranium phases is important for modelling of alteration processes occurring in the uranium deposits and geological radioactive waste repositories (Finch et al. 1999). Nowadays seven uranyl selenites are known as mineral species (Burns 2005; Krivovichev and Plášil 2013), whereas no uranium selenates have been found in nature to date. This can be explained by both high solubility of uranyl selenates in aqueous solutions and easy reduction of Se^{6+} to the Se^{4+} state under common natural conditions (Charykova et al. 2010, 2012; Krivovichev et al. 2011a, 2012). Synthetic members of the uranyl selenate group display an outstanding structural diversity. There are more than 120 purely inorganic or organically templated inorganic uranyl selenates (Burns 2005; Krivovichev et al. 2007; Krivovichev and Plášil 2013). Most of the uranyl-containing compounds, in particular uranyl selenate structures, are layered due to the specific coordination of U(VI) atoms (Burns et al. 1997). There are also well-known compounds with isolated, chain or framework structural units (Krivovichev et al. 2007; Krivovichev 2008, 2013). However, the most remarkable compounds in this group are uranyl selenate nanotubes (Krivovichev et al. 2005a, b; Alekseev et al. 2008), which have a unique structural architecture considered as being generated by folding of flat 2D units into single tubes. It is interesting that compounds containing nanotubes invariably contain K$^+$ ions in their structures. As it was suggested in the recent works (Krivovichev et al. 2009, 2011b; Krivovichev 2010), the presence of these ions plays a crucial role in formation of tubular morphologies of structural units, whereas water molecules in the interlayer space reduce the folding effect and may totally neutralize the curvature of uranyl selenate layers. There are eight K-containing uranyl selenates known so far (Krivovichev et al. 2005a, b; Alekseev et al. 2008; Gurzhiy et al. 2009, 2011, 2012; Ling et al. 2010), and it seems worthwhile to explore K-containing uranyl systems further in order to understand the role of K$^+$ ions in their structures and, in particular, the ability of these ions to induce curvature in otherwise planar structural units.

Herein, we report on the syntheses, crystal structures and spectroscopic investigations of two new potassium uranyl selenates: $K_3(H_3O)[(UO_2)_4(SeO_4)_6(H_2O)_4] \cdot 5H_2O$ (**I**) and $K_{2.5}(NO_3)_{0.5}[(UO_2)_2(SeO_4)_3(H_2O)] \cdot 4H_2O$ (**II**).

2. Experimental

2.1. Synthesis

Single crystals of the compounds **I** and **II** have been prepared by isothermal evaporation from aqueous solutions at room-temperature conditions. The crystals of compound **I** formed from the mixture of 2 ml of an aqueous solution of uranyl nitrate (0.48 g of $UO_2(NO_3)_2 \cdot 6H_2O$), selenic acid (0.2 ml of H_2SeO_4), potassium carbonate (0.068 g of K_2CO_3), and carbamide (0.018 g of CH_4ON_2). Prepared solution was heated at 60 °C for 35 min and then placed in a fume hood, where yellow-green crystals suitable for X-ray structural analysis grew within 6 days. Crystals of compound **II** formed from the mixture of 2 ml of an aqueous solution of uranyl nitrate (0.2 g of $UO_2(NO_3)_2 \cdot 6H_2O$), selenic acid (0.2 ml of H_2SeO_4) and potassium carbonate (0.048 g of K_2CO_3). The solution was heated at 60 °C for 35 min and then placed in a fume hood, where yellow-green crystals suitable for X-ray structural analysis grew after 4 days.

2.2. X-ray diffraction

Single yellow-green plates of **I** and **II** were mounted on thin glass fibres for X-ray diffraction analysis, which was carried out using a Bruker SMART single-crystal X-ray diffractometer equipped with an APEX II CCD planar detector operated with MoK$_\alpha$ radiation at 50 kV and 40 mA. More than a hemisphere of X-ray diffraction data (θ_{max} = 30.00 and 32.50° for **I** and **II**, respectively) were collected at 210 K for each crystal with frame widths of 0.5° in ω, and exposition of 20 s per each frame. Data were integrated and corrected for background, Lorentz, and polarization effects using an empirical spherical model (Bruker programs APEX and XPREP). Absorption corrections were applied using the SADABS program (Sheldrick 2007). The unit-cell parameters of **I** (Tab. 1) were determined and refined by the least-squares techniques on the basis of 28491 reflections with 2θ in the range of 3.14–60.00°. From the systematic absences and statistics of reflection distribution, the space group $P2_1/m$ was determined. The structure was solved by direct methods and refined to $R_1 = 0.029$ ($wR_2 = 0.084$) for 4865 reflections with $|F_o| \geq 4\sigma F$ using the SHELXL-97 program (Sheldrick 2008) incorporated in the *OLEX2* program package (Dolomanov et al. 2009). The unit-cell parameters of **II** (Tab. 1) were determined and refined by the least-squares techniques on the basis of 33,030 reflections with 2θ in the range 3.90°–65.00°. From the systematic absences and statistics of reflection distribution, the space group $C2/c$ was determined. The structure was solved by direct methods and refined to $R_1 = 0.027$ ($wR_2 = 0.066$) for 6405 reflections with $|F_o| \geq 4\sigma F$ using the SHELXL-97 program (Sheldrick 2008) incorporated in the *OLEX2* program package (Dolomanov et al. 2009). The final models included coordinates and anisotropic displacement parameters for all non-hydrogen atoms (Tabs 2 and 4 for **I** and **II**, respectively). Selected bond lengths and angles are given in Tabs 3 and 5 (for **I** and **II**, respectively). Positions of H atoms of H_2O molecules were localized from difference Fourier maps only for **II** and kept fixed during refinement. Oxygen atoms O22–O26 of H_2O molecules from the interlayer space of the compound **I** and atoms forming a nitrate group (N1, O22, O23 and O24) in the structure of **II** were refined with the same displacement parameters (using EADP instruction) due to a weak disorder. Supplementary crystallographic data for this paper have been deposited at

Tab. 1 Crystallographic data and refinement parameters for $K_3(H_3O)[(UO_2)_4(SeO_4)_6(H_2O)_4] \cdot 5H_2O$ (**I**) and $K_{2.5}(NO_3)_{0.5}[(UO_2)_2(SeO_4)_3(H_2O)] \cdot 4H_2O$ (**II**)

Parameter	I	II
a (Å)	12.001(3)	20.290(4)
b (Å)	13.613(3)	10.380(2)
c (Å)	13.753(3)	21.436(4)
β (°)	109.187(4)	103.446(3)
V (Å³)	2122.0(8)	4391.0(13)
Space group	$P2_1/m$	$C2/c$
μ, mm⁻¹	20.770	20.278
Z	2	4
D_{calc}, g cm⁻³	3.467	3.593
Crystal size, mm³	0.23×0.15×0.07	0.25×0.16×0.09
Radiation	MoK$_\alpha$	MoK$_\alpha$
Total number of reflections	28491	33030
Number of unique reflections	6432	7944
2θ range, deg	3.14–60.00	3.90–65.00
Reflections with $|F_o| \geq 4\sigma F$	4865	6405
R_{int}	0.0561	0.0548
R_σ	0.0467	0.0429
R_1 ($|F_o| \geq 4\sigma F$)	0.0289	0.0268
wR_2 ($|F_o| \geq 4\sigma F$)	0.0837	0.0657
R_1 (all data)	0.0431	0.0390
wR_2 (all data)	0.0867	0.0685
S	1.036	1.040
ρ_{min}, ρ_{max}, e/Å³	−1.399, 2.717	−2.013, 2.952

Note: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2 F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of the refined parameters

Tab. 2 Coordinates and displacement parameters (Å^2) of atoms forming the structure of $K_3(H_3O)[(UO_2)_4(SeO_4)_6(H_2O)_4]\cdot 5H_2O$ (**I**)

| Atom	x/a	y/b	z/c	U_{eq}
U(1)	0.22847(2)	0.48852(2)	0.433390(17)	0.01926(7)
U(2)	0.22135(2)	0.465616(19)	−0.068123(17)	0.01935(7)
Se(1)	0.09854(6)	0.49158(5)	0.14632(5)	0.02124(14)
Se(2)	−0.10023(6)	0.50992(5)	0.35368(5)	0.01924(13)
Se(3)	0.49279(6)	0.51073(6)	0.34348(5)	0.02508(16)
K(1)	0.0427(2)	3/4	0.26609(17)	0.0307(5)
K(2)	0.1481(3)	3/4	0.0149(2)	0.0584(8)
K(3)	0.0683(6)	1/4	0.3063(4)	0.0469(13)
K(4)	0.4949(8)	3/4	0.5156(5)	0.074(3)
O(1)	0.2501(4)	0.3634(4)	0.4676(4)	0.0298(11)
O(2)	0.2028(4)	0.6134(4)	0.3978(4)	0.0290(11)
O(3)	0.1974(4)	0.5260(4)	0.5930(3)	0.0281(12)
O(4)	0.3649(4)	0.4679(5)	0.3431(4)	0.0423(16)
O(5)	0.0250(4)	0.4519(4)	0.4117(3)	0.0250(10)
O(6)	0.1262(4)	0.4404(4)	0.2598(3)	0.0282(11)
O(7)	0.2891(4)	0.5800(4)	−0.0255(4)	0.0306(12)
O(8)	0.1533(5)	0.3530(4)	−0.1126(4)	0.0322(12)
H$_2$O(9)	0.3600(5)	0.4140(4)	−0.1532(4)	0.0391(14)
H$_2$O(10)	0.3889(5)	0.3854(5)	0.0587(4)	0.0413(14)
O(11)	0.1860(4)	0.4372(4)	0.0917(3)	0.0290(12)
O(12)	0.1159(5)	0.6093(4)	0.1523(4)	0.0344(12)
O(13)	−0.0387(4)	0.4580(4)	0.0821(3)	0.0246(10)
O(14)	−0.0837(5)	0.6277(4)	0.3550(4)	0.0321(12)
O(15)	−0.1506(4)	0.4661(4)	0.2347(3)	0.0279(11)
O(16)	0.5907(4)	0.4616(4)	0.4463(3)	0.0271(11)
O(17)	0.4958(6)	0.6291(5)	0.3469(5)	0.0508(16)
O(18)	0.5176(5)	0.4676(5)	0.2417(4)	0.0467(16)
H$_2$O(19)	0.4671(8)	3/4	0.9787(7)	0.050(2)
H$_2$O(20)	0.3121(8)	1/4	0.7215(7)	0.052(2)
H$_2$O(21)	0.3877(9)	3/4	0.1572(7)	0.059(3)
H$_2$O(22)	−0.0324(12)	1/4	0.4644(7)	0.086(3)
H$_2$O(23)	0.300(3)	3/4	0.6060(15)	0.086(3)
H$_2$O(24)	0.089(3)	1/4	0.0901(15)	0.086(3)
H$_2$O(25)	0.342(3)	1/4	0.2732(15)	0.086(3)
H$_2$O(26)	0.165(3)	3/4	−0.1795(15)	0.086(3)

Inorganic Crystal Structure Database (ICSD 427034 and 427035 for **I** and **II**, respectively) and can be obtained from Fachinformationszentrum Karlsruhe at http://*www.fiz-karlsruhe.de/request_for_deposited_data.html*.

2.3. Infrared spectroscopy

The infrared (IR) spectra of **I** and **II** were recorded using KBr pellets on the Bruker Vertex 70 spectrometer in the region 4000–300 cm^{-1} and are shown in Fig. 1. The band assignment confirms that the vibrational spectroscopic data are in a good agreement with the composition and single-crystal X-ray diffraction results.

Both spectra show characteristic absorption bands at 850–390 cm^{-1} (392, 459, 816, 851 cm^{-1} for **I** and 407, 472, 818, 834 and 850 cm^{-1} for **II**, respectively) due to the presence of $[SeO_4]^{2-}$ anions; these bands can be attributed to the stretches of the Se–O bonds. The bands at 950–850 cm^{-1} (in particular 851 and 943 cm^{-1} for **I** and 915, 931 and 950 cm^{-1} for **II**, respectively) are due to the vibrations of the $(UO_2)^{2+}$ cations (Nakamoto 1997). It should be noted that characteristic vibrations of the oxoselenate groups and uranyl ions overlap, so they cannot be clearly separated without structure-based calculations (Čejka 1999). The diffuse bands in the range of 3520–3200 cm^{-1} (3196, 3427 and 3522 cm^{-1}) correspond to the O–H stretching vibrations of water molecules or a strongly polarized H_2O group with strong H bonds. The band at 1635 cm^{-1} documents the presence of hydronium ions in the structure of **I**. Presence of the nitrate NO_3 group in the structure of **II** is confirmed by the multiple bands at 1630 and 1270–1260 cm^{-1}, whether the irregularly shaped band at 670 cm^{-1} can be assigned to vibrational modes of the $-NO_2$ group. Wide absorbance band of irregular shape in the range of 3500–3400 cm^{-1} corresponds to the stretching and bending vibrations of the H_2O molecules.
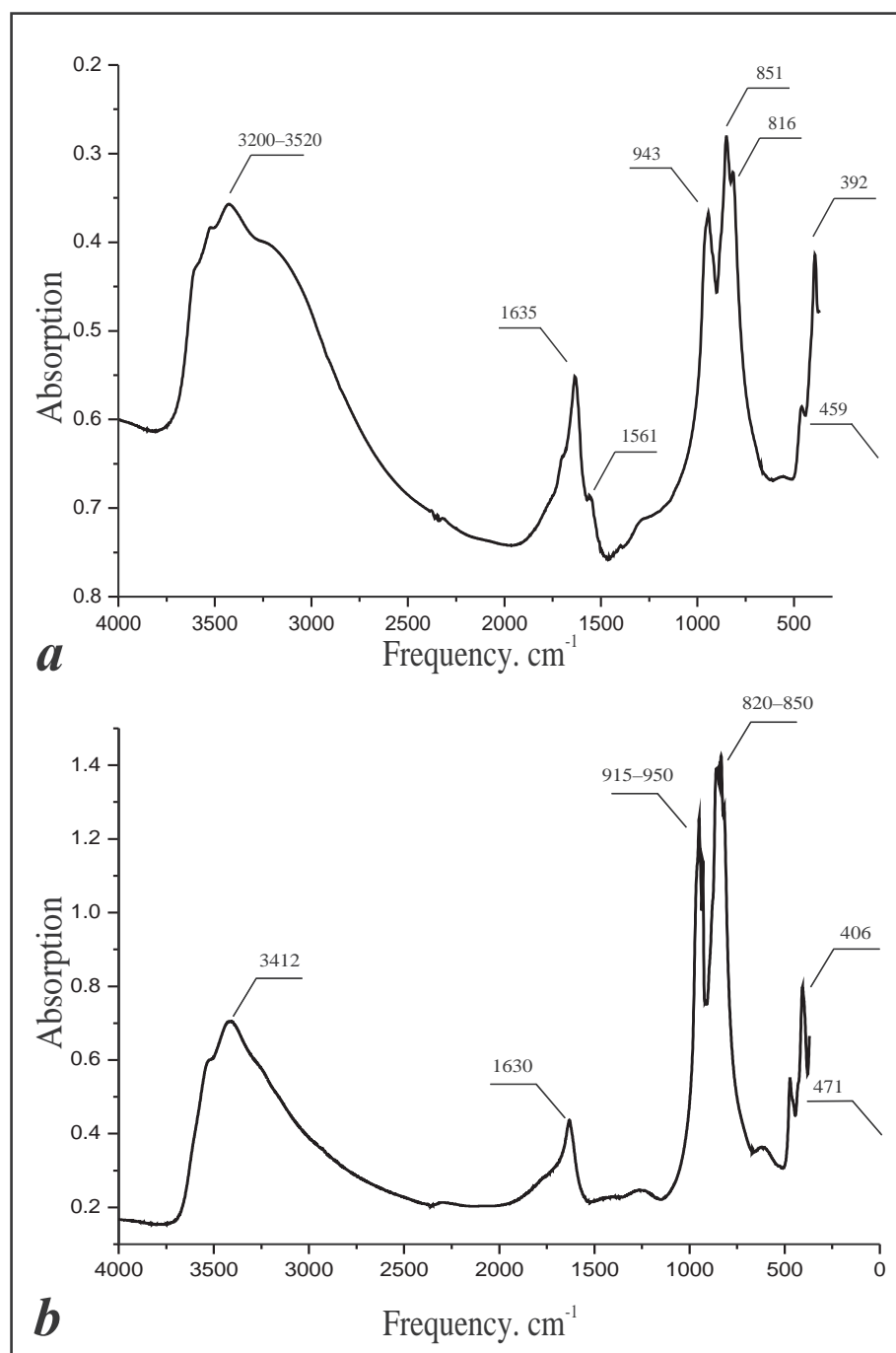
Fig. 1 Infrared spectra of $K_3(H_3O)[(UO_2)_4(SeO_4)_6(H_2O)_4]\cdot5H_2O$ (**a**) and $K_{2.5}(NO_3)_{0.5}[(UO_2)_2(SeO_4)_3(H_2O)]\cdot4H_2O$ (**b**)

3. Discussion

The structure of **I** (Fig. 2a) contains two symmetrically independent U atoms with two short $U^{6+}=O^{2-}$ bonds (1.763(5) and 1.768(5) Å for U1 and 1.750(5) and 1.765(5) Å for U2, respectively) forming approximately linear UO_2^{2+} uranyl ions (*Ur*). The $U(1)O_2^{2+}$ cation is coordinated by five oxygen atoms (U1–O_{eq} =

2.355(5)–2.413(5) Å) that belong to the selenate tetrahedra and that are arranged in the equatorial plane of the $Ur(1)O_5$ pentagonal bipyramid. The $U(2)O_2^{2+}$ cation is coordinated by three oxygen atoms (2.356(5)–2.403(4) Å) belonging to the selenate tetrahedra and two oxygen atoms of water molecules (the respective U(2)–$H_2O(9)$ and U(2)–$H_2O(10)$ bonds are elongated (2.432(5) Å and 2.444(5) Å, respectively) compared to other U–O_{eq} bonds, which is typical of hydrated uranyl complexes. Three symmetrically non-equivalent Se^{6+} atoms are tetrahedrally coordinated by four O^{2-} atoms each. The $[Se1O_4]^{2-}$ and $[Se2O_4]^{2-}$ groups are tridentate and $[Se3O_4]^{2-}$ groups are bidentate, sharing two and three vertices with adjacent uranium polyhedra, respectively. The Se–O bond lengths for the bridging oxygen atoms fall in the range of 1.641(4)–1.657(5) Å, 1.642(4)–1.658(4) Å and 1.640(5)–1.654(5) Å for Se(1), Se(2) and Se(3), respectively. Bond lengths for the terminal oxygen atoms are shorter and are equal to 1.614(5) Å, 1.616(5) Å and 1.612(6)–1.633(5) Å for Se(1), Se(2) and Se(3), respectively. The difference between Se–O bond-lengths for shared and non-shared O atoms is typical of uranyl oxysalts with hexavalent tetrahedrally coordinated cations (Krivovichev 2013). Non-shared vertices of the selenate tetrahedra are oriented either *up* or *down* relative to the planes of the layers.

The structure of **I** is based upon the $[(UO_2)_2(SeO_4)_3(H_2O)_2]^{2-}$ uranyl selenate layers formed by linkage of U and Se coordination polyhedra via common O atoms (Fig. 4a). The layers are parallel to (010). The charge of the layer is compensated by potassium and hydronium ions arranged in between the 2-D uranyl selenate units.

The linkage topology of the U and Se coordination polyhedra can be described using graphs where U and Se coordination polyhedra are symbolized by the black and white nodes, respectively (Fig. 4b). The two nodes are linked by an edge if the corresponding polyhedra have a shared O atom. Analysis of the topology of the uranyl selenate layers using graphs (Krivovichev 2004, 2008) indicates that the topology of the 2D layers belongs to the *cc*2–2:3–11 type (linkage of 4-membered rings creating 12-membered rings, Fig. 4c) and it is identical to those topologies found in the structures of $(H_3O)_2[(UO_2)_2(SeO_4)_3(H_2O)_2]$ $(H_2O)_{3.5}$ (Krivovichev and Kahlenberg 2005a) and $Rb_2[(UO_2)_2(SeO_4)_3(H_2O)_2](H_2O)_4$ (Krivovichev and Kahlenberg 2005b).

Crystal structure of **II** (Fig. 3a) contains two symmetrically independent U atoms with two short $U^{6+}=O^{2-}$ bonds (1.763(3) and 1.765(3) Å for U(1) and 1.761(4) and 1.767(4) Å for U(2), respectively). The $U(1)O_2^{2+}$ cation is coordinated by five oxygen atoms ($U1–O_{eq}$ = 2.355(3)–2.406(3) Å) of selenate tetrahedra arranged in the equatorial plane. The $U(2)O_2^{2+}$ cation is coordinated by four O atoms (2.358(3)–2.406(3) Å) of sel-

Tab. 3 Selected interatomic distances (d) and angles (ω) in the structure of $K_3(H_3O)[(UO_2)_4(SeO_4)_6$ $(H_2O)_4]·5H_2O$ (**I**)

	d, Å			d, Å
U(1)–O(1)	1.763(3)	K(1)–O(14)	×2	2.790(5)
U(1)–O(2)	1.765(3)	K(1)–O(12)	×2	2.792(5)
U(1)–O(16)	2.366(3)	K(1)–O(2)	×2	2.854(5)
U(1)–O(4)	2.384(3)	K(1)–O(8)	×2	2.948(5)
U(1)–O(6)	2.402(4)	<K1–O>		2.846
U(1)–O(3)	2.405(3)			
U(1)–O(5)	2.406(3)	K(2)–H$_2$O(24)		2.730(3)
<U(1)–O$_{Ur}$>	1.764	K(2)–H$_2$O(26)		2.750(2)
<U(1)–O$_{eq}$>	2.333	K(2)–O(12)	×2	2.806(6)
		K(2)–H$_2$O(21)		2.899(11)
U(2)–O(8)	1.761(4)	K(2)–O(7)	×2	3.024(6)
U(2)–O(7)	1.767(4)	<K(2)–O>		2.942
U(2)–O(15)	2.358(3)			
U(2)–O(13)	2.384(3)	K(3)–H$_2$O(26)		2.770(3)
U(2)–O(11)	2.386(3)	K(3)–O(6)	×2	2.811(6)
U(2)–H$_2$O(9)	2.406(3)	K(3)–H$_2$O(22)		2.813(12)
U(2)–H$_2$O(10)	2.412(4)	K(3)–O(1)	×2	2.980(7)
<U(2)–O$_{Ur}$>	1.764	K(3)–H$_2$O(24)		3.060(2)
<U(2)–O$_{eq}$>	2.389	<K(3)–O>		2.964
Se(1)–O(12)	1.613(4)	K(4)–O(17)	×2	2.847(8)
Se(1)–O(6)	1.638(3)	K(4)–H$_2$O(25)		2.920(2)
Se(1)–O(11)	1.639(3)	K(4)–H$_2$O(23)		2.990(3)
Se(1)–O(13)	1.645(3)	K(4)–O(16)	×2	3.160(6)
<Se(1)–O>	1.634	<K(4)–O>		2.901
Se(2)–O(14)	1.621(4)			
Se(2)–O(3)	1.635(3)	Angle		ω, °
Se(2)–O(5)	1.648(3)	U(1)– O(6)–Se(1)		135.4(3)
Se(2)–O(15)	1.650(3)	U(1)– O(5)–Se(2)		133.1(3)
<Se(2)–O>	1.638	U(1)– O(3)–Se(2)		133.8(3)
		U(1)– O(16)–Se(3)		135.7(3)
Se(3)–O(17)	1.613(4)	U(1)– O(4)–Se(3)		139.6(3)
Se(3)–O(18)	1.639(4)	U(2)– O(13)–Se(1)		130.6(3)
Se(3)–(O4)	1.641(3)	U(2)– O(11)–Se(1)		132.3(3)
Se(3)–O(16)	1.646(4)	U(2)– O(15)–Se(2)		135.7(3)
<Se(3)–O>	1.635			

enate tetrahedra and one water molecule ($U(2)–H_2O(17)$ = 2.412(4) Å). Three symmetrically non-equivalent Se^{6+} atoms are tetrahedrally coordinated by four O^{2-} anions, each with an average bond-length equal to 1.634, 1.638 and 1.635 Å for Se(1), Se(2) and Se(3), respectively. Tetrahedral complexes are tridentate having three vertices shared with the U polyhedra. Non-shared vertices of selenate tetrahedra are oriented either *up* or *down* relative to the planes of the layers.

The structure of **II** is based upon the $[(UO_2)_2(SeO_4)_3$ $(H_2O)]^{2-}$ layers formed by linkage of U and Se coordination polyhedra via shared O atoms (Fig. 4d). The structural layers are parallel to (–101). The negative charge of the layer is compensated by the K^+ ions arranged in

between the 2-D uranyl selenate units. Along with the potassium atoms, the interlayer contains four symmetrically independent H_2O molecules and disordered NO_3 groups.

Analysis of the topology of the uranyl selenate layers using graphs (Krivovichev 2004, 2008) indicates that the topology of the 2-D layers of the *cc*2–2:3–12 type (linkage of 4-membered rings and 8-membered rings with the latter ones forming rows along [010] – Fig. 4e–f) and is identical to that found in uranyl sulphate $[C_8H_{26}N_4]_{0.5}[(UO_2)_2(SO_4)_3(H_2O)]$ (Doran et al. 2004). However, the layer of this type had not been observed previously in uranyl selenates.

In the crystal structure of **I** there are four symmetrically independent K atoms that occupy special positions
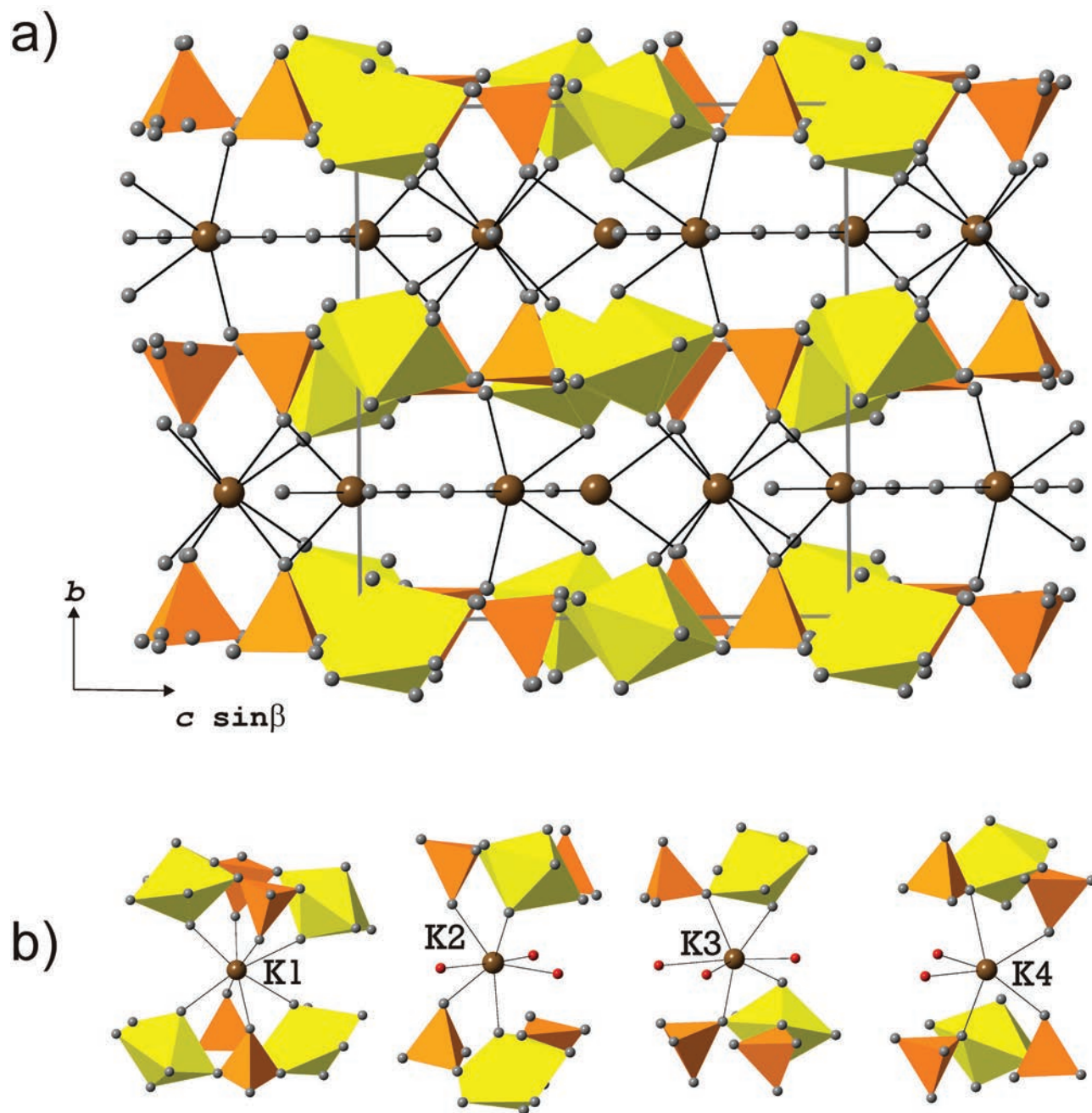
Fig. 2 Crystal structure of **I** (**a**) and coordination of K atoms in the structure of **I** (**b**). Legend: U polyhedra = yellow, Se tetrahedra = orange, K atoms = brown, O atoms = grey [in (**b**) H_2O groups are shown as red spheres].

on the mirror plane *m*. These K⁺ ions are surrounded by the O atoms belonging to the U–Se layers and also to the H_2O molecules in the interlayer. The K1 atom forms eight bonds to O atoms equally distributed between the two adjacent layers (K(1)–O bond lengths vary in the range of 2.790(5)–2.948(5) Å). Among the eight bonds, four are to the terminal O atoms of the selenate tetrahedra, whereas four others are to the O atoms of uranyl ions. The K(2) atom forms seven bonds (K(2)–O = 2.730(3)–3.024(6) Å) with four bonds to the terminal O atoms of the selenate

tetrahedra and O_{Ur} atoms from adjacent layers and three bonds to the interlayer H_2O molecules. The K(3) atom forms seven bonds (K(3)–O = 2.770(3)–3.060(2) Å): four bonds to O atoms from adjacent layers (two to the uranyl

⇨

Fig. 3 Crystal structure of **II** (**a**) and coordination of K atoms in the structure of **II** (**b**). Legend: U polyhedra = yellow, Se tetrahedra = orange, NO_3 groups = light-blue, K atoms = brown, O atoms = grey [in (**b**) H_2O groups are shown as red spheres and NO_3 groups in a stick--bond mode]. Hydrogen atoms are omitted for clarity.
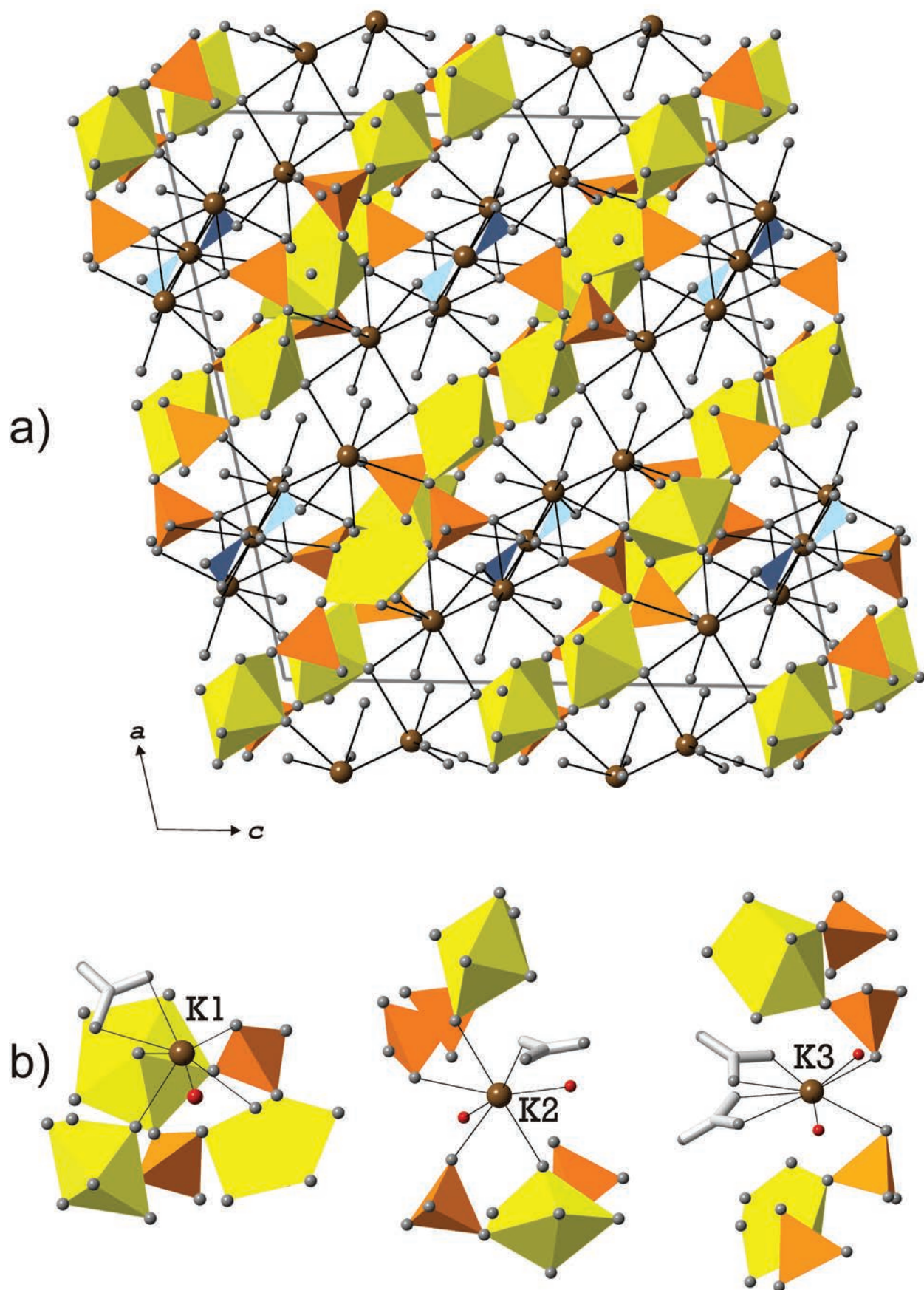
Tab. 4 Coordinates and displacement parameters ($Å^2$) of atoms forming the structure of $K_{2.5}(NO_3)_{0.5}[(UO_2)_2(SeO_4)_3(H_2O)] \cdot 4H_2O$ (**II**)

Atom	x/a	y/b	z/c	U_{eq}
U(1)	0.788786(8)	0.339121(14)	0.297341(8)	0.01423(4)
U(2)	0.585894(9)	0.252956(15)	0.047975(8)	0.01623(4)
Se(1)	0.86684(2)	0.66241(4)	0.28249(2)	0.01491(9)
Se(2)	0.70933(2)	0.49973(4)	0.14020(2)	0.01499(9)
Se(3)	0.56264(2)	−0.10793(4)	0.06678(2)	0.01800(9)
K(1)	0.70613(8)	0.66516(12)	0.39448(7)	0.0408(3)
K(2)	0.43450(7)	0.31267(14)	0.16243(7)	0.0402(3)
K(3)	0	0.45833(18)	1/4	0.0552(6)
O(1)	0.8135(2)	0.2426(3)	0.23893(17)	0.0243(7)
O(2)	0.7066(2)	0.6565(3)	0.13271(17)	0.0232(7)
O(3)	0.76367(19)	0.4374(3)	0.35480(16)	0.0218(7)
O(4)	0.81998(19)	0.7434(3)	0.22272(17)	0.0225(7)
O(5)	0.84342(18)	0.6982(3)	0.34893(16)	0.0204(7)
O(6)	0.7713(2)	0.4372(3)	0.11447(19)	0.0279(8)
O(7)	0.51462(19)	0.3064(3)	0.07445(19)	0.0261(8)
O(8)	0.65774(19)	0.2036(4)	0.02079(18)	0.0281(8)
O(9)	0.85402(19)	0.5088(3)	0.26689(18)	0.0247(8)
O(10)	0.71335(18)	0.4619(3)	0.21564(16)	0.0226(7)
O(11)	0.5983(2)	−0.1718(3)	0.13638(19)	0.0286(8)
O(12)	0.48700(19)	−0.1743(3)	0.04643(17)	0.0257(8)
O(13)	0.63656(18)	0.4472(3)	0.09601(17)	0.0236(7)
O(14)	0.5512(2)	0.0464(3)	0.07707(18)	0.0268(8)
O(15)	0.6076(2)	−0.1294(4)	0.01469(19)	0.0330(9)
O(16)	0.94523(18)	0.6961(4)	0.28594(19)	0.0267(8)
O(17)	0.5727(3)	0.4170(4)	−0.0337(2)	0.0450(12)
H(17A)	0.558(4)	0.505(4)	−0.025(4)	0.067
H(17B)	0.539(3)	0.408(7)	−0.0759(19)	0.067
O(18)	0.6362(2)	0.6375(4)	−0.0395(2)	0.0338(9)
H(18A)	0.680(2)	0.656(6)	−0.049(4)	0.051
H(18B)	0.628(4)	0.714(4)	−0.015(3)	0.051
O(19)	0.7599(2)	0.5295(5)	−0.0115(2)	0.0387(10)
H(19A)	0.760(4)	0.465(6)	0.022(3)	0.058
H(19B)	0.798(3)	0.557(7)	−0.030(4)	0.058
O(20)	0.4111(3)	0.0504(6)	0.1341(3)	0.0612(15)
H(20A)	0.434(5)	0.028(9)	0.099(3)	0.092
H(20B)	0.399(5)	−0.043(3)	0.129(5)	0.092
O(21)	0.4741(4)	0.4422(7)	−0.1395(3)	0.078(2)
H(21A)	0.513(2)	0.434(11)	−0.163(2)	0.118
H(21B)	0.438(2)	0.435(10)	−0.181(2)	0.118
N(1)*	0.4368(6)	0.6592(10)	0.2017(6)	0.0443(13)
O(22)*	0.4024(5)	0.5477(8)	0.2014(5)	0.0443(13)
O(23)*	0.4867(5)	0.6910(7)	0.2527(7)	0.0443(13)
O(24)*	0.4233(5)	0.7589(8)	0.1619(5)	0.0443(13)

* site-occupation factor is 0.5.

O atoms and two to the bridging O atoms between the U and Se atoms) and three more bonds to H_2O molecules in the interlayer. The K(4) atom forms six bonds (K(4)–O = 2.847(8)–3.160(6) Å): two to the terminal O atoms of the selenate tetrahedra, two to the bridging O atoms and two to the H_2O molecules in the interlayer.

In the crystal structure of **II** there are three symmetrically independent potassium atoms (Fig. 3b). The K(1) atom forms three bonds to O_{Ur} atoms and one bond

to terminal O atom of $[SeO_4]$ tetrahedra from the same layer, one bond (K(1)–O(19)) to water molecule and two bonds to the O atoms of the same nitrate group (K(1)–O(22), K(1)–O(24)). The K(1)–O bond lengths fall in the range of 2.799(10)–2.959(4) Å. The K(2) atom forms seven bonds (K(2)–O = 2.707(8) –2.997(4) Å): two to the terminal O atoms of the selenate groups from adjacent layers, one to bridging O atom, one to O_{Ur} atom, two to the interlayer water molecules and one to O atoms of

the NO_3 group. The K(3) atom forms eight bonds to O atoms (2.789(8)–2.984(9) Å) and is most isolated from the layers. It has two bonds with terminal O atoms of selenate tetrahedra and six other contacts are concentrated within the interlayer space: two bonds with H_2O molecules and four bonds with O atoms from two symmetrically equivalent nitrate groups.

It is worth noting that the K(1) atom in the structure of **I** is arranged in front of the U(1)–Se(2)–U(2)–Se(1) four-membered ring, forming bonds exclusively with the apical O atoms of the selenate tetrahedra and uranyl ions (Fig. 2b). This results in the observed local curvature of the U–Se–U–Se units (the angle between the equatorial planes of the uranyl bipyramids is equal to 132.2°). The K(4) atom is also arranged in front of the U(1)–Se(3)–U1–Se(3) four-membered ring, but, in this case, the equatorial planes of the U(1) bipyramids are parallel. The K(2) and K(3) atoms are shifted from the central position closer to uranyl polyhedron. Therefore, as shown also by the above-described coordination features, there is no exact effect of curvature induction for these positions.

Tab. 5 Selected interatomic distances (d) and angles (ω) in the structure of $K_{2.5}(NO_3)_{0.5}[(UO_2)_2 (SeO_4)_3(H_2O)]\cdot 4H_2O$ (**II**)

	d, Å		d, Å
U(1)–O(3)	1.763(3)	K(1)–O(24)	2.799(10)
U(1)–O(1)	1.765(3)	K(1)–O(3)	2.853(4)
U(1)–O(4)	2.366(3)	K(1)–O(6)	2.874(4)
U(1)–O(9)	2.384(3)	K(1)–O(19)	2.884(5)
U(1)–O(11)	2.402(4)	K(1)–O(1)	2.907(4)
U(1)–O(2)	2.405(3)	K(1)–O(22)	2.908(9)
U(1)–O(10)	2.406(3)	K(1)–O(8)	2.959(4)
<U(1)–O$_{Ur}$>	1.764	<K(1)–O>	2.883
<U(1)–O$_{eq}$>	2.333		
		K(2)–O(22)	2.707(8)
U(2)–O(7)	1.761(4)	K(2)–O(16)	2.718(4)
U(2)–O(8)	1.767(4)	K(2)–O(18)	2.741(5)
U(2)–O(12)	2.358(3)	K(2)–O(7)	2.762(4)
U(2)–O(14)	2.384(3)	K(2)–O(20)	2.806(6)
U(2)–O(13)	2.386(3)	K(2)–O(16)	2.873(4)
U(2)–O(5)	2.406(3)	K(2)–O(4)	2.997(4)
U(2)–H$_2$O(17)	2.412(4)	<K(2)–O>	2.801
<U(2)–O$_{Ur}$>	1.764		
<U(2)–O$_{eq}$>	2.389	K(3)–O(23) ×2	2.789(8)
		K(3)–O(20) ×2	2.873(6)
Se(1)–O(16)	1.613(4)	K(3)–O(16) ×2	2.884(4)
Se(1)–O(9)	1.638(3)	K(3)–O(24) ×2	2.984(9)
Se(1)–O(4)	1.639(3)	<K(3)–O>	2.882
Se(1)–O(5)	1.645(3)		
<Se(1)–O>	1.634		
Se(2)–O(6)	1.621(4)	Angle	ω, °
Se(2)–O(2)	1.635(3)	U(1)–O(4)–Se(1)	134.8(2)
Se(2)–O(10)	1.648(3)	U(1)–O(9)–Se(1)	137.3(2)
Se(2)–O(13)	1.650(3)	U(1)–O(2)–Se(2)	136.7(2)
<Se(2)–O>	1.638	U(1)–O(10)–Se(2)	136.0(2)
		U(1)–O(11)–Se(3)	132.7(2)
Se(3)–O(15)	1.613(4)	U(2)–O(5)–Se(1)	128.2(2)
Se(3)–O(11)	1.639(4)	U(2)–O(13)–Se(2)	139.9(2)
Se(3)–O(14)	1.641(3)	U(2)–O(12)–Se(3)	137.1(2)
Se(3)–O(12)	1.646(4)	U(2)–O(14)–Se(3)	141.5(2)
<Se(3)–O>	1.635		

4. Concluding remarks

As it was suggested by Gurzhiy et al. (2011), K atoms have specific ionic properties (Cartledge ionic potential) suitable for inducing the curvature of the uranyl selenate complexes in aqueous solutions. Latter, Gurzhiy et al. (2012) demonstrated that not only the pH of the solution (presence of the protonated water complexes in the structure) could control the modification of layers, but also the $K/(H_2O + H_3O + H_5O_2 + ...)$ ratio should be taken into account. It was also shown that if such ratio is equal or less than 1:2, the uranyl selenate layers are flat. The structures reported herein confirm these empirical observations. Interlayer space of the structure of **I** contains both

H_2O molecules and H_3O^+ ions along with K^+ cations; the $K/(H_2O + H_3O + H_5O_2 + ...)$ ratio equals to 1:2. The same ratio in the structure of **II** is 5:8, that is, more than 1:2, but no global layer curvature is observed. However, these layers contain significantly distorted regions with coordination environment of the K(1) atom very similar to those observed in structures with uranyl selenate nanotubes. We are inclined to ascribe the absence of the layer curvature to the presence of nitrate groups arranged in between the uranyl selenate layers and playing a considerable role in coordination of the K^+ ions. In addition, the position of nitrate anions inhibits the curvature electrostatically: apparently, the parallel orientation of the NO_3 groups favours repulsion between them and the layers, thus
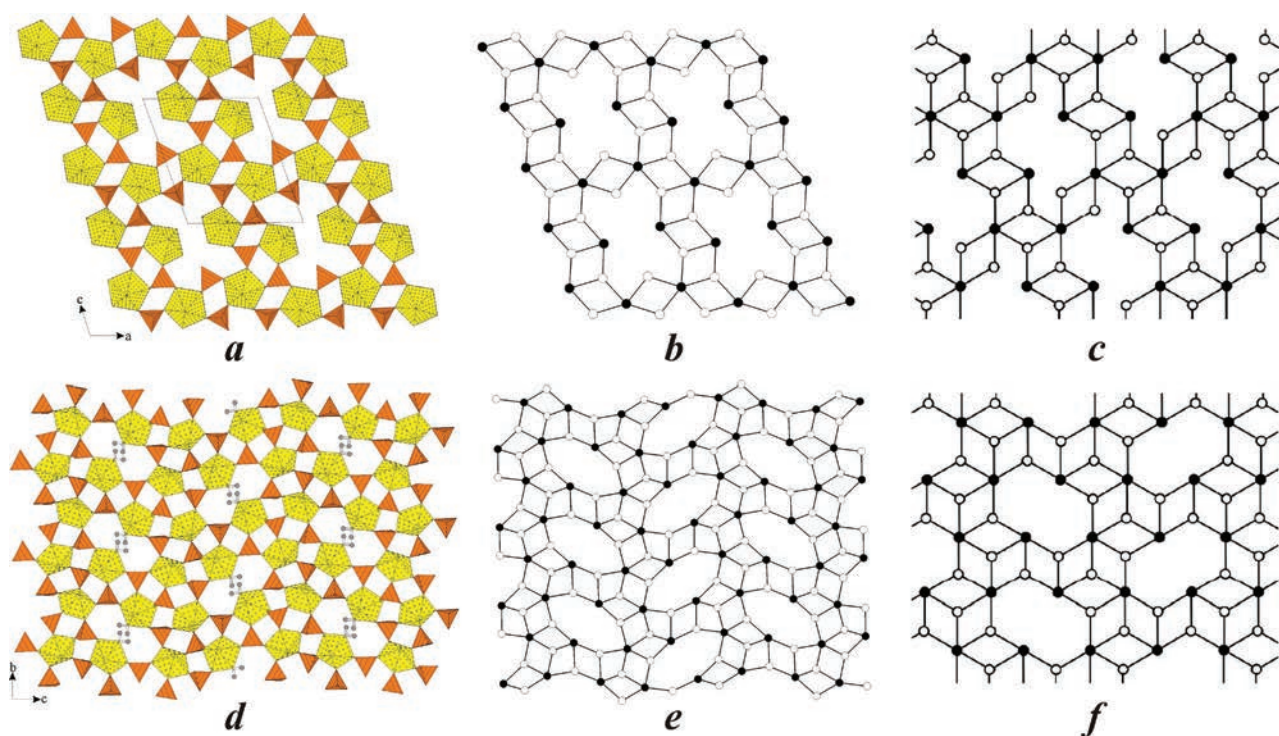
Fig. 4 Uranyl selenate layers in the structures of **I** (**a**) and **II** (**d**) and its real (**b** and **e**, respectively) and idealized (**c** and **f**, respectively) graphical representations.

supporting the flat architecture of uranyl selenate layers. It is interesting that the ratio $K:NO_3$ for the structure of $K_{2.5}(NO_3)_{0.5}[(UO_2)_2(SeO_4)_3(H_2O)] \cdot 4H_2O$ (**II**) is 5:1, i.e. the same as for the structure of $K_5[(UO_2)_3(SeO_4)_5](NO_3)(H_2O)_{3.5}$, which is based upon uranyl selenate nanotubules. However, the latter compound contains noticeably less water ($K:H_2O = 1:0.7$) compared to that observed in **II** ($K:H_2O = 1:1.6$), which may be considered a reason for the formation of layered instead of nanotubular structure. It is very probable that the relative amount of H_2O is of critical importance for the formation of particular structural topology. The synthesis of $K_5[(UO_2)_3(SeO_4)_5](NO_3)(H_2O)_{3.5}$ with the nanotubule-based structure was done at slightly elevated temperature (60 °C), which decreased the water amount in the structure.

Electronic supplementary material. Supplementary crystallographic data for this paper are available online at the Journal web site (http://dx.doi.org/10.3190/jgeosci.165).

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