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MINERALOGICAL CRYSTALLOGRAPHY

Crystal Chemistry of Selenates with Mineral-Like Structures: VIII. Butlerite Chains in the structure of $K(UO_2)(SeO_4)(OH)(H_2O)$

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Abstract—A new potassium uranyl selenate compound $K(UO_2)(SeO_4)(OH)(H_2O)$ has been synthesized for the first time using the technique of evaporation from water solution. Its crystal structure has been solved by direct methods (monoclinic, $P2_1/c$,a = 8.0413(9) Å, b = 8.0362(9) Å, c = 11.6032(14) Å, β = 106.925(2)°, V = 717.34(14) Å^3) and refined to R_1 = 0.0319 (wR_2 = 0.0824) for 1285 reflections with $|F_0| > 4\sigma_F$. The structure consists of $[(UO_2(SeO_4)(OH)(H_2O)]^-$ chains extending along axis b. In the chains, the uranyl pentagonal bipyramids are linked via bridged hydroxyl anions and tetrahedral oxoanions $[SeO_4]^{2-}$. Potassium ions are situated between these chains. No chains of that type have been observed in uranyl compounds earlier, but they had been detected in the structures of butlerite, parabutlerite, uklonskovite, fibroferrite, and a number of synthetic compounds.

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INTRODUCTION

In the previous papers of this series (Krivovichev, 2006a, 2006b, 2006c, 2006d, 2008a, 2008b, 2008c), the crystal structures of inorganic aluminum, magnesium, zinc, and uranyl selenates were described. In the structures of alunogen-type $[Al(H_2O)_6]_2(SeO_4)_3(H_2O)_4$ and $[Al(H_2O)_6](SeO_4)(NO_3)(H_2O)$ (Krivovichev, 2006a, 2006b), coordination polyhedrons of aluminum and selenate tetrahedrons are not linked to one another, whereas in the structures of $[Mg(H_2O)_4(SeO_4)]_2(H_2O)$, $Zn(SeO_4)(H_2O)_2$, $(H_3O)_2[(UO_2)(SeO_4)_2(H_2O)](H_2O)_2$, $(H_3O)_2[(UO_2)(SeO_4)_2(H_2O)](H_2O)$, $[(H_5O_2)(H_3O)(H_2O)][(UO_2)(SeO_4)_2]$, and $(H_3O)[(UO_2)(SeO_4)(SeO_2OH)]$, coordination polyhedrons of metals are combined with tetrahedral oxoanions $(SeO_4)^{2-}$ into one-, two-, and three-dimensional complexes (Krivovichev, 2006a, 2006d, 2008a, 2008b, 2008c). No direct link between coordination polyhedrons of metals via collectivization of bridged anions was, however, observed in any structure. In this paper, we present the results of investigation of a new compound, $K(UO_2)(SeO_4)(OH)(H_2O)$, where uranyl polyhedrons are linked to one another into one-dimensional chains added by selenate tetrahedrons according to the butlerite topological type.

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EXPERIMENTAL

Single crystals of $K(UO_2)(SeO_4)(OH)(H_2O)$ were obtained by evaporation of aqueous solution of uranyl, K selenate, and triethylenamine in a proportion of $UO_2(NO_3)_2 : K_2SeO_4 : (C_2H_5)_3N = 1 : 2 : 1$. Crystals of the compound also stably formed during other experiments involving these components. It is characteristic that triethylenamine molecules were not incorporated into crystallization products, probably due to the neutrality of the primary solution (pH ~7). Under these conditions, amine molecule are not protonated and do not play the role of structure-forming cations.

The unit-cell dimensions of $K(UO_2)(SeO_4)(OH)(H_2O)$ were determined using a Bruker SMART diffractometer equipped with a 1K CCD flat image plate detector and refined by the least squares procedure on the basis of 3916 unique reflections with 2θ = 5.2°–56.06° (Table 1). Extinction laws and statistics of reflection distribution correspond to space group $P2_1/c$. The absorption correction was introduced with regard for the shape of the crystal. The structure was solved by direct methods and refined to R_1 = 0.032 (wR_2 = 0.082) for 1285 reflections with $|F_0| > 4\sigma_F$. The final model involved the coordinates and anisotropic displacement parameters for all atoms (Table 2). Localization of hydrogen atoms failed. The interatomic distances are given in Table 3.

Table 1. Crystal data and refinement parameters of $K(UO_2)(SeO_4)(OH)(H_2O)$

Parameter	Value	Parameter	Value
a (Å)	8.0413(9)	Unique reflections	1600
b (Å)	8.362(9)	Measurement area 2θ, deg	5.2–56.06
c (Å)	11.6032(14)	Reflections with $\|F_0\| \geq 4\sigma_F$	1285
β (deg)	106.925(2)	R_{int}	0.0379
V (Å^3)	717.34(14)	R_σ	0.0543
Space group	$P2_1/c$	$R_1(\|F_0\| \geq 4\sigma_F)$	0.0319
μ, mm^{-1}	33.399	$wR_2(\|F_0\| \geq 4\sigma_F)$	0.0824
Z	4	R_1 (all data)	0.0468
D_{calc} (g/cm^3)	5.538	wR_2 (all data)	0.0862
Size of crystal, mm^3	0.18 × 0.14 × 0.08	S	1.024
Jrrediation	MoK_α	ρ_{min}, ρ_{max}, e/Å^3	–1.458, 1.772
Total reflections	3916		

Notes: $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, where $P = (F_0^2 - 2F_c^2)/3$; $S = \{\Sigma[w(F_0^2 - F_c^2)]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

RESULTS

The crystal structure of $K(UO_2)(SeO_4)(OH)(H_2O)$ contains one crystallographic nonequivalent U atom that forms two short bonds U^{6+}–O [1.770(7)–1.778(7) Å] making up uranyl cation UO_2^{2+}. In the equatorial plane, uranyl ion is surrounded by five anions with the formation of a pentagonal bipyramid typical of hexavelent uranium. Cation UO_2^{2+} is coordinated by two oxygen atoms pertaining to selenate groups (bond length U–O = 2.397(7)–2.423(7) Å), two hydroxyl groups (U–OH = 2.297(7)–2.378(7) Å), and one water molecule (U–H_2O = 2.494(8) Å). In the structure, there is one crystallographically independent selenium atom tetrahedrally coordinated by four oxygen atoms. Selenate tetrahedrons SeO_4 are bidentate-bridged. The bond length of bridged oxygen atoms is 1.617(7)–1.635(7) Å.The bond length of bridged oxygen atoms is shorter and ranges from 1.608(7) to 1.612(7) Å as is typical of tetrahedral oxoanions TO_4 (T = S, Cr, Se, Mo) in uranyl compounds (Krivovichev, 2004). A crystallographically independent K atom is coordinated by ten oxygen atoms in the structure (Table 3).

Table 2. Atomic coordinates and displacement parameters, Å^2 in the structure of $K(UO_2)(SeO_4)(OH)(H_2O)$

Atom	x	y	z	U_{eq}
U	0.07567(5)	0.10804(5)	0.29888(4)	0.01648(16)
Se	–0.29971(13)	0.23716(12)	0.03793(9)	0.0119(2)
K	–0.4382(3)	0.5323(3)	–0.2041(2)	0.0209(5)
O1	–0.2840(10)	0.4382(9)	0.0603(7)	0.0218(17)
O2	–0.0902(10)	0.0241(9)	0.3537(7)	0.0247(17)
O3	–0.3587(9)	0.2055(9)	–0.1051(6)	0.0188(16)
O4	–0.4416(10)	0.1722(10)	0.1011(6)	0.0263(18)
O5	0.2486(9)	0.1831(10)	0.2464(6)	0.0208(17)
OH6	0.0791(10)	–0.1398(8)	0.2010(7)	0.0198(17)
O7	–0.1133(10)	0.1490(9)	0.0961(7)	0.0221(17)
H_2O8	0.2153(11)	0.2735(10)	0.4835(7)	0.031(2)

The crystal structure is based on the $[(UO_2)(SeO_4)(OH)(H_2O)]^-$ chains, which consist of apex-sharing coordination polyhedrons of uranium and selenium (Fig. 1). In the chains, pentagonal bipyramids $[(UO_2)(SeO_4)(OH)(H_2O)]$ are linked by bridged hydroxyl anions and tetrahedral oxoanions $[SeO_4]^{2-}$. The chains are packed into lagers parallel to $(\bar{1}01)$ (Fig. 2).

Table 3. Selected interatomic distances, Å and angles, degree in the structure of $K(UO_2)(SeO_4)(OH)(H_2O)$

U–O2	1.770(7)	K–O2	2.718(8)
U–O5	1.778(7)	K–O3	2.721(7)
U–OH6	2.297(7)	K–O4	2.790(8)
U–OH6	2.378(7)	K–O3	2.866(7)
U–O1	2.397(7)	K–O5	2.867(7)
U–O7	2.423(7)	K–O4	2.939(8)
U–H_2O8	2.494(8)	K–O5	2.972(8)
⟨U–O_{Ur}⟩	1.774	K–O1	3.049(8)
⟨U–O_{eq}⟩	2.397	K–O1	3.162(8)
		K–H_2O8	3.294(8)
Se–O4	1.612(7)	⟨K–O⟩	2.938
Se–O3	1.608(7)		
Se–O7	1.617(7)	U–O6–U	131.1(3)
Se–O1	1.635(7)	U–O1–Se	132.6(4)
⟨Se–O⟩	1.618	U–O7–Se	134.0(4)

DISCUSSION

As a result of examination of the $K(UO_2)(SeO_4)(OH)(H_2O)$ structure, a new, previously unknown geometric type of the chain complex was revealed. This type is distinguished by a uranyl subcomplex with a one-dimensional bond chain … ellipsis –U–OH–U–OH–U–OH– … ellipsis, where neighboring uranyl ions are linked via bridged anions OH^-. It is noteworthy that the topological structure of selenate–uranyl chains is identical to that in the structures of butlerite, parabutlerite, uklonskovite, fibroferrite, and a number of synthetic compounds (Table 4). In the structures of these compounds, metal cations are octahedrally coordinated in contrast to the pentagonal bipyramidal coordination observed in $K(UO_2)(SeO_4)(OH)(H_2O)$. Metal octahedrons are linked via apexes into infinite chains encrusted by tetrahedral oxoanions according to graph shown in Fig. 1c. Note that the chain selenate–uranyl complexes with bridged hydroxyl anions were not previously observed and thus allow further extension of the topological diversity of uranyl complexes, providing insight into the basic features of self-organization of matter in actinide-bearing systems.

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Table 4. Minerals and inorganic compounds containing the butlerite-type chains

Mineral	Chemical formula	Space group	*a*, Å	*b*, Å/β, °	*c*, Å	Source
Butlerite	$[Fe(OH)(H_2O_2)_2(SO_4)]$	$P2_1/m$	6.50(1)	7.37(1)/108.38(8)	5.84(1)	Fanfani et al., 1971
Parabutlerite	$[Fe(OH)(H_2O_2)_2(SO_4)]$	$Pmnb$	7.38(2)	20.130(40)	7.22(1)	Borene, 1970
Uklonskovite	$Na[MgF(H_2O)_2(SO_4)]$	$P2_1/m$	7.202(1)	7.214(1)/113.23(1)	5.734(1)	Sabelli, 1981
Fibroferrite	$[Fe(OH)(H_2O)_5(SO_4)]$	$R\bar{3}$	24.17699	24.17699	7.656	Scordari, 1981
	$InOHSO_4(H_2O)_2$	$P2_1/m$	6.058(6)	7.894(7)/107.5(1)	12.665(12)	Johansson, 1961
	$Mn(OH)SO_4(H_2O)_2$	$P2_1/n$	10.63	7.12/97.69	7.149	Mereiter, 1979
	$NH_4(VO_2)(HPO_4)$	$Pbca$	6.8064(6)	9.2567(7)	17.732(2)	Amoros et al., 1988
	α-$NH_4(VO_2)(HPO_4)$	$Pb2_1a$	6.830(1)	9.233(2)	8.817(2)	Amoros and LeBail, 1992
	$K(VO_2)(HPO_4)$	$Pbca$	6.7550(3)	9.1026(4)	17.0808(6)	Amoros et al., 1988
	$Rb(VO_2)(HPO_4)$	$Pbca$	6.8182(8)	9.291(1)	17.631(2)	The same

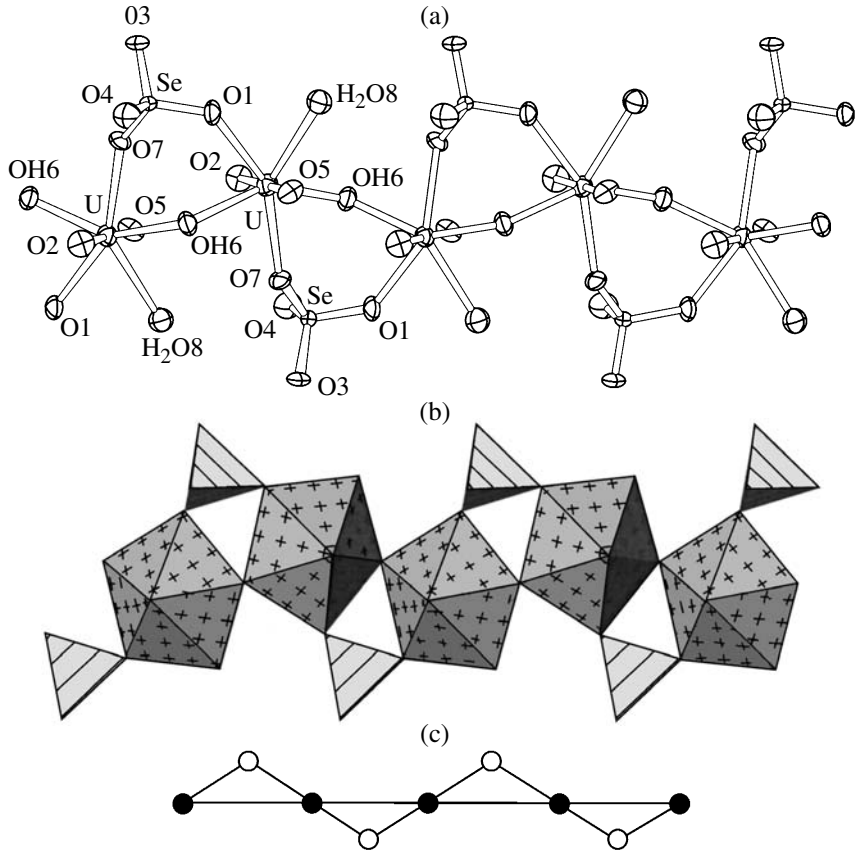

Fig. 1. Uranylselanate chain in the crystal structure of $K(UO_2)(SeO_4)(OH)(H_2O)$: (a) image in ellipsoids of atomic displacements (probability of 50%); (b) image in a polyhedral aspect (uranyl polyhedrons are marked by crosses, selenate tetrahedrons are lined); (c) topological structure of the chain shown as a graph (uranyl and selanate polyhedrons are shown by black and white apexes, respectively).

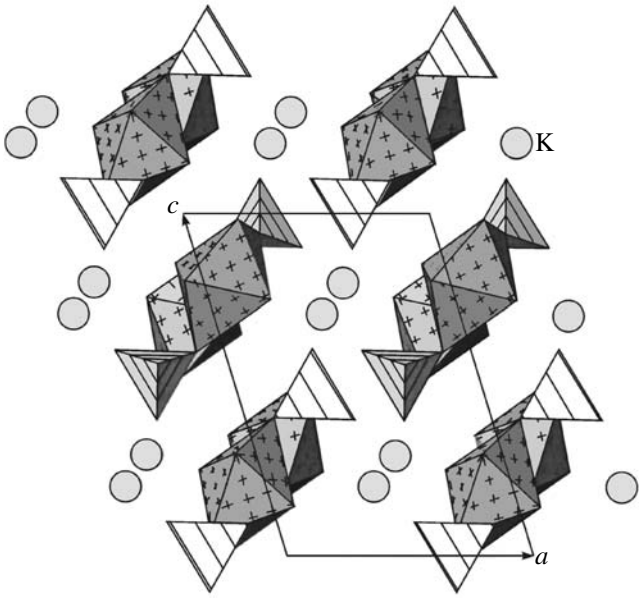

Fig. 2. Crystal structure of $K(UO_2)(SeO_4)(OH)(H_2O)$ projected along axis *b*.

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