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Synthesis and crystal structure of two new uranyl oxychloro-vanadate layered compounds: $M_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ with $M = \text{Rb}, \text{Cs}$

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Abstract

Two new alkali uranyl oxychloro vanadates $M_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ with $M = \text{Rb}, \text{Cs}$, have been synthesized by solid-state reactions and their structures determined from single-crystal X-ray diffraction data. They crystallize in the orthorhombic system with space groups $Pm\bar{c}n$ and $Pnmm$, respectively. The a and b unit cell parameters are almost identical in both compounds while the c parameter in the Rb compound is doubled: Rb— $a = 21.427(5) \text{ \AA}$, $b = 11.814(3) \text{ \AA}$, $c = 14.203(3) \text{ \AA}$, $V = 3595.1(1) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{mes}} = 5.93(2) \text{ g/cm}^3$, $\rho_{\text{cal}} = 5.82(1) \text{ g/cm}^3$; Cs— $a = 21.458(3) \text{ \AA}$, $b = 11.773(2) \text{ \AA}$, $c = 7.495(1) \text{ \AA}$, $V = 1893.6(5) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{mes}} = 6.09(2) \text{ g/cm}^3$, $\rho_{\text{cal}} = 6.11(1) \text{ g/cm}^3$. A full-matrix least-squares refinement yielded $R_1 = 0.0221$, $wR_2 = 0.0562$ for 2675 independent reflections and $R_1 = 0.0386$, $wR_2 = 0.1042$ for 2446 independent reflections, for the Rb and Cs compounds, respectively. Data were collected with $\text{Mo}(K\alpha)$ radiation and a charge coupled device (CCD) detector of a Bruker diffractometer. Both structures are characterized by $[(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}]_n^{7n-}$ layers parallel to the (001) plane. The layers are built up from VO_4 tetrahedra, UO_7 and UO_6Cl pentagonal bipyramids, and UO_6 distorted octahedra. The UO_7 and UO_6Cl pentagonal bipyramids are associated by sharing opposite equatorial edges to form infinite chains $(\text{UO}_5-\text{UO}_4\text{Cl}-\text{UO}_5)_n$ parallel to the a axis. These chains are linked together by VO_4 tetrahedra, UO_6 octahedra, UO_7 corner sharing and UO_6Cl , Cl sharing. Both structures differ simply by the symmetry of the layers. The unit cell contains one centrosymmetric layer in the Cs compound, whereas in the two-layer unit cell of the Rb compound, two non-centrosymmetric consecutive layers are related by an inversion center. The layers appear to be held together by the alkali ions. The mobility of the M^+ ions within the interlayer space in $M_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ and carnotite analog compounds is compared.

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1. Introduction

Our interest in uranyl compounds stems from their tendency to form layered structures of polyhedra of higher bond valence and to display exchange properties and good electrical ionic conductivity due to interlayer cation mobility. For example, hydrogen uranyl phosphate tetrahydrate $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (HUP) has been shown to have the best selective proton conductivity at room temperature and has received much attention because of its potential applications in electrochemical systems [1–4]. On the other hand, numerous studies on the synthesis and crystal structure determination of uranyl compounds were motivated because they form during the oxidation of uranium deposits and so their

knowledge is important to the environment [5–9]. Recently, new uranyl compound with low-dimensional inorganic architectures or open-framework structures were obtained by hydrothermal synthesis [10–14].

In most of the U^{6+} oxides, the approximately linear $(\text{U}^{6+}\text{O}_2)^{2+}$ uranyl ion is coordinated in the equatorial plane by four, five or six oxygen atoms to form rhombic, pentagonal or hexagonal bipyramids, respectively. The structure of the compounds can be often described as sheets of approximately parallel uranyl ions connected via coordinated oxygens of the sheets either directly or through oxo-anions such as $(\text{PO}_4)^{3-}$, $(\text{VO}_4)^{3-}$, $(\text{MoO}_4)^{2-}$, The crystal structure of several oxides containing uranyl ions is built from $(\text{UO}_5)_\infty$ zig-zag chains resulting from UO_7 pentagonal bipyramids sharing two opposite edges. The fifth oxygen atom of the pentagonal base alternates on both sides of the chain. Thus one unit cell parameter is twice the distance

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between the middle of two O–O bridges of one pentagon, that is to say $2 \times 3.8 = 7.6 \text{ \AA}$. The parallel $(\text{UO}_5)_\infty$ chains are connected together to form layers, either directly by corner sharing as in $\alpha\text{-U}_3\text{O}_8$ [15] or by VO_5 square pyramids in UVO_5 [16], by SbO_6 octahedra in USbO_5 [17], by ReO_3 -type slabs two octahedra wide in UMo_2O_8 [18], by divanadate groups in $\text{U}_2\text{V}_2\text{O}_{11}$ [19,20], by tetrahedra in $\text{U}_2\text{P}_2\text{O}_{10}$ [21], $\text{U}_3\text{V}_2\text{O}_{14} \cdot 5\text{H}_2\text{O}$ [22] and $\text{U}_3\text{P}_2\text{O}_{14} \cdot 4\text{H}_2\text{O}$ [23]. Finally in $M_6\text{U}_5\text{V}_2\text{O}_{23}$ ($M = \text{Na}, \text{K}$), the parallel chains are connected alternatively either by VO_4 tetrahedra or both by corner sharing and by UO_6 octahedra [24].

On the other hand, in several oxychloride compounds of uranyl, some of the atoms of the equatorial plane of coordination of the uranyl ion are chlorine atoms leading to UO_6Cl , UO_5Cl_2 , UO_4Cl_3 or UO_3Cl_4 pentagonal bipyramids. Both oxygen and chlorine are involved in the sharing between the pyramids. Similar zig-zag chains of edge shared pentagonal bipyramids are sometimes obtained as for example in uranyl chlorides UO_2Cl_2 [25] and $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ [26] in which $(\text{UO}_3\text{Cl}_2)_\infty$ chains are formed by sharing two opposite Cl–Cl edges between UO_3Cl_4 pentagonal bipyramids.

Our attempt to synthesize $\text{H}(\text{UO}_2)\text{VO}_4 \cdot x\text{H}_2\text{O}$ (HUV) led us to prepare a new compound $(\text{UO}_2)_3(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$ [22], which is a pentahydrated uranyl orthovanadate. Its structure shows $[(\text{UO}_2)(\text{VO}_4)]_n^{n-}$ sheets which are bridged together by other uranyl groups. This material was employed in excess fused salt for ion exchange reactions to prepare other new layered compounds. In potassium chloride, the reaction is not a simple exchange but single crystals of a new layered phase $\text{K}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$ were obtained [24]. Its sodium analogous has been synthesized and studied too [24]. Curiously, in melted rubidium or cesium chloride the reactions are different and lead to single crystals of two new layered compounds $M_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ ($M = \text{Rb}, \text{Cs}$). In this paper we describe the synthesis and the crystal structure of these compounds built from zig-zag chains of oxygen bridged UO_7 and UO_6Cl pentagonal bipyramids, the chlorine atom being substituted for $\frac{1}{3}$ of the fifth non-shared oxygen of the $(\text{UO}_5)_\infty$ chains.

2. Experimental

2.1. Synthesis

$\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ was prepared as a yellow powder by reacting a mixture of $\text{UO}_3 \cdot \text{H}_2\text{O}$ (Prolabo Rectapur, 8 mol), V_2O_5 (Aldrich, 1 mol), CsCl (Aldrich, 1 mole) and Cs_2CO_3 (Aldrich, 3 mol) in a shaken aqueous suspension (500 ml of water), at 60°C , during 4 days in air. The solution was evaporated to near dryness and the precipitate transferred to an alumina

boat. The boat is then placed in a furnace at 450°C for 12 h to improve the crystallization of the product. The product of reaction was identified by X-ray powder diffraction using a Guinier–Dewolff focusing camera and $\text{CuK}\alpha$ radiation. Attempts to prepare this compound by a solid-state reaction between the stoichiometric mixture preheated at 300°C in air to dehydrate the uranium trioxide and afterwards heated at different temperatures between 625°C and 725°C during a maximum time of 15 days with several intermediate grindings failed, the X-ray pattern of the compound was always accompanied by weak unidentified reflections.

Pure $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ powder was prepared both by solid-state reaction at 600°C , under air, from the quaternary mixtures U_3O_8 (Merck), V_2O_5 , RbCl (Merck), Rb_2CO_3 (Aldrich) in molar ratios 2.67:1:1:3 and by reaction of stoichiometric mixture in shaken aqueous suspension heated at 60°C during 4 days. In this second method, uranium is introduced as hydrated trioxide $\text{UO}_3 \cdot 1\text{H}_2\text{O}$ and a yellow amorphous powder is obtained after dry evaporation. By heating at 600°C , during one half-day, the powder became well crystallized and the X-ray diffraction pattern is identical to that of crushed single crystals.

$\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ crystals were obtained by heating in a platinum crucible a mixture of CsCl and $(\text{UO}_2)_3(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$ prepared as described in (11) in a 30:1 molar ratio at 750°C for 2 h. The mixture was cooled by cutting off the furnace. The product of the reaction was washed with water to remove CsCl excess and filtered, giving an homogeneous sample containing yellow single crystals of the title compound. The same process was used to obtain yellow single crystals of $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ except the heating time at 750°C (4 days) and the cooling rate ($5^\circ\text{C}/\text{h}$).

2.2. Structure determinations

For X-ray structure determinations well-shaped crystals of $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ ($0.13 \times 0.24 \times 0.035 \text{ mm}^3$) and $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ ($0.12 \times 0.018 \times 0.32 \text{ mm}^3$) were selected. Preliminary film methods indicated for both compounds an orthorhombic symmetry. Systematic absences of $hk0$ ($h+k=2n+1$) revealed $Pm2_1n$ or $Pmnm$ space group for Cs compound. For Rb, the $P2_1cn$ and $Pmcn$ possible space groups were deduced from systematic absences $hk0$ ($h+k=2n+1$) and $h0l$ ($l=2n+1$). The crystal structures were solved in the centrosymmetric space groups $Pmmm$ and $Pmcn$, respectively.

Room temperature single-crystal X-ray diffraction intensity data collections were carried out on a Bruker Smart charge coupled device (CCD) diffractometer (graphite-monochromated $\text{MoK}\alpha$ radiation) for both Cs and Rb compounds. Crystal data, conditions of data

collection, and structure refinement parameters are reported in Table 1. The unit cell parameters were also refined by a least-squares procedure from the indexed powder diffraction patterns of crushed single crystals, collected with a Siemens D5000 diffractometer (CuK α radiation) equipped with a back end monochromator and corrected for K α_2 contribution. The figures of merit, as defined by Smith and Snyder [27], were $F_{20} = 39.00$ (0.0102, 41) and 41.25 (0.0101, 48) for the Cs and Rb compounds, respectively.

The densities measured with an automated Micromeritics Accupyc 1330 helium pycnometer using a 1-cm³ cell indicated $Z = 2$ formula per unit cell ($\rho_{\text{exp}} = 6.09(2)$ g cm⁻³, and $\rho_{\text{cal}} = 6.11(1)$ g cm⁻³) for the Cs compound and $Z = 4$ ($\rho_{\text{exp}} = 5.93(2)$ g cm⁻³, $\rho_{\text{cal}} = 5.82(1)$ g cm⁻³) for the Rb compound.

The measured intensities were corrected for Lorentz and polarization effects and for absorption, using the analytical method of Demeulenaer and Tompa [28]. The structures were solved by direct methods using SHELXTL program [29] that localize the heavy U atoms. The positions of V, Cs or Rb, Cl and O were deduced from subsequent refinements and difference Fourier syntheses. Neutral-atom scattering factors were taken from the ‘‘International Tables for X-ray Crystallography’’ [30] and the values for the anomalous dispersion correction from Cromer and Liberman [31]. Refinement of atomic coordinates and anisotropic displacement parameters for all the atoms yielded to final $R_1 = 0.0386$ and $wR_2 = 0.1042$ for 2446 independent reflections for the Cs compound and to $R_1 = 0.0221$ and $wR_2 = 0.0562$ for 2675 independent

Table 1
Crystal data, intensity collection and structure refinement parameters for $M_7(\text{UO}_2)_8(\text{VO}_4)_2\text{ClO}_8$ ($M = \text{Cs, Rb}$)

	$M = \text{Cs}$		$M = \text{Rb}$	
<i>Crystal data</i>				
Crystal symmetry	Orthorhombic		Orthorhombic	
Space group	$Pm\bar{m}n$		$Pm\bar{c}n$	
Unit cell refined from	$a = 21.458(3)$ Å		$21.427(5)$ Å	
Single-crystal data	$b = 11.773(2)$ Å		$11.814(3)$ Å	
	$c = 7.495(1)$ Å		$14.203(3)$ Å	
	$V = 1893.6(5)$ Å ³		$3595.1(1)$ Å ³	
Z	2		4	
Calculated density	$\rho = 6.11(1)$ g cm ⁻³		$5.82(1)$ g cm ⁻³	
Measured density	$\rho = 6.09(2)$ g cm ⁻³		$5.93(2)$ g cm ⁻³	
<i>Data collection</i>				
Temperature (K)	293(2)		293(2)	
Equipment	Bruker SMART CCD		Bruker SMART CCD	
Radiation MoK α	0.71073 Å		0.71073 Å	
Scan mode	ω		ω	
Recording θ min/max (deg)	1.90/30.02		2.44/23.30	
Recording reciprocal space	$-29 \leq h \leq 29$		$-23 \leq h \leq 23$	
	$-16 \leq k \leq 16$		$-13 \leq k \leq 13$	
	$-10 \leq l \leq 10$		$-15 \leq l \leq 15$	
No. of measured reflections	13709		21554	
No. of independent reflections	2446		2675	
μ (cm ⁻¹) (for $\lambda_{K\alpha} = 0.71073$ Å)	413.38		459.76	
Limiting faces and distances (mm)	1 0 0	0.070	1 0 0	0.059
From an arbitrary origin	$\bar{1}$ 0 0	0.059	$\bar{1}$ 0 0	0.059
	0 1 0	0.141	$\bar{1}$ 5 0	0.148
	0 $\bar{1}$ 0	0.095	1 $\bar{5}$ 0	0.171
	0 0 1	0.018	0 0 1	0.014
	0 0 $\bar{1}$	0.017	0 0 $\bar{1}$	0.004
Transmission factor range	0.020–0.280		0.006–0.202	
R merging factor	0.056		0.057	
<i>Refinement</i>				
Refined parameters/restraints	133/0		239/0	
Goodness of fit on F^2	1.093		1.004	
R_1 [$I > 2\sigma(I)$]	0.0386		0.0221	
wR_2 [$I > 2\sigma(I)$]	0.1042		0.0562	
R_1 for all data	0.0401		0.0284	
wR_2 for all data	0.1064		0.0589	
Largest diff. peak and hole (e Å ⁻³)	2.66/–2.06		1.49/–1.51	

$$R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|, \quad wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}, \quad w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], \quad \text{where } a \text{ and } b \text{ are refinable parameters and } P = (F_o^2 + 2F_c^2)/3.$$

Table 2

Atomic positions and equivalent isotropic displacement parameters for Cs₇(UO₂)₈(VO₄)₂ClO₈

Atom	Site	x	y	z	U _{eq} (Å ²)
U(1)	8g	0.57574(2)	0.55698(3)	0.05215(5)	0.015(1)
U(2)	4e	$\frac{3}{4}$	0.46318(5)	0.05185(8)	0.017(1)
U(3)	4f	0.59516(2)	$\frac{1}{4}$	0.00261(8)	0.014(1)
Cs(1)	8g	0.14952(4)	0.55827(7)	0.44917(9)	0.032(1)
Cs(2)	4f	0.47685(8)	$\frac{1}{4}$	0.46155(15)	0.036(1)
Cs(3)	2a	$\frac{1}{4}$		0.23858(30)	0.061(1)
V	4f	0.8376(1)	$\frac{1}{4}$	0.2287(4)	0.017(1)
Cl	2b	$\frac{3}{4}$		-0.1273(9)	0.043(2)
O(1)	4f	0.8334(6)	$\frac{1}{4}$	0.446(1)	0.035(3)
O(2)	8g	0.8145(3)	0.8762(7)	0.134(1)	0.024(2)
O(3)	4f	0.9163(4)	$\frac{3}{4}$	0.163(2)	0.018(2)
O(4)	8g	0.5916(4)	0.5991(8)	-0.177(1)	0.027(2)
O(5)	8g	0.5623(4)	0.5254(7)	0.284(1)	0.024(2)
O(6)	8g	0.5248(3)	0.3931(7)	-0.014(1)	0.022(2)
O(7)	8g	0.6500(3)	0.4139(7)	0.022(1)	0.022(2)
O(8)	4e	$\frac{3}{4}$	0.5121(9)	-0.178(2)	0.036(3)
O(9)	4e	$\frac{3}{4}$	0.4101(9)	0.277(2)	0.031(3)
O(10)	4f	0.5929(5)	$\frac{1}{4}$	0.245(2)	0.023(2)
O(11)	4f	0.5985(6)	$\frac{1}{4}$	-0.245(2)	0.026(2)

Note. The U_{eq} values are defined by $U_{eq} = \frac{1}{3}(\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j)$.

reflections for the Rb compound. The atomic positions and equivalent isotropic displacement parameters are reported in Tables 2 and 3 for Cs and Rb compounds, respectively. The refined anisotropic displacement parameters are given in Tables 4 and 5.

Investigations of the electrical properties were carried out on cylindrical pellets (diameter, 5 mm; thickness, ca. 3 mm) obtained using a conventional cold press and sintered at 650°C for 12 h in a gold-foil boat. Gold electrodes were vacuum-deposited on both flat surfaces of the pellets. Conductivity measurements were carried out by ac impedance spectroscopy over the range 1–10⁶ Hz with a Solartron 1170 frequency-response analyzer. Measurements were at 20°C intervals over the range 200–700°C on both heating and cooling. Each set of values was recorded at a given temperature after a 1-h stabilization time.

3. Description of the structures and discussion

Table 6 provides for Cs₇(UO₂)₈(VO₄)₂O₈Cl the most significant distances, angles and bond valence sums. In the crystal structure of Cs₇(UO₂)₈(VO₄)₂O₈Cl, uranium atoms occupy three independent crystallographic sites U(1), U(2), and U(3). Uranium are each bonded to two oxygen atoms at short distances, O(4) and O(5) for U(1), O(8) and O(9) for U(2), O(10) and O(11) for U(3), respectively, forming nearly linear (176°, 178° and 179°, respectively) uranyl ions UO₂²⁺. Uranyl ion U(1)O₂²⁺ and U(2)O₂²⁺ are surrounded in the equatorial plane by a pentagonal environment of oxygen atoms for U(1) and

Table 3

Atomic positions and equivalent displacement isotropic parameters U_{eq} for Rb₇(UO₂)₈(VO₄)₂ClO₈

Atom	Site	x	y	z	U _{eq} (Å ²)
U(1)	8d	0.57659(1)	-0.06975(3)	0.72130(3)	0.014(1)
U(2)	8d	0.42407(1)	0.04271(3)	0.77138(3)	0.014(1)
U(3)	4c	$\frac{1}{4}$	-0.04901(4)	0.76955(4)	0.013(1)
U(4)	4c	$\frac{3}{4}$	0.01922(4)	0.72247(4)	0.013(1)
U(5)	8d	0.59418(2)	0.23636(3)	0.75110(2)	0.013(1)
Rb(1)	8d	0.65356(4)	0.04582(8)	0.97171(7)	0.026(1)
Rb(2)	8d	0.64659(4)	0.07853(7)	0.47639(7)	0.025(1)
Rb(3)	8d	0.52352(5)	-0.24395(9)	0.98065(8)	0.040(1)
Rb(4)	4c	$\frac{1}{4}$	0.23530(11)	0.63240(11)	0.041(1)
V	8d	0.66204(7)	-0.26681(11)	0.63341(12)	0.015(1)
Cl	4c	$\frac{1}{4}$	-0.2660(3)	0.6796(3)	0.024(1)
O(1)	8d	0.6693(4)	-0.2751(7)	0.5182(6)	0.031(2)
O(2)	8d	0.6857(3)	-0.1391(6)	0.6819(5)	0.024(2)
O(3)	8d	0.6858(3)	-0.3903(6)	0.6892(6)	0.024(2)
O(4)	8d	0.5835(3)	-0.2648(5)	0.6667(6)	0.017(2)
O(5)	8d	0.5661(3)	-0.0407(6)	0.5961(5)	0.022(2)
O(6)	8d	0.5905(3)	-0.1090(6)	0.8433(5)	0.019(2)
O(7)	8d	0.5248(3)	0.0931(6)	0.7553(5)	0.019(2)
O(8)	8d	0.4748(3)	-0.1212(6)	0.7377(5)	0.018(2)
O(9)	8d	0.6502(3)	0.0717(6)	0.7371(5)	0.019(2)
O(10)	8d	0.4354(3)	0.0110(6)	0.8950(5)	0.022(2)
O(11)	8d	0.4104(3)	0.0860(6)	0.6505(6)	0.025(2)
O(12)	8d	0.3502(3)	-0.0991(6)	0.7538(5)	0.017(2)
O(13)	4c	$\frac{1}{4}$	-0.0968(9)	0.8900(7)	0.020(2)
O(14)	4c	$\frac{1}{4}$	0.0007(9)	0.6479(7)	0.021(2)
O(15)	4c	$\frac{1}{4}$	-0.0311(8)	0.8445(7)	0.017(2)
O(16)	4c	$\frac{1}{4}$	0.0720(9)	0.6036(8)	0.028(3)
O(17)	8d	0.5917(4)	0.2392(6)	0.6228(6)	0.024(2)
O(18)	8d	0.5967(4)	0.2309(6)	0.8805(6)	0.020(2)

Note. The U_{eq} values are defined by $U_{eq} = \frac{1}{3}(\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j)$.

Table 4

Anisotropic displacement parameters (Å² × 10³) for Cs₇(UO₂)₈(VO₄)₂ClO₈

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
U(1)	5(1)	18(1)	20(1)	1(1)	-1(1)	0(1)
U(2)	4(1)	27(1)	20(1)	-2(1)	0	0
U(3)	7(1)	17(1)	19(1)	0	0(1)	0
Cs(1)	24(1)	46(1)	25(1)	5(1)	0(1)	-2(1)
Cs(2)	19(1)	59(1)	29(1)	0	4(1)	0
Cs(3)	98(2)	50(1)	35(1)	0	0	0
V	6(1)	23(1)	23(1)	0	1(1)	0
Cl	25(3)	31(3)	73(5)	0	0	0
O(1)	31(7)	54(8)	22(6)	0	6(5)	0
O(2)	13(3)	25(4)	35(5)	4(3)	2(3)	0(3)
O(3)	5(4)	24(5)	26(6)	0	2(4)	0
O(4)	20(4)	39(5)	22(4)	9(4)	-2(3)	2(3)
O(5)	15(3)	33(4)	25(4)	1(4)	-2(3)	1(3)
O(6)	11(3)	21(3)	34(4)	2(3)	-5(3)	3(3)
O(7)	4(3)	27(4)	35(5)	-5(3)	2(3)	1(3)
O(8)	24(6)	61(9)	23(6)	5(6)	0	0
O(9)	16(5)	35(6)	42(8)	8(6)	0	0
O(10)	20(5)	29(6)	20(6)	0	-14(4)	0
O(11)	32(6)	30(6)	15(5)	0	3(5)	0

Note. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2 a^*^2 U_{11} + \dots + 2hka^* b^* U_{12}]$.

Table 5
Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{ClO}_8$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	8(1)	10(1)	22(1)	0(1)	0(1)	0(1)
U(2)	8(1)	11(1)	23(1)	0(1)	1(1)	-1(1)
U(3)	7(1)	11(1)	21(1)	0(1)	0	0
U(4)	7(1)	11(1)	21(1)	1(1)	0	0
U(5)	9(1)	9(1)	21(1)	-1(1)	0(1)	0(1)
Rb(1)	21(1)	31(1)	27(1)	3(1)	1(1)	-2(1)
Rb(2)	22(1)	27(1)	27(1)	4(1)	-1(1)	0(1)
Rb(3)	26(1)	63(1)	31(1)	8(1)	-6(1)	-7(1)
Rb(4)	82(2)	17(1)	26(1)	1(1)	0	0
V	9(1)	11(1)	26(1)	-1(1)	0(1)	1(1)
Cl	21(2)	10(2)	40(3)	1(2)	0	0
O(1)	36(5)	39(5)	17(5)	2(3)	4(4)	2(4)
O(2)	14(3)	19(4)	38(5)	-6(4)	2(3)	-2(3)
O(3)	9(3)	21(4)	43(5)	4(4)	-3(3)	2(3)
O(4)	10(4)	13(3)	29(5)	1(3)	2(3)	0(3)
O(5)	22(4)	21(4)	24(4)	0(3)	-6(3)	-1(3)
O(6)	18(3)	30(4)	9(4)	0(3)	0(3)	-4(3)
O(7)	6(3)	11(4)	39(5)	-2(3)	7(3)	-1(3)
O(8)	14(4)	10(4)	30(4)	0(3)	4(3)	-1(3)
O(9)	10(4)	7(4)	41(5)	-5(3)	-2(3)	2(3)
O(10)	19(4)	22(4)	25(4)	3(3)	-2(3)	0(3)
O(11)	20(4)	25(4)	30(5)	5(4)	2(3)	-5(3)
O(12)	9(3)	10(4)	32(4)	1(3)	2(3)	-1(3)
O(13)	20(5)	29(6)	12(5)	6(5)	0	0
O(14)	11(5)	30(6)	21(6)	5(5)	0	0
O(15)	19(5)	14(5)	18(6)	-5(4)	0	0
O(16)	19(5)	30(6)	34(7)	2(5)	0	0
O(17)	33(5)	23(4)	15(5)	-5(3)	-2(4)	-1(3)
O(18)	24(4)	23(4)	15(4)	0(3)	-1(3)	-2(3)

Note. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

four oxygen atoms and one chlorine atom for U(2). Thus, the coordination polyhedra of U(1) and U(2) are pentagonal bipyramids UO_7 and UO_6Cl , respectively. The U(3)O_2^{2+} uranyl ion is surrounded in the equatorial plane by four oxygen atoms, U(3) coordination polyhedron is thus a strongly distorted UO_6 octahedron. The pentagonal bipyramid is the most common environment for U^{6+} ions in oxides. The pentagonal bipyramids are either isolated or related by corner and/or edge sharing in the equatorial plane to form different chains or sheets. Linear one-dimensional chains most usually met results from sharing two opposite pentagonal edges (Fig. 1a). Several compounds where chlorine atoms participate to the uranium equatorial coordination are known leading to $(\text{UO}_2)_4\text{O}_4\text{Cl}_1$, $(\text{UO}_2)_3\text{O}_3\text{Cl}_2$, $(\text{UO}_2)_2\text{O}_2\text{Cl}_3$ pentagonal bipyramidal geometries, for example, in $\text{U}_5\text{O}_{12}\text{Cl}$ [32], UO_2Cl_2 [24] and $\text{Cs}_x(\text{UO}_2)\text{OCl}_x$ ($x \approx 0.9$) [33]. Once again, in anhydrous uranyl chloride UO_2Cl_2 [25] and in uranyl chloride monohydrate $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ [26] linear chains are formed by Cl–Cl edge-sharing (Fig. 1b). In $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ the U(1)O_7 and $\text{U(2)O}_6\text{Cl}$ bipyramids are connected only by O–O edges to form linear chains

Table 6
Bond distances (\AA), UO_2 angles (deg) and bond valences for $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{ClO}_8$

U–O	d (\AA)	s_{ij}	U–O	d (\AA)	s_{ij}
U(1)–O(4)	1.820(8)	1.564	U(2)–O(8)	1.816(9)	1.567
U(1)–O(5)	1.800(8)	1.613	U(2)–O(9)	1.799(9)	1.622
U(1)–O(6)	2.272(8)	0.653	U(2)–O(7)	2.234(7)	0.703
U(1)–O(6) $_{110}^{\text{ii}}$	2.254(7)	0.676	U(2)–O(7) $_{000}^{\text{iii}}$	2.234(7)	0.703
U(1)–O(7)	2.330(7)	0.584	U(2)–O(2) $_{010}^{\text{iv}}$	2.423(8)	0.489
U(1)–O(2) $_{110}^{\text{ii}}$	2.558(7)	0.376	U(2)–O(2) $_{110}^{\text{iii}}$	2.423(8)	0.489
U(1)–O(3) $_{100}^{\text{iii}}$	2.426(3)	0.485	U(2)–Cl	2.846(3)	0.349
Σs_{ij}		5.951	Σs_{ij}		5.922
U–O					
U(3)–O(10)	1.817(9)	1.564			
U(3)–O(11)	1.857(9)	1.462	UO_2 angles		
U(3)–O(6)	2.266(8)	0.661	O(4)–U(1)–O(5)		176(1)
U(3)–O(6) $^{\text{v}}$	2.266(8)	0.661	O(8)–U(2)–O(9)		178(1)
U(3)–O(7) $^{\text{v}}$	2.265(8)	0.662	O(10)–U(3)–O(11)		179(1)
U(3)–O(7)	2.265(8)	0.662			
Σs_{ij}		5.738			
Cs–O (Cl)			Cs–O		
Cs(1)–O(5) $_{110}^{\text{iv}}$	2.911(8)	0.265	Cs(2)–O(10)	2.972(9)	0.224
Cs(1)–O(11) $_{110}^{\text{iv}}$	2.939(9)	0.243	Cs(2)–O(3) $_{111}^{\text{iv}}$	3.099(9)	0.160
Cs(1)–O(9) $_{111}^{\text{iv}}$	3.000(9)	0.207	Cs(2)–O(4) $_{110}^{\text{iv}}$	3.140(8)	0.141
Cs(1)–O(4) $_{110}^{\text{iv}}$	3.023(8)	0.194	Cs(2)–O(4) $_{110}^{\text{v}}$	3.140(8)	0.141
Cs(1)–O(8) $_{110}^{\text{ii}}$	3.077(9)	0.168	Cs(2)–O(1) $_{111}^{\text{v}}$	3.155(9)	0.136
Cs(1)–O(10) $_{110}^{\text{iv}}$	3.439 (9)	0.063	Cs(2)–O(5) $_{111}^{\text{ii}}$	3.367(9)	0.077
Cs(1)–O(7) $_{110}^{\text{iv}}$	3.547(9)	0.047	Cs(2)–O(5) $_{111}^{\text{v}}$	3.367(9)	0.077
Cs(1)–O(1) $_{111}^{\text{ii}}$	3.731(9)	0.029	Cs(2)–O(11) $_{001}^{\text{v}}$	3.413(9)	0.067
Cs(1)–Cl	3.945(4)	0.045			
Σs_{ij}		1.261	Σs_{ij}		1.023
Cs–O					
Cs(3)–O(8) $_{110}^{\text{ii}}$	2.837(9)	0.321			
Cs(3)–O(8) $_{110}^{\text{vi}}$	2.837(9)	0.321			
Cs(3)–O(1) $_{111}^{\text{ii}}$	2.965(9)	0.227	V–O		
Cs(3)–O(1) $_{111}^{\text{v}}$	2.965(9)	0.227	V–O(1)	1.631(8)	1.592
Cs(3)–O(2) $_{110}^{\text{ii}}$	3.453(9)	0.061	V–O(2)	1.720(8)	1.248
Cs(3)–O(2) $_{110}^{\text{iv}}$	3.453(9)	0.061	V–O(2) $_{010}^{\text{v}}$	1.720(8)	1.248
Cs(3)–O(2) $_{110}^{\text{v}}$	3.453(9)	0.061	V–O(3)	1.759(9)	1.126
Cs(3)–O(2) $_{110}^{\text{iii}}$	3.453(9)	0.061			
Σs_{ij}		1.340	Σs_{ij}		1.340

Symmetry codes: (ii) $-x, -y, -z$; (iii) $\frac{1}{2}-x, y, z$; (iv) $\frac{1}{2}+x, -y, -z$; (v) $x, \frac{1}{2}-y, z$; (vi) $-x, \frac{1}{2}+y, -z$; (vii) $\frac{1}{2}-x, \frac{1}{2}-y, z$; (viii) $\frac{1}{2}+x, \frac{1}{2}+y, -z$. Note: $\text{O}(n)_{pq}^m$ represent atom $\text{O}(n)$ to which the symmetry m has been applied, followed by a translation $pa + qb + rc$.

running along the a -axis of the unit cell with the sequence U(1)–U(2)–U(1) , thus the non-bridging equatorial atoms succeed one another on each side of the chain according to the sequence O(3)–O(3)–Cl (Fig. 1c). The odd number of atoms in this sequence implies that chlorine atoms alternate on both sides of the chain, so the basic unit of the chain is formed from six bipyramids and the corresponding a parameter is close to $6 \times 3.8 \text{\AA}$. Two successive parallel chains are related by an m mirror in the (010) plane containing the Cl and O(3) atoms which are so shared between chains to form a sheet of pentagonal bipyramids parallel to the (001)

plane (Fig. 2). The sheet has a pseudo-hexagonal symmetry, the ratio a/b of the corresponding C-centered base is close to $\sqrt{3}$ (1.82). This arrangement creates very distorted hexagonal rings better described as a rhombic

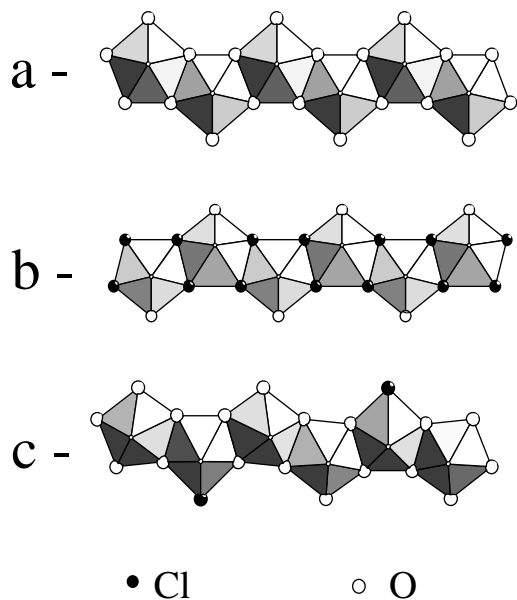


Fig. 1. (a) $[\text{UO}_5]_\infty$ linear one-dimensional chain built from edge-sharing UO_7 pentagonal bipyramids that extends down the c -axis for example in UVO_5 (5), (b) $[\text{UO}_3\text{Cl}_4]_\infty$ linear one-dimensional chain built from edge-sharing UO_3Cl_4 pentagonal bipyramids that extends down the b -axis in UO_2Cl_2 (13), (c) $[\text{U}_3\text{O}_{14}\text{Cl}]_\infty$ linear one-dimensional chain built from edge-sharing UO_7 and UO_6Cl_1 pentagonal bipyramids that extends down the a -axis in $M_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ ($M = \text{Rb}, \text{Cs}$) compounds.

site flanked by two triangular sites which are of two types, O_6 and O_5Cl . The rhombic site for the O_5Cl ring is occupied by $\text{U}(3)$ atom when the triangular sites are empty. Conversely, the rhombic site for the O_6 ring is empty when the two triangular sites are occupied by vanadium atoms. The $\text{U}(3)$ atoms belongs to an uranyl ion approximately parallel to the $\text{U}(1)\text{O}_2$ and $\text{U}(2)\text{O}_2$ uranyl ions. So the coordination around $\text{U}(3)$ is a distorted octahedron. Finally sheets of formula $\text{U}_8\text{V}_2\text{O}_{32}\text{Cl}^{7-}$ are formed (Fig. 3). The Cs^+ ions are located in the available space between the layers (Fig. 4).

It is interesting to compare the uranyl vanadate sheets in $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$, to those in $M_6\text{U}_5\text{V}_2\text{O}_{23}$ ($M = \text{Na}, \text{K}$) compounds [24] and $\text{U}_3\text{V}_2\text{O}_{14} \cdot 5\text{H}_2\text{O}$ [22] (Fig. 5). In $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ all the linear one-dimensional chains are related two–two by a mirror symmetry and are connected only by corner sharing, on the opposite in $\text{U}_3\text{V}_2\text{O}_{14} \cdot 5\text{H}_2\text{O}$ they are related only by translations and are connected by VO_4 tetrahedra, finally in $M_6\text{U}_5\text{V}_2\text{O}_{23}$ ($M = \text{Na}, \text{K}$) compounds both situations coexist, the direct connection between two plane symmetry-related chains is limited to two chains leading to ribbons which are linked together by VO_4 tetrahedra. O_6 rings are also formed in the ribbons, the rhombic site is occupied by an U atom when the triangular sites are empty.

The crystal structure of $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ is very similar to that of $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$. Table 7 provides the most significant distances, angles and bond valence sums. The main differences concern the symmetry elements connecting the basic blocks of the structure. First, in the Cs compound the

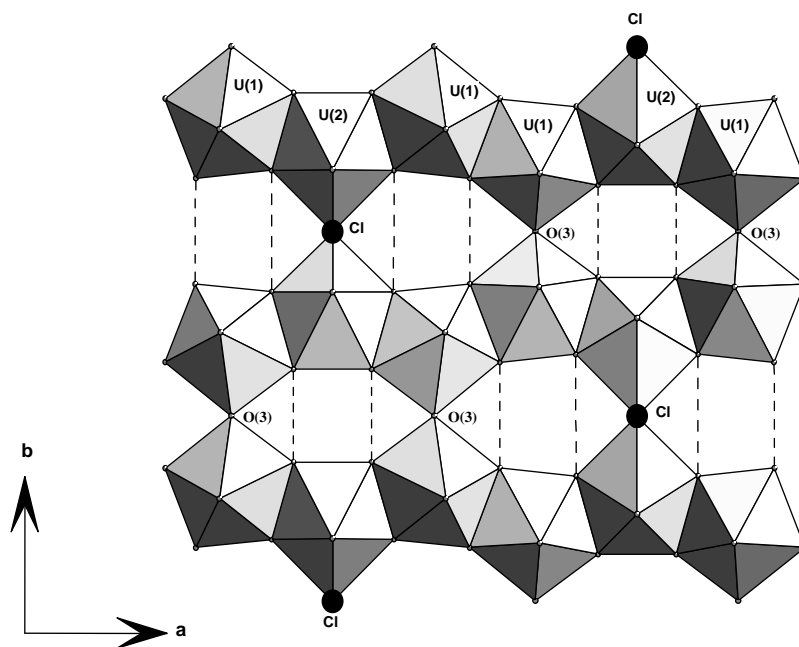


Fig. 2. Pseudo-hexagonal layer built from UO_7 and UO_6Cl_1 pentagonal bipyramids in $M_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ ($M = \text{Rb}, \text{Cs}$) compounds: two parallel $[\text{U}_3\text{O}_{14}\text{Cl}]$ linear one-dimensional chains are connected by Cl and $\text{O}(3)$ atoms and creates very distorted hexagonal rings.

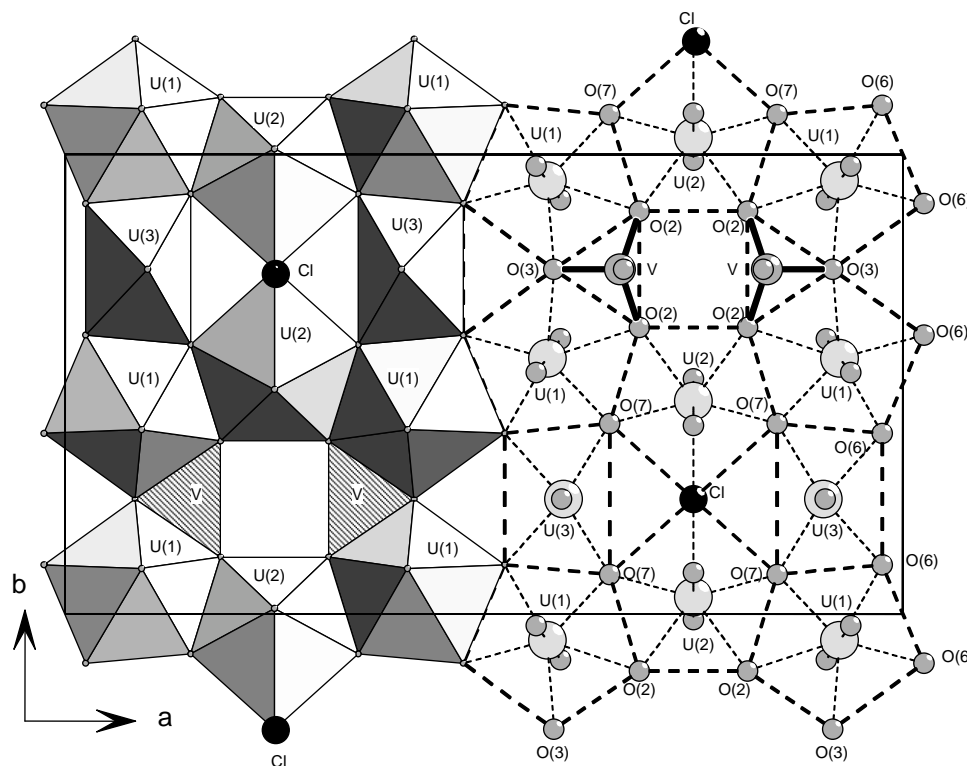


Fig. 3. Projection of the crystal structure of $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ on the (001) plane showing the connection between the polyhedra and the labeled scheme.

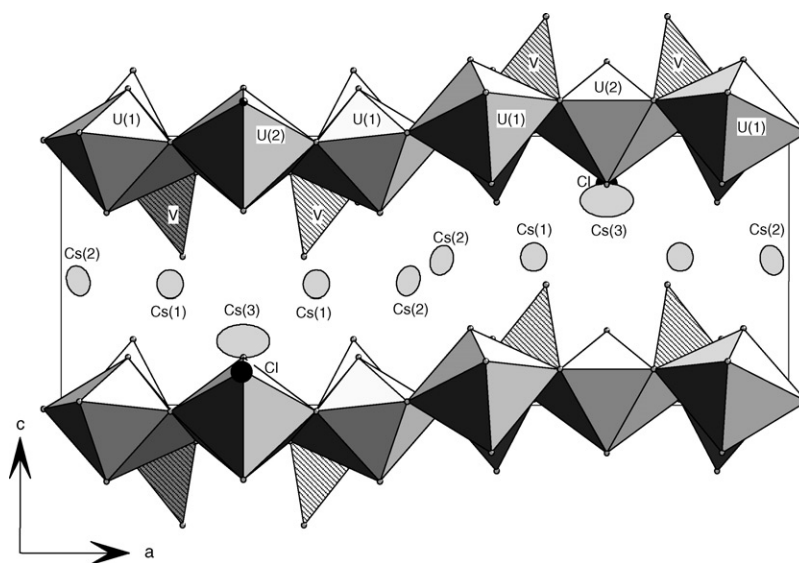


Fig. 4. Projection of the crystal structure of $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ on the (010) plane showing the $\text{U}_8\text{V}_2\text{O}_{32}\text{Cl}^{7-}$ layers stacked along c and interlayer Cs atoms.

one-dimensional $\text{U}(\text{O},\text{Cl})_5$ chains are built from one-type of $\text{U}(1)\text{U}(2)\text{U}(1)$ trinuclear entity possessing a m -mirror symmetry element containing $\text{U}(2)$ and Cl atoms, two successive trinuclear entities are related by an inversion center, in the Rb compound two successive trinuclear entities (which the m -mirror symmetry element containing $\text{U}(3)$, $\text{U}(4)$ and Cl) are crystallographi-

cally independent, $\text{U}(1)\text{U}(4)\text{U}(1)$ and $\text{U}(2)\text{U}(3)\text{U}(2)$ (Fig. 6). Second, while in the Cs compound two parallel chains are related by the m mirror perpendicular to b and containing the Cl atom, in the Rb compound they are related by the n plane perpendicular to c . As a consequence, the $\text{U}(5)\text{O}_6$ rhombic entity loses the m symmetry present in the $\text{U}(2)\text{O}_6$ entity of the Cs

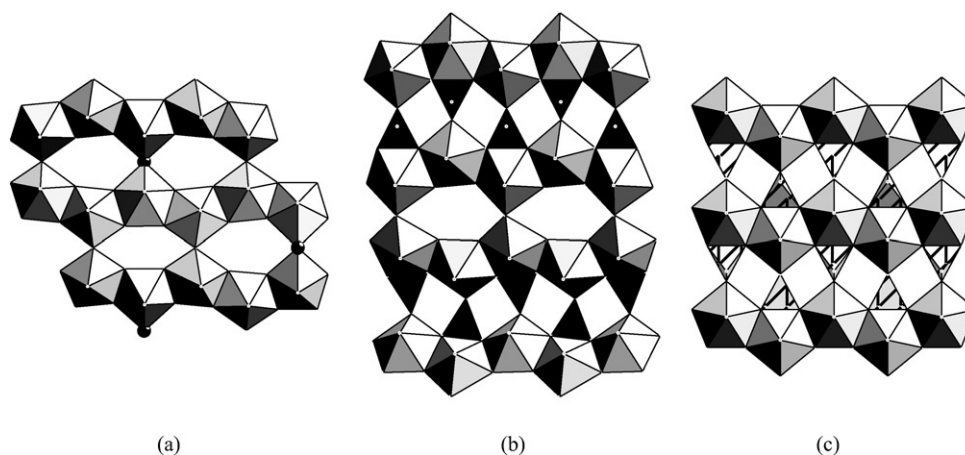


Fig. 5. Representation of the linkage between one-dimensional pentagonal chains (a) by corner-sharing in $M_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ ($M = \text{Rb}, \text{Cs}$) compounds, (b) both by corner-sharing and through VO_4 tetrahedra in $M_6\text{U}_5\text{V}_2\text{O}_{23}$ ($M = \text{Na}, \text{K}$) compounds and (c) only by VO_4 tetrahedra in $\text{U}_3\text{V}_2\text{O}_{14} \cdot 5\text{H}_2\text{O}$.

compound. So, there are five independent uranium atoms in the Rb compound instead three in the Cs compound. Finally, two successive layers deduct one from the other by c lattice translation for the Cs compound and by c glide-reflection plane for the Rb compound leading to a doubling of the c parameter for the Rb unit cell (Fig. 7).

In the two compounds the layers are slightly corrugated. The mean plane equations were calculated for the equatorial atoms of the uranyl groups.¹ For the octahedral uranium atoms the mean planes are nearly parallel to the (001) plane (5.7° and 5.5° for the Cs and Rb compounds, respectively), while for the other uranium atoms the angle between the mean plane and (001) one is in the range 16.5 – 23.3° . As a consequence only the $\text{U}(3)\text{O}_2$ and $\text{U}(5)\text{O}_2$ uranyl ions are perpendicular to the (001) plane in the Cs and Rb compounds, respectively.

The uranyl-ion bond lengths range from 1.799(9) to 1.857(9) Å with an average value of 1.82 Å. The uranyl-ion bond lengths are insensitive to the number and the chemical nature of the equatorial atoms. The infrared spectrum revealed strong and sharp band at about 865 cm^{-1} assignable to the asymmetric stretching frequency of the $\text{O}=\text{U}=\text{O}$ uranyl group. Application of Veal et al.'s equation [34], relating bond length (R) to the asymmetric stretching frequency (ν) for uranyl groups:

$$R = (81.2/\nu^{2/3}) + 0.895.$$

leads to a predicted uranyl bond length of 1.79 Å, in good agreement with the values calculated from X-ray structure results. The uranyl-ion bond angles are close to 180° for UO_6 and UO_6Cl polyhedra, in contrast, in

the UO_7 polyhedra, the uranyl-ion bond angles, although being close to linear, show a tendency to be distorted away from 180° , this could be due to different amounts of electrostatic repulsion from the equatorial anions. The remaining equatorial oxygen ligands show significant variation for UO_7 polyhedra with U–O distances ranging from 2.254(7) to 2.558(7) Å for $\text{U}(1)\text{O}_7$ bipyramid in the Cs-compound and from 2.273(7) to 2.540(7) Å and 2.251(7) to 2.546(6) Å for $\text{U}(1)\text{O}_7$ and $\text{U}(2)\text{O}_7$, respectively, in the Rb compound, the largest values corresponds to the oxygens strongly bonded to V atoms. For the UO_6Cl bipyramids, the equatorial U–O bond lengths are 2.234(7) Å ($\times 2$) and 2.423(8) Å ($\times 2$) in the Cs-compound and 2.238(7)–2.398(7) Å and 2.236(7)–2.393(7) Å for $\text{U}(3)$ and $\text{U}(4)$, respectively, in the Rb compound, once again the largest values correspond to oxygen atoms shared with V atoms. The U–Cl distances for the UO_6Cl polyhedra (average value, 2.87 Å) are slightly higher than usual, 2.73–2.75 Å in UO_2Cl_2 (25), 2.75–2.80 Å in $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (26), 2.70 Å in $\text{U}_5\text{O}_{12}\text{Cl}$ (32), 2.75 Å in $(\text{UO}_2)_2(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_4$ [35], however, longest distances have already been observed for example, 2.87 Å in $\text{K}_2(\text{UO}_2)_4\text{O}_2(\text{OH})_2\text{Cl}_4(\text{H}_2\text{O})_6$ [36] and 2.98 Å in $\text{Cs}_x(\text{UO}_2)\text{OCl}_x$ [33]. Finally, for the UO_6 distorted octahedra the equatorial U–O bond lengths are significantly shorter than for UO_7 and UO_6Cl bipyramids (average 2.267 Å) and in good accordance with the average value calculated for 16 UO_6 polyhedra that contain typical uranyl anions, 2.28(5) Å [37], the range is also very narrowed (2.245–2.294 Å) and the observed distances correspond to the lower distances obtained for the other U polyhedra. The $\text{U}(3)$ –Cl (Cs-compound) and the $\text{U}(5)$ –Cl (Rb compound) bonds are long (3.462(2) and 3.481(1) Å, respectively) and chlorine atoms definitively do not play a role in the coordination, especially since they are very outside of the mean plane

¹The mean-plane equations are available upon request from the authors.

Table 7
Bond distances (Å), UO₂ angles (deg) and bond valences for Rb₇(UO₂)₈(VO₄)₂ClO₈

U–O	<i>d</i> (Å)	<i>s_{ij}</i>	U–O	<i>d</i> (Å)	<i>s_{ij}</i>
U(1)–O(5)	1.825(8)	1.549	U(2)–O(10)	1.812(7)	1.585
U(1)–O(6)	1.818(7)	1.564	U(2)–O(11)	1.815(8)	1.576
U(1)–O(7)	2.273(7)	0.653	U(2)–O(7)	2.251(7)	0.682
U(1)–O(8)	2.276(7)	0.649	U(2)–O(8)	2.272(7)	0.653
U(1)–O(9)	2.309(7)	0.608	U(2)–O(12)	2.318(7)	0.597
U(1)–O(4)	2.436(6)	0.476	U(2)–O(4) ₁₀₁ ^{vii}	2.444(6)	0.470
U(1)–O(2)	2.540(7)	0.389	U(2)–O(3) ₁₀₁ ^{vii}	2.546(6)	0.385
Σ <i>s_{ij}</i>		5.888	Σ <i>s_{ij}</i>		5.948
U–O			U–O		
U(3)–O(13)	1.802(9)	1.616	U(4)–O(16)	1.800(9)	1.625
U(3)–O(14)	1.825(9)	1.546	U(4)–O(15)	1.832(9)	1.525
U(3)–O(12)	2.238(7)	0.697	U(4)–O(9)	2.236(7)	0.519
U(3)–O(12) ₁₀₁ ^{vi}	2.238(7)	0.697	U(4)–O(9) ₁₀₁ ^{vi}	2.236(7)	0.519
U(3)–O(3) ₁₀₁ ^{vii}	2.398(7)	0.512	U(4)–O(2) ₁₀₀ ^{vi}	2.393(7)	0.517
U(3)–O(3) ₁₀₁ ^{iv}	2.398(1)	0.512	U(4)–O(2)	2.393(7)	0.517
U(3)–Cl	2.864(4)	0.335	U(4)–Cl ₁₀₁ ^{iv}	2.894(4)	0.309
Σ <i>s_{ij}</i>		5.915	Σ <i>s_{ij}</i>		5.895
U–O			UO ₂ angles		
U(5)–O(17)	1.823(8)	1.552	O(5)–U(1)–O(6)		175(1)
U(5)–O(18)	1.840(8)	1.505	O(10)–U(2)–O(11)		175(1)
U(5)–O(8) ₁₀₁ ^{vii}	2.245(7)	0.687	O(13)–U(3)–O(14)		180(1)
U(5)–O(7)	2.253(7)	0.676	O(15)–U(4)–O(16)		179(1)
U(5)–O(12) ₁₀₁ ^{vii}	2.281(7)	0.642	O(17)–U(5)–O(18)		179(1)
U(5)–O(9)	2.294(7)	0.627			
Σ <i>s_{ij}</i>		5.689			
Rb–O			Rb–O		
Rb(1)–O(10) ₁₀₂ ⁱⁱ	2.769(7)	0.253	Rb(2)–O(5)	2.802(7)	0.231
Rb(1)–O(18)	2.818(7)	0.221	Rb(2)–O(18) ₁₀₀ ^{viii}	2.840(7)	0.209
Rb(1)–O(15)	2.891(7)	0.182	Rb(2)–O(16)	2.860(8)	0.197
Rb(1)–O(13) ₁₀₂ ⁱⁱ	2.914(7)	0.171	Rb(2)–O(11) ₁₀₁ ⁱⁱ	2.918(8)	0.169
Rb(1)–O(6)	2.914(7)	0.171	Rb(2)–O(14) ₁₀₁ ⁱⁱ	2.984(7)	0.142
Rb(1)–O(1) ₁₀₀ ^{viii}	3.283(8)	0.063	Rb(2)–O(17)	3.051(8)	0.117
Rb(1)–O(9)	3.347(8)	0.053	Rb(2)–O(12) ₁₀₁ ⁱⁱ	3.279(7)	0.064
Rb(1)–Cl ₁₀₁ ^{vii}	3.719(3)	0.056	Rb(2)–Cl ₁₀₁ ⁱⁱ	3.837(3)	0.041
Σ <i>s_{ij}</i>		1.170	Σ <i>s_{ij}</i>		1.170
Rb–O			Rb–O		
Rb(3)–O(17) ₁₁₁ ^{vii}	2.880(8)	0.188	Rb(4)–O(15) ₁₀₁ ^{iv}	2.780(9)	0.246
Rb(3)–O(6)	2.899(7)	0.171	Rb(4)–O(14)	2.779(9)	0.245
Rb(3)–O(4) ₁₀₀ ^{viii}	2.940(8)	0.159	Rb(4)–O(1) ₁₀₁ ⁱⁱ	2.791(8)	0.239
Rb(3)–O(11) ₁₁₁ ^{vii}	3.084(7)	0.108	Rb(4)–O(1) ₁₀₁ ^v	2.791(8)	0.239
Rb(3)–O(5) ₁₀₀ ^{viii}	3.161(7)	0.087	Rb(4)–O(3) ₁₀₁ ^{iv}	3.242(8)	0.070
Rb(3)–O(1) ₁₀₂ ^{viii}	3.177(9)	0.084	Rb(4)–O(3) ₁₀₀ ⁱⁱⁱ	3.242(8)	0.070
Rb(3)–O(18) ₁₀₂ ^{iv}	3.248(8)	0.068	Rb(4)–O(2) ₁₀₁ ^{iv}	3.325(8)	0.056
Rb(3)–O(10) ₁₀₂ ⁱⁱ	3.386(7)	0.048	Rb(4)–O(2) ₁₀₁ ^{viii}	3.325(8)	0.056
Σ <i>s_{ij}</i>		0.9210	Σ <i>s_{ij}</i>		1.221
V–O					
V–O(1)	1.646(8)	1.520			
V–O(2)	1.734(7)	1.205			
V–O(3)	1.737(7)	1.199			
V–O(4)	1.748(7)	1.163			
Σ <i>s_{ij}</i>		0.9210			

Symmetry codes: (ii) $-x, -y, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $\frac{1}{2}+x, -y, -z$; (vi) $\frac{1}{2}-x, y, z$; (vii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

Note. O(*n*)_{paq}^{*m*} represent atom O(*n*) to which the symmetry *m* has been applied, followed by a translation $pa + qb + rc$.

of the equatorial oxygen atoms (1.139(4) and 1.308(4) for Cs and Rb compounds, respectively).

While in other uranyl vanadates such as U₃V₂O₁₄·5H₂O (22) and M₆U₅V₂O₂₃ (M = Na, K) [24] the VO₄ tetrahedra participate in the connection of chains sharing an edge with one pentagonal bipyramid of one chain and a vertex with a bipyramid of an other chain, in M₇(UO₂)₈(VO₄)₂O₈Cl compounds VO₄ tetrahedra are not indispensable to the forming of sheets and only come to strengthen the solidity of these sheets, sharing two edges with two UO₇ polyhedra already connected by sharing an oxygen atoms. Thus, the two pentagonal bipyramids and the VO₄ tetrahedron form a condensed cluster with short U–V distances [3.221(2) Å for U(1)–V in Cs-compound and 3.214(1) Å and 3.209(1) Å for U(1)–V and U(2)–V, in Rb compound]. The competitiveness between the bonds do that the valence electrons are less available for the V–O bond when the oxygen atom is already engaged in U–O bond leading to three V–O distances with the bridging oxygen (in the range 1.720(8)–1.759(9) Å) significantly larger than the V–O bond with the O(1) atom not involved in the formation of the layer (1.631(8) and 1.646(8) Å for the Cs and the Rb compounds, respectively). Fig. 8 compares the VO₄ tetrahedra in different uranyl vanadate sheets. The V–O bond with the non-bridging oxygen atom is directed towards the interlayer space and the corresponding O(1) oxygen participates only in the coordination of some alkaline ions (Cs(1), Rb(4) and more weakly Rb(1) and Rb(3)). The strong distortion of the VO₄ tetrahedra is also represented by angles deviating strongly from 109.7°, particularly the O–O edges shared between VO₄ and UO₇ polyhedra are shorter (2.651(10) Å for the Cs-compound, for example) than the other edges which are not shared, according to the theory of Pauling [38] and Baur [39], so the corresponding O–V–O angles are particularly lower than 109.7°.

Bond valence sums calculated using Brese and O'Keeffe's data [40] with $b = 0.37$ Å except for U–O bonds where the coordination independent parameters ($R_{ij} = 2.051$ Å, $b = 0.519$ Å) were taken from Burns et al. [37] are reported in Tables 6 and 7 for Cs and Rb compounds respectively. These results are consistent with formal valences of U⁶⁺ and V⁵⁺. The values obtained for the six-coordinated U atoms although a little bit weak are in good agreement with the maximum of distribution of bond valence sums which is in the range 5.7–5.8 vu [37].

The Cs ions are distributed into three crystallographic sites: Cs(1) is coordinated by six uranyl-ion oxygen atoms, five at distances ranging from 2.911(8) to 3.077(9) Å and the sixth at longer distance 3.439(9) Å, the average distance, 3.06 Å is in good accordance with $r_{\text{Cs}^+}^{\text{VI}} + r_{\text{O}^{2-}}^{\text{IV}} = 3.05$ Å [41]. Cs(2) is coordinated by eight oxygen atoms at distances ranging from 2.972(9) to

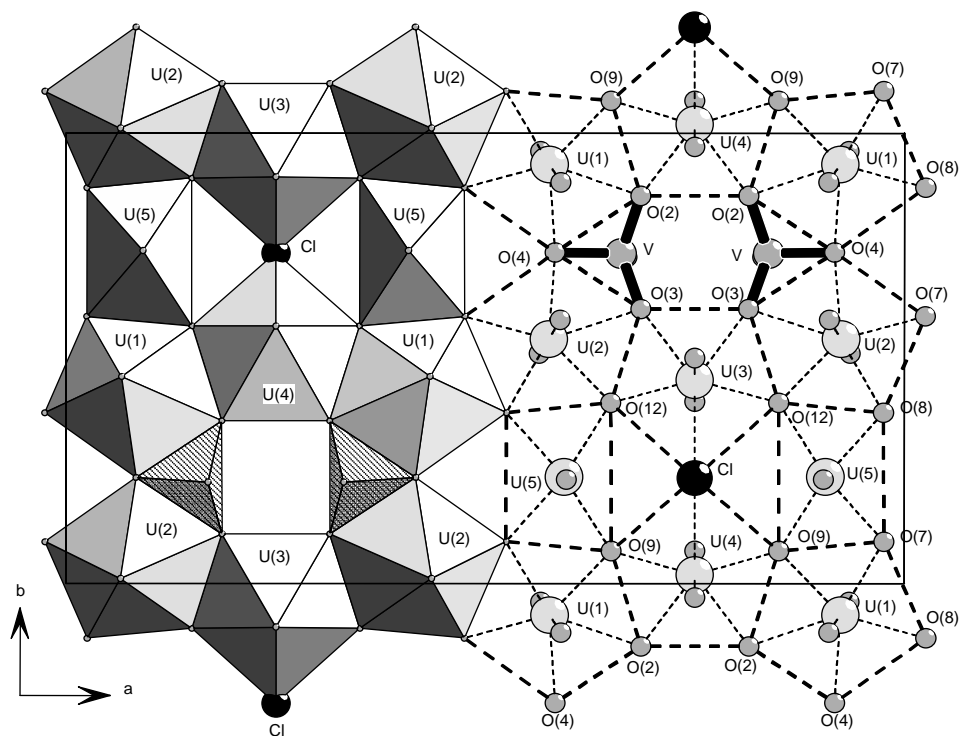


Fig. 6. Projection of the crystal structure of $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ on the (001) plane showing the connection between the polyhedra and the labeled scheme.

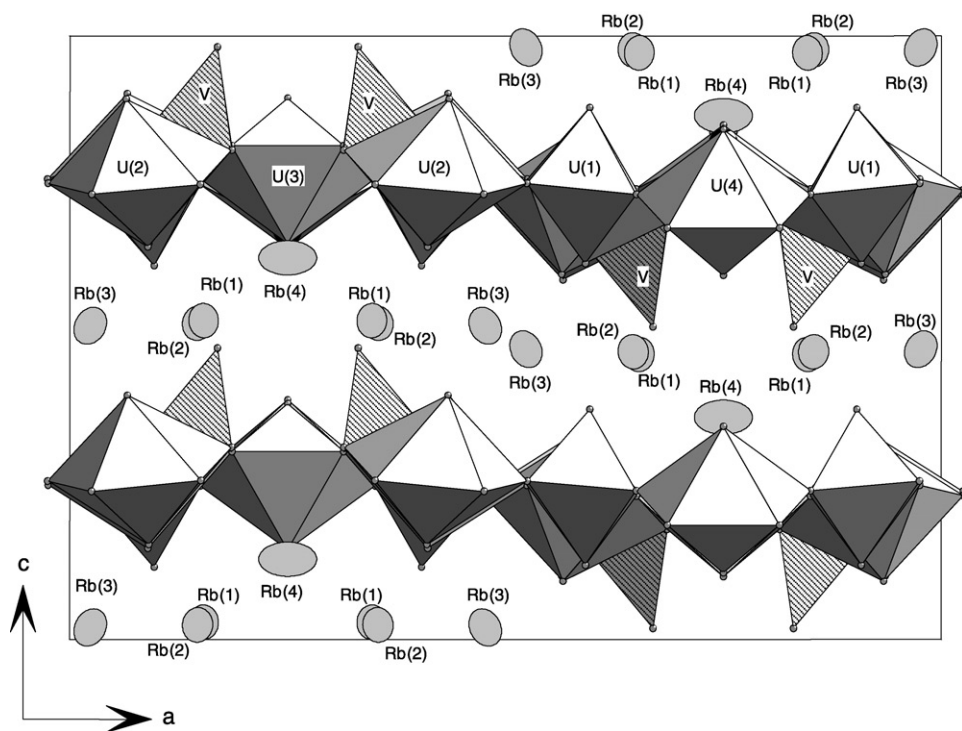


Fig. 7. Projection of the crystal structure of $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ on the (010) plane showing the $\text{U}_8\text{V}_2\text{O}_{32}\text{Cl}^{7-}$ layers stacked along c and interlayer Rb atoms.

$3.413(9) \text{ \AA}$, six uranyl-ion oxygen atoms, one O(1) atom which strongly bonded to V and one O(3) that participates to the layer formation. Eight oxygen atoms

form a very distorted cube around Cs(3) with four short distances, $2.837(9) (2 \times) \text{ \AA}$ with two O(8) atoms of $\text{U}(2)\text{O}_2$ uranyl-ions and $2.965(9) (2 \times) \text{ \AA}$ with two O(1)

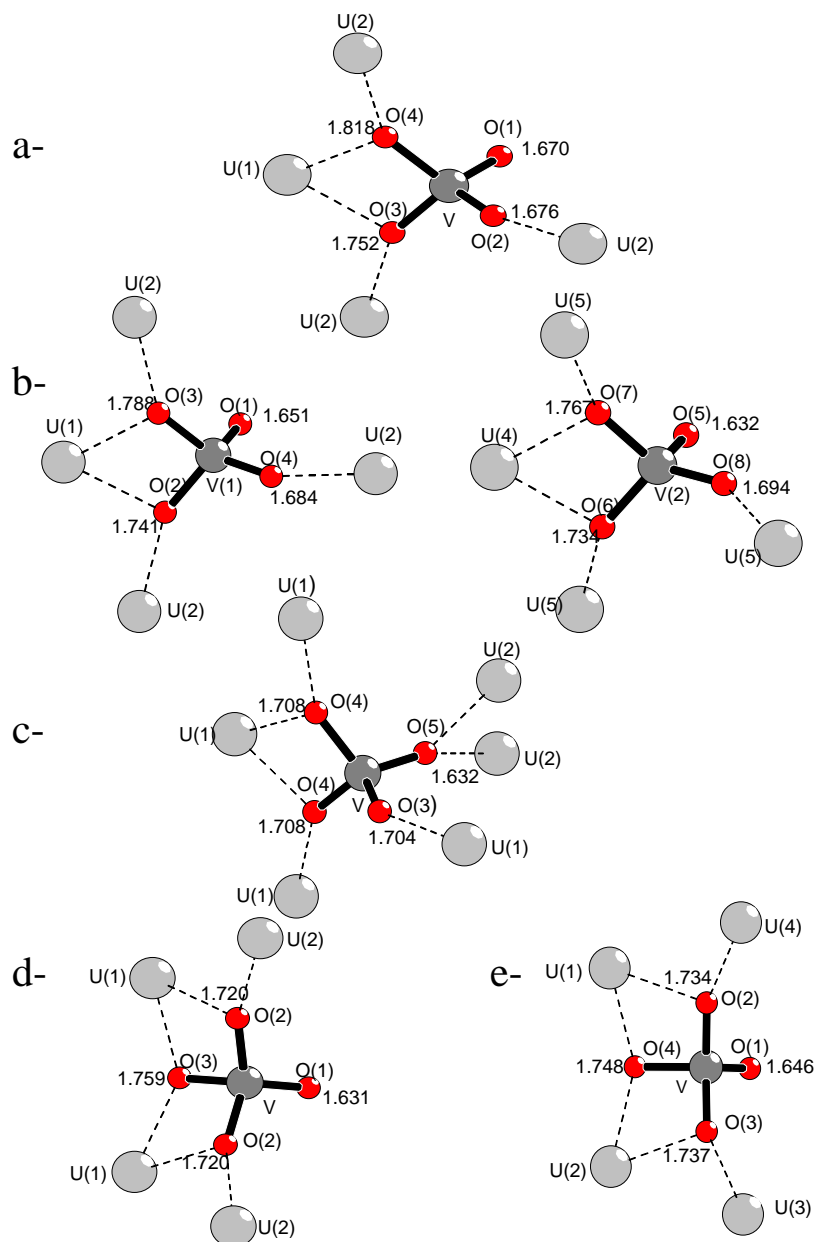


Fig. 8. A schematic representation of VO_4^{3-} tetrahedra in uranyl-vanadates showing the values of V–O distances for sharing and non-sharing oxygen atoms: (a) in $\text{K}_6\text{U}_5\text{V}_2\text{O}_{23}$, (b) in $\text{Na}_6\text{U}_3\text{V}_2\text{O}_{23}$, (c) in $\text{U}_3\text{V}_2\text{O}_{14} \cdot 5\text{H}_2\text{O}$, (d) in $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$, and (e) in $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$.

atoms that pertains only to VO_4 tetrahedra, and four longer, 3.453(9) ($4 \times$) Å, with O(2) atoms shared between two uranium polyhedra and one VO_4 tetrahedron. The Cs(3) atom is overbonded (Table 6) and the atomic displacement is high along the [100] direction, one can imagine that the Cs(3) atom is moved on both sides by the m -mirror in the (100) plane to increase the Cs–O(8) distances. The same observation can be made for the Rb(4) atom in $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$.

The layered structure of $M_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ allows us to consider some mobility of the alkali metals ions. Fig. 9 indicates the temperature dependence of the

conductivity of Rb and Cs compounds. For the two compounds, the variation vs. temperature agrees with an Arrhenius law over the studied temperature range. The conduction activation energy is 0.81 and 0.83 eV for Rb and Cs compounds, respectively, with a logical but weak better conductivity of about a factor of 2 for Rb compound, understandable by the mobility and cation size. Conductivity variations with temperature of two other layered uranyl vanadate compounds in which Cs ions are in the interlayer, the Cs carnotite, $\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$, and $\text{CsUV}_3\text{O}_{11}$ [42], are also reported in Fig. 9 for comparison. The conductivity properties of these two

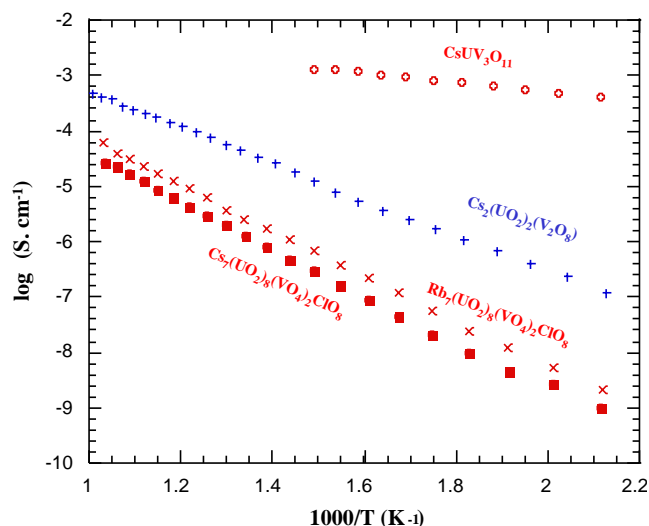


Fig. 9. Temperature dependence of conductivity of $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ and $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$. For comparison the conductivity vs. temperature for two other layered uranyl vanadates containing Cs in the interlayer space are reported.

compounds are significantly better. For the Cs carnotite, the same activation energy (0.83 eV) is observed but the conductivity values are increased by a factor 100. For $\text{CsUV}_3\text{O}_{11}$ better conductivity values are obtained associated with a lower activation energy (0.18 eV). In these two compounds the vanadium coordination is a square pyramid and the role of vanadium polyhedra are different, they link together the UO_7 or UO_8 bipyramids to form planar layers. On the contrary in the present compound the O(1) atoms of the VO_4 tetrahedra are directed towards the interlayer space and come to obstruct the conduction path.

4. Conclusion

The reaction of uranyl orthovanadate $(\text{UO}_2)_3(\text{VO}_4)_2$ in large excess of molten cesium or rubidium chlorides led to single-crystals growth of new layered compounds $M_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ with $M = \text{Cs}$ and Rb . This result differs from the one obtained with analog conditions in sodium or potassium chloride, the layered compounds being $M_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$ ($M = \text{Na}, \text{K}$). The two structures have been solved from single crystals. Unit cells are orthorhombic with space group $Pmnm$ and $Pm\bar{c}n$, respectively. In $\text{Cs}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ the unit cell contains one centrosymmetric uranyl vanadate layer whereas in $\text{Rb}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ the layers are almost similar but no centrosymmetric; the unit cell is double and thus contains two layers related by an inversion center. One common feature to the crystal structure of the starting uranyl vanadate and the Na or K oxyvanadate is the $(\text{UO}_5)_\infty$ chains formed from edge shared UO_7 pentagonal bipyramids. In $(\text{UO}_2)_3$

$(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$ the chains are connected via VO_4 tetrahedra, in $M_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$ ($M = \text{Na}, \text{K}$) compounds they are connected either by VO_4 tetrahedra or by oxygen corner sharing. With largest cations such as Rb and Cs the reaction in molten chlorides led to the substitution of chlorine for some equatorial oxygen of the UO_7 bipyramids, the so-obtained chains are connected together only by oxygen or chlorine atoms. Studies of reaction between $(\text{UO}_2)_3(\text{VO}_4)_2$ and salts of larger anions are plane.

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