

# Synthesis, Crystal Structure, and Comparison of Two New Uranyl Vanadate Layered Compounds: $M_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$ with $M = \text{Na}, \text{K}$

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Two new alkali uranyl vanadates,  $M_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  with  $M = \text{Na}, \text{K}$ , have been synthesized by solid state reactions and their structures determined from single-crystal X-ray diffraction data. They crystallize in the monoclinic system with space group  $P2_1/c$ . Unit cell  $b$ ,  $c$ , and  $\beta$  parameters are almost identical in both compounds while the  $a$  parameter in the Na compound is doubled: Na— $a = 12.584(1) \text{ \AA}$ ,  $b = 24.360(2) \text{ \AA}$ ,  $c = 7.050(1) \text{ \AA}$ ,  $\beta = 100.61(1)^\circ$ ,  $V = 2124.2 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{mes}} = 5.60(2) \text{ g/cm}^3$ ,  $D_{\text{cal}} = 5.63 \text{ g/cm}^3$ ; K— $a = 6.856(1) \text{ \AA}$ ,  $b = 24.797(3) \text{ \AA}$ ,  $c = 7.135(1) \text{ \AA}$ ,  $\beta = 98.79(8)^\circ$ ,  $V = 1198.8 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{mes}} = 5.25(2) \text{ g/cm}^3$ ,  $D_{\text{cal}} = 5.25 \text{ g/cm}^3$ . A full-matrix least-squares refinement yielded, respectively,  $R = 0.039$ ,  $R_w = 0.043$  and  $R = 0.037$ ;  $R_w = 0.046$  for 3293 and 2096 independent reflections with  $I > 3\sigma$  collected on a Philips PW 1100 diffractometer (MoK $\alpha$  radiation). Both structures are characterized by  $[(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5]_n^{6n-}$  corrugated layers parallel to the (100) plane. The layers are built up from  $\text{VO}_4$  tetrahedra,  $\text{UO}_7$  pentagonal bipyramids, and  $\text{UO}_6$  distorted octahedra. The  $\text{UO}_7$  pentagonal bipyramids are associated by sharing opposite equatorial edges to form zig-zag infinite chains  $(\text{UO}_5)_n$  parallel to the  $c$  axis. These chains are linked together on one side by  $\text{VO}_4$  tetrahedra and on other side by  $\text{UO}_6$  octahedra and  $\text{UO}_7$  corner sharing. Both structures differ simply by the symmetry of the layers. The unit cell contains one centrosymmetric layer in the K compound, whereas in the two-layer unit cell of the Na compound two noncentrosymmetric 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  $M_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  and carnotite analog compounds is compared. © 2000 Academic Press

## INTRODUCTION

Layered compounds are generally favorable for good electrical ionic conductivity. For example, in  $\beta$ -alumina, where fast  $\text{Na}^+$  ion transport has been initially observed (1), alkali ions are able to move freely within the conduction planes but cannot penetrate the dense spinel blocks. Numerous uranyl phosphate, arsenate, or vanadate compounds adopt layered structures. In the P and As compounds, generally the layers result from the association between  $\text{XO}_4$  tetrahedra ( $X = \text{P}, \text{As}$ ) and  $\text{UO}_7$  or  $\text{UO}_8$  bipyramids involving the equatorial oxygen atoms in the plane perpendicular to the uranyl ion. This is the case of, for example, hydrogen uranyl phosphate tetrahydrate,  $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ , also simply called HUP, which is among the best ionic electrical conductors actually known. In HUP, protons  $\text{H}^+$  jump between interlayer water molecules. HUP has received much attention because of its potential applications in electrochemical systems (2–7). In the V compounds, generally the  $\text{UO}_7$  or  $\text{UO}_8$  polyhedra are linked by  $\text{VO}_5$  square pyramids. We have already studied monovalent metal uranyl vanadates with a molar ratio  $\text{U}/\text{V} = 1$  (8, 9). These materials are characterized by  $(\text{UO}_2\text{VO}_4)_\infty$  sheets held together by interlayer cations alone or surrounded with water molecules. They belong to the large class of compounds of the general formula  $M_{1/n}^{n+} \text{UO}_2\text{XO}_4 \cdot x\text{H}_2\text{O}$ , where  $X$  can be P, As, and V (10). In P and As compounds, the  $\text{UO}_2^{2+}$  ions are connected by  $\text{PO}_4^{3-}$  or  $\text{AsO}_4^{3-}$  tetrahedra, whereas in V compounds they are linked by  $\text{V}_2\text{O}_8^{6-}$  units formed by two inverse  $\text{VO}_5$  square pyramids sharing an edge. They therefore have the general formula  $M_{2/n}^{n+}(\text{UO}_2)_2 \text{V}_2\text{O}_8 \cdot x\text{H}_2\text{O}$ . We have recently reported the structure of the synthetic carnotite  $\text{K}(\text{UO}_2)\text{VO}_4$ , its Na analog, the properties of  $\text{Na}_{1-x}\text{K}_x\text{UO}_2\text{VO}_4$  ( $0 \leq x \leq 1$ ) solid solution, and

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a relatively high mobility of the alkali metal ions. For all metal uranyl vanadates of ratio U/V = 1 whose structure has been determined, the same layers  $[(\text{UO}_2)_2\text{V}_2\text{O}_8]_n^{2n-}$  are observed. It is particularly the case for anhydrous compounds with  $M^+ = \text{Na}^+, \text{K}^+, \text{Cs}^+, \text{Ag}^+$  (11–13) and hydrated ones with  $M^{2+} = \text{Pb}^{2+}$  (14),  $\text{Ba}^{2+}$  (15),  $\text{Ni}^{2+}$  (16),  $\text{Cu}^{2+}$  (17). This family derived from carnotite seems particularly homogeneous from a structural view point.

Another type of layer appears when U/V = 1/3 and has been recently described for  $\text{CsUV}_3\text{O}_{11}$  (18). The layers are built from  $\text{VO}_5$  square pyramids and  $\text{UO}_8$  hexagonal bipyramids sharing edges and corners that extend into infinite sheets formulated as  $[\text{UV}_3\text{O}_{11}]_n^{n-}$  similar to the layers found in  $\text{UV}_3\text{O}_{10}$  (19). The mobility of  $\text{Cs}^+$  ions sandwiched between two layers is higher than that in Cs carnotite and these encouraging results induced us to study other monovalent compounds formulated as  $M(\text{UO}_2)(\text{VO}_3)_3$  with  $M^+ = \text{Na}^+, \text{NH}_4^+ \dots$

In sheets  $[\text{UO}_2\text{VO}_4]_n^{n-}$  and  $[\text{UV}_3\text{O}_{11}]_n^{n-}$ , vanadium atoms are pentacoordinated and form square pyramids  $\text{VO}_5$  but the association of  $\text{VO}_5$  polyhedra differs. In carnotite, two  $\text{VO}_5$  pyramids related by an inversion center sharing an edge form a  $\text{V}_2\text{O}_8$  group while in  $\text{CsUV}_3\text{O}_{11}$  the shared oxygen atoms of  $\text{VO}_5$  pyramids create equilateral triangles and hexagons whose centers are occupied by linear uranyl ions perpendicular to this plane. The coordination polyhedron is then an uncommon hexagonal bipyramid  $\text{UO}_8$  while it is a classical pentagonal bipyramid  $\text{UO}_7$  in the carnotite family.

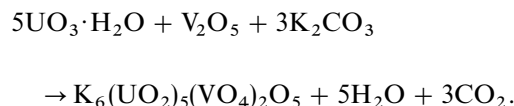
For  $\text{V}^{5+}$ , the most prevalent coordination is obviously tetrahedral and curiously this coordination seems nonobserved in metal uranyl vanadate structures known today. But in some mixed oxides such  $\text{U}_2\text{V}_2\text{O}_{11}$ , which can be structurally considered a uranyl divanadate  $(\text{UO}_2)_2\text{V}_2\text{O}_7$ , units  $\text{V}_2\text{O}_7$  are built from two  $\text{VO}_4$  tetrahedra sharing a corner (20, 21). In the recently published pentahydrated uranyl orthovanadate,  $(\text{UO}_2)_3(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$  (22), layers  $[\text{UO}_2(\text{VO}_4)]_n^{n-}$  are built from  $\text{VO}_4$  tetrahedra and  $\text{UO}_7$  pentagonal bipyramids. The connection between the layers is achieved by disordered  $\text{UO}_2$  uranyl ions and water molecules. Dehydration to  $(\text{UO}_2)_3(\text{VO}_4)_2$  is reversible so, if we assumed that the layered structure is preserved in the anhydrous species  $(\text{UO}_2)_3(\text{VO}_4)_2$ , ion exchange reactions may lead to new uranyl vanadate layered families built from  $\text{VO}_4$  tetrahedra. Towards this goal, attempts at ion exchange reactions have been investigated in molten alkali chlorides.

From potassium chloride, orange single crystals of a new compound that is not the result of a simple cationic exchange are prepared. The formula was deduced from the structural study of single-crystal X-ray diffraction data. Independently, single crystals of the structurally related sodium analog have been synthesized by solid state reaction. The crystal structures of both compounds have been

determined. They are reported and compared in this paper.  $\text{K}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  structure being more simple than  $\text{Na}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$ , it is described first for educational reasons.

## EXPERIMENTAL

Attempts at ion "exchange" reactions in uranyl orthovanadate  $(\text{UO}_2)_3(\text{VO}_4)_2$  have been investigated in molten potassium chloride. The mixture of uranyl orthovanadate pentahydrated with a large excess (accounts 30/1 in moles) of potassium chloride is slowly heated to allow dehydration of the uranyl salt in a platinum crucible to 775°C for 3 days, the heating temperature is below the melting point (800°C) of pure anhydrous uranyl orthovanadate but just above the potassium chloride melting point (770°C). The molten salt was cooled slowly and washed with water to dissolve the excess potassium chloride, giving orange single crystals. The crystals were crushed and characterized by X-ray powder diffraction using a Guinier-deWolff focusing camera with  $\text{CuK}\alpha$  radiation. A distinctive X-ray diffraction pattern was observed that characterized a new compound. The formula  $\text{K}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  was deduced from the structural study and the powder compound was synthesized by a solid state reaction between a stoichiometric mixture of  $\text{V}_2\text{O}_5$  (Aldrich),  $\text{UO}_3 \cdot \text{H}_2\text{O}$  (Prolabo Rectapur), and  $\text{K}_2\text{CO}_3$  (Aldrich) according to the following reaction:



The homogeneous mixture was preheated at 300°C in air to dehydrate the uranium trioxide and then heated at 620°C for 2 days in an aluminum crucible with an intermediate grinding. The X-ray diffraction pattern of the as-obtained powder is identical to that of crushed single crystals.

$\text{Na}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  single crystals were prepared independently from a mixture  $\text{Na}_2\text{UO}_4\text{-V}_2\text{O}_5$  of molar ratio 3/2, heated during 48 h at 800°C in a platinum crucible, and slowly cooled (5°C/h) to room temperature. The  $b$ ,  $c$  and  $\beta$  lattice parameters are very similar to those of  $\text{K}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  while the  $a$  parameter is approximately doubled. This indicated clearly at the start that Na and K compounds probably have the same formula with layers parallel to the (100) plane and that the unit formula number per cell is double for the Na compound. Further structural study confirms this forecast. Like previously for the K compound, direct synthesis by solid state reaction has been realized at 700°C from the ternary mixtures  $\text{UO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{CO}_3$  in molar ratios 5/1/3. The X-ray diffraction pattern of the as-prepared powder is identical to that of crushed single crystals.

Well-shaped crystals of  $K_6(UO_2)_5(VO_4)_2O_5$  ( $0.35 \times 0.06 \times 0.03$  mm<sup>3</sup>) and  $Na_6(UO_2)_5(VO_4)_2O_5$  ( $0.28 \times 0.08 \times 0.03$  mm<sup>3</sup>) were selected for structure determinations. Preliminary Weissenberg photographs were taken and indicated for both compounds a monoclinic symmetry, and systematic absences of  $0\ k\ 0$  ( $k = 2n + 1$ ) and  $h\ 0\ l$  ( $l = 2n + 1$ ) reflections revealed the same  $P2_1/c$  space group.

Single crystal X-ray diffraction data were collected on an automated Philips PW 1100 diffractometer (MoK $\alpha$  radiation). Crystal data, conditions of data collection, and structure refinement parameters are reported in Table 1. For

educational reasons  $K_6(UO_2)_5(VO_4)_2O_5$  will always be described first because its structure is more simple. The unit cell parameters of the crushed single crystals were refined by a least-squares procedure from the indexed powder diffraction pattern, collected with a Siemens D5000 diffractometer (CuK $\alpha$  radiation) equipped with a back end monochromator and corrected for  $K\alpha_2$  contribution. The figures of merit, as defined by Smith and Snyder (23), were  $F_{20} = 84$  (0.0053, 45) and 133 (0.0047, 33) for the K and Na compounds, respectively. The powder X-ray diffraction pattern data are reported in Tables 2 and 3, respectively.

The density, measured with an automated Micromeritics Accupyc 1330 helium pycnometer using a 1-cm<sup>3</sup> cell indicated  $Z = 2$  formula per unit cell ( $\rho_{\text{exp}} = 5.25(2)$  g cm<sup>-3</sup>,  $\rho_{\text{cal}} = 5.25$  g cm<sup>-3</sup>) for the K compound and  $Z = 4$  ( $\rho_{\text{exp}} = 5.60(2)$  g cm<sup>-3</sup>,  $\rho_{\text{cal}} = 5.63$  g cm<sup>-3</sup>) for the Na compound.

The measured intensities were corrected for Lorentz and polarization effects and for absorption, using the analytical method of De Meulenaer and Tompa (24).

The structures were solved by direct methods using SHELXS program (25) that localize the heavy U atoms. The positions of V, K, or Na and O were deduced from

**TABLE 1**  
Crystal Data, Intensity Collection, and Structure Refinement Parameters for  $M_6(UO_2)_5(VO_4)_2O_5$  ( $M = K, Na$ )

	$M = K$	$M = Na$
Crystal data		
Crystal symmetry	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell refined on powder	$a = 6.856(1)$ Å $b = 24.797(3)$ Å $c = 7.135(1)$ Å $\beta = 98.79(8)^\circ$	$a = 12.584(1)$ Å $b = 24.360(2)$ Å $c = 7.050(1)$ Å $\beta = 100.61(1)^\circ$
Volume	1198.8 Å <sup>3</sup>	2124.2 Å <sup>3</sup>
$Z$	2	4
Calculated density	$\rho = 5.25$ g cm <sup>-3</sup>	$\rho = 5.63$ g cm <sup>-3</sup>
Measured density	$\rho = 5.25(2)$ g cm <sup>-3</sup>	$\rho = 5.60(2)$ g cm <sup>-3</sup>
Data collection		
Equipment	Philips PW 1100	Philips PW 1100
Radiation MoK $\alpha$	0.7107 Å	0.7107 Å
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$
Scan width (°)	1.2	1.2
Recording angular range (°)	2–27	2–25
Standard reflections	$\bar{1}\ \bar{1}\ 0, 1\ \bar{3}\ 0, 0\ 7\ 1$	$\bar{2}\ 2\ 2, 0\ 0\ 2, \bar{2}\ 3\ 0$
Recording reciprocal space	$-8 \leq h \leq 8$ $-31 \leq k \leq 31$ $0 \leq l \leq 9$	$-14 \leq h \leq 14$ $-28 \leq k \leq 28$ $0 \leq l \leq 8$
Number of measured reflections	5655	8150
Number of reflections with $I > 3\sigma(I)$	4274	7189
Number of independent reflections	2096	3293
$\mu$ (cm <sup>-1</sup> ) (for $\lambda_{K\alpha} = 0.7107$ Å)	345.45	370.20
Limiting faces and distances (cm) from an arbitrary origin	$1\ 0\ 0, \bar{1}\ 0\ 0\ 0.0014$ $0\ 1\ 0, 0\ \bar{1}\ 0\ 0.0029$ $\bar{1}\ 1\ 5, 1\ \bar{1}\ \bar{5}\ 0.0170$	$1\ 0\ 0, \bar{1}\ 0\ 0\ 0.0037$ $0\ 1\ 0, 0\ \bar{1}\ 0\ 0.0016$ $1\ 0\ \bar{1}, \bar{1}\ 0\ 1\ 0.0138$
Transmission factor range	0.14–0.39	0.06–0.17
$R$ merging factor	0.027	0.063
Refinement parameters		
Number of refined parameters	105	210
Goof = $S$ (goodness of fit)	4.3	2.0
$R = \sum[ F_o  -  F_c ]/\sum F_o $	0.037	0.039
$R_w = [\sum w( F_o  -  F_c )^2 / \sum F_o^2]^{1/2}$ with $w = 1/\sigma(F_o)$	0.046	0.043

**TABLE 2**  
Observed and Calculated X-Ray Powder Diffraction Pattern for  $K_6(UO_2)_5(VO_4)_2O_5$

$h$	$k$	$l$	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	$I_{\text{obs}}/I_0$	$h$	$k$	$l$	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	$I_{\text{obs}}/I_0$
0	2	0	7.130	7.129	9	2	3	1	32.853	32.846	1
1	0	0	13.060	13.061	100	2	5	-1	32.890	32.900	4
1	1	0	13.544	13.541	75	1	8	-1	33.467	33.455	5
0	4	0	14.300	14.280	34	2	4	1	34.233	34.246	2
1	2	0	14.883	14.892	34	1	8	1	34.999	35.002	4
0	3	1	16.905	16.911	24	1	5	2	35.392	35.394	2
1	4	0	19.399	19.396	6	2	5	1	35.982	35.977	1
0	5	1	21.900	21.900	12	1	9	-1	36.717	36.725	1
1	5	0	22.214	22.199	7	1	10	0	38.638	38.637	2
1	4	1	24.248	24.248	5	2	1	2	39.769	39.756	2
1	5	-1	24.543	24.550	6	1	3	-3	40.113	40.121	2
1	6	0	25.230	25.225	25	1	10	-1	40.107	40.107	2
1	5	1	26.568	26.568	63	3	1	-1	40.164	40.156	1
2	2	0	27.269	27.271	5	3	2	0	40.573	40.572	2
1	2	-2	27.601	27.612	5	3	3	0	41.405	41.415	8
0	7	1	28.168	28.172	83	3	4	0	42.566	42.572	13
2	3	0	28.454	28.454	27	2	5	2	43.734	43.743	1
1	3	-2	28.789	28.783	4	2	10	0	45.286	45.286	6
1	6	1	29.178	29.170	9	2	4	-3	45.871	45.860	13
2	4	0	30.030	30.039	4	3	4	1	46.401	46.388	16
1	7	-1	30.308	30.314	27	1	12	-1	47.159	47.162	1
2	4	-1	31.011	31.018	5	1	12	1	48.335	48.338	3
0	5	2	31.111	31.104	2	2	11	0	48.463	48.468	3
1	2	2	31.150	31.160	2	0	8	3	48.580	48.577	1
1	7	1	32.000	31.996	5	1	13	0	49.607	49.613	1

Note.  $\lambda = 1.54056$  Å, refined zero-point correction 0.003(2) for  $\theta$ ;  $a = 6.856(1)$  Å;  $b = 24.797(3)$  Å;  $c = 7.135(1)$  Å;  $\beta = 98.79(8)^\circ$ ;  $F_{20} = 84$  (0.0053,45).

**TABLE 3**  
Observed and Calculated X-Ray Powder Diffraction Pattern  
for  $\text{Na}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}$	$2\theta_{\text{cal}}$	$I_{\text{obs}}/I_0$	<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}$	$2\theta_{\text{cal}}$	$I_{\text{obs}}/I_0$
0	1	1	13.275	13.272		2	2	1	27.312	27.311	2
1	0	-1	13.436	13.435		1	3	1	27.358	27.355	8
1	1	-1	13.920	13.921		2	1	3	27.674	27.675	8
2	0	0	14.316	14.310		92	2	5	27.865	27.862	25
0	4	0	14.543	14.560		40	1	0	27.968	27.969	5
0	2	1	14.694	14.694		4	2	2	28.052	28.051	5
2	1	0	14.770	14.766		100	3	2	28.097	28.093	11
1	2	-1	15.284	15.283		10	1	1	28.211	28.212	1
1	0	1	15.755	15.754		5	3	5	28.338	28.334	7
2	2	0	16.047	16.060		32	0	7	28.683	28.682	99
0	3	1	16.796	16.806		3	4	0	28.856	28.849	1
1	3	-1	17.327	17.324		1	1	7	28.998	28.997	3
2	0	-1		17.358		1	4	1	29.075	29.086	17
1	2	1	17.360	17.363		1	2	3	29.247	29.246	6
2	1	-1	17.740	17.738		4	1	4	29.354	29.355	1
2	3	0	18.001	18.015		26	3	5	29.454	29.450	3
2	2	-1	18.835	18.833		1	0	4	29.638	29.639	3
2	4	0	20.455	20.450		2	4	2	29.767	29.786	16
3	0	0	21.527	21.536		2	1	3	30.080	30.094	6
0	6	0	21.875	21.873		2	4	2	30.285	30.279	2
2	2	1	22.172	22.170		2	2	6		30.449	
0	5	1	22.275	22.287		15	3	0	30.452	30.465	8
1	5	-1	22.686	22.685		1	3	1	30.692	30.690	2
2	4	-1	22.716	22.711		4	4	3	30.925	30.919	18
3	2	0	22.756	22.751		3	2	7	31.079	31.077	25
3	0	-1	22.964	22.961		1	1	5	31.390	31.394	1
1	6	0	23.039	23.037		1	2	0	31.817	31.872	2
2	5	0	23.209	23.223		7	3	6	31.923	31.920	3
3	1	-1	23.256	23.252		1	0	8	32.081	32.080	6
2	3	1	23.644	23.642		1	3	3	32.436	32.441	4
3	2	-1	24.112	24.108		1	2	2	32.677	32.676	4
3	3	0	24.178	24.190		1	4	4	32.903	32.904	9
2	5	-1	25.250	25.248		14	2	7	33.278	33.271	9
2	4	1		25.569		4	1	8	33.443	33.441	2
0	7	0	25.571	25.576		1	6	-2	33.736	33.735	3
1	1	-2	25.630	25.632		1	4	1	34.031	34.026	3
0	0	2	25.688	25.690		9	2	8	34.251	34.261	9
1	6	-1	25.725	25.757		25	4	5	34.753	34.757	5
0	1	2	25.951	25.952		4	4	1	35.337	35.329	3
3	4	0	26.083	26.078		1	4	3	35.618	35.631	5
1	2	-2	26.413	26.415		1	4	2	35.924	35.920	2
1	7	0	26.589	26.586		4	5	0	36.292	36.286	3
0	2	2	26.726	26.727		1	1	7	36.331	36.330	3
3	0	1	27.107	27.104		23	5	2	36.987	36.978	2
3	4	-1	27.284	27.280		4	3	2	37.577	37.557	1

Note.  $\lambda = 1.54056 \text{ \AA}$ , refined zero-point correction  $-0.002(1)$  for  $\theta$ ;  $a = 12.584(1) \text{ \AA}$ ;  $b = 24.360(2) \text{ \AA}$ ;  $c = 7.050(1) \text{ \AA}$ ;  $\beta = 100.61(1)^\circ$ ;  $F_{20} = 133(0.0047, 33)$ .

subsequent refinements and difference Fourier syntheses. The full-matrix least-squares refinement was performed with a local modification of the SFLS-5 program (26). The atomic scattering factors for neutral atoms were taken from the "International Tables for X-ray Crystallography" (27) and the values for the anomalous dispersion correction from

**TABLE 4**  
Atomic Positions, Isotropic Displacement Parameters (O atoms), and Equivalent Isotropic Displacement Parameters (U, K, V atoms) for  $\text{K}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	B or $B_{\text{eq}}$ ( $\text{\AA}^2$ )
U(1)	4e	0.40712(11)	0.58161(3)	0.48557(12)	0.57(2)
U(2)	4e	0.65489(11)	0.35810(3)	0.02824(12)	0.61(2)
U(3)	2d	$\frac{1}{2}$	$\frac{1}{2}$	0	0.67(2)
V	4e	0.7880(5)	0.2033(1)	0.0457(5)	0.87(8)
K(1)	4e	0.8671(7)	0.6127(2)	0.2297(7)	1.4(1)
K(2)	4e	0.9494(7)	0.9606(2)	0.2324(7)	1.5(1)
K(3)	4e	0.7518(12)	0.7889(3)	0.2101(9)	4.3(2)
O(1)	4e	0.034(2)	0.207(1)	0.077(2)	2.0(3)
O(2)	4e	0.687(2)	0.265(1)	0.036(2)	1.8(3)
O(3)	4e	0.706(2)	0.162(1)	0.217(2)	1.2(3)
O(4)	4e	0.690(2)	0.160(1)	-0.152(2)	1.4(3)
O(5)	4e	0.146(2)	0.560(1)	0.442(2)	1.2(2)
O(6)	4e	0.661(2)	0.607(1)	0.531(2)	1.4(3)
O(7)	4e	0.763(2)	0.521(1)	0.029(2)	1.1(2)
O(8)	4e	0.397(2)	0.339(1)	0.002(2)	1.4(3)
O(9)	4e	0.920(2)	0.372(1)	0.067(2)	1.3(3)
O(10)	2b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.1(3)
O(11)	4e	0.406(2)	0.570(1)	0.796(2)	0.7(2)
O(12)	4e	0.438(2)	0.573(1)	0.175(2)	0.8(2)

Note. Equivalent isotropic temperature factors are computed according to the relation  $B_{\text{eq}} = 4/3 \sum_{ij} \beta_{ij} a_i a_j$ .

Cromer and Liberman (28). Refinement of atomic positional parameters, anisotropic displacement for U, V, K, or Na atoms, and isotropic displacement parameters for O atoms yielded to final  $R = 0.037$  and  $R_w = 0.046$  for 2096 independent reflections for the K compound and to  $R = 0.039$ ,  $R_w = 0.043$  for 3293 independent reflections for the Na compound. The atomic positions and equivalent isotropic displacement factors and anisotropic displacement parameters for metals are reported in Tables 4 and 5 for the K and in Tables 6 and 7 for the Na compounds, respectively.

**TABLE 5**  
Anisotropic Displacement Parameters ( $\times 10^4$ ) for  
 $\text{K}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
U(1)	90(4)	41(3)	85(4)	12(3)	13(3)	-0.9(3)
U(2)	92(4)	48(3)	91(4)	11(3)	10(3)	2(3)
U(3)	93(6)	33(5)	131(6)	13(4)	20(5)	6(4)
V	162(20)	78(16)	90(17)	-29(13)	22(16)	-6(13)
K(1)	159(25)	160(23)	206(26)	19(17)	-13(21)	1(19)
K(2)	209(26)	164(21)	197(26)	33(18)	45(22)	23(18)
K(3)	827(57)	536(40)	359(37)	489(39)	327(40)	197(32)

Note. The anisotropic temperature factor is defined by  $\exp[-2\pi^2((U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*))]$ .

**TABLE 6**  
Atomic Positions, Thermal Isotropic Factor (O), and Equivalent Thermal Isotropic (U, V, Na) of  $\text{Na}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$

Atom	Site	x	y	z	B or $B_{\text{eq}}$ ( $\text{\AA}^2$ )
U(1)	4e	0.81315(5)	0.07375(2)	0.02283(9)	0.75(1)
U(2)	4e	0.83400(4)	0.36029(2)	0.03880(9)	0.78(1)
U(3)	4e	0.76281(5)	0.50718(2)	-0.01270(9)	0.86(2)
U(4)	4e	0.70735(5)	0.91180(2)	-0.01266(9)	0.79(2)
U(5)	4e	0.65359(4)	0.64718(2)	-0.02754(9)	0.80(1)
V(1)	4e	0.1094(2)	0.7052(1)	0.4516(4)	1.04(7)
V(2)	4e	0.5609(2)	0.7010(1)	0.4502(4)	1.10(7)
Na(1)	4e	0.0227(5)	0.4619(3)	0.2726(11)	2.0(2)
Na(2)	4e	0.5739(5)	0.0998(3)	0.2585(11)	2.0(2)
Na(3)	4e	0.5243(5)	0.4661(3)	0.2620(11)	2.2(2)
Na(4)	4e	0.0768(5)	0.1222(3)	0.2855(12)	2.4(2)
Na(5)	4e	0.1155(6)	0.2943(4)	0.2707(13)	3.3(2)
Na(6)	4e	0.6241(8)	0.3087(6)	0.2504(17)	6.8(4)
O(1)	4e	-0.020(1)	0.718(1)	0.446(2)	2.6(3)
O(2)	4e	0.124(1)	0.661(1)	0.264(2)	1.9(2)
O(3)	4e	0.171(1)	0.661(1)	0.643(2)	1.5(2)
O(4)	4e	0.176(1)	0.765(1)	0.447(2)	2.2(2)
O(5)	4e	0.435(1)	0.686(1)	0.455(2)	2.7(3)
O(6)	4e	0.646(1)	0.672(1)	0.646(2)	2.1(2)
O(7)	4e	0.607(1)	0.660(1)	0.275(2)	1.8(2)
O(8)	4e	0.568(1)	0.770(1)	0.425(2)	2.1(2)
O(9)	4e	0.666(1)	0.084(1)	-0.031(2)	1.7(2)
O(10)	4e	0.961(1)	0.064(1)	0.071(2)	1.4(2)
O(11)	4e	0.795(1)	-0.014(1)	0.063(2)	1.3(2)
O(12)	4e	0.803(1)	0.069(1)	0.334(2)	1.6(2)
O(13)	4e	0.818(1)	0.059(1)	-0.290(2)	1.3(2)
O(14)	4e	0.688(1)	0.350(1)	-0.010(2)	1.5(2)
O(15)	4e	0.981(1)	0.366(1)	0.104(2)	1.4(2)
O(16)	4e	0.621(1)	0.485(1)	-0.048(2)	1.6(2)
O(17)	4e	0.902(1)	0.532(1)	0.025(2)	1.1(2)
O(18)	4e	0.726(1)	0.577(1)	0.180(2)	1.3(2)
O(19)	4e	0.710(1)	0.580(1)	-0.195(2)	1.5(2)
O(20)	4e	0.835(1)	0.874(1)	0.025(2)	1.6(2)
O(21)	4e	0.576(1)	0.948(1)	-0.059(2)	1.3(2)
O(22)	4e	0.786(1)	0.680(1)	0.030(2)	1.8(2)
O(23)	4e	0.521(1)	0.616(1)	-0.084(2)	1.6(2)

Note. Equivalent isotropic temperature factors are computed according to the relation  $B_{\text{eq}} = 4/3 \sum_{ij} \beta_{ij} a_i a_j$ .

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 850°C for 48 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 1–10<sup>6</sup> Hz with a Solartron 1170 frequency-response analyzer. Measurements were made at 20°C intervals over the range 350–650°C on both heating and cooling. Each set of values was recorded at a given temperature after a 1-h stabilization time.

**TABLE 7**  
Anisotropic Displacement Parameters for  $\text{Na}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
U(1)	118(3)	34(3)	128(3)	-8(2)	13(2)	1(2)
U(2)	128(3)	33(3)	129(3)	11(2)	9(2)	4(2)
U(3)	115(3)	26(3)	176(4)	18(2)	2(3)	1(2)
U(4)	126(3)	40(3)	127(4)	-16(2)	8(2)	-7(2)
U(5)	128(3)	43(3)	127(3)	14(2)	6(2)	1(2)
V(1)	200(14)	21(14)	173(16)	18(10)	27(12)	7(12)
V(2)	198(14)	61(15)	159(16)	22(10)	36(12)	4(12)
Na(1)	204(36)	313(46)	259(43)	-92(30)	51(32)	-43(35)
Na(2)	243(36)	142(38)	350(46)	-24(28)	-33(33)	-14(34)
Na(3)	283(38)	163(41)	323(46)	36(29)	-71(34)	-4(33)
Na(4)	202(35)	228(43)	418(51)	-20(29)	-71(34)	-74(37)
Na(5)	393(45)	407(56)	427(55)	-103(37)	54(41)	-118(43)
Na(6)	497(60)	1612(136)	460(68)	-441(71)	57(52)	-281(76)

Note. The anisotropic temperature factor is defined by  $\exp[-2\pi^2((U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*))]$ .

## DESCRIPTION OF THE STRUCTURES AND DISCUSSION

Table 8 provides for  $\text{K}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  the most significant distances, angles, and bond valence sums calculated using Brown and Altermatt's data (29)

The three independent uranium atoms U(1), U(2), and U(3) are bonded to two oxygen atoms at short distances, O(5) and O(6) for U(1), O(8) and O(9) for U(2), O(7) and O(7)<sub>ii10</sub> for U(3), respectively, forming nearly linear uranyl ions, U(1)O<sub>2</sub><sup>2+</sup>, U(2)O<sub>2</sub><sup>2+</sup>, and a perfectly linear ion U(3)O<sub>2</sub><sup>2+</sup> (Fig. 1). U(1) and U(2) are in general sites 4e and U(3) is in particular site 2d, respectively. Uranyl ions U(1)O<sub>2</sub><sup>2+</sup> and U(2)O<sub>2</sub><sup>2+</sup> are surrounded in the equatorial plane by a pentagonal environment of oxygen atoms. Coordination polyhedra of U(1) and U(2) are pentagonal bipyramids UO<sub>7</sub>. The uranyl ion, U(3)O<sub>2</sub><sup>2+</sup>, is surrounded in the equatorial plane by four oxygen atoms at 2.28–2.29 Å forming a rectangle. U(3) coordination is thus a distorted octahedron UO<sub>6</sub>. The linear group O–U–O with two short U–O bonds (about 1.8 Å) and an equatorial group of O atoms at longer distances (2.1 to 2.7 Å) are very common in so-called uranyl compounds. The equatorial group is constituted more often of five atoms leading to a UO<sub>7</sub> pentagonal bipyramid or sometimes of six O atoms forming a hexagonal bipyramid such as in CsUV<sub>3</sub>O<sub>11</sub> (18); in some less usual cases it contains only four atoms. A distorted octahedral environment of U atoms is found, for example, in BaUO<sub>4</sub> (30) or in HUP (3).

Bipyramids, U(1)O<sub>7</sub> and U(2)O<sub>7</sub>, share two edges O(4)–O(11) and O(3)–O(12) of equatorial pentagons, creating zig-zag infinite chains (UO<sub>5</sub>)<sub>∞</sub> running along the c axis and simply called U(1)–U(2). These chains are similar to those found in well-known compounds such as α-U<sub>3</sub>O<sub>8</sub> (31), UVO<sub>5</sub> (13), USbO<sub>5</sub> (32), UMo<sub>2</sub>O<sub>8</sub> (33), and other recently

**TABLE 8**  
**Bond Distances (Å), Angles (°) in  $K_6(UO_2)_5(VO_4)_2O_5$ , and  $S_{ij}$  Calculations**

V (tetrahedral environment)											
V–O(1)	1.67(1)	$S_{ij}$	1.43	O(1)–V–O(2)	111(2)						
V–O(2)	1.68(1)		1.39	O(1)–V–O(3)	111(2)						
V–O(3)	1.75(2)		1.15	O(1)–V–O(4)	112(2)						
V–O(4)	1.82(1)		0.96	O(2)–V–O(3)	113(2)						
		$\sum S_{ij} = 4.92$		O(2)–V–O(4)	113(2)						
				O(3)–V–O(4)	94(1)						
U(1) (pentagonal bipyramid environment)											
U(1)–O(5)	1.85(1)	$S_{ij}$	1.84	O(5)–U(1)–O(6)	177(11)						
U(1)–O(6)	1.83(1)		1.93	O(5)–U(1)–O(10)	90(1)						
U(1)–O(10)	2.12(1)		0.88	O(5)–U(1)–O(11)	89(1)						
U(1)–O(11)	2.23(1)		0.65	O(5)–U(1)–O(4) <sub>100</sub> <sup>iii</sup>	89(1)						
U(1)–O(4) <sub>100</sub> <sup>iii</sup>	2.42(2)		0.39	O(5)–U(1)–O(3) <sub>100</sub> <sup>iii</sup>	86(1)						
U(1)–O(3) <sub>100</sub> <sup>iii</sup>	2.51(2)		0.31	O(5)–U(1)–O(12)	92(1)						
U(1)–O(12)	2.27(1)		0.59								
		$\sum S_{ij} = 6.59$									
O(6)–U(1)–O(10)	93(1)			O(10)–U(1)–O(11)	83(1)						
O(6)–U(1)–O(11)	91(1)			O(11)–U(1)–O(4) <sub>100</sub> <sup>iii</sup>	65(1)						
O(6)–U(1)–O(4) <sub>100</sub> <sup>iii</sup>	88(1)			O(4) <sub>100</sub> <sup>iii</sup> –U(1)–O(3) <sub>100</sub> <sup>iii</sup>	64(1)						
O(6)–U(1)–O(3) <sub>100</sub> <sup>iii</sup>	92(1)			O(3) <sub>100</sub> <sup>iii</sup> –U(1)–O(12)	65(1)						
O(6)–U(1)–O(12)	89(1)			O(12)–U(1)–O(10)	83(1)						
U(2) (pentagonal bipyramid environment)											
U(2)–O(8)	1.81(1)	$S_{ij}$	2.05	O(8)–U(2)–O(9)	174(10)						
U(2)–O(9)	1.83(1)		1.93	O(8)–U(2)–O(2)	80(1)						
U(2)–O(2)	2.32(2)		0.52	O(8)–U(2)–O(4) <sup>iv</sup>	90(1)						
U(2)–O(4) <sup>iv</sup>	2.30(1)		0.54	O(8)–U(2)–O(11) <sub>111</sub> <sup>ii</sup>	90(1)						
U(2)–O(11) <sub>111</sub> <sup>ii</sup>	2.26(2)		0.61	O(8)–U(2)–O(12) <sub>110</sub> <sup>ii</sup>	88(1)						
U(2)–O(12) <sub>110</sub> <sup>ii</sup>	2.27(2)		0.59	O(8)–U(2)–O(3) <sub>001</sub> <sup>iv</sup>	98(1)						
U(2)–O(3) <sub>001</sub> <sup>iv</sup>	2.35(1)		0.48								
		$\sum S_{ij} = 6.72$									
O(9)–U(2)–O(2)	95(1)			O(2)–U(2)–O(4) <sup>iv</sup>	78(1)						
O(9)–U(2)–O(4) <sup>iv</sup>	86(1)			O(4) <sub>000</sub> <sup>iv</sup> –U(2)–O(11) <sub>111</sub> <sup>ii</sup>	67(1)						
O(9)–U(2)–O(11) <sub>111</sub> <sup>ii</sup>	92(1)			O(11) <sub>111</sub> <sup>ii</sup> –U(2)–O(12) <sub>110</sub> <sup>ii</sup>	73(1)						
O(9)–U(2)–O(12) <sub>110</sub> <sup>ii</sup>	97(1)			O(12) <sub>110</sub> <sup>ii</sup> –U(2)–O(3) <sub>001</sub> <sup>iv</sup>	68(1)						
O(9)–U(2)–O(3) <sub>001</sub> <sup>iv</sup>	84(1)			O(3) <sub>001</sub> <sup>iv</sup> –U(2)–O(2)	78(1)						
U(3) (octahedral distorted environment)											
U(3)–O(7)	1.86(1)	$S_{ij}$	1.79	O(7)–U(3)–O(7) <sub>110</sub> <sup>ii</sup>	180						
U(3)–O(7) <sub>110</sub> <sup>ii</sup>	1.86(1)		1.79	O(7)–U(3)–O(11) <sub>111</sub> <sup>ii</sup>	88(1)						
U(3)–O(11) <sub>111</sub> <sup>ii</sup>	2.29(2)		0.56	O(7)–U(3)–O(12)	89(1)						
U(3)–O(12)	2.28(2)		0.57	O(7)–U(3)–O(11) <sub>001</sub>	92(1)						
U(3)–O(11) <sub>001</sub>	2.29(2)		0.56	O(7)–U(3)–O(12) <sub>110</sub> <sup>ii</sup>	91(1)						
U(3)–O(12) <sub>110</sub> <sup>ii</sup>	2.28(2)		0.57								
		$\sum S_{ij} = 5.84$									
O(7) <sub>110</sub> <sup>ii</sup> –U(3)–O(11) <sub>111</sub> <sup>ii</sup>	92(1)			O(11) <sub>111</sub> <sup>ii</sup> –U(3)–O(12)	108(1)						
O(7) <sub>110</sub> <sup>ii</sup> –U(3)–O(12)	91(1)			O(12)–U(3)–O(11) <sub>001</sub>	71(1)						
O(7) <sub>110</sub> <sup>ii</sup> –U(3)–O(11) <sub>001</sub>	88(1)			O(11) <sub>001</sub> –U(3)–O(12) <sub>110</sub> <sup>ii</sup>	108(1)						
O(7) <sub>110</sub> <sup>ii</sup> –U(3)–O(12) <sub>110</sub> <sup>ii</sup>	89(1)			O(12) <sub>110</sub> <sup>ii</sup> –U(3)–O(11) <sub>111</sub> <sup>ii</sup>	72(1)						
Environment of K											
K(1)–O(8) <sub>110</sub> <sup>ii</sup>	2.56(2)	$S_{ij}$	0.31	K(2)–O(7) <sub>010</sub> <sup>iv</sup>	2.67(1)	$S_{ij}$	0.23	K(3)–O(1) <sub>110</sub> <sup>ii</sup>	2.70(2)	$S_{ij}$	0.21
K(1)–O(5) <sub>100</sub>	2.60(2)		0.28	K(2)–O(5) <sub>111</sub> <sup>iv</sup>	2.69(1)		0.22	K(3)–O(8) <sub>100</sub> <sup>iii</sup>	2.73(2)		0.20
K(1)–O(7)	2.72(2)		0.20	K(2)–O(9) <sub>200</sub> <sup>iii</sup>	2.70(1)		0.21	K(3)–O(1) <sub>200</sub> <sup>iii</sup>	2.81(2)		0.16
K(1)–O(6)	2.75(2)		0.19	K(2)–O(5) <sub>100</sub> <sup>iii</sup>	2.79(1)		0.17	K(3)–O(6) <sub>011</sub> <sup>iv</sup>	2.90(2)		0.13
K(1)–O(1) <sub>200</sub> <sup>iii</sup>	2.75(2)		0.19	K(2)–O(6) <sub>011</sub> <sup>iv</sup>	2.81(1)		0.16	K(3)–O(4) <sub>110</sub> <sup>i</sup>	3.25(2)		0.05
K(1)–O(9) <sub>210</sub> <sup>iii</sup>	2.78(1)		0.17	K(2)–O(7) <sub>200</sub> <sup>iii</sup>	2.83(1)		0.15	K(3)–O(9) <sub>200</sub> <sup>iii</sup>	3.28(2)		0.04
		$\sum S_{ij} = 1.34$				$\sum S_{ij} = 1.14$				$\sum S_{ij} = 0.79$	

Note. O(n)<sub>paq</sub><sup>m</sup> represents atom O(n) to which the symmetry m has been applied, followed by a translation pa + qb + rc. Symmetry code: (i): x, y, z; (ii)  $\bar{x}$ ,  $\bar{y}$ ,  $\bar{z}$ ; (iii):  $\bar{x}$ ,  $\frac{1}{2} + y$ ,  $\frac{1}{2} - z$ ; (iv):  $x$ ,  $\frac{1}{2} - y$ ,  $\frac{1}{2} + z$ .

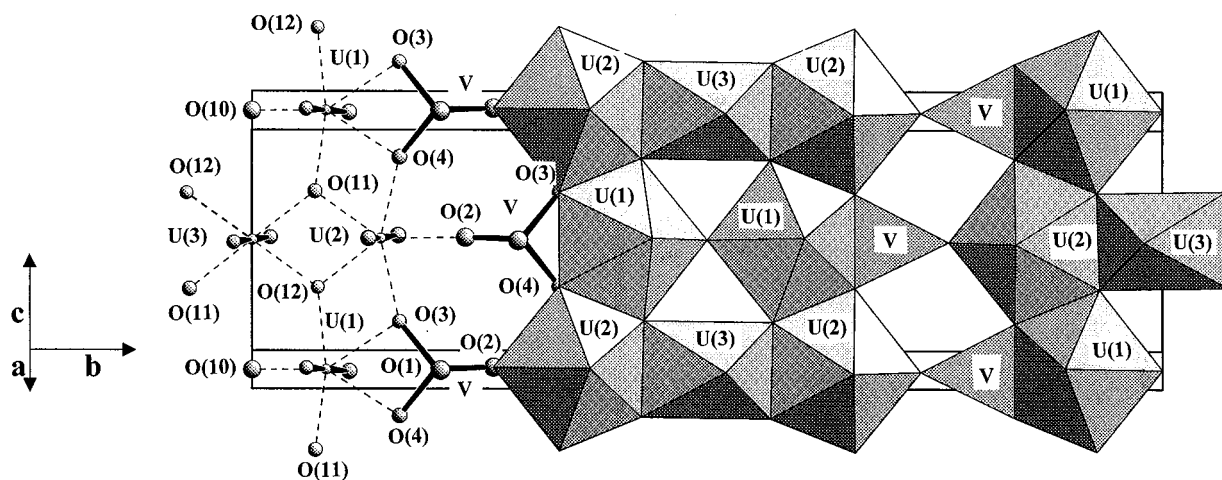


FIG. 1. Projection of the crystal structure of  $K_6(UO_2)_5(VO_4)_2O_5$  on the (100) plane showing the connection between U(1)–U(2) zig-zag chains either by  $VO_4$  or by O(10) oxygen atoms and U(3)O<sub>6</sub> distorted octahedra.

studied compounds like  $U_2P_2O_{10}$  (34), uranyl divanadate  $(UO_2)_2V_2O_7$  (11, 12), and pentahydrated uranyl orthovanadate  $(UO_2)_3(VO_4)_2 \cdot 5H_2O$  (22).

Two parallel chains related by an inversion center are linked together by O(10) oxygen atoms occupying the inversion center (site 2b) and by U(3)O<sub>6</sub> distorted octahedra. The O(10) oxygen atom is common to two equatorial pentagons of U(1)O<sub>7</sub> bipyramids. U(3)O<sub>6</sub> distorted octahedra link two U(2)O<sub>7</sub> bipyramids of two U(1)–U(2) chains by sharing symmetrical edges O(11)–O(12). The U(3) atom occupies a particular 2d site. It results in ribbons three uranium polyhedra in width, developed along the *c* axis, and nearly parallel to the (110) plane, formed from  $[(UO_2)_5O_{11}]$  building units.

Two  $(U_5O_{21})_n$  ribbons related by the  $2_1$  screw axis are linked together by  $VO_4$  tetrahedra. Each  $VO_4$  tetrahedron shares an O(3)–O(4) edge with a U(1)O<sub>7</sub> equatorial pentagon of one ribbon and an O(2) corner with a U(2)O<sub>7</sub> bipyramid of the neighboring ribbon. This results in corrugated layers of  $(U_5V_2O_{23})_n^{6n-}$  of mean plane (100) and developed in waves along the *b* axis. The layers are stacked along *a*. Fig. 2 represents an orthogonal projection of the layers in the (001) plane. The connection of two parallel U(1)–U(2) zig-zag chains by  $VO_4$  tetrahedra is very similar to that found in  $(UO_2)_3(VO_4)_2 \cdot 5H_2O$ .

Vanadium atoms have a strongly distorted tetrahedral environment of oxygen atoms with two long V–O distances with O(3) and O(4) atoms shared between two  $UO_7$  polyhedra and two shorter distances with O(2) atom shared with only one  $UO_7$  polyhedron and with O(1) atom that participates only to the potassium K(1) and K(3) ions coordination. The O(3)–O(4) edge shared between  $VO_4$  and U(1)O<sub>7</sub> bipyramid is shorter than the other O–O edges that are not shared so the O(3)–V–O(4) angle is particularly lower than 109.7°.

The  $K^+$  ions are located in the available space between the layers. The three crystallographically independent potassium atoms are hexacoordinated with oxygen atoms in the following ranges: K–O, 2.56 Å–2.78 Å for K(1); 2.67 Å–2.83 Å for K(2); and 2.70 Å–3.28 Å for K(3). The anisotropic thermal vibration of K(3) is greater than that of K(1) and K(2) in accordance with the higher K(3)–O average length.

Bond valence sums calculated using Brown and Altermatt's data (29) are reported in Table 8. Results confirm oxidation state +5 for vanadium. K(1) is overbonded when K(3) is underbonded as previously evidenced by high values of displacement parameters and average K(3)–O distance. For the U(1) and U(2) atoms in pentagonal bipyramidal coordination, the high values calculated confirm the conclusion of Dickens *et al.* (13) which points out that new parameters are needed to apply the valence bond model to uranium in uranyl ions. However the value tabulated for  $U^{6+}$  gives a very acceptable valence sum value for U(3) involved in a uranyl ion but in a distorted octahedral coordination. In fact the valence bond sum is very sensitive to the U–O distances for the uranyl anion.

The crystal structure of  $Na_6(UO_2)_5(VO_4)_2O_5$  is very similar to that of  $K_6(UO_2)_5(VO_4)_2O_5$ . The most significant distances and angles are reported in Table 9. The main difference between the two structures lies in the symmetry relations between the  $UO_7$  zig-zag chains. In the K compound the O(10) oxygen atom shared by two U(1)O<sub>7</sub> bipyramids occupied an inversion center. In the Na compound all the atoms occupied a general crystallographic site, so two corner-shared zig-zag chains are crystallographically independent, U(1)–U(2) and U(4)–U(5), respectively (Fig. 3). The U(3) atom doesn't occupy an inversion center any more; as a consequence the octahedral polyhedron around U(3) is more distorted than in the K compound, in particular the U(3)O<sub>2</sub> uranyl ion is no longer perfectly

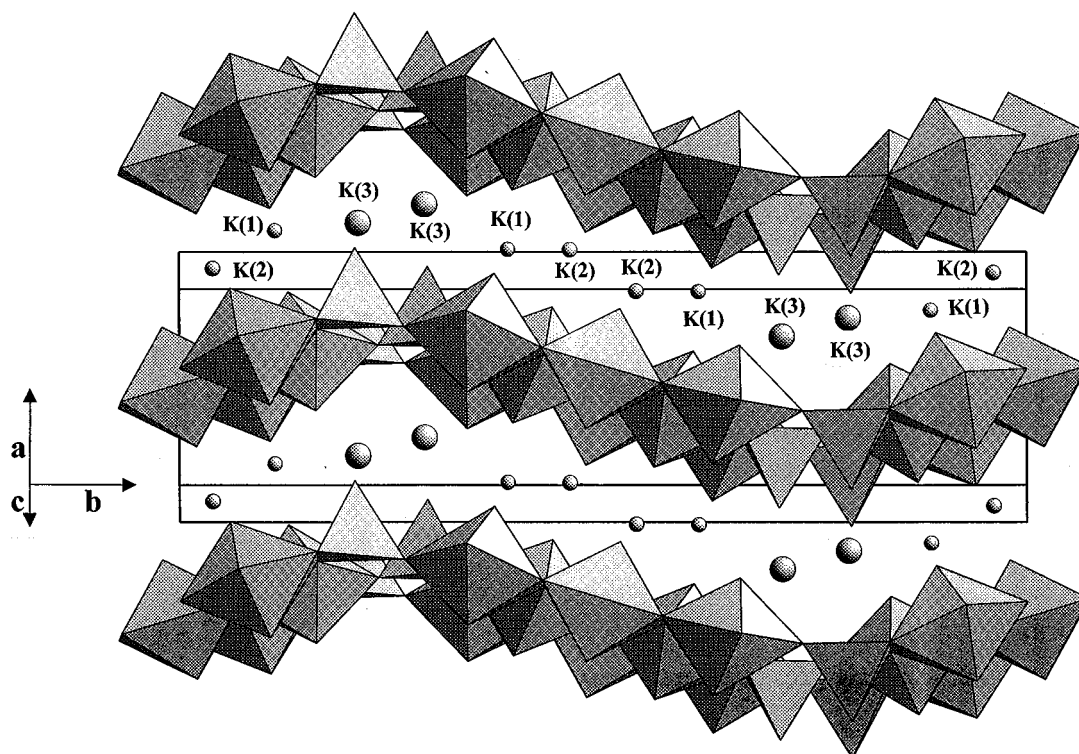


FIG. 2. Projection of the crystal structure of  $K_6(UO_2)_5(VO_4)_2O_5$  on the (001) plane showing the corrugated  $(U_5V_2O_{23})_n^{6n-}$  layers stacked along  $a$  and interlayer K atoms.

centrosymmetric. The  $(U_5O_{21})_n$  ribbons are no longer related by the  $2_1$  screw axis but only by the  $c$  mirror. In fact, two consecutive U(1)–U(2) chains related by the  $c$  mirror at  $y = 1/4$  are connected by V(1)O<sub>4</sub> tetrahedra when two U(4)–U(5) chains related by the  $c$  mirror at  $y = 3/4$  are connected by V(2)O<sub>4</sub> tetrahedra.

Two parallel corrugated  $(U_5V_2O_{23})_n^{6n-}$  layers are related by an inversion center (and a  $2_1$  screw axis). The Na sheets between two consecutive uranyl vanadate layers are also crystallographically independent (Fig. 4).

In summary, the  $M_2[(UO_2)_5(VO_4)_2O_5]$  structures for  $M = Na$  and  $K$  present an important relationship. Both structures are centrosymmetric and built from the layers  $[(UO_2)_5(VO_4)_2O_5]_n^{6n-}$ . The difference comes from the layer that is alone and thus centrosymmetric in the  $K$  compound while in the  $Na$  compound it is individually not centrosymmetric but the two layers of a unit cell are related by an inversion center. Thus the  $Na$  compound contains twice as many atoms.

The layered structure of  $M_6(UO_2)_5(VO_4)_2O_5$  compounds with large  $Na$  and  $K$  displacement parameters particularly for the underbonded K(3), Na(5), and Na(6) atoms allows us to consider some mobility of the alkali metal ions. Conductivity measurements were performed by ac impedance spectroscopy on sintered materials over the range 350–650°C. Figure 5 indicates the temperature dependence

of the conductivity of  $K$  and  $Na$  compounds; for comparison conductivity values for  $K$  and  $Na$  carnotites are also reported. For  $K_6(UO_2)_5(VO_4)_2O_5$  the conductivity variation versus temperature agrees with an Arrhenius law over the studied temperature range with values lower about a factor of 10 compared to those of carnotite. However the activation energy for conduction of 0.56 eV is very close to the value calculated for the  $K$  carnotite (0.57 eV); thus the undulation of the uranyl vanadate layers doesn't seem to restrict the pathway for  $K^+$  ions' mobility. Up to 500°C  $Na_6(UO_2)_5(VO_4)_2O_5$  presents conductivity values close to those of  $Na$  carnotite but with a higher activation energy (0.78 eV compared to 0.52 eV). There is a weak jump on the conductivity curve at 550°C; above this temperature, the activation energy is lower (0.50 eV) and very close to that calculated for the  $K$  compound. Thus the anomaly at 550°C could be attributed to a transition to the  $K$ -type structure. Unfortunately, so far this transition could not be detected by DSC or high-temperature X-ray diffraction. A similar and more important jump was observed on the  $Na$  carnotite curve at about the same temperature. In conclusion, in both families, electrical conductivity is better for  $Na^+$  than  $K^+$  ions, in accordance with size and mobility. For the same alkali metal ( $Na$  or  $K$ ) electrical conductivity is better in the carnotite family compounds than in the  $M_6(UO_2)_5(VO_4)_2O_5$  family and the difference is decreased for the  $Na$



**TABLE 9**  
**Bond Distances (Å), Angles (°) in Na<sub>6</sub>(UO<sub>2</sub>)<sub>5</sub>(VO<sub>4</sub>)<sub>2</sub>O<sub>5</sub>, and S<sub>ij</sub> Calculations**

V(1) (tetrahedral environment)				
		<i>S<sub>ij</sub></i>		
V(1)–O(1)	1.65(1)	1.51	O(1)–V(1)–O(2)	110(2)
V(1)–O(2)	1.74(2)	1.19	O(1)–V(1)–O(3)	115(2)
V(1)–O(3)	1.79(2)	1.04	O(1)–V(1)–O(4)	109(2)
V(1)–O(4)	1.68(2)	1.39	O(2)–V(1)–O(3)	96(1)
		$\sum s_{ij} = 5.13$	O(2)–V(1)–O(4)	113(2)
			O(3)–V(1)–O(4)	113(2)
V(2) (tetrahedral environment)				
		<i>S<sub>ij</sub></i>		
V(2)–O(5)	1.63(3)	1.59	O(5)–V(2)–O(6)	111(1)
V(2)–O(6)	1.73(2)	1.22	O(5)–V(2)–O(7)	109(2)
V(2)–O(7)	1.77(2)	1.09	O(5)–V(2)–O(8)	107(2)
V(2)–O(8)	1.69(2)	1.36	O(6)–V(2)–O(7)	95(2)
		$\sum s_{ij} = 5.26$	O(6)–V(2)–O(8)	117(2)
			O(7)–V(2)–O(8)	117(3)
U(1) (pentagonal bipyramid environment)				
		<i>S<sub>ij</sub></i>		
U(1)–O(9)	1.84(1)	1.89	O(9)–U(1)–O(10)	179(12)
U(1)–O(10)	1.84(1)	1.89	O(9)–U(1)–O(2) <sub>110</sub> <sup>iii</sup>	101(1)
U(1)–O(2) <sub>110</sub> <sup>iii</sup>	2.64(2)	0.22	O(9)–U(1)–O(12)	88(1)
U(1)–O(12)	2.22(2)	0.66	O(9)–U(1)–O(11)	92(1)
U(1)–O(11)	2.17(2)	0.77	O(9)–U(1)–O(13)	92(1)
U(1)–O(13)	2.25(2)	0.62	O(9)–U(1)–O(3) <sub>110</sub> <sup>iii</sup>	87(1)
U(1)–O(3) <sub>110</sub> <sup>iii</sup>	2.45(2)	0.36		
		$\sum s_{ij} = 6.41$		
O(10)–U(1)–O(2) <sub>110</sub> <sup>iii</sup>	79(1)		O(2) <sub>110</sub> <sup>iii</sup> –U(1)–O(12)	63(1)
O(10)–U(1)–O(12)	93(1)		O(12)–U(1)–O(11)	78(1)
O(10)–U(1)–O(11)	89(1)		O(11)–U(1)–O(13)	90(1)
O(10)–U(1)–O(13)	87(1)		O(13)–U(1)–O(3) <sub>110</sub> <sup>iii</sup>	70(1)
O(10)–U(1)–O(3) <sub>110</sub> <sup>iii</sup>	92(1)		O(3) <sub>110</sub> <sup>iii</sup> –U(1)–O(2) <sub>110</sub> <sup>iii</sup>	62(1)
U(2) (pentagonal bipyramid environment)				
		<i>S<sub>ij</sub></i>		
U(2)–O(14)	1.82(1)	1.99	O(14)–U(2)–O(15)	175(9)
U(2)–O(15)	1.83(1)	1.94	O(14)–U(2)–O(12) <sub>001</sub> <sup>iv</sup>	86(1)
U(2)–O(12) <sub>001</sub> <sup>iv</sup>	2.24(2)	0.64	O(14)–U(2)–O(13) <sup>iv</sup>	92(1)
U(2)–O(13) <sup>iv</sup>	2.34(2)	0.49	O(14)–U(2)–O(3) <sub>111</sub> <sup>ii</sup>	87(1)
U(2)–O(3) <sub>111</sub> <sup>ii</sup>	2.32(1)	0.52	O(14)–U(2)–O(4) <sub>110</sub> <sup>iii</sup>	79(1)
U(2)–O(4) <sub>110</sub> <sup>iii</sup>	2.33(2)	0.52	O(14)–U(2)–O(2) <sub>110</sub> <sup>ii</sup>	101(1)
U(2)–O(2) <sub>110</sub> <sup>ii</sup>	2.35(1)	0.48		
		$\sum s_{ij} = 6.58$		
O(15)–U(2)–O(12) <sub>001</sub> <sup>iv</sup>	99(1)		O(12) <sub>001</sub> <sup>iv</sup> –U(2)–O(13) <sup>iv</sup>	70(1)
O(15)–U(2)–O(13) <sup>iv</sup>	89(1)		O(13) <sup>iv</sup> –U(2)–O(3) <sub>111</sub> <sup>ii</sup>	71(1)
O(15)–U(2)–O(3) <sub>111</sub> <sup>ii</sup>	89(1)		O(3) <sub>111</sub> <sup>ii</sup> –U(2)–O(4) <sub>110</sub> <sup>iii</sup>	74(1)
O(15)–U(2)–O(4) <sub>110</sub> <sup>iii</sup>	97(1)		O(4) <sub>110</sub> <sup>iii</sup> –U(2)–O(2) <sub>110</sub> <sup>ii</sup>	81(1)
O(15)–U(2)–O(2) <sub>110</sub> <sup>ii</sup>	82(1)		O(2) <sub>110</sub> <sup>ii</sup> –U(2)–O(12) <sub>001</sub> <sup>iv</sup>	68(1)
U(3) (octahedral distorted environment)				
		<i>S<sub>ij</sub></i>		
U(3)–O(16)	1.84(1)	1.88	O(16)–U(3)–O(17)	178(12)
U(3)–O(17)	1.83(1)	1.94	O(16)–U(3)–O(12) <sub>001</sub> <sup>iv</sup>	89(1)
U(3)–O(12) <sub>001</sub> <sup>iv</sup>	2.25(2)	0.62	O(16)–U(3)–O(13) <sup>iv</sup>	93(1)
U(3)–O(13) <sup>iv</sup>	2.27(2)	0.59	O(16)–U(3)–O(18)	90(1)
U(3)–O(18)	2.28(2)	0.57	O(16)–U(3)–O(19)	89(1)
U(3)–O(19)	2.22(2)	0.68		
		$\sum s_{ij} = 6.31$		
O(17)–U(3)–O(12) <sub>001</sub> <sup>iv</sup>	93(1)		O(12) <sub>001</sub> <sup>iv</sup> –U(3)–O(13) <sup>iv</sup>	71(1)
O(17)–U(3)–O(13) <sup>iv</sup>	88(1)		O(13) <sup>iv</sup> –U(3)–O(18)	101(1)
O(17)–U(3)–O(18)	88(1)		O(18)–U(3)–O(19)	71(1)
O(17)–U(3)–O(19)	90(1)		O(19)–U(3)–O(12) <sub>001</sub> <sup>iv</sup>	117(2)

TABLE 9—Continued

U(4) (pentagonal bipyramid environment)								
		$s_{ij}$						
U(4)—O(20)	1.83(2)	1.94	O(20)—U(4)—O(21)		178(13)			
U(4)—O(21)	1.85(2)	1.84	O(20)—U(4)—O(11) <sub>010</sub> <sup>i</sup>		89(2)			
U(4)—O(11) <sub>010</sub> <sup>i</sup>	2.13(2)	0.86	O(20)—U(4)—O(19) <sub>010</sub> <sup>iv</sup>		93(1)			
U(4)—O(19) <sub>010</sub> <sup>iv</sup>	2.24(1)	0.64	O(20)—U(4)—O(6) <sub>011</sub> <sup>iv</sup>		82(1)			
U(4)—O(6) <sub>011</sub> <sup>iv</sup>	2.52(2)	0.30	O(20)—U(4)—O(7) <sub>011</sub> <sup>iv</sup>		94(1)			
U(4)—O(7) <sub>011</sub> <sup>iv</sup>	2.49(2)	0.33	O(20)—U(4)—O(18) <sub>011</sub> <sup>iv</sup>		87(1)			
U(4)—O(18) <sub>011</sub> <sup>iv</sup>	2.24(1)	0.64						
		$\sum s_{ij} = 6.58$						
O(21)—U(4)—O(11) <sub>010</sub> <sup>i</sup>	93(1)		O(11) <sub>010</sub> <sup>i</sup> —U(4)—O(19) <sub>010</sub> <sup>iv</sup>		76(1)			
O(21)—U(4)—O(19) <sub>010</sub> <sup>iv</sup>	89(1)		O(19) <sub>010</sub> <sup>iv</sup> —U(4)—O(6) <sub>011</sub> <sup>iv</sup>		65(1)			
O(21)—U(4)—O(6) <sub>011</sub> <sup>iv</sup>	97(1)		O(6) <sub>011</sub> <sup>iv</sup> —U(4)—O(7) <sub>011</sub> <sup>iv</sup>		62(1)			
O(21)—U(4)—O(7) <sub>011</sub> <sup>iv</sup>	84(1)		O(7) <sub>011</sub> <sup>iv</sup> —U(4)—O(18) <sub>011</sub> <sup>iv</sup>		69(1)			
O(21)—U(4)—O(18) <sub>011</sub> <sup>iv</sup>	91(1)		O(18) <sub>011</sub> <sup>iv</sup> —U(4)—O(11) <sub>010</sub> <sup>i</sup>		90(1)			
U(5) (pentagonal bipyramid environment)								
		$s_{ij}$						
U(5)—O(22)	1.82(1)	1.99	O(22)—U(5)—O(23)		179(14)			
U(5)—O(23)	1.81(1)	2.05	O(22)—U(5)—O(6) <sub>001</sub> <sup>i</sup>		89(1)			
U(5)—O(6) <sub>001</sub> <sup>i</sup>	2.36(2)	0.46	O(22)—U(5)—O(8) <sub>011</sub> <sup>iv</sup>		92(1)			
U(5)—O(8) <sub>011</sub> <sup>iv</sup>	2.28(2)	0.57	O(22)—U(5)—O(7)		96(1)			
U(5)—O(7)	2.33(1)	0.50	O(22)—U(5)—O(18)		87(1)			
U(5)—O(18)	2.32(2)	0.52	O(22)—U(5)—O(19)		94(1)			
U(5)—O(19)	2.21(2)	0.69						
		$\sum s_{ij} = 6.78$						
O(23)—U(5)—O(6) <sub>001</sub> <sup>i</sup>	91(1)		O(6) <sub>001</sub> <sup>i</sup> —U(5)—O(8) <sub>011</sub> <sup>iv</sup>		72(1)			
O(23)—U(5)—O(8) <sub>011</sub> <sup>iv</sup>	87(1)		O(8) <sub>011</sub> <sup>iv</sup> —U(5)—O(7)		80(1)			
O(23)—U(5)—O(7)	83(1)		O(7)—U(5)—O(18)		70(1)			
O(23)—U(5)—O(18)	94(1)		O(18)—U(5)—O(19)		70(1)			
O(23)—U(5)—O(19)	87(1)		O(19)—U(5)—O(6) <sub>001</sub> <sup>i</sup>		68(1)			
Environment of Na								
		$s_{ij}$		$s_{ij}$		$s_{ij}$		$s_{ij}$
Na(1)—O(11) <sub>100</sub> <sup>iii</sup>	2.44(1)	0.18	Na(2)—O(14) <sup>iv</sup>	2.32(2)	0.25	Na(3)—O(23) <sub>110</sub> <sup>ii</sup>	2.37(2)	0.22
Na(1)—O(10) <sub>100</sub> <sup>iv</sup>	2.45(1)	0.17	Na(2)—O(21) <sub>110</sub> <sup>ii</sup>	2.43(2)	0.18	Na(3)—O(9) <sup>iv</sup>	2.42(2)	0.19
Na(1)—O(17) <sub>110</sub> <sup>iii</sup>	2.46(2)	0.17	Na(2)—O(16) <sup>iv</sup>	2.49(2)	0.16	Na(3)—O(16) <sub>110</sub> <sup>ii</sup>	2.45(2)	0.17
Na(1)—O(13) <sub>100</sub> <sup>iv</sup>	2.58(1)	0.12	Na(2)—O(5) <sub>110</sub> <sup>iii</sup>	2.57(2)	0.13	Na(3)—O(21) <sub>100</sub> <sup>iv</sup>	2.47(2)	0.16
Na(1)—O(15) <sub>100</sub>	2.63(2)	0.11	Na(2)—O(9)	2.56(2)	0.13	Na(3)—O(21) <sub>110</sub> <sup>iii</sup>	2.67(2)	0.10
Na(1)—O(17) <sub>100</sub>	2.70(2)	0.09	Na(2)—O(7) <sub>110</sub> <sup>iii</sup>	2.68(2)	0.09	Na(3)—O(16)	2.73(2)	0.08
Na(1)—O(10) <sub>100</sub> <sup>iii</sup>	2.71(2)	0.09	Na(2)—O(23) <sub>110</sub> <sup>iii</sup>	2.80(2)	0.07	Na(3)—O(19) <sub>110</sub> <sup>ii</sup>	3.11(2)	0.03
Na(1)—O(1) <sub>110</sub> <sup>iii</sup>	2.98(2)	0.04	Na(2)—O(12)	2.93(2)	0.05			
		$\sum s_{ij} = 0.97$		$\sum s_{ij} = 1.05$				$\sum s_{ij} = 0.95$
		$s_{ij}$		$s_{ij}$		$s_{ij}$		$s_{ij}$
Na(4)—O(10) <sub>100</sub>	2.37(2)	0.22	Na(5)—O(20) <sub>110</sub> <sup>iii</sup>	2.43(2)	0.18	Na(6)—O(5) <sub>111</sub> <sup>ii</sup>	2.33(2)	0.24
Na(4)—O(22) <sub>110</sub> <sup>iii</sup>	2.41(2)	0.19	Na(5)—O(1) <sub>011</sub> <sup>ii</sup>	2.53(2)	0.14	Na(6)—O(14)	2.36(2)	0.22
Na(4)—O(17) <sub>110</sub> <sup>iii</sup>	2.56(2)	0.13	Na(5)—O(15) <sub>100</sub>	2.56(2)	0.13	Na(6)—O(3) <sub>111</sub> <sup>ii</sup>	2.65(2)	0.10
Na(4)—O(20) <sub>110</sub> <sup>iii</sup>	2.63(2)	0.11	Na(5)—O(1) <sub>010</sub> <sup>iii</sup>	2.56(2)	0.13	Na(6)—O(8) <sub>110</sub> <sup>iii</sup>	2.68(2)	0.09
Na(4)—O(2) <sub>010</sub> <sup>iii</sup>	2.66(2)	0.10	Na(5)—O(22) <sub>110</sub> <sup>ii</sup>	2.72(2)	0.08	Na(6)—O(23) <sub>110</sub> <sup>ii</sup>	2.70(2)	0.09
Na(4)—O(15) <sub>100</sub> <sup>iv</sup>	2.75(2)	0.08	Na(5)—O(6) <sub>111</sub> <sup>ii</sup>	3.06(2)	0.03	Na(6)—O(9) <sup>iv</sup>	3.03(2)	0.04
Na(4)—O(1) <sub>010</sub> <sup>iii</sup>	2.86(2)	0.06	Na(5)—O(22) <sub>110</sub> <sup>iii</sup>	3.26(2)	0.02	Na(6)—O(4) <sub>110</sub> <sup>iii</sup>	3.27(2)	0.02
		$\sum s_{ij} = 0.89$		$\sum s_{ij} = 0.71$				$\sum s_{ij} = 0.80$

Note. O( $n$ )<sub>*paq*</sub><sup>*m*</sup> represents atom O( $n$ ) to which the symmetry  $m$  has been applied, followed by a translation  $pa + qb + rc$ . Symmetry code: (i)  $x, y, z$ ; (ii)  $\bar{x}, \bar{y}, \bar{z}$ ; (iii)  $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iv)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ .

compounds. It is more difficult to explain this fact. The comparison of alkali ions' environments in  $M_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  and  $M_2(\text{UO}_2)_2\text{V}_2\text{O}_8$  can perhaps explain these observations. In our new compounds interlayer alkali

metals can be considered hexacoordinated by oxygen atoms.  $\text{K}^+$  ions are surrounded by six oxygen ions situated, respectively, in the ranges 2.56–2.78 Å for K(1), 2.67–2.83 Å for K(2), and 2.70–3.28 Å for K(3). In a radius of 3.40 Å only

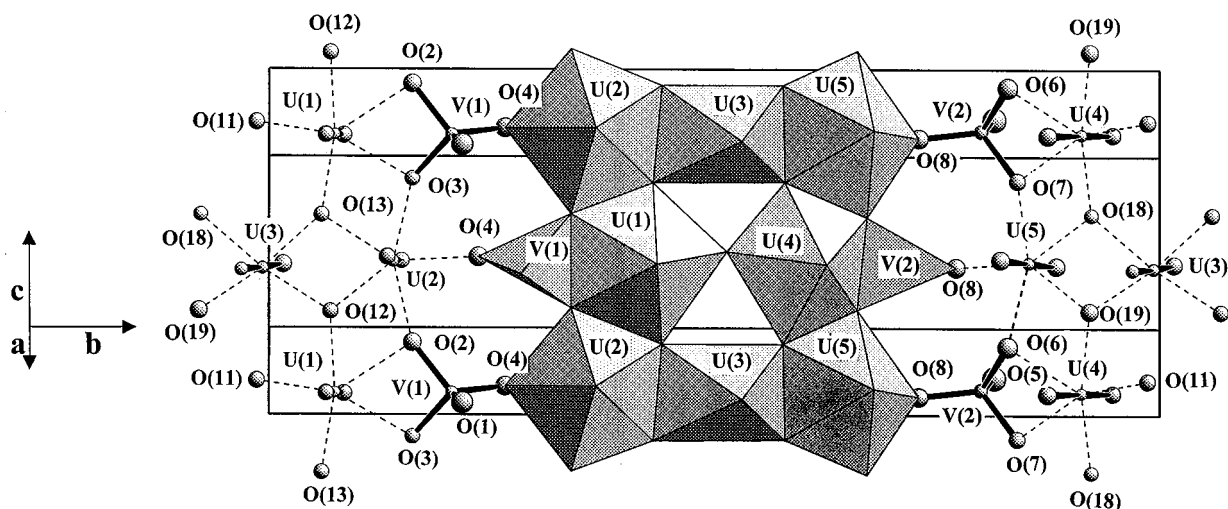


FIG. 3. Projection of the crystal structure of  $\text{Na}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  on the (100) plane showing the two independent U(1)–U(2) and U(4)–U(5) zig-zag chains.

two additional oxygen atoms are found around K(1) and K(2) and not any around K(3) which is probably the most mobile ion. Oxygen atoms are less numerous but at shorter distances than in carnotite where  $\text{K}^+$  ions are surrounded by 11 oxygen atoms in the range 2.62–3.43 Å. For  $\text{Na}^+$  ions, an identical situation is observed with seven or eight oxygen atoms, respectively, in the ranges 2.44–2.98 Å for Na(1), 2.32–2.93 Å for Na(2), 2.37–3.11 Å for Na(3), 2.37–2.86 Å for Na(4), 2.43–3.26 Å for Na(5), and 2.33–3.27 for Na(6). In Na analog carnotite, metal alkali atoms are surrounded by 11 oxygen atoms at distances ranging from 2.73 to 3.40 Å. This environment of alkali ions by oxygen atoms less numerous but at shorter distances can explain electrical conductivity lower than that in carnotites.

## CONCLUSION

The reaction of uranyl orthovanadate  $(\text{UO}_2)_3(\text{VO}_4)_2$  in a large excess of molten potassium chloride does not lead to the expected ion exchange reaction but to single crystals of a new layered compound,  $\text{K}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$ . It can be directly synthesized by heating the mixture  $\text{UO}_3\text{--V}_2\text{O}_5\text{--K}_2\text{CO}_3$  in molar accounts 5/1/3. The Na analog has been obtained from a binary system  $\text{Na}_2\text{UO}_4\text{--V}_2\text{O}_5$  study. The two structures have been solved from single crystals. Unit cells are monoclinic with the same space group  $P2_1/c$ . Both structures are centrosymmetric. In  $\text{K}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  the unit cell contains one centrosymmetric uranyl vanadate layer. In  $\text{Na}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  the layers are very similar

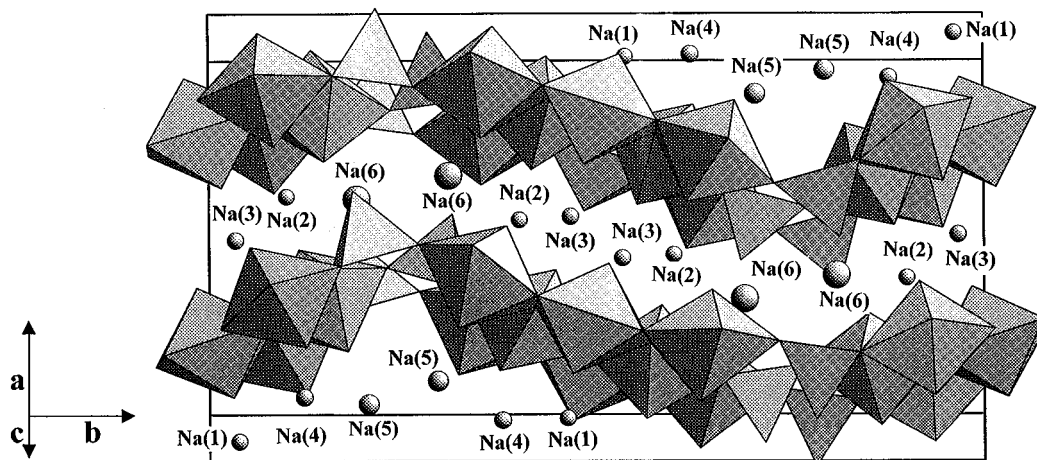


FIG. 4. Projection of the crystal structure of  $\text{Na}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  on the (001) plane. Two parallel corrugated layers are related by an inversion center. The Na ions in two consecutive sheets along  $a$  are crystallographically independent.

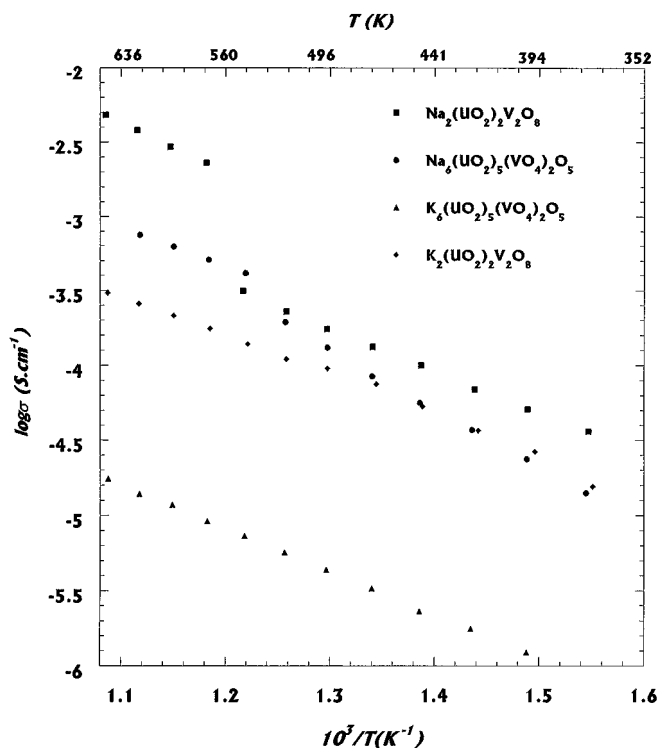


FIG. 5. Comparison of conductivity vs temperature between  $M_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$  and  $M$  analog carnotites ( $M = \text{Na}, \text{K}$ ).

but not centrosymmetric; the unit cell is double and thus contains two layers related by an inversion center.

The  $\text{K}^+$  or  $\text{Na}^+$  ions exhibit a relatively good mobility in the interlayer space; however, the electrical conductivity is slightly inferior to that of the Na analog of carnotite. Results are therefore interesting because comparison of different types of layers could bring a better understanding of the factors influencing the ionic electrical conductivity properties of the layered uranyl vanadate compounds.

## REFERENCES

1. Y. F. Yao and J. T. Kummer, *J. Inorg. Nuclear. Chem.* **29**, 2453 (1967).
2. B. Morosin, *Phys. Lett.* **65A**, 53 (1978).

3. A. T. Howe and M. G. Shilton, *J. Solid State Chem.* **28**, 345 (1979).
4. P. E. Childs, A. T. Howe, and M. G. Shilton, *J. Solid State Chem.* **34**, 341 (1980).
5. C. M. Johnson, M. G. Shilton, and A. T. Howe, *J. Solid State Chem.* **37**, 37 (1981).
6. M. Phan-Thi and Ph. Colomban, *Solid State Ionics* **17**, 295 (1985).
7. J. Benavente, J. R. Ramos-Barrado, M. Martinez, and S. Bruque, *J. Appl. Electrochem.* **25**, 68 (1995).
8. F. Abraham, C. Dion, and M. Saadi, *J. Mater. Chem.* **3**(5), 459 (1993).
9. F. Abraham, C. Dion, N. Tancret, and M. Saadi, *Adv. Mater. Res.* **1-2**, 511 (1994).
10. Weigel and G. Hoffmann, *J. Less-Common Met.* **44**, 99 (1976).
11. P. B. Barton, *J. Am. Miner.* **43**, 799 (1958).
12. D. E. Appleman and H. T. Evans, *J. Am. Miner.* **50**, 825 (1965).
13. P. G. Dickens, G. P. Stuttard, R. G. J. Ball, A. V. Powell, S. Hull, and S. Patat, *J. Mater. Chem.* **2**(2), 161 (1992).
14. F. Cesbron, thesis, Paris, 1970.
15. D. P. Shashkim, *Dokl. Akad. Nauk SSSR* **220**, 1410 (1974).
16. J. Borene and F. Cesbron, *Bull. Soc. Fr. Miner. Cristallogr.* **93**, 426 (1970).
17. P. Piret, P. Declercq, and D. Wauters-Stoop, *Bull. Miner.* **103**, 176 (1980).
18. I. Duribreux, C. Dion, F. Abraham, and M. Saadi, *J. Solid State Chem.* **146**, 258 (1999).
19. A. M. Chippindale, S. J. Crennell, and P. G. Dickens, *J. Mater. Chem.* **3**, 33 (1993).
20. A. M. Chippindale, P. G. Dickens, G. J. Flynn, and G. P. Stuttard, *J. Mater. Chem.* **5**(1), 141 (1995).
21. N. Tancret, S. Obbade, and F. Abraham, *Eur. J. Solid State Inorg. Chem.* **32**, 195 (1995).
22. M. Saadi, C. Dion, and F. Abraham, *J. Solid State Chem.* **150**, 72 (2000).
23. G. Smith and R. J. Snyder, *J. Appl. Crystallogr.* **12**, 60 (1979).
24. J. De Meulenaer and H. Tompa, *Acta Crystallogr.* **19**, 1014 (1965).
25. G. M. Sheldrick, SHELXS-86, Program for Crystal Structure Determination, University of Göttingen, Germany, 1986.
26. C. T. Prewitt, SFLS-5, Report ORNL-TM 305, Oak Ridge National Laboratory, Oak Ridge, TN, 1966.
27. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, UK, 1974.
28. D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53**, 1891 (1970).
29. I. D. Brown and D. Altermatt, *Acta Crystallogr. B* **41**, 244 (1985).
30. B. O. Loopstra and H. M. Rietveld, *Acta Crystallogr. B* **25**, 787 (1969).
31. B. O. Loopstra, *Acta Crystallogr.* **17**, 651 (1964).
32. P. G. Dickens and G. P. Stuttard, *J. Mater. Chem.* **2**, 691 (1992).
33. T. L. Creemers, P. G. Eller, R. A. Penneman, and C. C. Herrick, *Acta Crystallogr.* **39**, 1163 (1983).
34. P. Benard, D. Loüer, N. Dacheux, V. Brandel, and M. Genet, *Chem. Mater.* **6**, 1049 (1994).