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$CsUV_3O_{11}$, a New Uranyl Vanadate with a Layered Structure

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A new cesium uranyl vanadate $CsUV_3O_{11}$ has been synthesized by solid state reaction. Its crystal structure has been determined from single-crystal X-ray diffraction data. It crystallizes in the monoclinic system with space group $P2_1/a$ and unit cell parameters $a = 11.904(2)$ Å, $b = 6.8321(6)$ Å, $c = 12.095(2)$ Å, $\beta = 106.989(5)^\circ$, $Z = 4$, and $D_{exp} = 4.89(2)$ g/cm^3. A full-matrix least squares refinement yielded $R = 0.046$ and $R_w = 0.045$ for 1831 independent reflections with $I > 3\sigma(I)$ collected on a Nonius CAD4 diffractometer (Mo$K\alpha$ radiation). The structure of $CsUV_3O_{11}$ is characterized by $[UV_3O_{11}]_\infty$ layers parallel to the (001) plane. The layers, very similar to those found in UV_3O_{10}, are built up from VO_5 square pyramids sharing corners of their equatorial bases and UO_8 hexagonal bipyramids, the U atoms occupying the hexagonal holes created by the VO_5 array. The Cs^+ ions are located between two successive layers and hold them together; the Cs^+ ions and two layers constitute a neutral "sandwich" $\{(UV_3O_{11}^-)–(Cs)_2^{2+}–(UV_3O_{11}^-)\}$. In this unusual structure, the neutral sandwiches are stacked one above another along the [104] direction with no formal chemical bonds between the neutral sandwiches. The Cs mobilities in $CsUV_3O_{11}$ and Cs carnotite are compared. © 1999 Academic Press

Key Words: **uranyl vanadate; crystal structure; layered structure; uvanite.**

INTRODUCTION

Layered structures are generally favorable for good electrical ionic conductivity. Among the layered compounds, hydrogen uranyl phosphate tetrahydrate, $HUO_2PO_4 \cdot 4H_2O$, also called HUP, has been evidenced to have good selective proton conductivity at room temperature and has received much attention because of its potential applications in electrochemical systems (1–5). With the aim of preparing new layered compounds, we have already studied uranyl vanadates with a molar ratio of U/V = 1 (6, 7). These materials are characterized by $(UO_2VO_4)_\infty$ sheets held together by interlayer cations alone or surrounded by H_2O molecules. They belong to the large class of compounds of the general formula $M_{1/n}^{n+}UO_2XO_4 \cdot xH_2O$, where X can be P, As, or V (8).

However, uranyl vanadates are quite different from phosphates and arsenates in the building of the layers. In P and As compounds, the UO_2^{2+} ions are connected by PO_4^{3-} or AsO_4^{3-} tetrahedra, whereas in V compounds, they are linked by $V_2O_8^{6-}$ units formed by two inverse VO_5 square pyramids sharing an edge.

Compounds of ratio U/V = 1/3 are also known to exist with the general formula $MUO_2(XO_3)_3$ where X can be P or V and M is commonly a monovalent cation: H_3O^+, Na^+, Cs^+, or NH_4^+ (9–12).

For X = P, uranyl polyphosphate acid $HUO_2(PO_3)_3$ (9) and monovalent cations salts, Na^+ (10) and Cs^+ (11), have been isolated and their structures established. Uranyl phosphate layers linked into a three-dimensional framework by polyphosphate chains are distinguished in the structure of H or Na compounds. In contrast, the structure of $CsUO_2(PO_3)_3$ involves cyclohexaphosphate rings $(P_6O_{18})^{6-}$ (with proper symmetry $\bar{1}$) which constitute the basis of the structure, together with the UO_2^{2+} and Cs^+ ions. Uranyl phosphate layers linked in a three-dimensional skeleton through –P–O–P– bridges can also be distinguished. In the three compounds, the uranyl group has a pseudosymmetric, linear structure, with five other oxygen atoms at greater distances in the equatorial plane to constitute a U seven-vertex polyhedron.

In summary, in the compounds where X = P, the structure results from the association of pentagonal bipyramids,

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UO_7, and tetrahedra, PO_4, linked in polyphosphate chains or in cyclohexaphosphate rings, $(P_6O_{18})^{6-}$.

For $X = \mathrm{V}$, a natural variety (called Uvanite) exists, and different derivated salts belonging to the class of compounds of the general formula $M^{n+}_{1/n}UO_2(VO_3)_3 \cdot xH_2O$ with $M = H_3O^+$, Na^+, NH_4^+, or Mg^{2+} (12) are suspected to have a layered structure on the basis of their exchange properties. The cations, found between the $[UO_2V_3O_9]^-$ layers, can be exchanged for inorganic and organic cations and some water molecules can be replaced by other solvent molecules (13).

No crystal structure has been established for this series of compounds. We have investigated methods of synthesis leading to single crystals of different monovalent cations and obtained single crystals for $M = \mathrm{Cs}$. The crystal structure of the anhydrous compound $Cs(UO_2)(VO_3)_3$ has been determined and is reported in this paper.

EXPERIMENTAL

$CsUV_3O_{11}$ was synthesized by a solid state reaction between a stoichiometric mixture of V_2O_5 (Aldrich), $UO_3 \cdot H_2O$ (Prolabo Rectapur), and Cs_2CO_3 (Aldrich) according to the following reaction:

$$2UO_3 \cdot H_2O + 3V_2O_5 + Cs_2CO_3 \rightarrow 2CsUV_3O_{11} + 2H_2O + CO_2.$$

The mixture was preheated at 300°C in air to dehydrate the uranium trioxide and then heated at 550°C for 2 days in an alumina crucible with an intermediate grinding. After such treatment, a new compound is formed with a distinctive X-ray diffraction pattern. The as-prepared powder was heated at 650°C (melting temperature: 575°C) in a platinum crucible and cooled at the rate of 3°C/h to room temperature, to obtain brown-colored single crystals. The crystals were crushed and characterized by X-ray powder diffraction using a Guinier-Dewolff focusing camera with Cu$K\alpha$ radiation. The X-ray diffraction pattern is identical to that of the powder previously prepared.

A well-shaped crystal of $CsUV_3O_{11}$ ($0.20 \times 0.19 \times 0.02\ \mathrm{mm}^3$) was selected for structure determination. Preliminary Weissenberg photographs indicated a monoclinic symmetry, systematic absences of $0k0$ ($k = 2n + 1$) and $h0l$ ($h = 2n + 1$) reflections revealed the $P2_1/a$ space group.

TABLE 1
Crystal Data, Intensity Measurement, and Structure Refinement Parameters for a $CsUV_3O_{11}$ Single Crystal

Crystal Data		
Crystal symmetry	Monoclinic	
Space group	$P2_1/a$	
Cell dimensions (Å)	$a = 11.904(2)$	
	$b = 6.8321(6)$	
	$c = 12.095(2)$	
	$\beta = 106.989(5)°$	
Volume (Å^3)	941(2)	
Z	4	
Calculated density	$\rho = 4.94\ \mathrm{g\,cm^{-3}}$	
Experimental density	$\rho = 4.89(2)\ \mathrm{g\,cm^{-3}}$	
Data Collection		
Equipment	Nonius CAD4	
λ Mo$K\alpha$ (graphite monochromator)	0.7107 Å	
Scan mode	ω–2θ	
Scan width (°)	$1.0 + 0.34 \tan \theta$	
Recording angular range (°)	2–30	
Standard reflections	$\bar{2}\bar{2}0$, $22\bar{1}$, $\bar{2}21$	
Recording reciprocal space	$-16 \leq h \leq 16$, $-9 \leq k \leq 9$, $0 \leq l \leq 16$	
Number of measured reflections	4118	
Number of reflections with $I > 3\sigma(I)$	3464	
Number of independent reflections	1831	
μ (cm^{-1}) (for $\lambda K\alpha = 0.7107$ Å)	235.11	
Limiting faces and distance (cm) from an arbitrary origin	001, $00\bar{1}$	0.0012
	$1\bar{1}0$, $\bar{1}10$	0.0102
	100, $\bar{1}00$	0.0096
Transmission factor range	0.058–0.553	
R merging factor	0.032	
Refinement		
Number of refined parameters	91	
$R = \sum[\lvert F_o\rvert - F_c\rvert]/\sum\lvert F_o\rvert$	0.046	
$R_W = [\sum w(\lvert F_o\rvert - F_c\rvert)^2/\sum F_o]^{1/2}$ with $w = 1$	0.045	
Goof = S (Goodness of fit)	3.58	

Single-crystal X-ray diffraction data were collected on a Nonius CAD4 diffractometer using graphite monochromatized Mo$K\alpha$ radiation. Crystal data, details of data collection, and structure refinement parameters are reported in Table 1. 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 (Cu$K\alpha$ radiation) equipped with a back monochromator and corrected for $K\alpha_2$ contribution (no displacement or zero-point correction). The figure of merit, as defined by Smith and Snyder (14), was $F_{20} = 63$ (0.0084, 38). The powder X-ray diffraction pattern data are reported in Table 2.

The density, measured with an automated Micromeritics Accupyc 1330 helium pycnometer using a 1-cm^3 cell, indicated $Z = 4$ formula per unit cell ($\rho_{exp} = 4.89(2)\ \mathrm{g\,cm^{-3}}$; $\rho_{cal} = 4.94\ \mathrm{g\,cm^{-3}}$).

The measured intensities were corrected for Lorentz and polarization effects and for absorption, using the analytical method of De Meulenaer and Tompa (15).

The structure was solved by the heavy-atom method. Uranium atoms are located from the Patterson function. The positions of Cs, V, and O atoms were deduced from subsequent refinements and difference Fourier syntheses. The full-matrix least-squares refinement was performed

TABLE 2

Observed and Calculated X-Ray Powder Diffraction Pattern for $CsUV_3O_{11}$ ($\lambda = 1.54056$ Å) ($a = 11.904(2)$ Å, $b = 6.8321(6)$ Å, $c = 12.095(2)$ Å, $\beta = 106.989(5)°$, $F_{20} = 63$ (0.0084, 38))

hkl	d_{obs}	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}/I_o	*hkl*	d_{obs}	$2\theta_{obs}$	$2\theta_{calc}$	I_{ob}/I_o
110	5.8617	15.102	15.111	2	402	2.3013	39.110	39.112	2
$20\bar{1}$	5.8276	15.191	15.194	3	$41\bar{4}$	2.2729	39.619	39.606	2
002	5.7833	15.308	15.308	86	$11\bar{5}$	2.2712	39.650	39.645	4
200	5.6960	15.544	15.554	8	313	2.2468	40.099	40.096	< 1
$11\bar{1}$	5.5644	15.914	15.884	10	$42\bar{1}$	2.2434	40.163	40.180	2
111	4.9400	17.941	17.957	13	$51\bar{1}$	2.2380	40.263	40.256	4
$11\bar{2}$	4.4655	19.866	19.868	12	$51\bar{2}$			40.281	
$21\bar{1}$	4.4345	20.006	20.012	7	$22\bar{4}$	2.2318	40.381	40.367	3
012	4.4092	20.122	20.099	3	$42\bar{2}$	2.2169	40.663	40.670	5
210	4.3757	20.278	20.289	4	$13\bar{1}$			40.673	
$21\bar{2}$	3.9369	22.566	22.550	3	420	2.1874	41.237	41.251	2
003	3.8558	23.047	23.048	100	412	2.1809	41.365	41.367	3
112	3.8401	23.143	23.160	6	223			41.386	
211	3.8166	23.287	23.284	2	$31\bar{5}$	2.1755	41.473	41.458	2
$20\bar{3}$	3.7391	23.777	23.773	9	131	2.1703	41.576	41.591	5
202	3.5691	24.927	24.928	8	510	2.1589	41.807	41.781	7
013	3.3577	26.524	26.523	21	$51\bar{3}$	2.1568	41.849	41.852	4
310	3.3175	26.852	26.851	4	$13\bar{2}$	2.1234	42.540	42.516	2
$21\bar{3}$	3.2794	27.170	27.161	4	$42\bar{3}$	2.1169	42.676	42.676	2
021	3.2757	27.201	27.197	13	421	2.0653	43.797	43.789	2
$31\bar{2}$	3.2595	27.339	27.340	3	115	2.0488	44.169	44.163	1
212	3.1613	28.205	28.186	7	132	2.0444	44.269	44.272	< 1
113	3.0181	29.573	29.565	1	231	2.0413	44.338	44.343	< 1
311	2.9949	29.808	29.829	3	511	2.0244	44.730	44.724	< 1
$40\bar{1}$	2.9732	30.030	30.036	44	$20\bar{6}$	2.0132	44.991	44.986	3
$22\bar{1}$	2.9465	30.309	30.305	24	$22\bar{5}$	1.9649	46.160	46.163	2
022	2.9418	30.359	30.364	28	033	1.9610	46.257	46.261	3
220	2.9290	30.494	30.493	20	205	1.9532	46.454	46.450	3
$40\bar{2}$	2.9136	30.660	30.664	1	330			46.465	
$31\bar{3}$	2.9111	30.687	30.711	3	$23\bar{3}$	1.9451	46.658	46.658	1
$22\bar{2}$	2.7861	32.099	32.083	2	413	1.9406	46.773	46.758	2
$11\bar{4}$	2.7629	32.376	32.373	3	$33\bar{2}$			46.771	
221	2.7438	32.608	32.618	4	006	1.9283	47.090	47.276	4
$40\bar{3}$	2.6969	33.191	33.187	1	232	1.9189	47.334	47.310	2
014	2.6625	33.633	33.626	4	224			47.340	
401	2.5946	34.540	34.554	1	025	1.9164	47.398	47.423	2
023	2.5563	35.074	35.067	1	512	1.8611	48.899	48.886	1
$22\bar{3}$	2.5236	35.544	35.565	2	$33\bar{3}$	1.8580	48.985	48.977	1
222	2.4670	36.388	36.375	1	515	1.8565	49.028	49.034	3
114	2.4507	36.639	36.635	2	016	1.8553	49.061	49.059	6
404	2.4114	37.258	37.263	5	$60\bar{4}$	1.8543	49.089	49.089	1
005	2.3136	38.894	38.898	24	$13\bar{4}$	1.8194	50.094	50.119	2

with a local modification of the SFLS-5 program (16). The atomic scattering factors for neutral atoms were taken from the "International Tables for X-ray Crystallography" (17) and the values for the anomalous dispersion correction from Cromer and Liberman (18). Refinement of atomic positional parameters, anisotropic displacement for U, Cs, and V atoms, and isotropic displacement parameters for O atoms yielded the final $R = 0.046$ and $R_w = 0.045$ for 1831 independent reflections. The atomic positions and equivalent displacement isotropic factors are given in Table 3. Anisotropic factors for metal atoms are given in Table 4.

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 560°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 1–10^6 Hz with a Solartron 1170 frequency-response analyzer. Measurements were made at 20°C intervals over the range 100–400°C on both heating and cooling. Each set of values was recorded at a given temperature after a 1-h stabilization time.

TABLE 3
Atomic Positions, Displacement Isotropic Parameters (O Atoms), and Equivalent Displacement Isotropic Parameters (U, Cs, and V atoms) for $CsUV_3O_{11}$

Atom	Site	x	y	z	B or B_{eq} (Å^2)
U	4e	0.30312(4)	0.0008(1)	0.18227(4)	0.501(9)
Cs	4e	0.1202(2)	0.7337(2)	0.4434(1)	4.72(5)
V(1)	4e	0.3162(2)	0.5040(4)	0.2268(2)	0.76(5)
V(2)	4e	0.0672(2)	0.2501(3)	0.2297(2)	0.77(6)
V(3)	4e	0.5407(2)	0.7494(3)	0.1384(2)	1.09(6)
O(1)	4e	0.2596(8)	0.003(2)	0.0305(9)	1.3(2)
O(2)	4e	0.3463(8)	− 0.008(2)	0.3352(9)	1.3(2)
O(3)	4e	0.3556(9)	0.516(2)	0.365(1)	2.1(2)
O(4)	4e	0.1088(9)	0.251(2)	0.370(1)	1.9(2)
O(5)	4e	0.002(1)	0.248(1)	− 0.001(1)	2.1(2)
O(6)	4e	0.4069(9)	0.692(1)	0.185(1)	0.8(2)
O(7)	4e	0.2004(9)	0.691(1)	0.182(1)	1.0(2)
O(8)	4e	0.4097(9)	0.309(1)	0.194(1)	1.0(2)
O(9)	4e	0.2035(8)	0.309(1)	0.1935(9)	0.7(2)
O(10)	4e	0.0984(7)	− 0.003(2)	0.1911(8)	0.9(1)
O(11)	4e	0.0126(7)	0.503(2)	0.1903(8)	0.8(1)

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

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Table 5 provides selected distances, angles, and bond valence sums calculated using Brown and Altermatt's data (19).

The three independent vanadium atoms are pentacoordinated, surrounded by five oxygen atoms in square pyramidal arrangements (Fig. 1). In all cases, the apical oxygen atom [O(3) for V(1), O(4) for V(2), and O(5) for V(3)] is at a shorter distance than oxygen atoms of the square base. These short V–O distances (1.60, 1.62, and 1.60 Å, respectively) indicate the existence of vanadyl V=O groups. Because of this, the sum of bond valences is a little higher than the expected value for the three V atoms, but remains however acceptable.

This type of coordination is typical of V^{4+} ions involved in VO^{2+} groups. In $K_2(VO)[V_2O_7]$ (20) and $(NH_4)_2VO[P_2O_7]$ (21) $V^{4+}O_5$ square pyramids are linked

TABLE 4
Anisotropic Displacement Parameters (×10^4) for $CsUV_3O_{11}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	38(2)	32(2)	126(2)	3(2)	33(1)	2(3)
Cs	970(12)	463(8)	268(8)	58(9)	25(8)	− 43(7)
V(1)	64(8)	38(8)	196(12)	− 10(13)	54(8)	10(14)
V(2)	30(9)	41(9)	239(15)	3(8)	65(10)	2(10)
V(3)	109(11)	97(11)	221(15)	1(9)	65(11)	− 3(11)

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

TABLE 5
Bond Distances (Å), Angles (°), and Bond Valences for $CsUV_3O_{11}$

		s_{ij}		
		U Environment		
U–O(1)	1.75(1)	**2.38**	O(1)–U–O(2)	178(11)
U–O(2)	1.77(1)	**2.29**	O(1)–U–O(6)$^{i}_{0\bar{1}0}$	91.0(7)
U–O(6)$^{i}_{0\bar{1}0}$	2.434(9)	**0.38**	O(1)–U–O(7)$^{i}_{0\bar{1}0}$	90.3(8)
U–O(7)$^{i}_{0\bar{1}0}$	2.44(1)	**0.38**	O(1)–U–O(8)	92.6(7)
U–O(8)	2.44(1)	**0.38**	O(1)–U–O(9)	92.8(8)
U–O(9)	2.434(9)	**0.38**	O(1)–U–O(10)	92.6(8)
U–O(10)	2.460(9)	**0.35**	O(1)–U–O(11)^{iv}	91.9(6)
U–O(11)^{iv}	2.458(9)	**0.35**		
		$\sum s_{ij} =$ **6.89**		
O(2)–U–O(6)$^{i}_{0\bar{1}0}$	87.9(7)			
O(2)–U–O(7)$^{i}_{0\bar{1}0}$	88.2(7)			
O(2)–U–O(8)	88.8(8)			
O(2)–U–O(9)	88.4(7)			
O(2)–U–O(10)	87.2(6)			
O(2)–U–O(11)^{iv}	88.3(7)			
		V(1) Environment		
		s_{ij}		
V(1)–O(3)	1.60(1)	**1.75**	O(3)–V(1)–O(6)	103(1)
V(1)–O(6)	1.83(1)	**0.92**	O(3)–V(1)–O(7)	104(1)
V(1)–O(7)	1.84(1)	**0.91**	O(3)–V(1)–O(8)	104(1)
V(1)–O(8)	1.85(1)	**0.89**	O(3)–V(1)–O(9)	104(1)
V(1)–O(9)	1.844(9)	**1.89**	O(6)–V(1)–O(7)	83.2(8)
average	1.79	$\sum s_{ij} =$ **5.37**	O(7)–V(1)–O(9)	90.0(7)
			O(9)–V(1)–O(8)	83.0(7)
			O(8)–V(1)–O(6)	90.4(7)
		V(2) Environment		
		s_{ij}		
V(2)–O(4)	1.62(1)	**1.63**	O(4)–V(2)–O(8)$^{iv}_{\bar{1}00}$	104(1)
V(2)–O(8)$^{iv}_{\bar{1}00}$	1.84(1)	**0.91**	O(4)–V(2)–O(9)	103(1)
V(2)–O(9)	1.84(1)	**0.92**	O(4)–V(2)–O(10)	104(1)
V(2)–O(10)	0.85(1)	**0.88**	O(4)–V(2)–O(11)	104(1)
V(2)–O(11)	1.85(1)	**0.88**	O(10)–V(2)–O(8)$^{iv}_{\bar{1}00}$	89.9(8)
V(2)–O(4)	2.66(1)	**0.13**	O(8)$^{iv}_{\bar{1}00}$–V(2)–O(11)	83.4(7)
		$\sum s_{ij} =$ **5.35**	O(11)–V(2)–O(9)	90.1(8)
			O(9)–V(2)–O(10)	83.8(7)
		V(3) Environment		
		s_{ij}		
V(3)–O(5)^{iii}	1.60(1)	**1.73**	O(5)^{iii}–V(3)–O(6)	106(1)
V(3)–O(6)	1.87(1)	**0.84**	O(5)^{iii}–V(3)–O(7)$^{iv}_{010}$	107(1)
V(3)–O(7)$^{iv}_{010}$	1.86(1)	**0.86**	O(5)^{iii}–V(3)–O(10)^{iv}	109(1)
V(3)–O(10)^{iv}	1.86(1)	**0.86**	O(5)^{iii}–V(3)–O(11)$^{iv}_{010}$	109(1)
V(3)–O(11)$^{iv}_{010}$	1.86(1)	**0.86**	O(6)–V(3)–O(10)^{iv}	88.2(8)
V(3)–O(5)	2.98(1)	**0.08**	O(10)^{iv}–V(3)–O(7)$^{iv}_{010}$	81.8(7)
		$\sum s_{ij} =$ **5.23**	O(7)$^{iv}_{010}$–V(3)–O(11)$^{iv}_{010}$	88.4(8)
			O(11)$^{iv}_{010}$–V(3)–O(6)	80.9(8)

TABLE 5—*Continued*

Cs Environment		
		s_{ij}
Cs–O(2)$^{\text{iii}}_{001}$	3.07(1)	**0.17**
Cs–O(2)$^{\text{iv}}_{\bar{1}00}$	3.49(1)	**0.05**
Cs–O(3)	3.52(1)	**0.05**
Cs–O(3)$^{\text{iii}}_{001}$	2.96(1)	**0.23**
Cs–O(3)$^{\text{iv}}_{\bar{1}10}$	3.46(1)	**0.06**
Cs–O(4)	3.40(1)	**0.07**
Cs–O(4)$^{\text{iii}}_{001}$	3.36(1)	**0.08**
Cs–O(6)$^{\text{iv}}_{\bar{1}10}$	3.45(1)	**0.06**
Cs–O(10)$_{010}$	3.48(1)	**0.06**
Cs–O(11)	3.35(1)	**0.08**
		$\sum s_{ij}$ = **0.92**

Note. O$(n)^{m}_{pqr}$ represents atom O(n) to which the symmetry m has been applied, followed by a translation $p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$. Symmetry code: (i) x, y, z; (ii) $-x, -y, -z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z$.

by divanadate or diphosphate groups to form layers. In CsV_2O_5 (22), layers are formed by pairs of edge-sharing $V^{4+}O_5$ square pyramids and bridging $V^{5+}O_4$ tetrahedra. In $VOSb_2O_4$ (23), the $V^{4+}O_5$ pyramids form one-dimensional chains. Finally, in the recently published new polymorph of VO_2 prepared by soft chemistry from $VO_2 \cdot \frac{1}{2}H_2O$ (24), each pyramid shares its four basal edges with four VO_5 pyramids to form layers. In all the examples, the vanadyl V=O groups are perpendicular to the plane of the layer. In some cases, the $V^{4+}O_5$ pyramid is completed by a sixth longer oxygen atom to form a distorted octahedron such as in $M_2(VO)(VO_4)_2$ (M = Ba, Sr, or Pb) (25, 26). For V^{5+}, the most prevalent coordination is obviously tetrahedral. However, there are some examples of square pyramidal coordination for V^{5+} ions with the formation of the V=O vanadyl bond with the apical oxygen. For example, the carnotite-type compounds contain a pair of edge-sharing $V^{5+}O_5$ square pyramids (6, 7). As for V^{4+}, the coordination is often completed by a longer V^{5+}–O bond to form a distorted octahedron such as in α-VPO_5 (27).

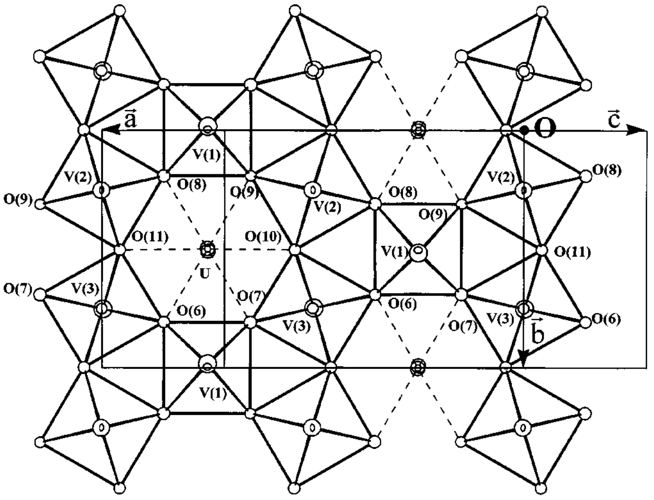

FIG. 1. Structure of $CsUV_3O_{11}$: Projection of the $[UV_3O_{11}]_n^{n-}$ layer on (001) plane.

In the uranium environment, two particular short distances, U–O(1) = 1.75 Å and U–O(2) = 1.77 Å, unambiguously indicate the existence of a nearly symmetrical and linear U^{VI} uranyl group, O(1)–U–O(2) = 178°. The U atom is surrounded in the equatorial plane by six oxygen atoms located at an average distance of 2.44(1) Å. The coordination polyhedron of uranium is thus a hexagonal bipyramid, UO_8. This coordination is rarely observed for uranium, bipyramidal, UO_7, coordination being more usual. However, examples are known, especially α-$UO_2(OH)_2$ and UO_2F_2 (28, 29). In α-$UO_2(OH)_2$, the uranyl ion, UO_2^{2+}, is surrounded, in the equatorial plane, by six OH^- ions oxygen atoms located at the corners of a hexagon, with U–O equatorial distances of 2.43–2.46 Å. The apical oxygen atoms of the uranyl ion is at 1.71 Å.

As previously observed for uranyl ions, the sum of bond valences around the uranium atom is once again higher than the expected value of six. These results corroborate the Dickens *et al.* conclusions (30) about the necessity of special parameters when applying the bond valence model to the uranium atoms of uranyl ions.

The V(2)O_5 and V(3)O_5 pyramids are linked together by diametrically opposite corners O(10) and O(11), to form infinite chains $[VO_4]_\infty$ running along the **b** axis (Fig. 1). The pyramidal bases of VO_5 polyhedra are parallel to the (001) plane and the apical oxygen atoms, O(4) and O(5), alternate on opposite sides of the plane. These chains are linked together by the V(1)O_5 pyramids. A V(1)O_5 pyramid exchanges two oxygen atoms, O(9) and O(7), of the square plane with one V(2)O_5 and one V(3)O_5 of a chain and the two others O(8) and O(6) with the VO_5 pyramids of a parallel chain. The apical oxygen atom, O(3), of the V(1)O_5 polyhedron projects in the same direction as O(4) of V(2)O_5. The VO_5 are thus linked in sheets formulated $[(VO_3)_3]_n^{3n-}$ and parallel to the (001) plane. Thus, the building unit of the structure is a triangular trivanadate entity V(1)V(2)V(3).

The shared oxygen atoms of VO_5 pyramids create equilateral triangles and hexagons whose centers are occupied by linear uranyl ions perpendicular to this (001) plane.

The layers can be described as being built from VO_5 pyramids and UO_8 hexagonal bipyramids and formulated as $[UV_3O_{11}]_n^{n-}$; they are located at about z = 0.18 and 0.82 in the cell (Fig. 2). Two consecutive layers at z = ± 0.18 are related by a center of symmetry and form double sheets.

The Cs^+ ions are located in the available space between successive double layers at z = 0.18 and z = 0.82. The coordination polyhedra of the Cs^+ ions consist of 10 oxygen atoms at 2.96–3.52 Å (mean 3.35 Å), including O(2) oxygen

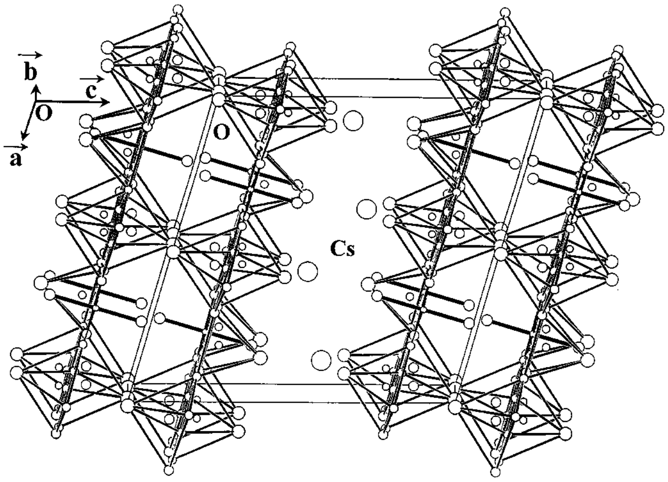

FIG. 2. Perspective view of $CsUV_3O_{11}$ along **b** axis showing the double-layer sheets connected by Cs^+ ions.

atoms of the O=U=O group, the apical atoms O(3) and O(4) of the square pyramids $V(1)O_5$ and $V(2)O_5$, and the O(6), O(10), and O(11) atoms of the layers. The thermal vibration of cesium atoms is particularly high ($B = 4.7$ Å^2).

Except for the oxygen atoms of the linear UO_2 group and the apical oxygen atoms of the vanadium square pyramids involved in U=O uranyl and V=O vanadyl bonds, respectively, all other oxygen atoms are shared by VO_5 pyramids and UO_8 bipyramids. Thus, the formula could be written as $CsUO_2(VO_3)_3$, which is in agreement with the use of the "metavanadate" name often given for this series, but which does not represent the crystal structure; in fact, the (001) layer is well described as an extended covalent solid.

It is interesting to compare the structure of $CsUV_3O_{11}$ with that of UV_3O_{10} (31). The structures of the oxides UV_3O_{10}, UNb_3O_{10}, and $UTi_xNb_{3-x}O_{10}$ have been determined by X-ray and neutron diffraction (31, 32). All these compounds and $CsUV_3O_{11}$ have an identical arrangement in the *ab* plane of the $U(V, Nb)_3O_6$ atoms (see Fig. 3 of the present paper and Fig. 4 of Ref. 31). The *a* and *b* lattice parameters are very similar and the up and down displacements of V(2) and V(3) are the same (V(2) and V(3) in $CsUV_3O_{11}$ correspond to one crystallographic site, V(2), with double multiplicity, in UV_3O_{10}). The only difference between the (001) arrangements of the two compounds is that in UV_3O_{10} the V(1) atom has no close vanadyl O atom associated with it; in fact, in UV_3O_{10}, V(1) is tetravalent vanadium and is surrounded by an elongated octahedron of oxygen atoms with four V–O bonds in the *ab* plane, of length 1.837 Å, and two perpendicular to the plane, of length 2.012 Å. Both structures have vanadyl O atoms associated with V(2) and V(3). The three V=O bonds in $CsUV_3O_{11}$ (1.60 × 2 and 1.62 Å) are shorter than the V(2)=O bond in UV_3O_{10} (1.698 Å); in fact, in this compound, the V(2) coordination is completed by a sixth oxygen atom opposite to the V(2)=O bond at 2.619 Å to form a very distorted octahedron.

The extended planar array of VO_4 squares in the *ab* plane is very similar to that of WO_4 squares (bases of WO_6 octahedra) in hexagonal tungsten trioxide which has been obtained by dehydration of $WO_3 \cdot \frac{1}{3}H_2O$ (33) or in hexagonal tungsten bronze. The geometrical relationhship between the structure of the (001) layer in UNb_3O_{10} and the corresponding layer in the hexagonal tungsten bronze phase was discussed in detail by Deschanvres *et al.* (34). The hexagonal site of the MO_4 layer (M = Nb, V, and W) is occupied by U^{VI} in UV_3O_{10} and $CsUV_3O_{11}$ and by U^{V} in UNb_3O_{10} but is empty in hexagonal tungsten bronzes; however, in the analogous $(BiO)TaW_2O_9$, this site is occupied by the bismuth atom which is in a hexagonal–pyramidal coordination of oxygen atoms (34).

The monoclinic base cell (**a**, **b**) of $CsUV_3O_{11}$ corresponds to the C-centered orthorhombic multiple cell of the hexagonal primitive one (Fig. 3) and the cell parameters are linked by the relation $a_{\text{mono}} = \sqrt{3}b_{\text{mono}}$, with $b_{\text{mono}} = b_{\text{hex}}$; actually, the $a_{\text{mono}}/b_{\text{mono}}$ ratio is 1.743. However, the layer itself lacks hexagonal symmetry since four apical oxygens of VO_5 pyramids of one six-membered ring are on one side of the mean plane of the square bases and the two latters on the other side. It is noticeable that natural uvanite and NH_4^+, H_3O^+, and Mg^{2+} analogous adopt a hexagonal unit cell with a parameter close to 6.84 Å (12). It is worth mentioning that Hilke *et al.* (12) determined the same U and V positions for the (001) plane in $NaUV_3O_{10}$ by powder X-ray diffraction; however, the hexagonal symmetry requires another orientation of some vanadyl bonds.

In UV_3O_{10}, the successive layers are linked together by metal–oxygen chains running perpendicular to them. The interlayer chain sequence along the [001] direction is V(1)—O(2)=V(2) ··· O(3)=U=O(3) ··· V(2)=O(2)—V(1) as shown in Fig. 3 of Ref. 31. The lengths of the "long" bonds V(1)—O(2) and V(2) ··· O(3) are 2.01 and 2.62 Å, respectively. In $CsUV_3O_{11}$, the closest contacts between the $[UV_3O_{11}]$ layers at $z = \pm 0.18$ fall along the [104] direction and are of two types, U=O(1) ··· V(1)=O(3) and V(3)=O(5) ··· V(2)=O(4) for which the "long" bonds are 2.98 and 2.66 Å, respectively (Fig. 4). Their corresponding contributions to the bond valence sums about vanadium are only 0.08 and 0.13, and they thus correspond to much weaker bonds than those in UV_3O_{10}. The occurrence of such weak bonding between the components of the double layer could account for the variable stacking in the *c* direction reported for other uvanites by Hilke *et al.* (12).

As a matter of fact, $CsUV_3O_{11}$ is composed of neutral sandwiches of oppositely charged infinite layers $\{(UV_3O_{11}^-)\text{-}(Cs)_2^{2+}\text{-}(UV_3O_{11}^-)\}$ stacked one above another along [104], with any "bonds" between the neutral sandwiches being very weak (as is the case in the "talc" silicate minerals).

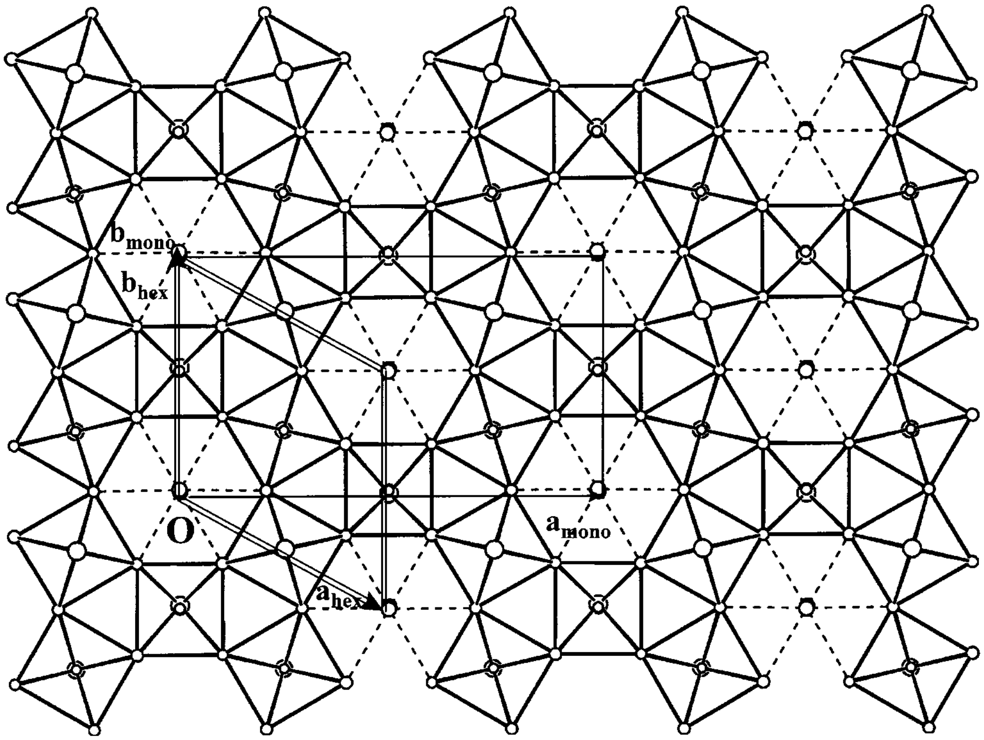

FIG. 3. Orthorhombic and hexagonal pseudocells relationship in the (001) plane of the $CsUV_3O_{11}$ structure.

It is also interesting to compare the layered structure of $CsUV_3O_{11}$ with the carnotite family of compounds for U/V = 1, $M_2[(UO_2)_2V_2O_8]$ with M = Na, K, Rb, Cs, T1, Ag, or NH_4. Sheets are respectively $[UV_3O_{11}]_n^{n-}$ in the title compound and $[UVO_6]_n^{2n-}$ in carnotites. Layers are linked in both cases by interlayer monovalent cations. In the two compounds, vanadium atoms are pentacoordinated (square pyramidals VO_5), but the associations of VO_5 polyhedra differ. In carnotite, two VO_5 pyramids related by an inversion center, sharing an edge, form a V_2O_8 group. The V_2O_8 groups are connected by uranium polyhedra. But while the coordination geometry of the vanadium atoms is preserved, uranium displays a different behavior. In carnotite, uranium atoms adopt classic UO_7 pentagonal bipyramidal geometry, while in $CsUV_3O_{11}$ they present a most uncommon hexagonal bipyramidal, UO_8, structure.

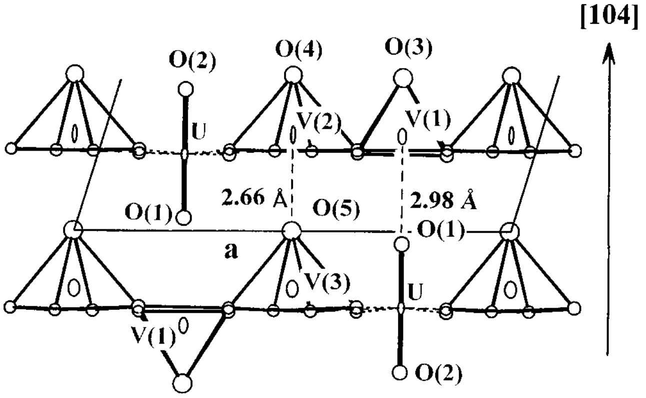

FIG. 4. Parallel strings of uranyl and vanadyl moieties with "long" bonds running along the [1 0 4] direction for two $[UV_3O_{11}]$ layers at $z = \pm 0.18$.

Finally, when we compare the two phosphorus analogs, $M[UO_2PO_4]$ and $M[UO_2(PO_3)_3]$, we observe that coordination polyhedra of phosphorus and uranium atoms are similar and are respectively PO_4 tetrahedra and UO_7 pentagonal bipyramids. But the layered structure, well known in uranyl phosphate tetrahydrate, HUP, and other compounds with U/P = 1, is not observed in $CsUO_2(PO_3)_3$ where a three-dimensional framework is obtained.

The layered structure of $CsUV_3O_{11}$ with a large Cs displacement coefficient ($B = 4.7$ Å^2) allows us to consider some mobility of the alkali-metal ion. Conductivity measurements were performed by ac impedance spectroscopy on sintered material over the range 30–400°C. The conductivity obeys the Arrhenius law over the studied temperature range with high conductivity values (about $5 \times 10^{-4}\ \Omega^{-1}\,cm^{-1}$ at 200°C) and a low activation energy of 0.18 eV (Fig. 5). The conductivity properties of $CsUV_3O_{11}$ are better than those of Cs carnotite in spite of the similar coordination of Cs atoms. In Cs carnotite, the Cs–O distances are ranging between 3.05 and 3.56 Å (average value, 3.30 Å), but the displacement parameter of the Cs atom is

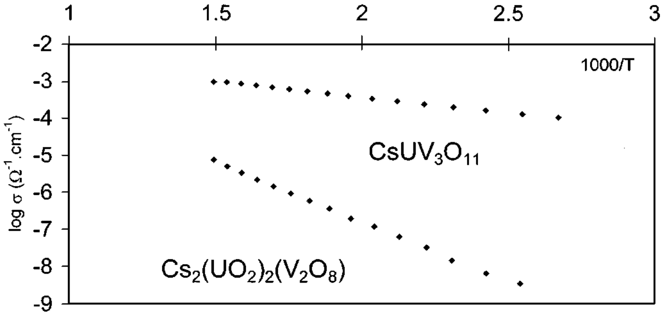

FIG. 5. Comparison between $CsUV_3O_{11}$ and Cs carnotite conductivity vs temperature.

significantly lower (0.84 Å^2) (30). Conductivity variations with temperature for Cs carnotite is also reported in Fig. 5 for comparison.

CONCLUSION

The structure of $CsUV_3O_{11}$ consists of edge- and corner-sharing UO_8 and VO_5 polyhedra which extend into infinite sheets, $UV_3O_{11}^-$, similar to the layers found in UV_3O_{10}. These layers are stacked in a parallel fashion with Cs^+ ion layers in the sequence $\{UV_3O_{11}^-\text{–}(Cs)_2^{2+}\text{–}UV_3O_{11}^-\}\text{–}\{UV_3O_{11}^-\text{–}(Cs)_2^{2+}\text{–}UV_3O_{11}^-\}\text{–}\cdots$, Astonishingly, there are on one hand, no formal chemical bonds between two consecutive layers. On the other hand, the mobility of Cs^+ ions sandwiched between two layers is particularly high. These two encouraging results incite us to study other monovalent compounds with the formula $M(UO_2)(VO_3)_3$ ($M = Na^+$, NH_4^+, $H_3O^+, \ldots$) which, from previously published results (12), adopt a hexagonal cell with parameters corresponding to the same kind of UO_8 and VO_5 layers with different stackings.

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