The Canadian Mineralogist
Vol. 40, pp. 193-200 (2002)

CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. V. TOPOLOGICALLY DISTINCT URANYL DIMOLYBDATE SHEETS IN THE STRUCTURES OF $Na_2[(UO_2)(MoO_4)_2]$ AND $K_2[(UO_2)(MoO_4)_2](H_2O)$

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ABSTRACT

Two alkali uranyl dimolybdates, $Na_2[(UO_2)(MoO_4)_2]$ and $K_2[(UO_2)(MoO_4)_2](H_2O)$, have been synthesized by high-temperature solid-state reactions and hydrothermal methods, respectively. The structures of both compounds were solved by direct methods and refined on the basis of F^2 for all unique data collected with monochromatic Mo$K\alpha$ X-radiation and a CCD (charge-coupled device) detector. The structure of $Na_2[(UO_2)(MoO_4)_2]$ was refined to an agreement factor ($R1$) of 3.1%, calculated from 2089 unique reflections ($|F_o| \geq 4\sigma_F$); it is orthorhombic, space group $P2_12_12_1$, a 7.2298(5), b 11.3240(8), c 12.0134(8) Å, V 983.5(1) Å^3, $Z = 4$. The structure of $K_2[(UO_2)(MoO_4)_2](H_2O)$ was refined to an $R1$ of 3.7%, calculated from 2181 unique reflections ($F_o \geq 4\sigma_F$); it is monoclinic, space group $P2_1/c$, a 7.893(2), b 10.907(2), c 13.558(3) Å, β 98.70(3)°, V 1153.8(4) Å^3, $Z = 4$. Both structures are based upon sheets of uranyl pentagonal bipyramids and molybdate tetrahedra. The structural sheets in the two compounds are isochemical but topologically distinct.

Keywords: uranyl molybdate, crystal structure, uranium crystal chemistry.

SOMMAIRE

Nous avons synthétisé deux dimolybdates uranylés à alcalins, $Na_2[(UO_2)(MoO_4)_2]$ et $K_2[(UO_2)(MoO_4)_2](H_2O)$, par réactions à température élevée à l'état solide et par voie hydrothermale, respectivement. Nous avons résolu les structures des deux composés par méthodes directes, et nous les avons affiné en utilisant les facteurs F^2 pour toutes les données uniques prélevées en diffraction X avec rayonnement monochromatique Mo$K\alpha$ et un détecteur à charges couplées. La structure de $Na_2[(UO_2)(MoO_4)_2]$ a été affinée jusqu'à un facteur de concordance ($R1$) de 3.1%, calculé à partir des 2089 réflexions uniques ($|F_o| \geq 4\sigma_F$); il s'agit d'une phase orthorhombique, groupe spatial $P2_12_12_1$, a 7.2298(5), b 11.3240(8), c 12.0134(8) Å, V 983.5(1) Å^3, $Z = 4$. La structure de $K_2[(UO_2)(MoO_4)_2](H_2O)$ a été affinée jusqu'à un facteur de concordance $R1$ de 3.7%, calculé à partir de 2181 réflexions uniques ($F_o \geq 4\sigma_F$); c'est une phase monoclinique, groupe spatial $P2_1/c$, a 7.893(2), b 10.907(2), c 13.558(3) Å, β 98.70(3)°, V 1153.8(4) Å^3, $Z = 4$. Les deux structures possèdent des feuillets contenant des bipyramides pentagonales à uranyle et des tétraèdres de molybdate. Les feuillets structuraux sont isochimiques dans les deux composés, mais topologiquement distincts.

(Traduit par la Rédaction)

Mots-clés: molybdate d'uranyle, structure cristalline, cristallochimie de l'uranium.

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INTRODUCTION

Our interest in uranyl molybdates arises from their mineralogical and environmental importance. Uranyl molybdate minerals occur in the oxidized portions of U–Mo deposits in the U.S. and the Russian Federation (Finch & Murakami 1999) and are components of mine and mill tailings that are the result of resource utilization. Uranyl molybdates may also be significant in a geological repository for nuclear waste, because Mo is a relatively abundant nuclear-fission product in spent nuclear fuel. In laboratory experiments designed to simulate conditions relevant to those expected in the proposed nuclear-waste repository at Yucca Mountain, Nevada, the compound $(Cs_{2x}Ba_{1-x})$ $[(UO_2)_5(MoO_6)(OH)_6]{\bullet}nH_2O$ ($x \approx 0.4$, $n \approx 6$) has been identified as an alteration product of spent nuclear fuel during corrosion in water at 90°C (Buck *et al.* 1997, Finch & Buck 1998, Finch *et al.* 1999). As part of our continuing work on uranyl molybdates (Krivovichev & Burns 2000a, b, 2001a, b), we report the synthesis and crystal-structure determination for two alkali uranyl dimolybdates, both of which have structural sheets with the composition $[(UO_2)(MoO_4)_2]$, but with different sheet-topologies.

PREVIOUS STUDIES OF RELATED URANYL MOLYBDATES

Compounds containing uranyl dimolybdate sheets, $[(UO_2)(MoO_4)_2]$, have been the subject of several studies. Krasovskaya *et al.* (1981) reported syntheses of anhydrous uranyl molybdates with the general formula $M_2[(UO_2)(MoO_4)_2]$ (M = K, Rb, Cs), and Dion & Noël (1981) discovered the compound $Na_2[(UO_2)(MoO_4)_2]$ in the system UO_2MoO_4 – Na_2MoO_4. Sadikov *et al.* (1988) reported the crystal structure of $K_2[(UO_2)(MoO_4)_2]$, and Tatarinova *et al.* (1991) demonstrated that it is isostructural with $Rb_2[(UO_2)(MoO_4)_2]$. A series of hydrated uranyl molybdates, with the general formula $M_2[(UO_2)(MoO_4)_2](H_2O)$ (M = NH_4, K, Rb, Cs), were characterized by Fedoseev *et al.* (2001), and structures of compounds with M = Cs, NH_4, Rb were reported by Rastsvetaeva *et al.* (1999), Andreev *et al.* (2001) and Khrustalev *et al.* (2000), respectively.

EXPERIMENTAL

Synthesis of $Na_2[(UO_2)(MoO_4)_2]$

Crystals of $Na_2[(UO_2)(MoO_4)_2]$ were obtained by high-temperature solid-state reaction. A mixture of Na_2CO_3, MoO_3 and UO_3 with the Na:U:Mo molar ratio 2:1:2 was placed in an alumina crucible and heated to 850°C, followed by cooling to 650°C over 5 hours, and then to 50°C over 100 hours. The product contained greenish yellow transparent tablets of $Na_2[(UO_2)(MoO_4)_2]$ as much as 1.5 mm in diameter and 0.2 mm thick.

Synthesis of $K_2[(UO_2)(MoO_4)_2](H_2O)$

Potassium (as KCl) was added to an aqueous solution that contained equal molar proportions of U (as uranyl acetate hexahydrate) and Mo (as MoO_3) in deionized water, to give a solution composition of approximately $10^{-3.5}$ M U and Mo and 10^{-1} M K. This solution was put into a covered stainless-steel vessel, placed into a 150°C oven, and allowed to evaporate. After two hours, the vessel was removed and abundant translucent yellow, tabular to blocky crystals of $K_2[(UO_2)(MoO_4)_2](H_2O)$ were recovered, along with an unidentified white K-rich powder that is readily soluble in deionized water.

Single-crystal X-ray diffraction

Crystals selected for data collection were mounted on a Bruker three-circle diffractometer equipped with a SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 5 cm. Data were collected using monochromated Mo*K*α X-radiation and frame widths of 0.3° in ω. Unit-cell dimensions (Table 1) were refined from 3351 and 3323 reflections for $Na_2[(UO_2)(MoO_4)_2]$ and $K_2[(UO_2)(MoO_4)_2](H_2O)$, respectively, using least-squares techniques. More than a hemisphere of data was collected for each crystal, and three-dimensional data were reduced and filtered for statistical outliers using the Bruker program SAINT. Data were corrected for Lorentz, polarization and background effects. A semi-empirical absorption correction of data for $Na_2[(UO_2)(MoO_4)_2]$ was done by modeling the crystal as a {010} plate, which lowered R_{int} for 2310 intense reflections from 22.0 to 7.3%. A semi-empirical absorption correction of data for $K_2[(UO_2)(MoO_4)_2](H_2O)$ was done by modeling the crystal as a {100} plate, which reduced R_{int} for 2131 intense reflections from 13.3 to 4.9%. In each case, reflections with a plate-glancing angle of 3° or less were discarded. Additional information pertinent to data collections on both crystals is given in Table 1.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR $Na_2[(UO_2)(MoO_4)_2]$ AND $K_2[(UO_2)(MoO_4)_2](H_2O)$

	$Na_2[(UO_2)(MoO_4)_2]$	$K_2[(UO_2)(MoO_4)_2](H_2O)$
a (Å)	7.2298(5)	7.893(2)
b (Å)	11.3240(8)	10.907(2)
c (Å)	12.0134(8)	13.558(3)
β (°)	-	98.70(3)
V (Å^3)	983.5(1)	1153.8(4)
Space group	$P2_12_12_1$	$P2_1/c$
F_{000}	1112	1216
Crystal size (mm)	0.24 x 0.20 x 0.03	0.34 x 0.16 x 0.10
Radiation	Mo*K*α	Mo*K*α
Total Ref.	5501	6317
Unique Ref.	2272	2736
Unique $\lvert F_o\rvert \geq 4\sigma_F$	2089	2181
$R1$	0.031	0.037
$wR2$	0.067	0.102
S	1.020	1.061
μ (cm^{-1})	190.6	169.0
D_{calc} (g/cm^3)	4.69	3.95

$R1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for m observations and n parameters

$wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $Na_2[(UO_2)(MoO_4)_2]$

	x	y	z	$*U_{eq}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.82238(4)	0.76038(3)	0.23117(3)	0.0177(1)	0.0125(2)	0.0285(2)	0.0121(1)	0.0008(1)	-0.00(1)	0.0009(2)
Mo(1)	0.3355(1)	0.71338(9)	0.09927(6)	0.0214(2)	0.0106(3)	0.0396(6)	0.0141(3)	-0.0027(3)	-0.0003(3)	0.0019(4)
Mo(2)	0.5802(1)	0.66610(9)	0.48552(6)	0.0206(2)	0.0159(4)	0.0279(5)	0.0179(3)	0.0000(4)	0.0019(3)	-0.0016(4)
Na(1)	0.5822(6)	0.9483(4)	0.5702(4)	0.034(1)	0.032(0)	0.031(3)	0.041(2)	-0.003(2)	-0.009(2)	-0.005(2)
Na(2)	0.4098(7)	0.9395(5)	0.3055(4)	0.044(1)	0.049(3)	0.045(3)	0.038(2)	-0.011(2)	-0.003(2)	0.022(3)
O(1)	0.790(1)	0.6035(6)	0.2488(5)	0.026(2)	0.029(4)	0.022(4)	0.027(4)	-0.002(3)	-0.004(3)	0.004(3)
O(2)	0.853(1)	0.9156(7)	0.2153(6)	0.030(2)	0.026(4)	0.030(4)	0.034(4)	0.003(3)	0.002(3)	-0.004(3)
O(3)	0.395(1)	0.5652(9)	0.0950(6)	0.044(2)	0.027(4)	0.063(7)	0.042(4)	-0.003(5)	-0.001(4)	0.004(4)
O(4)	0.5156(8)	0.7372(9)	0.6135(5)	0.026(2)	0.021(3)	0.042(5)	0.016(3)	0.000(3)	0.007(2)	-0.005(4)
O(5)	0.6318(8)	0.7830(7)	0.3881(5)	0.025(2)	0.014(3)	0.038(5)	0.023(3)	0.003(3)	0.009(2)	0.006(3)
O(6)	0.311(1)	0.7666(9)	-0.0375(5)	0.047(2)	0.033(4)	0.091(7)	0.017(3)	-0.002(4)	0.006(3)	0.007(6)
O(7)	0.775(1)	0.5805(8)	0.5097(6)	0.033(2)	0.026(4)	0.041(5)	0.032(4)	0.004(4)	0.002(3)	0.009(3)
O(8)	0.402(1)	0.5806(8)	0.4337(7)	0.043(2)	0.036(4)	0.041(5)	0.052(5)	-0.001(5)	-0.003(4)	-0.013(4)
O(9)	0.5100(8)	0.7949(8)	0.1727(6)	0.031(2)	0.013(3)	0.052(6)	0.029(3)	0.005(4)	-0.010(3)	0.004(3)
O(10)	0.1256(9)	0.731(1)	0.1719(7)	0.054(3)	0.015(3)	0.101(9)	0.047(4)	-0.015(6)	0.011(3)	0.014(5)

$U = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})] \times 10^4$ Å^2

$* \ U_{eq} = (1/3)\ \Sigma\Sigma\ U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF $Na_2[(UO_2)(MoO_4)_2]$

U-O(2)	1.782(8)	Na(1)-O(8)b	2.334(9)
U-O(1)	1.805(7)	Na(1)-O(2)d	2.373(9)
U-O(10)a	2.329(6)	Na(1)-O(3)e	2.39(1)
U-O(4)b	2.331(6)	Na(1)-O(7)f	2.440(8)
U-O(6)c	2.348(6)	Na(1)-O(4)	2.49(1)
U-O(5)	2.349(6)	Na(1)-O(5)	2.902(9)
U-O(9)	2.397(6)	<Na(1)-O>	2.49
Mo(1)-O(3)	1.73(1)	Na(2)-O(3)e	2.33(1)
Mo(1)-O(6)	1.759(7)	Na(2)-O(9)	2.40(1)
Mo(1)-O(10)	1.761(7)	Na(2)-O(7)f	2.435(8)
Mo(1)-O(9)	1.795(7)	Na(2)-O(1)e	2.440(9)
<Mo(1)-O>	1.76	Na(2)-O(5)	2.588(9)
		<Na(2)-O>	2.44
Mo(2)-O(8)	1.729(8)		
Mo(2)-O(7)	1.735(7)		
Mo(2)-O(4)	1.797(7)		
Mo(2)-O(5)	1.806(7)		
<Mo(2)-O>	1.77		

a = x + 1, y, z ; b = x + 1/2, -y + 3/2, -z + 1 ; c = x + 1/2, -y + 3/2, -z ; d = -x + 3/2, -y + 2, z + 1/2 ; e = -x + 1, y + 1/2, -z + 1/2 ; f = x - 1/2, -y + 3/2, -z + 1

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from International Tables for X-Ray Crystallography, Vol. IV (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for structure determination and refinement. The positions of U and Mo atoms in both structures were determined by direct methods, and anion positions were located from difference-Fourier maps that were calculated after least-squares refinement of partial-structure models. Each structure was refined on the basis of F^2 for all unique reflections. Both final refinements included positional parameters of all atoms, with allowance for their anisotropic displacement, and a weighting scheme for structure factors. Refinement of the structure of $Na_2[(UO_2)(MoO_4)_2]$ converged to an agreement index (*R*1) of 3.1%, calculated for 2089 unique reflections ($F_o > 4\sigma_F$). Final atom-parameters and selected interatomic distances in $Na_2[(UO_2)(MoO_4)_2]$ are presented in Tables 2 and 3, respectively. The refinement of the structure of $K_2[(UO_2)(MoO_4)_2](H_2O)$ converged to an *R*1 of 3.7%, calculated for 2181 unique reflections ($F_o > 4\sigma_F$). Final atom-parameters and selected interatomic distances in $Na_2[(UO_2)(MoO_4)_2]$ are presented in Tables 4 and 5, respectively. Observed and calculated structure-factors for both compounds are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

Cation polyhedra

The structures of $Na_2[(UO_2)(MoO_4)_2]$ and $K_2[(UO_2)(MoO_4)_2](H_2O)$ each contain one symmetrically independent U^{6+} cation as part of an approximately linear $(UO_2)^{2+}$ uranyl ion (*Ur*). All uranyl ions are coordinated by five anions located at the equatorial positions of pentagonal bipyramids. There are two symmetrically distinct Mo^{6+} cations in both structures. Each is tetrahedrally coordinated by four O atoms, which is typical for synthetic uranyl molybdates (*e.g.*, Krivovichev & Burns 2001a, b).

There are two symmetrically independent Na cations in the structure of $Na_2[(UO_2)(MoO_4)_2]$. The Na(1) cation is coordinated by six atoms of O in a distorted octahedral arrangement, whereas Na(2) is coordinated by five O atoms located at the vertices of a tetragonal pyramid. Mean bond-lengths are 2.49 and 2.44 Å for the Na(1) and Na(2) polyhedra, respectively.

There are two symmetrically independent K atoms in the structure of $K_2[(UO_2)(MoO_4)_2](H_2O)$. K(1) and K(2) are coordinated by nine and seven anions, respectively, with mean polyhedron bond-lengths of 3.07 and 2.95 Å for K(1) and K(2), respectively.

TABLE 4. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $K_2[(UO_2)(MoO_4)_2](H_2O)$

	x	y	z	$*U_{eq}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.47673(5)	0.74106(3)	0.14526(2)	0.0198(1)	0.0258(2)	0.0194(2)	0.0146(2)	-0.00(1)	0.00(1)	0.00(1)
Mo(1)	0.5111(1)	0.60157(7)	-0.09570(6)	0.0221(2)	0.0356(5)	0.0174(4)	0.0143(4)	-0.0001(3)	0.0075(3)	-0.0022(3)
Mo(2)	0.7606(1)	0.95588(7)	-0.14068(6)	0.0217(2)	0.0260(4)	0.0202(4)	0.0194(4)	-0.0008(3)	0.0055(3)	0.0010(3)
K(1)	0.2420(7)	0.9161(4)	-0.1276(3)	0.091(1)	0.098(3)	0.098(3)	0.076(3)	0.002(2)	0.009(2)	0.014(3)
K(2)	0.9363(6)	0.6679(5)	0.0946(4)	0.100(1)	0.062(3)	0.147(4)	0.089(3)	0.000(3)	0.007(2)	0.011(3)
O(1)	0.4234(9)	0.4488(5)	-0.0834(4)	0.022(1)	0.031(4)	0.019(3)	0.016(3)	0.003(2)	0.005(3)	0.004(3)
O(2)	0.429(1)	0.7235(6)	-0.0303(5)	0.035(2)	0.062(6)	0.026(3)	0.015(3)	0.001(3)	0.002(3)	0.016(3)
O(3)	0.280(1)	0.6679(7)	0.1561(6)	0.036(2)	0.027(4)	0.042(4)	0.041(4)	-0.006(4)	0.014(4)	-0.005(3)
O(4)	0.671(1)	0.0829(6)	-0.0827(5)	0.033(2)	0.051(5)	0.028(4)	0.016(3)	-0.000(3)	-0.001(3)	0.013(3)
O(5)	0.675(1)	0.8148(7)	0.1392(6)	0.035(2)	0.038(5)	0.033(4)	0.036(4)	-0.001(3)	0.012(4)	-0.005(3)
O(6)	0.432(1)	0.6336(6)	-0.2214(5)	0.034(2)	0.059(5)	0.028(4)	0.015(3)	-0.004(3)	0.008(3)	-0.013(4)
O(7)	0.868(1)	0.8709(7)	-0.0442(5)	0.037(2)	0.039(5)	0.038(4)	0.034(4)	-0.002(3)	0.004(4)	0.005(4)
O(8)	0.598(1)	0.8628(6)	-0.2118(5)	0.035(2)	0.050(5)	0.029(4)	0.026(4)	0.001(3)	-0.001(3)	-0.007(3)
O(9)	0.731(1)	0.6029(7)	-0.0853(5)	0.033(2)	0.034(4)	0.034(4)	0.033(4)	0.000(3)	0.010(3)	-0.004(3)
O(10)	0.910(1)	0.9994(8)	-0.2150(6)	0.047(2)	0.043(5)	0.060(5)	0.042(5)	0.019(4)	0.020(4)	0.005(4)
$H_2O(11)$	0.979(2)	0.209(1)	-0.311(1)	0.084(4)						

$U = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]\times10^4$ Å^2

$* U_{eq} = (1/3)\, \Sigma\Sigma\, U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF $K_2[(UO_2)(MoO_4)_2](H_2O)$

U-O(3)	1.772(8)	K(1)-O(2)	2.784(8)
U-O(5)	1.774(8)	K(1)-O(4)b	2.830(7)
U-O(8)a	2.324(7)	K(1)-O(10)f	2.859(10)
U-O(6)a	2.335(7)	K(1)-H_2O(11)g	2.900(15)
U-O(4)b	2.339(7)	K(1)-O(5)h	3.015(9)
U-O(2)	2.360(7)	K(1)-O(3)i	3.129(9)
U-O(1)b	2.411(6)	K(1)-O(8)	3.243(10)
<U-O_{Ur}>	1.773	K(1)-O(7)f	3.352(10)
<U-O_{eq}>	2.354	K(1)-O(7)h	3.492(9)
		<K(1)-O>	3.07
Mo(1)-O(9)	1.718(8)		
Mo(1)-O(6)	1.759(7)	K(2)-O(3)j	2.715(9)
Mo(1)-O(2)	1.774(7)	K(2)-O(5)	2.749(9)
Mo(1)-O(1)	1.822(6)	K(2)-O(9)	2.809(9)
< Mo(1)-O>	1.77	K(2)-O(7)	2.903(9)
		K(2)-O(1)b	3.094(9)
Mo(2)-O(7)	1.720(7)	K(2)-O(10)a	3.193(10)
Mo(2)-O(10)	1.727(8)	K(2)- H_2O(11)k	3.205(15)
Mo(2)-O(4)c	1.790(7)	<K(2)-O>	2.95
Mo(2)-O(8)	1.796(7)		
<Mo(2)-O>	1.76		
H_2O(11)-O(10)d	2.73(2)		
H_2O(11)-O(7)e	3.02(2)		
H_2O(11)-O(9)e	3.09(2)		

a = $x, -y + 3/2, z + 1/2$; b = $-x + 1, -y + 1, -z$; c = $x, y + 1, z$; d = $x, y - 1, z$; e = $-x + 2, y - 1/2, -z - 1/2$; f = $x - 1, y, z$; g = $-x + 1, y + 1/2, -z - 1/2$; h = $-x + 1, -y + 2, -z$; i = $x, -y + 3/2, z - 1/2$; j = $x + 1, y, z$; k = $-x + 2, -y + 1, -z$.

TABLE 6. BOND-VALENCE* ANALYSIS FOR $Na_2[(UO_2)(MoO_4)_2]$ (*vu*)

	U	Mo(1)	Mo(2)	Na(1)	Na(2)	Σ
O(1)	1.60				0.18	1.78
O(2)	1.68			0.21		1.89
O(3)		1.60		0.20	0.24	2.04
O(4)	0.57		1.35	0.15		2.07
O(5)	0.55		1.31	0.05	0.12	2.03
O(6)	0.55	1.49				2.04
O(7)			1.59	0.18	0.18	1.95
O(8)			1.62	0.24		1.86
O(9)	0.50	1.35			0.20	2.05
O(10)	0.57	1.48				2.05
Σ	6.02	5.92	5.87	1.03	0.92	

* Values calculated using the parameters for U^{6+}-O from Burns *et al.* (1997) and Mo^{6+}-O and Na-O from Brese & O'Keeffe (1991).

TABLE 7. BOND-VALENCE* ANALYSIS FOR $K_2[(UO_2)(MoO_4)_2](H_2O)$ (*vu*)

Atom	U	Mo(1)	Mo(2)	K(1)	K(2)	Σ
O(1)	0.49	1.26			0.07	1.82
O(2)	0.54	1.43		0.17		2.14
O(3)	1.71			0.07	0.21	1.99
O(4)	0.56		1.37	0.15		2.08
O(5)	1.70			0.09	0.19	1.98
O(6)	0.57	1.49				2.06
O(7)			1.66	0.04, 0.03	0.12	1.85
O(8)	0.58		1.35	0.05		1.98
O(9)		1.67			0.16	1.83
O(10)			1.63	0.14	0.06	1.83
H_2O(11)				0.13	0.06	0.19
Σ	6.15	5.85	6.01	0.87	0.87	

* Values calculated using the parameters for U^{6+}-O from Burns *et al.* (1997) and Mo^{6+}-O and K-O from Brese & O'Keeffe (1991).

Bond-valence analysis

Bond-valence analyses for the structures of $Na_2[(UO_2)(MoO_4)_2]$ and $K_2[(UO_2)(MoO_4)_2](H_2O)$ are presented in Tables 6 and 7, respectively. Bond-valence sums were calculated using parameters for U^{6+}–O bonds in Burns *et al.* (1997), and for Na–O, K–O and Mo^{6+}–O in Brese & O 'Keeffe (1991). Bond-valence sums for cations and O atoms are in agreement with their expected values. The bond-valence sum at the $H_2O(11)$ site in the structure of $K_2[(UO_2)(MoO_4)_2](H_2O)$ is 0.19 *vu* and is consistent with assignment as an H_2O group.

Topology of the uranyl molybdate sheets

The structures of $K_2[(UO_2)(MoO_4)_2](H_2O)$ and $Na_2[(UO_2)(MoO_4)_2]$ contain sheets formed by sharing vertices between *Ur*O_5 pentagonal bipyramids and MoO_4 tetrahedra (Figs. 1a, b). Although the composition of the structural sheet in both compounds is $[(UO_2)$

$(MoO_4)_2$], the topologies of the sheets are different. The structural sheets are illustrated in Figure 1 as polyhedral representations (Figs. 1a, b), and graphical representations where each vertex corresponds to a coordination polyhedron (Figs. 1c, d). Sheet anion-topologies, obtained following the procedure suggested by Burns *et al.* (1996), are shown in Figures 1e and f.

Both sheets involve UrO_5 bipyramids that are 5-connected; each equatorial oxygen is shared with a MoO_4 tetrahedron. The MoO_4 tetrahedra are 2- and 3-connected to (UrO_5) bipyramids, with a ratio of 1:1, in both sheets. Although the local topological structure (nearest-neighbor polyhedra) is identical in these sheets, the arrangement of the next-nearest neighbor polyhedra is distinct.

The sheet anion-topology of $Na_2[(UO_2)(MoO_4)_2]$ has not previously been described. It contains hexagons, pentagons, squares and triangles (Fig. 1e). Pentagons and hexagons share edges, forming chains that extend along [100] that are two polygons wide. Chains of hexagons and pentagons are separated by chains of alternating squares and triangles that share edges. Identical chains of triangles and squares occur in the uranophane and phosphuranylite anion-topologies (Burns *et al.* 1996). The structural sheet in $Na_2[(UO_2)(MoO_4)_2]$ is derived from the anion topology shown in Figure 1e by populating each pentagon with a uranyl ion, thereby producing the uranyl pentagonal bipyramids. Chains of triangles and squares are populated by MoO_4 tetrahedra, with each triangle in the chain corresponding to one face of a tetrahedron. Additional MoO_4 tetrahedra occur in the sheet, with their edges corresponding to shared edges between hexagons in the anion topology.

The sheet anion-topology in $K_2[(UO_2)(MoO_4)_2](H_2O)$ (Fig. 1f) has already been described by Burns *et al.* (1996). In addition to triangles, squares and pentagons, this anion topology also contains an eight-sided polygon. The sheet is derived from the anion topology by populating each pentagon with a uranyl ion, and each triangle with a MoO_4 tetrahedron, such that triangles correspond to faces of tetrahedra. Additional MoO_4 tetrahedra are inserted such that an edge of a tetrahedron connects adjacent UrO_5 pentagonal bipyramids.

Structure connectivities

The $[(UO_2)(MoO_4)_2]$ sheets in $Na_2[(UO_2)(MoO_4)_2]$ are linked through Na^+ cations located between the structural sheets (Fig. 2). Uranyl molybdate sheets in $K_2[(UO_2)(MoO_4)_2](H_2O)$ are linked through K^+ cations, with hydrogen bonding involving the $H_2O(11)$ group providing additional linkage (Fig. 3a). As is common in analyses of the structures of H-bearing uranium compounds, we were unable to locate the positions of the two H atoms in the structure of $K_2[(UO_2)(MoO_4)_2](H_2O)$. The O atom of the $H_2O(11)$ group is close to three O atoms, O(10), O(7) and O(9), which occur 2.73, 3.03 and 3.09 Å, respectively, from $H_2O(11)$ (Table 5). Two of these three O atoms might act as acceptors of hydrogen bonds donated by the two H atoms of the $H_2O(11)$ group; however, we cannot discern which two. All three O atoms are equally underbonded according to our bond-valence analysis (Table 7), but all three are also closely bonded to Mo^{6+} ions (Table 5). The proposed hydrogen-bonding scheme in $K_2[(UO_2)(MoO_4)_2](H_2O)$, showing all three possible H bonds, is illustrated in Figure 3b. Finally, the fact that no uranyl O atoms participate in the network of H bonds makes $K_2[(UO_2)(MoO_4)_2](H_2O)$ unusual among hydrous uranyl compounds (Finch 1997).

DISCUSSION

Crystallographic information for uranyl dimolybdates that contain $[(UO_2)(MoO_4)_2]$ sheets is given in Table 8. The structures of compounds with the general formulae $M_2[(UO_2)(MoO_4)_2]$ (M = K, Rb) and $M_2[(UO_2)(MoO_4)_2](H_2O)$ (M = NH_4, K, Rb, Cs) contain sheets with topologies identical to those in $K_2[(UO_2)(MoO_4)_2](H_2O)$ (Figs. 1b, d). Of the compounds listed in Table 8, only $Na_2[(UO_2)(MoO_4)_2]$ contains the uranyl dimolybdate sheet shown in Figure 1a. It is interesting that the same topology was observed for the $[(NpO_2)(MoO_4)_2]$ sheet in the structure of $K_3[(NpO_2)(MoO_4)_2]$ (Grigor'ev *et al.* 1992).

Recently, Shiv Halasayamani *et al.* (1999) reported crystal structures of four uranyl molybdates that have uranyl molybdate sheets separated by cationic organic templates. Two of those, $(C_4H_{12}N_2)(UO_2)(MoO_4)_2$ and $(C_5H_{14}N_2)(UO_2)(MoO_4)_2{\bullet}H_2O$, contain structural sheets that are topologically identical to those in $Na_2[(UO_2)(MoO_4)_2]$ and $K_2[(UO_2)(MoO_4)_2](H_2O)$, respectively.

Compounds with structures based on $[(UO_2)(MoO_4)_2]$ structural sheets may be common. For example, Burnell (1970) synthesized and characterized two hydrated alkali uranyl dimolybdates, $Na_2[UO_2(MoO_4)_2]{\bullet}6H_2O$ and $K_2[UO_2(MoO_4)_2]{\bullet}4H_2O$, and Fedoseev *et al.* (1998) synthesized $Na_2[UO_2(MoO_4)_2]{\bullet}4H_2O$. In addition, the anhydrous dimolybdate $Cs_2[(UO_2)(MoO_4)_2]$, which was first studied by Krasovskaya *et al.* (1980), has two polymorphs (Misra *et al.* 1995). To our knowledge, however, none of these compounds has been structurally characterized.

Our experience as well as literature descriptions indicate that uranyl dimolybdate sheets can form relatively easily, even under ambient near-surface conditions. It therefore seems reasonable to expect uranyl dimolybdates with $[(UO_2)(MoO_4)_2]$ sheets to form in geological repositories for spent nuclear fuel.

ACKNOWLEDGEMENTS

This research was supported by the Environmental Management Sciences Program of the United States Department of Energy (DE–FG07–97ER14820) and by the Russian Foundation for Basic Research (RFBR) that supports SVK (grants 01–05–64883 and 01–05–06195).

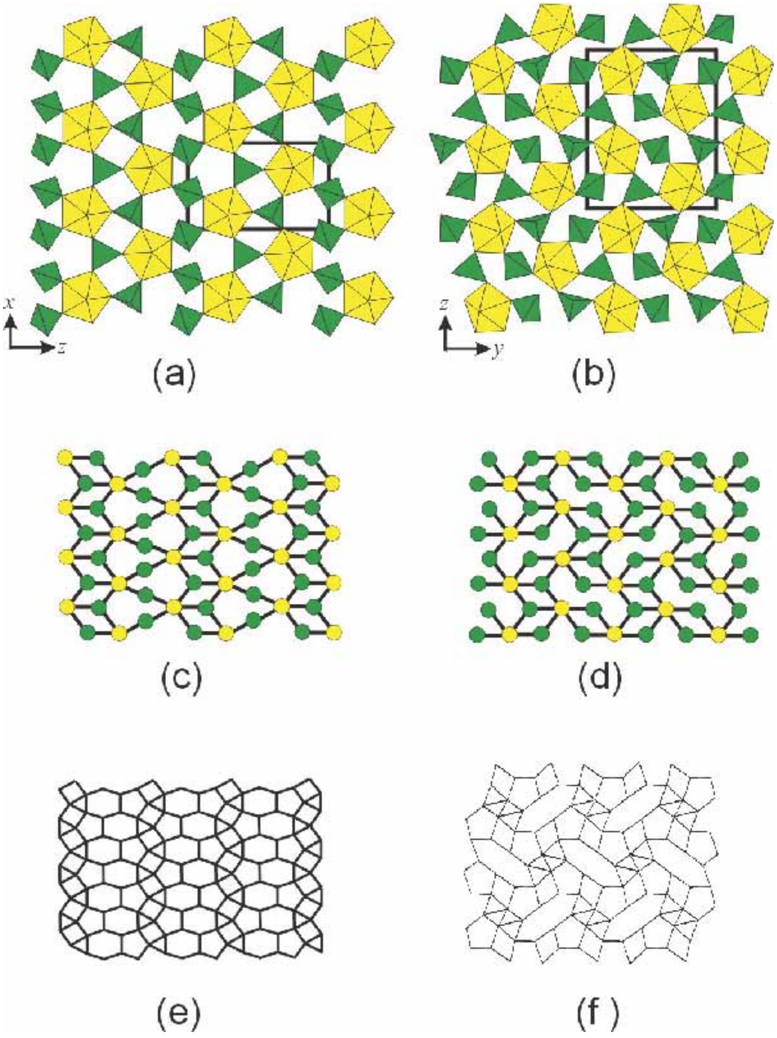

FIG. 1. The sheets of uranyl and molybdate polyhedra in the structures of $Na_2[(UO_2)(MoO_4)_2]$ (left) and $K_2[(UO_2)(MoO_4)_2](H_2O)$ (right) shown in polyhedral (a, b) and graphical (c, d) representations, respectively. Anion topologies produced according to the procedure suggested by Burns *et al.* (1996) are shown in e and f, respectively.

TABLE 8. CRYSTALLOGRAPHIC DATA FOR INORGANIC URANYL DIMOLYBDATES

Formula	Sp. gr.	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	Ref.
$Na_2[(UO_2)(MoO_4)_2]$	$P2_12_12_1$	7.2298(5)	11.3240(8)	12.0134(8)	-	this work
$K_2[(UO_2)(MoO_4)_2]$	$P2_1/c$	12.269(5)	13.468(5)	12.857(6)	95.1	1
$Rb_2[(UO_2)(MoO_4)_2]$	$P2_1/c$	12.30(1)	13.63(1)	13.49(1)	95.28(4)	2
$K_2[(UO_2)(MoO_4)_2](H_2O)$	$P2_1/c$	7.893(2)	10.907(2)	13.558(3)	98.70(3)	this work
$Rb_2[(UO_2)(MoO_4)_2](H_2O)$	$P2_1/c$	7.967(3)	10.956(4)	13.679(5)	96.69(3)	3
$Cs_2[(UO_2)(MoO_4)_2](H_2O)$	$P2_1$	8.272(2)	11.067(2)	14.031(3)	95.63	4
$(NH_4)_2[(UO_2)(MoO_4)_2](H_2O)$	$P2_1/c$	7.916(2)	10.885(2)	13.476(2)	98.40(2)	5

Refs.: 1: Sadikov *et al.* (1988); 2: Tatarinova *et al.* (1991); 3: Khrustalev *et al.* (2000); 4: Rastsvetaeva *et al.* (1999); 5: Andreev *et al.* (2001).

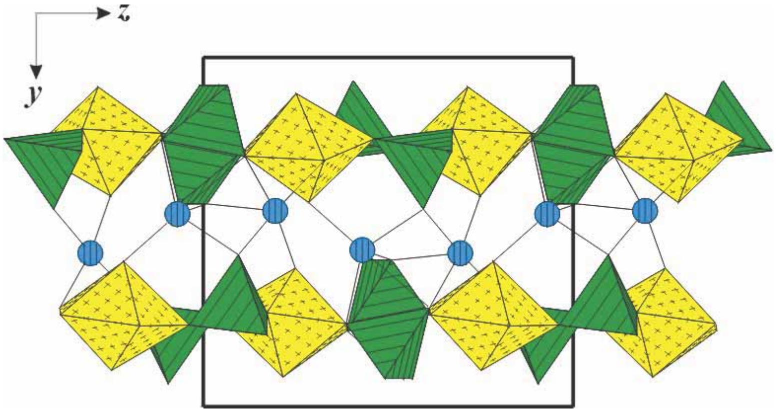

FIG. 2. The structure of $Na_2[(UO_2)(MoO_4)_2]$ projected along [100]. Legend: (UrO_5) pentagonal bipyramids: yellow; (MoO_4) tetrahedra: green; Na: blue circles.

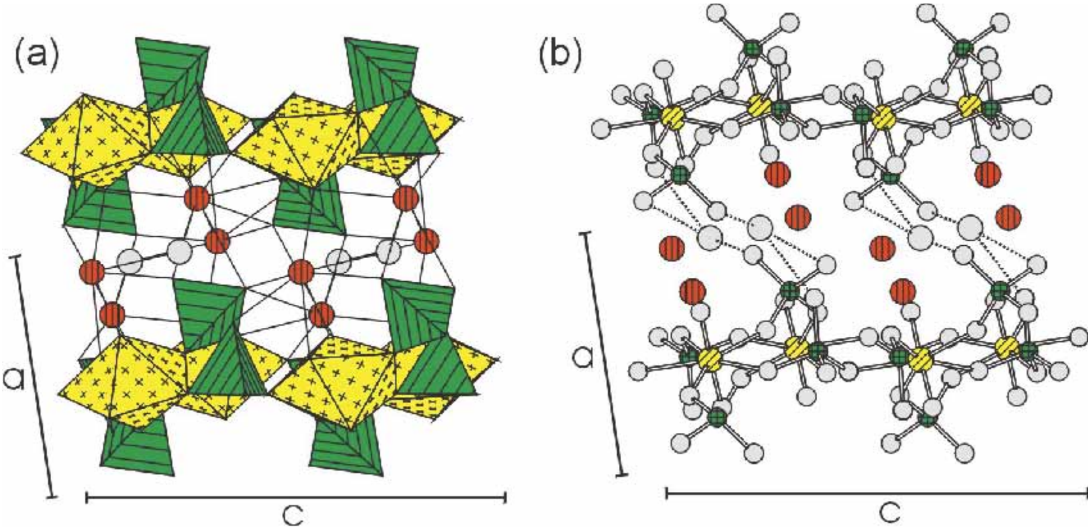

FIG. 3. The structure of $K_2[(UO_2)(MoO_4)_2](H_2O)$ projected along [010] in polyhedral (a) and ball-and-stick (b) representations. Legend: (UrO_5) pentagonal bipyramids: yellow; (MoO_4) tetrahedra: green; K cations: red circles; O atoms and H_2O molecules: grey circles; U atoms: yellow circles; Mo atoms: green circles. The proposed scheme of hydrogen bonding is shown in (b) as dashed lines.

Collaboration between PCB and SVK is supported by the NATO Science program (grant EST.CLG.977834). Drs. N.V. Chukanov and M.D. Welch reviewed the manuscript.

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Received August 8, 2001, revised manuscript accepted January 9, 2002.