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CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. III. NEW STRUCTURAL THEMES IN $Na_6[(UO_2)_2O(MoO_4)_4]$, $Na_6[(UO_2)(MoO_4)_4]$ AND $K_6[(UO_2)_2O(MoO_4)_4]$

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ABSTRACT

Two Na uranyl molybdates, $Na_6[(UO_2)_2O(MoO_4)_4]$ and $Na_6[(UO_2)(MoO_4)_4]$, and one K uranyl molybdate, $K_6[(UO_2)_2O(MoO_4)_4]$, have been synthesized by high-temperature solid-state reactions of mixtures of Na_2CO_3, K_2CO_3, UO_3 and MoO_3. All three structures 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 $Na_6[(UO_2)_2O(MoO_4)_4]$ was refined to an agreement factor ($R1$) of 4.1%, calculated using the 1969 unique observed reflections ($F_o \geq 4\sigma_F$), and a goodness-of-fit (S) of 1.06. It is triclinic, space group $P1$, a 7.637(2), b 8.164(2), c 8.746(2) Å, α 72.329(5), β 79.364(5), γ 65.795(4)°, V 472.7(2) Å^3, $Z = 1$. The structure of $Na_6[(UO_2)(MoO_4)_4]$ was refined to an $R1$ of 3.3%, calculated using the 3268 unique observed reflections ($F_o \geq 4\sigma_F$), and a S of 0.97. It is triclinic, space group $P1$, a 7.0958(8), b 9.566(1), c 13.415(2) Å, α 73.692(2), β 86.621(2), γ 82.940(2)°, V 867.0(2) Å^3, $Z = 2$. The structure of $K_6[(UO_2)_2O(MoO_4)_4]$ was refined to an $R1$ index of 4.9%, calculated using the 1833 unique observed reflections ($F_o \geq 4\sigma_F$), and a S of 0.90. It is triclinic, space group $P1$, a 7.8282(8), b 7.8298(8), c 10.302(1) Å, α 83.893(2), β 73.131(2), γ 80.338(2)°, V 594.6(1) Å^3, $Z = 1$. The structural connectivity of these three compounds is notable in that each exhibits themes not previously observed in uranyl compounds. The structures of both $Na_6[(UO_2)_2O(MoO_4)_4]$ and $K_6[(UO_2)_2O(MoO_4)_4]$ contain chains of polyhedra of composition $[(UO_2)_2O(MoO_4)_4]^{6-}$. These chains have not been previously observed and are composed of $[UrO_4OUrO_4]$ dimers consisting of two UrO_5 (Ur: uranyl ion) pentagonal bipyramids sharing a common O atom. The dimers are connected into a chain by sharing vertices with MoO_4 tetrahedra, with the chains linked by Na^+ or K^+ cations. The structure of $Na_6[(UO_2)(MoO_4)_4]$ consists of finite clusters of composition $[(UO_2)_2(MoO_4)_8]^{12-}$ composed of two UrO_5 pentagonal bipyramids connected by sharing vertices with MoO_4 tetrahedra. The clusters in $Na_6[(UO_2)(MoO_4)_4]$ are oriented parallel to the (001) plane and are linked through Na^+ cations.

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

SOMMAIRE

Nous avons synthétisé deux molybdates uranylés de sodium, $Na_6[(UO_2)_2O(MoO_4)_4]$ et $Na_6[(UO_2)(MoO_4)_4]$, et un molybdate uranylé de potassium, $K_6[(UO_2)_2O(MoO_4)_4]$, par réaction à l'état solide à température élevée de mélanges de Na_2CO_3, K_2CO_3, UO_3 et MoO_3. Chacune des trois structures a été résolue et affinée par méthodes directes en utilisant les facteurs F^2 pour chaque réflexion unique mesurée avec rayonnement monochromatique Mo$K\alpha$ et un détecteur à couplage de charges (CCD). La structure de $Na_6[(UO_2)_2O(MoO_4)_4]$ a été affinée jusqu'à un résidu ($R1$) de 4.1%, calculé en utilisant les 1969 réflexions uniques observées ($F_o \geq 4\sigma_F$), et un indice de concordance (S) de 1.06. Ce composé est triclinique, groupe spatial $P1$, a 7.637(2), b 8.164(2), c 8.746(2) Å, α 72.329(5), β 79.364(5), γ 65.795(4)°, V 472.7(2) Å^3, $Z = 1$. La structure de $Na_6[(UO_2)(MoO_4)_4]$ a été affinée jusqu'à un résidu $R1$ of 3.3%, calculé sur la base de 3268 réflexions uniques observées ($F_o \geq 4\sigma_F$), et un S de 0.97. Ce composé est triclinique, groupe spatial $P1$, a 7.0958(8), b 9.566(1), c 13.415(2) Å, α 73.692(2), β 86.621(2), γ 82.940(2)°, V 867.0(2) Å^3, $Z = 2$. La structure de $K_6[(UO_2)_2O(MoO_4)_4]$ a été affinée jusqu'à un indice $R1$ de 4.9%, calculé sur la base de 1833 réflexions uniques observées ($F_o \geq 4\sigma_F$), et un S de 0.90. Ce composé est aussi triclinique, groupe spatial $P1$, a 7.8282(8), b 7.8298(8), c 10.302(1) Å, α 83.893(2), β 73.131(2), γ 80.338(2)°, V 594.6(1) Å^3, $Z = 1$. Les schémas de connectivité structurale de ces trois composés n'avaient pas été signalés parmi les composés à uranyle. La structure de $Na_6[(UO_2)_2O(MoO_4)_4]$ et de $K_6[(UO_2)_2O(MoO_4)_4]$ contient des chaînes de polyèdres de composition $[(UO_2)_2O(MoO_4)_4]^{6-}$. Ces chaînes, inconnues jusqu'à ce point, contiennent des dimères $[UrO_4OUrO_4]$ faits de deux bipyramides pentagonales UrO_5 (Ur: ion uranyle) partageant un atome commun d'oxygène. Les dimères sont agencés en chaînes par partage d'arêtes avec des tétraèdres MoO_4, ces chaînes étant

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liées par des cations Na^+ ou K^+. La structure de $Na_6[(UO_2)(MoO_4)_4]$ contient des groupes finis de composition $[(UO_2)_2(MoO_4)_8]^{12-}$ ayant deux bipyramides pentagonales UrO_5 agencés par partage d'arêtes avec des tétraèdres MoO_4. Les groupes du composé $Na_6[(UO_2)(MoO_4)_4]$ ont une orientation parallèle au plan (001) et sont liés par les cations Na^+.

(Traduit par la Rédaction)

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

INTRODUCTION

Uranyl molybdates are important constituents of the oxidized zones of U–Mo deposits (Finch & Murakami 1999). They may also be important phases in a geological repository for nuclear waste because ^{97}Mo is a fission product that forms during irradiation of nuclear fuel in a reactor. Recently, the phase $(Cs_{2x}Ba_{1-x})[(UO_2)_5(MoO_6)(OH)_6]\bullet nH_2O$ ($x \approx 0.4$, $n \approx 6$) was found as an alteration-induced phase on spent nuclear fuel at 90°C in tests designed to simulate conditions expected in the proposed nuclear waste repository at Yucca Mountain, Nevada (Buck *et al.* 1997). As part of our continuing work on uranyl molybdates (Krivovichev & Burns 2000a, b), we have determined the structures of two synthetic Na uranyl molybdates and one synthetic K uranyl molybdate. These new structures exhibit topologies unlike other known uranyl phases, providing new insights into the structural hierarchy of uranyl compounds.

PREVIOUS STUDIES OF NA AND K URANYL MOLYBDATES

The phase relations in the system Na–U–Mo–O were studied by Dion and his coauthors (Dion *et al.* 1977, Dion & Noël 1981a, b, c, 1982), who reported the synthesis of eight Na uranyl molybdates that they distinguished on the basis of X-ray powder-diffraction patterns. No structures have been reported for any of these compounds.

Krasovskaya *et al.* (1981) and Dion & Noël (1983, 1985) studied the phase relations in the system K–U–Mo–O, and reported the synthesis of seven K uranyl molybdates, as distinguished by X-ray powder diffraction. Of these, a structure has been reported for $K_2[(UO_2)(MoO_4)_2]$ only (Sadikov *et al.* 1988).

EXPERIMENTAL

Syntheses of the crystals

Crystals of the Na uranyl molybdates used in the current study were obtained by high-temperature solid-state reaction in alumina crucibles at 850°C in air followed by cooling to 650°C over 5 hours and then to 50°C over 100 hours. Crystals of the K uranyl molybdate were obtained in a similar fashion, except that reaction at 850°C in air was followed by cooling to 450°C over 60 hours, and then to 50°C over 18 hours.

$Na_6[(UO_2)_2O(MoO_4)_4]$: The reactants were Na_2CO_3, MoO_3 and UO_3 powders with a Na:U:Mo molar ratio of 8:3:5. The resulting transparent orange crystals attain 4 mm in maximum length.

$Na_6[(UO_2)(MoO_4)_4]$: The reactants were Na_2CO_3, MoO_3 and UO_3 powders with a Na:U:Mo molar ratio of 6:1:4. Intergrowths of greenish yellow transparent elongate crystals were obtained, with individual crystals as much as 1.5 mm across and up to 6 mm in length.

$K_6[(UO_2)_2O(MoO_4)_4]$: The reactants were K_2CO_3, MoO_3 and UO_3 powders with a K:U:Mo molar ratio of 4:1:3. Transparent yellow crystals with maximum dimensions of 2 mm were obtained.

X-ray data collection

Small crystal fragments of each phase were selected for data collection and 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 monochromatized Mo$K\alpha$ X-radiation with frame widths in ω of 0.3°. 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. Unit-cell parameters were refined using least-squares methods (Table 1). Empirical absorption-corrections were done with each crystal modeled as an ellipsoid; details are presented in Table 1.

Structure solutions and refinements

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 the determination and refinement of all three structures. Each was solved by direct methods, which gave the positions of the U, Mo, Na and K atoms. Anions were located in difference-Fourier maps calculated after least-squares refinement of the partial-structure models. Each structure was refined on the basis of F^2 for all unique data. For each structure, the final refinement included all atomic positional parameters with an allowance for anisotropic displacement of all atoms, and included a weighting scheme of the structure factors. For

TABLE 1. MISCELLANEOUS INFORMATION FOR $Na_6[(UO_2)_2O(MoO_4)_4]$, $Na_6[(UO_2)(MoO_4)_4]$ AND $K_6[(UO_2)_2O(MoO_4)_4]$

	$Na_6[(UO_2)_2O(MoO_4)_4]$	$Na_6[(UO_2)(MoO_4)_4]$	$K_6[(UO_2)_2O(MoO_4)_4]$
a (Å)	7.637(2)	7.0958(8)	7.8282(8)
b (Å)	8.164(2)	9.566(1)	7.8298(8)
c (Å)	8.746(2)	13.415(2)	10.302(1)
α (°)	72.329(5)	73.692(2)	83.893(2)
β (°)	79.364(5)	86.621(2)	73.131(2)
γ (°)	65.795(4)	82.940(2)	80.338(2)
V (Å^3)	472.7(2)	867.0(2)	594.6(1)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Crystal size (mm^3)	0.34 x 0.34 x 0.30	0.30 x 0.22 x 0.08	0.20 x 0.10 x 0.03
Z	1	2	1
F_{000}	586	940	634
D_{calc} (g/cm^3)	4.69	4.01	4.00
μ (cm^{-1})	198.8	123.6	167.7
Abs. corr.	6.6 → 4.5%	14.8 → 4.2	14.6 → 8.6
Ref. for abs. corr.	1084	1334	568
Ref. for cell	967	2898	1422
Total Ref.	2846	5447	3746
Unique Ref.	2079	3929	2713
Unique $\lvert F_o \rvert \geq 4\sigma_F$	1969	3268	1833
$R1$ (%)	4.1	3.3	4.9
S	1.06	0.97	0.90

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

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{½}$, for m observations and n parameters

$w = 1/[\sigma^2(F_o^2) + (0.0217 \times P)^2]$, $P = (\max(F_o^2,0) + 2 \times F_c^2)/3$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF $Na_6[(UO_2)_2O(MoO_4)_4]$

U-O(2)	1.828(7)	Mo(2)-O(9)	1.724(7)	Na(2)-O(10)	2.313(9)
U-O(1)	1.833(8)	Mo(2)-O(10)	1.742(8)	Na(2)-O(6)	2.335(9)
U-O(11)b	2.1142(5)	Mo(2)-O(3)	1.805(6)	Na(2)-O(4)f	2.449(8)
U-O(3)a	2.357(7)	Mo(2)-O(5)	1.826(7)	Na(2)-O(1)f	2.47(1)
U-O(5)b	2.360(7)	<Mo(2)-O>	1.77	Na(2)-O(2)h	2.483(9)
U-O(7)c	2.386(6)			Na(2)-O(1)i	2.603(9)
U-O(8)n	2.498(7)	Na(1)-O(3)a	2.424(8)	<Na(2)-O>	2.44
<U-O$_{Ur}$>	1.83	Na(1)-O(6)	2.458(9)		
<U-ϕ_{eq}>	2.34	Na(1)-O(7)f	2.512(8)	Na(3)-O(8)	2.299(8)
		Na(1)-O(7)	2.647(9)	Na(3)-O(9)m	2.307(9)
Mo(1)-O(4)	1.745(7)	Na(1)-O(10)	2.66(1)	Na(3)-O(2)m	2.349(9)
Mo(1)-O(8)	1.757(7)	Na(1)-O(1)f	2.815(9)	Na(3)-O(4)a	2.422(8)
Mo(1)-O(6)l	1.764(8)	Na(1)-O(9)	2.95(1)	Na(3)-O(2)i	2.718(9)
Mo(1)-O(7)	1.819(6)	<Na(1)-O>	2.64	Na(3)-O(5)	2.772(9)
<Mo(1)-O>	1.77			Na(3)-O(10)m	2.78(1)
				<Na(3)-O>	2.52

a: 1-x, 1-y, -z; b: x, y+1, z; c: -x, 2-y, 1-z; d: x-1, y+1, z; e: x-1, y, z; f: 1-x, 1-y, 1-z; g: 1-x, -y, 1-z; h: -x, 1-y, 1-z; i: x, y-1, z; j: -x, 2-y, -z; k: 1-x, 2-y, -z; l: x+1, y, z; m: -x, 1-y, -z; n: 1+x, y, 1+z

$Na_6[(UO_2)_2O(MoO_4)_4]$, the refinement converged to an agreement index ($R1$) of 4.1%, calculated for the 1969 unique observed reflections ($F_o \geq 4\sigma_F$), with a goodness-of-fit (S) of 1.06. Final atomic parameters and selected interatomic distances are presented in Tables 2 and 3, respectively. For $Na_6[(UO_2)(MoO_4)_4]$, the refinement converged to an $R1$ of 3.3%, calculated for the 3268 unique observed reflections ($F_o \geq 4\sigma_F$), with a S of 0.97. Final atomic parameters and selected interatomic distances are presented in Tables 4 and 5, respectively. For $K_6[(UO_2)_2O(MoO_4)_4]$, the final $R1$ is 4.9%, calculated for the 1833 unique observed reflections ($F_o \geq 4\sigma_F$), and S is 0.90. Final atomic parameters are given in Table 6, with selected interatomic distances in Table 7. Observed and calculated structure-factors for each compound are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS: $Na_6[(UO_2)_2O(MoO_4)_4]$

Cation polyhedra

The structure of $Na_6[(UO_2)_2O(MoO_4)_4]$ contains a single symmetrically unique U^{6+} cation. It is strongly bonded to two O atoms, forming a $(UO_2)^{2+}$ uranyl ion (Ur) with a <U–O$_{Ur}$> bond-length of 1.83 Å. The uranyl ion is coordinated by five additional O atoms arranged at the equatorial corners of UrO$_5$ pentagonal bipyramids that are capped by the O$_{Ur}$ atoms. The mean <U–O$_{eq}$> (eq: equatorial) bond length is 2.34 Å. The geometry of the polyhedron is consistent with mean values for UrO$_5$ pentagonal bipyramids in many well-

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $Na_6[(UO_2)_2O(MoO_4)_4]$

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.21256(5)	0.92437(4)	0.31422(4)	0.0063(2)	0.0055(2)	0.0075(2)	0.0061(2)	-0.0017(1)	0.0005(1)	-0.0031(2)
Mo(1)	0.9372(1)	0.4135(1)	0.35573(9)	0.0075(2)	0.0063(4)	0.0080(4)	0.0067(4)	0.0008(3)	-0.0016(3)	-0.0026(3)
Mo(2)	0.4451(1)	0.2474(1)	0.0140(1)	0.0096(2)	0.0097(4)	0.0102(4)	0.0076(4)	0.0011(3)	0.0007(3)	-0.0054(3)
Na(1)	0.4562(7)	0.3998(6)	0.3463(6)	0.0182(9)	0.016(2)	0.015(2)	0.023(2)	-0.002(2)	-0.001(2)	-0.007(2)
Na(2)	0.2695(7)	0.0953(6)	0.6555(6)	0.0193(9)	0.019(2)	0.012(2)	0.021(2)	0.002(2)	-0.002(2)	-0.004(2)
Na(3)	-0.0551(7)	0.2465(6)	-0.0116(5)	0.021(1)	0.032(3)	0.017(2)	0.014(2)	-0.006(2)	-0.004(2)	-0.007(2)
O(1)	0.393(1)	0.936(1)	0.4189(9)	0.017(2)	0.022(4)	0.009(3)	0.018(4)	-0.001(3)	-0.007(3)	-0.003(3)
O(2)	0.043(1)	0.908(1)	0.2028(9)	0.014(1)	0.011(3)	0.010(3)	0.023(4)	-0.004(3)	-0.005(3)	-0.004(3)
O(3)	0.549(1)	0.2974(9)	-0.1891(8)	0.012(1)	0.015(4)	0.011(3)	0.010(3)	0.000(3)	0.003(3)	-0.007(3)
O(4)	0.855(1)	0.6369(9)	0.2286(8)	0.014(1)	0.016(4)	0.008(3)	0.016(3)	0.000(3)	0.000(3)	-0.006(3)
O(5)	0.324(1)	0.083(1)	0.0685(8)	0.015(1)	0.014(3)	0.016(3)	0.013(3)	-0.001(3)	0.003(3)	-0.009(3)
O(6)	0.150(1)	0.358(1)	0.4448(9)	0.019(2)	0.013(4)	0.015(4)	0.025(4)	0.001(3)	-0.003(3)	-0.006(3)
O(7)	0.745(1)	0.3670(9)	0.4956(8)	0.011(1)	0.012(3)	0.012(3)	0.009(3)	-0.002(3)	0.006(3)	-0.009(3)
O(8)	0.004(1)	0.261(1)	0.2316(8)	0.015(1)	0.021(4)	0.011(3)	0.014(3)	-0.001(3)	0.001(3)	-0.008(3)
O(9)	0.282(1)	0.454(1)	0.0514(9)	0.022(2)	0.019(4)	0.017(4)	0.025(4)	-0.007(3)	0.005(3)	-0.005(3)
O(10)	0.621(1)	0.179(1)	0.147(1)	0.022(2)	0.021(4)	0.026(4)	0.021(4)	0.004(3)	-0.013(3)	-0.012(4)
O(11)	0	0	½	0.051(5)	0.06(1)	0.017(6)	0.020(6)	0.010(5)	0.015(6)	0.024(6)

refined structures: <U–O$_{Ur}$> = 1.79(4) Å, <U–O$_{eq}$> = 2.37(9) Å (Burns *et al.* 1997).

The structure contains two symmetrically unique Mo^{6+} cations, each of which is tetrahedrally coordinated by O atoms. The <Mo–O> bond-lengths of each tetrahedron are 1.77 Å, which is identical to the value obtained from sums of ionic radii (Shannon 1976).

The structure contains three symmetrically distinct Na^{+} cations. The coordination polyhedra about these cations are irregular (Fig. 1) and contain six or seven O atoms within 3 Å of the Na^{+} cation.

Bond-valence analysis

Bond-valence sums incident upon the cation positions in the structure of $Na_6[(UO_2)_2O(MoO_4)_4]$, calculated using the parameters for U^{6+}–O given by Burns *et al.* (1997) and for Na–O and Mo^{6+}–O given by Brese & O'Keeffe (1991), are: U = 5.91, Mo(1) = 5.79, Mo(2) = 5.76, Na(1) = 0.81, Na(2) = 1.09, Na(3) = 1.15 *vu.* Bond-valence sums incident upon the O atoms range from 1.76 to 2.17 *vu* (valence units).

Structural connectivity

The structure of $Na_6[(UO_2)_2O(MoO_4)_4]$ is based upon chains of $Ur\mathrm{O}_5$ pentagonal bipyramids and MoO_4 tetrahedra that are parallel to $[\bar{1}01]$ (Fig. 2). Each chain, which has the composition $[(UO_2)_2O(MoO_4)_4]^{6-}$, contains a dimer of $Ur\mathrm{O}_5$ pentagonal bipyramids that share the O(11) vertex. The O(11) atom only bonds to two U^{6+} cations; thus the U–O(11) bond-length of 2.1142(4) Å is considerably shorter than is typical for $^{[7]}$U–O$_{eq}$ bonds, giving a total of 1.75 *vu* incident upon this anion position. The dimers, with composition $[Ur\mathrm{O}_4\mathrm{O}Ur\mathrm{O}_4]^{14-}$, are linked into chains by sharing vertices with MoO_4 tetrahedra. The resulting chains are parallel to (101) and are linked through bonds to Na^{+} cations (Fig. 3a).

RESULTS: $Na_6[(UO_2)(MoO_4)_4]$

Cation polyhedra

The single symmetrically unique U^{6+} cation in the structure of $Na_6[(UO_2)(MoO_4)_4]$ is part of a uranyl ion that is coordinated by five additional O atoms, resulting in a $Ur\mathrm{O}_5$ pentagonal bipyramid. The <U–O$_{Ur}$> and <U–O$_{eq}$> bond-lengths of 1.80 and 2.35 Å, respectively, are consistent with geometries of $Ur\mathrm{O}_5$ pentagonal bipyramids in well-refined structures (Burns *et al.* 1997).

There are four symmetrically unique Mo^{6+} cations, each of which is tetrahedrally coordinated by O atoms,

TABLE 4. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $Na_6[(UO_2)(MoO_4)_4]$

Atom	*x*	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.07313(4)	0.81676(3)	0.32694(2)	0.0138(1)	0.0160(1)	0.0145(2)	0.0117(2)	-0.0047(1)	0.0001(1)	- 0.0029(1)
Mo(1)	0.52738(9)	0.49016(7)	0.67448(5)	0.0179(2)	0.0149(3)	0.0202(3)	0.0194(4)	-0.0081(3)	0.0002(2)	0.0004(2)
Mo(2)	0.23814(9)	0.90941(7)	0.56699(5)	0.0180(2)	0.0236(3)	0.0170(3)	0.0141(3)	-0.0066(3)	-0.0027(3)	0.0019(3)
Mo(3)	-0.34364(9)	0.98742(7)	0.15007(5)	0.0186(2)	0.0169(3)	0.0231(3)	0.0146(3)	-0.0029(3)	-0.0020(3)	-0.0026(3)
Mo(4)	-0.07375(9)	0.37198(8)	0.90483(5)	0.0217(2)	0.0219(3)	0.0322(4)	0.0151(3)	-0.0109(3)	0.0032(3)	-0.0105(3)
Na(1)	0.0239(4)	0.5886(4)	0.6129(3)	0.0338(8)	0.022(2)	0.031(2)	0.057(3)	-0.026(2)	0.003(2)	-0.006(1)
Na(2)	0.3959(4)	0.2488(4)	0.5616(3)	0.0270(7)	0.023(2)	0.037(2)	0.021(2)	-0.009(1)	0.004(1)	-0.006(1)
Na(3)	-0.2080(5)	0.3176(4)	0.1605(3)	0.0317(8)	0.040(2)	0.033(2)	0.022(2)	-0.006(1)	-0.007(1)	-0.002(1)
Na(4)	-0.1878(5)	0.9665(4)	-0.0725(3)	0.0386(9)	0.033(2)	0.059(2)	0.022(2)	-0.005(2)	-0.001(1)	-0.009(2)
Na(5)	-0.2730(5)	0.7915(4)	0.7202(3)	0.0403(9)	0.028(2)	0.051(2)	0.056(3)	-0.039(2)	-0.002(2)	-0.002(2)
Na(6)	-0.5726(5)	0.3404(4)	0.9682(3)	0.0395(9)	0.027(2)	0.040(2)	0.050(3)	-0.005(2)	-0.005(2)	-0.013(2)
O(1)	0.0025(7)	0.6443(5)	0.4051(4)	0.022(1)	0.028(3)	0.016(3)	0.024(3)	-0.009(2)	0.005(2)	-0.008(2)
O(2)	0.1169(7)	0.0919(5)	0.5429(4)	0.020(1)	0.025(3)	0.014(2)	0.019(3)	-0.006(2)	0.002(2)	0.001(2)
O(3)	0.2681(7)	0.8459(6)	0.4537(4)	0.023(1)	0.022(3)	0.033(3)	0.017(3)	-0.013(2)	-0.003(2)	0.001(2)
O(4)	0.1350(8)	0.9946(5)	0.2517(4)	0.023(1)	0.033(3)	0.018(3)	0.019(3)	-0.002(2)	0.001(2)	-0.008(2)
O(5)	-0.2430(7)	0.8813(6)	0.2730(4)	0.024(1)	0.017(3)	0.034(3)	0.018(3)	-0.002(2)	-0.004(2)	0.002(2)
O(6)	-0.2779(7)	0.3982(6)	0.9801(4)	0.026(1)	0.025(3)	0.034(3)	0.018(3)	-0.006(2)	0.003(2)	-0.005(2)
O(7)	0.6918(7)	0.6165(6)	0.6200(5)	0.028(1)	0.020(3)	0.022(3)	0.041(4)	-0.007(3)	0.002(3)	-0.003(2)
O(8)	-0.0887(8)	0.2449(6)	0.8294(5)	0.032(1)	0.037(3)	0.041(4)	0.025(3)	-0.021(3)	0.001(3)	-0.010(3)
O(9)	0.4437(8)	0.5125(6)	0.7943(5)	0.034(1)	0.039(4)	0.035(3)	0.029(3)	-0.013(3)	0.001(3)	0.005(3)
O(10)	0.6305(7)	0.3051(6)	0.6876(5)	0.026(1)	0.025(3)	0.023(3)	0.030(3)	-0.007(2)	0.002(2)	-0.002(2)
O(11)	0.1138(8)	0.3069(7)	0.9905(5)	0.034(1)	0.031(3)	0.043(4)	0.034(4)	-0.019(3)	-0.001(3)	-0.010(3)
O(12)	-0.0344(9)	0.5427(7)	0.8164(5)	0.044(2)	0.057(4)	0.050(4)	0.027(4)	-0.011(3)	0.015(3)	-0.024(3)
O(13)	-0.5086(9)	0.1351(7)	0.1584(5)	0.038(2)	0.049(4)	0.036(4)	0.024(3)	-0.005(3)	0.003(3)	0.011(3)
O(14)	0.3398(7)	0.5212(6)	0.5901(5)	0.030(1)	0.022(3)	0.043(4)	0.026(3)	-0.013(3)	-0.003(2)	0.002(3)
O(15)	-0.4496(9)	0.8769(7)	0.0919(5)	0.037(1)	0.054(4)	0.035(3)	0.023(3)	-0.004(3)	-0.017(3)	-0.008(3)
O(16)	0.1133(9)	0.7919(6)	0.6647(5)	0.032(1)	0.057(4)	0.019(3)	0.019(3)	-0.002(2)	0.002(3)	-0.005(3)
O(17)	-0.1589(8)	0.0626(7)	0.0699(5)	0.034(2)	0.020(3)	0.042(4)	0.027(3)	0.013(3)	0.000(2)	-0.007(3)
O(18)	0.4636(9)	0.9067(7)	0.6101(5)	0.039(2)	0.038(4)	0.052(4)	0.034(4)	-0.026(3)	-0.020(3)	0.011(3)

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF $Na_6[(UO_2)(MoO_4)_4]$

U-O(1)	1.801(5)	Na(1)-O(14)	2.282(6)	Na(5)-O(13)l	2.372(7)
U-O(4)	1.809(5)	Na(1)-O(1)b	2.337(6)	Na(5)-O(18)d	2.407(7)
U-O(10)a	2.302(5)	Na(1)-O(7)d	2.338(6)	Na(5)-O(7)d	2.466(7)
U-O(8)b	2.326(6)	Na(1)-O(16)	2.405(7)	Na(5)-O(4)c	2.501(6)
U-O(3)	2.350(5)	Na(1)-O(12)	2.656(8)	Na(5)-O(12)	2.782(8)
U-O(5)	2.353(5)	Na(1)-O(1)	2.697(7)	Na(5)-O(16)	2.798(7)
U-O(2)b	2.433(5)	<Na(1)-O>	2.45	<Na(5)-O>	2.55
<U-O_{Ur}>	1.80				
<U-ϕ_{eq}>	2.35	Na(2)-O(3)a	2.462(6)	Na(6)-O(6)	2.253(6)
		Na(2)-O(5)b	2.479(6)	Na(6)-O(11)d	2.278(7)
Mo(1)-O(9)	1.741(6)	Na(2)-O(7)a	2.491(7)	Na(6)-O(15)l	2.417(7)
Mo(1)-O(14)	1.742(6)	Na(2)-O(10)	2.642(7)	Na(6)-O(9)d	2.454(7)
Mo(1)-O(7)	1.762(5)	Na(2)-O(2)e	2.691(6)	Na(6)-O(13)n	2.771(7)
Mo(1)-O(10)	1.795(5)	Na(2)-O(14)	2.717(7)	Na(6)-O(6)k	2.845(7)
<Mo(1)-O>	1.76	Na(2)-O(1)b	2.938(6)	<Na(6)-O>	2.50
		<Na(2)-O>	2.63		
Mo(2)-O(18)	1.728(6)				
Mo(2)-O(16)	1.745(6)	Na(3)-O(9)b	2.361(7)		
Mo(2)-O(3)	1.781(5)	Na(3)-O(16)b	2.384(7)	a: 1-x, 1-y, 1-z;	
Mo(2)-O(2)m	1.800(5)	Na(3)-O(6)o	2.386(7)	b: -x, 1-y, 1-z;	
<Mo(2)-O>	1.76	Na(3)-O(12)b	2.388(8)	c: -x, 2-y, 1-z;	
		Na(3)-O(13)	2.924(8)	d: x-1, y, z ;	
Mo(3)-O(15)	1.738(6)	Na(3)-O(17)	2.993(8)	e: x, y-1, z ;	
Mo(3)-O(17)m	1.739(5)	<Na(3)-O>	2.57	f: -x, 1-y, 2-z;	
Mo(3)-O(13)m	1.745(6)			g: x, y-1, z+1;	
Mo(3)-O(5)	1.811(5)	Na(4)-O(4)h	2.342(7)	h: -x, 2-y, -z ;	
<Mo(3)-O>	1.76	Na(4)-O(17)	2.369(8)	i: x, y+1, z–1;	
		Na(4)-O(17)h	2.443(6)	j: 1-x, 2-y, -z ;	
Mo(4)-O(11)	1.747(6)	Na(4)-O(11)b	2.538(7)	k: -x-1, 1-y, 2-z;	
Mo(4)-O(6)	1.750(5)	Na(4)-O(8)i	2.775(7)	l: -x-1, 1-y, 1-z;	
Mo(4)-O(12)	1.771(6)	Na(4)-O(15)j	2.801(7)	m: x, y+1, z;	
Mo(4)-O(8)	1.803(6)	Na(4)-O(15)	2.810(8)	n: x, y, z+1;	
<Mo(4)-O>	1.77	Na(4)-O(13)p	2.889(8)	o: x, y, z-1;	
		<Na(4)-O>	2.62	p: -x-1, 1-y, -z	

with <Mo–O> bond-lengths in the range 1.76 to 1.77 Å. Six symmetrically independent Na^+ cations occupy irregular coordination polyhedra (Fig. 4), and are coordinated by from six to eight O atoms with Na–O bond-lengths of less than 3 Å.

Bond-valence analysis

Bond-valence sums incident upon the cation positions in the structure of $Na_6[(UO_2)(MoO_4)_4]$, calculated as for $Na_6[(UO_2)_2O(MoO_4)_4]$, are: U = 5.95, Mo(1) = 5.96, Mo(2) = 5.92, Mo(3) = 6.00, Mo(4) = 5.83, Na(1) = 1.11, Na(2) = 0.80, Na(3) = 0.93, Na(4) = 1.02, Na(5) = 0.86, Na(6) = 0.83 *vu*. Bond-valence sums incident upon the O atoms range from 1.81 to 2.13 *vu*.

Structural connectivity

The structure of $Na_6[(UO_2)(MoO_4)_4]$ is based upon a finite cluster with composition $[(UO_2)_2(MoO_4)_8]^{12-}$ (Fig. 5). The cluster contains two $\mathit{Ur}O_5$ pentagonal bipyramids and eight MoO_4 tetrahedra. The $\mathit{Ur}O_5$ pentagonal bipyramids are linked by sharing their equato-

TABLE 6. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $K_6[(UO_2)_2O(MoO_4)_4]$

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.21675(7)	0.48425(7)	0.31435(5)	0.0196(2)	0.0172(3)	0.0258(3)	0.0138(3)	-0.0085(2)	0.0028(2)	-0.0055(2)
Mo(1)	0.3649(2)	0.7436(2)	-0.0340(1)	0.0181(3)	0.0182(6)	0.0190(6)	0.0140(6)	-0.0043(5)	0.0002(4)	-0.0009(5)
Mo(2)	-0.1510(2)	0.8456(2)	0.3938(1)	0.0238(3)	0.0234(7)	0.0225(7)	0.0207(6)	-0.0031(5)	0.0006(5)	-0.0008(5)
K(1)	0.8381(5)	0.7060(4)	0.0294(4)	0.0340(8)	0.037(2)	0.025(2)	0.036(2)	-0.011(1)	-0.005(1)	0.003(1)
K(2)	0.2735(4)	0.6026(4)	-0.3421(3)	0.0308(8)	0.033(2)	0.030(2)	0.026(2)	-0.006(1)	-0.001(1)	-0.004(1)
K(3)	0.6072(4)	0.0678(4)	-0.2778(3)	0.0318(8)	0.029(2)	0.027(2)	0.035(2)	-0.010(1)	-0.000(1)	-0.004(1)
O(1)	0.069(1)	0.447(1)	0.218(1)	0.031(2)	0.021(5)	0.037(6)	0.040(6)	-0.018(5)	-0.012(5)	-0.004(5)
O(2)	0.373(1)	0.535(1)	0.398(1)	0.034(3)	0.038(6)	0.056(7)	0.022(5)	-0.008(5)	-0.017(5)	-0.024(5)
O(3)	0.405(1)	0.645(1)	0.120(1)	0.024(2)	0.024(5)	0.029(5)	0.017(5)	0.004(4)	-0.009(4)	0.003(4)
O(4)	-0.272(1)	0.755(2)	0.307(1)	0.036(3)	0.029(6)	0.052(7)	0.030(6)	-0.012(5)	-0.012(5)	0.001(5)
O(5)	-0.225(1)	0.797(1)	0.573(1)	0.036(3)	0.042(6)	0.031(6)	0.027(6)	-0.005(5)	0.001(5)	0.002(5)
O(6)	0.564(1)	0.718(1)	-0.168(1)	0.037(3)	0.034(6)	0.021(6)	0.038(6)	-0.011(5)	0.013(5)	0.013(4)
O(7)	0.084(1)	0.782(1)	0.3188(9)	0.027(2)	0.026(5)	0.025(5)	0.025(5)	-0.002(4)	0.000(4)	-0.006(4)
O(8)	0.200(1)	0.653(1)	-0.072(1)	0.035(3)	0.026(6)	0.051(7)	0.032(6)	-0.002(5)	-0.016(5)	-0.005(5)
O(9)	0.300(1)	0.962(1)	-0.013(1)	0.038(3)	0.044(7)	0.021(6)	0.042(7)	-0.004(5)	-0.007(5)	0.007(5)
O(10)	-0.202(2)	0.066(1)	0.374(1)	0.049(3)	0.051(7)	0.032(7)	0.052(8)	0.006(6)	-0.003(6)	0.005(5)
O(11)	0	½	½	0.060(5)	0.063(8)	0.045(8)	0.049(8)	-0.021(7)	0.029(6)	-0.010(7)

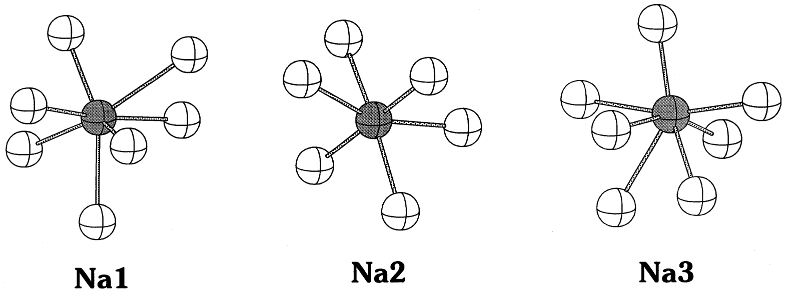

FIG. 1. The coordination of Na atoms in the structure of $Na_6[(UO_2)_2O(MoO_4)_4]$ (dark circles: Na; light circles: O).

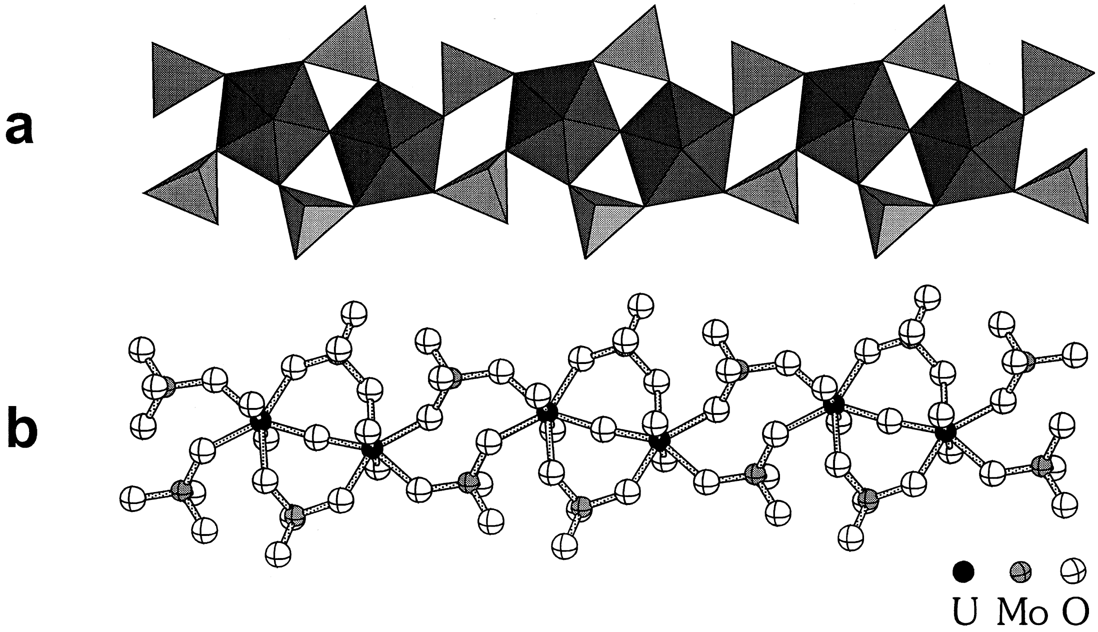

FIG. 2. The chains of composition $[(UO_2)_2O(MoO_4)_4]^{6-}$ in the structure of $Na_6[(UO_2)_2O(MoO_4)_4]$ shown in polyhedral (*a*) and ball-and-stick (*b*) representations.

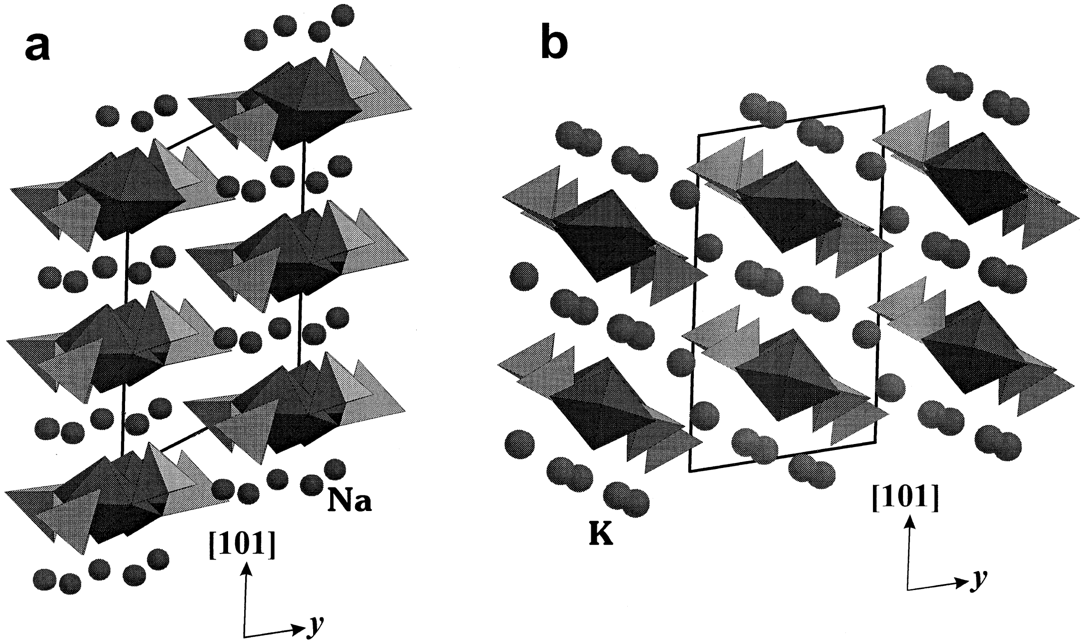

FIG. 3. The structures of (a) $Na_6[(UO_2)_2O(MoO_4)_4]$ and (b) $K_6[(UO_2)_2O(MoO_4)_4]$ projected down [$\bar{1}$01] (dark circles: Na and K atoms).

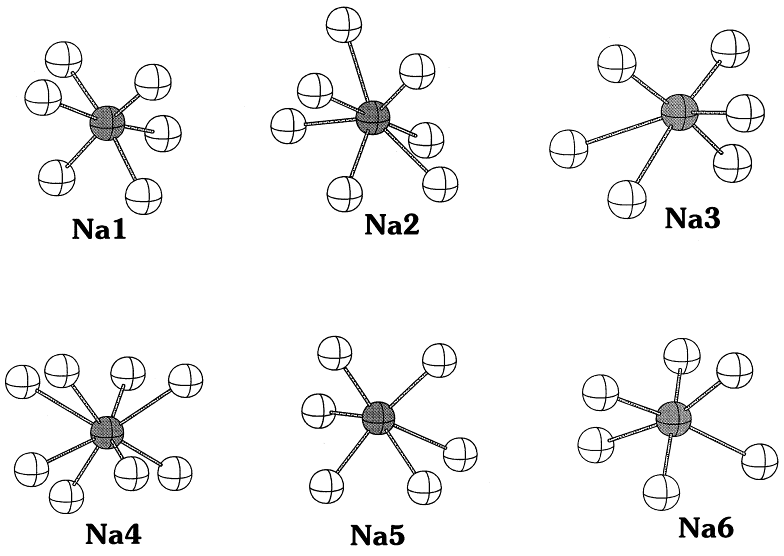

FIG. 4. The coordination of Na atoms in the structure of $Na_6[(UO_2)(MoO_4)_4]$ (dark circles: Na; light circles: O).

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF $K_6[(UO_2)_2O(MoO_4)_4]$

U-O(2)	1.799(9)	Mo(2)-O(10)c	1.71(1)	K(2)-O(10)f	2.57(1)
U-O(1)	1.804(9)	Mo(2)-O(4)	1.74(1)	K(2)-O(2)g	2.65(1)
U-O(11)	2.1560(5)	Mo(2)-O(7)	1.783(9)	K(2)-O(1)f	2.69(1)
U-O(5)a	2.38(1)	Mo(2)-O(5)	1.79(1)	K(2)-O(2)b	2.71(1)
U-O(7)	2.39(1)	<Mo(2)-O>	1.76	K(2)-O(8)	2.73(1)
U-O(6)b	2.408(8)			K(2)-O(4)f	2.79(1)
U-O(3)	2.478(9)	K(1)-O(9)d	2.65(1)	K(2)-O(11)g	3.279(3)
$<U\text{-}O_{Ur}>$	1.80	K(1)-O(8)e	2.70(1)	<K(2)-O>	2.77
$<U\text{-}\phi_{eq}>$	2.36	K(1)-O(1)b	2.78(1)		
		K(1)-O(4)e	2.79(1)	K(3)-O(5)h	2.68(1)
Mo(1)-O(9)	1.72(1)	K(1)-O(8)b	2.85(1)	K(3)-O(7)b	2.77(1)
Mo(1)-O(8)	1.72(1)	K(1)-O(1)e	3.34(1)	K(3)-O(4)f	2.84(1)
Mo(1)-O(6)	1.759(9)	K(1)-O(6)	3.34(1)	K(3)-O(3)b	2.88(1)
Mo(1)-O(3)	1.776(9)	K(1)-O(3)	3.35(1)	K(3)-O(6)i	2.89(1)
<Mo(1)-O>	1.74	<K(1)-O>	2.98	K(3)-O(9)i	3.21(1)
a : $-x, -y+1, -z+1$; b : $-x+1, -y+1, -z$; c : $x, y+1,$				K(3)-O(2)b	3.24(1)
z; d : $-x+1, -y+2, -z$; e : $x+1, y, z$; f : $-x, -y+1, -z$;				K(3)-O(9)b	3.26(1)
g : $x, y, z-1$; h : $x+1, y-1, z-1$; i : $x, y-1, z$				<K(3)-O>	2.97

rial vertices with two MoO_4 tetrahedra. Additional MoO_4 tetrahedra attach to the cluster by sharing single equatorial vertices of the UrO_5 pentagonal bipyramids. The clusters are oriented approximately parallel to $(\bar{1}01)$ and are linked through bonds to the interstitial Na^+ cations (Fig. 6).

RESULTS: $K_6[(UO_2)_2O(MoO_4)_4]$

Cation polyhedra

The cation polyhedra in the structure of $K_6[(UO_2)_2O(MoO_4)_4]$ are similar to those found in $Na_6[(UO_2)_2O(MoO_4)_4]$. The $<U–O_{Ur}>$ and $<U–O_{eq}>$ bond-lengths of the single symmetrically unique uranyl pentagonal bipyramid are 1.80 and 2.36 Å, respectively. The <Mo–O> bond lengths of the two MoO_4 tetrahedra are 1.74 and 1.76 Å. The three symmetrically distinct K cations are coordinated by seven to eight O atoms (Fig. 7), with <K–O> bond-lengths ranging from 2.77 to 2.97 Å.

Bond-valence analysis

Bond-valence sums at the cation positions in the structure of $K_6[(UO_2)_2O(MoO_4)_4]$, calculated as for $Na_6[(UO_2)_2O(MoO_4)_4]$, are: U = 5.97, Mo(1) = 6.23, Mo(2) = 6.04, K(1) = 1.06, K(2) = 1.39, K(3) = 0.96 *vu*. Bond-valence sums at the anion positions range from 1.70 to 2.21 *vu*.

Structural connectivity

The structure of $K_6[(UO_2)_2O(MoO_4)_4]$ contains a chain of composition $[(UO_2)_2O(MoO_4)_4]^{6-}$ parallel to $[\bar{1}01]$ that is topologically identical to that found in $Na_6[(UO_2)_2O(MoO_4)_4]$ (Fig. 2). Owing to the different ionic radii of the Na and K cations ($^{IV}Na^+ = 1.02$, $^{VIII}K^+ = 1.51$ Å, Shannon 1976), the arrangement of chains is different in $K_6[(UO_2)_2O(MoO_4)_4]$ and $Na_6[(UO_2)_2O(MoO_4)_4]$ (Fig. 3), as reflected by rather different unit-cell parameters for the two phases (Table 1).

DISCUSSION

The compound $Na_6[(UO_2)(MoO_4)_4]$ corresponds to "phase B" that was synthesized by Dion *et al.* (1977).

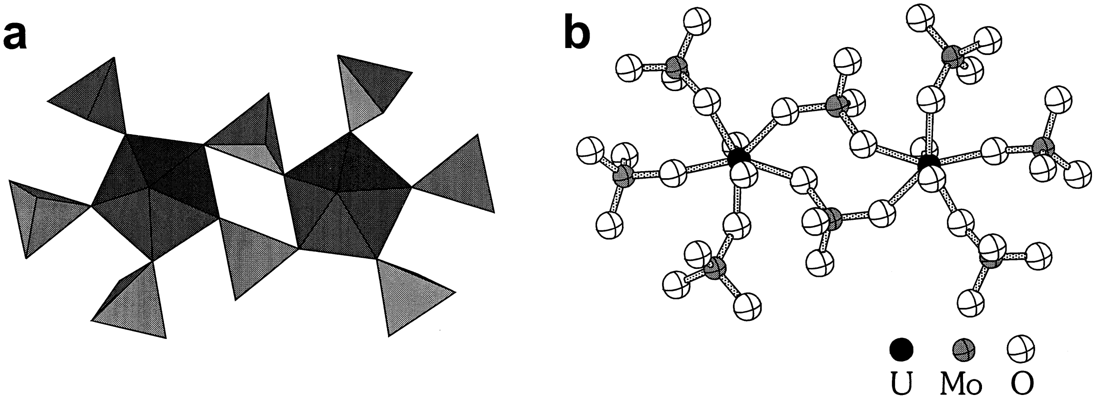

FIG. 5. The finite cluster of composition $[(UO_2)_2(MoO_4)_8]^{12-}$ in the structure of $Na_6[(UO_2)(MoO_4)_4]$ shown in polyhedral (*a*) and ball-and-stick (*b*) representations.

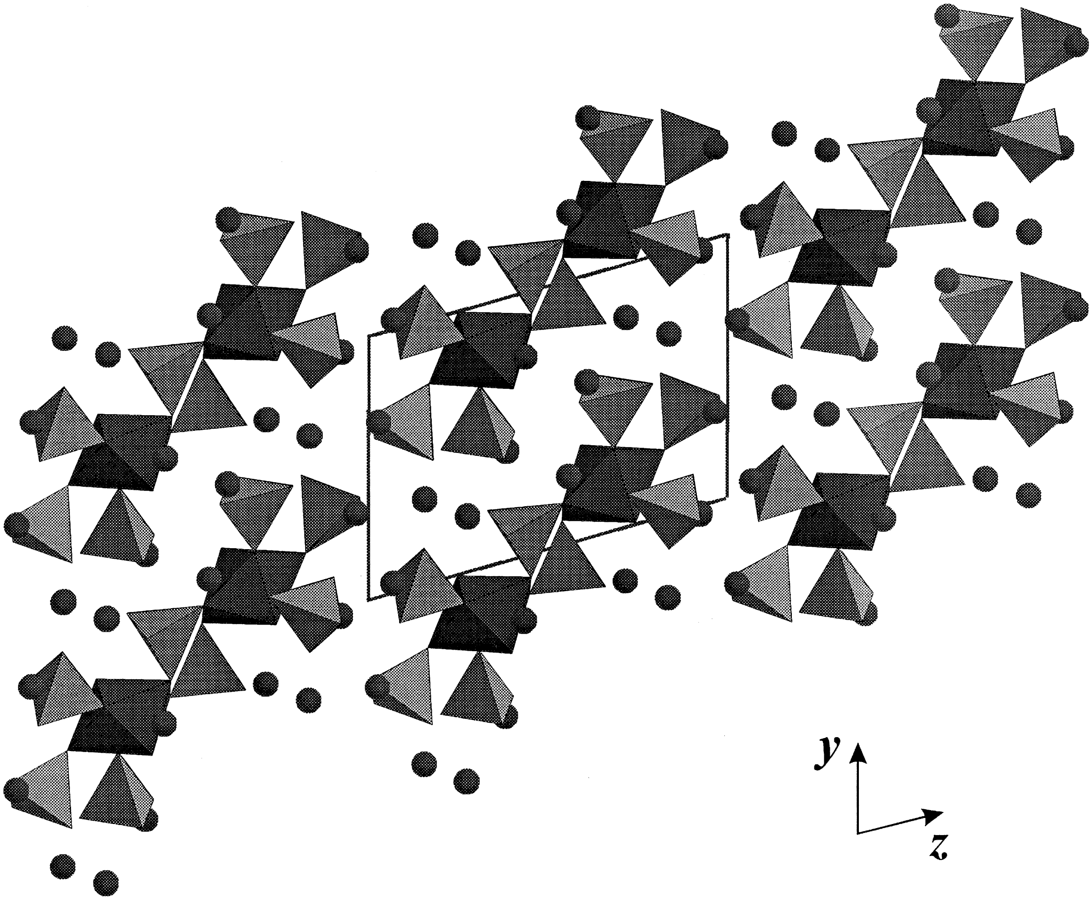

FIG. 6. The structure of $Na_6[(UO_2)(MoO_4)_4]$ projected along [100] (circles: Na atoms).

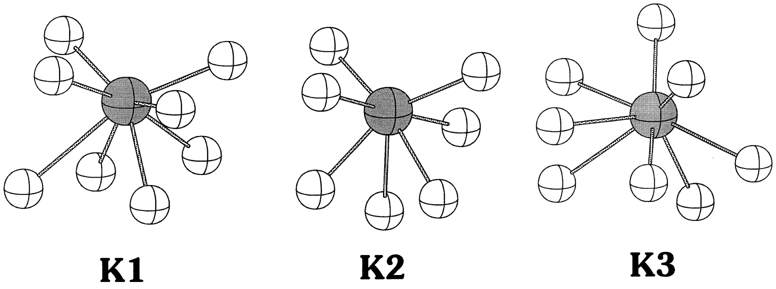

FIG. 7. The coordination of the K atoms in the structure of $K_6[(UO_2)_2O(MoO_4)_4]$ (dark circles: K atoms, light circles: O atoms).

On the basis of the X-ray-diffraction data, $Na_6[(UO_2)_2O(MoO_4)_4]$ probably corresponds to the low-temperature modification of the "E phase" reported by Dion & Noël (1981b), although they reported the formula as $Na_2UMo_2O_{10}$, which may be rewritten as $Na_4[(UO_2)_2(MoO_4)_4]$. We have not been able to find reference to the compound $K_6[(UO_2)_2O(MoO_4)_4]$ in the literature.

The structural hierarchy for uranyl phases proposed by Burns *et al.* (1996) and Burns (1999) is based upon polymerization of those polyhedra of higher bond-valence. In the case of the new uranyl molybdate structures reported here, the polyhedra of higher bond-valence are UrO_5 pentagonal bipyramids and MoO_4 tetrahedra. The structures of $Na_6[(UO_2)_2O(MoO_4)_4]$ and $K_6[(UO_2)_2O(MoO_4)_4]$ are classified as structures based upon chains, whereas $Na_6[(UO_2)(MoO_4)_4]$ corresponds to the class of structures based upon finite clusters of polyhedra of higher bond-valence. These two structural classes are uncommon in uranyl compounds owing to the dominance of sheets of polyhedra.

The structures of each of the three uranyl molybdates reported in the current study provide insight into possible structural arrangements in uranyl phases, as each contains a novel structural unit. The uranyl molybdate chains that occur in $Na_6[(UO_2)_2O(MoO_4)_4]$ and $K_6[(UO_2)_2O(MoO_4)_4]$ are topologically distinct, although several chains of polyhedra of higher bond-valence are known in uranyl phases (Burns *et al.* 1996), including the uranyl molybdate chain found in $Cu_4[(UO_2)(MoO_4)_2](OH)_6$ (Tali *et al.* 1993) and deloryite (Pushcharovsky *et al.* 1996). In $Cu_4[(UO_2)(MoO_4)_2](OH)_6$, the chains are relatively simple, involving UrO_4 square bipyramids, each of which shares an equatorial vertex with a MoO_4 tetrahedron, with each MoO_4 tetrahedron bridging two UrO_4 square bipyramids.

Finite clusters of polyhedra of higher bond-valence are the basis of the structures of several uranyl phases (Burns *et al.* 1996), but the cluster in $Na_6[(UO_2)(MoO_4)_4]$ is unique. It is interesting to note that finite clusters found in all other uranyl compounds involve both vertex- and edge-sharing between polyhedra, in contrast to the cluster in $Na_6[(UO_2)(MoO_4)_4]$ that involves only the sharing of polyhedron vertices.

The structure of deloryite contains a uranyl molybdate chain (Pushcharovsky *et al.* 1996), and both umohoite and iriginite have structures that involve sheets of uranyl and molybdate polyhedra (Krivovichev & Burns 2000a, b). The current study demonstrates that other structural themes are possible in uranyl molybdates.

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REFERENCES

BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.

BUCK, E.C., WRONKIEWICZ, D.J., FINN, P.A. & BATES, J.K. (1997): A new uranyl oxide hydrate phase derived from spent fuel alteration. *J. Nucl. Mater.* **249**, 70-76.

BURNS, P.C. (1999): The crystal chemistry of uranium. *In* Uranium: Mineralogy, Geochemistry and the Environment (P.C. Burns & R. Finch, eds.). *Rev. Mineral.* **38**, 23-90.

________, HAWTHORNE, F.C. & EWING, R.C. (1997): The crystal chemistry of hexavalent uranium: polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. *Can. Mineral.* **35**, 1551-1570.

________, MILLER, M.L. & EWING, R.C. (1996): U^{6+} minerals and inorganic phases: a comparison and hierarchy of structures. *Can. Mineral.* **34**, 845-880.

DION, C. & NOËL, A. (1981a): Étude et interprétation du diagramme Na_2MoO_4–UO_3 dans le cadre du système ternaire UO_3–MoO_3–Na_2O. *Bull. Soc. Chim. Fr.* **1981**, I, 185-192.

________ & ________ (1981b): Étude et interprétation de la ligne UO_2MoO_4–Na_2MoO_4 dans le cadre du système UO_3–MoO_3–Na_2O. *Bull. Soc. Chim. Fr.* **1981**, I, 371-376.

________ & ________ (1981c): Étude du processus de réduction, par hydrogène, du molybdate d'uranyle UO_2MoO_4, des molybdates de sodium: $Na_2Mo_4O_{13}$, $Na_2Mo_2O_7$, Na_2MoO_4 et des composés du système UO_3–MoO_3–Na_2O. *Bull. Soc. Chim. Fr.* **1981**, I, 413-418.

________ & ________ (1982): Interprétation du diagramme MoO_3–UO_2MoO_4–Na_2MoO_4 dans le cadre du système MoO_3–UO_3–Na_2O. *Bull. Soc. Chim. Fr.* **1982**, I, 188-192.

________ & ________ (1983): Le système ternaire UO_3–MoO_3–K_2O: mise au point relative aux phases des binaires UO_3–K_2O, MoO_3–K_2O, étude du domaine UO_2MoO_4–K_2MoO_4–MoO_3. *Bull. Soc. Chim. Fr.* **1983**, I, 257-266.

________ & ________ (1985): Le système ternaire UO_3–MoO_3–K_2O: étude du domaine UO_2MoO_4–K_2MoO_4–$K_2U_2O_7$. *Bull. Soc. Chim. Fr.* **1985**, I, 735-741.

________, ________ & LAUREYNS, J. (1977): Contribution à l'etude du système UO_3–MoO_3–Na_2O. Ètude du domaine $Na_2U_2O_7$–$Na_2Mo_2O_7$–Na_2O. *Bull. Soc. Chim. Fr.* **1977**, I, 1115-1120.

FINCH, R.J. & MURAKAMI, T. (1999): Systematics and paragenesis of uranium minerals. *In* Uranium: Mineralogy, Geochemistry and the Environment (P.C. Burns & R. Finch, eds.). *Rev. Mineral.* **38**, 91-179.

IBERS, J.A. & HAMILTON, W.C., eds. (1974): *International Tables for X-ray Crystallography* IV. The Kynoch Press, Birmingham, U.K.

KRASOVSKAYA, T.I., POLYAKOV, YU.A. & ROZANOV, I.A. (1981): Alkali metal dimolybdate uranates. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **17**, 695-698 (in Russ.).

KRIVOVICHEV, S.V. & BURNS, P.C. (2000a): The crystal chemistry of uranyl molybdates. I. The structure and formula of umohoite. *Can. Mineral.* **38**, 717-726.

________ & ________ (2000b): The crystal chemistry of uranyl molybdates. II. The crystal structure of iriginite. *Can. Mineral.* **38**, 847-851.

PUSHCHAROVSKY, D.YU., RASTSVETAEVA, R.K. & SARP, H. (1996): Crystal structure of deloryite, $Cu_4(UO_2)(Mo_2O_8)(OH)_6$. *J. Alloys Compounds* **239**, 23-26.

SADIKOV, G.G., KRASOVSKAYA, T.I., POLYAKOV, YU.A. & NIKOLAEV, V.P. (1988): Structure and spectral analysis of potassium uranyl dimolybdate. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **24**, 109-115 (in Russ.).

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

TALI, R., TABACHENKO, V.V. & KOVBA, L.M. (1993): Crystal structure of $Cu_4UO_2(MoO_4)_2(OH)_6$. *Zh. Neorg. Khim.* **38**, 1450-1452 (in Russ.).

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