The Canadian Mineralogist
Vol. 40, pp. 201-209 (2002)

CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. VI. NEW URANYL MOLYBDATE UNITS IN THE STRUCTURES OF $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ AND $Cs_6[(UO_2)(MoO_4)_4]$

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Abstract

Two Cs uranyl molybdates, $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ and $Cs_6[(UO_2)(MoO_4)_4]$, have been synthesized by high-temperature solid-state reactions. The structures of these compounds were solved by direct methods and refined on the basis of F^2 for all unique data collected with monochromatic Mo*K*α X-radiation and a CCD (charge-coupled device) detector. The structure of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ was refined to an agreement factor (*R*1) of 4.4%, calculated using the 4873 unique observed reflections ($F_o \geq 4\sigma_F$). It is triclinic, space group *P*1, *a* 7.510(2), *b* 7.897(2), *c* 9.774(2) Å, α 79.279(5), β 81.269(5), γ 87.251(5)°, *V* 562.8(2) Å^3, *Z* = 1. The structure of $Cs_6[(UO_2)(MoO_4)_4]$ was refined to an *R*1 of 4.9%, calculated using the 4275 unique observed reflections ($F_o \geq 4\sigma_F$). It is triclinic, space group *P*1, *a* 11.613(3), *b* 12.545(3), *c* 14.466(3) Å, α 102.713(6), β 95.281(6), γ 106.182(6)°, *V* 1947.7(8) Å^3, *Z* = 3. These compounds are based upon uranyl molybdate structural units not previously observed in uranyl compounds. The structure of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ contains sheets of composition $[(UO_2)_3Mo_3O_{14}]^{4-}$ that contain UrO_5 pentagonal bipyramids (*Ur*: uranyl ion), MoO_4 tetrahedra and MoO_5 polyhedra. The sheets are parallel to (100) and Cs cations are located in the interlayer. The structure of $Cs_6[(UO_2)(MoO_4)_4]$ is based upon two symmetrically distinct finite clusters of composition $[(UO_2)(MoO_4)_4]^{6-}$, each of which contains a central UrO_4 square bipyramid that shares all four of its equatorial vertices with MoO_4 tetrahedra. Three-dimensional connectivity is provided by Cs cations located between the clusters.

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

Sommaire

Nous avons synthétisé deux molybdates uranylés de césium, $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ et $Cs_6[(UO_2)(MoO_4)_4]$, par réactions à haute température à l'état solide. Nous avons résolu les structures de ces deux composés par méthodes directes, et nous les avons affinées en utilisant les facteurs F^2 de toutes les données uniques prélevées avec un rayonnement monochromatique Mo*K*α et un détecteur à charges couplées. La structure de $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ a été affinée jusqu'à un facteur de concordance *R*1 de 4.4%, calculé en utilisant les 4873 réflexions uniques observées ($F_o \geq 4\sigma_F$). Il s'agit d'une phase triclinique, groupe spatial *P*1, *a* 7.510(2), *b* 7.897(2), *c* 9.774(2) Å, α 79.279(5), β 81.269(5), γ 87.251(5)°, *V* 562.8(2) Å^3, *Z* = 1. La structure du composé $Cs_6[(UO_2)(MoO_4)_4]$ a été affinée jusqu'à un facteur de concordance *R*1 de 4.9%, calculé en utilisant les 4275 réflexions uniques observées ($F_o \geq 4\sigma_F$). C'est une phase triclinique, groupe spatial *P*1, *a* 11.613(3), *b* 12.545(3), *c* 14.466(3) Å, α 102.713(6), β 95.281(6), γ 106.182(6)°, *V* 1947.7(8) Å^3, *Z* = 3. Ces composés sont fondés sur des unités structurales à molybdate uranylé qui n'avaient pas été observées antérieurement dans des composés d'uranyle. La structure de $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ contient des feuillets de composition $[(UO_2)_3Mo_3O_{14}]^{4-}$ ayant des bipyramides pentagonales UrO_5 (*Ur*: ion uranyle), des tétraèdres MoO_4 et des polyèdres MoO_5. Ces feuillets sont parallèles à (100), et les cations Cs logent entre les feuillets. La structure de $Cs_6[(UO_2)(MoO_4)_4]$ est fondée sur deux groupements limités symétriquement distincts, de composition $[(UO_2)(MoO_4)_4]^{6-}$, chacun ayant une bipyramide carrée UrO_4 au centre qui partage chacun de ses coins équatoriaux avec un tétraèdre MoO_4. La connectivité en trois dimensions est assurée par les cations Cs situés entre les groupements.

(Traduit par la Rédaction)

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

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INTRODUCTION

The Cs–U–Mo–O and Cs–U–Mo–O–H_2O systems have been extensively studied recently, owing to their importance in processes that occur during burnup of nuclear fuels in reactors (Misra *et al.* 1995) and alteration of spent nuclear fuel (Buck *et al.* 1997, Finch *et al.* 1999). Krasovskaya *et al.* (1980) reported the existence of $Cs_2[(UO_2)_2(MoO_4)_3]$, $Cs_2[(UO_2)(MoO_4)_2]$, $Cs_4[(UO_2)(MoO_4)_3]$ and $Cs_6[(UO_2)(MoO_4)_4]$. Serezhkin *et al.* (1987) investigated the tetragonal modification of $Cs_2[(UO_2)_2(MoO_4)_3]$ and suggested that it is closely related structurally to $Cs_2[(UO_2)_2(SO_4)_3]$ (Ross & Evans 1960). Misra *et al.* (1995) reported results of thermal, powder diffraction, chemical and infrared (IR) spectroscopic studies of two modifications of $Cs_2[(UO_2)(MoO_4)_2]$ and of $Cs_2[(UO_2)_2(MoO_4)_3]$. The first structure reported for a Cs uranyl molybdate was that of $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ (Rastsvetaeva *et al.* 1999). The IR spectrum and thermal behavior of this compound were later reported by Fedoseev *et al.* (2001). Recently, we have reported syntheses and crystal-structure determinations of $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ (Krivovichev & Burns 2001b) and two modifications of $Cs_2[(UO_2)_2(MoO_4)_3]$ (Krivovichev *et al.* 2002b).

As part of our ongoing studies of uranyl molybdates (Krivovichev & Burns 2000a, b, 2001a, b, Krivovichev *et al.* 2002a, b), we have synthesized $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ and $Cs_6[(UO_2)(MoO_4)_4]$ and determined their crystal structures.

EXPERIMENTAL

Synthesis of the crystals

Crystals of the Cs uranyl molybdates used in the current study were obtained by high-temperature solid-state reaction. A mixture of 0.038 g of $CsOOCCH_3$, 0.029 g of $UO_2(CH_3COO)_2{\bullet}2H_2O$, and 0.029 g MoO_3 (molar ratio Cs:U:Mo = 2:1:2) was placed in a platinum crucible and heated to 850°C in air, followed by cooling to 400°C over 100 hours, and then to 50°C over 10 hours. Transparent orange crystals of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ and transparent yellow crystals of $Cs_6[(UO_2)(MoO_4)_4]$ with maximum dimensions up to 0.5 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 APEX CCD (charge-coupled device) detector. Data were collected using monochromatized Mo*K*α X-radiation with frame widths of 0.3° in ω. More than a hemisphere of data was collected for each crystal, and the data were reduced 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). Semi-empirical corrections for absorption 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 the structures. Each was solved by direct methods, which gave the positions of the U, Cs and Mo atoms. Anions were located on difference-Fourier maps calculated following least-squares refinement of the partial-structure models. Each structure was refined on the basis of F^2 for all unique data. Final refinements for each structure included all atomic positional parameters, with an allowance for anisotropic displacement of all atoms, and a weighting scheme of the structure factors. For $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$, the refinement converged to an agreement index ($R1$) of 4.4%, calculated for the 4873 unique observed reflections. Final atomic parameters and selected interatomic distances are presented in Tables 2 and 3, respectively. For $Cs_6[(UO_2)(MoO_4)_4]$, the refinement converged to an $R1$ of 4.9%, calculated for the 4275 unique observed reflections ($F_o > 4\sigma_F$). Final atom-parameters and selected interatomic distances are presented in Tables 4 and 5, respectively. Observed and calculated structure-factors for each compound are available from the Depository of Unpublished Data,

TABLE 1. MISCELLANEOUS INFORMATION FOR $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ AND $Cs_6[(UO_2)(MoO_4)_4]$

Compound	$Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$	$Cs_6[(UO_2)(MoO_4)_4]$
a (Å)	7.510(2)	11.613(3)
b (Å)	7.897(2)	12.545(3)
c (Å)	9.774(2)	14.466(3)
α (°)	79.279(5)	102.713(6)
β (°)	81.269(5)	95.281(6)
γ (°)	87.251(5)	106.182(6)
V (Å^3)	562.8(2)	1947.7(8)
Z	1	3
Space group	$P1$	$P\bar{1}$
F_{000}	782	2202
μ (cm^{-1})	295.79	164.45
D_{calc} (g/cm^3)	5.47	4.37
Crystal size (mm)	0.16 x 0.10 x 0.05	0.14 x 0.04 x 0.03
Radiation	Mo*K*α	Mo*K*α
Abs. corr.	25.0 → 6.7 %	11.8 → 4.8 %
Ref. for abs. corr.	1275	419
Ref. for cell	2328	1166
Total Ref.	6357	21,655
Unique Ref.	5306	15,104
Unique $\|F_o\| \geq 4\sigma_F$	4873	4275
$R1$	0.044	0.049
S	1.00	0.58

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

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

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.01499(8)	0.85419(7)	0.80084(6)	0.0126(1)	0.0160(3)	0.0131(3)	0.0086(2)	-0.0008(2)	-0.0030(2)	-0.0009(2)
U(2)	-0.02434(9)	0.01907(7)	0.14717(6)	0.0118(1)	0.0162(3)	0.0090(2)	0.0104(2)	-0.0017(2)	-0.0030(2)	-0.0006(2)
U(3)	-0.01698(8)	0.53349(7)	0.15619(6)	0.0111(1)	0.0148(3)	0.0084(2)	0.0103(2)	-0.0014(2)	-0.0034(2)	-0.0001(2)
Mo(1)	-0.0832(2)	0.1966(2)	0.4992(1)	0.0150(3)	0.0192(7)	0.0139(6)	0.0116(6)	0.0005(5)	-0.0044(5)	-0.0006(5)
Mo(2)	-0.1489(2)	0.3483(2)	0.8845(2)	0.0166(3)	0.0262(8)	0.0107(6)	0.0147(6)	-0.0022(5)	-0.0095(6)	0.0011(6)
Mo(3)	0.2000(2)	0.7235(2)	0.4407(1)	0.0131(3)	0.0127(6)	0.0163(6)	0.0105(6)	-0.0020(5)	-0.0031(5)	-0.0001(5)
Cs(1)	-0.5249(2)	0.2528(2)	0.2754(1)	0.0251(3)	0.0231(6)	0.0212(5)	0.0325(6)	-0.0056(5)	-0.0085(5)	0.0024(5)
Cs(2)	-0.3163(2)	0.7101(2)	0.5148(1)	0.0313(3)	0.0181(6)	0.0458(8)	0.0304(6)	-0.0043(6)	-0.0070(5)	-0.0049(6)
Cs(3)	0.4843(2)	0.7837(2)	0.0417(1)	0.0269(3)	0.0182(6)	0.0338(7)	0.0266(6)	0.0000(5)	-0.0035(5)	-0.0004(5)
Cs(4)	0.3548(2)	0.2762(2)	0.7544(2)	0.0456(6)	0.0357(9)	0.057(1)	0.0424(9)	0.0010(8)	-0.0091(7)	-0.0170(8)
O(1)	-0.258(2)	0.966(2)	0.193(1)	0.021(3)	0.021(7)	0.017(6)	0.027(7)	-0.002(6)	-0.006(6)	-0.004(5)
O(2)	0.219(2)	0.487(2)	0.109(1)	0.022(3)	0.021(7)	0.024(7)	0.023(7)	-0.009(6)	-0.003(6)	0.000(6)
O(3)	-0.048(2)	0.125(2)	0.906(1)	0.022(3)	0.037(8)	0.014(6)	0.017(6)	-0.005(5)	-0.008(6)	-0.003(6)
O(4)	-0.253(2)	0.578(2)	0.216(1)	0.024(3)	0.025(8)	0.022(7)	0.024(7)	-0.005(6)	-0.001(6)	0.006(6)
O(5)	0.259(2)	0.854(2)	0.791(1)	0.022(3)	0.013(6)	0.039(8)	0.012(6)	-0.002(6)	-0.001(5)	0.006(6)
O(6)	0.054(2)	0.731(2)	0.601(1)	0.021(3)	0.027(7)	0.021(6)	0.017(6)	-0.008(5)	-0.004(5)	0.000(6)
O(7)	0.073(2)	0.740(2)	0.293(1)	0.015(2)	0.018(6)	0.014(5)	0.013(5)	0.002(4)	-0.008(5)	0.000(5)
O(8)	0.050(2)	0.101(2)	0.630(1)	0.017(2)	0.025(7)	0.012(5)	0.012(5)	0.004(4)	-0.004(5)	-0.005(5)
O(9)	0.332(2)	0.540(2)	0.462(2)	0.030(3)	0.029(8)	0.028(7)	0.034(8)	-0.008(6)	-0.013(7)	0.013(7)
O(10)	-0.221(2)	0.862(2)	0.793(1)	0.020(3)	0.013(6)	0.026(7)	0.026(7)	-0.016(6)	-0.007(5)	0.002(5)
O(11)	-0.104(2)	0.291(2)	0.113(1)	0.018(3)	0.023(7)	0.014(5)	0.019(6)	-0.003(5)	-0.006(5)	-0.003(5)
O(12)	-0.031(2)	0.546(2)	0.902(1)	0.021(3)	0.039(8)	0.006(5)	0.018(6)	0.001(4)	-0.010(6)	0.001(5)
O(13)	-0.043(3)	0.050(2)	0.382(1)	0.040(5)	0.08(1)	0.025(7)	0.014(6)	-0.002(6)	-0.009(8)	0.003(9)
O(14)	0.006(2)	0.801(2)	0.029(1)	0.019(3)	0.037(8)	0.010(5)	0.009(5)	-0.001(4)	-0.002(5)	-0.001(5)
O(15)	-0.133(3)	0.385(2)	0.703(2)	0.044(6)	0.10(2)	0.014(6)	0.019(7)	-0.001(6)	-0.025(9)	-0.004(9)
O(16)	0.350(2)	0.890(2)	0.405(1)	0.025(3)	0.024(7)	0.030(7)	0.017(6)	0.007(5)	-0.001(5)	-0.012(6)
O(17)	-0.009(2)	0.394(2)	0.396(1)	0.028(3)	0.05(1)	0.020(6)	0.015(6)	0.003(5)	-0.012(6)	-0.007(7)
O(18)	0.212(2)	0.070(2)	0.105(2)	0.025(3)	0.024(8)	0.013(6)	0.033(8)	0.008(6)	-0.003(6)	-0.003(6)
O(19)	-0.376(2)	0.356(3)	0.939(2)	0.041(4)	0.023(8)	0.04(1)	0.06(1)	-0.008(9)	-0.016(8)	-0.004(8)
O(20)	-0.310(3)	0.200(3)	0.549(2)	0.043(5)	0.023(8)	0.07(1)	0.024(8)	0.013(8)	-0.005(7)	-0.011(9)

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$

U(1)-O(10)	1.78(1)	Mo(2)-O(19)	1.71(2)	Cs(3)-O(10)g	3.02(2)
U(1)-O(5)	1.82(1)	Mo(2)-O(15)	1.73(1)	Cs(3)-O(4)h	3.02(1)
U(1)-O(14)a	2.18(1)	Mo(2)-O(3)	1.87(1)	Cs(3)-O(18)b	3.06(2)
U(1)-O(6)	2.31(1)	Mo(2)-O(12)	1.89(1)	Cs(3)-O(2)	3.06(2)
U(1)-O(8)b	2.32(1)	Mo(2)-O(11)a	2.27(1)	Cs(3)-O(5)d	3.13(1)
U(1)-O(12)	2.47(1)	<Mo(2)-O>	1.89	Cs(3)-O(1)h	3.15(1)
U(1)-O(3)b	2.54(1)			Cs(3)-O(14)	3.61(2)
<U(1)-O_{Ur}>	1.80	Mo(3)-O(9)	1.71(1)	Cs(3)-O(7)	3.63(1)
<U(1)-O_{eq}>	2.36	Mo(3)-O(16)	1.72(2)	Cs(3)-O(19)g	3.76(2)
		Mo(3)-O(6)	1.78(1)	Cs(3)-O(16)	3.78(1)
U(2)-O(1)c	1.79(2)	Mo(3)-O(7)	1.83(1)	<Cs(3)-O>	3.32
U(2)-O(18)	1.81(2)	<Mo(3)-O>	1.76		
U(2)-O(11)	2.18(1)			Cs(4)-O(19)h	3.07(2)
U(2)-O(14)c	2.23(1)	Cs(1)-O(2)c	3.04(1)	Cs(4)-O(20)h	3.09(2)
U(2)-O(13)	2.34(1)	Cs(1)-O(16)f	3.04(2)	Cs(4)-O(8)	3.22(1)
U(2)-O(3)d	2.38(1)	Cs(1)-O(1)c	3.09(1)	Cs(4)-O(9)	3.23(2)
U(2)-O(7)c	2.53(1)	Cs(1)-O(9)e	3.22(1)	Cs(4)-O(3)	3.33(2)
<U(2)-O_{Ur}>	1.80	Cs(1)-O(4)	3.27(2)	Cs(4)-O(5)c	3.39(2)
<U(2)-O_{eq}>	2.33	Cs(1)-O(19)d	3.27(2)	Cs(4)-O(18)a	3.54(2)
		Cs(1)-O(20)	3.28(2)	Cs(4)-O(12)	3.78(1)
U(3)-O(2)	1.80(2)	Cs(1)-O(18)e	3.30(2)	Cs(4)-O(15)	3.81(2)
U(3)-O(4)	1.82(2)	Cs(1)-O(11)	3.31(2)	<Cs(4)-O>	3.38
U(3)-O(11)	2.18(1)	<Cs(1)-O>	3.20		
U(3)-O(14)	2.24(1)				
U(3)-O(17)	2.41(1)	Cs(2)-O(6)	3.05(1)	a = $x, y, z + 1$;	
U(3)-O(7)	2.47(1)	Cs(2)-O(16)e	3.06(1)	b = $x, y + 1, z$;	
U(3)-O(12)d	2.49(1)	Cs(2)-O(9)e	3.17(2)	c = $x, y - 1, z$;	
<U(3)-O_{Ur}>	1.81	Cs(2)-O(4)	3.24(1)	d = $x, y, z - 1$;	
<U(3)-O_{eq}>	2.36	Cs(2)-O(15)	3.25(1)	e = $x - 1, y, z$;	
		Cs(2)-O(10)	3.35(1)	f = $x - 1, y - 1, z$;	
Mo(1)-O(20)	1.70(2)	Cs(2)-O(7)	3.35(1)	g = $x + 1, y, z - 1$;	
Mo(1)-O(13)	1.75(2)	Cs(2)-O(1)	3.39(1)	h = $x + 1, y, z$	
Mo(1)-O(17)	1.75(1)	Cs(2)-O(13)b	3.40(2)		
Mo(1)-O(8)	1.78(1)	Cs(2)-O(17)	3.55(2)		
<Mo(1)-O>	1.75	<Cs(2)-O>	3.28		

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Results: $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$

Cation polyhedra

The structure of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ contains three symmetrically independent U^{6+} cations. Each cation is bonded to two O atoms, forming $(UO_2)^{2+}$ uranyl ions (*Ur*) with <U–O_{Ur}> bond lengths of 1.80, 1.80 and 1.81 Å for U(1), U(2) and U(3), respectively. Each uranyl ion is coordinated by five O atoms arranged at the equatorial vertices of UrO_5 pentagonal bipyramids. The <U–O_{eq}> (eq: equatorial) bond distances range from 2.33 to 2.36 Å, which is consistent with the value of 2.37(9) Å obtained for uranyl pentagonal bipyramids from numerous well-refined structures (Burns *et al.* 1997).

There are three symmetrically independent Mo^{6+} cations in the structure. The Mo(1) and Mo(3) cations are coordinated by four atoms of O located at the vertices of tetrahedra. The <Mo–O> distances for these tetrahedra are 1.75 and 1.76 Å, in good agreement with values in uranyl molybdates containing MoO_4 tetrahedra (Krivovichev & Burns 2001a, b). The Mo(2) cation

TABLE 4. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $Cs_6[(UO_2)(MoO_4)_4]$

Atom	*x*	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.49766(5)	0.75078(5)	0.49960(5)	0.0191(1)	0.0199(3)	0.0213(3)	0.0175(3)	0.0050(2)	0.0044(2)	0.0082(2)
U(2)	0	0	0	0.0199(2)	0.0195(4)	0.0180(4)	0.0233(5)	0.0059(4)	0.0044(3)	0.0068(3)
Mo(1)	0.8026(1)	0.1934(1)	-0.0250(1)	0.0216(3)	0.0170(6)	0.0237(7)	0.0258(8)	0.0075(6)	0.0043(6)	0.0081(5)
Mo(2)	0.8005(1)	0.6884(1)	-0.0265(1)	0.0222(3)	0.0179(7)	0.0202(7)	0.0285(9)	0.0073(6)	0.0032(6)	0.0052(5)
Mo(3)	0.5975(1)	0.2177(1)	0.2468(1)	0.0255(3)	0.0307(8)	0.0286(8)	0.0168(8)	0.0044(6)	0.0043(6)	0.0093(6)
Mo(4)	0.1605(1)	0.6623(1)	0.4213(1)	0.0272(3)	0.0215(7)	0.0351(8)	0.0244(9)	0.0086(7)	0.0035(6)	0.0071(6)
Mo(5)	0.5803(1)	0.7158(1)	0.2440(1)	0.0272(3)	0.0345(8)	0.0304(8)	0.0176(8)	0.0050(6)	0.0056(6)	0.0120(6)
Mo(6)	0.1692(1)	0.1766(1)	0.4394(1)	0.0262(3)	0.0226(7)	0.0299(8)	0.0272(9)	0.0103(7)	0.0045(6)	0.0073(6)
Cs(1)	0.62409(8)	0.91593(8)	0.05655(8)	0.0270(2)	0.0218(5)	0.0336(6)	0.0253(6)	0.0071(5)	0.0032(4)	0.0086(4)
Cs(2)	0.37111(8)	0.58264(8)	-0.06254(8)	0.0272(2)	0.0238(5)	0.0303(5)	0.0279(6)	0.0073(5)	0.0059(4)	0.0088(4)
Cs(3)	0.62299(9)	0.07383(9)	-0.29694(8)	0.0346(3)	0.0294(6)	0.0348(6)	0.0360(7)	0.0058(5)	0.0016(5)	0.0076(5)
Cs(4)	0.62220(9)	0.58160(9)	-0.29980(8)	0.0347(3)	0.0292(6)	0.0374(6)	0.0375(7)	0.0110(5)	0.0038(5)	0.0096(5)
Cs(5)	0.96117(9)	0.26020(9)	0.25343(8)	0.0359(3)	0.0306(6)	0.0486(7)	0.0296(7)	0.0108(5)	0.0041(5)	0.0137(5)
Cs(6)	0.96309(9)	0.8327(1)	0.25071(8)	0.0398(3)	0.0356(6)	0.0508(7)	0.0317(7)	0.0013(6)	0.0059(5)	0.0185(5)
Cs(7)	0.22546(9)	0.96973(9)	0.58646(9)	0.0349(3)	0.0370(6)	0.0333(6)	0.0377(7)	0.0096(5)	0.0101(5)	0.0143(5)
Cs(8)	0.2137(1)	0.47257(9)	0.59664(9)	0.0384(3)	0.0432(7)	0.0319(6)	0.0376(8)	0.0049(5)	0.0067(5)	0.0105(5)
Cs(9)	0.0696(1)	0.55393(9)	0.13668(9)	0.0400(3)	0.0552(7)	0.0320(6)	0.0350(7)	0.0097(5)	0.0016(6)	0.0181(5)
O(1)	0.0619(8)	0.0454(8)	0.1291(7)	0.020(2)	0.025(5)	0.029(6)	0.007(5)	0.005(4)	-0.008(4)	0.010(4)
O(2)	0.8702(9)	0.1041(8)	0.0338(8)	0.032(3)	0.036(6)	0.036(6)	0.034(8)	0.020(6)	0.005(5)	0.019(5)
O(3)	0.4418(9)	0.8727(9)	0.5200(8)	0.038(3)	0.033(7)	0.048(7)	0.037(8)	0.006(6)	0.009(6)	0.023(6)
O(4)	0.3072(9)	0.1330(9)	0.4265(8)	0.038(3)	0.040(7)	0.048(7)	0.022(7)	0.000(6)	-0.002(5)	0.018(6)
O(5)	0.8578(9)	0.6133(9)	0.0441(9)	0.041(3)	0.036(7)	0.029(6)	0.06(1)	0.012(6)	0.001(6)	0.016(5)
O(6)	0.3046(9)	0.6324(9)	0.4239(9)	0.040(3)	0.041(7)	0.042(7)	0.039(9)	0.009(6)	0.019(6)	0.014(6)
O(7)	0.8638(8)	0.8423(8)	0.0233(8)	0.028(3)	0.018(5)	0.028(6)	0.030(7)	0.005(5)	0.003(5)	-0.002(4)
O(8)	0.5523(9)	0.6297(8)	0.4799(8)	0.037(3)	0.046(7)	0.028(6)	0.036(8)	0.000(6)	0.009(6)	0.014(5)
O(9)	0.8620(9)	0.3381(8)	0.0389(8)	0.031(3)	0.038(7)	0.019(6)	0.030(7)	0.001(5)	0.004(5)	0.004(5)
O(10)	0.8395(9)	0.6504(9)	-0.1399(8)	0.038(3)	0.034(7)	0.043(7)	0.030(8)	-0.008(6)	0.011(5)	0.013(5)
O(11)	0.5427(9)	0.7811(9)	0.3594(8)	0.036(3)	0.039(7)	0.044(7)	0.029(8)	0.011(6)	0.018(6)	0.014(5)
O(12)	0.1784(8)	0.3004(8)	0.4006(8)	0.032(3)	0.025(6)	0.034(6)	0.035(8)	0.012(6)	-0.002(5)	0.004(5)
O(13)	0.5498(9)	0.2783(9)	0.3569(8)	0.038(3)	0.044(7)	0.043(7)	0.035(8)	0.019(6)	0.017(6)	0.016(6)
O(14)	0.618(1)	0.594(1)	0.245(1)	0.060(4)	0.09(1)	0.052(8)	0.05(1)	0.010(7)	0.012(8)	0.044(8)
O(15)	0.649(1)	0.1451(9)	-0.0298(9)	0.041(3)	0.043(7)	0.046(7)	0.039(9)	0.012(6)	0.013(6)	0.018(6)
O(16)	0.6475(9)	0.6480(9)	-0.032(1)	0.048(4)	0.030(7)	0.037(7)	0.07(1)	0.010(7)	0.017(7)	0.004(5)
O(17)	0.8394(9)	0.1883(9)	-0.1398(8)	0.038(3)	0.038(7)	0.046(7)	0.033(8)	0.011(6)	0.015(6)	0.016(5)
O(18)	0.1461(9)	0.203(1)	0.5597(9)	0.043(3)	0.036(7)	0.064(8)	0.034(8)	0.020(7)	0.010(6)	0.016(6)
O(19)	0.0406(9)	0.070(1)	0.369(1)	0.053(4)	0.021(6)	0.053(8)	0.07(1)	0.016(8)	-0.004(6)	0.000(6)
O(20)	0.702(1)	0.815(1)	0.2184(9)	0.048(4)	0.040(7)	0.061(8)	0.06(1)	0.028(8)	0.021(7)	0.025(6)
O(21)	0.1673(9)	0.778(1)	0.3735(9)	0.045(3)	0.030(6)	0.064(8)	0.052(9)	0.043(8)	0.006(6)	0.008(6)
O(22)	0.480(1)	0.192(1)	0.1557(9)	0.065(4)	0.063(9)	0.11(1)	0.021(8)	0.005(8)	-0.006(7)	0.033(8)
O(23)	0.455(1)	0.686(1)	0.154(1)	0.079(5)	0.10(1)	0.10(1)	0.024(9)	-0.007(8)	-0.024(8)	0.04(1)
O(24)	0.7250(9)	0.3222(9)	0.2285(9)	0.040(3)	0.041(7)	0.035(7)	0.041(9)	0.007(6)	0.013(6)	0.005(5)
O(25)	0.639(1)	0.095(1)	0.2492(9)	0.062(4)	0.14(1)	0.040(7)	0.037(9)	0.012(7)	0.042(9)	0.057(8)
O(26)	0.124(1)	0.6905(9)	0.5356(9)	0.041(3)	0.057(8)	0.032(7)	0.037(8)	0.006(6)	0.009(6)	0.021(6)
O(27)	0.047(1)	0.5442(9)	0.342(1)	0.054(4)	0.034(7)	0.043(7)	0.07(1)	-0.011(7)	0.008(7)	0.003(6)

is in a strongly distorted coordination polyhedron containing five O atoms. It consists of four Mo(2)–O bond lengths in the range 1.71 to 1.89 Å, and one Mo(2)–O bond length of 2.27 Å. According to the bond-valence curves provided by Brese & O'Keeffe (1991), the Mo(2)–O bond-length of 2.27 Å corresponds to 0.37 *vu*, and exclusion of this bond would result in serious deficiencies in the bond-valence sums incident at both of the Mo(2) and O(11) sites (Table 6). A similar environment of coordination was found about the Mo^{6+} cation in the structure of deloryite, where there are four Mo–O bonds in the range 1.71 to 1.88 Å, and one at 2.58 Å (Pushcharovsky *et al.* 1996).

The structure of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ contains four symmetrically independent Cs cations. Cs(1) and Cs(4) are coordinated by nine O atoms, whereas Cs(2) and Cs(3) are each coordinated by ten O atoms within 3.8 Å.

Structural connectivity

The three UrO_5 pentagonal bipyramids are linked through a single vertex [O(14)], resulting in a trimer of polyhedra that share edges (Fig. 1a). The trimers share vertices, forming chains that extend along [010]. The $Mo(2)O_5$ polyhedra are attached to these chains by sharing edges with two uranyl polyhedra, and the chains are cross-linked by the sharing of vertices with the $Mo(1)O_4$ and $Mo(2)O_4$ tetrahedra, resulting in sheets that are parallel to (100).

The uranyl molybdate sheet in $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ (Fig. 1a) has not been observed in any

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF $Cs_6[(UO_2)(MoO_4)_4]$

U(1)-O(8)	1.781(9)	Mo(6)-O(12)	1.744(9)	Cs(4)-O(10)	3.05(1)	Cs(7)-O(25)a	3.11(1)
U(1)-O(3)	1.799(9)	Mo(6)-O(19)	1.75(1)	Cs(4)-O(12)e	3.057(9)	Cs(7)-O(19)m	3.14(1)
U(1)-O(11)	2.23(1)	Mo(6)-O(18)	1.76(1)	Cs(4)-O(13)e	3.17(1)	Cs(7)-O(3)	3.217(9)
U(1)-O(13)a	2.28(1)	Mo(6)-O(4)	1.84(1)	Cs(4)-O(6)e	3.25(1)	Cs(7)-O(26)	3.26(1)
U(1)-O(6)	2.33(1)	<Mo(6)-O>	1.77	Cs(4)-O(8)e	3.30(1)	Cs(7)-O(20)n	3.30(1)
U(1)-O(4)a	2.33(1)			Cs(4)-O(14)e	3.32(1)	Cs(7)-O(21)	3.34(1)
<U(1)-O_{Ur}>	1.79	Cs(1)-O(15)e	3.01(1)	Cs(4)-O(8)i	3.44(1)	Cs(7)-O(11)n	3.39(1)
<U(1)-O_{eq}>	2.29	Cs(1)-O(22)e	3.05(1)	Cs(4)-O(22)e	3.68(1)	Cs(7)-O(18)g	3.39(1)
		Cs(1)-O(20)	3.08(1)	Cs(4)-O(16)	3.74(1)	Cs(7)-O(4)g	3.44(1)
U(2)-O(1), b	1.840(9) 2x	Cs(1)-O(25)g	3.13(1)	<Cs(4)-O>	3.33	<Cs(7)-O>	3.29
U(2)-O(2)c, d	2.273(9) 2x	Cs(1)-O(7)	3.212(9)				
U(2)-O(7)e, f	2.275(8) 2x	Cs(1)-O(2)g	3.256(9)	Cs(5)-O(12)j	3.00(1)	Cs(8)-O(24)a	3.05(1)
<U(2)-O_{Ur}>	1.84	Cs(1)-O(15)g	3.33(1)	Cs(5)-O(10)k	3.06(1)	Cs(8)-O(12)	3.08(1)
<U(2)-O_{eq}>	2.27	Cs(1)-O(16)	3.42(1)	Cs(5)-O(24)	3.06(1)	Cs(8)-O(18)	3.16(1)
		Cs(1)-O(23)	3.65(1)	Cs(5)-O(2)	3.25(1)	Cs(8)-O(27)m	3.19(1)
Mo(1)-O(15)	1.71(1)	<Cs(1)-O>	3.24	Cs(5)-O(26)a	3.28(1)	Cs(8)-O(14)a	3.28(1)
Mo(1)-O(17)	1.74(1)			Cs(5)-O(27)j	3.33(1)	Cs(8)-O(13)a	3.42(1)
Mo(1)-O(9)	1.75(1)	Cs(2)-O(16)	3.05(1)	Cs(5)-O(1)j	3.465(9)	Cs(8)-O(26)	3.438(9)
Mo(1)-O(2)	1.840(9)	Cs(2)-O(23)	3.07(1)	Cs(5)-O(19)j	3.47(1)	Cs(8)-O(8)a	3.48(1)
<Mo(1)-O>	1.76	Cs(2)-O(14)e	3.09(1)	Cs(5)-O(9)	3.63(1)	Cs(8)-O(6)	3.59(1)
		Cs(2)-O(24)e	3.15(1)	Cs(5)-O(25)	3.72(1)	<Cs(8)-O>	3.30
Mo(2)-O(16)	1.70(1)	Cs(2)-O(5)e	3.15(1)	<Cs(5)-O>	3.33		
Mo(2)-O(5)	1.74(1)	Cs(2)-O(9)e	3.16(1)			Cs(9)-O(9)b	3.03(1)
Mo(2)-O(10)	1.74(1)	Cs(2)-O(16)e	3.43(1)	Cs(6)-O(19)l	2.93(1)	Cs(9)-O(27)	3.04(1)
Mo(2)-O(7)	1.813(9)	Cs(2)-O(15)e	3.46(1)	Cs(6)-O(17)k	2.96(1)	Cs(9)-O(10)e	3.04(1)
<Mo(2)-O>	1.75	Cs(2)-O(22)e	3.49(1)	Cs(6)-O(20)	2.96(1)	Cs(9)-O(5)b	3.04(1)
		<Cs(2)-O>	3.23	Cs(6)-O(21)j	3.15(1)	Cs(9)-O(17)e	3.10(1)
Mo(3)-O(22)	1.72(1)			Cs(6)-O(18)a	3.19(1)	Cs(9)-O(9)e	3.19(1)
Mo(3)-O(25)	1.74(1)	Cs(3)-O(17)	3.01(1)	Cs(6)-O(7)	3.42(1)	Cs(9)-O(5)e	3.31(1)
Mo(3)-O(24)	1.768(9)	Cs(3)-O(21)e	3.08(9)	Cs(6)-O(5)	3.44(1)	Cs(9)-O(21)	3.77(1)
Mo(4)-O(26)	1.73(1)	Cs(3)-O(3)e	3.50(1)				
Mo(4)-O(27)	1.77(1)	Cs(3)-O(23)e	3.65(1)				
Mo(4)-O(6)	1.81(1)	Cs(3)-O(15)	3.73(1)				
<Mo(4)-O>	1.76	<Cs(3)-O>	3.34				
Mo(5)-O(14)	1.70(1)						
Mo(5)-O(20)	1.74(1)						
Mo(5)-O(23)	1.75(1)						
Mo(5)-O(11)	1.84(1)						
<Mo(5)-O>	1.76						

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

TABLE 6. BOND VALENCE ANALYSIS* (*vu*) FOR $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$

	Cs(1)	Cs(2)	Cs(3)	Cs(4)	U(1)	U(2)	U(3)	Mo(1)	Mo(2)	Mo(3)	Σ
O(1)	0.16	0.07	0.14			1.65					2.02
O(2)	0.19		0.18				1.62				1.99
O(3)				0.09	0.38	0.52			1.10		2.09
O(4)	0.10	0.11	0.20				1.55				1.96
O(5)			0.15	0.07	1.55						1.77
O(6)		0.18			0.59					1.41	2.18
O(7)		0.08	0.04			0.39	0.43			1.23	2.17
O(8)				0.12	0.58			1.41			2.11
O(9)	0.12	0.13		0.11						1.70	2.06
O(10)		0.08	0.20		1.68						1.96
O(11)	0.09					0.77	0.77		0.37		2.00
O(12)				0.03	0.43		0.42		1.04		1.92
O(13)		0.07				0.56		1.52			2.15
O(14)			0.04		0.77	0.70	0.68				2.19
O(15)		0.11		0.02					1.61		1.74
O(16)	0.19	0.18	0.03							1.65	2.05
O(17)		0.05					0.49	1.52			2.06
O(18)	0.09		0.18	0.05		1.59					1.91
O(19)	0.10		0.03	0.17					1.70		2.00
O(20)	0.10			0.16				1.75			2.01
Σ	1.14	1.06	1.19	0.82	5.98	6.18	5.96	6.20	5.82	5.99	

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

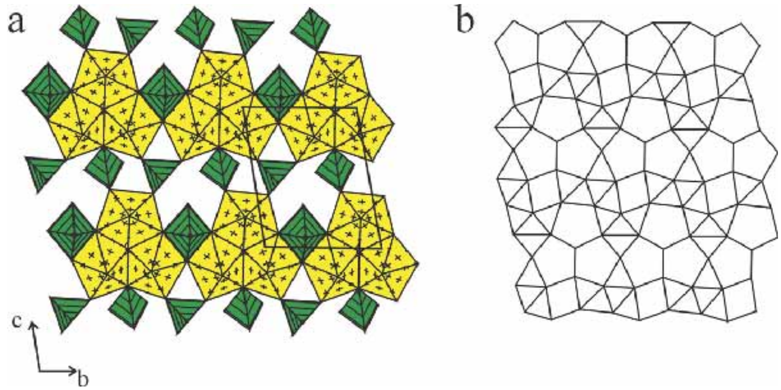

FIG. 1. The sheet of uranyl and molybdate polyhedra in the structure of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ (a) and its corresponding anion-topology (b). Legend: *Ur*O_5 polyhedra: yellow, MoO_n polyhedra: green.

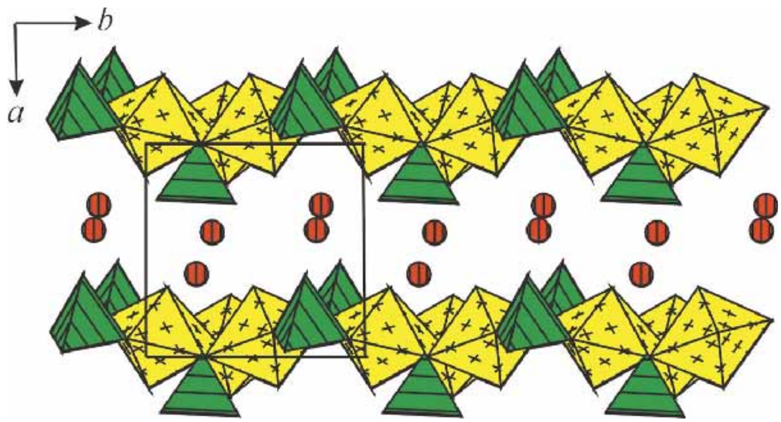

FIG. 2. The structure of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ projected approximately along the *c* axis. Legend: *Ur*O_5 polyhedra: yellow, MoO_n polyhedra: green, Cs cations: red.

other structure. The sheet anion-topology, obtained using the method of Burns *et al.* (1996), is novel (Fig. 1b). The sheets are connected through Cs cations located in the interlayer (Fig. 2).

RESULTS: $Cs_6[(UO_2)(MoO_4)_4]$

Cation polyhedra

The structure of $Cs_6[(UO_2)(MoO_4)_4]$ contains two symmetrically independent U^{6+} cations, each of which forms part of an approximately linear $(UO_2)^{2+}$ uranyl ion (*Ur*). In contrast to $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$, each uranyl ion in this structure is coordinated by four O atoms arranged at the equatorial vertices of *Ur*O_4 square bipyramids. The <U–O_{eq}> bond lengths are 2.29 and 2.27 Å for U(1) and U(2), respectively, in good agreement with the average value of 2.28(5) Å given for (*Ur*O_4) square bipyramids by Burns *et al*. (1997).

There are six symmetrically independent Mo^{6+} cations in the structure, each of which is tetrahedrally coordinated by four O atoms. The <Mo–O> bond lengths range from 1.75 to 1.77 Å (Table 5). Nine symmetrically non-equivalent Cs atoms in the structure are coordinated by eight to ten atoms of O.

Structural connectivity

The structure of $Cs_6[(UO_2)(MoO_4)_4]$ is based upon finite clusters of composition $[(UO_2)(MoO_4)_4]^{6-}$

(Fig. 3a) that involve a central UrO_4 square bipyramid that shares all four of its equatorial vertices with MoO_4 tetrahedra. This is the first documented occurrence of this finite cluster in a uranyl compound (Burns *et al.* 1996). The extended structure contains two symmetrically independent $[(UO_2)(MoO_4)_4]$ clusters. The cluster involving the U(1) cation (Fig. 3b) is non-centrosymmetric and is aligned parallel to (010) (Fig. 4), whereas the cluster containing the U(2) cation is centrosymmetric, and is oriented parallel to (001) (Fig. 4). There are twice as many clusters that contain U(1) as U(2).

The three-dimensional connectivity of the structure is provided by Cs cations located between the clusters (Fig. 4).

Discussion

Burns *et al.* (1996) developed a structural hierarchy of uranyl minerals and inorganic compounds that is based upon the polymerization of cation polyhedra of high bond-valence. The uranyl molybdate sheet in $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$, and the uranyl molyb-

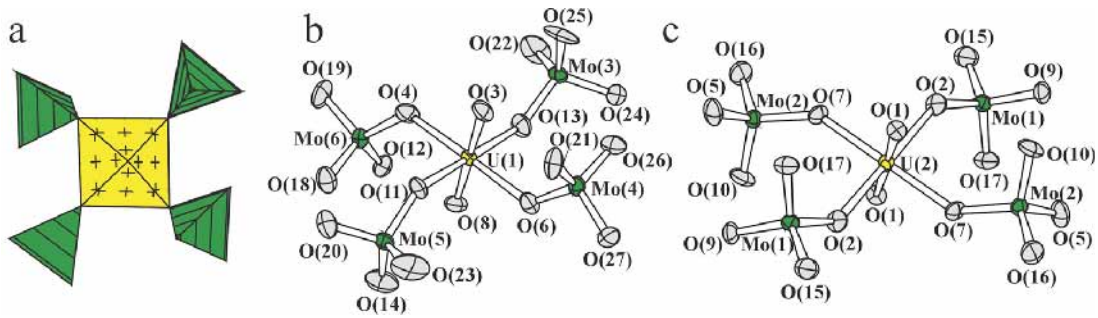

FIG. 3. The $[(UO_2)(MoO_4)_4]^{6-}$ finite cluster in $Cs_6[(UO_2)(MoO_4)_4]$ shown in polyhedral representation (a) and ball-and-stick representations of the two symmetrically independent clusters (b, c).

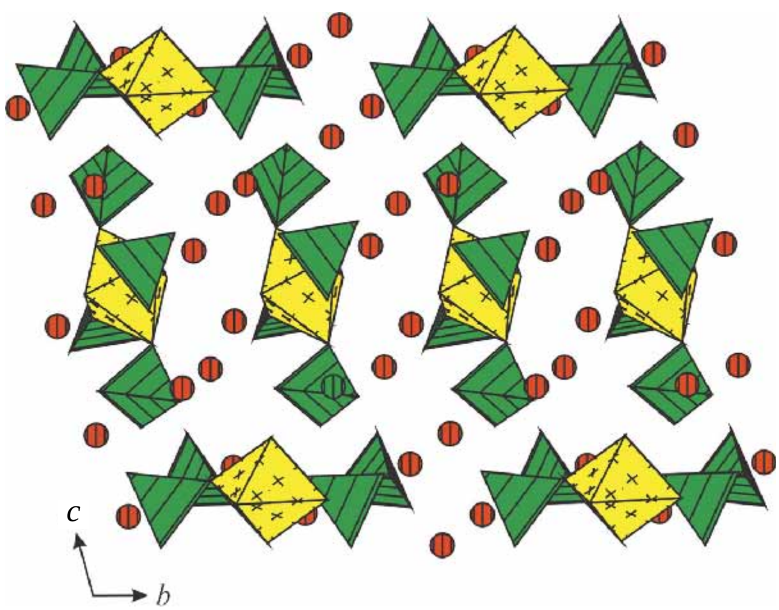

FIG. 4. The structure of $Cs_6[(UO_2)(MoO_4)_4]$ projected approximately along the *a* axis. The legend is as in Figure 2.

TABLE 7. BOND VALENCE ANALYSIS* (v.u.) FOR $Cs_6[(UO_2)(MoO_4)_4]$

	Cs(1)	Cs(2)	Cs(3)	Cs(4)	Cs(5)	Cs(6)	Cs(7)	Cs(8)	Cs(9)	U(1)	U(2)	Mo(1)	Mo(2)	Mo(3)	Mo(4)	Mo(5)	Mo(6)	Σ
O(1)					0.06	0.05					$1.53^{2\downarrow}$							1.64
O(2)	0.10				0.11						$0.70^{2\downarrow}$	1.20						2.11
O(3)			0.09, 0.05				0.12			1.64								1.90
O(4)			0.12				0.06			0.63							1.20	2.01
O(5)		0.14				0.06			0.19, 0.09				1.57					2.05
O(6)				0.11				0.04		0.63					1.30			2.08
O(7)	0.12					0.07					$0.70^{2\downarrow}$		1.29					2.18
O(8)				0.09, 0.06				0.06		1.70								1.91
O(9)		0.14			0.04				0.19, 0.12			1.52						2.01
O(10)				0.18	0.18				0.19				1.57					2.12
O(11)			0.12				0.07			0.75						1.20		2.14
O(12)				0.18	0.21			0.17									1.55	2.12
O(13)				0.13				0.07		0.69				1.30				2.19
O(14)		0.16		0.09				0.10								1.75		2.10
O(15)	0.20, 0.09	0.06	0.03									1.70						2.08
O(16)	0.07	0.18, 0.07		0.03									1.75					2.10
O(17)			0.20			0.23			0.16			1.57						2.16
O(18)						0.12	0.07	0.14									1.48	1.81
O(19)					0.06	0.25	0.14										1.52	1.97
O(20)	0.17					0.23	0.09									1.57		2.06
O(21)			0.17			0.14	0.08		0.03						1.62			2.04
O(22)	0.18	0.06		0.03										1.65				1.92
O(23)	0.04	0.17	0.04													1.52		1.77
O(24)		0.14			0.18			0.18						1.45				1.95
O(25)	0.15		0.07		0.03		0.16							1.57				1.98
O(26)					0.10		0.10	0.06							1.61			1.87
O(27)					0.09			0.12	0.19						1.44			1.84
Σ	1.12	1.12	0.89	0.90	1.06	1.15	0.89	0.94	1.16	6.04	5.86	5.99	6.18	5.97	5.97	6.04	5.75	

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

date cluster in $Cs_6[(UO_2)(MoO_4)_4]$ place these compounds in the sheet and finite-cluster classes, respectively. Neither of these specific structural units have been reported previously in uranyl compounds, and their discovery provides insight into the crystal chemistry of uranyl molybdates and uranyl compounds in general.

The structure of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ is remarkable in that it is the first uranyl molybdate to contain Mo^{6+} in both fourfold and fivefold coordination. The single symmetrically distinct Mo^{6+} cation in the structure of deloryite, $Cu_4[(UO_2)(MoO_4)_2](OH)_6$, is also in fivefold coordination, although the longest Mo–O bond (2.57 Å) is substantially longer than in $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ (Pushcharovsky *et al.* 1996).

The compound $Cs_6[(UO_2)(MoO_4)_4]$ is only the second uranyl molybdate structure that contains uranium in square bipyramidal coordination, the other being deloryite. The structure of deloryite involves uranyl square bipyramids linked through vertex sharing with MoO_5 polyhedra to form chains (Tali *et al.* 1993, Pushcharovsky *et al.* 1996).

Despite their similar formulae, $Cs_6[(UO_2)(MoO_4)_4]$ is not isostructural with $Na_6[(UO_2)(MoO_4)_4]$ (Krivovichev *et al*. 2002a). The structure of $Na_6[(UO_2)(MoO_4)_4]$ also contains finite clusters of uranyl and molybdate polyhedra, but each cluster involves two (UrO_5) uranyl pentagonal bipyramids that are linked by the sharing of vertices with two molybdate tetrahedra.

Among the structures of Cs uranyl molybdates, $Cs_6[(UO_2)(MoO_4)_4]$ is the first that contains finite uranyl molybdate clusters. The structures of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ (reported here), $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ (Rastsvetaeva *et al.* 1999) and β–$Cs_2[(UO_2)_2(MoO_4)_3]$ (Krivovichev *et al.* 2002b) are each based upon uranyl molybdate sheets, whereas those of $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ (Krivovichev & Burns 2001b) and α–$Cs_2[(UO_2)_2(MoO_4)_3]$ (Krivovichev *et al.* 2002b) contain frameworks of UrO_5 pentagonal bipyramids and MoO_4 tetrahedra.

The current study demonstrates that the exceptional structural diversity of uranyl molybdates is controlled not only by the combinatorics of polyhedron linkage but also by the diversity of coordination polyhedra of U^{6+} and Mo^{6+} cations.

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). Collaboration between PCB and SVK is supported by the NATO Science program (grant EST.CLG.977834). The manuscript was improved following reviews by Dr. Mickey Gunter and an anonymous referee, and editorial work by Dr. Robert Martin and Associate Editor Dr. John Hughes.

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