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CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. IV. THE STRUCTURES OF $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ (M = Cs, NH_4)

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ABSTRACT

Two new uranyl molybdate hydrates, $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ (M = Cs, NH_4), have been synthesized using hydrothermal methods. The crystals occur as transparent yellow needles and yellow elongate plates for M = Cs and NH_4, respectively. Their structures were solved by direct methods and refined on the basis of F^2 for all unique data collected with Mo$K\alpha$ X-radiation and a CCD (charge-coupled device) detector. Final $R1$ values are 4.1 and 3.9% for M = Cs and M = NH_4, respectively, calculated for 2178 and 2969 unique observed ($|F_o| \le 4\sigma_F$) reflections, respectively. The compound $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ is orthorhombic, space group *Pbcm*, *a* 13.990(2), *b* 10.808(1), *c* 25.671(3) Å, *V* 3881.6(9) Å^3, Z = 4. The compound $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ is isostructural with the Cs analogue, *a* 13.970(1), *b* 10.747(1), *c* 25.607(2) Å, *V* 3844.4(6) Å^3, Z = 4. The four symmetrically independent U^{6+} cations in $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ are part of approximately linear $(UO_2)^{2+}$ uranyl ions (*Ur*) that are further coordinated by five ligands at the equatorial positions of uranyl pentagonal bipyramids that are capped by O_{Ur} atoms. The four symmetrically identical Mo^{6+} cations are tetrahedrally coordinated by O atoms. The uranyl and molybdate polyhedra link by vertex sharing to form a framework, with the low-valence M cations located in voids within the framework.

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

SOMMAIRE

Nous avons synthétisé deux nouveaux molybdates uranylés hydratés, $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ (M = Cs, NH_4) par méthodes hydrothermales. Les cristaux se présentent en aiguilles jaunes transparentes (M = Cs) et en plaquettes allongées jaunes (M = NH_4). Nous avons aussi résolu leurs structures par méthodes directes et nous les avons affinées sur la base de facteurs F^2 calculés pour toutes les réflexions uniques, prélevées avec rayonnement Mo$K\alpha$ et un détecteur à couplage de charges (CCD). Les valeurs du résidu final $R1$ sont de 4.1 et 3.9% pour M = Cs et M = NH_4, respectivement; elles sont calculées en utilisant les 2178 et 2969 réflexions uniques observées ($|F_o| \le 4\sigma_F$), respectivement. Le composé $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ est orthorhombique, groupe spatial *Pbcm*, *a* 13.990(2), *b* 10.808(1), *c* 25.671(3) Å, *V* 3881.6(9) Å^3, Z = 4. Le composé $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ est isostructural avec ce dernier, *a* 13.970(1), *b* 10.747(1), *c* 25.607(2) Å, *V* 3844.4(6) Å^3, Z = 4. Les quatre cations U^{6+} symétriquement indépendants dans $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ font partie d'ions d'uranyle $(UO_2)^{2+}$ presque linéaires; ils ont de plus cinq ligands disposés de façon équatoriale pour former des bipyramides pentagonales à uranyle (*Ur*) ayant les atomes O_{Ur} à leurs sommets. Les quatres cations Mo^{6+}, symétriquement identiques, ont une coordinence tétraédrique avec des atomes d'oxygène. Les polyèdres à uranyle et à molybdate sont interliés par partage d'arêtes pour former une trame, les cations M à valence faible occupant des trous au sein de cette trame.

(Traduit par la Rédaction)

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

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Introduction

Uranyl molybdates are common constituents of U–Mo deposits (Finch & Murakami 1999), and as such are important for understanding the genesis of U deposits. Recent studies have shown that uranyl molybdates also form from the corrosion of spent nuclear fuel under conditions similar to those expected in the proposed geological repository at Yucca Mountain (Buck *et al.* 1997, Finch *et al.* 1999). These compounds thus may be important radionuclide-bearing phases during evolution of the repository. Inspired by the significance of uranyl molybdates, we have undertaken a detailed study of their crystal chemistry. The first three papers of the series present a redetermination of the structure of umohoite (Krivovichev & Burns 2000a), a refinement of the structure of iriginite (Krivovichev & Burns 2000b), and the synthesis and structure determinations for $Na_6[(UO_2)_2O(MoO_4)_4]$, $Na_6[(UO_2)(MoO_4)_4]$ and $K_6[(UO_2)_2O(MoO_4)_4]$ (Krivovichev & Burns 2001). In the current contribution, we report the synthesis and structures of the isostructural compounds $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ and $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$.

Cs and Mo are both fission products of uranium where nuclear fuel is burned in a reactor, and spent nuclear fuel contains radioactive ^{137}Cs, ^{135}Cs and ^{93}Mo. 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 product on spent fuel exposed to a moist, oxidizing environment at 90°C (Buck *et al.* 1997). This occurrence demonstrates the potential importance of uranyl phases in determining the mobility of radionuclides under conditions in a geological repository, as uranyl phases may incorporate a variety of fission products and transuranic elements into their structures (Burns *et al.* 1997a, Chen *et al.* 1999, 2000). Uranyl phases are likely also to be important in determining the mobility of radionuclides in low-temperature aqueous environments, such as in the vadose zone of the Hanford site in Washington, and in and about the 4th block of the Chernobyl nuclear power plant.

Experimental

The crystals used in the current study were synthesized by hydrothermal methods. Crystals of the compound $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ were grown from a solution of CsCl, MoO_3 and $UO_2(CH_3COO)_2\bullet 2H_2O$ (0.0816, 0.0864 and 0.1176 g, respectively) in 5 mL of water. The solution was placed in a Teflon-lined Parr bomb and heated to 230°C for 10 days, followed by cooling to ambient temperature. The crystals occur as aggregates of transparent yellow needles up to 0.02 mm across and 0.5 mm in maximum length.

The compound $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ was obtained from a solution of $(NH_4)_6Mo_7O_{24}$ and $UO_2(CH_3COO)_2\bullet 2H_2O$ (0.0388 and 0.0392 g, respectively) in 5 mL of water. The solution was placed in a Teflon-lined Parr bomb and heated to 180°C for 5 days, followed by cooling to ambient temperature. Transparent yellow plates resulted, up to 0.1 and 0.5 mm in maximum thickness and diameter, respectively.

One crystal of each compound was selected for data collection. The crystals 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 Mo$K\alpha$ X-radiation and frame widths of 0.3° in ω, with 10 s spent counting per frame. The unit-cell dimensions (Table 1) were refined from 1686 and 4136 reflections for M = Cs and M = NH_4, respectively, using least-squares techniques. A comparison of unit-cell parameters indicated that these phases are probably isostructural. More than a hemisphere of data was collected for each crystal, and the three-dimensional data were reduced and filtered for statistical outliers using the Bruker program SAINT. Data were corrected for Lorentz, polarization, and background effects. Semi-empirical corrections for adsorption were done for each crystal using intense reflections, with the crystals modeled as plates; reflections with plate-glancing angles less than 3° were discarded, which lowered R_{int} from 7.4 to 3.7% for $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ and from 14.7 to 6.8% for $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$. Additional information pertinent to the data collections is given in Table 1.

Structure Solutions and Refinement

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. Reflection statistics for each crystal indicated space group *Pbcm*. Both structures were solved by direct methods, which

TABLE 1. CRYSTALLOGRAPHIC DATA FOR $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ (M = Cs, NH_4)

	M = Cs	M = NH_4
a (Å)	13.990(2)	13.970(1)
b (Å)	10.808(1)	10.747(1)
c (Å)	25.671(3)	25.607(2)
V (Å^3)	3881.6(9)	3844.4(6)
Z	4	4
Space group	*Pbcm*	*Pbcm*
F_{000}	5184	4832
μ (mm^{-1})	29.07	27.49
D_{calc} (g/cm^3)	5.205	4.858
Crystal size (mm)	0.38 x 0.04 x 0.01	0.38 x 0.06 x 0.03
Total Ref.	21,916	21,266
Unique Ref.	4828	4768
Unique $\lvert F_o\rvert \geq 4\sigma_F$	2178	2969
$R1$ (%)	4.1	3.9
S	0.711	0.896

$R1 = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$

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

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

gave the positions of the U, Mo and Cs atoms. Anion positions were located on difference-Fourier maps calculated after refinement of the models using least-squares techniques. Both structures were refined on the basis of F^2 for all unique data. The final models included anisotropic-displacement parameters for U, Mo and Cs, isotropic-displacement parameters for the other atoms, and weighting schemes (Table 1) of the structure factors. Final agreement factors ($R1$) were 4.1% and 3.9%, calculated for observed reflections ($F_o > 4\sigma_F$) for $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ and $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$, respectively. The final atomic positional and displacement parameters for the structures are presented in Tables 2 to 5, selected interatomic distances are in Tables 6 and 7, and a bond-valence analysis for $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ is in Table 8. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

The structure determinations demonstrate that $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ and $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ are isostructural. Projection of the structure of $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ along [010] (Fig. 1a) reveals a framework of vertex-sharing uranyl and molybdate polyhedra, with Cs cations located in voids within the framework. The structure of $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ has the same framework, but NH_4 replaces the Cs cations in the voids within the framework.

TABLE 2. ATOMIC PARAMETERS FOR $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$

	x	y	z	U_{eq}
Cs(1)	-0.3817(1)	-¼	½	0.0224(4)
Cs(2)*	0.1447(2)	-0.2682(2)	0.1850(1)	0.064(1)
U(1)	0.13221(7)	0.09692(8)	¼	0.0165(2)
U(2)	-0.36884(5)	-0.57221(6)	0.41534(2)	0.0115(2)
U(3)	-0.13429(5)	-0.06128(5)	0.42750(2)	0.0137(2)
U(4)	-0.39274(7)	-0.98710(7)	¼	0.0147(2)
Mo(1)	-0.1712(1)	¼	½	0.0147(5)
Mo(2)	-0.39019(9)	-0.9156(1)	0.40159(5)	0.0120(3)
Mo(3)	-0.3347(1)	-0.2612(1)	0.34624(5)	0.0123(3)
Mo(4)	0.10653(9)	0.0810(1)	0.40084(5)	0.0147(3)
O(1)	-0.271(1)	-0.001(1)	¼	0.023(4)
O(2)	-0.4281(7)	-0.7723(8)	0.4305(3)	0.011(2)
O(3)	-0.1153(7)	-0.0157(8)	0.3620(3)	0.017(2)
O(4)	-0.3882(8)	-0.5203(8)	0.4806(3)	0.019(2)
O(5)	-0.1612(7)	-0.1115(9)	0.4922(3)	0.023(3)
O(6)	-0.517(1)	-0.970(1)	¼	0.027(4)
O(7)	-0.3466(7)	-0.6245(9)	0.3501(3)	0.019(3)
O(8)	-0.2743(7)	-0.9445(9)	0.4259(3)	0.017(3)
O(9)	-0.1031(8)	0.1395(8)	0.4667(3)	0.017(2)
O(10)	-0.4037(8)	-0.1573(9)	0.3090(3)	0.020(3)
O(11)	0.2293(7)	0.0512(8)	0.4084(4)	0.020(3)
O(12)	-0.3775(7)	-0.8988(8)	0.3336(3)	0.018(2)
O(13)	0.0777(7)	0.2384(9)	0.4127(4)	0.021(3)
O(14)	-0.2695(7)	-0.1788(9)	0.3940(4)	0.020(3)
O(15)	-0.2549(8)	-0.3328(9)	0.3043(4)	0.021(3)
O(16)	-0.4610(6)	-0.0474(8)	0.4138(3)	0.012(2)
O(17)	-0.4084(7)	-0.3714(9)	0.3778(3)	0.017(2)
O(18)	-0.2420(8)	0.180(1)	0.5488(4)	0.025(3)
H_2O(19)	-0.036(1)	0.008(2)	¼	0.036(5)
O(20)	0.0332(6)	-0.0271(8)	0.4343(3)	0.010(2)
H_2O(21)	-0.369(1)	-0.754(1)	¼	0.028(4)
O(22)	0.0805(8)	0.0588(9)	0.3344(4)	0.031(3)
O(23)	0.075(1)	0.242(1)	¼	0.036(4)
O(24)	0.185(1)	-0.052(1)	¼	0.025(4)

*s.o.f. = 0.5

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS FOR $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs(1)	0.034(1)	0.0158(8)	0.0178(8)	-0.0020(6)	0	0
Cs(2)	0.066(2)	0.034(2)	0.091(2)	-0.033(1)	0.018(2)	-0.017(2)
U(1)	0.0204(5)	0.0180(5)	0.0112(4)	0	0	-0.0046(5)
U(2)	0.0122(3)	0.0095(3)	0.0129(3)	-0.0001(2)	-0.0012(3)	0.0004(3)
U(3)	0.0137(4)	0.0128(3)	0.0144(3)	0.0009(3)	0.0005(3)	-0.0006(3)
U(4)	0.0211(5)	0.0128(5)	0.0103(4)	0	0	0.0004(4)
Mo(1)	0.011(1)	0.014(1)	0.019(1)	0.0018(9)	0	0
Mo(2)	0.0147(8)	0.0102(7)	0.0110(6)	-0.0010(5)	0.0008(6)	-0.0018(7)
Mo(3)	0.0146(8)	0.0117(8)	0.0105(7)	0.0006(6)	0.0010(6)	0.0001(7)
Mo(4)	0.0137(8)	0.0147(8)	0.0156(7)	0.0006(6)	0.0026(6)	-0.0018(7)

TABLE 4. ATOMIC PARAMETERS FOR $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$

Atom	x	y	z	U_{eq}
NH_4(1)	-0.395(1)	-¼	½	0.042(4)
NH_4(2)*	-0.152(2)	-0.778(2)	0.3031(8)	0.045(5)
U(1)	0.13485(5)	0.09365(6)	¼	0.0204(2)
U(2)	-0.36907(3)	-0.56850(4)	0.41631(2)	0.0147(1)
U(3)	-0.13501(3)	-0.05950(4)	0.42683(2)	0.0167(1)
U(4)	-0.39610(5)	-0.98456(6)	¼	0.0174(2)
Mo(1)	-0.1714(1)	¼	½	0.0169(3)
Mo(2)	-0.39167(8)	-0.91311(8)	0.40233(4)	0.0152(2)
Mo(3)	-0.33638(8)	-0.25915(9)	0.34638(4)	0.0156(2)
Mo(4)	0.10636(8)	0.08069(9)	0.40006(4)	0.0180(2)
O(1)	-0.2701(9)	-0.002(1)	¼	0.026(3)
O(2)	-0.4305(6)	-0.7729(7)	0.4328(3)	0.018(2)
O(3)	-0.1147(6)	-0.0092(7)	0.3617(3)	0.027(2)
O(4)	-0.3875(6)	-0.5088(7)	0.4796(3)	0.024(2)
O(5)	-0.1607(6)	-0.1095(7)	0.4913(3)	0.026(2)
O(6)	-0.5234(8)	-0.970(1)	¼	0.021(3)
O(7)	-0.3469(6)	-0.6274(7)	0.3527(3)	0.023(2)
O(8)	-0.2746(6)	-0.9381(7)	0.4250(3)	0.024(2)
O(9)	-0.1020(6)	0.1386(7)	0.4657(3)	0.021(2)
O(10)	-0.4055(6)	-0.1549(7)	0.3082(3)	0.028(2)
O(11)	0.2310(6)	0.0522(7)	0.4075(3)	0.026(2)
O(12)	-0.3815(6)	-0.8961(8)	0.3348(3)	0.028(2)
O(13)	0.0784(7)	0.2388(8)	0.4112(3)	0.032(2)
O(14)	-0.2714(6)	-0.1762(7)	0.3942(3)	0.021(2)
O(15)	-0.2546(6)	-0.3295(8)	0.3041(3)	0.031(2)
O(16)	-0.4624(6)	-0.0465(6)	0.4148(3)	0.016(2)
O(17)	-0.4096(6)	-0.3715(7)	0.3784(3)	0.023(2)
O(18)	-0.2437(6)	0.1767(8)	0.5474(4)	0.030(2)
H_2O(19)	-0.030(1)	-0.002(1)	¼	0.042(4)
O(20)	0.0339(6)	-0.0267(7)	0.4336(3)	0.019(2)
H_2O(21)	-0.3751(9)	-0.750(1)	¼	0.028(3)
O(22)	0.0805(7)	0.0531(8)	0.3344(4)	0.041(3)
O(23)	0.078(1)	0.241(1)	¼	0.044(4)
O(24)	0.190(1)	-0.055(1)	¼	0.038(3)

* s.o.f. = 0.5

Cation polyhedra

There are four symmetrically distinct U sites in each of the structures of $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ (M = Cs, NH_4); they are occupied by U^{6+} cations, each of which forms part of approximately linear $(UO_2)^{2+}$ uranyl ions

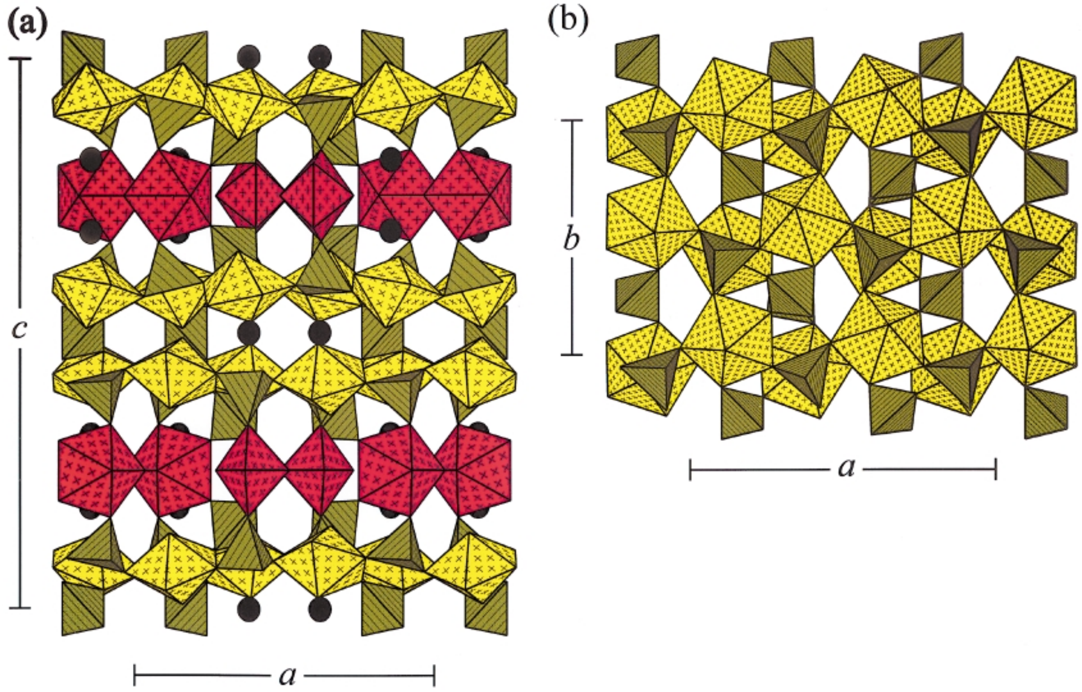

FIG. 1. Polyhedral representations of the structure of $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ (a) projected along [010]. (b) The complex sheet of uranyl and molybdate polyhedra projected along [001]. Uranyl and molybdate polyhedra are shaded with crosses and parallel lines, respectively. The $Ur(2)\phi_5$ and $Ur(3)\phi_5$ polyhedra are shown in yellow, the $Ur(1)\phi_5$ and $Ur(4)\phi_5$ polyhedra are shown in red, molybdate polyhedra are shown in green, and Cs cations are represented by black circles.

(designated *Ur*), as is almost invariably observed for uranyl compounds (Burns *et al.* 1997b). Each uranyl ion is coordinated by five additional ligands arranged at the equatorial corners of pentagonal bipyramids that are capped by O_{Ur} atoms. The equatorial ligands in the $Ur(2)\phi_5$ and $Ur(3)\phi_5$ polyhedra (ϕ: unspecified ligand) are all O atoms, whereas in the $Ur(1)\phi_5$ and $Ur(4)\phi_5$ pentagonal bipyramids, the equatorial ligands correspond to four O atoms and one H_2O group. The $\langle U–\phi_{eq}\rangle$ (eq: equatorial) bond-lengths (Tables 6, 7) range from 2.35 to 2.41 Å in the $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ structures, in good agreement with the $\langle {}^{[7]}U^{6+}–\phi_{eq}\rangle$ bond-length of 2.37(9) Å obtained from numerous well-refined structures (Burns *et al.* 1997b).

There are four symmetrically distinct Mo^{6+} cations in each of the structures of $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$; all are tetrahedrally coordinated by O atoms, with $\langle Mo–O\rangle$ bond-lengths ranging from 1.76 to 1.78 Å (Tables 6, 7).

Each of the structures of $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ contain two symmetrically distinct *M* cations. The *M*(1) sites are fully occupied. The occupancy of the *M*(2) sites is 0.5, and separations of symmetrically related *M*(2) sites are 3.31(1) and 2.72(4) Å for *M* = Cs and NH_4, respectively. This is in accord with the partial occupancies observed for the *M*(2) sites, as only one of each pair of symmetrically related *M*(2) sites may be occupied locally. The coordination polyhedra of *M*(1) and *M*(2) are listed in Tables 6 and 7.

Structural formula

Consideration of the bond-valence sums incident upon O atom positions (Table 8) indicates that each structure contains two symmetrically distinct H_2O

TABLE 5. ANISOTROPIC DISPLACEMENT PARAMETERS FOR $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.0247(4)	0.0179(3)	0.0184(3)	0	0	-0.0057(3)
U(2)	0.0155(2)	0.0114(2)	0.0171(2)	0.0000(2)	-0.0013(2)	0.0004(2)
U(3)	0.0169(2)	0.0135(2)	0.0195(2)	0.0019(2)	0.0002(2)	-0.0014(2)
U(4)	0.0229(4)	0.0143(3)	0.0149(3)	0	0	0.0010(3)
Mo(1)	0.0138(8)	0.0126(7)	0.0244(8)	0.0025(6)	0	0
Mo(2)	0.0178(6)	0.0121(5)	0.0157(5)	-0.0011(4)	0.0019(5)	-0.0021(4)
Mo(3)	0.0181(6)	0.0122(5)	0.0167(5)	0.0011(4)	0.0019(4)	0.0004(4)
Mo(4)	0.0161(6)	0.0163(5)	0.0214(5)	0.0028(4)	0.0018(5)	-0.0020(4)

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$

U(1)-O(23)	1.75(2)	Mo(2)-O(12)	1.763(8)
U(1)-O(24)	1.77(1)	Mo(2)-O(16)h	1.763(9)
U(1)-O(22),a	2.32(1) 2x	Mo(2)-O(8)	1.76(1)
U(1)-O(15)b, c	2.34(1) 2x	Mo(2)-O(2)	1.798(9)
U(1)-H_2O(19)	2.54(2)	<Mo(2)-O>	1.77
<U(1)-O_{Ur}>	1.76		
<U(1)-ϕ_{eq}>	2.37	Mo(3)-O(15)	1.73(1)
		Mo(3)-O(10)	1.76(1)
U(2)-O(4)	1.788(8)	Mo(3)-O(14)	1.77(1)
U(2)-O(7)	1.794(9)	Mo(3)-O(17)	1.771(9)
U(2)-O(18)d	2.31(1)	<Mo(3)-O>	1.76
U(2)-O(2)	2.348(9)		
U(2)-O(11)e	2.37(1)	Mo(4)-O(11)	1.76(1)
U(2)-O(16)f	2.396(9)	Mo(4)-O(22)	1.76(1)
U(2)-O(17)	2.438(9)	Mo(4)-O(20)	1.777(9)
<U(2)-O_{Ur}>	1.79	Mo(4)-O(13)	1.77(1)
<U(2)-ϕ_{eq}>	2.37	<Mo(4)-O>	1.77
U(3)-O(3)	1.772(8)	Cs(1)-O(4),d	2.965(9) 2x
U(3)-O(5)	1.788(9)	Cs(1)-O(2)k,l	3.212(9) 2x
U(3)-O(8)g	2.33(1)	Cs(1)-O(14),d	3.233(9) 2x
U(3)-O(13)e	2.34(1)	Cs(1)-O(16),d	3.304(9) 2x
U(3)-O(20)	2.379(9)	Cs(1)-O(17),d	3.421(9) 2x
U(3)-O(9)	2.432(9)	Cs(1)-O(5),d	3.43(1) 2x
U(3)-O(14)	2.44(1)	<Cs(1)-O>	3.26
<U(3)-O_{Ur}>	1.78		
<U(3)-ϕ_{eq}>	2.38	Cs(2)-O(24)m	2.93(1)
		Cs(2)-O(3)h	2.964(9)
U(4)-O(1)h	1.71(1)	Cs(2)-O(19)h	3.31(1)
U(4)-O(6)	1.75(1)	Cs(2)-O(7)	3.35(1)
U(4)-O(12),a	2.359(8) 2x	Cs(2)-O(1)h	3.49(1)
U(4)-O(10)h,i	2.388(9) 2x	Cs(2)-O(23)h	3.50(1)
U(4)-H_2O(21)	2.54(1)	Cs(2)-O(21)	3.56(1)
<U(4)-O_{Ur}>	1.73	Cs(2)-O(12)	3.58(1)
<U(4)-ϕ_{eq}>	2.41	Cs(2)-O(22)e	3.68(1)
		Cs(2)-O(22)h	3.70(1)
Mo(1)-O(9),j	1.751(9) 2x	<Cs(2)-O>	3.41
Mo(1)-O(18),j	1.77(1) 2x		
<Mo(1)-O>	1.76		

a : $x, y, -z + 1/2$; b : $-x, y + 1/2, z$; c : $-x, y + 1/2, -z + 1/2$; d : $x, -y -1/2, -z + 1$; e : $-x, y - 1/2, z$; f : $-x - 1, y - 1/2, z$; g : $x, y + 1, z$; h : $x, y - 1, z$; i : $x, y - 1, -z + 1/2$; j : $x, -y + 1/2, -z + 1$; k : $-x - 1, y + 1/2, z$; l : $-x - 1, -y - 1, -z + 1$; m : $-x, y - 1/2, -z + ½$

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$

U(1)-O(23)	1.77(1)	Mo(2)-O(12)	1.745(8)
U(1)-O(24)	1.77(1)	Mo(2)-O(8)	1.756(9)
U(1)-O(15)b, c	2.324(9) 2x	Mo(2)-O(16)h	1.770(7)
U(1)-O(22),a	2.33(1) 2x	Mo(2)-O(2)	1.781(7)
U(1)-H_2O(19)	2.52(1)	<Mo(2)-O>	1.76
<U(1)-O_{Ur}>	1.77		
<U(1)-ϕ_{eq}>	2.37	Mo(3)-O(15)	1.746(9)
		Mo(3)-O(14)	1.766(8)
U(2)-O(4)	1.762(8)	Mo(3)-O(10)	1.773(8)
U(2)-O(7)	1.775(8)	Mo(3)-O(17)	1.782(8)
U(2)-O(18)d	2.299(9)	<Mo(3)-O>	1.77
U(2)-O(11)e	2.335(8)		
U(2)-O(2)	2.396(7)	Mo(4)-O(22)	1.745(9)
U(2)-O(16)f	2.367(8)	Mo(4)-O(20)	1.759(8)
U(2)-O(17)	2.397(8)	Mo(4)-O(13)	1.767(9)
<U(2)-O_{Ur}>	1.77	Mo(4)-O(11)	1.778(9)
<U(2)-ϕ_{eq}>	2.36	<Mo(4)-O>	1.76
U(3)-O(3)	1.776(8)	NH_4(1)-O(4),d	2.832(8) 2x
U(3)-O(5)	1.773(8)	NH_4(1)-O(2)k,l	2.99(2) 2x
U(3)-O(8)g	2.347(8)	NH_4(1)-O(16),d	3.229(9) 2x
U(3)-O(13)e	2.342(9)	NH_4(1)-O(14),d	3.31(1) 2x
U(3)-O(20)	2.392(8)	NH_4(1)-O(17),d	3.383(8) 2x
U(3)-O(9)	2.395(7)	< NH_4(1)-O>	3.15
U(3)-O(14)	2.429(8)		
<U(3)-O_{Ur}>	1.77	NH_4(2)-O(24)m	2.81(2)
<U(3)-ϕ_{eq}>	2.38	NH_4(2)-O(3)h	2.95(2)
		NH_4(2)-O(19)h	3.25(2)
U(4)-O(1)h	1.77(1)	NH_4(2)-O(1)h	3.22(2)
U(4)-O(6)	1.79(2)	NH_4(2)-O(7)c	3.41(2)
U(4)-O(10)h,i	2.364(8) 2x	NH_4(2)-O(21)	3.41(2)
U(4)-O(12),a	2.379(8) 2x	NH_4(2)-O(23)h	3.49(2)
U(4)-H_2O(21)	2.54(1)	NH_4(2)-O(12)	3.54(2)
<U(4)-O_{Ur}>	1.78	< NH_4(2)-O>	3.26
<U(4)-ϕ_{eq}>	2.41		
Mo(1)-O(9),j	1.773(8) 2x		
Mo(1)-O(18),j	1.765(9) 2x		
<Mo(1)-O>	1.77		

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

groups. The bond-valence sums confirm the valence of 6+ for all U and Mo cations. The structural formula for the two isostructural compounds is therefore $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$, with the constituents of the framework enclosed in square braces.

Description of the structure

The structures of $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ possess a framework of vertex-sharing uranyl pentagonal bipyramids and molybdate tetrahedra (Fig. 1). The connectivity of the framework results from the distribution of bond-valences in uranyl pentagonal bipyramids. The O_{Ur} atoms receive ~1.7 *vu* from the $U^{6+}–O_{Ur}$ bond, whereas the equatorial ligands only receive ~0.5 *vu* from the bond to the U^{6+} cation at the center of the polyhedron. Where the equatorial ligands correspond to O atoms, an additional ~1.5 *vu* is required to satisfy their bonding requirements. Each vertex in a molybdate tetrahedron receives ~1.5 *vu* from the bond to the Mo^{6+} cation, thus the sharing of an equatorial O atom of a uranyl pentagonal bipyramid with a molybdate tetrahedron results in ~2.0 *vu* incident upon the O atom, which satisfies its bonding requirements. In the case where an equatorial ligand of a uranyl pentagonal bipyramid is an H_2O group, additional bonding is not required, and it is not possible for this ligand to be shared with a molybdate tetrahedron. Owing to the strength of the bonds within the uranyl ion, it is also not possible for O_{Ur} atoms to bond to Mo^{6+} cations; O_{Ur} atoms may only form weak bonds to low-valence cations.

Each of the molybdate tetrahedra in the structures of $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ share all ligands with uranyl pentagonal bipyramids. The $Ur(2)\phi_5$ and $Ur(3)\phi_5$ uranyl pentagonal bipyramids, in which all equatorial ligands correspond to O atoms, are shown in yellow in Figure 1a. Each of the equatorial O atoms of these pentagonal bipyramids is shared with molybdate tetrahedra, and in each polyhedron the uranyl ion is oriented subparallel to [001]. The $Ur(1)\phi_5$ and $Ur(4)\phi_5$ uranyl pentagonal bipyramids each contain a single H_2O group; these polyhedra are shown in red in Figure 1a. Only the four O atoms that are equatorial ligands in these uranyl polyhedra are shared with molybdate tetrahedra; the

TABLE 8. BOND-VALENCE* ANALYSIS (*vu*) FOR $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$

	U(1)	U(2)	U(3)	U(4)	Mo(1)	Mo(2)	Mo(3)	Mo(4)	Cs(1)	Cs(2)	Σ
O(1)				1.93						0.06	1.99
O(2)		0.55				1.34			$0.12^{x2\downarrow}$		2.01
O(3)			1.71							0.23	1.94
O(4)		1.66							$0.23^{x2\downarrow}$		1.89
O(5)			1.66						$0.07^{x2\downarrow}$		1.72
O(6)				1.78							1.78
O(7)		1.64								0.08	1.72
O(8)			0.57			1.49					2.06
O(9)			0.47		$1.52^{x2\downarrow}$						1.99
O(10)				$0.51^{x2\downarrow}$			1.49				2.00
O(11)		0.53						1.49			2.02
O(12)				$0.54^{x2\downarrow}$		1.48				0.04	2.06
O(13)			0.56					1.45			2.01
O(14)			0.46				1.45		$0.11^{x2\downarrow}$		2.02
O(15)	$0.56^{x2\downarrow}$						1.61				2.17
O(16)		0.50				1.48			$0.09^{x2\downarrow}$		2.07
O(17)		0.46					1.45		$0.07^{x2\downarrow}$		1.98
O(18)		0.59			$1.45^{x2\downarrow}$						2.04
$H_2O(19)$	0.38									0.09	0.47
O(20)			0.52					1.42			1.94
$H_2O(21)$				0.37						0.05	0.42
O(22)	$0.58^{x2\downarrow}$							1.49		$0.03^{x2\downarrow}$	2.10
O(23)	1.75									0.05	1.80
O(24)	1.71									0.25	1.96
Σ	6.14	5.93	5.95	6.18	5.94	5.79	6.00	5.85	1.38	0.91	

* bond-valence parameters for U^{6+} from Burns *et al.* (1997b), for Cs and Mo from Brese & O'Keeffe (1991).

remaining ligands correspond to the H_2O groups, which are weakly bonded to *M* cations. In the $Ur(1)\phi_5$ and $Ur(4)\phi_5$ polyhedra, the uranyl ions are oriented subperpendicular to [001].

The structures of $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ may be conveniently described with reference to complex sheets of uranyl and molybdate polyhedra that are parallel to (001). These sheets contain all of the molybdate tetrahedra, as well as the $Ur(2)\phi_5$ and $Ur(3)\phi_5$ pentagonal bipyramids (Fig. 1a). The sheet is shown projected along [001] in Figure 1b. Note that each uranyl pentagonal bipyramid shares vertices with five molybdate tetrahedra, but polymerization does not involve the sharing of polyhedron edges, nor does it involve the direct sharing of polyhedron elements between uranyl polyhedra. Those vertices of molybdate tetrahedra that are not shared within the sheets are shared with $Ur(1)\phi_5$ or $Ur(4)\phi_5$ pentagonal bipyramids that occur between the sheets (Fig. 1a), resulting in the framework structure.

The structures of $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ contain *M* cations that are located within voids in the framework. It is notable that there are no channels in the framework; thus the *M* cations are not likely to be susceptible to rapid exchange of ions where the crystals are in contact with a fluid phase. *M*(1) occurs within the complex sheets that contain the molybdate tetrahedra and $Ur(2)\phi_5$ and $Ur(3)\phi_5$ polyhedra, whereas *M*(2) is located between the sheets, and is coordinated by anions of the $Ur(1)\phi_5$ and $Ur(4)\phi_5$ polyhedra (Fig. 1a).

Discussion

Burns *et al.* (1996) proposed a structural hierarchy for uranyl phases based upon the connectivity between those cation polyhedra of higher bond-valence. The structures were grouped into those containing isolated clusters, infinite chains, infinite sheets, and frameworks of polyhedra. Owing to the uneven distribution of bond-valences in uranyl polyhedra, sharing of edges and vertices between uranyl polyhedra and other cation polyhedra of higher valence occurs only through the equatorial polyhedron elements, favoring the formation of sheets of polyhedra. In the case of uranyl minerals, approximately 80% of known structures are based upon sheets of cation polyhedra of higher bond-valence.

It is interesting to note that uranyl molybdates crystallize in each of the four main structure-types. Isolated clusters occur in $Na_6[(UO_2)(MoO_4)_4]$ (Krivovichev & Burns 2001). Infinite chains occur in $Na_6[(UO_2)_2O(MoO_4)_4]$ and $K_6[(UO_2)_2O(MoO_4)_4]$ (Krivovichev & Burns 2001), as well as in $Cu_4[(UO_2)(MoO_4)_2](OH)_6$ (Tali *et al.* 1993) and deloryite (Pushcharovsky *et al.* 1996). Sheets of uranyl and molybdate polyhedra are found in the structures of umohoite (Krivovichev & Burns 2000a), iriginite (Krivovichev & Burns 2000b), $[Ca(UO_2)MoO_4O_{14}]$ (Lee & Jaulmes 1987), $K_2[(UO_2)(MoO_4)]$ (Sadikov *et al.* 1988) and $Cs_2(UO_2)(MoO_4)_2(H_2O)$ (Rastsvetaeva *et al.* 1999). Frameworks occur in several uranyl molybdates, including $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ (this work), $(UO_2)(MoO_4)$ (Serezhkin *et al.* 1980a), $(UO_2)(MoO_4)(H_2O)_2$ (Serezhkin *et al.* 1980b), $M(UO_2)_3(MoO_4)_4(H_2O)_8$ (M = Mg, Zn; Tabachenko *et al.* 1983), $Mg(UO_2)_3(MoO_4)_4(H_2O)_{18}$ and $Sr(UO_2)_3(MoO_4)_4(H_2O)_{15}$ (Tabachenko *et al.* 1984a), $Ba(UO_2)_3(MoO_4)_4(H_2O)_4$ (Tabachenko *et al.* 1984b), $(UO_2)_3(MoO_4)_2(OH)_2(H_2O)_{10}$ and $(UO_2)_4(MoO_4)_3(OH)_2(H_2O)_4$ (Tali *et al.* 1994).

The structural diversity in uranyl molybdates arises in part because Mo^{6+} occurs in two coordination polyhedra: a tetrahedron and a distorted octahedron. The bond-valences associated with the individual $Mo^{6+}–\phi$ bonds in these polyhedra are rather different, ~1.5 *vu* in the case of the tetrahedron, but ~1.0 *vu* for the octahedron. This is significant because an O atom that is part of a $Mo^{6+}\phi_6$ octahedron may be shared with two uranyl polyhedra, thus permitting the formation of relatively dense sheets (*e.g.,* the umohoite- and iriginite-type sheets). Conversely, the O atom of a $Mo^{6+}O_4$ tetrahedron can be shared with only a single uranyl polyhedron. As such, molybdate tetrahedra are not compatible with dense sheets, but rather tend to occur in open frameworks, isolated clusters, chains or open sheets.

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