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CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. XI. CRYSTAL STRUCTURES OF $Cs_2[(UO_2)(MoO_4)_2]$ AND $Cs_2[(UO_2)(MoO_4)_2](H_2O)$

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ABSTRACT

Crystals of $Cs_2[(UO_2)(MoO_4)_2]$ have been synthesized by high-temperature solid-state reactions. The structure [orthorhombic, *Pbca*, *a* 11.762(2), *b* 14.081(2), *c* 14.323(2) Å, *V* 2372.3(6), *Z* = 8] was solved by direct methods and refined to *R*1 = 0.034 (*wR*2 = 0.044), calculated for 2577 unique observed reflections ($|F_o| \geq 4\sigma_F$). Crystals of $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ were prepared by hydrothermal reaction. The structure [monoclinic, $P2_1/c$, *a* 8.2222(9), *b* 11.0993(10), *c* 13.9992(13) Å, β 95.155(8)°, *V* 1272.4(2) Å^3, *Z* = 4] was refined to *R*1 = 0.048 (*wR*2 = 0.099), calculated for 2487 unique observed reflections ($|F_o| \geq 4\sigma_F$). The space group is $P2_1/c$, in contrast to $P112_1$ reported for this compound by Rastsvetaeva *et al*. (1999). The structures of $Cs_2[(UO_2)(MoO_4)_2]$ and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ both contain topologically identical sheets of corner-sharing UrO_5 pentagonal bipyramids and MoO_4 tetrahedra with composition $[(UO_2)(MoO_4)_2]^{2-}$. The $[(UO_2)(MoO_4)_2]^{2-}$ sheets are oriented parallel to (001) in $Cs_2[(UO_2)(MoO_4)_2]$, and to (100) in $Cs_2[(UO_2)(MoO_4)_2](H_2O)$. The sheets are linked by bonds to Cs^+ cations located in the interlayer, and also by H bonds to H_2O groups located in the interlayer in the case of $Cs_2[(UO_2)(MoO_4)_2](H_2O)$. The $[(UO_2)(MoO_4)_2]^{2-}$ sheets in $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ are more distorted than those observed in $Cs_2[(UO_2)(MoO_4)_2]$.

Keywords: uranyl molybdate, crystal structure, cesium.

SOMMAIRE

Nous avons synthétisé des cristaux de $Cs_2[(UO_2)(MoO_4)_2]$ à température élevée par réaction à l'état solide. Sa structure [orthorhombique, *Pbca*, *a* 11.762(2), *b* 14.081(2), *c* 14.323(2) Å, *V* 2372.3(6), *Z* = 8] a été résolue et affinée par méthodes directes jusqu'à un résidu *R*1 de 0.034 (*wR*2 = 0.044), calculé en utilisant 2577 réflexions uniques observées ($|F_o| \geq 4\sigma_F$). Nous avons préparé les cristaux de $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ par voie hydrothermale. Sa structure [monoclinique, $P2_1/c$, *a* 8.2222(9), *b* 11.0993(10), *c* 13.9992(13) Å, β 95.155(8)°, *V* 1272.4(2) Å^3, *Z* = 4] a été affinée jusqu'à un résidu *R*1 de 0.048 (*wR*2 = 0.099), calculé en utilisant 2487 réflexions uniques observées ($|F_o| \geq 4\sigma_F$). Le groupe spatial est $P2_1/c$, et non $P112_1$ comme l'ont proposé Rastsvetaeva *et al*. (1999). Les structures de $Cs_2[(UO_2)(MoO_4)_2]$ et $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ contiennent des feuillets topologiquement identiques de bipyramides pentagonales UrO_5 et de tétraèdres MoO_4 à coins partagés, ayant une composition $[(UO_2)(MoO_4)_2]^{2-}$. Ces feuillets sont orientés parallèles à (001) dans le cas de $Cs_2[(UO_2)(MoO_4)_2]$, et à (100) dans le cas de $Cs_2[(UO_2)(MoO_4)_2](H_2O)$. Les feuillets sont connectés l'un à l'autre par liaisons aux cations Cs^+ situés dans l'interfeuillet, et aussi par liaisons hydrogène aux groupes H_2O situés aussi dans l'interfeuillet dans le cas de $Cs_2[(UO_2)(MoO_4)_2](H_2O)$. Les feuillets $[(UO_2)(MoO_4)_2]^{2-}$ dans le composé $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ sont plus difformes que ceux du composé $Cs_2[(UO_2)(MoO_4)_2]$.

(Traduit par la Rédaction)

Mots-clés: molybdate uranylé, structure cristalline, césium.

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Introduction

Both ^{135}Cs and ^{99}Mo are long-lived products of radioactive fission. These isotopes are present in significant concentrations in radioactive waste and spent nuclear fuel. Indeed, one metric tonne of the waste uranium fuel from a light-water reactor (LWR) at discharge from reprocessing contains as much as 3.13 kg of Mo and 2.50 kg of Cs (Benedict *et al*. 1981). According to Baluev *et al*. (2000), waste from reprocessing of spent nuclear fuel contains 8.49 wt.% of Mo and 4.79 wt.% of Cs. The formation of Cs uranyl molybdates in alteration products of spent nuclear fuel was observed by Buck *et al*. (1997), who reported the phase $(Cs_{2x}Ba_{1-x})[(UO_2)_5(MoO_6)(OH)_6]\bullet nH_2O$ ($x \approx 0.4$, $n \approx 6$). It formed owing to the alteration of spent nuclear fuel during hydrologically unsaturated tests designed to simulate conditions expected in the proposed nuclear-waste repository at Yucca Mountain, Nevada. Thus, investigations of Cs uranyl molybdates are important for our understanding of the processes of alteration of radioactive waste and spent nuclear fuel.

In this paper, which is a continuation of our studies of the crystal chemistry of uranyl molybdates (Krivovichev & Burns 2000a, b, 2001a, b, 2002a, b, c, d, 2003a, b, c, d, e, Krivovichev *et al*. 2002a, b, 2003), we report the first crystal-structure determination for $Cs_2[(UO_2)(MoO_4)_2]$ and a refinement of the structure of $Cs_2[(UO_2)(MoO_4)_2](H_2O)$.

Background Information

At least seven Cs uranyl molybdates have been mentioned in the literature. 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 structurally closely related to $Cs_2[(UO_2)_2(SO_4)_3]$ (Ross & Evans 1960). Krivovichev *et al.* (2002a) reported the structures of two modifications of $Cs_2[(UO_2)_2(MoO_4)_3]$ [of which the β phase was studied by Serezhkin *et al*. (1987)]. Krivovichev & Burns (2002a) prepared crystals of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ and $Cs_6[(UO_2)(MoO_4)_4]$, and provided their structures. The compound $Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ and its structure were reported by Krivovichev & Burns (2001b).

Misra *et al*. (1995) reported results of thermal, X-ray powder diffraction, chemical and infrared (IR) spectroscopic studies of two modifications of $Cs_2[(UO_2)(MoO_4)_2]$ and of $Cs_2[(UO_2)_2(MoO_4)_3]$. On the basis of X-ray powder-diffraction studies, Misra *et al*. (1995) determined the following unit-cell dimensions for the two modifications of $Cs_2[(UO_2)(MoO_4)_2]$: phase A, orthorhombic, *a* 11.764(6), *b* 18.14(1), *c* 11.538(7) Å; phase B, orthorhombic, *a* 19.18(1), *b* 13.67(1), *c* 4.431(5) Å.

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). Rastsvetaeva *et al*. (1999) indicated that the structure is non-centrosymmetric, space group $P112_1$, *a* 14.031(3), *b* 8.272(2), *c* 11.067(2) Å, γ 95.63°, and that it is isostructural to other uranyl molybdates with general composition $A_2[(UO_2)(MoO_4)_2](H_2O)$ (A = K, Rb, NH_4) (Khrustalev *et al*. 2000, Andreev *et al*. 2001, Krivovichev *et al*. 2002). However, in contrast to $Cs_2[(UO_2)(MoO_4)_2](H_2O)$, all these compounds crystallize in the centrosymmetric space-group $P2_1/c$.

Synthesis of crystals

$Cs_2[(UO_2)(MoO_4)_2]$. Crystals of $Cs_2[(UO_2)(MoO_4)_2]$ were obtained by a high-temperature solid-state reaction. A mixture of Cs_2CO_3 (0.065 g), MoO_3 (0.057 g) and UO_3 (0.058 g) were heated in a platinum crucible to 600°C, followed by cooling to 100°C over 75 h, after which the furnace was turned off. The products of the synthesis included yellow crystals of $Cs_4[(UO_2)_3O(MoO_4)_2(MoO_5)]$ and $Cs_6[(UO_2)(MoO_4)_4]$ (Krivovichev & Burns 2002a), and greenish yellow crystals of $Cs_2[(UO_2)(MoO_4)_2]$. The latter crystals were found to be imperfect, and it was a challenge to find a crystal appropriate for the collection of data.

$Cs_2[(UO_2)(MoO_4)_2](H_2O)$. One mL of 0.075 M solution of $(UO_2)(NO_3)_2\bullet 6H_2O$, 1 mL of solution of $Na_2MoO_4\bullet H_2O$ [acidified by addition of concentrated HNO_3 (assay 69.2%) according to the ratio: 0.35 mg HNO_3 per 10 mL of 1M solution of $Na_2MoO_4\bullet 4H_2O$] and 0.33 mL of 0.2 M solution of $Cs(NO_3)$ were placed in a 23 mL Teflon-lined container. The reaction vessel was heated at 120°C for 2 h. The resulting precipitate was dissolved in ultrapure water, and insoluble greenish yellow equant crystals of $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ were recovered.

The collection of X-ray data

Crystals selected for data collection were mounted on a Bruker three-circle diffractometer equipped with a SMART APEX CCD (charge-coupled device) detector with a crystal-to-detector distance of 4.67 cm. More than a hemisphere of data was collected using monochromated Mo$K\alpha$ X-radiation and frame widths of 0.3° in ω. The unit-cell dimensions (Table 1) were refined using least-squares techniques. The data were reduced and filtered for statistical outliers using the Bruker program SAINT, and were corrected for Lorentz, polarization and background effects. Empirical absorption-corrections for $Cs_2[(UO_2)(MoO_4)_2]$ and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ were done for the crystals by modeling each as an ellipsoid, which lowered R_{int} from 11.7 to 4.0% and from 7.5 to 3.4%, respectively. Additional

information pertinent to the data collection is given in Table 1.

Structure solution 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. Each was solved by direct methods, which gave the positions of the U, Mo and Cs atoms. Oxygen atoms were located in difference-Fourier maps calculated following least-squares refinements of the partial-structure models. The structures were refined on the basis of F^2 for all unique data. The final refinements included positional parameters of all atoms, with an allowance for anisotropic displacement of all atoms except the H_2O group in the structure of $Cs_2[(UO_2)(MoO_4)_2](H_2O)$, and included a weighting scheme of the structure factors. The refinement of the structure of $Cs_2[(UO_2)(MoO_4)_2]$ converged to an agreement index ($R1$) of 3.4%, which was calculated for the 2577 unique observed reflections ($F_o \geq 4\sigma_{Fo}$). The refinement of the structure of $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ converged to an agreement index ($R1$) of 4.8%, which was calculated for the 2487 unique observed reflections ($F_o \geq 4\sigma_{Fo}$). Final positional and displacement parameters of all atoms in the structures of $Cs_2[(UO_2)(MoO_4)_2]$ and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ are presented in Tables 2 and 3, respectively, and selected interatomic distances are presented in Tables 4 and 5, respectively. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR $Cs_2[(UO_2)(MoO_4)_2]$ AND $Cs_2[(UO_2)(MoO_4)_2](H_2O)$

	$Cs_2[(UO_2)(MoO_4)_2]$	$Cs_2[(UO_2)(MoO_4)_2](H_2O)$
a (Å)	11.762(2)	8.2222(9)
b (Å)	14.081(2)	11.0993(10)
c (Å)	14.323(2)	13.9992(13)
β (°)	-	95.155(8)
V (Å^3)	2372.3(6)	1272.4(2)
Space group	*Pbca*	$P2_1/c$
F_{000}	2928	1504
Z	8	4
μ (cm^{-1})	217.80	203.14
D_{calc} (g/cm^3)	4.79	4.56
Crystal size (mm)	0.05 × 0.02 × 0.01	0.16 × 0.10 × 0.06
Radiation	Mo$K\alpha$	Mo$K\alpha$
Total Ref.	25229	13704
Unique Ref.	4952	5214
Unique $\|F_o\| \geq 4\sigma_F$	2577	2487
R_1	0.034	0.048
wR_2	0.044	0.099
S	0.771	1.083

Note: $R1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

RESULTS

Cation polyhedra

There is one symmetrically independent U^{6+} cation in the structures of both $Cs_2[(UO_2)(MoO_4)_2]$ and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$, each of which is strongly bonded to two O atoms, forming approximately linear uranyl ions with U–O_{Ur} bond lengths of ~1.8 Å. The uranyl ions are further coordinated by five atoms of O arranged at the equatorial vertices of UrO_5 pentagonal bipyramids. Average U^{6+}–O_{eq} (O_{eq}: equatorial O atom) bond lengths are 2.37 Å in both structures.

There are two symmetrically independent Mo^{6+} cations in each structure. These are tetrahedrally coordinated by four O atoms with the average <Mo–O> bond lengths of 1.75–1.76 Å. This coordination is typical for many uranyl molybdates (*e.g.*, Krivovichev & Burns 2001a, b).

TABLE 2. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR $Cs_2[(UO_2)(MoO_4)_2]$

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.17552(2)	0.16084(2)	0.46766(2)	0.01593(6)	0.0164(1)	0.0121(1)	0.0193(1)	0.0001(1)	0.0005(1)	0.0003(1)
Cs(1)	0.00956(5)	0.33525(4)	0.68449(4)	0.0322(1)	0.0406(3)	0.0235(3)	0.0325(3)	0.0026(2)	0.0034(2)	0.0006(3)
Cs(2)	0.24206(5)	0.42296(4)	0.29032(4)	0.0333(1)	0.0337(3)	0.0369(3)	0.0293(3)	-0.0028(2)	0.0043(2)	0.0012(3)
Mo(1)	0.34902(5)	0.39475(4)	0.54950(4)	0.0172(1)	0.0153(3)	0.0134(3)	0.0228(4)	-0.0004(2)	0.0021(2)	-0.0005(2)
Mo(2)	-0.04971(6)	0.36110(4)	0.40357(5)	0.0209(2)	0.0196(3)	0.0153(3)	0.0278(4)	0.0041(3)	0.0026(3)	0.0033(3)
O(1)	0.2182(4)	0.1588(4)	0.3483(3)	0.0234(11)	0.025(3)	0.016(3)	0.029(3)	-0.003(2)	0.004(2)	-0.006(2)
O(2)	0.1322(4)	0.1625(3)	0.5868(3)	0.0248(11)	0.027(3)	0.018(3)	0.030(3)	-0.002(2)	0.008(2)	0.001(2)
O(3)	0.4925(4)	0.3830(3)	0.5852(3)	0.0246(12)	0.025(3)	0.019(3)	0.030(3)	-0.002(2)	-0.004(2)	-0.001(2)
O(4)	-0.1439(4)	0.3974(3)	0.4938(3)	0.0247(12)	0.022(3)	0.016(3)	0.037(3)	-0.003(2)	0.008(2)	-0.005(2)
O(5)	0.3383(4)	0.4928(3)	0.4717(3)	0.0215(11)	0.023(3)	0.011(2)	0.031(3)	0.000(2)	0.005(2)	0.004(2)
O(6)	0.3045(4)	0.2938(3)	0.4860(3)	0.0248(13)	0.023(3)	0.021(3)	0.030(3)	0.002(2)	-0.006(2)	-0.010(2)
O(7)	0.2649(5)	0.4157(4)	0.6443(4)	0.0324(13)	0.027(3)	0.031(3)	0.038(3)	0.004(3)	0.011(3)	0.004(3)
O(8)	0.0742(4)	0.3026(4)	0.4481(4)	0.0323(14)	0.027(3)	0.021(3)	0.049(4)	-0.002(3)	-0.007(3)	0.000(2)
O(9)	-0.0065(5)	0.4581(4)	0.3380(4)	0.039(2)	0.040(4)	0.026(3)	0.051(4)	0.022(3)	0.017(3)	0.005(3)
O(10)	-0.1190(5)	0.2861(4)	0.3279(4)	0.0338(14)	0.036(4)	0.035(3)	0.029(3)	-0.007(3)	-0.007(3)	0.004(3)

In the structure of $Cs_2[(UO_2)(MoO_4)_2]$, both of the Cs(1) and Cs(2) sites are coordinated by nine O atoms each, whereas in the structure of $Cs_2[(UO_2)(MoO_4)_2](H_2O)$, the Cs(1) and Cs(2) sites are coordinated by ten and seven O atoms, respectively. Individual Cs^+–O bond distances range from 2.927 to 3.517 Å.

Bond-valence analysis

The bond-valence sums for the atoms in the structures (Table 6) were calculated using parameters given by Burns *et al.* (1997) for U^{6+}–O bonds and by Brown (2002) for Mo^{6+}–O and Cs^+–O bonds. The bond-valence sums obtained are in good agreement with the values expected for the respective ions in the structures.

Description of the structures

The structures of $Cs_2[(UO_2)(MoO_4)_2]$ and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ are based upon sheets of corner-sharing UrO_5 pentagonal bipyramids and MoO_4 tetrahedra, with the composition $[(UO_2)(MoO_4)_2]^{2-}$ (Figs. 1a, b). The $[(UO_2)(MoO_4)_2]^{2-}$ sheets are oriented parallel to (001) in $Cs_2[(UO_2)(MoO_4)_2]$ and (100) in $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ (Fig. 2). The sheets are linked by bonds to Cs^+ cations located in the interlayer, and by H bonds to interlayer H_2O groups in $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ (Fig. 2b).

TABLE 3. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR $Cs_2[(UO_2)(MoO_4)_2](H_2O)$

Atom	*x*	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.47609(6)	0.72547(4)	0.15249(3)	0.0201(1)	0.0271(3)	0.0156(2)	0.0173(2)	-0.0008(2)	-0.0001(2)	0.0021(2)
Mo(1)	0.49952(14)	0.60953(8)	-0.09714(7)	0.0227(2)	0.0366(7)	0.0141(5)	0.0172(5)	-0.0005(4)	0.0012(4)	-0.0014(4)
Mo(2)	0.74909(13)	0.96972(8)	-0.15144(7)	0.0205(2)	0.0234(6)	0.0169(4)	0.0208(5)	-0.0017(4)	-0.0003(4)	0.0018(4)
Cs(1)	0.23257(11)	0.92489(7)	-0.11853(5)	0.0308(2)	0.0340(5)	0.0315(4)	0.0262(4)	-0.0004(3)	-0.0009(3)	0.0056(4)
Cs(2)	0.9515(2)	0.66308(13)	0.07868(9)	0.0809(4)	0.0463(8)	0.112(1)	0.0816(9)	0.0085(8)	-0.0082(6)	0.0097(7)
O(1)	0.4240(10)	0.4579(6)	-0.0894(5)	0.024(2)	0.030(5)	0.023(4)	0.019(4)	0.007(3)	0.006(4)	-0.001(4)
O(2)	0.4191(11)	0.7119(7)	-0.0165(5)	0.034(2)	0.055(7)	0.024(4)	0.023(4)	0.000(4)	-0.001(4)	0.010(4)
O(3)	0.2927(10)	0.6503(7)	0.1683(6)	0.029(2)	0.024(5)	0.033(5)	0.032(5)	0.002(4)	0.003(4)	0.001(4)
O(4)	0.6657(13)	0.0978(7)	-0.1004(6)	0.041(3)	0.079(8)	0.024(5)	0.019(4)	-0.008(4)	-0.002(5)	0.017(5)
O(5)	0.6635(12)	0.7994(7)	0.1401(6)	0.038(2)	0.048(6)	0.022(5)	0.045(5)	0.007(4)	0.010(5)	-0.015(4)
O(6)	0.4209(12)	0.6573(7)	-0.2131(5)	0.038(2)	0.065(7)	0.029(5)	0.018(4)	0.004(4)	-0.001(4)	-0.016(4)
O(7)	0.8444(11)	0.8936(7)	-0.0559(5)	0.029(2)	0.034(5)	0.029(4)	0.021(4)	0.003(3)	-0.007(4)	0.008(4)
O(8)	0.5949(10)	0.8784(7)	-0.2139(6)	0.030(2)	0.030(5)	0.032(5)	0.027(4)	-0.008(4)	-0.005(4)	-0.012(4)
O(9)	0.7082(12)	0.6160(8)	-0.0916(6)	0.040(2)	0.042(7)	0.032(5)	0.047(6)	-0.001(4)	0.006(5)	-0.003(4)
O(10)	0.9001(11)	0.0071(8)	-0.2254(6)	0.042(2)	0.032(6)	0.051(6)	0.043(6)	0.013(5)	0.005(4)	-0.001(5)
$H_2O(11)$	0.9877(22)	0.1940(15)	-0.3370(12)	0.132(6)						

TABLE 4. SELECTED BOND-LENGTHS (Å) IN THE STRUCTURE OF $Cs_2[(UO_2)(MoO_4)_2]$

U-O(2)	1.782(5)	Cs(1)-O(9)d	2.927(5)
U-O(1)	1.782(5)	Cs(1)-O(10)e	3.069(5)
U-O(8)	2.342(5)	Cs(1)-O(2)	3.155(5)
U-O(4)a	2.343(5)	Cs(1)-O(7)	3.261(5)
U-O(3)b	2.364(5)	Cs(1)-O(3)f	3.372(5)
U-O(5)c	2.372(4)	Cs(1)-O(4)	3.390(5)
U-O(6)	2.423(5)	Cs(1)-O(1)e	3.396(5)
<U-O_{Ur}>	1.782	Cs(1)-O(1)b	3.461(5)
<U-O_{eq}>	2.37	Cs(1)-O(8)	3.501(6)
		<Cs(1)-O>	3.28
Mo(1)-O(7)	1.706(5)		
Mo(1)-O(6)	1.767(5)	Cs(2)-O(5)	3.000(5)
Mo(1)-O(3)	1.771(5)	Cs(2)-O(10)g	3.042(5)
Mo(1)-O(5)	1.779(5)	Cs(2)-O(9)	3.043(6)
<Mo(1)-O>	1.76	Cs(2)-O(7)h	3.089(6)
		Cs(2)-O(2)i	3.408(5)
Mo(2)-O(10)	1.719(5)	Cs(2)-O(6)	3.421(5)
Mo(2)-O(9)	1.734(5)	Cs(2)-O(8)	3.447(5)
Mo(2)-O(4)	1.777(5)	Cs(2)-O(1)j	3.455(5)
Mo(2)-O(8)	1.791(5)	Cs(2)-O(9)g	3.517(6)
<Mo(2)-O>	1.76	<Cs(2)-O>	3.27

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

TABLE 5. SELECTED BOND-LENGTHS (Å) IN THE STRUCTURE OF $Cs_2[(UO_2)(MoO_4)_2](H_2O)$

U-O(3)	1.754(8)	Cs(1)-O(2)d	3.096(8)
U-O(5)	1.768(9)	Cs(1)-O(4)e	3.114(8)
U-O(8)a	2.336(7)	Cs(1)-O(10)	3.132(9)
U-O(4)b	2.363(8)	Cs(1)-$H_2O(11)$f	3.17(2)
U-O(6)a	2.365(8)	Cs(1)-O(3)g	3.180(8)
U-O(2)	2.375(8)	Cs(1)-O(5)e	3.199(7)
U-O(1)c	2.393(7)	Cs(1)-O(7)e	3.270(8)
<U-O_{Ur}>	1.761	Cs(1)-O(7)	3.403(9)
<U-O_{eq}>	2.37	Cs(1)-O(8)d	3.411(9)
		<Cs(1)-O>	3.22
Mo(1)-O(9)	1.712(10)		
Mo(1)-O(2)	1.771(8)	Cs(2)-O(3)d	2.972(8)
Mo(1)-O(6)	1.774(8)	Cs(2)-O(5)	3.00(1)
Mo(1)-O(1)	1.800(7)	Cs(2)-O(9)	3.017(9)
<Mo(1)-O>	1.76	Cs(2)-O(7)	3.251(7)
		Cs(2)-O(1)c	3.383(8)
Mo(2)-O(7)	1.712(7)	Cs(2)-O(10)a	3.388(9)
Mo(2)-O(10)	1.737(9)	Cs(2)-$H_2O(11)$f	3.48(2)
Mo(2)-O(4)	1.758(8)	<Cs(2)-O>	3.21
Mo(2)-O(8)	1.789(7)		
<Mo(2)-O>	1.75		

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

Discussion

Topology and flexibility of uranyl molybdate sheets

The topology of linkage of coordination polyhedra of the $[(UO_2)(MoO_4)_2]^{2-}$ sheets in the structures of $Cs_2[(UO_2)(MoO_4)_2]$ and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ is identical and can be represented using a nodal description (Fig. 1c). In Figure 1c, black and white nodes correspond to the UrO_5 and MoO_4 polyhedra, respectively. Two nodes are linked where the two respective polyhedra share a common corner. The graph depicted in Figure 1c is an idealized version of the topologies of the sheets shown in Figures 1a, b. This graph may be obtained from the highly symmetrical graph (**3.6.3.6**) shown in Figure 1d by elimination of some nodes and of the linkages incident upon these nodes. This topology is fundamental to a number of uranyl compounds (see Krivovichev & Burns 2002c for more details). In general, the (**3.6.3.6**) graph shown in Figure 1d is a parent graph for at least 35 different sheet-topologies observed in crystal structures of inorganic oxysalts (Krivovichev 2004).

It is interesting to note that the topology shown in Figure 1c can be obtained by merging four-membered rings (4MRs) of black and white nodes taken in the sequence "black–white–black–white". The 4MRs are known as basic building blocks for heteropolyhedral structures such as zinc and aluminum phosphates that contain tetrahedral units consisting of MO_4 (M = Zn, Al) and PO_4 tetrahedra. Rao *et al*. (2001) pointed out that 4MRs play a role of synthons (building units) in construction of different structures and their transformations under hydrothermal conditions. It is quite possible that the 4MRs in uranyl molybdates play a similar role in the process of crystallization.

It is noteworthy that the topological structure of the $[(UO_2)(MoO_4)_2]^{2-}$ sheets in $Cs_2[(UO_2)(MoO_4)_2]$ and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ is identical, whereas their geometrical parameters are different. The U^{6+}–O and Mo^{6+}–O bond lengths are very similar in both structures and cannot seriously affect the degree of distortion of the sheets. The main factor controlling distortion of the sheets is the Mo–O_{br}–U angles, where O_{br} is the O atom shared between UrO_5 and MoO_4 polyhedra. Figure 3 shows a ball-and-stick representation of the $[(UO_2)(MoO_4)_2]^{2-}$ sheet in $Cs_2[(UO_2)(MoO_4)_2](H_2O)$. The UO_2^{2+} ion is coordinated by five equatorial O atoms that are also vertices of the MoO_4 tetrahedra. Thus, there are five different Mo–O–U angles in both structures; in Figure 3, we provide appropriate notations for the bridging O atoms. A comparison of the corresponding Mo–O–U angles in the structures of $Cs_2[(UO_2)(MoO_4)_2]$ and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ is given in Table 7. These data show that the Mo–O–U angles vary by 5 to 13°. In general, the $[(UO_2)(MoO_4)_2]^{2-}$ sheet in $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ is more distorted, as deduced from the smaller values of the Mo–O–U angles. This distortion also can be estimated from the surface area occupied by the $[(UO_2)(MoO_4)_2]^{2-}$ sheets in both structures. This area can be expressed as $S_{sheet} = a. \times b.$, where *a*. and *b*. are defined in Figure 3. The area occupied by the $[(UO_2)(MoO_4)_2]^{2-}$ sheet in $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ is about 6% smaller than that in $Cs_2[(UO_2)(MoO_4)_2]$ (Table 7).The higher degree of distortion of the $[(UO_2)(MoO_4)_2]^{2-}$ sheet in $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ is a consequence of the presence of an additional H_2O group in the interlayer. From the similarity of the sheet topologies in the structures under consideration, one may expect that $Cs_2[(UO_2)(MoO_4)_2]$ forms as a result of dehydration of $Cs_2[(UO_2)(MoO_4)_2](H_2O)$. However, more experimental evidence is needed to confirm this suggestion.

Comparison with previous studies and related compounds

Phases with the composition $Cs_2[(UO_2)(MoO_4)_2]$ were previously studied by Misra *et al*. (1995). However, the unit-cell dimensions obtained for $Cs_2[(UO_2)(MoO_4)_2]$ in the present study do not correspond to any reported by Misra *et al*. (1995). The calculated X-ray powder-diffraction pattern calculated from our crystal-structure data is in good agreement with that reported by Misra *et al*. (1995) for $Cs_2[(UO_2)(MoO_4)_2]$, designated phase A.

The structure of $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ was first reported by Rastsvetaeva et al. (1999), who refined it in the non-centrosymmetric space-group $P112_1$. We were unable to find any deviation of the structure of this compound from group $P2_1/c$, which is characteristic of other compounds with the general formula $A_2[(UO_2)(MoO_4)_2](H_2O)$ (*A* = K, Rb, NH_4) (Khrustalev *et al*. 2000, Andreev *et al*. 2001, Krivovichev *et al*. 2002b).

It is noteworthy that $Cs_2[(UO_2)(MoO_4)_2]$ is not isotypic with the compounds with the general formula

TABLE 6. BOND-VALENCE ANALYSIS (*v.u.*) FOR $Cs_2[(UO_2)(MoO_4)_2]$ AND $Cs_2[(UO_2)(MoO_4)_2](H_2O)$

Atom (group)	$Cs_2[(UO_2)(MoO_4)_2]$	$Cs_2[(UO_2)(MoO_4)_2](H_2O)$
Cs	0.99, 1.05	1.07, 0.94
U	5.97	6.12
Mo	6.04, 6.05	5.91, 6.15
O	1.86-2.14	1.80-2.18
H_2O	-	0.19

TABLE 7. SELECTED GEOMETRICAL PARAMETERS OF THE $[(UO_2)(MOO_4)_2]^{2-}$ SHEETS IN THE STRUCTURES OF $Cs_2[(UO_2)(MoO_4)_2]$ AND $Cs_2[(UO_2)(MoO_4)_2](H_2O)$

	$Cs_2[(UO_2)(MoO_4)_2]$	$Cs_2[(UO_2)(MoO_4)_2](H_2O)$
Mo(2)-O_{t1}-U (°)	148.1	153.9
Mo(1)-O_{t2}-U (°)	149.6	144.3
Mo(2)-O_{t3}-U (°)	129.5	138.2
Mo(1)-O_{t4}-U (°)	142.6	128.6
Mo(1)-O_{t5}-U (°)	143.0	129.9
$S_{sheet} = a' \times b'$	14.081 × 11.763 = 165.6 Å^2	13.999 × 11.099 = 155.4 Å^2

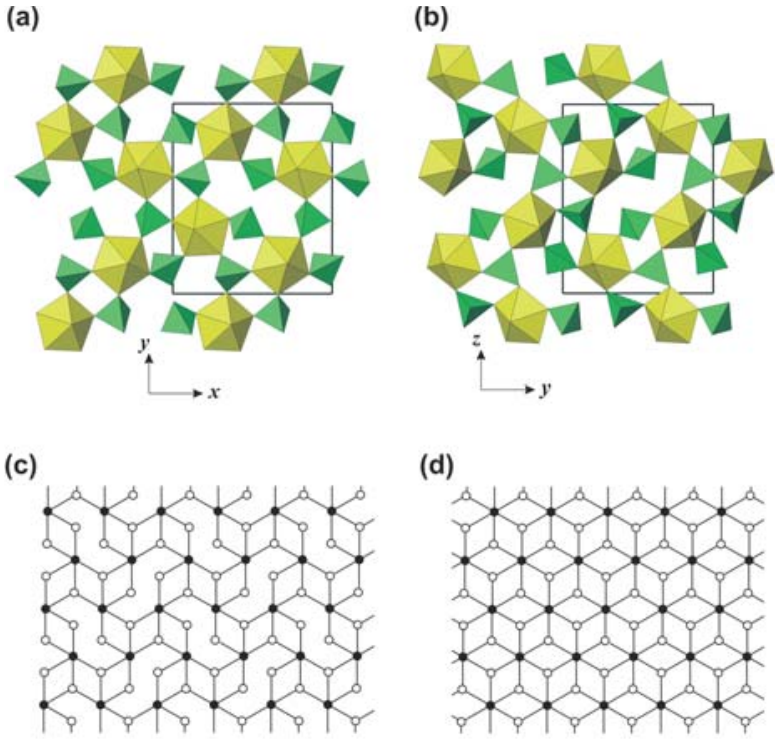

FIG. 1. The $[(UO_2)(MoO_4)_2]^{2-}$ sheets in the structures of $Cs_2[(UO_2)(MoO_4)_2]$ (a) and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ (b), a black-and-white graph with black and white nodes corresponding to UrO_5 and MoO_4 polyhedra, respectively (c). The graph shown in (c) can be obtained from more regular graph (**3.6.3.6**) (d) by elimination of some links between black and white nodes. Legend for (a) and (b): UrO_5 polyhedra: yellow, MoO_4 polyhedra: green.

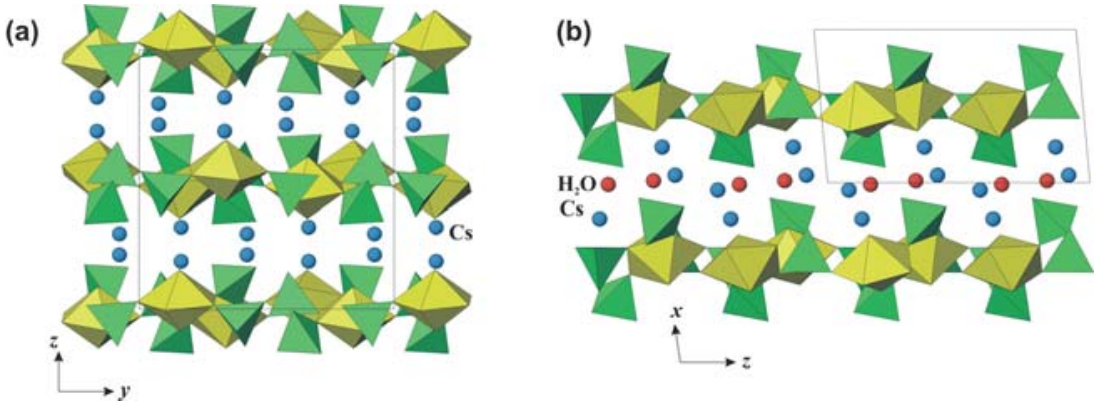

FIG. 2. The structures of $Cs_2[(UO_2)(MoO_4)_2]$ (a) and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$ (b) projected along the *a* and *b* axes, respectively. Legend: UrO_5 polyhedra: yellow, MoO_4 polyhedra: green, Cs^+ cations: blue, H_2O groups: red.

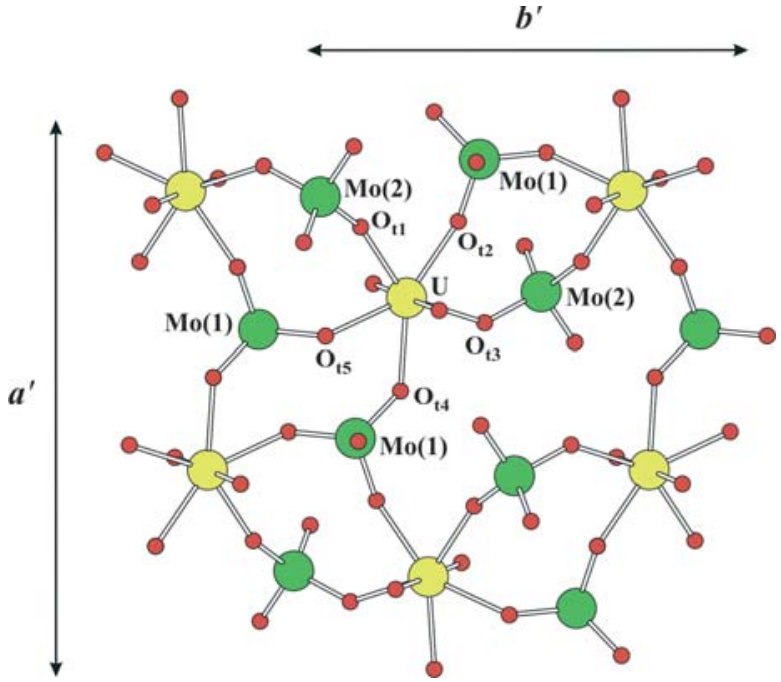

FIG. 3. Ball-and-stick representation of the $[(UO_2)(MoO_4)_2]^{2-}$ sheet in $Cs_2[(UO_2)(MoO_4)_2](H_2O)$. Legend: U^{6+} cations: yellow, Mo^{6+} cations: green, O^{2-} anions: red. See text for details.

$A_2[(UO_2)(MoO_4)_2]$ (A = K, Rb) (Sadikov *et al*. 1988, Krivovichev & Burns 2002b). The structures of $A_2[(UO_2)(MoO_4)_2]$ (A = K, Rb) are based upon $[(UO_2)(MoO_4)_2]^{2-}$ sheets with the same topology as that observed in $Cs_2[(UO_2)(MoO_4)_2]$ and $Cs_2[(UO_2)(MoO_4)_2](H_2O)$. However, they crystallize in space group $P2_1/c$, in contrast to the orthorhombic symmetry of $Cs_2[(UO_2)(MoO_4)_2]$. The structure of $Na_2[(UO_2)(MoO_4)_2]$ consists of $[(UO_2)(MoO_4)_2]^{2-}$ sheets whose topology differs from that observed for $Cs_2[(UO_2)(MoO_4)_2]$ [see Krivovichev *et al*. (2002b) for details]. The structure of $Li_2[(UO_2)(MoO_4)_2]$ (Krivovichev & Burns 2003a) is based upon $[(UO_2)(MoO_4)_2]^{2-}$ chains of corner-sharing UrO_4 square bipyramids and MoO_4 tetrahedra.

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