

CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. IX. A NOVEL URANYL MOLYBDATE SHEET IN THE STRUCTURE OF $\text{Th}_2[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$

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ABSTRACT

Crystals of a new thallium uranyl molybdate, $\text{Th}_2[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$, have been synthesized by high-temperature solid-state reactions. The structure [monoclinic, $P2_1/n$, a 8.2527(3), b 28.5081(12), c 9.1555(4) Å, β 104.122(1)°, V 2088.91(15) Å³, $Z = 8$] was solved by direct methods and refined to $R1 = 0.039$ ($wR2 = 0.081$) on the basis of 8609 unique reflections. The structure is novel in that Mo^{6+} cations occur in both tetragonal pyramidal and trigonal bipyramidal coordination environments, and it contains a uranyl molybdate sheet of composition $[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$ with more uranium than molybdenum. The uranyl molybdate sheets are composed of UrO_5 (Ur : uranyl ion, UO_2^{2+}) pentagonal bipyramids and MoO_5 polyhedra that are linked by the sharing of edges. Within the sheet, eight UrO_5 bipyramids share edges, resulting in a Z-shaped complex that is oriented approximately parallel to [010]. The MoO_5 polyhedra each contain one O atom that is not shared within the sheet; these are oriented both up and down relative to the plane of the sheet. The anion topology of the sheet consists of pentagons, squares and triangles. In the sheet, all pentagons are populated by U, four-fifths of the squares contain Mo, and the triangles are empty. The uranyl molybdate sheets are parallel to (101) and are linked *via* Th^+ cations located in the interlayer.

Keywords: uranyl molybdate, crystal structure, thallium.

SOMMAIRE

Nous avons synthétisé un nouveau molybdate uranylé de thallium, $\text{Th}_2[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$, par réactions à l'état solide à température élevée. La structure [monoclinique, $P2_1/n$, a 8.2527(3), b 28.5081(12), c 9.1555(4) Å, β 104.122(1)°, V 2088.91(15) Å³, $Z = 8$] a été résolue par méthodes directes et affinée jusqu'à un résidu $R1$ de 0.039 ($wR2 = 0.081$) en utilisant 8609 réflexions uniques. La structure présente un aspect original à cause de la présence des cations Mo^{6+} en polyèdres de coordination sous forme de pyramides tétraogonales et de bipyramides trigonales. De plus, elle contient un feuillet de molybdate uranylé de composition $[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$, donc avec plus d'uranium que de molybdène. Ces feuillets contiennent des bipyramides pentagonales UrO_5 (Ur : ion uranyle, UO_2^{2+}) et des polyèdres MoO_5 qui sont connectés par partage d'arêtes. Au sein du feuillet, huit bipyramides UrO_5 partagent des arêtes, et définissent un complexe en forme de Z qui est orienté à peu près parallèle à [010]. Chacun des polyèdres MoO_5 contient un atome d'oxygène non partagé avec les feuillets. Ces atomes sont orientés alternativement vers le haut et vers le bas par rapport au plan du feuillet. La topologie du feuillet contient des pentagones, des carrés et des triangles. Dans le feuillet, tous les pentagones contiennent un atome d'uranium, quatre cinquièmes des carrés contiennent un atome de Mo, et les triangles sont vides. Les feuillets de molybdate uranylé sont parallèles à (101) et sont interliés grâce aux cations Th^+ situés dans l'interfeuillet.

(Traduit par la Rédaction)

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

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INTRODUCTION

In our previous papers concerning the crystal chemistry of uranyl molybdates (Krivovichev & Burns 2000a, b, 2001a, b, 2002a, b, c, d, 2003a, b, c, Krivovichev *et al.* 2002a, b), we have established that structural diversity of uranyl molybdates is controlled by several factors, including the coordination geometry of U and Mo. The most common coordination polyhedra for U and Mo in uranyl molybdates are the UrO_5 pentagonal bipyramid (Ur : uranyl ion, UO_2^{2+}) and the MoO_4 tetrahedron, respectively. The coordination about Mo is more flexible than that about U, and varies from fourfold (tetrahedral) to sixfold (distorted octahedral). In this contribution, we report the crystal structure of $Tl_2[(UO_2)_2O(MoO_5)]$, in which Mo^{6+} cations occur in two types of fivefold coordination: trigonal bipyramidal and tetragonal pyramidal.

Krivovichev & Burns (2003a) reported the structures of the Tl uranyl molybdates $Na_3Tl_3[(UO_2)(MoO_4)_4]$, $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$) and $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$. We have recently prepared crystals of $Tl_2(UO_2)(MoO_4)_2$, $Tl_2(UO_2)_2(MoO_4)_3$ and $Tl_2[(UO_2)_6(MoO_4)_7(H_2O)](H_2O)$, the structures of which will be reported elsewhere.

EXPERIMENTAL

Synthesis of crystals

Crystals of $Tl_2[(UO_2)_2O(MoO_5)]$ were obtained by high-temperature solid-state reactions. A mixture of $TlNO_3$ (0.1064 g), MoO_3 (0.0432 g) and UO_3 (0.0286 g) were heated in a platinum crucible to 600°C, followed by cooling to 300°C over 50 h, after which the furnace was turned off. Dark red plates of $Tl_2[(UO_2)_2O(MoO_5)]$ were obtained, together with equidimensional yellow crystals of $Tl_2[(UO_2)(MoO_4)_2]$.

Collection of X-ray data

A crystal of $Tl_2[(UO_2)_2O(MoO_5)]$ was mounted on a Bruker three-circle diffractometer equipped with a

SMART APEX CCD (charge-coupled device) detector with a crystal-to-detector distance of 4.5 cm. More than a hemisphere of data was collected using monochromated $MoK\alpha$ X-radiation and framewidths of 0.3° in ω . The unit-cell dimensions (Table 1) were refined using least-squares techniques. The three-dimensional dataset was reduced and filtered for statistical outliers using the Bruker program SAINT. The data were corrected for Lorentz, polarization and background effects. An empirical absorption-correction was done for the crystal by modeling it as an ellipsoid, which lowered R_{int} from 12.0 to 4.6%. 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 structure. The structure was solved by direct methods, which gave the positions of the U, Mo and Tl atoms. Oxygen atoms were located in difference-Fourier maps calculated following least-squares refinement of the partial-structure model. The structure was refined on the basis of F^2 for all 8609 unique data. The final refinement included the positional parameters of all atoms, with an allowance for anisotropic displacement of all atoms except the partially occupied Tl(5) site, and included a weighting scheme of the structure factors. The refinement converged to an agreement index ($R1$) of 3.9%, which was calculated for the 6255 unique observed reflections ($F_o > 4\sigma F_o$). The goodness-of-fit (S) was 1.077. Final positional and displacement parameters of all atoms, and selected interatomic distances are shown in Tables 2 and 3, respectively. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

Cation polyhedra

There are four symmetrically independent U^{6+} cations in the structure, 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 in the range of 2.33 to 2.34 Å.

There are two symmetrically independent Mo^{6+} cations in the structure, and each is coordinated by five O atoms (Fig. 1). Each of the MoO_5 polyhedra has one

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR $Tl_2[(UO_2)_2O(MoO_5)]$

a (Å)	8.2527(3)	D_{calc} (g/cm ³)	7.25
b (Å)	28.5081(12)	Crystal size (mm)	0.18 × 0.10 × 0.05
c (Å)	9.1555(4)	Radiation	$MoK\alpha$
β (°)	104.122(1)	Total Ref.	23244
V (Å ³)	2088.91(15)	Unique Ref.	8609
Space group	$P2_1/n$	Unique $ F_o \geq 4\sigma_F$	6255
F_{000}	3744	R_1	0.039
Z	8	wR_2	0.081
μ (cm ⁻¹)	628.56	S	1.077

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

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $\text{Ti}_2[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.41320(4)	0.09965(1)	0.91820(4)	0.00917(7)	0.0100(2)	0.0063(2)	0.00980(15)	-0.0002(1)	-0.00043(12)	0.00018(13)
U(2)	-0.17362(4)	0.16754(1)	0.28007(4)	0.00908(7)	0.0095(2)	0.0071(2)	0.00918(14)	0.0010(1)	-0.00051(11)	0.00080(13)
U(3)	0.17917(4)	0.18742(1)	0.63612(4)	0.00960(7)	0.0109(2)	0.0061(2)	0.01013(14)	0.0002(1)	-0.00083(12)	0.00006(13)
U(4)	0.01842(4)	0.06801(1)	0.52999(4)	0.00872(7)	0.0106(2)	0.0057(2)	0.00873(14)	0.0002(1)	0.00027(11)	-0.00030(13)
Tl(1)	-0.07176(6)	0.12421(2)	0.89186(5)	0.0228(1)	0.0274(2)	0.0206(2)	0.0222(2)	-0.0008(2)	0.0096(2)	0.0006(2)
Tl(2)	-0.24059(6)	-0.01384(2)	0.81425(5)	0.0312(1)	0.0366(3)	0.0345(3)	0.0237(2)	-0.0060(2)	0.0094(2)	-0.0049(2)
Tl(3)	-0.47944(6)	0.09974(2)	0.47969(6)	0.0357(1)	0.0295(3)	0.0323(3)	0.0457(3)	0.0057(2)	0.0099(2)	-0.0022(2)
Tl(4)*	0.81118(9)	0.29198(3)	0.70214(9)	0.0392(3)	0.0380(4)	0.0345(4)	0.0506(5)	0.0109(3)	0.0217(3)	-0.0020(3)
Tl(5)**	0.7347(10)	0.2765(3)	0.6039(10)	0.090(3)						
Mo(1)	0.6007(1)	0.20996(3)	0.93957(9)	0.0092(2)	0.0106(3)	0.0056(4)	0.0095(3)	0.0003(3)	-0.0008(3)	-0.0004(3)
Mo(2)	-0.2279(1)	0.03084(3)	0.18158(9)	0.0101(2)	0.0125(4)	0.0060(4)	0.0095(3)	0.0001(3)	-0.0019(3)	-0.0008(3)
O(1)	0.1791(9)	0.0690(3)	0.4266(8)	0.017(2)	0.016(3)	0.014(4)	0.023(4)	0.001(3)	0.008(3)	-0.003(3)
O(2)	-0.1118(9)	0.0044(3)	0.3692(8)	0.019(2)	0.029(4)	0.007(4)	0.015(3)	0.004(3)	-0.007(3)	-0.001(3)
O(3)	0.0005(9)	0.1609(3)	0.1961(8)	0.019(2)	0.016(3)	0.024(5)	0.019(4)	0.005(3)	0.007(3)	0.000(3)
O(4)	-0.3552(8)	0.1765(3)	0.3575(8)	0.018(2)	0.015(3)	0.022(5)	0.019(4)	0.001(3)	0.005(3)	0.003(3)
O(5)	0.6398(8)	0.1517(2)	0.0444(7)	0.0131(14)	0.018(3)	0.004(3)	0.014(3)	0.006(3)	-0.003(3)	-0.001(3)
O(6)	0.7450(8)	0.2331(3)	0.1216(7)	0.0146(15)	0.015(3)	0.007(4)	0.016(3)	0.004(3)	-0.007(3)	0.000(3)
O(7)	0.4948(9)	0.2664(3)	0.9222(8)	0.017(2)	0.019(4)	0.010(4)	0.017(3)	-0.002(3)	-0.005(3)	-0.003(3)
O(8)	-0.1448(9)	0.0644(3)	0.6339(8)	0.018(2)	0.021(4)	0.015(4)	0.018(4)	0.000(3)	0.003(3)	-0.004(3)
O(9)	0.0545(9)	0.2049(3)	0.7647(8)	0.023(2)	0.022(4)	0.030(5)	0.019(4)	-0.003(3)	0.009(3)	-0.001(4)
O(10)	0.2883(9)	0.1165(3)	0.0480(7)	0.017(2)	0.021(4)	0.019(4)	0.010(3)	-0.002(3)	0.002(3)	0.004(3)
O(11)	0.1982(9)	0.1103(3)	0.7204(7)	0.0144(15)	0.020(4)	0.011(4)	0.009(3)	-0.003(3)	-0.003(3)	-0.003(3)
O(12)	-0.1836(8)	0.0884(3)	0.3081(7)	0.0134(14)	0.015(3)	0.009(4)	0.013(3)	-0.001(3)	-0.004(3)	0.003(3)
O(13)	-0.0238(8)	0.1456(3)	0.5025(7)	0.0144(14)	0.017(3)	0.010(4)	0.014(3)	-0.003(3)	0.000(3)	-0.003(3)
O(14)	0.4016(9)	0.1792(3)	0.8411(8)	0.023(2)	0.027(4)	0.011(4)	0.020(4)	0.008(3)	-0.014(3)	-0.004(3)
O(15)	0.5467(9)	0.0831(3)	0.7967(8)	0.024(2)	0.021(4)	0.034(5)	0.020(4)	-0.005(4)	0.012(3)	0.002(4)
O(16)	0.3140(10)	0.1748(3)	0.5098(8)	0.022(2)	0.029(4)	0.016(4)	0.023(4)	0.009(3)	0.012(3)	0.005(3)
O(17)	-0.0984(10)	0.0458(3)	0.0656(8)	0.024(2)	0.035(4)	0.021(5)	0.022(4)	-0.005(3)	0.018(3)	-0.005(4)
O(18)	-0.4370(9)	0.0528(3)	0.1129(8)	0.022(2)	0.018(4)	0.021(5)	0.023(4)	0.004(3)	-0.003(3)	-0.002(3)
O(19)	-0.2815(9)	-0.0283(3)	0.1118(8)	0.018(2)	0.025(4)	0.009(4)	0.017(4)	0.001(3)	0.000(3)	-0.004(3)
O(20)	0.7192(10)	0.2101(3)	0.8114(8)	0.023(2)	0.029(4)	0.023(5)	0.020(4)	0.003(3)	0.011(3)	-0.004(4)

* s.o.f. = 0.866(3). ** s.o.f. = 0.134(3); refined isotropically.

relatively short Mo–O bond (1.701 and 1.734 Å for Mo(1) and Mo(2), respectively). The remaining four Mo–O bonds are arranged differently for the two Mo cations. The geometries of each arrangement can be described using bond angles between two opposite Mo–O bonds (Fig. 1). In the Mo(1)O₅ polyhedron, these two angles are 146.4 and 149.4°, and the Mo(1)O₅ polyhedron may be described as a tetragonal pyramid. In contrast, the corresponding angles in the Mo(2)O₅ polyhedron (note that the short “apical” Mo–O bond is not considered) are 132.9 and 164.4°, which defines a distorted trigonal bipyramidal geometry (an ideal trigonal bipyramid has angles of 120 and 180°). Thus the structure of $\text{Ti}_2[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$ possesses two types of Mo coordination polyhedron: a tetragonal pyramid Mo(1)O₅, and a trigonal bipyramid Mo(2)O₅.

There are four symmetrically independent Ti⁺ cations in the structure. The Ti(1) and Ti(2) atoms are each coordinated by eight atoms of O, whereas the Ti(3) and Ti(4) atoms are each coordinated by six anions. The Ti⁺–O bond lengths range from 2.72 to 3.26 Å, and the Ti coordination polyhedra are distorted owing to the presence of the 6s² lone-electron pairs on the Ti⁺ cations.

However, owing to the relatively low charge of the Ti⁺ cations, the effect of the lone-electron pair is not as pronounced as is typical for Pb²⁺ and Bi³⁺ cations, for example.

The refined occupancy of the Ti(4) position is 0.886(3), and it has a complementary Ti(5) position ~1.05 Å away with an occupancy of 0.134(3). Only one of these sites is occupied locally.

Bond-valence analysis

The bond-valence sums for the atoms in the structures were calculated using parameters given by Burns *et al.* (1997) for U⁶⁺–O bonds and by Brown (2002) for Mo⁶⁺–O bonds. The bond-valence sums for Ti⁺–O bonds were calculated using new bond-valence parameters ($r_o = 1.801$ Å, $b = 0.56$ Å) recently derived by Locock & Burns (pers. commun.). The calculated bond-valence sums for cations are 6.03, 6.02, 6.03, 5.96, 6.06, 6.08, 1.04, 0.96, 0.85 and 0.81 valence units for U(1), U(2), U(3), U(4), Mo(1), Mo(2), Ti(1), Ti(2), Ti(3) and Ti(4), respectively. The bond-valence sums for O atoms are in the range of 1.81 to 2.20 valence units.

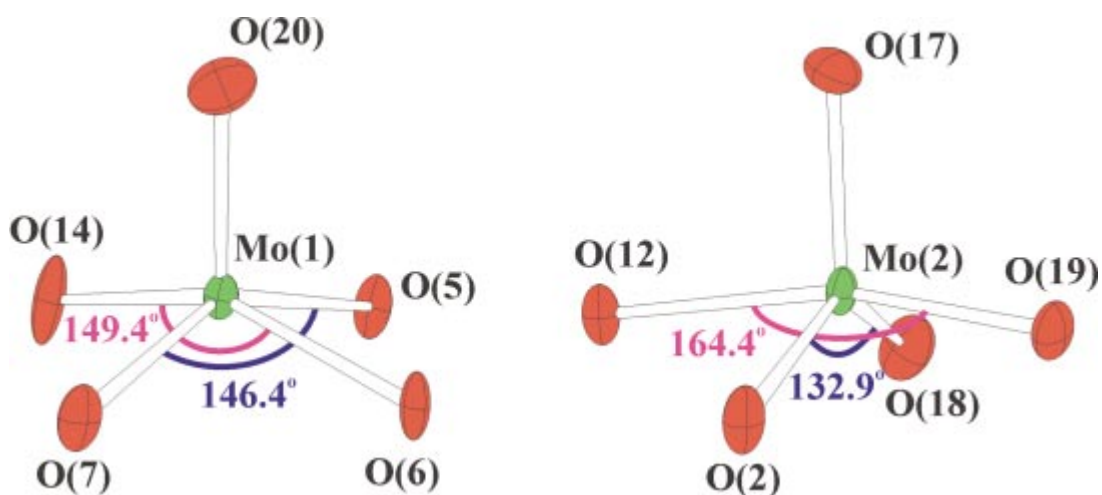


FIG. 1. Coordination of Mo atoms in the structure of $Tl_2[(UO_2)_2O(MoO_5)]$. According to the values of the bond angles, the $Mo(1)O_5$ and $Mo(2)O_5$ coordination polyhedra are designated as a tetragonal pyramid and trigonal bipyramid, respectively.

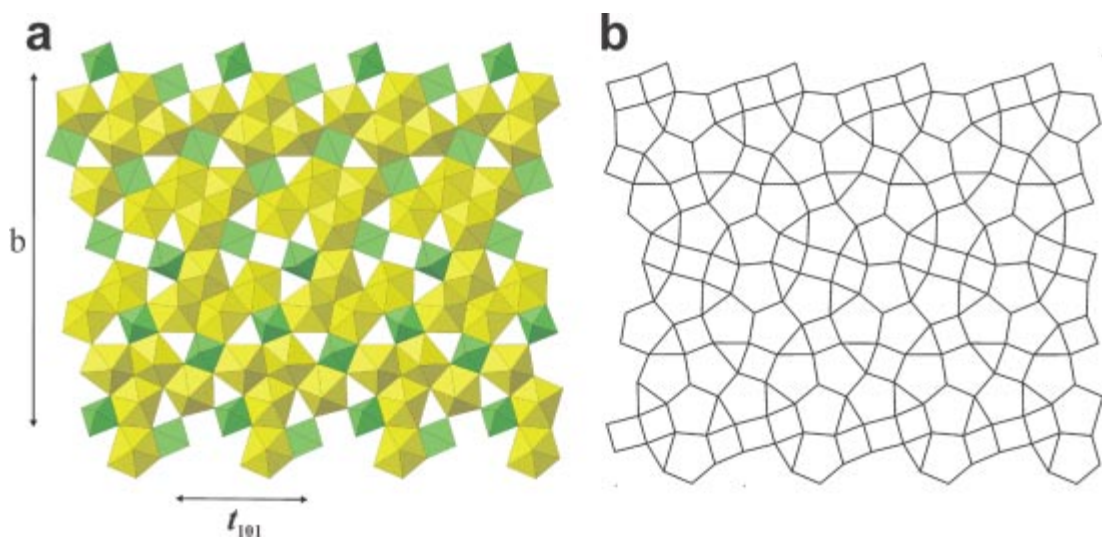


FIG. 2. The uranyl molybdate sheet in the structure of $Tl_2[(UO_2)_2O(MoO_5)]$ (a) and its anion topology (b). Legend: U polyhedra: yellow, Mo polyhedra: green, t_{101} = translation along [101].

Structure description

The structure of $Tl_2[(UO_2)_2O(MoO_5)]$ contains a dense sheet of composition $[(UO_2)_2O(MoO_5)]$ that involves UrO_5 pentagonal bipyramids and MoO_5 polyhedra that share edges (Fig. 2a). Within the sheet, eight UrO_5 bipyramids link by sharing edges, resulting in Z-shaped complexes that are oriented approximately par-

allel to [010]. The MoO_5 polyhedra each include one O atom that is not shared within the sheet; these alternate up and down relative to the plane of the sheet.

The anion topology of the $[(UO_2)_2O(MoO_5)]$ sheet, constructed according to the procedure described by Burns *et al.* (1996), is shown in Figure 2b. It consists of pentagons, squares and triangles. In the corresponding sheet, each pentagon contains a U atom, four-fifths of

the squares are populated by Mo atoms, and the triangles are empty. Among the uranyl molybdates, related anion-topologies have been observed for $\text{Cs}_4[(\text{UO}_2)_3\text{O}(\text{MoO}_4)_2(\text{MoO}_5)]$ (Krivovichev & Burns 2002a) and $\text{Ag}_6[(\text{UO}_2)_3\text{O}(\text{MoO}_4)_5]$ (Krivovichev & Burns 2002c).

The structure is shown projected onto (010) in Figure 3. The uranyl molybdate sheets are parallel to (101) and are linked *via* Tl^+ cations located in the interlayer.

DISCUSSION

The $[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$ sheet in the structure of $\text{Tl}_2[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$ is an example of a uranyl molybdate structural unit with more U than Mo (U:Mo = 2:1). Recently, Obbade *et al.* (2003b) reported two new K uranyl molybdates, $\text{K}_2(\text{UO}_2)_2(\text{MoO}_4)_2\text{O}_2$ and $\text{K}_8(\text{UO}_2)_8(\text{MoO}_5)_3\text{O}_6$. Crystal structures of these compounds contain new uranyl molybdate sheets with the U:Mo ratios of 2:1 and 8:3, respectively. Uranyl molybdates with

U:Mo greater than 1 are of interest because of their potential relationships to the structure of the phase $(\text{Cs}_{2x}\text{Ba}_{1-x})[(\text{UO}_2)_5(\text{MoO}_6)(\text{OH})_6] \cdot n\text{H}_2\text{O}$ ($x \approx 0.4$, $n \approx 6$), which formed owing to the alteration of spent nuclear fuel during hydrologically unsaturated tests designed to simulate conditions expected in the nuclear waste repository at Yucca Mountain, Nevada (Buck *et al.* 1997). Buck *et al.* suggested that the structure of this phase is based upon sheets of U and Mo polyhedra; however, complete determination of the structure was impossible owing to the poor quality of the material available. The characteristic feature of the uranyl molybdate sheets observed in $\text{Tl}_2[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$ (this work) and $\text{K}_2(\text{UO}_2)_2(\text{MoO}_4)_2\text{O}_2$ and $\text{K}_8(\text{UO}_2)_8(\text{MoO}_5)_3\text{O}_6$ (Obbade *et al.* 2003b) is that U polyhedra are arranged in complex islands that are further interlinked *via* Mo polyhedra. It is very likely that the U–Mo sheets in $(\text{Cs}_{2x}\text{Ba}_{1-x})[(\text{UO}_2)_5(\text{MoO}_6)(\text{OH})_6] \cdot n\text{H}_2\text{O}$ share this feature as well.

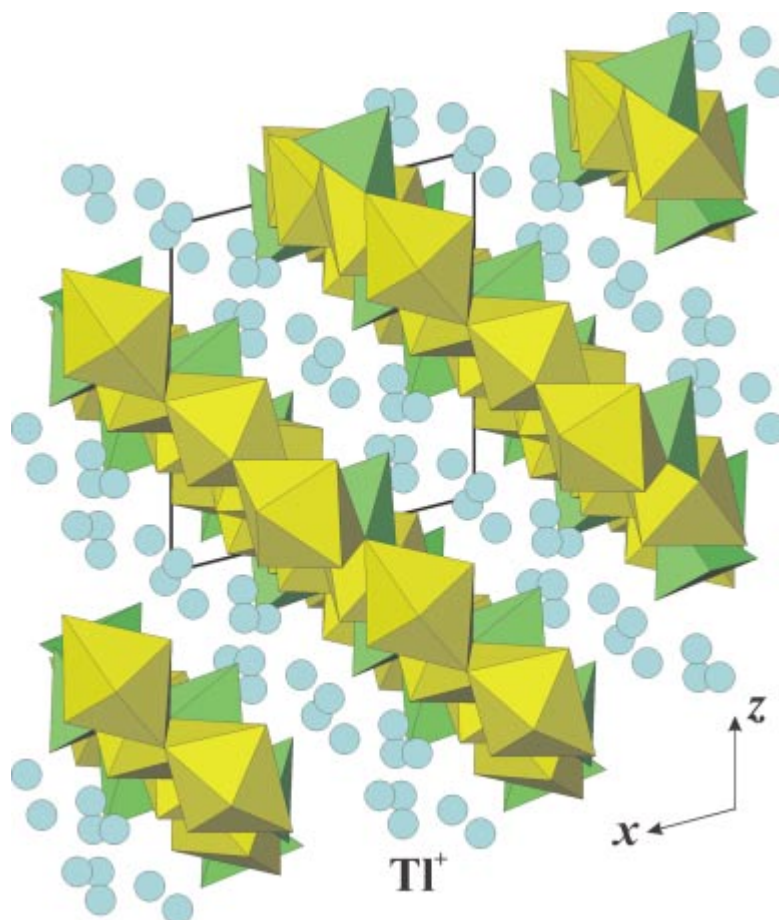


FIG. 3. Projection of the structure of $\text{Tl}_2[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$ onto the plane (010). Legend: U polyhedra: yellow, Mo polyhedra: green, and Tl^+ cations are shown as blue circles.

TABLE 3. SELECTED BOND LENGTHS (Å) IN THE STRUCTURE OF $Tl_2[(UO_2)_2O(MoO_5)]$

U(1)-O(15)	1.808(7)	Mo(2)-O(17)	1.734(7)
U(1)-O(10)e	1.817(7)	Mo(2)-O(18)	1.799(7)
U(1)-O(11)	2.226(6)	Mo(2)-O(19)	1.819(8)
U(1)-O(19)a	2.291(8)	Mo(2)-O(2)	1.906(7)
U(1)-O(18)b	2.328(8)	Mo(2)-O(12)	1.990(7)
U(1)-O(14)	2.370(8)	<Mo(2)-O>	1.85
U(1)-O(5)	2.445(7)		
<U(1)-O _{ir} >	1.81	Tl(1)-O(17)e	2.783(8)
<U(1)-O _{sq} >	2.33	Tl(1)-O(8)	2.856(7)
		Tl(1)-O(9)	2.886(8)
U(2)-O(3)	1.797(7)	Tl(1)-O(3)e	2.899(7)
U(2)-O(4)	1.825(7)	Tl(1)-O(10)e	2.975(7)
U(2)-O(13)	2.199(7)	Tl(1)-O(20)f	2.981(9)
U(2)-O(12)	2.275(7)	Tl(1)-O(11)	3.048(7)
U(2)-O(6)c	2.362(7)	Tl(1)-O(5)	3.139(7)
U(2)-O(5)c	2.369(6)	<Tl(1)-O>	2.95
U(2)-O(7)d	2.509(7)		
<U(2)-O _{ir} >	1.81	Tl(2)-O(1)a	2.853(7)
<U(2)-O _{sq} >	2.34	Tl(2)-O(19)e	2.855(7)
		Tl(2)-O(17)e	2.872(8)
U(3)-O(9)	1.812(7)	Tl(2)-O(17)a	2.892(8)
U(3)-O(16)	1.826(7)	Tl(2)-O(8)	2.993(7)
U(3)-O(13)	2.173(7)	Tl(2)-O(18)g	3.102(8)
U(3)-O(14)	2.295(7)	Tl(2)-O(10)e	3.248(8)
U(3)-O(11)	2.323(8)	Tl(2)-O(15)	3.257(8)
U(3)-O(6)d	2.341(7)	<Tl(2)-O>	3.01
U(3)-O(7)d	2.536(7)		
<U(3)-O _{ir} >	1.82	Tl(3)-O(4)	2.765(8)
<U(3)-O _{sq} >	2.33	Tl(3)-O(16)f	2.792(8)
		Tl(3)-O(1)f	2.878(7)
U(4)-O(1)	1.807(7)	Tl(3)-O(15)f	2.897(7)
U(4)-O(8)	1.832(7)	Tl(3)-O(8)	2.956(7)
U(4)-O(13)	2.245(8)	Tl(3)-O(12)	3.225(8)
U(4)-O(2)a	2.315(7)	<Tl(3)-O>	2.92
U(4)-O(11)	2.330(6)		
U(4)-O(12)	2.365(6)	Tl(4)-O(20)	2.721(8)
U(4)-O(2)	2.416(7)	Tl(4)-O(3)h	2.883(7)
<U(4)-O _{ir} >	1.82	Tl(4)-O(4)i	2.916(7)
<U(4)-O _{sq} >	2.33	Tl(4)-O(10)j	2.951(8)
		Tl(4)-O(16)h	2.966(7)
Mo(1)-O(20)	1.701(7)	Tl(4)-O(9)k	3.156(8)
Mo(1)-O(7)	1.818(8)	<Tl(4)-O>	2.93
Mo(1)-O(14)	1.886(7)		
Mo(1)-O(5)e	1.906(7)		
Mo(1)-O(6)e	1.914(6)		
<Mo(1)-O>	1.85		

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

The structure of $Tl_2[(UO_2)_2O(MoO_5)]$ is closely related to the structures of $M_2[(UO_2)_2O(WO_5)]$ ($M = K, Rb$) recently reported by Obbade *et al.* (2003a). In fact, these structures are based upon the $[(UO_2)_2O(WO_5)]$ sheets of the same topology as observed in the $[(UO_2)_2O(MoO_5)]$ sheets of our compound. Whereas no uranyl molybdate minerals with U:Mo > 1 have been reported so far, Walenta (1985) reported the only known natural uranyl tungstate, uranotungstite, $(Ba,Pb,Fe^{2+})(UO_2)_2(WO_4)(OH)_4(H_2O)_{12}$. The structure of this mineral is unknown, but it is remarkable that it has a U:W ratio of 2:1, *i.e.*, the same as observed for $M_2[(UO_2)_2O(WO_5)]$ ($M = K, Rb$) (Obbade *et al.* 2003a) and for $Tl_2[(UO_2)_2O(MoO_5)]$, reported herein.

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