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CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. VIII. CRYSTAL STRUCTURES OF $Na_3Tl_3[(UO_2)(MoO_4)_4]$, $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$), $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$ AND $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$

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ABSTRACT

Crystals of four sodium uranyl molybdates, $Na_3Tl_3[(UO_2)(MoO_4)_4]$ (**1**), $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$) (**2**), $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$ (**3**) and $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ (**4**), have been synthesized by hydrothermal methods. The structure of each was solved and refined on the basis of F^2 for all unique data collected using Mo$K\alpha$ X-radiation and a CCD-based detector. The structure of **1** [orthorhombic, *Pbcn*, *a* 20.5823(14), *b* 7.4391(5), *c* 26.2514(17) Å, *V* 4019.5(5) Å^3, $Z = 8$] was refined to an $R1$ of 0.060. It is based upon a finite cluster with composition $[(UO_2)_2(MoO_4)_8]^{12-}$ that contains two UrO_5 pentagonal bipyramids and eight MoO_4 tetrahedra. The clusters are linked into a framework through distorted $Na(1)O_6$ and $Na(2)O_6$ octahedra. The Tl atoms and partially occupied Na(3) and Na(4) sites are located within cavities in the framework. The structure of **2** [monoclinic, $P2/c$, *a* 19.7942(11), *b* 7.1913(4), *c* 22.8835(13) Å, β 97.828(1)º, *V* 3227.0(3) Å^3, $Z = 2$] was refined to an $R1$ of 0.050. It contains chains of composition $[(UO_2)(MoO_4)_3]^{4-}$ that are parallel to the *a* axis. The chains are linked into a three-dimensional framework by $Na\phi_5$ and $Na\phi_6$ polyhedra (ϕ: O^{2-}, H_2O) that share edges. The Tl atoms are located in cavities within the framework. The structure of **3** [orthorhombic, $P2_12_12_1$, *a* 10.7662(6), *b* 11.9621(6), *c* 12.8995(7) Å, *V* 1661.3(2) Å^3, $Z = 2$] was refined to an $R1$ of 0.063. It is based on chains of composition $[(UO_2)(MoO_4)_3]^{4-}$ parallel to the *c* axis that are linked into a framework by $Na(1)\phi_6$ octahedra. The Tl atoms and partially occupied Na(2) sites are located in cavities within the framework. The structure of **4** [monoclinic, $P2_1/n$, *a* 8.9023(5), *b* 11.5149(6), *c* 13.8151(7) Å, β 107.743(1)º, *V* 1348.8(1) Å^3, $Z = 4$] was refined to an $R1$ of 0.035. It contains sheets of composition $[(UO_2)(MoO_4)_2]^{2-}$ that are parallel to the (101) plane. $Na\phi_6$ octahedra share edges with each other, giving chains parallel to the *b* axis that link adjacent $[(UO_2)(MoO_4)_2]^{2-}$ sheets into a framework. The four structures are compared to those of related uranyl molybdates.

Keywords: uranyl molybdate, sodium, thallium, crystal structure.

SOMMAIRE

Nous avons synthétisé par voie hydrothermale des cristaux de quatre molybdates uranylés de sodium, $Na_3Tl_3[(UO_2)(MoO_4)_4]$ (**1**), $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$) (**2**), $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$ (**3**) et $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ (**4**). La structure de chaque composé a été résolue et affinée en utilisant les facteurs F^2 de toutes les données uniques, prélevées avec rayonnement Mo$K\alpha$ et un détecteur de type CCD. La structure de **1** [orthorhombique, *Pbcn*, *a* 20.5823(14), *b* 7.4391(5), *c* 26.2514(17) Å, *V* 4019.5(5) Å^3, $Z = 8$] a été affinée jusqu'à un résidu $R1$ de 0.060. Elle repose sur la présence d'un groupement fini ayant une composition $[(UO_2)_2(MoO_4)_8]^{12-}$, qui contient deux bipyramides pentagonales UrO_5 et huit tétraèdres MoO_4. Les groupements sont liés dans une trame grâce à des octaèdres difformes $Na(1)O_6$ et $Na(2)O_6$. Le site des atomes Tl et Na, ces derniers dans des sites partiellement occupés [Na(3) et Na(4)], sont situés dans des cavités dans la trame. La structure de **2** [monoclinique, $P2/c$, *a* 19.7942(11), *b* 7.1913(4), *c* 22.8835(13) Å, β 97.828(1)°, *V* 3227.0(3) Å^3, $Z = 2$] a été affinée jusqu'à un facteur $R1$ de 0.050. Elle contient des chaînes de composition $[(UO_2)(MoO_4)_3]^{4-}$ parallèles à l'axe *a*. Les chaînes sont interliées dans une trame tri-dimensionnelle par des polyèdres $Na\phi_5$ et $Na\phi_6$ (ϕ: O^{2-}, H_2O) partageant des arêtes. Les atomes Tl sont situés dans des cavités de cette trame. La structure de **3** [orthorhombique, $P2_12_12_1$, *a* 10.7662(6), *b* 11.9621(6), *c* 12.8995(7) Å, *V* 1661.3(2) Å^3, $Z = 2$] a été affinée jusqu'à un facteur $R1$ de 0.063. Elle est faite de chaînes de composition $[(UO_2)(MoO_4)_3]^{4-}$ parallèles à l'axe *c*, et liées dans une trame par des octaèdres $Na(1)\phi_6$. Les atomes Tl et les sites Na(2) partiellement occupés sont situés dans des cavités dans cette trame. La structure de **4** [monoclinique, $P2_1/n$, *a* 8.9023(5), *b* 11.5149(6), *c* 13.8151(7) Å, β 107.743(1)°, *V* 1348.8(1) Å^3, $Z = 4$] a été affinée jusqu'à un résidu $R1$ de 0.035. Elle contient des feuillets de composition $[(UO_2)(MoO_4)_2]^{2-}$ parallèles au plan (101). Les octaèdres $Na\phi_6$ partagent des arêtes entre eux, pour donner des chaînes parallèles

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à l'axe *b* qui lient les feuillets $[(UO_2)(MoO_4)_2]^{2-}$ adjacents en une trame. Les quatre structures sont comparées à celles de molybdates uranylés apparentés.

(Traduit par la Rédaction)

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

INTRODUCTION

Sodium- and Ca-bearing uranyl molybdate hydrates are common constituents of the altered zones of U–Mo deposits. Skvortsova *et al.* (1969) described a series of Na and Ca uranyl molybdate hydrates from an unidentified locality in the territory of the former U.S.S.R. They reported that crystals of $Na_2(UO_2)_5(MoO_4)_5(OH)_2{\bullet}8H_2O$ and $Na_2(UO_2)_4(MoO_4)_4(OH)_2{\bullet}12H_2O$ occur on the surfaces of umohoite, U-bearing powellite and sodium uranospinite. These Na uranyl molybdates were not fully characterized, and are not recognized as mineral species. However, their formation as products of alteration in U–Mo deposits is probable, and they may also form owing to oxidative alteration of spent nuclear fuel in a geological repository. Groundwater from the proposed repository at Yucca Mountain contains up to 45.8 mg/L of Na (Wronkiewicz & Buck 1999), and Na uranyl compounds are common products of alteration of spent nuclear fuel under simulated Yucca Mountain conditions (Finch *et al.* 1999).

Several synthetic Na uranyl molybdates have been reported (Dion *et al.* 1977, Dion & Noël 1981a, b, c), and some of their structures were recently determined (Krivovichev & Burns 2001a, Krivovichev *et al.* 2002b). However, the phases studied were obtained by high-temperature solid-state reactions and are anhydrous. The only known synthetic Na uranyl molybdate hydrate is $Na_2(UO_2)(MoO_4)_2(H_2O)_4$, which was first reported by Burnell (1970) and later obtained by Dion & Noël (1981b) by hydration of $Na_2(UO_2)(MoO_4)_2$. Fedoseev *et al.* (1998) also reported the hydrothermal synthesis of $Na_2(UO_2)(MoO_4)_2(H_2O)_4$, but its crystal structure remains unknown. Here, we report the synthesis and crystal structure of $Na_2(UO_2)(MoO_4)_2(H_2O)_4$. We also report the crystal structures of three other uranyl molybdates which, in addition to Na, contain Tl^+ cations.

Dahale *et al.* (1995) reported syntheses of $Tl_2(UO_2)(MoO_4)_2$ and $Tl_2(UO_2)_2(MoO_4)_3$, but a detailed characterization of these phases was not presented. We have synthesized and structurally characterized four Tl uranyl molybdates, $Tl_2(UO_2)(MoO_4)_2$, $Tl_2(UO_2)_2(MoO_4)_3$, $Tl_2[(UO_2)_2O(MoO_5)]$ and $Tl_2[(UO_2)_6(MoO_4)_7(H_2O)](H_2O)$, which will be reported elsewhere. Here we report the crystal structures of three mixed-metal Na and Tl uranyl molybdates. This contribution is a continuation of our series concerning the crystal chemistry of uranyl molybdates (Krivovichev & Burns 2000a, b, 2001a, b, 2002a, b, c, d, e, f, Krivovichev *et al.* 2002a, b).

EXPERIMENTAL

Syntheses of the crystals

In general, we followed the procedure described by Fedoseev *et al.* (1998, 2001) for the synthesis of $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ and $M_2[(UO_2)(MoO_4)_2](H_2O)$ (M = K, Rb, Cs, NH_4).

Crystals used in the current study were obtained by hydrothermal methods using solutions of $Na_2MoO_4{\bullet}4H_2O$, $Tl(NO_3)$ and $(UO_2)(NO_3)_2{\bullet}6H_2O$. For each syntheses, a 1M solution of $Na_2MoO_4{\bullet}4H_2O$ was acidified by addition of concentrated HNO_3 (assay 69.2%), with 0.35 mg HNO_3 added for each 10 mL of 1M solution of $Na_2MoO_4{\bullet}4H_2O$.

$Na_3Tl_3[(UO_2)(MoO_4)_4]$ and $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ (x = 0.1). One mL of 0.075 M solution of $(UO_2)(NO_3)_2{\bullet}6H_2O$, 1 mL of acidified solution of $Na_2MoO_4{\bullet}4H_2O$, and 0.5 mL of 0.2 M solution of $Tl(NO_3)$ were combined in a Teflon container. The solution was heated at 120°C for 2 h, and a yellowish white precipitate formed upon evaporation. The precipitate was suspended in ultrapure water, and insoluble yellow needles of $Na_3Tl_3[(UO_2)(MoO_4)_4]$ (designated **1**) and yellowish transparent plates of $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$) (designated **2**) were recovered.

$Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$. A mixture of 1.5 mL of 0.075 M solution of $(UO_2)(NO_3)_2{\bullet}6H_2O$, 1.5 mL of acidified solution of $Na_2MoO_4{\bullet}4H_2O$ and 1.5 mL of 0.2 M solution of $Tl(NO_3)$ were combined in a Teflon container, followed by heating at 180°C for 1 h. The resulting precipitate was suspended in ultrapure water, and insoluble dark yellow equant crystals of $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$ (designated **3**) were recovered.

$Na_2[(UO_2)(MoO_4)_2](H_2O)_4$. One mL of 0.075 M solution of $(UO_2)(NO_3)_2{\bullet}6H_2O$, 1 mL of acidified solution of $Na_2MoO_4{\bullet}4H_2O$, and 0.33 mL of 0.2 M solution of $Tl(NO_3)$ were combined in a Teflon container, which was heated at 120°C for 2 h. The resulting precipitate was suspended in ultrapure water, and insoluble greenish yellow equant crystals of $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ (designated **4**) were recovered.

The collection of X-ray data

Crystals of each phase were selected for data collection using 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.

Data were collected using monochromated Mo$K\alpha$ X-radiation and framewidths of 0.3° in ω. The unit-cell dimensions (Table 1) were refined using least-squares techniques. The three-dimensional data was reduced and filtered for statistical outliers using the Bruker program SAINT. The data were corrected for Lorentz, polarization and background effects. An empirical correction for absorption was done for each crystal. Additional information pertinent to the data collections is given 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 U, Mo and Tl atoms. Sodium atoms and anions were located in difference-Fourier maps calculated after least-squares refinement of the partial-structure models. Each structure was refined on the basis of F^2 for all unique data. Each final refinement included all atomic positional parameters, with an allowance for anisotropic displacement of all atoms [except for the partially occupied Na(3) and Na(4) sites in **1** and the interstitial H_2O(32) site in **2**], and included a weighting scheme of the structure factors. For **1**, the refinement converged to an agreement index ($R1$) of 6.0%, calculated for the 3508 unique observed reflections ($F_o > 4\sigma_{Fo}$). Final atomic positional and displacement parameters, and selected interatomic distances are in Tables 2 and 3, respectively. For **2**, the refinement converged to an $R1$ of 5.0%, calculated for the 5703 unique observed reflections ($F_o > 4\sigma_{Fo}$). Final atomic positional and displacement parameters, and selected interatomic distances are presented in Tables 4 and 5, respectively. For **3**, the refinement converged to an $R1$ of 6.3%, calculated for the 4100 unique observed reflections ($F_o > 4\sigma_{Fo}$). Final atomic positional and displacement parameters, and selected interatomic distances are shown in Tables 6 and 7, respectively. For **4**, the refinement converged to an $R1$ of 3.5%, calculated for the 3384 unique observed reflections ($F_o > 4\sigma_{Fo}$). Final atomic positional and displacement parameters, and selected interatomic distances are presented in Tables 8 and 9, respectively. Observed and calculated structure-factors for each compound are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

Cation polyhedra

Uranium. In each structure, all U^{6+} cations are strongly bonded to two O atoms each, forming approximately linear uranyl ions [UO_2^{2+}, designated *Ur*], with U–O_{Ur} bond lengths of ~1.8 Å. In all cases, the uranyl ions are coordinated by five anions arranged at the equatorial vertices of UrO_5 pentagonal bipyramids. The U^{6+}–O_{eq} (O_{eq}: equatorial O atom) bond lengths are in the range of 2.32 to 2.39 Å in all four structures.

Molybdenum. In each structure, the Mo^{6+} cations are tetrahedrally coordinated by four O atoms. The <Mo–

TABLE 1. MISCELLANEOUS INFORMATION FOR $Na_3Tl_3[(UO_2)(MoO_4)_4]$ (**1**), $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$) (**2**), $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$ (**3**) AND $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ (**4**)

Compound	**1**	**2**	**3**	**4**
Space group	*Pbcn*	*P*2/*c*	*P*2$_1$2$_1$2$_1$	*P*2$_1$/*n*
a (Å)	20.5823(14)	19.7942(11)	10.7662(6)	8.9023(5)
b (Å)	7.4391(5)	7.1913(4)	11.9621(6)	11.5149(6)
c (Å)	26.2514(17)	22.8835(13)	12.8995(7)	13.8151(7)
β (°)	-	97.828(1)	-	107.743(1)
V (Å^3)	4019.5(5)	3227.0(3)	1661.3(2)	1348.8(1)
Z	8	2	2	4
D_{calc} (g/cm^3)	5.26	4.17	5.29	3.49
μ (cm^{-1})	345.39	201.45	361.82	139.36
Crystal size (mm^3)	0.20 x 0.02 x 0.02	0.24 x 0.06 x 0.02	0.20 x 0.18 x 0.14	0.10 x 0.06 x 0.05
Ref. for cell refinement	5733	5223	4200	3542
Absorption correction	ellipsoid	(001) plate	ellipsoid	ellipsoid
Ref. for abs. corr.	1113	809	821	688
R_{int}	11.66 → 6.98	7.54 → 3.04	5.28 → 4.20	5.58 → 2.64
Total Ref.	41827	31981	18443	14748
Unique Ref.	8298	13134	6773	5543
Unique Ref. [$F_o > 4\sigma F_o$]	3508	5703	4100	3384
S	0.853	0.790	0.906	0.651
*R*1	0.060	0.050	0.063	0.035
*wR*2	0.131	0.086	0.107	0.057

O> bond lengths range from 1.74 to 1.78 Å, whereas individual Mo–O bond lengths vary from 1.718 to 1.84 Å.

Thallium. The coordination polyhedra about the Tl^+ cations are somewhat irregular, owing to the presence of a stereoactive $6s^2$ lone-electron pair on the cation. The coordination numbers for the Tl^+ cations in all structures vary from six to ten, and individual Tl^+–O bond lengths range from 2.55 to 3.44 Å.

Sodium. The coordination environment about the Na^+ cations in the four structures ranges from four to six, with average <Na–ϕ> (ϕ: O^{2-}, H_2O) bond lengths in the range of 2.38 to 2.53 Å. The most common Na coordination polyhedron is a distorted octahedron.

Na and Tl disorder

$Na_3Tl_3[(UO_2)(MoO_4)_4]$. During refinement of the structure of **1**, we noted that the anisotropic displacement parameters of the Na(3) site are strongly elongate, consistent with disorder of the cation over two sites. Subsequently, the Na(3) site was refined as two sites, designated Na(3) and Na(4), with a refined Na(3)–Na(4) distance of 0.90(4) Å, and refined occupancies of 0.35 and 0.65 for Na(3) and Na(4), respectively.

$Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$). There are two partially occupied Tl sites in the structure of **2**; the site occupancies for Tl(2) and Tl(3) are 0.70 and 0.20, respectively. The Tl(3) and $H_2O(32)$ sites are disordered and are separated by 1.59(2) Å. The Na(6) site-occupancy factor is 0.90. These partial occupancies suggest the charge-balance mechanism $Tl \rightarrow H_2O_{1-x} + Na_x$. In this model, the quantity of Tl varies *via* the Tl(3) site, and Na varies *via* Na(6). In the crystal studied, $x \approx 0.1$. Thus, the structural formula of the compound may be written as $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$).

$Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$. In the structure of **3**, Na^+–Tl^+ disorder occurs. The Na(2) and Tl(3) positions are both half-occupied and are separated by 0.89(2) Å.

Bond-valence analysis

Bond-valence sums for the atoms in the structures were calculated using parameters given by Burns *et al.* (1997) for U^{6+}–O bonds and by Brown (2002) for Mo^{6+}–O and Na^+–O bonds. The bond-valence sums for Tl^+–O bonds were calculated using new bond-valence parameters (r_o = 1.801 Å, b = 0.56 Å) recently derived by Locock & Burns (unpubl. results). The results are sum-

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $Na_3Tl_3[(UO_2)(MoO_4)_4]$ (**1**)

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.50971(3)	0.37338(9)	0.12930(2)	0.0155(1)	0.0090(2)	0.0218(3)	0.0156(3)	-0.0018(3)	0.0002(2)	-0.0010(2)
Mo(1)	0.40279(7)	0.7642(2)	-0.00948(6)	0.0187(3)	0.0138(7)	0.0230(8)	0.0192(7)	0.0012(7)	0.0006(5)	0.0017(6)
Mo(2)	0.39264(7)	0.3970(2)	0.24780(5)	0.0170(3)	0.0113(6)	0.0248(7)	0.0150(7)	0.0011(6)	0.0017(5)	0.0010(5)
Mo(3)	0.67391(7)	-0.3644(2)	0.12343(5)	0.0168(3)	0.0137(6)	0.0194(7)	0.0174(7)	0.0018(6)	0.0005(5)	-0.0029(6)
Mo(4)	0.34990(8)	0.1179(2)	0.11875(6)	0.0255(3)	0.0248(8)	0.0275(9)	0.0240(8)	-0.0056(7)	0.0057(6)	-0.0069(7)
Tl(1)	0.32829(4)	0.62135(12)	0.11755(3)	0.0348(2)	0.0309(4)	0.0412(5)	0.0323(4)	-0.0033(4)	-0.0017(3)	0.0026(4)
Tl(2)	0.57676(4)	-0.25801(11)	0.00878(3)	0.0302(2)	0.0239(4)	0.0364(4)	0.0303(4)	-0.0015(4)	-0.0096(3)	-0.0019(3)
Tl(3)	0.21487(4)	0.39732(10)	0.24619(3)	0.0338(2)	0.0291(4)	0.0315(4)	0.0409(5)	-0.0077(4)	-0.0018(3)	-0.0013(3)
Na(1)	0.8404(3)	-0.3695(8)	0.1344(3)	0.022(2)	0.013(3)	0.013(3)	0.040(4)	-0.013(3)	0.014(3)	-0.011(3)
Na(2)	0.2590(4)	0.0386(11)	-0.0162(3)	0.033(2)	0.018(4)	0.037(4)	0.046(5)	-0.009(4)	0.000(3)	-0.001(3)
Na(3)**	0.967(2)	-0.668(5)	0.1870(16)	0.070(15)*						
Na(4)***	0.9949(9)	-0.637(2)	0.1622(8)	0.059(7)*						
O(1)	0.4133(5)	0.2709(17)	0.0954(4)	0.024(3)	0.011(6)	0.040(8)	0.022(6)	0.009(6)	-0.001(5)	-0.004(5)
O(2)	0.3503(6)	0.5992(16)	0.0135(5)	0.024(3)	0.018(6)	0.022(7)	0.031(7)	0.000(6)	0.003(5)	-0.005(5)
O(3)	0.5411(5)	0.1478(16)	0.1409(4)	0.021(3)	0.012(5)	0.025(7)	0.027(7)	-0.004(5)	0.006(5)	-0.002(5)
O(4)	0.4686(6)	0.6544(15)	-0.0438(4)	0.020(3)	0.023(6)	0.018(6)	0.018(6)	-0.001(5)	-0.003(5)	-0.004(5)
O(5)	0.3591(7)	0.9173(17)	-0.0492(5)	0.031(3)	0.034(8)	0.030(8)	0.029(8)	0.005(6)	-0.005(6)	0.008(6)
O(6)	0.4387(6)	0.8817(18)	0.0392(5)	0.034(3)	0.023(7)	0.038(8)	0.040(8)	0.008(7)	-0.010(6)	0.009(6)
O(7)	0.7120(6)	-0.3029(17)	0.0666(5)	0.028(3)	0.023(7)	0.036(8)	0.026(7)	-0.005(6)	0.007(5)	-0.005(6)
O(8)	0.3401(7)	0.5621(17)	0.2267(5)	0.032(3)	0.035(8)	0.024(7)	0.037(8)	0.001(6)	-0.019(6)	0.006(6)
O(9)	0.6207(6)	-0.5466(18)	0.1128(5)	0.027(3)	0.017(6)	0.033(7)	0.031(7)	-0.001(6)	0.007(5)	0.003(5)
O(10)	0.4427(6)	0.4963(17)	0.2954(4)	0.026(3)	0.013(6)	0.040(8)	0.024(7)	0.000(6)	-0.010(5)	-0.008(5)
O(11)	0.6325(7)	-0.1813(17)	0.1496(5)	0.035(3)	0.041(9)	0.019(7)	0.044(9)	-0.002(6)	0.022(7)	-0.002(6)
O(12)	0.4820(6)	0.5961(19)	0.1198(5)	0.033(3)	0.015(6)	0.043(9)	0.041(8)	0.002(7)	0.003(5)	0.010(6)
O(13)	0.3457(6)	0.2273(18)	0.2763(5)	0.030(3)	0.032(8)	0.037(8)	0.021(7)	0.004(6)	0.006(5)	-0.010(6)
O(14)	0.2967(7)	0.235(2)	0.1601(6)	0.049(4)	0.022(8)	0.058(10)	0.068(11)	-0.016(9)	0.025(7)	-0.007(7)
O(15)	0.7351(7)	-0.428(2)	0.1668(6)	0.043(4)	0.029(8)	0.052(10)	0.049(10)	0.006(8)	-0.013(7)	-0.007(7)
O(16)	0.3808(9)	-0.0596(19)	0.1554(6)	0.050(4)	0.085(13)	0.028(8)	0.036(9)	0.000(7)	0.017(8)	-0.010(8)
O(17)	0.3060(7)	0.034(2)	0.0673(6)	0.044(4)	0.018(7)	0.065(10)	0.049(9)	-0.025(8)	0.011(6)	-0.016(7)
O(18)	0.4397(6)	0.3020(19)	0.1975(5)	0.035(3)	0.024(7)	0.051(9)	0.029(8)	-0.016(7)	0.006(6)	-0.002(7)

* refined isotropically. ** s.o.f. = 0.35(4). *** s.o.f. = 0.65(4).

marized in Table 10. The bond-valence sums for all atoms are in agreement with their expected formal valences. The sums for the H_2O sites are in the range of 0 to 0.41 *vu* (valence units), which is in agreement with their assignment as H_2O groups.

Description of the structures

$Na_3Tl_3[(UO_2)(MoO_4)_4]$. The structure of **1** contains a finite cluster of polyhedra with composition $[(UO_2)_2(MoO_4)_8]^{12-}$ (Fig. 1a). The cluster contains two *Ur*O_5 pentagonal bipyramids and eight MoO_4 tetrahedra. The *Ur*O_5 pentagonal bipyramids are linked by sharing equatorial vertices with two $Mo(2)O_4$ tetrahedra. The $Mo(1)O_4$, $Mo(3)O_4$ and $Mo(4)O_4$ tetrahedra are attached to the cluster by sharing single equatorial vertices of the *Ur*O_5 pentagonal bipyramids. The $[(UO_2)_2(MoO_4)_8]^{12-}$ clusters extend along [001] and are parallel to (010) (Fig. 2a). The clusters are linked into a framework through the $Na(1)O_6$ and $Na(2)O_6$ distorted octahedra (Fig. 2a). The Tl atoms and partially occupied Na(3) and Na(4) atoms are located in cavities within the framework.

$Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$). The structure of **2** is based upon chains of composition $[(UO_2)(MoO_4)_3]^{4-}$ that are parallel to the *a* axis (Fig. 1e). The chains contain *Ur*O_5 pentagonal bipyramids that share all of their equatorial corners with MoO_4 tetrahedra. The $Mo(1)O_4$, $Mo(2)O_4$, $Mo(4)O_4$ and $Mo(5)O_4$ tetrahedra bridge adjacent *Ur*O_5 bipyramids (and therefore are 2-connected), whereas the $Mo(3)O_4$ tetrahedra each share one corner with a *Ur*O_5 bipyramid (and are 1-connected tetrahedra). The chains are highly distorted, and have a somewhat helical structure (Figs. 1e, f). The $[(UO_2)(MoO_4)_3]^{4-}$ chains are linked into a three-dimensional framework through the $Na\phi_5$ and $Na\phi_6$ polyhedra, which share edges with each other (Fig. 2b). The Tl^+ cations are located in cavities within the framework.

$Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$. The structure of **3** contains chains of polyhedra with composition $[(UO_2)(MoO_4)_3]^{4-}$ that are parallel to the *c* axis (Figs. 1c, d). The chains are topologically identical to those in the structure of 2. The $Mo(2)O_4$, and $Mo(3)O_4$ tetrahedra are 2-connected, whereas the $Mo(1)O_4$ tetrahedra are 1-connected. In contrast to the chains in the structure of 2, the $[(UO_2)(MoO_4)_3]^{4-}$ chains in 3 are almost planar and parallel to (010) (Figs. 1d, 2c). The chains are linked into a three-dimensional framework by $Na(1)\phi_6$ octahedra (Fig. 2c), and the Tl^+ cations and partially occupied Na(2) sites are located in cavities within the framework.

$Na_2[(UO_2)(MoO_4)_2](H_2O)_4$. The structure of **4** is based upon sheets of composition $[(UO_2)(MoO_4)_2]^{2-}$ that contain *Ur*O_5 pentagonal bipyramids that share their equatorial corners with MoO_4 tetrahedra (Fig. 3a). Each *Ur*O_5 pentagonal bipyramid shares all five of its equatorial corners with MoO_4 tetrahedra, and thus is 5-connected, whereas the $Mo(1)O_4$ tetrahedra are 3-connected and the $Mo(2)O_4$ tetrahedra are 2-connected. The sheets are parallel to the (101) plane (Fig. 2d). $Na\phi_6$ octahedra share edges with each other, forming chains parallel to the *b* axis, which link adjacent $[(UO_2)(MoO_4)_2]^{2-}$ sheets into a three-dimensional framework. The $H_2O(9)$ and $H_2O(13)$ groups are bonded to Na^+ cations, whereas the $H_2O(14)$ groups are held in framework cavities by H bonds only.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) FOR $Na_3Tl_3[(UO_2)(MoO_4)_4]$ (1)

U-O(12)	1.77(1)	Tl(3)-O(8)j	2.79(1)
U-O(3)	1.82(1)	Tl(3)-O(15)m	2.82(1)
U-O(4)a	2.30(1)	Tl(3)-O(13)l	2.86(1)
U-O(1)	2.30(1)	Tl(3)-O(8)	2.90(1)
U-O(18)	2.36(1)	Tl(3)-O(14)	3.07(1)
U-O(10)b	2.39(1)	Tl(3)-O(13)	3.08(1)
U-O(9)c	2.40(1)	Tl(3)-O(16)l	3.11(2)
<U-O_{Ur}>	1.80	Tl(3)-O(11)p	3.27(2)
<U-O_{eq}>	2.35	Tl(3)-O(15)p	3.35(2)
		Tl(3)-O(14)l	3.39(2)
Mo(1)-O(6)	1.72(1)	<Tl(3)-O>	3.06
Mo(1)-O(2)	1.74(1)		
Mo(1)-O(5)	1.79(1)	Na(1)-O(5)d	2.30(2)
Mo(1)-O(4)	1.82(1)	Na(1)-O(15)	2.37(2)
<Mo(1)-O>	1.77	Na(1)-O(11)e	2.42(1)
		Na(1)-O(3)e	2.45(1)
Mo(2)-O(8)	1.73(1)	Na(1)-O(13)f	2.46(1)
Mo(2)-O(13)	1.76(1)	Na(1)-O(9)g	2.60(1)
Mo(2)-O(10)	1.78(1)	<Na(1)-O>	2.43
Mo(2)-O(18)	1.78(1)		
<Mo(2)-O>	1.76	Na(2)-O(17)	2.40(2)
		Na(2)-O(7)h	2.40(1)
Mo(3)-O(7)	1.74(1)	Na(2)-O(5)i	2.41(2)
Mo(3)-O(11)	1.75(1)	Na(2)-O(2)j	2.42(1)
Mo(3)-O(15)	1.76(1)	Na(2)-O(7)k	2.44(2)
Mo(3)-O(9)	1.76(1)	<Na(2)-O>	2.41
<Mo(3)-O>	1.75		
		Na(3)-O(11)e	2.27(4)
Mo(4)-O(17)	1.74(1)	Na(3)-O(10)n	2.59(4)
Mo(4)-O(16)	1.75(2)	Na(3)-O(3)e	2.65(4)
Mo(4)-O(14)	1.77(1)	Na(3)-O(12)o	2.70(4)
Mo(4)-O(1)	1.84(1)	<Na(3)-O>	2.55
<Mo(4)-O>	1.78		
		Na(4)-O(3)c	2.31(2)
Tl(1)-O(2)	2.77(1)	Na(4)-O(12)o	2.33(2)
Tl(1)-O(16)c	2.79(2)	Na(4)-O(16)e	2.63(3)
Tl(1)-O(8)	2.91(1)	Na(4)-O(11)e	2.66(2)
Tl(1)-O(14)l	2.93(2)	<Na(4)-O>	2.48
Tl(1)-O(17)l	3.13(1)		
Tl(1)-O(14)	3.15(2)		
Tl(1)-O(12)	3.17(1)		
Tl(1)-O(11)	3.19(1)		
Tl(1)-O(17)c	3.37(2)		
<Tl(1)-O>	3.05		
Tl(2)-O(4)i	2.70(1)		
Tl(2)-O(1)k	2.74(1)		
Tl(2)-O(2)k	3.01(1)		
Tl(2)-O(5)a	3.05(1)		
Tl(2)-O(6)a	3.09(1)		
Tl(2)-O(6)i	3.13(1)		
Tl(2)-O(7)	3.19(1)		
Tl(2)-O(4)k	3.23(1)		
<Tl(2)-O>	3.02		

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

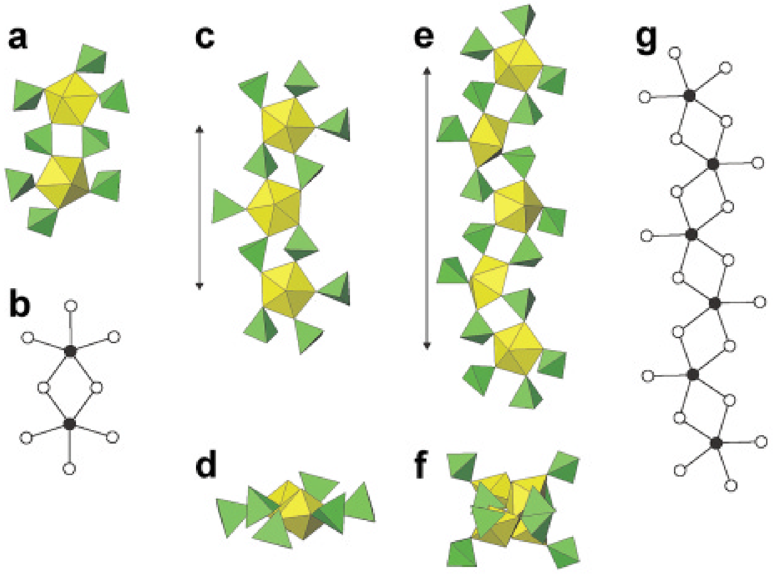

FIG. 1. (a) The $[(UO_2)_2(MoO_4)_8]^{12-}$ cluster in the structure of $Na_3Tl_3[(UO_2)(MoO_4)_4]$ (**1**) and (b) its nodal representation. (c, d) The $[(UO_2)(MoO_4)_3]^{4-}$ chain in the structure of $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$ (**3**). (e, f) The $[(UO_2)(MoO_4)_3]^{2-}$ chain in the structure of $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$) (**2**). (g) Nodal representation of the $[(UO_2)(MoO_4)_3]^{4-}$ chain.

DISCUSSION

Nodal representation of uranyl molybdate units

Krivovichev *et al.* (2002a, b) reported that the topological structure of uranyl molybdate units may be described using a nodal representation. Each node corresponds to a $Ur\phi_n$ bipyramid (ϕ: O^{2-}, H_2O; n = 4 or 5) (black circle) or a MoO_4 tetrahedron (white circle) (Fig. 1). Nodes are connected if the polyhedra share at least one common vertex, and the number of connecting lines corresponds to the number of anions common to the polyhedra. Thus, each uranyl molybdate structural unit can be associated with a black-and-white graph that represents a topology of polyhedron linkage. The graphs for uranyl molybdate units observed in the structures reported in this study are shown in Figures 1 and 3: the $[(UO_2)(MoO_4)_4]^{6-}$ cluster is shown in Figure 1b, the $[(UO_2)(MoO_4)_3]^{4-}$ chains, in Figure 1g, and the $[(UO_2)(MoO_4)_2]^{2-}$ sheet, in Figure 3c.

Comparison with related compounds

$Na_3Tl_3[(UO_2)(MoO_4)_4]$. The only other uranyl compound that contains a cluster with composition $[(UO_2)_2(TO_4)_8]$ (*T*: tetrahedrally coordinated cation) is $Na_6[(UO_2)(MoO_4)_4]$ (Krivovichev & Burns 2001a). Note that the compounds $M_6[(UO_2)(MoO_4)_4]$ (*M* = Rb, Cs) (Krivovichev & Burns 2002a, c), although chemically similar to $Na_6[(UO_2)(MoO_4)_4]$, contain a different cluster of composition $[(UO_2)(MoO_4)_4]^{6-}$, which consists of a UrO_4 tetragonal bipyramid that shares its equatorial vertices with four MoO_4 tetrahedra.

$Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ ($x = 0.1$) and $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$. These two compounds are based on topologically identical $[(UO_2)(MoO_4)_3]^{4-}$ chains of UrO_5 pentagonal bipyramids and MoO_4 tetrahedra. Topologically identical chains have not been previously observed in uranyl molybdates. However, similar chains with composition $[(UO_2)(CrO_4)_3]^{4-}$ were recently described in the structures of $K_5[(UO_2)(CrO_4)_3](NO_3)(H_2O)_3$ (Krivovichev & Burns 2002g) and $Na_4[(UO_2)(CrO_4)_3]$ (Krivovichev & Burns, in prep.). Chains in which the TO_4 tetrahedra are replaced by SeO_3 pyramids occur in the structure of demesmaekerite, $Pb_2Cu_5[(UO_2)(SeO_3)_3](OH)_6(H_2O)_2$ (Ginderow & Cesbron 1983).

$Na_2[(UO_2)(MoO_4)_2](H_2O)_4$. The $[(UO_2)(MoO_4)_2]^{2-}$ sheet observed in the structure of **4** is a member of a topological type that is abundant in the structures of uranyl molybdates (for more about the combinatorial topology of uranyl molybdate sheets, see Krivovichev & Burns 2002d). The structures of $M_2[(UO_2)(MoO_4)_2]$ [*M* = Cs (Krivovichev & Burns, in prep.), Rb (Krivo-

vichev & Burns 2002c), K (Sadikov *et al.* 1988), Tl (Krivovichev *et al.*, in prep.)], $M_2[(UO_2)(MoO_4)_2](H_2O)$ [*M* = K (Krivovichev *et al.* 2002b), Rb (Khrustalev *et al.* 2000), Cs (Rastsvetaeva *et al.* 1999), NH_4 (Andreev *et al.* 2001)], and $(C_5H_{14}N_2)[(UO_2)(MoO_4)_2](H_2O)$ (Shiv Halasayamani *et al.* 1999) all contain similar sheets. A sheet with composition $[(UO_2)(SeO_3)_2]^{2-}$ also has the same topology, and occurs in the structures of $M[(UO_2)(HSeO_3)(SeO_3)]$ (*M* = NH_4, K, Rb, Cs, Tl) (Koskenlinna & Valkonen 1996, Almond & Albrecht-Schmitt 2002) and $(NH_4)_2[(UO_2)(SeO_3)_2](H_2O)_{0.5}$ (Koskenlinna *et al.* 1997).

It is interesting to compare the uranyl molybdate sheet observed in the structure of **4** with that observed in its anhydrous analogue, $Na_2[(UO_2)(MoO_4)_2]$ (Krivovichev *et al.* 2002b). The corresponding $[(UO_2)(MoO_4)_2]^{2-}$ sheets are shown in Figures 3a and 3b, respectively. Their nodal representations are given in Figures 3c and 3d, respectively. It is clear that, despite their chemical identity, the sheets are topologically

TABLE 4. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ (x = 0.1) (**2**)

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.30498(2)	0.32356(7)	0.14435(2)	0.0119(1)	0.0121(2)	0.0133(2)	0.0103(2)	0.0001(2)	0.0020(2)	0.00111(19)
U(2)	-0.18434(2)	-0.34747(7)	0.13618(2)	0.0134(1)	0.0116(2)	0.0173(3)	0.0114(3)	0.0007(2)	0.0021(2)	-0.00128(19)
Tl(1)	0.48894(3)	0.52392(8)	0.09434(3)	0.0282(2)	0.0269(3)	0.0255(3)	0.0314(4)	-0.0053(3)	0.0008(3)	-0.0022(3)
Tl(2)*	0	-0.67522(18)	0.25	0.0255(3)	0.0247(5)	0.0343(7)	0.0201(6)	0	0.0122(5)	0
Tl(3)**	-0.21575(12)	0.1447(4)	0.07311(12)	0.0164(5)	0.0186(11)	0.0156(13)	0.0159(13)	0.003(1)	0.006(1)	0.0048(10)
Mo(1)	0.14674(5)	0.31323(16)	0.02706(5)	0.0134(2)	0.0150(5)	0.0150(6)	0.0105(6)	0.0006(5)	0.0025(5)	0.0013(4)
Mo(2)	0.67240(5)	0.34437(16)	0.18297(5)	0.0130(2)	0.0150(5)	0.0122(5)	0.0113(6)	0.0000(5)	-0.0002(4)	-0.0023(4)
Mo(3)	0.44974(5)	0.02633(16)	0.11037(5)	0.0153(2)	0.0145(5)	0.0174(6)	0.0147(6)	0.0001(5)	0.0048(5)	0.0034(5)
Mo(4)	0.65040(5)	0.62143(15)	0.02228(5)	0.0126(2)	0.0131(5)	0.0142(6)	0.0104(6)	0.0003(4)	0.0017(4)	-0.0005(4)
Mo(5)	-0.14739(5)	-0.42124(16)	0.31123(5)	0.0151(2)	0.0177(5)	0.0153(6)	0.0119(6)	0.0013(5)	0.0000(5)	-0.0028(5)
Mo(6)	-0.03768(6)	-0.02770(17)	0.11189(6)	0.0183(3)	0.0192(5)	0.0162(6)	0.0208(7)	-0.0014(5)	0.0078(5)	-0.0042(5)
Na(1)	0.0978(3)	-0.1927(8)	0.0406(3)	0.0285(14)	0.032(3)	0.020(3)	0.033(4)	-0.002(3)	0.003(3)	-0.002(3)
Na(2)	0.4007(3)	-0.1270(7)	-0.0321(3)	0.0243(13)	0.028(3)	0.019(3)	0.026(3)	0.004(2)	0.002(3)	0.006(2)
Na(3)	0.6297(3)	0.8592(7)	0.1612(2)	0.0213(12)	0.029(3)	0.020(3)	0.015(3)	-0.004(2)	0.002(2)	-0.005(2)
Na(4)	-0.0131(3)	0.4540(8)	0.0761(2)	0.0237(13)	0.024(3)	0.029(3)	0.019(3)	0.003(3)	0.006(3)	-0.009(2)
Na(5)	-0.1410(3)	-0.9132(8)	0.3305(3)	0.0281(14)	0.035(3)	0.025(3)	0.025(4)	0.003(3)	0.005(3)	-0.001(3)
Na(6)***	0.5	-0.2392(13)	0.25	0.029(2)	0.040(5)	0.040(6)	0.006(5)	0	0.002(4)	0
Na(7)	0.2700(4)	-0.2046(11)	0.0867(4)	0.069(3)	0.096(6)	0.045(5)	0.075(7)	-0.003(4)	0.040(5)	-0.009(4)
O(1)	0.5876(4)	0.4527(13)	0.0203(4)	0.026(2)	0.017(4)	0.023(6)	0.038(7)	-0.004(5)	-0.005(4)	-0.008(4)
O(2)	0.1189(5)	0.1294(12)	0.0654(4)	0.027(2)	0.043(6)	0.016(5)	0.024(6)	-0.004(4)	0.017(5)	-0.016(4)
O(3)	0.2716(4)	0.0931(11)	0.1360(4)	0.015(2)	0.017(4)	0.013(5)	0.014(5)	-0.002(4)	0.005(4)	-0.002(4)
O(4)	-0.1194(4)	-0.5088(13)	0.1212(4)	0.025(2)	0.024(5)	0.026(6)	0.028(6)	0.009(5)	0.008(5)	-0.002(4)
O(5)	0.2167(4)	0.4258(13)	0.0714(4)	0.022(2)	0.022(5)	0.027(6)	0.017(6)	-0.003(4)	0.000(4)	-0.001(4)
O(6)	0.0821(4)	0.4792(13)	0.0153(4)	0.017(2)	0.014(4)	0.026(5)	0.011(5)	0.001(4)	0.000(4)	0.006(4)
O(7)	0.4144(4)	0.1953(13)	0.1577(4)	0.021(2)	0.015(4)	0.030(6)	0.017(5)	-0.007(4)	0.000(4)	0.012(4)
O(8)	0.6438(4)	0.1692(13)	0.1350(4)	0.025(2)	0.032(5)	0.014(5)	0.025(6)	-0.006(4)	-0.004(5)	-0.007(4)
O(9)	0.3894(4)	-0.1198(13)	0.0737(4)	0.026(2)	0.027(5)	0.027(6)	0.024(6)	-0.013(5)	0.004(5)	-0.006(4)
O(10)	0.1700(4)	0.2251(13)	-0.0383(4)	0.022(2)	0.030(5)	0.030(6)	0.006(5)	0.000(4)	0.001(4)	-0.010(4)
O(11)	0.7585(4)	0.4047(12)	0.1769(4)	0.020(2)	0.025(5)	0.016(5)	0.018(6)	0.003(4)	0.000(4)	-0.001(4)
O(12)	0.3382(4)	0.5570(13)	0.1529(4)	0.022(2)	0.032(5)	0.023(5)	0.011(5)	0.004(4)	-0.002(4)	-0.003(4)
O(13)	0.7281(4)	0.5315(13)	0.0596(4)	0.023(2)	0.028(5)	0.025(6)	0.017(5)	0.006(4)	0.005(4)	0.002(4)
O(14)	-0.1074(4)	-0.1107(12)	0.1471(4)	0.022(2)	0.021(5)	0.024(6)	0.023(6)	0.005(4)	0.006(4)	-0.011(4)
O(15)	0.6192(4)	0.5394(13)	0.1687(5)	0.028(3)	0.021(5)	0.013(5)	0.046(7)	0.004(5)	-0.010(5)	0.000(4)
O(16)	0.6558(4)	0.6810(14)	-0.0549(4)	0.026(2)	0.015(4)	0.047(7)	0.016(5)	0.002(5)	0.004(4)	0.004(5)
O(17)	0.6231(4)	0.8149(13)	0.0579(4)	0.026(2)	0.034(5)	0.025(6)	0.015(5)	0.000(4)	-0.008(4)	0.003(5)
O(18)	-0.2476(4)	-0.1854(13)	0.1518(4)	0.024(2)	0.018(4)	0.023(6)	0.032(6)	0.003(5)	0.008(4)	-0.001(4)
O(19)	-0.0022(4)	-0.2106(12)	0.0750(4)	0.023(2)	0.021(5)	0.019(5)	0.029(6)	-0.004(4)	0.001(5)	0.007(4)
O(20)	-0.2108(5)	-0.5942(14)	0.3118(4)	0.029(3)	0.032(5)	0.039(7)	0.022(6)	-0.004(5)	0.022(5)	-0.012(5)
O(21)	0.5076(4)	-0.1155(13)	0.1560(5)	0.028(2)	0.026(5)	0.026(6)	0.031(7)	0.003(5)	0.007(5)	0.009(4)
O(22)	0.6631(4)	0.2655(13)	0.2563(4)	0.022(2)	0.020(5)	0.035(6)	0.011(5)	0.000(4)	0.005(4)	-0.011(4)
O(23)	-0.1409(4)	-0.3551(15)	0.2393(4)	0.033(3)	0.031(5)	0.044(7)	0.023(6)	0.005(5)	-0.001(5)	-0.026(5)
O(24)	0.4917(4)	0.1393(14)	0.0618(4)	0.031(3)	0.029(5)	0.036(7)	0.030(7)	0.003(5)	0.016(5)	0.007(5)
O(25)	-0.0717(4)	-0.5190(15)	0.3427(4)	0.034(3)	0.029(5)	0.038(7)	0.027(6)	-0.002(5)	-0.019(5)	0.008(5)
O(26)	-0.0623(5)	0.1481(13)	0.0601(5)	0.039(3)	0.062(7)	0.012(5)	0.046(8)	0.009(5)	0.019(6)	0.010(5)
H_2O(27)	0.6198(5)	0.8621(14)	0.2644(4)	0.034(3)	0.043(6)	0.040(7)	0.020(6)	-0.005(5)	0.005(5)	0.004(5)
H_2O(28)	-0.1408(5)	-0.8512(15)	0.2334(5)	0.038(3)	0.045(6)	0.039(7)	0.025(6)	-0.011(5)	-0.008(5)	0.014(5)
O(29)	-0.1650(5)	-0.2333(14)	0.3554(5)	0.034(3)	0.037(6)	0.027(6)	0.037(7)	-0.007(5)	-0.003(5)	0.005(5)
O(30)	0.0228(5)	0.0648(16)	0.1631(5)	0.048(3)	0.030(6)	0.061(9)	0.052(9)	-0.016(7)	0.002(6)	-0.031(6)
H_2O(31)	0.5	-0.572(2)	0.25	0.050(5)	0.039(9)	0.063(13)	0.043(12)	0	-0.013(8)	0
H_2O(32)S	-0.2158(7)	0.176(2)	0.0042(7)	0.058(4)						

*s.o.f. = 0.70 ** s.o.f. = 0.20. *** s.o.f. = 0.90. \$ s.o.f. – 0.80 (refined isotropically).

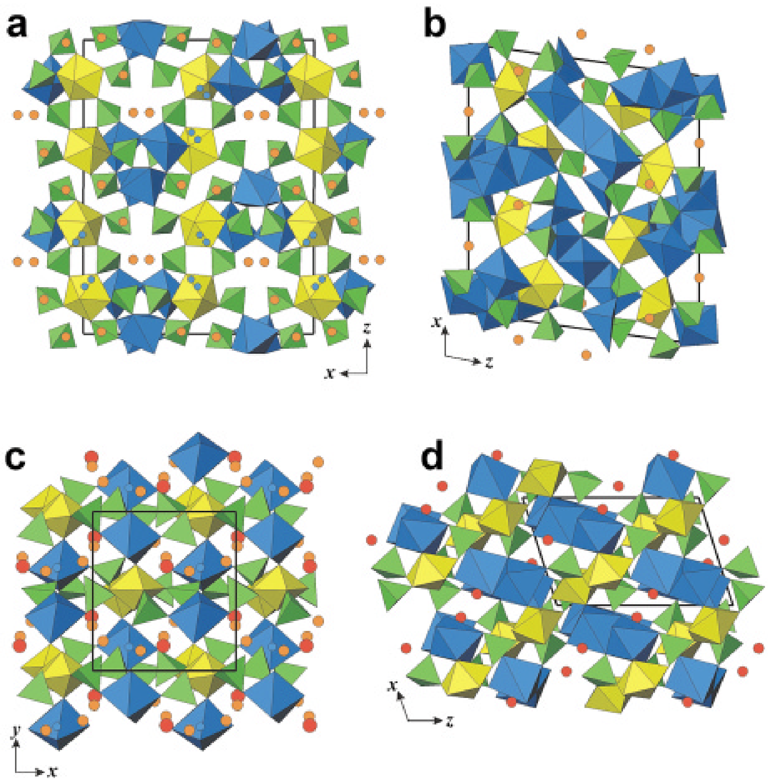

FIG. 2. (a) The structure of $Na_3Tl_3[(UO_2)(MoO_4)_4]$ (**1**) projected along the *b* axis. (b) The structure of $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ (x = 0.1) (**2**) projected along the *b* axis. (c) The structure of $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$ (**3**) projected along the *c* axis. (d) The structure of $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ (**4**) projected along the *b* axis. Legend: UrO$_5$ bipyramids: yellow; MoO_4 tetrahedra: green; Na polyhedra: blue; Tl atoms: orange; Na atoms: blue; H_2O groups: red.

different. Krivovichev & Burns (2002d) suggested that the topologies of uranyl molybdate sheets consisting of corner-sharing $Ur\phi_n$ bipyramids and MoO_4 tetrahedra be described as derivatives of the black-and-white graph shown in Figure 3f. By deleting elements of this graph (vertices and connecting lines), the range of topologies observed in uranyl compounds with tetrahedral or pseudotetrahedral oxyanions may be obtained. The idealized versions of the graphs shown in Figures 3c and 3d are given in Figures 3e and g. Each can be obtained from the graph shown in Figure 3f by deleting some of its connecting lines. Note that there is no topological transformation (*i.e.*, a transformation that conserves the topological structure of a graph) that can make the graph shown in Figure 3e into that in Figure 3g. This is interesting because Dion & Noël (1981b) obtained crystals of $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ during hydration of $Na_2(UO_2)(MoO_4)_2$. The calculated X-ray powder-diffraction pattern for **4** (based on structure data reported herein) is not identical to that reported by Dion & Noël (1981b) [PDF card 35–0349], although the strongest lines generally coincide. Thus the hydration involves not only incorporation of H_2O molecules into the interlayer, but also an essential topological reconstruction of the uranyl molybdate sheets.

Phase **4** is isotypic with $Na_2[(UO_2)(SeO_4)_2](H_2O)_4$ (Mikhailov *et al*. 2001; the space group reported by those authors is different from that for the current structure owing to the difference in unit-cell settings).

Flexibility of the $[(UO_2)(MoO_4)_3]^{4-}$ uranyl molybdate chains

As noted above, **2** and **3** contain topologically identical $[(UO_2)(MoO_4)_3]^{4-}$ chains. However, the geometrical parameters of the chains are rather different. Figures 1d and 1f provide views of the chains along their length. The uranyl pentagonal bipyramids in the chain in **3** (Fig.

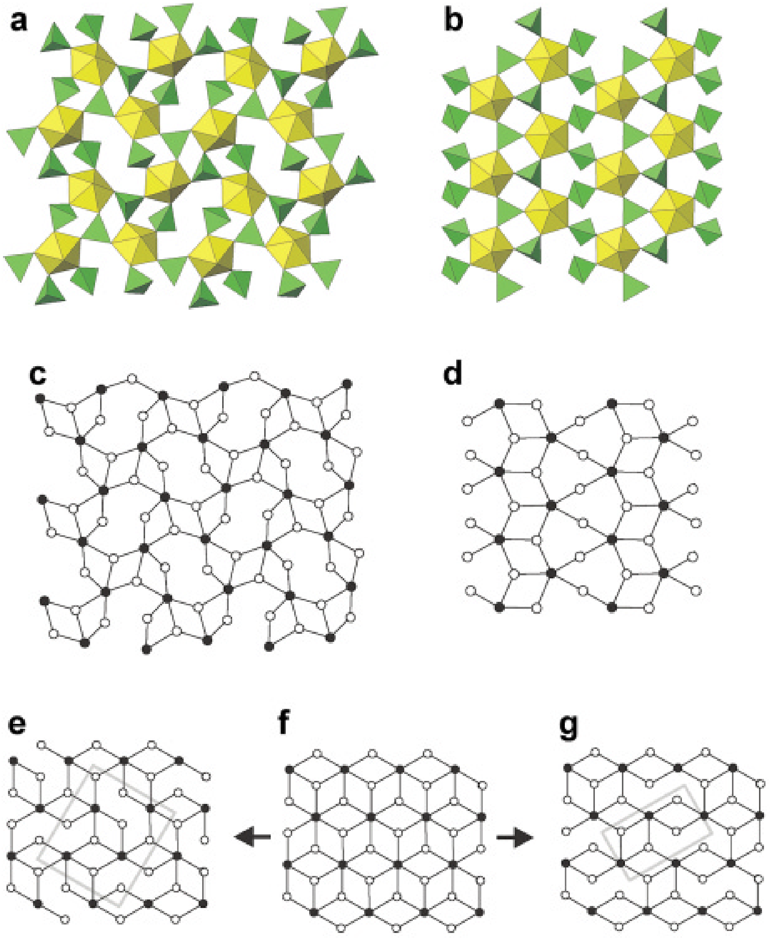

FIG. 3. (a) The $[(UO_2)(MoO_4)_2]^{2-}$ sheet in the structure of $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ (**4**). (b) The $[(UO_2)(MoO_4)_2]^{2-}$ sheet in the structure of $Na_2[(UO_2)(MoO_4)_2]$. (c) Nodal representation of the sheet shown in (a). (d) Nodal representation of the sheet shown in (b). (e) Idealized nodal representation of the sheet shown in (a). (f) Idealized parent black-and-white graph for the graphs shown in (e) and (g). (g) Idealized nodal representation of the sheet shown in (b).

1d) are approximately parallel to each other, and the chain is close to being planar, whereas the corresponding planes of adjacent uranyl bipyramids in the chain in **2** are almost perpendicular to each other. Consequently, the periodicity of the chain (the number of U polyhedra within the identity period of a chain) changes from two in **3** to four in **2**. It is interesting that the U–O–Mo angles are in the range of 125.8 to 147.9° in **3** and 134.1 to 158.5° in **2**. This difference is not dramatic, and indicates that, in this case, conformation of the uranyl molybdate units is not due to the flexibility of the U–O–Mo linkages, but rather to rotations of the uranyl polyhedra relative to each other. Thus, the chain shown in Figure 1e can be obtained from the chain in Figure 1c by rotation of adjacent uranyl polyhedra in the chain by ~90°. Note that rotation of polyhedra is responsible for conformation of topologically identical uranyl molybdate chains in the structures of $K_6[(UO_2)_2O(MoO_4)_4]$ (Krivovichev & Burns 2001a) and $Rb_6[(UO_2)_2O(MoO_4)_4]$ (Krivovichev & Burns 2002c). However, in that case, conformation is due to rotation of MoO_4 tetrahedra, but not UrO_5 bipyramids.

Structural diversity of uranyl molybdates

The following factors are responsible for the rich structural diversity observed in uranyl molybdates: (i) the possibility of different coordination about U^{6+} and Mo^{6+} cations, (ii) the different modes of linkage of U and Mo polyhedra (edge- or corner-sharing), (iii) the different dimensionality of uranyl molybdate units (finite clusters, chains, sheets and frameworks), (iv) the flexibility of U–O–Mo linkages, and (v) the conformation of uranyl molybdate units owing to the relative rotations of U or Mo polyhedra (or both).

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) FOR $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ (x = 0.1) (2)

U(1)-O(3)	1.784(8)	Tl(3)-O(10)e	2.95(1)
U(1)-O(12)	1.804(9)	Tl(3)-O(13)j	3.00(1)
U(1)-O(16)a	2.285(9)	Tl(3)-O(26)	3.09(1)
U(1)-O(20)b	2.312(8)	Tl(3)-O(18)	3.096(9)
U(1)-O(22)c	2.314(9)	Tl(3)-O(11)j	3.118(9)
U(1)-O(7)	2.336(8)	Tl(3)-O(14)	3.138(9)
U(1)-O(5)	2.364(9)	Tl(3)-O(4)f	3.24(1)
<U(1)-O_{Ur}>	1.79	Tl(3)-O(8)j	3.292(9)
<U(1)-O_{eq}>	2.32	<Tl(3)-O>	3.12
U(2)-O(18)	1.782(9)	Na(1)-O(19)	2.23(1)
U(2)-O(4)	1.799(9)	Na(1)-O(26)e	2.34(1)
U(2)-O(14)	2.275(8)	Na(1)-O(2)	2.41(1)
U(2)-O(11)d	2.369(8)	Na(1)-O(6)g	2.44(1)
U(2)-O(23)	2.40(1)	Na(1)-O(29)i	2.58(1)
U(2)-O(13)d	2.451(9)	Na(1)-H_2O(32)c	2.68(2)
U(2)-O(10)e	2.458(9)	<Na(1)-ϕ*>	2.45
<U(2)-O_{Ur}>	1.79		
<U(2)-O_{eq}>	2.39	Na(2)-O(24)k	2.32(1)
		Na(2)-O(17)a	2.35(1)
Mo(1)-O(2)	1.719(9)	Na(2)-O(1)k	2.37(1)
Mo(1)-O(10)	1.744(9)	Na(2)-O(8)k	2.42(1)
Mo(1)-O(6)	1.744(8)	Na(2)-O(9)	2.46(1)
Mo(1)-O(5)	1.794(9)	<Na(2)-O>	2.38
<Mo(1)-O>	1.75		
		Na(3)-O(15)	2.32(1)
Mo(2)-O(8)	1.716(9)	Na(3)-O(8)f	2.34(1)
Mo(2)-O(15)	1.758(9)	Na(3)-O(17)	2.37(1)
Mo(2)-O(11)	1.782(8)	Na(3)-H_2O(27)	2.40(1)
Mo(2)-O(22)	1.803(9)	Na(3)-O(21)f	2.41(1)
<Mo(2)-O>	1.76	Na(3)-O(18)l	2.488(9)
		<Na(3)-ϕ*>	2.39
Mo(3)-O(24)	1.684(9)		
Mo(3)-O(9)	1.721(9)	Na(4)-O(25)b	2.34(1)
Mo(3)-O(21)	1.766(9)	Na(4)-O(6)m	2.39(1)
Mo(3)-O(7)	1.829(8)	Na(4)-O(26)	2.41(1)
<Mo(3)-O>	1.75	Na(4)-O(19)f	2.42(1)
		Na(4)-O(4)f	2.48(1)
Mo(4)-O(1)	1.733(8)	Na(4)-O(6)	2.497(9)
Mo(4)-O(17)	1.736(9)	<Na(4)-O>	2.42
Mo(4)-O(13)	1.776(9)		
Mo(4)-O(16)	1.836(9)	Na(5)-H_2O(28)	2.27(1)
<Mo(4)-O>	1.77	Na(5)-O(30)h	2.33(1)
		Na(5)-O(2)h	2.38(1)
Mo(5)-O(25)	1.722(9)	Na(5)-O(29)g	2.43(1)
Mo(5)-O(23)	1.74(1)	Na(5)-O(20)	2.68(1)
Mo(5)-O(29)	1.75(1)	Na(5)-O(3)h	2.796(9)
Mo(5)-O(20)	1.769(9)	<Na(5)-ϕ*>	2.48
<Mo(5)-O>	1.74		
		Na(6)-O(21),c	2.35(1) 2x
Mo(6)-O(30)	1.69(1)	Na(6)-H_2O(31)	2.39(2)
Mo(6)-O(26)	1.76(1)	Na(6)-H_2O(27)g,n	2.46(1) 2x
Mo(6)-O(19)	1.759(9)	<Na(6)-ϕ*>	2.40
Mo(6)-O(14)	1.793(8)		
<Mo(6)-O>	1.75	Na(7)-H_2O(32)e	2.22(2)
		Na(7)-O(3)	2.42(1)
Tl(1)-O(1)	2.801(9)	Na(7)-O(9)	2.50(1)
Tl(1)-O(1)a	2.85(1)	Na(7)-O(12)g	2.55(1)
Tl(1)-O(24)	2.87(1)	Na(7)-O(29)i	2.62(1)
Tl(1)-O(15)	2.891(9)	Na(7)-O(5)g	2.86(1)
Tl(1)-O(21)f	2.95(1)	<Na(7)-ϕ*>	2.53
Tl(1)-O(9)f	3.227(9)		
Tl(1)-O(7)	3.232(9)		
Tl(1)-O(16)a	3.239(9)		
Tl(1)-O(12)	3.442(9)		
<Tl(1)-O>	3.06		
Tl(2)-O(30)g,h	2.81(1) 2x		
Tl(2)-O(25),i	2.93(1) 2x		
Tl(2)-H_2O(28),i	3.04(1) 2x		
<Tl(2)-ϕ*>	2.93		

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

* ϕ = O, H_2O

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TABLE 6. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$ (**3**)

Atom	*x*	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.29343(6)	0.52182(5)	0.07025(5)	0.0138(1)	0.0142(3)	0.0167(2)	0.0105(2)	0.0003(3)	0.0008(3)	-0.0004(2)
Tl(1)	-0.07078(8)	0.68815(7)	0.08152(8)	0.0357(2)	0.0321(4)	0.0381(5)	0.0368(5)	-0.0033(4)	-0.0024(4)	0.0053(4)
Tl(2)	0.49257(10)	0.21540(8)	-0.07094(10)	0.0475(3)	0.0542(6)	0.0413(5)	0.0471(6)	-0.0038(5)	0.0019(6)	-0.0030(4)
Tl(3)*	0.8298(3)	0.37234(18)	-0.17244(18)	0.0484(6)	0.0695(16)	0.0392(11)	0.0366(12)	-0.0033(9)	-0.0151(11)	0.0050(11)
Mo(1)	0.66663(14)	0.48353(14)	0.05762(13)	0.0200(3)	0.0152(6)	0.0231(7)	0.0217(8)	0.0062(7)	-0.0024(6)	-0.0032(6)
Mo(2)	0.46129(13)	0.51265(14)	-0.20599(12)	0.0162(3)	0.0138(7)	0.0225(7)	0.0123(6)	0.0000(6)	-0.0005(5)	0.0011(6)
Mo(3)	0.37730(15)	0.39293(14)	0.33171(13)	0.0189(3)	0.0169(8)	0.0236(8)	0.0163(8)	0.0012(6)	0.0013(6)	0.0028(6)
Na(1)	0.7591(8)	0.6618(6)	-0.1881(7)	0.026(2)	0.031(5)	0.019(4)	0.028(5)	0.004(3)	-0.007(4)	-0.001(3)
Na(2)*	0.751(2)	0.350(2)	-0.181(2)	0.075(10)	0.033(13)	0.075(17)	0.12(3)	-0.063(17)	-0.021(14)	-0.003(12)
O(1)	0.3542(13)	0.5058(11)	0.2407(10)	0.025(3)	0.028(7)	0.033(8)	0.014(6)	-0.010(6)	-0.002(5)	-0.006(6)
O(2)	0.2853(13)	0.3760(11)	0.0594(10)	0.032(3)	0.043(8)	0.037(7)	0.015(7)	-0.013(6)	0.001(7)	0.015(7)
O(3)	0.2984(14)	0.6702(9)	0.0840(10)	0.030(3)	0.065(10)	0.016(6)	0.009(6)	0.003(5)	0.015(7)	0.012(7)
O(4)	0.7353(15)	0.5002(13)	0.1784(12)	0.039(4)	0.050(10)	0.035(8)	0.033(8)	0.005(6)	-0.028(7)	0.009(7)
O(5)	0.3454(13)	0.5258(12)	-0.1101(9)	0.025(3)	0.024(7)	0.038(8)	0.013(6)	-0.006(6)	-0.001(5)	0.003(7)
O(6)	0.5609(13)	0.4004(12)	-0.1807(12)	0.033(4)	0.021(7)	0.038(8)	0.039(10)	-0.009(7)	0.002(7)	0.010(7)
O(7)	0.2734(14)	0.2825(10)	0.3101(11)	0.029(3)	0.043(9)	0.015(6)	0.029(8)	-0.003(6)	0.013(7)	0.009(6)
O(8)	0.3813(13)	0.4454(13)	0.4635(10)	0.031(4)	0.029(8)	0.055(10)	0.009(6)	0.003(6)	-0.004(5)	-0.002(7)
O(9)	0.3930(12)	0.4894(13)	-0.3279(10)	0.030(3)	0.024(7)	0.052(9)	0.013(6)	-0.009(7)	-0.004(5)	-0.002(7)
O(10)	0.5458(13)	0.6358(12)	-0.2084(13)	0.034(4)	0.027(8)	0.036(8)	0.041(10)	0.002(7)	0.006(7)	0.000(7)
O(11)	0.5236(13)	0.3437(13)	0.3036(12)	0.034(4)	0.019(7)	0.052(10)	0.032(9)	0.009(8)	0.007(6)	0.007(7)
O(12)	0.5041(12)	0.5196(15)	0.0547(11)	0.042(4)	0.015(6)	0.086(12)	0.024(8)	-0.010(9)	-0.004(6)	0.005(8)
H_2O(13)	0.7426(14)	0.7921(13)	-0.3248(12)	0.037(4)	0.035(9)	0.041(9)	0.035(9)	0.002(7)	0.001(7)	0.010(7)
O(14)	0.6793(16)	0.3419(13)	0.0198(13)	0.045(5)	0.058(12)	0.037(9)	0.041(10)	-0.003(7)	-0.030(9)	0.007(9)
O(15)	0.7489(17)	0.5658(16)	-0.0302(13)	0.054(5)	0.062(12)	0.070(12)	0.029(9)	0.014(9)	0.002(8)	-0.001(10)
H_2O(16)*	0.989(3)	0.342(2)	-0.172(3)	0.031(7)	0.031(16)	0.011(12)	0.05(2)	-0.001(12)	-0.015(15)	-0.003(11)

*s.o.f. = 0.50.

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) FOR $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$ (**3**)

U-O(2)	1.75(1)	Tl(2)-O(6)	2.73(2)
U-O(3)	1.78(1)	Tl(2)-O(14)	2.78(2)
U-O(12)	2.28(1)	Tl(2)-H_2O(13)f	3.01(2)
U-O(1)	2.30(1)	Tl(2)-O(10)f	3.03(2)
U-O(8)a	2.36(1)	Tl(2)-H_2O(16)g	3.21(3)
U-O(5)	2.39(1)	Tl(2)-O(9)f	3.24(2)
U-O(9)b	2.40(1)	Tl(2)-O(2)i	3.34(1)
<U-O_{Ur}>	1.77	Tl(2)-O(2)	3.39(1)
<U-O_{eq}>	2.35	<Tl(2)-ϕ*>	3.09
Mo(1)-O(4)	1.74(1)	Tl(3)-O(4)h	2.55(2)
Mo(1)-O(15)	1.74(2)	Tl(3)-O(7)i	2.64(1)
Mo(1)-O(14)	1.77(2)	Tl(3)-O(6)	2.92(1)
Mo(1)-O(12)	1.80(1)	Tl(3)-O(14)	2.98(2)
<Mo(1)-O>	1.76	Tl(3)-O(15)	3.08(2)
		Tl(3)-O(2)g	3.34(1)
Mo(2)-O(10)	1.73(4)	<Tl(3)-O>	2.92
Mo(2)-O(6)	1.75(4)		
Mo(2)-O(9)	1.76(1)	Na(1)-O(10)	2.33(2)
Mo(2)-O(5)	1.76(1)	Na(1)-O(15)	2.34(2)
<Mo(2)-O>	1.75	Na(1)-O(11)h	2.34(2)
		Na(1)-H_2O(13)	2.36(2)
Mo(3)-O(11)	1.72(1)	Na(1)-O(3)j	2.45(1)
Mo(3)-O(7)	1.75(1)	Na(1)-O(4)h	2.59(2)
Mo(3)-O(1)	1.81(1)	<Na(1)-ϕ*>	2.40
Mo(3)-O(8)	1.81(1)		
<Mo(3)-O>	1.77	Na(2)-O(6)	2.14(3)
		Na(2)-O(7)i	2.31(3)
Tl(1)-O(15)c	2.83(2)	Na(2)-O(4)h	2.56(4)
Tl(1)-O(7)d	2.83(2)	Na(2)-H_2O(16)	2.56(4)
Tl(1)-O(10)e	2.95(2)	Na(2)-O(14)	2.71(4)
Tl(1)-O(8)a	3.01(1)	<Na(2)-ϕ*>	2.46
Tl(1)-O(3)c	3.07(1)		
Tl(1)-O(9)b	3.09(1)		
Tl(1)-O(6)b	3.25(2)		
Tl(1)-O(4)c	3.31(2)		
<Tl(1)-O>	3.04		

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

* ϕ = O, H_2O

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TABLE 8. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ (4)

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.18365(3)	0.21151(2)	0.153504(16)	0.01401(5)	0.0162(1)	0.0128(1)	0.01238(9)	-0.0005(1)	0.00323(8)	-0.0008(1)
Mo(1)	0.40090(7)	0.38523(5)	0.41116(4)	0.0162(1)	0.0205(3)	0.0131(3)	0.0123(2)	0.0005(2)	0.0009(2)	-0.0011(2)
Mo(2)	0.35641(7)	0.51588(5)	0.12263(4)	0.0163(1)	0.0205(3)	0.0144(3)	0.0139(2)	-0.0026(2)	0.0051(2)	-0.0021(2)
Na(1)	0.7878(3)	0.4105(2)	0.16643(19)	0.0285(7)	0.0315(17)	0.0254(16)	0.0302(15)	0.0009(13)	0.0119(14)	0.0008(13)
Na(2)*	0.2981(3)	0.4150(2)	0.6447(2)	0.0311(7)	0.0296(17)	0.0364(18)	0.0303(15)	0.0005(14)	0.0134(14)	0.0017(14)
O(1)	0.5615(5)	0.2953(4)	0.4747(3)	0.0249(10)	0.040(3)	0.012(2)	0.020(2)	-0.0031(19)	0.006(2)	0.006(2)
O(2)	0.4571(5)	0.5338(3)	0.3971(3)	0.0187(9)	0.027(3)	0.011(2)	0.018(2)	-0.0019(17)	0.0061(19)	0.0000(18)
O(3)	0.0043(5)	0.2674(4)	0.1670(3)	0.0234(10)	0.026(3)	0.023(3)	0.020(2)	0.0020(19)	0.005(2)	0.000(2)
O(4)	0.2536(6)	0.3824(4)	0.0842(3)	0.0253(11)	0.041(3)	0.024(3)	0.012(2)	-0.0014(19)	0.009(2)	-0.013(2)
O(5)	0.3603(5)	0.1498(4)	0.1402(3)	0.0252(11)	0.021(3)	0.031(3)	0.026(2)	0.003(2)	0.010(2)	-0.002(2)
O(6)	0.2665(5)	0.5994(4)	0.1991(3)	0.0207(10)	0.030(3)	0.019(2)	0.012(2)	-0.0032(18)	0.0046(19)	0.002(2)
O(7)	0.5518(5)	0.4943(4)	0.1908(3)	0.0259(11)	0.020(3)	0.037(3)	0.021(2)	-0.005(2)	0.008(2)	-0.001(2)
O(8)	0.2501(5)	0.3796(4)	0.4647(3)	0.0272(11)	0.026(3)	0.032(3)	0.022(2)	-0.003(2)	0.006(2)	-0.007(2)
$H_2O(9)$	0.0927(6)	0.5392(4)	0.6496(3)	0.0344(12)	0.034(3)	0.036(3)	0.031(3)	-0.003(2)	0.008(2)	0.002(2)
O(10)	0.3489(6)	0.5953(4)	0.0147(3)	0.0276(11)	0.041(3)	0.022(3)	0.021(2)	0.004(2)	0.010(2)	-0.008(2)
O(11)	0.3272(5)	0.3311(4)	0.2859(3)	0.0271(11)	0.037(3)	0.023(3)	0.015(2)	0.0004(19)	-0.002(2)	-0.007(2)
O(12)	0.9297(6)	0.5649(4)	0.1316(3)	0.0372(13)	0.034(3)	0.041(3)	0.033(3)	0.009(3)	0.004(3)	-0.010(3)
$H_2O(13)$	0.1976(6)	0.2687(4)	0.7260(4)	0.0369(13)	0.034(3)	0.031(3)	0.051(3)	-0.003(3)	0.021(3)	0.002(2)
$H_2O(14)$	0.6078(7)	0.7461(4)	0.0680(3)	0.0446(15)	0.063(4)	0.050(4)	0.029(3)	-0.010(3)	0.026(3)	-0.020(3)

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TABLE 9. SELECTED INTERATOMIC DISTANCES (Å) FOR $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ (4)

U(1)-O(3)	1.783(4)	Na(1)-O(12)	2.315(5)
U(1)-O(5)	1.786(4)	Na(1)-O(7)	2.427(5)
U(1)-O(11)	2.335(4)	Na(1)-H_2O(13)c	2.446(5)
U(1)-O(6)a	2.336(4)	Na(1)-O(10)d	2.427(5)
U(1)-O(4)	2.354(4)	Na(1)-H_2O(9)e	2.506(5)
U(1)-O(1)b	2.378(4)	Na(1)-O(3)f	2.534(5)
U(1)-O(2)a	2.390(4)	<Na(1)-ϕ*>	2.44
<U-O_{Ur}>	1.78		
<U-O_{eq}>	2.36	Na(2)-H_2O(9)	2.338(6)
		Na(2)-H_2O (13)	2.349(5)
Mo(1)-O(8)	1.720(4)	Na(2)-O(8)	2.426(5)
Mo(1)-O(1)	1.767(4)	Na(2)-O(7)e	2.488(5)
Mo(1)-O(11)	1.767(4)	Na(2)-O(2)e	2.490(5)
Mo(1)-O(2)	1.809(4)	Na(2)-O(3)g	2.745(5)
<Mo(1)-O>	1.77	<Na(2)-ϕ*>	2.47
Mo(2)-O(7)	1.725(4)	a = $-x+1/2,y-1/2,-z+1/2$;	
Mo(2)-O(10)	1.733(4)	b = $x-1/2,-y+1/2,z-1/2$;	
Mo(2)-O(4)	1.785(4)	c = $x+1/2,-y+1/2,z-1/2$; d = -	
Mo(2)-O(6)	1.788(4)	$x-1,-y+1,-z$;	
<Mo(2)-O>	1.76	e = $-x+1,-y+1,-z+1$; f = $x+1,y,z$;	
		g = $x-1/2,-y+1/2,z+1/2$.	

* ϕ = O, H_2O

TABLE 10. BOND-VALENCE ANALYSIS (v.u.) FOR $Na_3Tl_3[(UO_2)(MoO_4)_4]$ (1), $Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$ (x = 0.1) (2), $Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$ (3) AND $Na_2[(UO_2)(MoO_4)_2](H_2O)_4$ (4)

	$Na_3Tl_3[(UO_2)(MoO_4)_4]$	$Na_{13-x}Tl_{3+x}[(UO_2)(MoO_4)_3]_4(H_2O)_{6+x}$	$Na_3Tl_5[(UO_2)(MoO_4)_3]_2(H_2O)_3$	$Na_2[(UO_2)(MoO_4)_2](H_2O)_4$
U	6.03	6.17, 5.85	6.22	6.05
Mo	5.87, 5.92, 6.08, 5.75	6.12, 5.90, 6.17, 5.82, 6.21, 6.14	6.07, 6.10, 5.78	5.88, 6.01
Tl	0.95, 0.97, 1.10	1.05, 0.82*, 0.79*	0.90, 0.88, 0.90*	-
Na	1.12, 0.95, 0.59*, 0.70*	1.12, 1.04, 1.25, 1.13, 1.07, 1.20*, 0.96	1.21, 1.00	1.07, 1.03
O**	1.83-2.16	1.78-2.22	1.84-2.16	1.66-2.03
H_2O**	-	0.20-0.41	0.21-0.34	0.00-0.40

* Partially occupied sites. ** Contributions from H bonds are not included.

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