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A Novel Open Framework Uranyl Molybdate: Synthesis and Structure of $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$

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Single crystals of $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$ have been synthesized hydrothermally using $(NH_4)_6Mo_7O_{24}$, $(UO_2)(CH_3COO)_2\cdot 2H_2O$, and H_2O at 180 °C. The phase has been characterized by single-crystal X-ray diffraction using a merohedrally twinned single crystal: it is hexagonal, $P6_1$, $a = 11.4067(5)$ Å, $c = 70.659(5)$ Å, $V = 7961.9(7)$ Å^3, and $Z = 6$. The structure is based upon an open framework with composition $[(UO_2)_5(MoO_4)_7]^{4-}$ that is composed of UO_7 pentagonal bipyramids that share vertexes with MoO_4 tetrahedra. The framework has large channels (effective pore size: 4.8×4.8 Å^2) parallel to the *c* axis and a system of smaller channels (effective pore size: 2.5×3.6 Å^2) parallel to [100], [110], [010], $[\bar{1}10]$, $[1\bar{1}0]$, and $[\bar{1}\bar{1}0]$. The channels are occupied by NH_4^+ cations and H_2O molecules. The topological structure of the uranyl molybdate framework can be described either in terms of fundamental chains of UO_7 pentagonal bipyramids and MoO_4 tetrahedra or in terms of tubular building units parallel to the *c* axis.

Introduction

Open-framework actinide-bearing materials have received considerable attention in recent years due to their possible relevance to corrosion, ion-exchange/sequestration, and other issues related to the long-term disposal of spent nuclear fuel.[1−15] Uranyl minerals and inorganic compounds with open-framework structures have been known for two decades,[16−20] and frameworks of UO_7 pentagonal bipyramids and MoO_4 tetrahedra are especially common in uranium

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molybdates.[21,22] This is a result of the ideal matching of U−O and Mo−O bonds from the perspective of bond-valence theory.[23−27] The U^{6+}−O bond in the equatorial plane of a UO_7 pentagonal bipyramid has a bond valence of ∼0.5 vu (valence units),[22,28] whereas the average Mo^{6+}−O bond valence in a MoO_4 tetrahedron is 1.5 vu. Thus, O atoms shared between UO_7 and MoO_4 groups have their bond-valence requirements satisfied, and the relative sizes of the adjacent coordination polyhedra permit considerable flexibility of the U−O−Mo linkages. This is reflected in the large range of observed U−O−Mo angles which vary from 120 to 180°. The bond-valence matching and linkage flexibility in uranyl molybdates result in a large variety of complex uranyl molybdate anions, ranging from finite clusters through chains and sheets to frameworks.[9,14,18−20,29−46]

The current study involves the NH_4−U−Mo−O−H_2O system, in which two compounds, $(NH_4)_2[(UO_2)(MoO_4)_2]$ and $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)]$, have been structurally characterized previously.[9,41] $(NH_4)_2[(UO_2)(MoO_4)_2]$ has a layered structure and is closely related to the structures based on uranyl dimolybdate sheets,[31,36,39,43] whereas $(NH_4)_2[(UO_2)_6(MoO_4)_7(H_2O)]$ contains a uranyl molybdate framework with channels occupied by NH_4 cations. Recently, we were able to synthesize a new NH_4−Bi uranyl molybdate with an interrupted framework structure; this compound will be reported elsewhere.[47] In this paper we report the synthesis and structure of an ammonium uranyl molybdate, $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$, which possesses a novel open framework with a three-dimensional system of channels unlike any observed in an actinide compound.

Experimental Section

Synthesis. $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$ (**1**) was synthesized in a 23 mL Teflon-lined steel autoclave by combining 0.058 g $(NH_4)_6Mo_7O_{24}$ (Alfa), 0.039 g of $(UO_2)(CH_3CO_2)_2{\cdot}2H_2O$ (Alfa-Aesar), and 5 mL of ultrapure water. The mixture was held static at 180 °C for 4 days, followed by cooling to room temperature over 2 h. The product, a greenish-yellow solid, was collected by filtration and washed with ethanol and ultrapure water and allowed to dry in air. The phase crystallized as hexagonal bipyramidal crystals. *While the $(UO_2)(CH_3CO_2)_2{\cdot}2H_2O$ contains depleted U, standard precautions for handling radioactive substances should be followed.* Powder X-ray diffraction (Rigaku Miniflex, 3.0−60.0° 2θ, 0.02 deg/step, 1.0 s/step, Cu Kα radiation) of the product indicated that this was a pure phase. The framework of **1** (below) could also be produced from a mixture of 0.03 g $KC_2H_3O_2$, 0.04 g MoO_3, 0.04 g $UO_2(CH_3COO)_2{\cdot}2H_2O$, and 5.0 g H_2O heated at 180 °C for 7 days. Identification of this phase was confirmed via powder diffraction and unit cell parameters obtained from single-crystal analysis, however a full structural refinement was not performed. Thermogravimetric analysis (Perkin-Elmer, Pyris TGA 1; 30−700 °C, 5.00 °C/min) on **1** yielded a single weight loss even between ∼250 and 500 °C of approximately 5.6 wt %.

Crystal Structure Determination. A single greenish-yellow hexagonal bipyramid was mounted on a thin glass fiber for X-ray diffraction analysis. More than a hemisphere of X-ray diffraction data ($2\theta_{max} = 34.44°$) was collected at room temperature using a Bruker SMART APEX CCD diffractometer with Mo Kα radiation. The data were integrated and corrected for absorption using an empirical ellipsoidal model ($R_{int} = 0.090$) using the Bruker programs SAINT and XPREP.[48,49] The observed systematic absences were consistent with space groups $P6_1$, $P6_5$, $P6_122$, and $P6_522$. The structure was solved in the space group $P6_1$ by direct methods and refined on the basis of F^2 for all unique data using SHELXTL[50] software. Refinement in other candidate spacegroups proved unsatisfactory. An initial refinement of the structure resulted in essential disorder of one of the Mo atoms; inspection of the calculated and experimental structure factors revealed that many $F_{exp}{}^2$ were much greater than $F_{calc}{}^2$, suggesting the crystal studied was twinned. The twin operator $[010/100/00\bar{1}]$ was applied, corresponding to merohedral twinning. The structure was refined according to the method of Jameson[51] on the basis of F^2 for all unique data. The final refinement converged to R1 = 0.055, wR2 = 0.1200, and GoF = 0.908 and a model that did not involve disorder of any atom positions. The refinement indicated two twin components with 50% fractions of the volume of the crystal. As $P6_1$ is a noncentrosymmetric space group, care was taken to determine absolute structure (the final value of the Flack parameter

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Table 1. Crystal and Structure Refinement Data for $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$

chem formula	$(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$
fw	2631.93
T, K	293(2)
λ, Å	0.710 73
space group	$P6_1$
a, Å	11.4067(5)
c, Å	70.659(5)
V, Å^3	7961.9(7)
Z	6
ρ_{calc}, mg/m^3	3.294
μ(Mo Kα), mm^{-1}	16.880
tot. reflcns	88 722
unique reflcns	21 776
obsd reflcns	12 592
final R indices [$I > 2\sigma(I)$]	R1^a = 0.0559; wR2^b = 0.1238
R indices (all data)	R1 = 0.1002; wR2 = 0.1393

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]]^{1/2}$.

$x = 0.006(6)$). To get reasonable geometry around U^{6+} cations, soft restraints were applied to some of the U−O distances in uranyl ions. After atomic positions of the framework atoms were determined, NH_4^+ and H_2O positions in the framework channels were extracted from the difference Fourier map. The NH_4 sites were found first as peaks with maximal electron density and by analysis of their local environment. The site occupancy factors for H_2O positions were fixed at 1.00 and isotropic displacement parameters at 0.05 Å^2 to get reasonable refinement. The number of H_2O molecules/formula unit determined from structure refinement is 5.0. This value, when considered with the four $NH4^+$ sites (6.1 wt %), is in agreement with the TGA results (above). The final model included anisotropic displacement parameters for U and Mo; attempts to refine O atoms anisotropically were not successful, most probably due to the large cell dimensions and twinning problems. Details of the data collection and refinement are given in Table 1, and selected bond lengths and angles are in Table 2. A complete listing of atomic coordinates and bond distances and angles is available in CIF format as Supporting Information.

Results and Discussion

U and Mo Coordination. The structure contains five symmetrically unique U^{6+} cations, each of which is strongly bonded to two oxygen atoms, giving nearly linear uranyl $(UO_2)^{2+}$ ions (Ur). Each uranyl ion is coordinated by five additional O atoms located at the equatorial vertexes of pentagonal bipyramids that are capped by the O_{Ur} atoms. Bond lengths within the uranyl ions range from 1.72 to 1.88 Å, whereas the U−O bond lengths corresponding to the equatorial ligands range from 2.24 to 2.53 Å, which is typical for UO_7 polyhedra in uranyl oxysalts.[22] Each equatorial O atom is shared with a Mo^{6+} cation. Each Mo^{6+} cation is tetrahedrally coordinated by four O atoms, with Mo−O bond lengths averaging 1.76 Å. All O atoms of the $Mo(1)O_4$, $Mo(3)O_4$, $Mo(4)O_4$, and $Mo(7)O_4$ tetrahedra are shared with UO_7 polyhedra, whereas the $Mo(2)O_4$, $Mo(5)O_4$, and $Mo(6)O_4$ tetrahedra each have three O atoms that are bonded to U^{6+}, as well as one terminal O atom. The Mo−O−U angles range from 123.7 to 166.7°, reflecting substantial flexibility of the Mo−O−U connections.

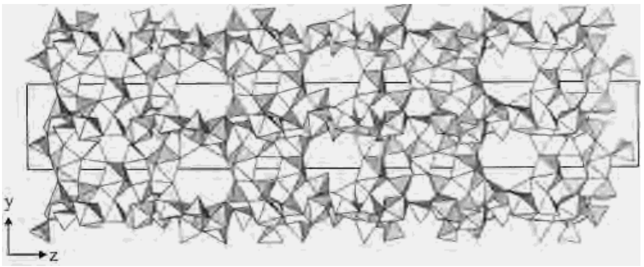

Figure 1. Open framework structure of $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$ (**1**) drawn projected along the a axis. The unit cell is shown (solid line) whereas the NH_4^+ cations and H_2O molecules residing in the channels have been omitted for clarity. Tetrahedra and pentagonal bipyramids are MoO_4 and UO_7 units, respectively.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$ (**1**)^a

U(1)−O(1)	1.80(2)	U(5)−O(35)c	2.43(2)
U(1)−O(2)	1.78(2)	U(5)−O(34)c	2.46(2)
U(1)−O(4)	2.29(1)	U(5)−O(31)	2.51(3)
U(1)−O(7)	2.38(2)	Mo(1)−O(3)	1.72(2)
U(1)−O(6)a	2.45(2)	Mo(1)−O(32)	1.78(1)
U(1)−O(3)	2.41(2)	Mo(1)−O(21)	1.81(1)
U(1)−O(5)b	2.48(2)	Mo(1)−O(10)	1.88(1)
U(2)−O(8)	1.88(2)	Mo(2)−O(36)	1.71(2)
U(2)−O(9)	1.86(2)	Mo(2)−O(6)	1.71(2)
U(2)−O(11)	2.28(1)	Mo(2)−O(11)	1.77(1)
U(2)−O(10)c	2.36(1)	Mo(2)−O(20)	1.95(2)
U(2)−O(12)c	2.39(1)	Mo(3)−O(26)	1.72(2)
U(2)−O(13)d	2.48(2)	Mo(3)−O(12)	1.80(1)
U(2)−O(14)d	2.47(1)	Mo(3)−O(33)	1.80(2)
U(3)−O(15)	1.73(2)	Mo(3)−O(7)	1.86(2)
U(3)−O(16)	1.84(2)	Mo(4)−O(35)	1.59(2)
U(3)−O(17)e	2.29(1)	Mo(4)−O(18)	1.62(2)
U(3)−O(19)	2.37(1)	Mo(4)−O(14)	1.78(1)
U(3)−O(20)e	2.43(2)	Mo(4)−O(27)	1.74(1)
U(3)−O(21)	2.44(1)	Mo(5)−O(17)h	1.72(1)
U(3)-O(18)f	2.49(2)	Mo(5)−O(37)h	1.75(3)
U(4)−O(22)	1.75(2)	Mo(5)−O(24)	1.84(2)
U(4)−O(23)	1.79(2)	Mo(5)−O(31)	1.87(3)
U(4)−O(24)	2.25(2)	Mo(6)−O(19)	1.70(1)
U(4)−O(27)	2.41(1)	Mo(6)−O(38)	1.77(2)
U(4)−O(26)g	2.41(2)	Mo(6)−O(28)	1.79(2)
U(4)−O(25)	2.44(2)	Mo(6)−O(4)	1.84(1)
U(4)−O(28)h	2.50(2)	Mo(7)−O(25)	1.64(2)
U(5)−O(30)	1.71(1)	Mo(7)−O(13)	1.66(2)
U(5)−O(29)	1.74(2)	Mo(7)−O(34)	1.70(2)
U(5)−O(33)g	2.32(2)	Mo(7)−O(5)	1.73(2)
U(5)−O(32)g	2.37(1)		
O(1)−U(1)−O(2)	171(1)	Mo(5)f−O(17)−U(3)c	151.9(8)
O(8)−U(2)−O(9)	174.7(8)	Mo(4)−O(18)−U(3)h	132(1)
O(15)−U(3)−O(16)	175.1(6)	Mo(6)−O(19)−U(3)	169(1)
O(22)−U(4)−O(23)	172(1)	Mo(2)−O(20)−U(3)c	130(1)
O(30)−U(5)−O(29)	172.9(8)	Mo(1)−O(21)−U(3)	124.8(7)
Mo(1)−O(3)−U(1)	150.5(9)	Mo(5)−O(24)−U(4)	142.9(9)
Mo(6)−O(4)−U(1)	124.9(7)	Mo(7)−O(25)−U(4)	146(1)
Mo(7)−O(5)−U(1)g	146.7(9)	Mo(3)−O(26)−U(4)b	155.4(9)
Mo(2)−O(6)−U(1)a	137.7(9)	Mo(4)−O(27)−U(4)	154.4(8)
Mo(3)−O(7)−U(1)	136.6(9)	Mo(6)−O(28)−U(4)f	122.6(9)
Mo(1)−O(10)−U(2)e	146.9(8)	Mo(5)−O(31)−U(5)	128(1)
Mo(2)−O(11)−U(2)	149.2(7)	Mo(1)−O(32)−U(5)b	128.5(7)
Mo(3)−O(12)−U(2)e	126.2(6)	Mo(3)−O(33)−U(5)b	165.8(9)
Mo(7)−O(13)−U(2)i	159(1)	Mo(7)−O(34)−U(5)e	130.6(9)
Mo(4)−O(14)−U(2)i	123.0(7)	Mo(4)−O(35)−U(5)e	169(1)

[a] Symmetry codes: a = x, $y - 1$, z; b = y, $-x + y$, $z + 5/6$; c = $x - 1$, y, z; d = y, $-x + y + 1$, $z + 5/6$; e = $x + 1$, y, z; f = x, y, $z + 1$; g = $x - y$, x, $z - 5/6$; h = x, y, $z - 1$; i = $x - y + 1$, x, $z - 5/6$.

Uranyl Molybdate Framework and Its Topological Structure. The structure of **1** comprises a three-dimensional framework of composition $[(UO_2)_5(MoO_4)_7]^{4-}$ that consists of UO_7 pentagonal bipyramids that share equatorial edges with MoO_4 tetrahedra (Figures 1 and 2a). The framework contains a three-dimensional system of channels. The largest

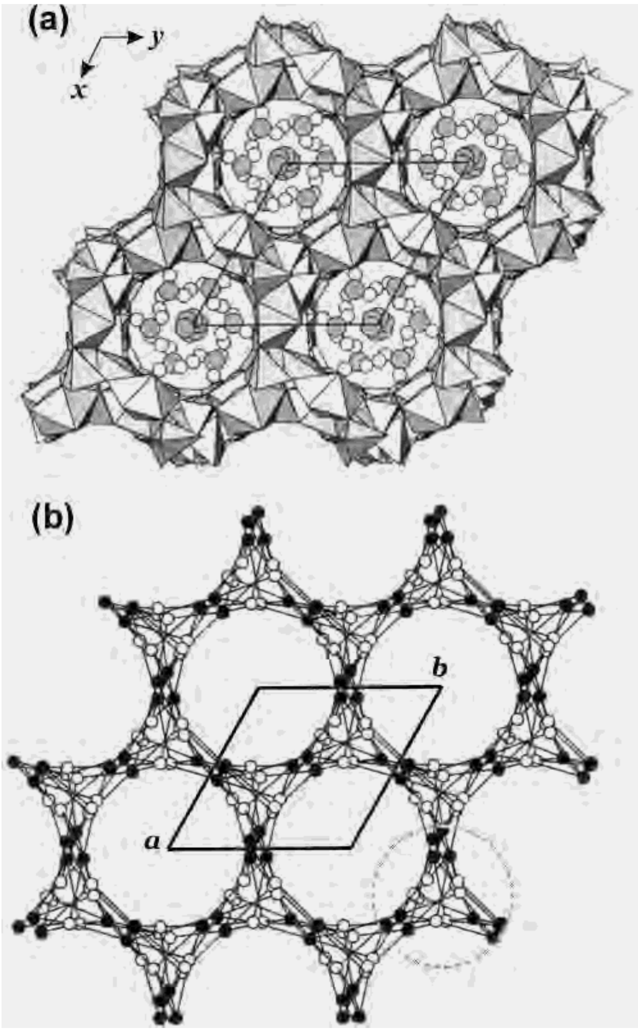

Figure 2. (a) Structure of **1** projected along the *c* axis (large gray circles = H_2O molecules; small circles = NH_4 groups). (b) Nodal representation of the uranyl molybdate framework (white circles = MoO_4 tetrahedra; black circles = UO_7 pentagonal bipyramids). The unit cell is shown, as is the fundamental chain of polyhedra (dashed line in (b)).

channel is parallel to [001] and has the dimensions 7.5 × 7.5 Å, which result in a crystallographic free diameter (effective pore width) of 4.8 × 4.8 Å (based on an oxygen radius of 1.35 Å) (Figure 2a). Smaller channels run parallel to [100], [110], [010], [$\bar{1}$10], [1$\bar{1}$0], and [$\bar{1}\bar{1}$0] and have dimensions 5.2 × 6.3 Å (giving an effective pore width of 2.5 × 3.6 Å) (Figure 1). Four symmetrically unique NH_4^+ cations and five unique H_2O molecules are located in the framework channels.

The $[(UO_2)_5(MoO_4)_7]^{4-}$ framework is unusually complex. The local structure of the framework may be described using a nodal representation (Figure 2b) in which each node corresponds to a UO_7 bipyramid (black) or a MoO_4 tetrahedron (white). Nodes are shown connected if the polyhedra share a common vertex (O atom). We have used this representation in describing other uranyl molybdate structures[14,43,46,56] and find it useful in delineating local systematics. As such, the uranyl molybdate framework of **1** is an infinite net, where all black vertexes are 5-connected and all white vertexes are either 3- or 4-connected (Figure 2b). The nodes corresponding to the Mo(2)O_4, Mo(5)O_4, and Mo(6)O_4 tetrahedra are 3-connected, whereas those corresponding to the Mo(1)O_4, Mo(3)O_4, Mo(4)O_4, and Mo(7)O_4 tetrahedra are 4-connected. All nodes corresponding to U polyhedra are 5-connected.

Using the nodal representation, the uranyl molybdate framework in the structure of $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$ (**1**) can be described in terms of either fundamental chains or tubular building units.[52,53] The concept of the fundamental chain was proposed by Liebau[54,55] for the description of complex silicate structures. Sheets and frameworks of polyhedra can be regarded as based upon appropriately chosen chains of polyhedra. This concept was recently applied to aid in the comparison of uranyl molybdate units in the structures of α- and β-$Cs_2(UO_2)_2(MoO_4)_3$.[14] The fundamental chain corresponding to the uranyl molybdate framework in the structure of **1** is shown in Figure 2b. It extends along [001]; its nodal representation is shown in Figure 3a. The chain is a sequence of 3- and 4-connected MoO_4 tetrahedra (white vertexes) linked through one, two, or three UO_7 pentagonal bipyramids (black vertexes). The graph shown in Figure 3a can be further reduced to the simplified isomorphic graph shown in Figure 3c. This reduction preserves all topological linkages between the polyhedra. Note that the graph shown in Figure 3c is periodic and its identity unit includes seven white vertexes, whereas, in the real structure, the identity period of the fundamental chain includes 21 white vertexes (Figure 3a). Thus, the topological structure of the fundamental chain is simpler than its geometrical realization. Note that the U:Mo ratio for this chain is 10:7.

Distinction of a fundamental chain permits the comparison of uranyl molybdate framework in $(NH_4)_4[(UO_2)_5(MoO_4)_7]$-$(H_2O)$ with the frameworks in $M[(UO_2)_6(MoO_4)_7](H_2O)_n$ (M = Sr, Mg,[19] Ca, Cu, Li[56]). The structures of the latter compounds are orthorhombic and involve open uranyl molybdate frameworks with nonlinear channels. The corresponding fundamental chain is parallel to [001] and contains seven white vertexes within its identity period (Figure 3b; see simplified graph in Figure 3d). All white vertexes are 4-connected. The U:Mo ratio is 12:7.

The use of nodal representations permits the derivation of relations between topological structures of the two fundamental chains. The graph shown in Figure 3d can be transformed into the graph shown in Figure 3c by deleting two black vertexes (which corresponds to the change of U:Mo ratio from 12:7 to 10:7) and addition of one more connection between the black and white vertexes (Figure 3e). The latter requirement shows that transition between the two fundamental chains involves not only stoichiometric changes (reflecting the change of the framework composition from

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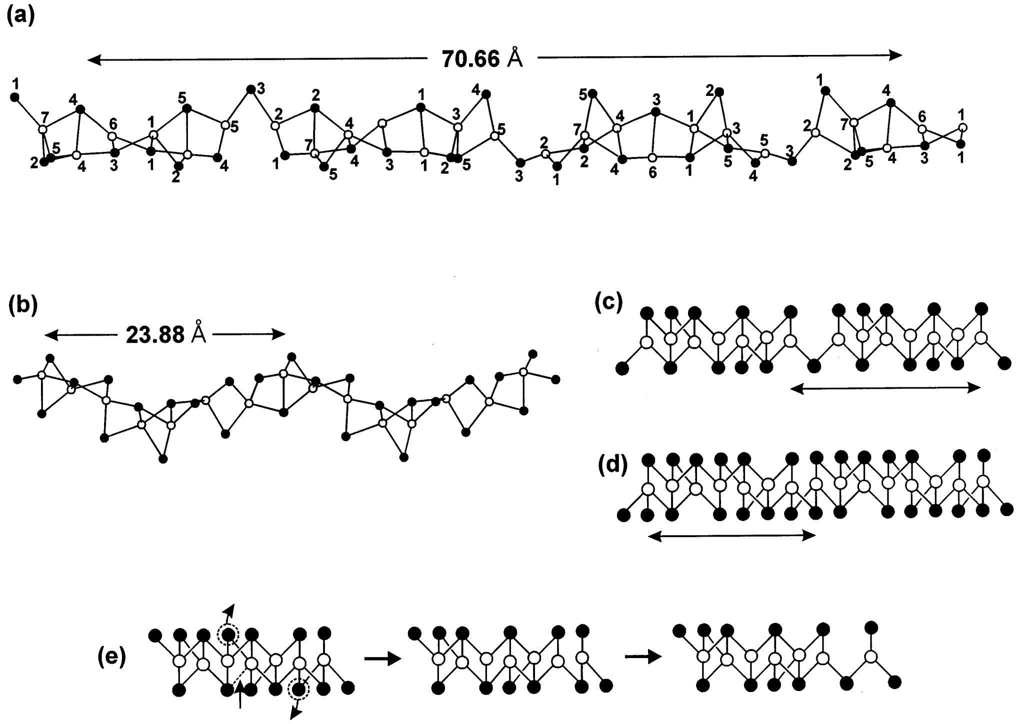

Figure 3. (a) Nodal representation of the fundamental chain of U and Mo polyhedra of the uranyl molybdate framework in $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$ (chain parallel to the *c* axis; see Figure 2b). (b) Same as (a) drawn for $M[(UO_2)_6(MoO_4)_7](H_2O)_n$ (M = Sr, Mg, Ca, Cu, Li). (c, d) Simplified graphs for the nodal representations of chains of polyhedra shown in (a) and (b), respectively. (e) Scheme of topological reconstruction needed to transform the graph of the chain shown in (b) to the graph of the chain shown in (a). The legend is as in Figure 2b.

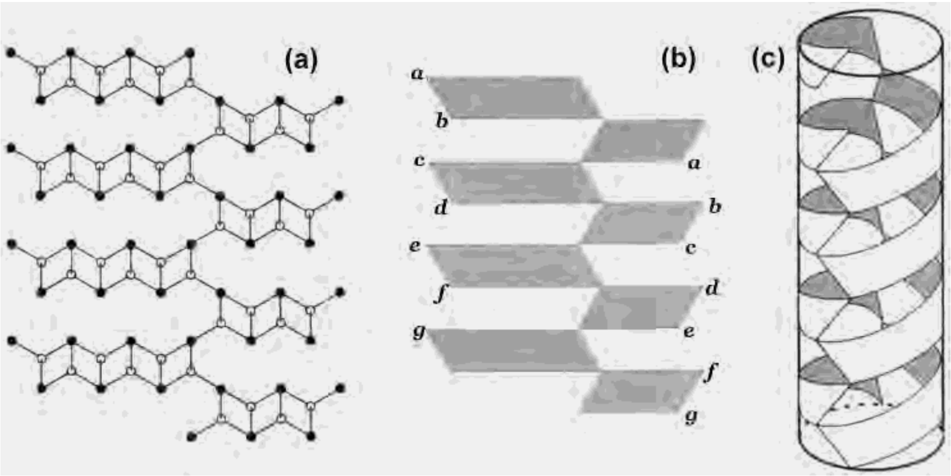

Figure 4. Construction of the tubular building unit (assemblage of U and Mo polyhedra around cylindrical channels) in the structure of **1**: (a) nodal representation of strip of U and Mo polyhedra; (b) its simplified image; (c) folding of the strips around a cylinder produces the tubular building unit observed in the structure. Note that the points denoted by identical letters in (b) should be joined to produce the unit shown in (c). The legend is as in Figure 2b.

$[(UO_2)_6(MoO_4)_7]^{2-}$ to $[(UO_2)_5(MoO_4)_7]^{4-}$) but also slight but essential topological reconstruction.

The uranyl molybdate framework in the structure of **1** can also be described in terms of tubular building units. These are an assemblage of polyhedral linkages around cylindrical channels. A tubular building unit for the channels in the structure of **1** can be constructed from the strips of UO_7 pentagonal bipyramids and MoO_4 tetrahedra. A nodal representation of the required strips is shown in Figure 4a. All white and black vertexes are 3-connected. The tubular building unit can be obtained by folding the strip around a cylinder and joining its corresponding points *a*−*a*, *b*−*b*, *c*−*c*, *d*−*d*, etc., as its shown in Figure 4b,c. Note that the tubular building unit is chiral, as required by space group $P6_1$. It should be noted that open frameworks with chiral channel topologies are not quite common but have been observed in several inorganic structures. For example, Stuckey et al.[57] reported the synthesis and structure of an open-framework sodium zincophosphate, $NaZnPO_4{\cdot}(H_2O)$, with a CZP framework topology, as well as a ferriborophosphate $Fe(H_2O)_2BP_2O_8{\cdot}H_2O$.[58] An example of octahedral−tetrahedral framework with chiral channel topology is a $[ASi_3O_9]$ framework

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observed in the structures of hilairite-group minerals, $A'_n[ASi_3O_9](H_2O)_3$ ($A' = Na, Ca, Ba$; $A = Zr, Ti, Y$),[59] space group *R*32. More recently, some chiral metal−organic framework compounds have been reported as candidates for enantioselective sensing, catalysis, and separations.[60−63] Efforts to examine the potential of $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$ (**1**) for these types of applications will be the focus of future investigations.

Conclusions

Consistent with both our and other groups' previous studies of the crystal chemistry of uranyl molybdates,[9,14,18−20,29−47,56] this study further demonstrates the structural complexity and variability of these materials. In particular, there is an exceptional number of topologically unique frameworks in the U−Mo family. We have shown the uranyl molybdate framework in $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$ (**1**) is topologically related to the open framework observed in the structures of $M[(UO_2)_6(MoO_4)_7](H_2O)_n$ ($M = Sr, Mg, Ca, Cu, Li$). The structure of **1** can be obtained from the others by topological reconstruction of a fundamental chain that involves elimination of some uranyl ions and additional connections of UO_7 pentagonal bipyramids and MoO_4 tetrahedra. Other examples in which topological reconstruction of fundamental chains leads to new open framework uranyl molybdates will be the subject of a forthcoming paper.

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Supporting Information Available: A thermal ellipsoid plot of $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$ and X-ray crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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