

Chiral open-framework uranyl molybdates.

2. Flexibility of the U:Mo = 6:7 frameworks: syntheses and crystal structures of (UO₂)_{0.82}[C₈H₂₀N]_{0.36}[(UO₂)₆(MoO₄)₇(H₂O)₂](H₂O)_n and [C₆H₁₄N₂][(UO₂)₆(MoO₄)₇(H₂O)₂](H₂O)_m

Sergey V. Krivovichev ^{a,*}, Peter C. Burns ^b, Th. Armbruster ^c,
Evgeniy V. Nazarchuk ^a, Wulf Depmeier ^d

^a Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia

^b Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame 46556 IN, USA

^c Laboratorium für chemische and mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3102 Bern, Switzerland

^d Institut für Geowissenschaften, Kiel Universität, Olshausenstrasse 40, D-24118 Kiel, Germany

Received 5 April 2004; received in revised form 7 October 2004; accepted 8 October 2004

Available online 30 November 2004

Abstract

Two new chiral open-framework uranyl molybdates, (UO₂)_{0.82}[C₈H₂₀N]_{0.36}[(UO₂)₆(MoO₄)₇(H₂O)₂](H₂O)_n (**1**) and [C₆H₁₄N₂][(UO₂)₆(MoO₄)₇(H₂O)₂](H₂O)_m (**2**) have been synthesized by hydrothermal methods. The structures of **1** and **2** have been refined using X-ray diffraction data collected at –127°C. The structure of **1** [orthorhombic, C222₁, *a* = 12.2303(15), *b* = 18.966(2), *c* = 22.392(3) Å, *V* = 5194.0(11) Å³] has been refined to *R*₁ = 0.043 on the basis of 4126 unique observed reflections. The structure of **2** [orthorhombic, C222₁, *a* = 11.3256(15), *b* = 19.860(3), *c* = 23.731(3) Å, *V* = 5337.8(12) Å³] has been refined to *R*₁ = 0.056 on the basis of 3519 unique observed reflections. The structures of **1** and **2** are based upon complex chiral [(UO₂)₆(MoO₄)₇(H₂O)₂] frameworks of corner-sharing UO₇ bipyramids and MoO₄ tetrahedra. In addition to framework U sites, the structure of **1** contains an additional, partially-occupied and disordered U(4) site, located within the framework cavities and coordinated by several disordered anions to form the complex [(UO₂)(H₂O)₅]²⁺ cation. The structure of **2** contains disordered DABCO (1,4-diazabicyclo[2.2.2]-octane) molecules. The geometrical parameters of the uranyl molybdate frameworks in the structures of **1** and **2** are significantly different. The *a* parameter of **1** is about 0.9 Å longer than that of **2**, whereas the *b* and *c* parameters of **1** are shorter than those of **2** (~0.9 and 1.3 Å, respectively). This occurs due to the adaptation of the [(UO₂)₆(MoO₄)₇(H₂O)₂]²⁻ framework to the shape of the complex [(UO₂)(H₂O)₅]²⁺ cation in **1**. Analysis of the U–O–Mo bond angles of the frameworks indicates the U–O(15)–Mo and U–O(20)–Mo links are the most flexible. The transition from **2** to **1** involves an increase of the U–O(15)–Mo and U–O(20)–Mo angles from 146.7° to 169.0° and from 151° to 171°, respectively.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Uranyl molybdates; Open framework; Crystal structure; Chiral; Flexibility

1. Introduction

As we have shown in the first paper of this series [1], there are three known topologically distinct types of

* Corresponding author.

E-mail address: skrivovi@mail.ru (S.V. Krivovichev).

chiral uranyl molybdate open frameworks. These three types are characterized by the U:Mo ratio of 5:7, 4:5 and 6:7. The 6:7 framework uranyl molybdates were first described by Tabachenko et al. [2] for $M_2(UO_2)_6(MoO_4)_7(H_2O)_n$ ($M = Sr, Mg; n = 15, 18$). Later, the same framework type was reported for the uranyl sulfate material $[NC_4H_{12}]_2[(UO_2)_6(H_2O)_2(SO_4)_7]$ [3]. The 6:7 uranyl molybdate framework, as with other frameworks of the series, is based upon corner-sharing UO_7 pentagonal bipyramids and MoO_4 tetrahedra. The $U-O_{br}-Mo$ links (O_{br} = bridging oxygen atom) are very flexible with $U-O-Mo$ bond angles in the range from 120° to 177° [4]. Due to this high degree of flexibility, uranyl molybdate units with the same topology may occur in a number of conformation states. Here we report the hydrothermal syntheses and crystal structures of two new 6:7 uranyl molybdate framework compounds prepared in the presence of amines. The $[(UO_2)_6(MoO_4)_7(H_2O)_2]$ frameworks in these compounds are topologically identical but have notably different geometrical parameters. We demonstrate that the geometrical differences originate from the flexibility of the $U-O-Mo$ links.

2. Experimental

2.1. Synthesis

Crystals of $(UO_2)_{0.82}[C_8H_{20}N]_{0.36}[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_n$ (**1**) and $[C_6H_{14}N_2]_2[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_m$ (**2**) were synthesized by hydrothermal methods. Crystals of **1** were prepared from a solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (0.1568 g), MoO_3 (0.0288 g), *n*-octylamine (0.035 g) and HCl (0.034 g) in 5 ml of H_2O (with an approximate U:Mo:*n*-octylamine:HCl: H_2O molar gel ratio of 4:2:3:9:2780). The solution was placed in a Teflon-lined Parr bomb and heated to $180^\circ C$ for 24 h, followed by cooling at the rate of $6^\circ h^{-1}$ to ambient temperature. The crystals occur as aggregates of dark-yellow transparent parallelepipeds. Crystals of **2** were prepared from a solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (0.0784 g), MoO_3 (0.0576 g), 1,4-diazabicyclo[2.2.2]-octane (DABCO; 0.07 g) and HCl (0.045 g) in 5 ml of H_2O (with an approximate U:Mo:DABCO:HCl: H_2O molar gel ratio of 2:4:5:12:2780). The solution was placed in a Teflon-lined Parr bomb and heated to $180^\circ C$ for 43 h, followed by cooling to ambient temperature. The crystals occur as yellow transparent plates.

2.2. Crystal-structure analysis

Crystals of **1** and **2** selected for X-ray data collection were mounted on thin glass fibers. More than a hemisphere of X-ray diffraction data ($\theta_{max} = 34.44^\circ$) were collected for each crystal at $-127^\circ C$ using a Bruker SMART 1K CCD diffractometer with $MoK\alpha$ radiation.

The data were integrated and corrected for absorption using an empirical ellipsoidal model using the Bruker programs SAINT and XPREP. The structures were solved by direct methods. At this stage, the general similarities of the structures of **1** and **2** to the structures of $M_2(UO_2)_6(MoO_4)_7(H_2O)_n$ ($M = Sr, Mg; n = 15, 18$) [2] were confirmed. However, it was observed that the uranyl molybdate frameworks in the structures of **1** and **2** have a different absolute configuration in comparison with the structures of the Sr and Mg analogues (the validity of our models was confirmed by the values of the Flack parameter [5] equal to 0.006(7) for **1** and 0.003(11) for **2**). For the structure of **1**, a large peak was found in the difference Fourier map that was attributed to an additional disordered U position located within the framework cavities. This partially-occupied U site (site-occupation factor (s.o.f.) = 0.407(3)) is coordinated by O atoms and H_2O molecules with a stereochemistry typical to that observed in a number of uranyl compounds [6]. We were unable to locate positions of amine molecules within the framework of either structure, presumably because they are disordered. This type of disorder is typical for framework materials [7,8]. Analysis of the difference-Fourier maps revealed the presence of several partially-occupied positions in the framework cavities that can be assigned to disordered organic and water molecules. These positions were introduced into the model and refined using O scattering factors. The final refinements converged to $R_1 = 0.043$ and 0.056 for **1** and **2**, respectively. The final model in-

Table 1
Crystallographic data and refinement parameters for **1** and **2** at $-127^\circ C$

	1	2
<i>a</i> (Å)	12.2303(15)	11.3256(15)
<i>b</i> (Å)	18.966(2)	19.860(3)
<i>c</i> (Å)	22.392(3)	23.731(3)
<i>V</i> (Å ³)	5194.0(11)	5337.8(12)
Space group	C222 ₁	C222 ₁
μ (cm ⁻¹)	229.07	198.06
<i>Z</i>	4	4
<i>D</i> _{calc} (g/cm ³)	4.08	3.61
Crystal size (mm)	0.16 × 0.14 × 0.12	0.10 × 0.04 × 0.02
Radiation	MoK α	MoK α
Ref. for cell refinement	837	817
Absorption correction	Ellipsoid	Ellipsoid
Ref. for abs. corr.	1852	736
Total Ref.	15083	15550
Unique Ref.	5831	5988
Unique $ F_o \geq 4\sigma_F$	4126	3519
<i>R</i> ₁	0.043	0.056
<i>wR</i> ₂	0.095	0.121
<i>S</i>	0.609	0.678

Note: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, 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 **1** at -127°C

Atom	<i>s.o.f.</i>	<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)		0.55660(6)	0.76843(4)	0.51032(3)	0.0264(2)	0.0319(4)	0.0313(3)	0.0160(3)	−0.0048(3)	−0.0042(3)	0.0093(3)
U(2)		0.13728(6)	0.53726(3)	0.87818(3)	0.0268(2)	0.0427(4)	0.0195(3)	0.0182(3)	0.0027(2)	0.0032(3)	0.0025(3)
U(3)		0.26918(6)	0.76677(4)	0.73627(3)	0.0292(2)	0.0356(4)	0.0330(4)	0.0189(3)	0.0027(3)	0.0002(3)	−0.0077(3)
Mo(1)		0	0.64161(11)	3/4	0.0250(5)	0.0293(12)	0.023(1)	0.023(1)	0	−0.0077(9)	0
Mo(2)		0.98837(13)	0.36161(7)	0.83798(6)	0.0245(3)	0.0342(9)	0.0243(7)	0.0149(7)	0.0026(6)	0.0033(6)	−0.0024(7)
Mo(3)		0.83595(11)	0.74948(7)	0.60488(6)	0.0205(3)	0.0219(7)	0.0237(7)	0.0159(7)	−0.0045(5)	−0.0016(5)	−0.0010(5)
Mo(4)		0.23209(13)	0.62308(8)	0.02225(6)	0.0236(3)	0.0262(8)	0.0222(7)	0.0223(7)	0.0030(6)	−0.0054(6)	−0.0019(6)
O(1)		0.2403(12)	0.5380(7)	0.8222(5)	0.042(3)	0.062(10)	0.032(7)	0.032(7)	0.004(6)	0.024(7)	−0.007(7)
O(2)		0.8813(10)	0.3501(7)	0.7843(5)	0.032(3)	0.039(8)	0.037(7)	0.021(6)	0.004(5)	0.005(5)	−0.007(6)
O(3)		0.9373(11)	0.3545(7)	0.9111(5)	0.033(3)	0.041(8)	0.035(7)	0.024(6)	−0.009(5)	0.003(6)	−0.002(6)
O(4)		0.6109(11)	0.8280(7)	0.4612(6)	0.040(3)	0.043(9)	0.051(8)	0.025(7)	−0.006(6)	0.010(6)	0.000(7)
O(5)		0.8141(11)	0.7956(7)	0.6716(6)	0.038(3)	0.037(8)	0.049(8)	0.028(7)	−0.006(6)	−0.005(6)	−0.003(7)
O(6)		0.0477(11)	0.4452(6)	0.8290(5)	0.034(3)	0.046(8)	0.028(7)	0.028(7)	0.001(5)	0.010(6)	0.001(6)
O(7)		0.2581(11)	0.5734(7)	0.9572(5)	0.036(3)	0.033(8)	0.047(8)	0.028(7)	−0.010(6)	−0.006(6)	0.008(6)
O(8)		0.1940(13)	0.8326(9)	0.7017(6)	0.055(4)	0.060(10)	0.082(12)	0.023(7)	0.025(7)	−0.004(7)	0.000(9)
O(9)		0.3489(12)	0.7019(6)	0.7723(6)	0.043(3)	0.064(10)	0.022(6)	0.043(8)	0.001(5)	−0.003(8)	0.003(7)
O(10)		0.0881(12)	0.2951(7)	0.8286(6)	0.044(4)	0.058(10)	0.044(8)	0.029(8)	0.008(6)	0.025(7)	0.012(7)
O(11)		0.9547(12)	0.7807(8)	0.5690(6)	0.048(4)	0.039(9)	0.062(10)	0.044(8)	−0.025(7)	0.000(7)	−0.019(8)
O(12)		0.1164(16)	0.6938(9)	0.7450(8)	0.069(5)	0.090(13)	0.069(10)	0.048(10)	0.012(8)	−0.016(9)	−0.039(10)
O(13)		0.9901(15)	0.5867(7)	0.6881(7)	0.054(4)	0.084(12)	0.034(8)	0.045(9)	−0.013(7)	0.009(8)	−0.011(8)
O(14)		0.2133(10)	0.5672(6)	0.0830(6)	0.032(3)	0.030(7)	0.028(7)	0.039(7)	0.002(5)	−0.003(6)	−0.002(6)
O(15)		0.8513(16)	0.6625(6)	0.6200(6)	0.060(5)	0.135(15)	0.017(6)	0.027(7)	−0.004(5)	−0.003(9)	−0.003(8)
O(16)		0.0317(11)	0.5357(6)	0.9340(5)	0.033(3)	0.048(9)	0.027(6)	0.025(6)	−0.005(5)	0.001(6)	0.000(6)
O(17)		0.1172(10)	0.6736(7)	0.0120(6)	0.036(3)	0.032(7)	0.043(7)	0.033(7)	0.012(6)	−0.006(6)	0.010(6)
O(18)		0.3430(12)	0.6772(8)	0.0369(6)	0.047(4)	0.053(9)	0.061(9)	0.027(7)	0.027(6)	−0.021(7)	−0.035(8)
O(19)		0.5012(15)	0.7056(7)	0.5612(6)	0.050(4)	0.083(12)	0.028(7)	0.039(9)	−0.003(6)	0.011(8)	−0.017(8)
O(20)		0.7233(13)	0.7583(9)	0.5586(6)	0.063(5)	0.052(10)	0.089(13)	0.048(9)	−0.036(9)	−0.021(7)	0.033(9)
H ₂ O(21)		0.2668(17)	0.6902(9)	0.6472(7)	0.072(5)	0.107(15)	0.065(11)	0.043(9)	−0.011(8)	−0.006(10)	−0.025(11)
Extra-framework positions											
U(4)	0.407(3)	0.8494(2)	0.01205(14)	0.50974(14)	0.0380(9)	0.0339(10)	0.030(2)	0.050(2)	−0.010(1)	0.002(1)	0.0036(8)
H ₂ O(22)	0.73(5)	0.660(3)	0.019(2)	0.4784(18)	0.148(8)*						
H ₂ O(23)	0.83(5)	0.012(3)	0.0241(19)	0.5674(18)	0.148(8)*						
H ₂ O(24)	0.59(5)	0.767(4)	0.051(3)	0.415(2)	0.148(8)*						
O(25)	0.56(6)	0.863(5)	0.064(3)	0.535(3)	0.148(8)*						
O(26)	0.43(5)	0.843(7)	0.086(4)	0.477(4)	0.148(8)*						
Peaks in the difference Fourier map											
Q(1)	5.6e [−]	0.026(4)	0.903(2)	0.633(2)	0.148(8)*						
Q(2)	6.4e [−]	0.481(3)	0.613(2)	0.6558(18)	0.148(8)*						
Q(3)	4.6e [−]	0.897(4)	0.950(3)	0.733(3)	0.148(8)*						
Q(4)	2.4e [−]	0.793(4)	0.511(2)	0.8185(19)	0.148(8)*						
Q(5)	2.6e [−]	0.041(8)	0.971(5)	0.665(4)	0.148(8)*						
Q(6)	2.6e [−]	0.031(8)	0.048(4)	0.730(4)	0.148(8)*						

* Fixed to be equal during refinement.

cluded anisotropic displacement parameters for U, Mo and framework O atoms, all atomic positional parameters, and isotropic-displacement parameters for the extraframework sites. Further details of the data collection and refinement are given in Table 1. Atomic coordinates are in Tables 2 and 3 for **1** and **2**, respectively (including extra-framework partially-occupied sites and their refined site scattering). Selected bond lengths are in Tables 4 and 5 for **1** and **2**, respectively.

2.3. Room- and high-temperature X-ray powder-diffraction study

X-ray powder-diffraction patterns of **1** and **2** were recorded at room temperature using a DRON-2 powder

diffractometer and CuK α radiation ($\lambda = 1.54059 \text{ \AA}$). The observed powder-diffraction patterns are in excellent agreement with theoretical powder diffraction pattern calculated from the crystal-structure data. The unit-cell parameters of **1** refined from powder data using least-squares methods and 37 reflections are $a = 11.369(1)$, $b = 19.899(2)$, $c = 23.798(3) \text{ \AA}$. The unit-cell parameters of **2** refined from powder data using least-squares methods and 46 reflections are $a = 12.3700(9)$, $b = 18.791(2)$, $c = 22.555(3) \text{ \AA}$. These parameters are in good agreement with the results of single-crystal diffraction analysis.

High-temperature X-ray powder diffraction study of **2** was performed in the range of temperatures from 20 to 700 °C by means of a DRON-3 powder diffractometer

Table 3
Atomic coordinates and displacement parameters for **2** at -127°C

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)	0.54011(7)	0.74890(5)	0.51910(4)	0.0186(2)	0.0218(4)	0.0145(4)	0.0195(5)	-0.0015(5)	-0.0007(4)	0.0024(4)
U(2)	0.11141(8)	0.52714(4)	0.88310(4)	0.0188(2)	0.0257(5)	0.0098(4)	0.0208(5)	0.0022(4)	-0.0048(4)	-0.0026(4)
U(3)	0.26305(8)	0.75183(6)	0.74089(4)	0.0252(2)	0.0329(5)	0.0221(5)	0.0207(5)	-0.0037(5)	0.0037(4)	-0.0115(5)
Mo(1)	0.0000	0.61480(14)	0.7500	0.0182(7)	0.0240(16)	0.010(1)	0.021(2)	0.000	-0.0028(15)	0.000
Mo(2)	0.98533(19)	0.34738(9)	0.83889(9)	0.0173(5)	0.0259(12)	0.0111(9)	0.015(1)	0.0007(8)	0.0011(10)	-0.0009(9)
Mo(3)	0.84047(18)	0.72545(9)	0.60397(9)	0.0157(5)	0.0210(11)	0.0104(9)	0.016(1)	0.0010(8)	0.0008(9)	-0.0005(8)
Mo(4)	0.23518(18)	0.61628(9)	0.0183(1)	0.0167(5)	0.0213(11)	0.0079(9)	0.021(1)	0.0003(9)	0.0006(10)	-0.0018(8)
O(1)	0.2299(16)	0.5339(9)	0.8351(7)	0.030(4)	0.043(8)	0.030(7)	0.017(7)	-0.006(7)	-0.003(7)	-0.001(7)
O(2)	0.8766(19)	0.3381(9)	0.7852(8)	0.033(5)	0.065(14)	0.018(9)	0.015(10)	-0.003(8)	0.015(10)	-0.017(10)
O(3)	0.9315(15)	0.3274(8)	0.9039(9)	0.031(5)	0.027(10)	0.015(9)	0.052(14)	-0.005(9)	-0.007(10)	0.004(7)
O(4)	0.6314(15)	0.8008(9)	0.4772(7)	0.026(4)	0.027(10)	0.045(11)	0.008(9)	0.004(8)	-0.005(8)	0.006(8)
O(5)	0.8183(14)	0.7655(7)	0.6687(7)	0.023(4)	0.026(9)	0.014(9)	0.030(10)	0.003(7)	-0.002(8)	-0.007(7)
O(6)	0.0363(17)	0.4296(8)	0.8363(8)	0.030(5)	0.047(12)	0.020(9)	0.023(11)	0.002(8)	-0.015(10)	-0.015(9)
O(7)	0.2327(16)	0.5660(9)	0.9573(7)	0.025(4)	0.030(8)	0.030(7)	0.016(7)	-0.002(6)	-0.015(7)	-0.003(6)
O(8)	0.1571(16)	0.8115(10)	0.7148(9)	0.039(5)	0.030(11)	0.053(13)	0.033(13)	0.020(10)	-0.006(10)	-0.013(10)
O(9)	0.3654(18)	0.6939(10)	0.7672(11)	0.050(7)	0.040(13)	0.028(11)	0.08(2)	0.005(11)	0.028(13)	-0.018(10)
O(10)	0.1046(17)	0.2919(9)	0.8254(8)	0.034(5)	0.036(11)	0.035(11)	0.031(12)	-0.003(9)	0.013(10)	0.012(9)
O(11)	0.9258(15)	0.7768(7)	0.5614(8)	0.023(4)	0.028(10)	0.011(8)	0.029(11)	-0.014(8)	0.007(8)	-0.003(7)
O(12)	0.129(2)	0.6654(9)	0.7517(9)	0.049(6)	0.075(16)	0.040(12)	0.032(13)	-0.004(11)	0.000(12)	-0.040(11)
O(13)	0.0081(16)	0.5650(7)	0.6900(7)	0.021(4)	0.037(11)	0.008(7)	0.019(10)	-0.006(7)	-0.005(9)	0.013(7)
O(14)	0.2075(16)	0.5663(9)	0.0784(8)	0.027(5)	0.026(11)	0.030(10)	0.026(11)	0.002(9)	0.003(9)	0.004(8)
O(15)	0.9093(14)	0.6472(7)	0.6158(7)	0.021(4)	0.040(11)	0.005(7)	0.019(10)	-0.003(7)	0.019(9)	-0.005(7)
O(16)	0.9961(17)	0.5215(8)	0.9303(7)	0.030(4)	0.046(8)	0.024(7)	0.019(7)	-0.003(6)	-0.016(7)	0.005(7)
O(17)	0.1189(19)	0.6778(8)	0.0126(9)	0.042(5)	0.063(14)	0.020(10)	0.042(13)	0.012(9)	0.013(12)	0.006(9)
O(18)	0.3714(15)	0.6541(9)	0.0257(8)	0.031(5)	0.027(10)	0.027(10)	0.039(13)	0.007(9)	-0.002(9)	-0.017(8)
O(19)	0.4483(15)	0.7002(8)	0.5619(8)	0.024(4)	0.029(10)	0.022(9)	0.021(10)	0.000(8)	0.005(9)	-0.012(8)
O(20)	0.6999(15)	0.7117(9)	0.5714(8)	0.030(5)	0.021(10)	0.047(12)	0.021(10)	0.005(9)	0.002(9)	-0.009(9)
H ₂ O(21)	0.248(2)	0.6907(11)	0.6452(10)	0.058(7)	0.085(18)	0.045(14)	0.045(15)	-0.011(11)	0.017(14)	-0.005(12)

Peaks in the difference Fourier map

	Height	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Q(1)	5.7e ⁻	0.647(4)	0.492(2)	0.908(2)	0.100*
Q(2)	3.9e ⁻	0.749(6)	0.458(3)	0.993(3)	0.100*
Q(3)	3.7e ⁻	0.665(10)	0.5000	0.0000	0.100*
Q(4)	2.9e ⁻	0.678(8)	0.476(4)	0.786(4)	0.100*
Q(5)	4.4e ⁻	0.499(6)	0.429(3)	0.842(3)	0.100*
Q(6)	4.9e ⁻	0.539(5)	0.488(3)	0.796(2)	0.100*
Q(7)	3.0e ⁻	0.538(7)	0.497(4)	0.032(3)	0.100*
Q(8)	2.4e ⁻	0.726(9)	0.501(5)	0.848(5)	0.100*
Q(9)	4.6e ⁻	0.543(5)	0.549(3)	0.858(2)	0.100*

* Fixed during refinement.

Table 4
Selected bond lengths (Å) in the structure of **1** at -127°C

U(1)–O(4)	1.71(1)	Mo(1)–O(13)	1.74(1) 2x
U(1)–O(19)	1.78(1)	Mo(1)–O(12)	1.74(2) 2x
U(1)–O(20)	2.32(1)	$\langle\text{Mo(1)–O}\rangle$	1.74
U(1)–O(11)	2.36(1)		
U(1)–O(18)	2.37(1)	Mo(2)–O(6)	1.76(1)
U(1)–O(17)	2.39(1)	Mo(2)–O(3)	1.76(1)
U(1)–O(3)	2.40(1)	Mo(2)–O(10)	1.77(1)
$\langle\text{U(1)–O}_{\text{Uir}}\rangle$	1.75	Mo(2)–O(2)	1.79(1)
$\langle\text{U(1)–O}_{\text{eq}}\rangle$	2.37	$\langle\text{Mo(2)–O}\rangle$	1.77
U(2)–O(1)	1.78(1)	Mo(3)–O(15)	1.69(1)
U(2)–O(16)	1.80(1)	Mo(3)–O(20)	1.73(1)
U(2)–O(6)	2.34(1)	Mo(3)–O(5)	1.75(1)
U(2)–O(13)	2.35(2)	Mo(3)–O(11)	1.76(1)
U(2)–O(14)	2.36(1)	$\langle\text{Mo(3)–O}\rangle$	1.73
U(2)–O(15)	2.38(1)		
U(2)–O(7)	2.41(1)	Mo(4)–O(17)	1.72(1)
$\langle\text{U(2)–O}_{\text{Uir}}\rangle$	1.79	Mo(4)–O(18)	1.73(1)
$\langle\text{U(2)–O}_{\text{eq}}\rangle$	2.37	Mo(4)–O(14)	1.74(1)
		Mo(4)–O(7)	1.76(1)
U(3)–O(8)	1.73(1)	$\langle\text{Mo(4)–O}\rangle$	1.75
U(3)–O(9)	1.77(1)		
U(3)–O(12)	2.33(2)	U(4)–O(25)	1.76(7)
U(3)–O(10)	2.33(1)	U(4)–O(26)	1.89(8)
U(3)–O(2)	2.35(1)	U(4)–H ₂ O(24)	2.31(5)
U(3)–O(5)	2.36(1)	U(4)–H ₂ O(23)	2.39(4)
U(3)–H ₂ O(21)	2.47(2)	U(4)–H ₂ O(22)	2.40(4)
$\langle\text{U(3)–O}_{\text{Uir}}\rangle$	1.75	U(4)–H ₂ O(22)	2.42(4)
$\langle\text{U(3)–O}_{\text{eq}}\rangle$	2.37	U(4)–H ₂ O(24)	2.47(5)
		U(4)–H ₂ O(23)	2.73(4)
		$\langle\text{U(4)–O}\rangle$	2.30

Table 5
Selected bond lengths (Å) in the structure of **2** at -127°C

U(1)–O(19)	1.75(2)	Mo(1)–O(13)	1.74(2) 2x
U(1)–O(4)	1.77(2)	Mo(1)–O(12)	1.77(2) 2x
U(1)–O(20)	2.31(2)	$\langle\text{Mo(1)–O}\rangle$	1.76
U(1)–O(17)	2.32(2)		
U(1)–O(11)	2.36(2)	Mo(2)–O(3)	1.71(2)
U(1)–O(18)	2.38(2)	Mo(2)–O(6)	1.73(2)
U(1)–O(3)	2.42(2)	Mo(2)–O(10)	1.77(2)
$\langle\text{U(1)–O}_{\text{Uir}}\rangle$	1.76	Mo(2)–O(2)	1.78(2)
$\langle\text{U(1)–O}_{\text{eq}}\rangle$	2.36	$\langle\text{Mo(2)–O}\rangle$	1.75
U(2)–O(16)	1.72(2)	Mo(3)–O(11)	1.73(2)
U(2)–O(1)	1.77(2)	Mo(3)–O(5)	1.75(2)
U(2)–O(13)	2.32(2)	Mo(3)–O(15)	1.76(2)
U(2)–O(14)	2.34(2)	Mo(3)–O(20)	1.79(2)
U(2)–O(7)	2.36(2)	$\langle\text{Mo(3)–O}\rangle$	1.76
U(2)–O(6)	2.39(2)		
U(2)–O(15)	2.40(1)	Mo(4)–O(18)	1.72(2)
$\langle\text{U(2)–O}_{\text{Uir}}\rangle$	1.75	Mo(4)–O(7)	1.76(2)
$\langle\text{U(2)–O}_{\text{eq}}\rangle$	2.36	Mo(4)–O(14)	1.77(2)
		Mo(4)–O(17)	1.80(2)
		$\langle\text{Mo(4)–O}\rangle$	1.76
U(3)–O(9)	1.75(2)		
U(3)–O(8)	1.80(2)		
U(3)–O(12)	2.31(2)		
U(3)–O(10)	2.31(2)		
U(3)–O(5)	2.35(2)		
U(3)–O(2)	2.39(2)		
U(3)–H ₂ O(21)	2.58(2)		
$\langle\text{U(3)–O}_{\text{Uir}}\rangle$	1.78		
$\langle\text{U(3)–O}_{\text{eq}}\rangle$	2.39		

equipped with a high-temperature KRV-1100 chamber. The phase is stable until $300 \pm 10^{\circ}\text{C}$. In between 300 and 500°C , no diffraction peaks are observed. At $500 \pm 10^{\circ}\text{C}$, the compound UO_2MoO_4 crystallizes. The compound **1** shows similar thermal behaviour.

3. Results

The structures of **1** and **2** are based upon complex chiral $[(\text{UO}_2)_6(\text{MoO}_4)_7(\text{H}_2\text{O})_2]$ frameworks of corner-sharing UO_7 bipyramids and MoO_4 tetrahedra (Fig. 1a). The topology of the frameworks is the same for

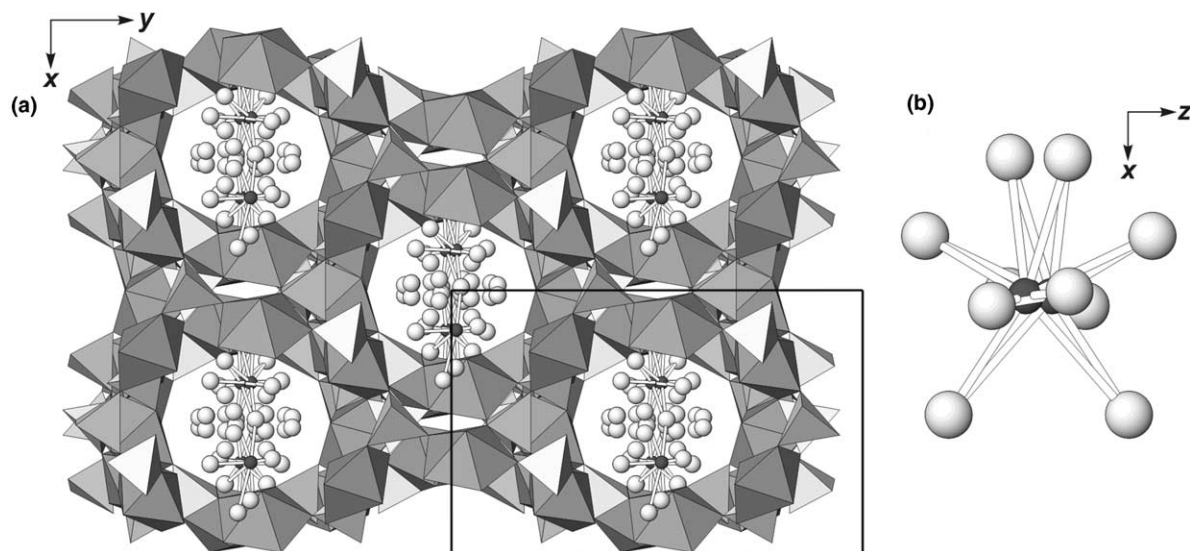


Fig. 1. The crystal structure of **1** viewed along the c axis (a) and disordered $[(\text{UO}_2)(\text{H}_2\text{O})_5]^{2+}$ extra-framework cation (b).

both structures and can be described using the fundamental chain approach discussed in [1,9].

The uranyl molybdate frameworks in each structure contain three symmetrically unique U^{6+} cations and four Mo^{6+} cations. Each of the U^{6+} cations 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 vertices of pentagonal bipyramids that are capped by the O_{Ur} atoms. Each Mo^{6+} cation is tetrahedrally coordinated by four O atoms. In addition to framework U sites, the structure of **1** contains an additional partially-occupied disordered U(4) site that is located within the framework cavities. The U(4) is coordinated by several disordered ligands with the approximate arrangement shown in Fig. 1b. Even high-quality low-temperature diffraction data did not allow complete resolution of the U(4)–O, H₂O configuration. However, from general crystal-chemical arguments and U(4)–O, H₂O bond lengths (Table 4), we propose that the U(4) site is coordinated by two O atoms that define the uranyl cation, UO_2^{2+} . The UO_2^{2+} cations are coordinated in the equatorial plane by five H₂O molecules that results in a complex $[(UO_2)(H_2O)_5]^{2+}$ cation that is held in the framework cavities by hydrogen bonds from H₂O groups to the framework O atoms. To achieve electroneutrality, the structure of **1** should contain some additional cations which are most likely protonated *n*-octylamine molecules. The total amount of extra-framework cations thus can be expressed as

$[(UO_2)_{0.82}[C_8H_{20}N]_{0.36}]^{2+}$. In contrast to **1**, the structure of **2** contains no additional extra-framework U sites. In this case, charge balance is provided by the disordered DABCO molecules located in the framework cavities.

Bond-valence sums for the U and Mo positions calculated using bond-valence parameters for the U^{6+} –O bonds taken from [6] and for the Mo^{6+} –O bonds taken from [9] are in the range from 5.80 to 6.43 valence units (v.u.).

4. Discussion

The $[(UO_2)_6(MoO_4)_7(H_2O)_2]^{2-}$ frameworks in the structures of **1** and **2** are topologically identical. However, their geometrical parameters are significantly different, as evidenced by the unit-cell parameters of **1** and **2** listed in Table 1. The *a* parameter of **1** is about 0.9 Å longer than that of **2**, whereas the *b* and *c* parameters of **1** are shorter than those of **2** (~0.9 and 1.3 Å, respectively). This behaviour of the uranyl molybdate framework can be explained on the basis of general structural arguments. The structure of **1** contains the $[(UO_2)(H_2O)_5]^{2+}$ cation as an extra-framework species, which is present as a pentagonal bipyramid that is strongly flattened along its apical axis (which is parallel to the linear uranyl cation, UO_2^{2+}). In the structure of **1**, the equatorial plane of the disordered $[(UO_2)(H_2O)_5]^{2+}$ bipyramid is parallel to the (010) plane, i.e., its axis is parallel to the *b* axis. Thus, the bipyramid can be

Table 6

U–O–Mo angles (deg) in uranyl molybdates based upon $[(UO_2)_6(MoO_4)_7(H_2O)_2]^{2-}$ frameworks (space group C222₁)

	1	2	3	4	5	<i>d</i> _{max} , deg
<i>a</i> (Å)	12.2303(15)	11.3256(15)	11.3196(4)	11.313(5)	11.166(5)	
<i>b</i> (Å)	18.966(2)	19.860(3)	20.0027(7)	20.163(10)	20.281(10)	
<i>c</i> (Å)	22.392(3)	23.731(3)	24.4606(10)	23.877(11)	24.061(12)	
<i>V</i> (Å ³)	5194.0(11)	5337.8(12)	5538.4(4)	5446.44	5448.8	
Temperature, K	146	146	293	293	293	
U(3)–O(2)–Mo(2)	144.6(7)	140(1)	148.4(7)	138.9	142.1	9.5
U(1)–O(3)–Mo(2)	136.4(7)	141.6(9)	153.1(7)	149.0	148.1	16.7
U(3)–O(5)–Mo(3)	134.0(7)	143.7(8)	148.9(6)	139.8	149.7	16.7
U(2)–O(6)–Mo(2)	144.5(6)	150(1)	148.6(7)	152.0	151.6	7.5
U(2)–O(7)–Mo(4)	130.5(7)	144(1)	144.7(7)	136.5	138.7	14.4
U(3)–O(10)–Mo(2)	138.9(7)	146(1)	152.0(8)	152.7	148.1	14.4
U(1)–O(11)–Mo(3)	130.2(7)	130.6(8)	130.4(6)	133.4	135.4	5.2
U(3)–O(12)–Mo(1)	178(1)	164(1)	165.0(10)	164.9	165.8	15.0
U(2)–O(13)–Mo(1)	142(1)	139.9(9)	140.4(7)	148.8	140.1	9.0
U(2)–O(14)–Mo(4)	148.6(7)	148(1)	150.4(7)	149.4	156.1	8.1
U(2)–O(15)–Mo(3)	169.0(8)	146.7(9)	148.2(6)	160.3	144.3	24.7
U(1)–O(17)–Mo(4)	138.9(6)	132(1)	128.9(6)	137.8	132.1	10.0
U(1)–O(18)–Mo(4)	170.3(7)	171(1)	170.3(8)	165.5	169.5	5.5
U(1)–O(20)–Mo(3)	171(1)	151(1)	151.4(7)	157.9	153.2	20.0

1 = $(UO_2)_{0.82}[C_8H_{20}N]_{0.36}[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_n$, *n* ≈ 4–6 (this work).

2 = $[C_6H_{14}N_2]_2[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_m$, *m* ≈ 2 (this work).

3 = $[C_6H_{16}N]_2[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_2$ [10].

4 = $Mg[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_{12}$ [2].

5 = $Sr[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_{17}$ [2].

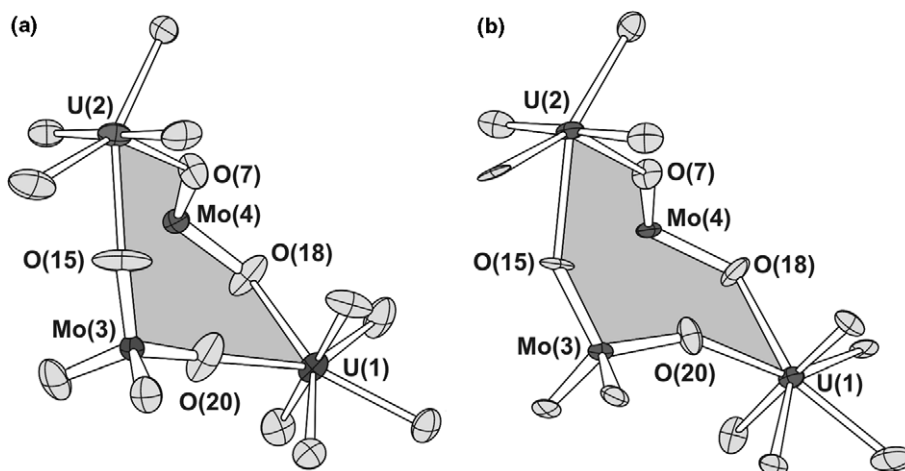


Fig. 2. Configurations of $-U(2)-O(7)-Mo(4)-O(18)-U(1)-O(20)-Mo(3)-O(15)-$ in the structures of **1** (a) and **2** (b).

thought as a disc with its rotation axis oriented along [010]. In order to adapt to this configuration, the $[(UO_2)_6(MoO_4)_7(H_2O)_2]^{2-}$ framework contracts along b and expands along the a axis (Fig. 1), which results in the shorter b and longer a unit-cell parameters of **1** in comparison with those of **2**.

The proposed mechanism of adaptation of the $[(UO_2)_6(MoO_4)_7(H_2O)_2]^{2-}$ framework to the form of extra-framework species is possible because of the high flexibility of uranyl molybdate units consisting of corner-sharing U and Mo coordination polyhedra. Table 6 provides a comparison of the unit-cell parameters and U–O–Mo angles in the structures of uranyl molybdates based upon $[(UO_2)_6(MoO_4)_7(H_2O)_2]^{2-}$ frameworks. For each U–O–Mo angle, the value Δ_{\max} was calculated as the difference between the maximum and minimum values in the structures of the five compounds listed:

$$\Delta_{\max} = (\langle U-O-Mo \rangle_{\max} - \langle U-O-Mo \rangle_{\min}) \quad [\text{deg}].$$

The Δ_{\max} parameter helps to identify the U–O(15)–Mo and U–O(20)–Mo links as the most flexible in the uranyl molybdate frameworks under consideration. Fig. 2 shows configurations of $-U(2)-O(7)-Mo(4)-O(18)-U(1)-O(20)-Mo(3)-O(15)-$ in the structures of **1** and **2**. Transition from **2** to **1** involves an increase of the U–O(15)–Mo and U–O(20)–Mo angles from 146.7° to 169.0° and from 151° to 171° , respectively. The fact that such a transition is energetically possible provides additional evidence of the high degree of flexibility of the U–O–Mo links in uranyl molybdates.

5. Conclusions

In this contribution, we have demonstrated that the 6:7 open-framework uranyl molybdates may have different conformation states of their uranyl molybdate units.

Due to the high flexibility of the U–O–Mo links, the framework adapts to the geometrical shape of complex extra-framework cations, which is manifested by significantly different unit-cell parameters of the 6:7 open-framework uranyl molybdates. It was suggested in [11] that the flexibility of uranyl molybdate units may result in interesting physical behavior such as highly anisotropic thermal expansion and displacive phase transitions. In the next paper of the series, we report the discovery of the $C222_1 \rightarrow P2_12_1$ phase transition in the structure of another new amine-templated 6:7 open-framework uranyl molybdate [10].

Acknowledgments

This research was supported by the Environmental Management Sciences Program of the United States Department of Energy (Grant DE-FG07-97ER14820). S.V.K. thanks Alexander von Humboldt Foundation and Swiss National Foundation for financial support during his stay at Bern.

References

- [1] S.V. Krivovichev, C.L. Cahill, E.V. Nazarchuk, P.C. Burns, T. Armbruster, W. Depmeier, *Micropor. Mesopor. Mater.* 78 (2005) 209.
- [2] V.V. Tabachenko, L.M. Kovba, V.N. Serezhkin, *Koord. Khim.* 10 (1984) 558.
- [3] M. Doran, A.J. Norquist, D. O'Hare, *Chem. Commun.* 22 (2002) 2946.
- [4] S.V. Krivovichev, *Radiochem.* 46 (2004) 401.
- [5] H.D. Flack, *Acta Crystallogr. A* 39 (1983) 876.
- [6] P.C. Burns, F.C. Hawthorne, R.C. Ewing, *Can. Mineral.* 35 (1997) 1551.
- [7] J. Kim, B. Chen, T.M. Reineke, H. Li, M. Eddaoudi, D.B. Moler, M. O'Keeffe, O. Yaghi, *J. Am. Chem. Soc.* 123 (2001) 8239.

- [8] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, *Acc. Chem. Res.* 34 (2001) 319.
- [9] I.D. Brown, *The Chemical Bond in Inorganic Chemistry. The Bond Valence Model*, Oxford University Press, Oxford New York, 2002.
- [10] S.V. Krivovichev, T. Armbruster, D.Yu. Chernyshov, P.C. Burns, E.V. Nazarchuk, W. Depmeier, *Micropor. Mesopor. Mater.* 78 (2005) 225.
- [11] E.V. Nazarchuk, S.V. Krivovichev, S.K. Filatov, *Radiochemistry* 46 (2004) 405.