Original paper

K$_2$Na$_8$(UO$_2$)$_8$Mo$_4$O$_{24}$[(S,Mo)O$_4$], the first uranium molybdosulfate: synthesis, crystal structure, and comparison to related compounds

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Orange platy crystals of K$_2$Na$_8$(UO$_2$)$_8$Mo$_4$O$_{24}$[(S,Mo)O$_4$], the first known uranium molybdosulfate, have been prepared by high-temperature solid-state reactions. The structure (monoclinic, *C*2/*c*, *a* = 24.282(4), *b* = 12.1170(18), *c* = 13.6174(17) Å, β = 106.33(1)º, *V* = 3845.0(9) Å^3, *Z* = 4) has been solved by direct methods and refined to R_1 = 0.058 on the basis of 2837 unique observed reflections. The structure consists of a three-dimensional heteropolyhedral framework based upon the [(UO$_2$)$_4$O$_4$(Mo$_2$O$_{10}$)] layers parallel to (010). The layers are formed by linkage of chains of edge-sharing UO$_7$ bipyramids running along the *c* axis via the Mo$_2$O$_{10}$ dimers of edge-sharing MoO$_6$ octahedra. Linkage of the layers into a three-dimensional framework is provided by the MoO$_4$ and SO$_4$ tetrahedra that share corners with the MoO$_6$ octahedra. The Na$^+$ and K$^+$ cations reside in framework cavities in between the uranyl molybdate layers. The structure of K$_2$Na$_8$(UO$_2$)$_8$Mo$_4$O$_{24}$[(S,Mo)O$_4$] is yet another complex derivative of the U$_2$MoO$_8$ structure type.

1. Introduction

Uranium molybdates and uranium sulfates represent two groups of important secondary minerals formed in the oxidation zones of uranium deposits (Čejka and Urbanec 1990; Finch and Murakami 1999; Krivovichev and Plášil 2013). Recent studies by Czech colleagues led to considerable advances in knowledge and understanding of formation and crystal chemistry of uranium sulfates, both with tetra- and hexavalent uranium ions (Plášil et al. 2010, 2011a, b, c, 2012a, b, c, 2013). On the other hand, recent synthetic investigations on uranium molybdate and uranium sulfate systems with the wide range of inorganic and organic cations supplied considerable amount of data on structure, topology and composition of this class of uranium compounds (Norquist et al. 2002, 2003a, b, c, 2005; Burns et al. 2003; Doran et al. 2003; Krivovichev and Burns 2007; Krivovichev 2008, 2010, etc.). However, no uranium oxocompounds with both S^{6+} and Mo^{6+} have been described to date. In this paper, we report on the synthesis and single-crystal structure study of the first uranium molybdosulfate obtained via solid-state reaction method.

2. Experimental

2.1. Synthesis

The initial mixture of Na$_2$SO$_4$ (0.037 g), uranyl acetate hydrate (0.112 g), and MoO$_3$ (0.038 g) (corresponding to the hypothetic formula Na$_2$(UO$_2$)(SO$_4$)(MoO$_4$)) was placed into a platinum crucible and heated to 700 ºC. After 3 hours it was cooled down to 300 ºC with the cooling rate of 12 ºC/h and then to room temperature with the cooling rate of 10 ºC/min. The product consisted of yellowish-green elongated crystals of Na$_2$(UO$_2$)$_3$(MoO$_4$)$_4$ with few transparent orange plates of the title phase. Crystal-structure determination of the orange crystals confirmed the chemical formula K$_2$Na$_8$(UO$_2$)$_8$Mo$_4$O$_{24}$[(S,Mo)O$_4$], where the presence of K was ascribed to the admixtures of K$_2$SO$_4$ to Na$_2$SO$_4$, verified by the qualitative electron microprobe analysis. The low content of S compared to the composition of initial reaction mixture can be explained by the evaporation of S under high-temperature conditions.

2.2. Single-crystal X-ray diffraction

The selected crystal of K$_2$Na$_8$(UO$_2$)$_8$Mo$_4$O$_{24}$[(S,Mo)O$_4$] was mounted on a STOE IPDS II X-ray diffractometer equipped with Image Plate area detector and operated at 50 kV and 40 mA. More than a hemisphere of three-dimensional data was collected using monochromatic MoK_α radiation, with frame widths of 2° in ω, and with a 5 minutes count for each frame. The unit-cell parameters (Tab. 1) were refined using least-squares techniques. The intensity data were integrated and corrected for Lorentz, polarization, and background effects using the STOE X-Red program (STOE and Cie 2002). An analytical absorption correction was made on the basis of experimentally determined crystal shape.

Tab. 1 Crystal data, data collection and structure refinement parameters for $K_2Na_8(UO_2)_8Mo_4O_{24}[(S,Mo)O_4]$

Crystal data	
Temperature	293 K
Radiation, wavelength	MoK_α, 0.71073 Å
Crystal system	monoclinic
Space group	$C2/c$
Unit-cell dimensions a, b, c (Å), β (°)	24.282(4), 12.1170(18), 13.6174(17), 106.33(1)
Unit-cell volume (Å³)	3845.0(9)
Z	4
Calculated density (g/cm³)	5.677
Absorption coefficient (mm⁻¹)	35.287
Crystal size (mm³)	$0.22 \times 0.12 \times 0.02$
Data collection	
θ range	1.75−27.31°
h, k, l ranges	$-30 \to 31, -15 \to 15, -17 \to 16$
Total reflections collected	14743
Unique reflections (R_{int})	4237 (0.065)
Unique reflections $F > 4\sigma(F)$	2837
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients a, b	0.0415, 643.0607
Extinction coefficient	0.000138(10)
Data/restraints/parameters	4237/0/201
R_1 [$F > 4\sigma(F)$], wR_2 [$F > 4\sigma(F)$],	0.058, 0.130
R_1 all, wR_2 all	0.086, 0.145
Goodness-of-fit on F^2	1.134
Largest diff. peak and hole, e Å⁻³	3.239, −4.255

The SHELX programs (Sheldrick 2008) were used for determination and refinement of the crystal structure. The structure was solved in the monoclinic space group $C2/c$ by direct methods and refined to an R_1 value of 0.058, calculated for the 2837 unique observed ($|F_o| \geq 4\sigma_F$) reflections. During the refinement, one of the positions initially assigned to Na appeared to have unreasonably small isotropic displacement parameter with cation–anion distances larger than 2.7 Å, which is more characteristic of K than of Na. Refinement of its occupancy using mixed Na–K scattering curve resulted in the refined site-occupation factor $K_{0.68(6)}Na_{0.42(6)}$. Structure refinement also indicated the presence of two tetrahedrally coordinated sites with rather different average bond lengths of c. 1.52 and 2.06 Å. These sites were considered as occupied by S and Mo, respectively, and pairwise constrained refinement of their occupancies provided satisfactory displacement parameters and site-occupation factors of 0.85(1) and 0.15(1), respectively. All cation sites were refined in an anisotropic approximation. Attempts to refine positions of O atoms anisotropically resulted in physically unrealistic parameters for several sites, most probably due to the disorder observed for the cation sites mentioned above.

Final atom coordinates and displacement parameters of the atoms are given in Tab. 2, selected interatomic

distances are in Tab. 3. Table 4 provides bond-valence analysis for the structure, with bond valences calculated using parameters provided by Burns et al. (1997) for the U^{6+}–O bonds and by Brese and O'Keeffe (1991) for other ones. As it can be seen, bond-valence sums incident upon the atom sites are in good agreement with the expected values, except for the low-occupied Mo3 and S sites.

3. Results

3.1. Cation coordination

The structure of the title compound contains four symmetrically independent U^{6+} cations, which form uranyl cations, $(UO_2)^{2+}$, with the U=O distances in the range of 1.80–1.89 Å. The uranyl ions are equatorially coordinated by five O atoms each, which results in the formation of UO_7 pentagonal bipyramids. The equatorial coordination is rather distorted, which manifests itself in relatively broad range of the U–O bond lengths (2.17–2.55 Å). This distortion can be explained by the chemical bonding inequivalence of the equatorial O ligands. The equatorial O atoms bonded to Mo (O1, O2, O14, O16, O17, O18) display fairly usual U–O bond lengths in the range of 2.37–2.52 Å, whereas the O10, O12, O13, and O15 sites are bonded to U atoms only and show comparably short U–O bond lengths (2.17–2.22 Å), in some cases complemented by longer U–O bonds (2.50–2.56 Å).

There are three Mo sites in the structure of $K_2Na_8(UO_2)_8Mo_4O_{24}[(S,Mo)O_4]$. The Mo1 and Mo2 sites are octahedrally coordinated with the four short and two long Mo–O bonds. This coordination geometry is typical of Mo^{6+} cations in natural and synthetic uranyl molybdates (Krivovichev and Burns 2000a, b). The Mo3 site is coordinated tetrahedrally and is rather low occupied (SOF = 0.15). As a consequence, the average <Mo3–O> bond length of 2.06 Å is much higher than the usual Mo–O bond length of 1.762(2) Å observed for MoO_4 tetrahedra in uranyl molybdates (Krivovichev 2013). One symmetrically independent S site in the structure is coordinated tetrahedrally by four O atoms. Its low occupation factor of 0.85 results in comparably longer

Tab. 2 Atom coordinates, site-occupation factors (SOF) and displacement parameters (Å^2) in the structure of K$_2$Na$_8$(UO$_2$)$_8$Mo$_4$O$_{24}$[(S,Mo)O$_4$]

Atom	SOF	x/a	y/b	z/c	U_{iso}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	U	0.37836(2)	0.49799(7)	0.03422(5)	0.0114(2)	0.0074(3)	0.0163(3)	0.0102(3)	0.0008(3)	0.0021(2)	−0.0001(3)
U2	U	0.21716(3)	0.49449(7)	−0.06373(5)	0.0141(2)	0.0091(3)	0.0237(4)	0.0093(3)	−0.0006(3)	0.0025(2)	−0.00003(3)
U3	U	0.12162(2)	0.50010(7)	−0.34417(5)	0.0117(2)	0.0072(3)	0.0173(3)	0.0106(3)	0.0001(3)	0.0026(2)	−0.0003(2)
U4	U	0.28279(3)	0.49771(7)	0.21899(5)	0.0154(2)	0.0082(3)	0.0293(4)	0.0091(3)	0.0001(3)	0.0027(2)	0.0011(3)
Mo1	Mo	0.04933(7)	0.4916(2)	−0.64055(12)	0.0242(4)	0.0078(7)	0.0529(12)	0.0123(7)	0.0012(9)	0.0035(5)	−0.0013(8)
Mo2	Mo	0.45064(7)	0.4918(2)	−0.19005(12)	0.0251(4)	0.0064(7)	0.0574(13)	0.0114(7)	0.0012(9)	0.0025(5)	−0.00038(8)
Mo3	Mo$_{0.15}$	0	0.248(2)	1/4	0.032(7)	0.022(11)	0.046(13)	0.027(12)	0	0.005(8)	0
S	S$_{0.85}$	1/2	0.2496(8)	1/4	0.027(2)	0.031(5)	0.013(4)	0.039(6)	0	0.012(4)	0
Na1	Na	0.3673(4)	0.2521(8)	0.1860(8)	0.027(2)	0.021(5)	0.026(5)	0.039(6)	0.011(4)	0.016(4)	−0.003(4)
Na2	Na	0.3673(4)	0.2483(8)	−0.3183(7)	0.025(2)	0.028(5)	0.019(4)	0.021(5)	0.001(4)	−0.003(4)	0.002(4)
Na3	Na	0.2980(4)	0.2511(9)	−0.1029(8)	0.033(2)	0.035(5)	0.026(5)	0.043(6)	0.001(4)	0.018(5)	0.005(4)
Na4	Na	0.2023(4)	0.7485(9)	0.0994(8)	0.032(2)	0.022(5)	0.032(5)	0.038(6)	0.017(4)	0.002(4)	0.003(4)
K	K$_{0.68}$Na$_{0.32}$	0.4995(4)	0.2501(7)	−0.0001(6)	0.047(3)	0.075(5)	0.043(4)	0.027(3)	−0.002(3)	0.025(3)	−0.001(4)
O1	O	−0.0310(5)	0.4977(12)	−0.6920(9)	0.012(2)						
O2	O	0.5308(6)	0.4978(13)	−0.1616(10)	0.017(3)						
O3	O	0.2837(8)	0.3416(16)	0.2243(15)	0.034(4)						
O4	O	0.2153(8)	0.3408(16)	−0.0653(15)	0.038(4)						
O5	O	0.3748(8)	0.6481(17)	0.0355(15)	0.037(4)						
O6	O	0.3822(7)	0.3497(14)	0.0313(13)	0.026(3)						
O7	O	0.2857(7)	0.6488(14)	0.2162(13)	0.026(3)						
O8	O	0.1175(8)	0.3505(16)	−0.3537(14)	0.035(4)						
O9	O	0.2148(7)	0.6464(14)	−0.0651(13)	0.027(4)						
O10	O	0.3116(6)	0.5066(13)	0.3881(10)	0.018(3)						
O11	O	0.1239(7)	0.6492(15)	−0.3359(14)	0.031(4)						
O12	O	0.1895(6)	0.4944(13)	0.0756(10)	0.019(3)						
O13	O	0.2050(6)	0.4874(14)	−0.2301(10)	0.022(3)						
O14	O	0.4412(7)	0.5214(14)	−0.0696(12)	0.028(3)						
O15	O	0.2944(7)	0.4888(15)	0.0639(11)	0.027(3)						
O16	O	0.0591(7)	0.5190(15)	−0.5120(13)	0.035(4)						
O17	O	0.1194(7)	0.5136(15)	−0.6606(12)	0.031(4)						
O18	O	0.3802(6)	0.5159(13)	−0.2816(11)	0.024(3)						
O19	O	0.053(1)	0.338(2)	−0.633(2)	0.060(6)						
O20	O	0.4605(8)	0.1781(17)	0.1661(16)	0.042(5)						
O21	O	0.4447(9)	0.3380(18)	−0.1885(17)	0.046(5)						
O22	O	0.5371(8)	0.3210(16)	0.2056(15)	0.038(4)						

Tab. 3 Selected bond lengths (in Å) in the structure of $K_2Na_8(UO_2)_8Mo_4O_{24}[(S,Mo)O_4]$

U1–O6	1.801(17)	U2–O9	1.841(17)	U3–O11	1.811(18)
U1–O5	1.82(2)	U2–O4	1.86(2)	U3–O8	1.818(19)
U1–O10	2.186(13)	U2–O15	2.171(15)	U3–O13	2.184(13)
U1–O15	2.190(16)	U2–O12	2.183(14)	U3–O12	2.220(14)
U1–O14	2.371(17)	U2–O13	2.202(14)	U3–O16	2.372(17)
U1–O2	2.392(13)	U2–O17	2.371(16)	U3–O1	2.386(12)
U1–O18	2.501(15)	U2–O10	2.555(14)	U3–O17	2.521(17)
U4–O7	1.832(17)	Mo1–O16	1.731(18)	Mo2–O14	1.755(17)
U4–O3	1.89(2)	Mo1–O17	1.818(17)	Mo2–O18	1.836(15)
U4–O13	2.195(14)	Mo1–O19	1.86(3)	Mo2–O21	1.87(2)
U4–O15	2.210(15)	Mo1–O1	1.880(12)	Mo2–O2	1.876(13)
U4–O10	2.213(13)	Mo1–O1	2.198(12)	Mo2–O2	2.191(13)
U4–O18	2.372(15)	Mo1–O20	2.29(2)	Mo2–O22	2.30(2)
U4–O12	2.541(13)				
		Na1–O4	2.48(2)	Na2–O11	2.38(2)
Mo3–O21	2.06(3) 2×	Na1–O3	2.48(2)	Na2–O5	2.40(2)
Mo3–O19	2.06(3) 2×	Na1–O22	2.52(2)	Na2–O19	2.44(3)
		Na1–O20	2.52(2)	Na2–O21	2.44(2)
S-O22	1.49(2) 2×	Na1–O6	2.53(2)	Na2–O7	2.50(2)
S-O20	1.54(2) 2×	Na1–O8	2.54(2)	Na2–O9	2.50(2)
Na3–O4	2.46(2)	Na4–O7	2.51(2)	K–O19	2.74(3)
Na3–O3	2.47(2)	Na4–O9	2.53(2)	K–O21	2.75(2)
Na3–O11	2.59(2)	Na4–O5	2.55(2)	K–O22	2.82(2)
Na3–O6	2.62(2)	Na4–O3	2.59(2)	K–O20	2.83(2)
Na3–O4	2.65(2)	Na4–O8	2.61(2)	K–O14	3.14(2)
Na3–O7	2.69(2)	Na4–O9	2.65(2)	K–O16	3.15(2)
				K–O8	3.18(2)
				K–O6	3.23(2)

(a)

MoO6 UO7

SO4 Na

b

a sinβ

(b)

c

a
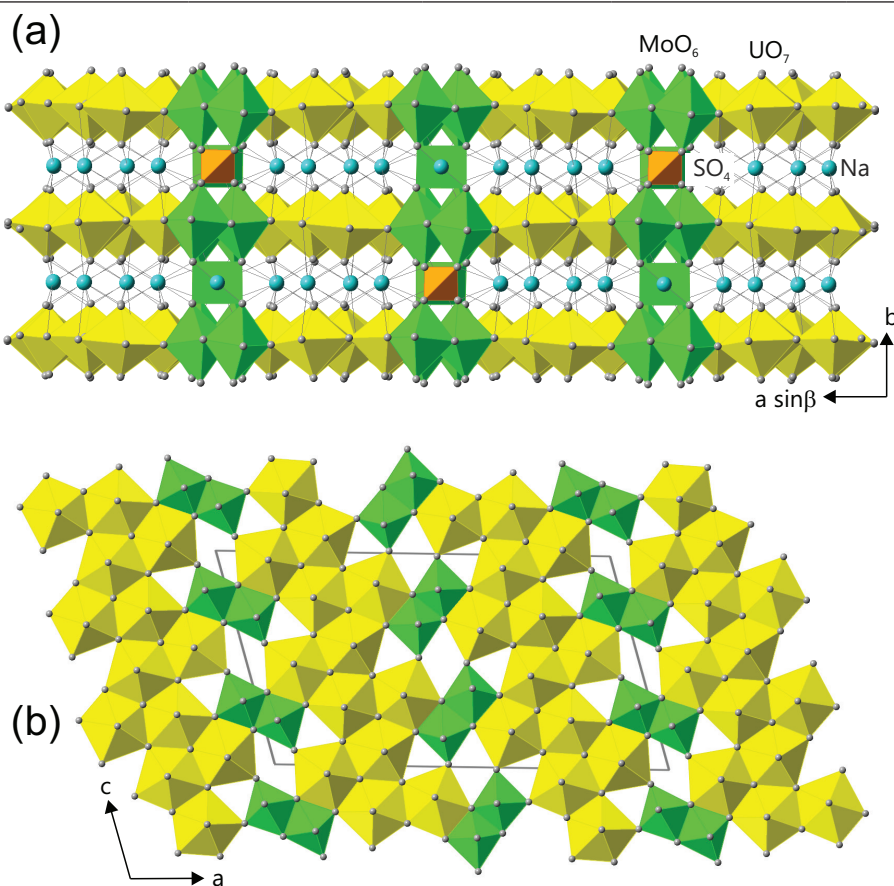
average <S–O> bond length of 1.52 Å, which can be compared to the average <S–O> distance in sulfates (1.475 Å: Hawthorne et al. 2000) and in uranyl sulfates in particular (1.473(2) Å: Krivovichev 2013).

The structure contains four symmetrically independent Na sites octahedrally coordinated by six O atoms each, and one mixed K–Na site coordinated by eight O atoms.

3.2. Structure description

The basis of the structure of $K_2Na_8(UO_2)_8Mo_4O_{24}[(S,Mo)O_4]$ is a three-dimensional hetero-polyhedral framework formed by UO7 pentagonal bipyramids, MoO6 octahedra, MoO4 and SO4

Fig. 1a – Projection of the crystal structure of $K_2Na_8(UO_2)_8Mo_4O_{24}[(S,Mo)O_4]$ along the *c* axis. **b** – Uranyl molybdate layer projected onto the (010) plane.

Tab. 4 Bond-valence analysis (in v.u. = valence units) for the structure of $K_2Na_8(UO_2)_8Mo_4O_{24}[(S,Mo)O_4]$

	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	O11	O12	O13	O14	O15	O16	O17	O18	O19	O20	O21	O22	ΣBV
U1		0.51			1.55	1.61				0.76				0.53	0.75			0.41					6.12
U2				1.44					1.49	0.37		0.76	0.74		0.78		0.53						6.11
U3	0.51							1.56			1.58	0.71	0.76			0.53	0.39						6.04
U4			1.36				1.52			0.72		0.38	0.75		0.72			0.53					5.98
Mo1	1.08, 0.46															1.61	1.27		1.14	0.36			5.92
Mo2		1.09, 0.46												1.51				1.21			1.11	0.35	5.73
Mo3																			$0.66^{2\rightarrow}$		$0.66^{2\rightarrow}$		2.64*
S																				$1.25^{2\rightarrow}$		$1.44^{2\rightarrow}$	5.38*
Na1			0.16	0.16		0.14		0.14												0.14		0.14	0.88
Na2					0.20		0.15		0.15		0.21								0.18		0.18		1.07
Na3			0.16	0.17, 0.10		0.11	0.09				0.12												0.75
Na4			0.12		0.13		0.15	0.11	0.14, 0.10														0.75
K						0.05		0.06						0.07		0.06			0.19	0.15	0.19	0.16	0.93
	2.05	2.06	1.80	1.87	1.88	1.91	1.91	1.87	1.88	1.85	1.91	1.85	2.25	2.11	2.25	2.20	2.19	2.15	2.17	1.90	2.14	2.09	

* partially occupied sites

tetrahedra (Fig. 1a). In turn, the framework can be considered as based upon the $[(UO_2)_4O_4(Mo_2O_{10})]$ layers parallel to (010) (Fig. 1b). The layers are formed by linkage of chains of edge-sharing UO_7 bipyramids running along the *c* axis via the Mo_2O_{10} dimers of edge-sharing MoO_6 octahedra. Linkage of the layers into a three-dimensional framework is provided by the MoO_4 and SO_4 tetrahedra that share corners with the MoO_6 octahedra.

Alternatively, the framework can be described as constructed by cross-linkage of chains of edge-sharing UO_7 bipyramids parallel to [001] and octahedral–tetrahedral molybdosulfate chains parallel to [010]. The latter are arranged in the (100) plane as shown in Fig. 2. Note that tetrahedral sites are partially occupied; so, in the real arrangement, the chains are not continuous but interrupted at every second tetrahedron position.

The Na^+ and K^+ cations reside in framework cavities in between the uranyl molybdate layers.

4. Discussion

The structure of $K_2Na_8(UO_2)_8Mo_4O_{24}[(S,Mo)O_4]$ is yet another complex derivative of the U_2MoO_8 structure type (Serezhkin et al. 1973). In the structure of the latter compound, the uranium molybdate layers of the type shown in Fig. 1b are linked together by sharing apical vertices of the UO_7 and MoO_6 coordination polyhedra. In derivative structures (Krivovichev 2013; Krivovichev and Plášil 2013), the layers are separated from each other by the insertion of additional TO_4 tetrahedra and monovalent cations into the interlayer. This is the case in the title compound, $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$ (Krivovichev and Burns 2003) and $Cs_2Na_8[(UO_2)_8O_8(Mo_5O_{20})]$ (Nazarchuk et al. 2009). Alternatively, they can be separated by monovalent cations only, as in $CsNa_3[(UO_2)_4O_4Mo_2O_8]$ (Nazarchuk et al. 2009). It is noteworthy that the uranyl molybdate layer shown in Fig. 1b can be considered as a derivative of the protasite anion topology (Krivovichev 2013).

5. Conclusions

In this paper, we report on the synthesis and crystal-structure determination of $K_2Na_8(UO_2)_8Mo_4O_{24}[(S,Mo)O_4]$, the first uranium molybdosulfate. This work provides general positive conclusion on the possibility of combination of U, Mo, and S in the same oxocompound. No similar compounds have been found in nature so far, though their formation is theoretically possible, as demonstrated by the present work.
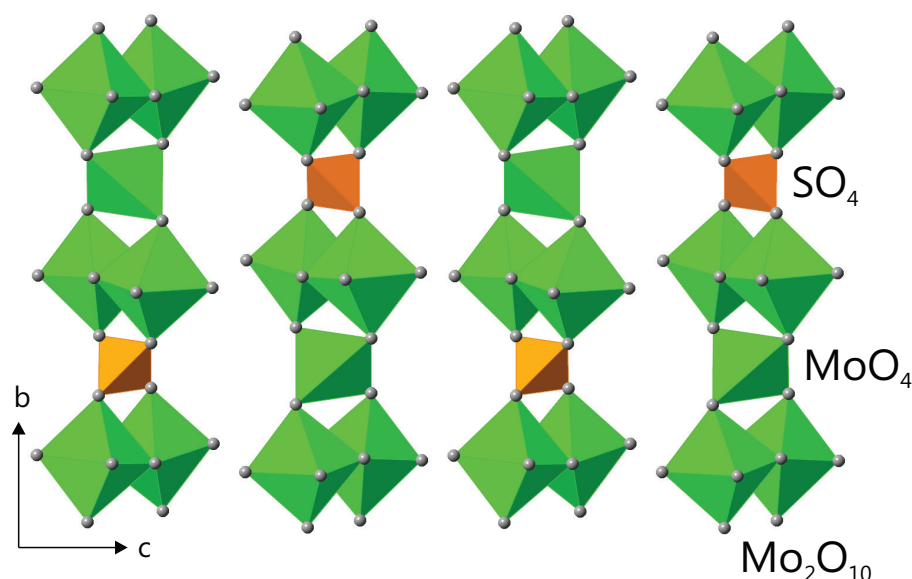
Fig. 2 Orientation of the molybdosulfate chains in the structure of $K_2Na_8(UO_2)_8Mo_4O_{24}[(S,Mo)O_4]$ within the (100) plane.

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