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CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. X. THE CRYSTAL STRUCTURE OF $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$

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ABSTRACT

Crystals of a new silver uranyl molybdate, $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$, have been synthesized by high-temperature solid-state reaction. The structure [monoclinic, $C2/c$, a 24.672(2), b 23.401(2), c 6.7932(4) Å, β 94.985(2)°, V 3907.3(4) Å^3, $Z = 4$] was solved by direct methods and refined to $R1 = 0.049$ ($wR2 = 0.101$) on the basis of 4317 unique observed reflections using a crystal twinned on (001). The twinning causes overlap of the reflections with $l = 3n$. The structure is based upon complex double sheets of UrO_5 pentagonal bipyramids and Mo polyhedra. The double sheets are parallel to (100) and consist of two $[(UO_2)_2O_2(MoO_5)]$ sheets of UrO_5 bipyramids and MoO_6 octahedra. Within the $[(UO_2)_2O_2(MoO_5)]$ sheets, UrO_5 bipyramids share edges to produce complex chains parallel to the c axis and linked *via* pairs of edge-sharing MoO_6 octahedra. The two $[(UO_2)_2O_2(MoO_5)]$ sheets are linked into double $[(UO_2)_8O_8(Mo_5O_{20})]$ sheets *via* the Mo(3)O_4 tetrahedron located between the sheets. The MoO_4 tetrahedra share two corners with two MoO_6 octahedra of the sheet above and two corners with MoO_6 octahedra from the sheet below, so that Mo_5O_{20} pentanuclear clusters are formed. The uranyl molybdate sheets found in the structure have not been previously observed in uranyl minerals and inorganic compounds. The Ag(2), Ag(3), Ag(6), Ag(7), and Ag(8) atoms are located within the double sheets, whereas the Ag(1), Ag(4), and Ag(5) are in between the double sheets.

Keywords: uranyl molybdate, crystal structure, silver.

SOMMAIRE

Nous avons synthétisé des cristaux d'un nouveau molybdate uranylé d'argent, $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$, par réaction à l'état solide à température élevée. La structure [monoclinique, $C2/c$, a 24.672(2), b 23.401(2), c 6.7932(4) Å, β 94.985(2)°, V 3907.3(4) Å^3, $Z = 4$] a été résolue par méthodes directes et affinée jusqu'à un résidu $R1$ de 0.049 ($wR2 = 0.101$) en utilisant 4317 réflexions uniques observées sur un cristal maclé selon (001). Les macles causent une surimposition de réflexions ayant $l = 3n$. La structure contient des feuillets doubles complexes de bipyramides pentagonales UrO_5 et de polyèdres contenant le Mo. Les feuillets doubles sont parallèles à (100) et sont faits de deux feuillets $[(UO_2)_2O_2(MoO_5)]$ contenant des bipyramides UrO_5 et les octaèdres MoO_6. Dans ces feuillets les bipyramides UrO_5 partagent des arêtes pour former des chaînes complexes parallèles à l'axe c qui sont interliées par des paires d'ocatèdres partageant une arête. Les deux feuillets $[(UO_2)_2O_2(MoO_5)]$ sont agencés en feuillets doubles $[(UO_2)_8O_8(Mo_5O_{20})]$ par un tétraèdre Mo(3)O_4 situé entre les feuillets. Ces tétraèdres MoO_4 partagent deux coins avec deux octaèdres MoO_6 du feuillet supérieur et deux coins avec les octaèdres MoO_6 du feuillet inférieur, de sorte qu'il en résulte des groupements pentanucléaires de composition Mo_5O_{20}. De tels feuillets de molybdate uranylé n'avaient pas été signalés dans la nature ou les produits de synthèse. Les atomes Ag(2), Ag(3), Ag(6), Ag(7), et Ag(8) sont situés au sein des feuillets doubles, tandis que Ag(1), Ag(4), et Ag(5) sont situés dans l'interfeuillet.

(Traduit par la Rédaction)

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

INTRODUCTION

Uranyl molybdates of monovalent cations show remarkable structural variability. Recently, Krivovichev & Burns (2002a) reported the synthesis and crystal structure of the first silver uranyl molybdate, $Ag_6[(UO_2)_3O(MoO_4)_5]$: that compound is based upon a unique sheet consisting of triuranyl clusters $(UO_2)_3O$ and MoO_4 tetrahedra. Compared to known alkali metal, ammonium and thallium uranyl molybdates (Krivovichev & Burns 2001a, b, 2002b, c, d, 2003a, b, Krivovichev *et al.* 2002a, b, 2003, Obbade *et al.* 2003a, and references therein), the structure of $Ag_6[(UO_2)_3O(MoO_4)_5]$ is quite unusual as a consequence of the

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small size of the Ag^+ cation and features of its electronic configuration. Together with crystals of $Ag_6[(UO_2)_3O(MoO_4)_5]$, we synthesized several crystals of another silver uranyl molybdate, $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$, the structure of which we report here. Its novel structure provides new important insights into crystal chemistry of uranyl molybdates and uranyl compounds in general.

EXPERIMENTAL

Synthesis

Crystals of $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$ were obtained by loading $AgNO_3$ (0.068 g), MoO_3 (0.058 g) and UO_3 (0.057 g) into a platinum crucible. The mixture was heated at 650°C for 5 h in air, followed by cooling to 300°C over 50 h and then to 50°C over 10 h. The product consisted of orange tabular transparent crystals of $Ag_6[(UO_2)_3O(MoO_4)_5]$ with several dark red plates of $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$.

X-ray data collection

A small crystal of $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$ was mounted on a Bruker three-circle diffractometer equipped with a SMART APEX CCD (charge-coupled device) detector with a crystal-to-detector distance of 4.67 cm. More than a hemisphere of data was collected using monochromated Mo$K\alpha$ X-radiation and frame-widths of 0.3° in ω. The unit-cell dimensions (Table 1) were refined using least-squares techniques. The three-dimensional data were reduced and filtered for statistical outliers using the Bruker program SAINT. The data were corrected for Lorentz, polarization and background effects. An empirical absorption-correction was done for the crystal by modeling it as an ellipsoid, which lowered R_{int} from 9.6 to 4.4%. Additional information pertinent to the data collection 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 structure. Initial attempts to solve the structure in the monoclinic system space, group $C2/c$, were unsuccessful. The positions of U and Mo atoms were located by direct methods, but large residual electron-density peaks were invariably present around the positions of the heavy cation. Lowering the symmetry to space group $C1$ did not improve the situation. We concluded that the crystals are twinned on (001), and inspection of the reciprocal space showed that reflections with $l = 3n$ overlap (Fig. 1). This twinning can be described as being pseudo-merohedral, with the $l = 3n$ reflections overlapped. Such twinning cannot be taken into account by simple application of the TWIN instruction in the current or previous versions of the SHELXTL system of programs. Thus, reflections with $l = 3n$ and $l \neq 3n$ were placed in separate datasets. The structure was easily solved in the space group $C2/c$ using only reflections with $l \neq 3n$. The structure was refined to $R1 = 0.047$ on the basis of 2878 unique observed reflections with $l \neq 3n$. The largest peak on the difference Fourier map was 4.80 e^-. The model was further refined using all reflections to $R1$ of 0.056 on the basis of 4317 unique observed reflections. This model resulted in nine large peaks (5.0–12.5 e^-) in the difference-Fourier maps, close to the positions of the U, Mo and Ag atoms. The scale factors for the datasets with $l = 3n$ and $l \neq 3n$ were subsequently refined, and all data were adjusted to the same scale factor by multiplying F^2_{hkl} by 0.8354 for the reflections with $l = 3n$, *i.e.*, reflections for which overlap in the reciprocal space has been observed (Fig. 1). The modified dataset was used in the final refinement that included the positional parameters of all atoms with an allowance for anisotropic displacement of cations, and a weighting scheme of the structure factors.

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$

a (Å)	24.672(2)	D_{calc} (g/cm^3)	7.08
b (Å)	23.401(2)	Crystal size (mm)	0.10 x 0.04 x 0.02
c (Å)	6.7932(4)	Radiation	Mo$K\alpha$
β (°)	94.985(2)	Total Ref.	21613
V (Å^3)	3907.3(4)	Unique Ref.	8009
Space group	$C2/c$	Unique $\lvert F_o\rvert \geq 4\sigma_F$	4317
F_{000}	7072	R_1	0.049
Z	4	wR_2	0.101
μ (cm^{-1})	395.60	S	0.863

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

The refinement of anisotropic parameters of anions resulted in physically unrealistic parameters for some of the O atoms, most likely due to the effects of twinning: the reciprocal lattices of the two twin components do not completely overlap in reciprocal space, and their separation cannot be achieved perfectly. On the basis of the structure refinement, the chemical formula of the compound was determined to be $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$. The final refinement converged to an agreement index ($R1$) of 0.049, calculated for the 4317 unique observed reflections ($F_o > 4\sigma_{Fo}$), with a goodness-of-fit (S) of 0.863. In the final refinement, the largest residue in the difference-Fourier map was 2.3 e^-. Final positional and displacement parameters of the atoms, and selected interatomic distances, are reported in Tables 2 and 3, 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

There are four symmetrically independent U^{6+} cations in the structure, each of which is strongly bonded to two O atoms, forming approximately linear uranyl ions with U–O_{Ur} bond lengths of ~1.8 Å. Uranyl ions are coordinated by five anions arranged at the vertices of UrO_5 pentagonal bipyramids. It is interesting that some of the U^{6+}–O bonds in the uranyl ions are essentially longer than 1.8 Å. This can be explained as a result of external influence of Ag^+ cations that form relatively strong Ag^+–O bonds to the O atoms of the uranyl ions. For instance, the relatively long U(2)–O(2) bond, 1.90(1) Å, is probably a result of formation of two short Ag(2)–O(2) and Ag(3)–O(2) bonds (2.47 and 2.48 Å, respectively) and one longer Ag(3)–O(2) bond (2.62 Å).

There are three symmetrically independent Mo^{6+} cations in the structure. The Mo(1) and Mo(2) are each coordinated by six O atoms in strongly distorted octahedral arrangements. The $Mo(1)O_6$ and $Mo(2)O_6$ coordination polyhedra each consist of two short (1.68–1.77 Å), two intermediate (1.83–1.88 Å) and two long (2.23–2.36 Å) Mo^{6+}–O bonds. A similarly distorted octahedral coordination of the Mo^{6+} cations occurs in the structures of umohoite, iriginite, and a low hydrate analogue of iriginite (Krivovichev & Burns 2000a, b, 2002b). The Mo(3) atom is tetrahedrally coordinated by four O atoms with a <Mo(3)–O> bond of 1.73 Å.

There are eight symmetrically independent Ag sites in the structure, of which Ag(5) and Ag(8) are partially occupied. The Ag(4), Ag(5), and Ag(8) atoms are coordinated by six anions each, whereas the Ag(1), Ag(2), Ag(3), Ag(6), and Ag(7) are coordinated by eight anions each. The <Ag–O> average bond-lengths are in the range of 2.60 to 2.73 Å.

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.87540(2)	0.12838(3)	0.50536(8)	0.0082(1)	0.0147(3)	0.0044(3)	0.0058(3)	-0.0001(2)	0.0029(2)	-0.0001(2)
U(2)	0.87310(3)	-0.03357(3)	0.54066(9)	0.0087(1)	0.0148(3)	0.0061(3)	0.0055(2)	0.0004(2)	0.0019(2)	0.0000(2)
U(3)	0.62419(2)	-0.12832(3)	0.59042(8)	0.0081(1)	0.0142(3)	0.0036(3)	0.0064(3)	-0.0003(2)	0.0008(2)	-0.0002(2)
U(4)	0.62692(3)	0.03342(3)	0.62694(8)	0.0081(1)	0.0140(3)	0.0055(3)	0.0050(2)	-0.0007(2)	0.0017(2)	-0.0004(2)
Ag(1)	0.74727(7)	-0.04640(7)	0.8264(2)	0.0245(3)	0.0240(8)	0.0250(8)	0.0250(8)	0.0022(6)	0.0041(6)	0.0022(6)
Ag(2)	0	-0.10751(10)	-¼	0.0244(5)	0.0275(12)	0.0183(11)	0.0292(11)	0	0.0126(9)	0
Ag(3)	0	-0.04924(10)	¼	0.0256(5)	0.0280(12)	0.0253(12)	0.0231(11)	0	-0.0011(9)	0
Ag(4)	0.75459(6)	-0.11720(7)	0.3144(2)	0.0236(3)	0.0244(8)	0.0179(8)	0.0281(8)	0.0004(6)	-0.0005(6)	0.0021(6)
Ag(5)*	0.75897(9)	-0.28430(10)	0.2190(3)	0.0321(5)	0.0290(12)	0.0267(12)	0.0419(12)	0.0094(10)	0.0111(10)	0.0128(9)
Ag(6)	½	-0.10711(10)	¼	0.0252(5)	0.0281(12)	0.0175(11)	0.0286(11)	0	-0.0051(9)	0
Ag(7)	½	-0.04981(10)	¾	0.0236(5)	0.0239(11)	0.0211(11)	0.0270(11)	0	0.0087(9)	0
Ag(8)**	0	-0.2022(4)	¼	0.073(2)	0.077(5)	0.089(7)	0.056(4)	0	0.020(4)	0
Mo(1)	0.63527(6)	-0.20220(6)	0.1194(2)	0.0087(3)	0.0144(7)	0.0046(6)	0.0075(6)	0.0004(5)	0.0032(5)	-0.0003(5)
Mo(2)	0.63392(6)	-0.29817(6)	0.4749(2)	0.0083(3)	0.0141(7)	0.0041(6)	0.0066(6)	0.0004(4)	0.0001(5)	0.0009(5)
Mo(3)	0	-0.25144(10)	-¼	0.0181(5)	0.0075(9)	0.0134(11)	0.0327(12)	0	-0.0020(9)	0
O(1)	0.7985(6)	-0.0386(6)	0.5160(19)	0.023(3)						
O(2)	0.9504(6)	-0.0297(6)	0.5684(19)	0.022(3)						
O(3)	0.8024(5)	0.1342(6)	0.4889(18)	0.019(3)						
O(4)	0.6968(5)	-0.1336(6)	0.6191(18)	0.022(3)						
O(5)	0.6244(4)	-0.2191(5)	0.4365(15)	0.009(2)						
O(6)	0.7005(6)	0.0394(6)	0.6482(20)	0.026(3)						
O(7)	0.5494(5)	0.0310(6)	0.6070(18)	0.021(3)						
O(8)	0.9509(5)	0.1252(6)	0.5294(17)	0.019(3)						
O(9)	0.7032(6)	-0.3004(6)	0.5031(19)	0.026(3)						
O(10)	0.5473(5)	-0.1265(6)	0.5646(18)	0.024(3)						
O(11)	0.7035(6)	-0.2016(6)	0.1387(19)	0.027(3)						
O(12)	0.6163(5)	-0.3090(6)	0.7190(17)	0.017(3)						
O(13)	0.6247(5)	-0.2813(6)	0.1480(16)	0.015(2)						
O(14)	0.9616(6)	-0.2088(7)	-0.4137(21)	0.033(4)						
O(15)	0.8766(5)	-0.0631(6)	0.2357(18)	0.024(3)						
O(16)	0.6231(5)	-0.0625(6)	0.8199(18)	0.019(3)						
O(17)	0.6192(5)	-0.1898(6)	-0.1353(17)	0.018(3)						
O(18)	0.9585(5)	-0.2949(6)	-0.1226(19)	0.024(3)						
O(19)	0.8720(5)	-0.0441(6)	0.8581(18)	0.017(3)						
O(20)	0.6215(5)	-0.1318(6)	0.2206(16)	0.015(2)						
O(21)	0.6246(7)	0.0468(7)	0.9422(23)	0.037(4)						
O(22)	0.6148(6)	-0.3684(7)	0.3623(20)	0.030(3)						

* s.o.f. = 0.75. ** s.o.f. = 0.50.

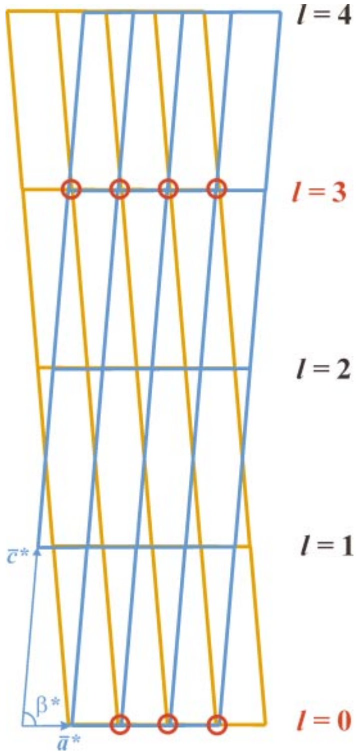

FIG. 1. Schematic representation of the overlap of reciprocal lattices of two twin components (orange and blue lattices) of the crystal of $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$ twinned on (001). The overlapped lattice points are marked by red circles. The overlap occurs for the reflections with $l = 3n$.

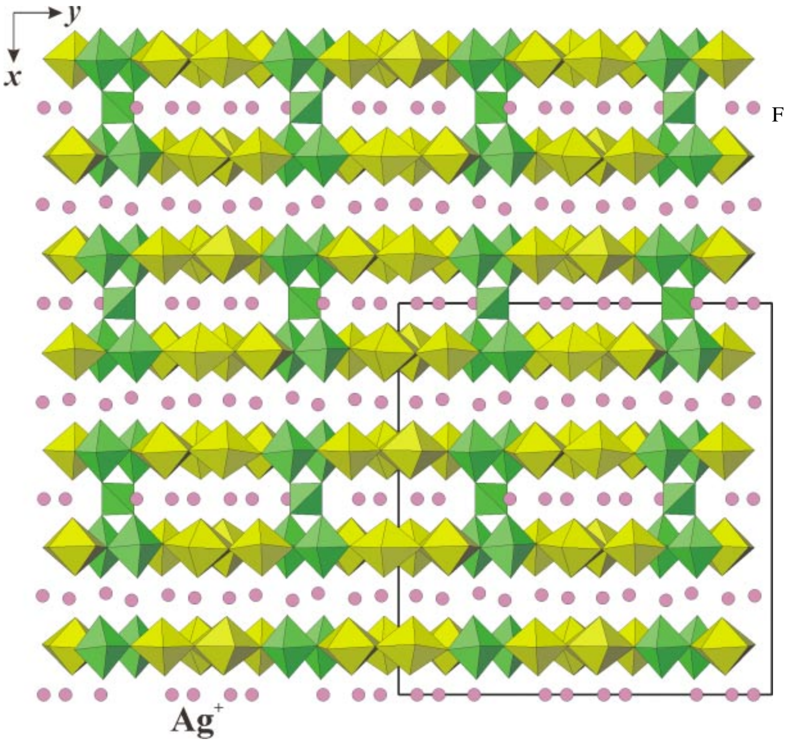

FIG. 2. The crystal structure of $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$ projected along the c axis. Legend: U polyhedra are yellow, Mo polyhedra are green, Ag^+ cations are lavender.

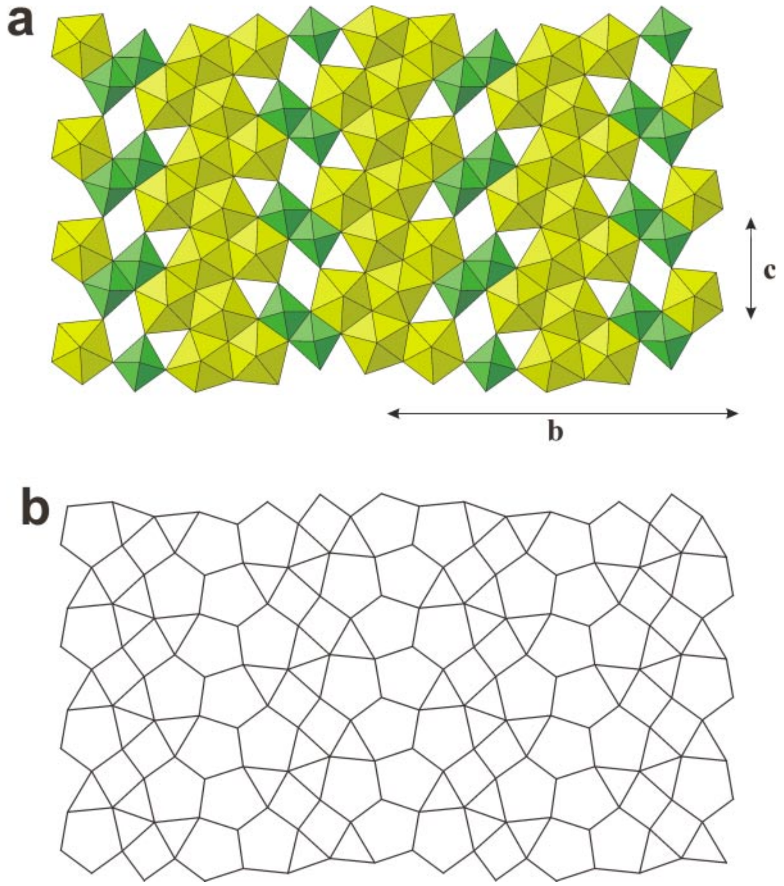

FIG. 3. The single uranyl molybdate sheet in the structure of $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$ (a) and its anion topology (b), presented according to the method by Burns *et al*. (1996). Legend: U polyhedra are yellow, Mo polyhedra are green.

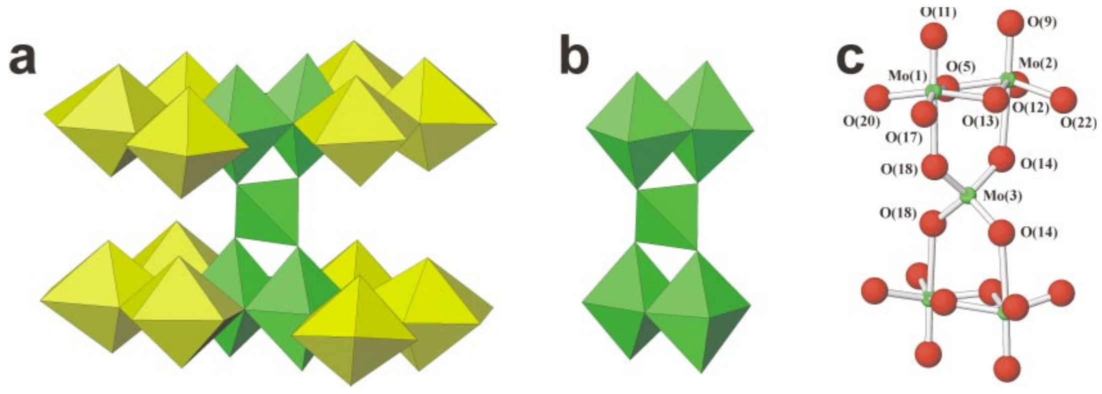

FIG. 4. Diagram demonstrating linkage of two adjacent uranyl molybdate sheets into double sheet *via* $Mo(3)O_4$ tetrahedron (a), and Mo_5O_{20} cluster shown in polyhedral (b) and ball-and-stick representations. Legend: U polyhedra are yellow, Mo polyhedra are green, Mo atoms are green spheres, and O atoms are red spheres.

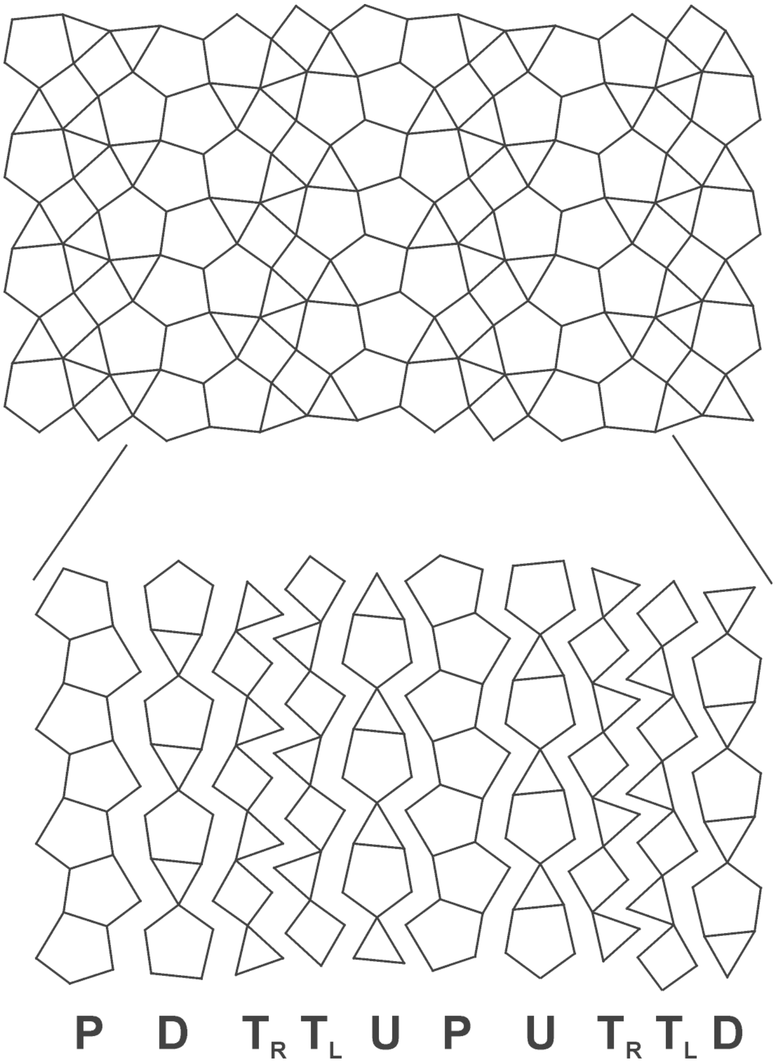

FIG. 5. Anion topology of uranyl molybdate sheet in the structure of $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$ (a) and its construction from chains of polygons (b).

Bond-valence analysis

The 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 Ag^+–O and Mo^{6+}–O bonds. The calculated bond-valence sums for hexavalent cations are 5.98, 5.92, 6.01, 5.91, 6.35, 6.05, and 6.54 *vu* (valence units) for U(1), U(2), U(3), U(4), Mo(1), Mo(2), and Mo(3), respectively. The bond-valence sums for Ag atoms are in the range of 0.61–1.05 *vu* (the lowest bond-valence sums correspond to partially occupied Ag sites). The bond-valence sums for the O atoms are in the range of 1.61–2.26 *vu*.

Description of the structure

The structure of $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$ (Fig. 2) contains complex double sheets of UrO_5 pentagonal bipyramids and Mo polyhedra. The double sheets are parallel to (100) and consist of two sheets of composition $[(UO_2)_2O_2(MoO_5)]$ that contain UrO_5 bipyramids and MoO_6 octahedra (Fig. 3a). Within these sheets, UrO_5 bipyramids share equatorial edges, resulting in

TABLE 3. SELECTED BOND LENGTHS (Å) IN THE STRUCTURE OF Ag$_{10}$[(UO$_2$)$_8$O$_8$(Mo$_5$O$_{20}$)]

U(1)-O(3)	1.80(1)	Ag(1)-O(1)	2.56(1)
U(1)-O(8)	1.86(1)	Ag(1)-O(6)a	2.56(1)
U(1)-O(15)a	2.19(1)	Ag(1)-O(6)	2.57(1)
U(1)-O(19)b	2.21(1)	Ag(1)-O(1)a	2.63(1)
U(1)-O(13)c	2.36(1)	Ag(1)-O(3)a	2.65(1)
U(1)-O(12)d	2.37(1)	Ag(1)-O(4)	2.72(1)
U(1)-O(22)c	2.53(1)	Ag(1)-O(19)	3.07(1)
<U(1)-O$_{Ur}$>	2.33	Ag(1)-O(16)	3.08(1)
<U(1)-O$_{eq}$>	1.83	<Ag(1)-O>	2.73
U(2)-O(1)	1.84(1)	Ag(2)-O(8)j,k	2.38(1) 2x
U(2)-O(2)	1.90(1)	Ag(2)-O(2)l,q	2.47(1) 2x
U(2)-O(19)	2.17(1)	Ag(2)-O(14)h,i	2.75(2) 2x
U(2)-O(15)	2.19(1)	Ag(2)-O(22)m,n	2.93(1) 2x
U(2)-O(19)b	2.20(1)	<Ag(2)-O>	2.63
U(2)-O(22)e	2.40(1)		
U(2)-O(15)a	2.62(1)	Ag(3)-O(2)o,k	2.48(1) 2x
<U(2)-O$_{Ur}$>	2.32	Ag(3)-O(8)k,o	2.56(1) 2x
<U(2)-O$_{eq}$>	1.87	Ag(3)-O(2)h,q	2.62(1) 2x
		Ag(3)-O(15)h,q	3.06(1) 2x
U(3)-O(4)	1.79(1)	<Ag(3)-O>	2.68
U(3)-O(10)	1.89(1)		
U(3)-O(21)b	2.16(2)	Ag(4)-O(6)b	2.47(1)
U(3)-O(16)	2.19(1)	Ag(4)-O(9)e	2.47(1)
U(3)-O(17)f	2.37(1)	Ag(4)-O(1)	2.49(1)
U(3)-O(5)	2.37(1)	Ag(4)-O(11)	2.58(2)
U(3)-O(20)	2.51(1)	Ag(4)-O(3)b	2.63(1)
<U(3)-O$_{Ur}$>	1.84	Ag(4)-O(4)	2.64(1)
<U(3)-O$_{eq}$>	2.32	<Ag(4)-O>	2.55
U(4)-O(6)	1.81(1)	Ag(5)-O(11)	2.41(2)
U(4)-O(7)	1.91(1)	Ag(5)-O(4)e	2.42(1)
U(4)-O(21)	2.17(2)	Ag(5)-O(9)	2.50(1)
U(4)-O(16)b	2.19(1)	Ag(5)-O(11)g	2.70(1)
U(4)-O(21)b	2.26(2)	Ag(5)-O(3)p	2.75(1)
U(4)-O(20)a	2.40(1)	Ag(5)-O(9)e	2.84(1)
U(4)-O(16)	2.61(1)	<Ag(5)-O>	2.60
<U(4)-O$_{Ur}$>	1.86		
<U(4)-O$_{eq}$>	2.33	Ag(6)-O(10),q	2.39(1) 2x
		Ag(6)-O(7)o,b	2.41(1) 2x
Mo(1)-O(11)	1.68(1)	Ag(6)-O(18)r,g	2.68(1) 2x
Mo(1)-O(17)	1.77(1)	Ag(6)-O(20),q	3.08(1) 2x
Mo(1)-O(20)	1.83(1)	<Ag(6)-O>	2.68
Mo(1)-O(13)	1.88(1)		
Mo(1)-O(5)	2.23(1)	Ag(7)-O(7),s	2.49(1) 2x
Mo(1)-O(18)_$20	2.32(1)	Ag(7)-O(10),s	2.54(1) 2x
<Mo(1)-O>	1.95	Ag(7)-O(7)a,o	2.65(1) 2x
		Ag(7)-O(16),s	3.05(1) 2x
Mo(2)-O(9)	1.71(1)	<Ag(7)-O>	2.64
Mo(2)-O(12)	1.77(1)		
Mo(2)-O(22)	1.86(2)	Ag(8)-O(14)t,i	2.55(1) 2x
Mo(2)-O(5)	1.88(1)	Ag(8)-O(8)o,k	2.58(1) 2x
Mo(2)-O(13)	2.25(1)	Ag(8)-O(12)n,u	2.91(1) 2x
Mo(2)-O(14)g	2.36(2)	<Ag(8)-O>	2.68
<Mo(2)-O>	1.97		
Mo(3)-O(14)h,i	1.72(2) 2x		
Mo(3)-O(18)h,i	1.73(1) 2x		
<Mo(3)-O>	1.73		

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

complex chains parallel to the *c* axis. The chains are linked by a sharing of edges and vertices with pairs of edge-sharing MoO$_6$ octahedra.

The anion-topology of the [(UO$_2$)$_2$O$_2$(MoO$_5$)] sheet, derived using method of Burns *et al.* (1996), is depicted in Figure 3b. It consists of pentagons, squares and triangles. The pentagons and squares are populated by U and Mo atoms, respectively, whereas triangles are empty. This sheet is novel in uranyl minerals and inorganic compounds.

Two [(UO$_2$)$_2$O$_2$(MoO$_5$)] sheets are linked into double sheets of composition [(UO$_2$)$_8$O$_8$(Mo$_5$O$_{20}$)] by sharing vertices with the Mo(3)O$_4$ tetrahedron, located between the sheets (Fig. 4a). The MoO$_4$ tetrahedron shares two corners with two MoO$_6$ octahedra in the sheet above, and two with MoO$_6$ octahedra of the sheet below. Thus four MoO$_6$ octahedra and a MoO$_4$ tetrahedron form pentanuclear clusters of composition Mo$_5$O$_{20}$, as shown in Figures 4b and 4c. The structure can be described as based upon chains of edge-sharing *Ur*O$_5$ pentagonal bipyramids that are joined into double sheets by linkages to Mo$_5$O$_{20}$ clusters.

The Ag(2), Ag(3), Ag(6), Ag(7), and Ag(8) atoms are located within the double sheets, whereas the Ag(1), Ag(4), and Ag(5) are located in between the double sheets (Fig. 2).

DISCUSSION

Miller *et al.* (1996) introduced the concept of anion-topologies, in the description of sheets, as stacking sequences of one-dimensional chains of polygons, and this approach was extended by Burns (1999). This approach is advantageous because it provides a means to compare complex topologies, as only a small number of chain types is required to construct topologies that differ mainly in the sequences of the chains. The novel anion-topology in the structure of Ag$_{10}$[(UO$_2$)$_8$O$_8$(Mo$_5$O$_{20}$)] can also be described as stacking sequence of chains of polygons (Fig. 5). Construction of the anion topology requires the previously known **P**, **D**, and **U** chains (Miller *et al.* 1996), and $\mathbf{T_R}$ and $\mathbf{T_L}$ chains that are introduced here for the first time. The **P** chains are chains of edge-sharing pentagons, whereas **D** and **U** chains are based upon edge-sharing pentagons and triangles with two possible orientations, either up (**U**) or down (**D**). The new $\mathbf{T_R}$ and $\mathbf{T_L}$ chains consist of corner-sharing squares and triangles with two possible orientations, either right (**R**) or left (**L**) (Fig. 5). The anion topology has the repeat $\ldots\mathbf{DPDT_RT_LUPUT_LT_R}\ldots$

As was mentioned above, the single [(UO$_2$)$_2$O$_2$(MoO$_5$)] sheets in Ag$_{10}$[(UO$_2$)$_8$O$_8$(Mo$_5$O$_{20}$)] can also be described as consisting of complex chains of *Ur*O$_5$ bipyramids linked by sharing edges and vertices with pairs of edge-sharing MoO$_6$ octahedra. It is interesting that structurally similar chains of *Ur*O$_5$ bipyramids have been observed recently in the structures of uranyl iodates of composition *M*[(UO$_2$)$_2$(IO$_3$)$_2$O$_2$](H$_2$O), *M* = Ba, Sr, Pb (Bean *et al.* 2001, Bean & Albrecht-Schmitt 2001). In these compounds, however, these chains are surrounded by IO$_3$ trigonal pyramids and, as a result, form one-dimensional [(UO$_2$)$_2$(IO$_3$)$_2$O$_2$]$^{2-}$ complex anionic chains.

It should be noted that the structure of Ag$_{10}$[(UO$_2$)$_8$O$_8$(Mo$_5$O$_{20}$)] reported here is closely related to the structure of Na$_{10}$(UO$_2$)$_8$(W$_5$O$_{20}$)O$_8$ (Obbade *et al.* 2003b). The close relationships between these structures demonstrate similarity of uranyl tungstates and uranyl molybdates with octahedral coordination of hexavalent cations.

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