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CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. VII. AN IRIGINITE-TYPE SHEET OF POLYHEDRA IN THE STRUCTURE OF $[(UO_2)Mo_2O_7(H_2O)_2]$

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ABSTRACT

A new uranyl molybdate hydrate, $[(UO_2)Mo_2O_7(H_2O)_2]$, has been synthesized by hydrothermal methods. The crystals are dark yellow elongate plates that are invariably twinned on (100). The structure was solved by direct methods and refined on the basis of F^2 for all unique reflections collected with monochromated Mo*K*α X-radiation and a CCD (charge-coupled device) detector. The compound is monoclinic, space group *C*2/*c*, *a* 35.071(6), *b* 6.717(1), *c* 11.513(2) Å, β 90.069(6)°, *V* 2712.0(8) Å^3, *Z* = 12, *R*1 = 0.055, *S* = 0.91. The two symmetrically distinct U^{6+} cations are part of $(UO_2)^{2+}$ uranyl ions that are coordinated by five atoms of O arranged at the equatorial vertices of pentagonal bipyramids. The three symmetrically independent Mo^{6+} cations are coordinated by five O atoms and one H_2O group in distorted octahedral arrangements. The $(UO_2)O_5$ pentagonal bipyramids and $MoO_5(H_2O)$ octahedra are linked by vertex- and edge-sharing, resulting in electroneutral $[(UO_2)Mo_2O_7(H_2O)_2]^0$ sheets that are based upon the iriginite anion-topology. Unlike iriginite, $[(UO_2)Mo_2O_7(H_2O)_2](H_2O)$, the structure does not contain H_2O groups in the interlayer. The sheets are linked to each other by hydrogen bonding involving H_2O groups that are part of the $MoO_5(H_2O)$ octahedra. $[(UO_2)Mo_2O_7(H_2O)_2]$ is a lower hydrate of iriginite that forms under basic conditions, whereas iriginite usually forms under more acidic conditions.

Keywords: uranyl molybdate, iriginite, crystal structure.

SOMMAIRE

Nous avons synthétisé un nouveau molybdate hydraté d'uranyle, $[(UO_2)Mo_2O_7(H_2O)_2]$, par voie hydrothermale. Les cristaux sont longs, jaune foncé, et maclés sur (100). Nous en avons résolu la structure par méthodes directes et nous l'avons affinée en utilisant les facteurs F^2 de toutes les réflexions uniques prélevées avec rayonnement monochromatisé Mo*K*α et un détecteur à couplage de charges CCD. Il s'agit d'un composé monoclinique, groupe spatial *C*2/*c*, *a* 35.071(6), *b* 6.717(1), *c* 11.513(2) Å, β 90.069(6)°, *V* 2712.0(8) Å^3, *Z* = 12, *R*1 = 0.055, *S* = 0.91. Les deux cations U^{6+} symétriquement distincts font partie d'ions uranyle, $(UO_2)^{2+}$, qui sont coordonnés par cinq atomes d'oxygène agencés aux coins équatoriaux de bipyramides pentagonales. Les trois cations Mo^{6+} symétriquement indépendents sont coordonnés à cinq atomes d'oxygène et un groupe H_2O dans des agencements octaédriques difformes. Les bipyramides pentagonales $(UO_2)O_5$ et les octaèdres $MoO_5(H_2O)$ sont liés par partage de coins et d'arêtes, pour donner des feuillets $[(UO_2)Mo_2O_7(H_2O)_2]^0$ électrostatiquement neutres et fondés sur la topologie de l'anion dans l'iriginite. Contrairement au cas de l'iriginite, $[(UO_2)Mo_2O_7(H_2O)_2](H_2O)$, la structure ne contient pas de groupes H_2O entre les feuillets. Ceux-ci sont liés l'un à l'autre par liaisons hydrogène impliquant des groupes H_2O faisant partie des octaèdres $MoO_5(H_2O)$. Le composé $[(UO_2)Mo_2O_7(H_2O)_2]$, hydrate "inférieur" de l'iriginite, est stable à des conditions basiques, tandis que les conditions plus fortement acides favorisent généralement l'iriginite.

(Traduit par la Rédaction)

Mots-clés: molybdate d'uranyle, iriginite, structure cristalline.

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INTRODUCTION

Uranyl molybdate hydrate minerals are common constituents of the altered zones of U–Mo deposits. At least three mineral species have been described in the literature: umohoite, $[(UO_2)MoO_4(H_2O)]$ (Krivovichev & Burns 2000a, and references therein), iriginite, $[(UO_2)Mo_2O_7(H_2O)_2](H_2O)$ (Krivovichev & Burns 2000b, and references therein), and mourite, $UO_{2.5}MoO_{3.5}H_2O$ (Kopchenova *et al.* 1962, Smith *et al.* 1971, Serezhkin *et al.* 1980b). The only other known uranium molybdate mineral that does not contain additional cations is sedovite, $U(MoO_4)_2$, which is reported to contain U^{4+} (Skvortsova & Sidorenko 1965). There are several synthetic uranyl molybdate hydrates for which structures have been reported: $(UO_2)_3(MoO_4)_2(OH)_2 \bullet 10H_2O$ (Tali *et al.* 1994), $(UO_2)_4(MoO_4)_3(OH)_2 \bullet 4H_2O$ (Tali *et al.* 1994) and $UO_2MoO_4 \bullet 2H_2O$ (Serezhkin *et al.* 1980a). The structures of these synthetic phases contain uranyl pentagonal bipyramids, UrO_5 (*Ur*: uranyl ion, UO_2^{2+}) and MoO_4 tetrahedra, whereas in the structures of umohoite and iriginite, Mo^{6+} cations occur in a distorted octahedral coordination (Krivovichev & Burns 2000a, b).

As a part of our continuing studies of uranyl molybdates (Krivovichev & Burns 2000a, b, 2001a, b, 2002, Krivovichev *et al.* 2002a, b), we report the synthesis and structure of a new uranyl molybdate hydrate, $[(UO_2)Mo_2O_7(H_2O)_2]$, which is chemically and topologically related to iriginite.

EXPERIMENTAL

Crystals were obtained by hydrothermal methods. A mixture of Ag_2SO_4, MoO_3 and $UO_2(CH_3COO)_2 \bullet 2H_2O$ (0.0624, 0.0720 and 0.1254 g, respectively), together with 5 mL of water, was placed in a 23 mL Teflon-lined Parr bomb. The mixture was heated to 230°C for 6 days and then cooled to ambient temperature. Dark yellow, transparent, elongate, platy crystals up to 0.1 mm across and 0.5 mm in maximum length were obtained.

The crystal selected for data collection was mounted on a Bruker three-circle diffractometer equipped with a SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 5 cm. The data were collected using monochromated Mo$K\alpha$ X-radiation and frame widths of 0.3° in ω. The unit-cell dimensions (Table 1) were refined from 2490 reflections using least-squares techniques. More than a hemisphere of data was collected, and the 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 by modeling the crystal as a {100} plate, which reduced R_{INT} of 142 intense reflections from 24.8 to 7.6%. Additional information pertinent to the data collection is given in Table 1.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR $[(UO_2)Mo_2O_7(H_2O)_2]$

a (Å)	35.071(6)	D_{calc} (g/cm³)	4.45
b (Å)	6.717(1)	Crystal size (mm)	0.34 x 0.08 x 0.03
c (Å)	11.513(2)	Radiation	Mo$K\alpha$
β (°)	90.069(6)	Total Ref.	7202
V (Å³)	2712.0(8)	Unique Ref.	3068
Space group	$C2/c$	Unique $\|F_o\| \geq 4\sigma_F$	1480
F_{000}	3168	$R1$	0.055
μ (cm⁻¹)	206.45	$wR2$	0.157
Z	12	S	0.914

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.1027P)^2]$ 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.

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. It was solved by direct methods, and an initial structure-model containing only heavy atoms was refined to an $R1$ of 0.329. Twinning with operator [$\bar{1}$00, 010, 001] was incorporated using the method of Jameson (1982) and Herbst-Irmer & Sheldrick (1998) and resulted in a substantial improvement of the refinement ($R1$ = 0.147). Difference-Fourier maps calculated at this stage revealed the positions of the anions, and refinement of a model that included anisotropic displacement parameters for the U and Mo atoms, as well as all atomic positions, resulted in an $R1$ of 0.055. A model that included anisotropic displacement parameters for the anions was tried but resulted in non-positive-definite parameters for several anions. The final positional and displacement parameters of the atoms, and selected interatomic distances are presented in Tables 2 and 3, respectively. Calculated and observed structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

Cation polyhedra

The cation coordination polyhedra in the structure of $[(UO_2)Mo_2O_7(H_2O)_2]$ are similar to those in iriginite, $[(UO_2)Mo_2O_7(H_2O)_2](H_2O)$. The two symmetrically unique U^{6+} cations are each bonded to two atoms of O, resulting in $(UO_2)^{2+}$ uranyl ions with U–O_{Ur} bond lengths of ~1.8 Å. The U^{6+} cations are each further coordinated by five atoms of O arranged at the equatorial vertices of uranyl pentagonal bipyramids that are capped by the O_{Ur} atoms. There are three unique Mo^{6+} cations in the structure, each of which is coordinated by five O atoms and one H_2O group in distorted octahedral arrangements. Such distortions are typical for uranyl molybdates with octahedrally coordinated Mo atoms (Krivovichev & Burns 2000a, b).

The structure of $[(UO_2)Mo_2O_7(H_2O)_2]$ consists of electroneutral sheets of composition $(UO_2)Mo_2O_7(H_2O)_2$ that are parallel to (100) (Fig. 1a). The sheets are based upon the iriginite anion-topology (Fig. 1b) (Burns *et al.* 1996) and are topologically identical to the iriginite sheet.

Bond-valence analysis

A bond-valence analysis for the structure, calculated using parameters from Burns *et al.* (1997) for U^{6+}–O bonds and Brese & O'Keeffe (1991) for Mo^{6+}–O bonds, is presented in Table 4. The contributions of proposed H bonds (see below) were estimated from the O...O bond lengths using the method given by Ferraris & Ivaldi (1988). The O atoms with incident bond-valence sums of 0.26, 0.28 and 0.36 valence units (*vu*) correspond to $H_2O(6)$, $H_2O(14)$ and $H_2O(17)$, respectively. The bond-valence sums at O sites are in the range of 1.61–2.24 *vu*. The sums at O(7) and O(13) are 1.61 and 1.66 *vu*, respectively. These low values may imply that these anions accept stronger H bonds, although undersaturated anions could be observed in the structure of hydrated oxysalts (see, for example, Cooper & Hawthorne 2000).

Hydrogen bonding

Linkage of the uranyl molybdate sheets in $[(UO_2)Mo_2O_7(H_2O)_2]$ involves H bonding only. As is typical for uranyl compounds, the positions of the H atoms were not obtainable directly from the X-ray data. A H-bonding network is proposed on the basis of crystal-chemical arguments, including O...O contacts that are of appropriate distances for H bonds. The most probable H-bonding network in the structure of $[(UO_2)Mo_2O_7(H_2O)_2]$ is depicted in Figure 2; the corresponding H_2O...O distances are given in Table 3. Each of the three H_2O groups donates two H bonds: $H_2O(6)$ to O(7) and O(13), $H_2O(14)$ to O(3) and O(9), and $H_2O(17)$ to O(1) and O(8). O(1), O(3) and O(17) are O_{Ur} atoms, whereas O(7), O(9) and O(13) are terminal atoms of the $MoO_5(H_2O)$ distorted octahedra.

The structure of $[(UO_2)Mo_2O_7(H_2O)_2]$ contains two symmetrically distinct interlayers (Fig. 2); one consists of the O(3), O(7), O(9) and O(13) atoms, and $H_2O(6)$

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR $[(UO_2)Mo_2O_7(H_2O)_2]$

Atom	x	y	z	U_{eq}
U(1)	0	0.7931(4)	¼	0.0137(6)
U(2)	0.16654(6)	0.2926(2)	0.9170(2)	0.0126(4)
Mo(1)	0.1587(1)	0.1738(6)	0.2598(4)	0.020(1)
Mo(2)	0.0088(1)	0.6744(5)	0.9072(4)	0.0119(9)
Mo(3)	0.1750(1)	0.1731(7)	0.5742(4)	0.0161(9)
O(1)	0.2164(9)	0.305(5)	0.914(3)	0.032(9)
O(2)	0.1686(7)	0.153(5)	0.102(3)	0.019(8)
O(3)	-0.0495(8)	0.797(4)	0.257(3)	0.022(8)
O(4)	0	0.564(5)	½	0.008(9)
O(5)	0.1636(7)	0.071(3)	0.417(3)	0.014(6)
$H_2O(6)$	-0.0594(8)	0.627(5)	0.897(3)	0.031(8)
O(7)	0.1082(8)	0.152(5)	0.256(3)	0.030(9)
O(8)	0.2239(7)	0.153(5)	0.580(3)	0.026(8)
O(9)	0.0557(7)	0.682(3)	0.905(2)	0.017(6)
O(10)	0.1669(9)	0.427(6)	0.295(3)	0.034(9)
O(11)	0.1639(7)	0.419(4)	0.540(2)	0.015(6)
O(12)	0.0056(7)	0.924(4)	0.869(2)	0.023(6)
O(13)	0.1143(8)	0.290(4)	0.928(3)	0.022(7)
$H_2O(14)$	0.1079(6)	0.128(4)	0.565(3)	0.014(6)
O(15)	-0.0061(5)	0.648(3)	0.068(2)	0.000(4)
O(16)	0.1681(7)	0.144(4)	0.731(3)	0.022(8)
$H_2O(17)$	0.2238(7)	0.170(4)	0.266(2)	0.025(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.022(1)	0.010(1)	0.009(2)	0	-0.002(1)	0
U(2)	0.0217(7)	0.0084(7)	0.0077(8)	-0.000(1)	-0.0018(6)	0.0018(8)
Mo(1)	0.048(2)	0.005(2)	0.007(3)	-0.001(2)	-0.006(2)	0.002(2)
Mo(2)	0.018(2)	0.011(2)	0.007(2)	0.001(2)	0.001(2)	-0.002(2)
Mo(3)	0.030(2)	0.010(2)	0.009(3)	0.000(2)	-0.004(2)	-0.002(2)

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF $[(UO_2)Mo_2O_7(H_2O)_2]$

U(1)-O(3)a	1.74(3) 2x	Mo(1)-O(10)	1.77(4)	Mo(3)-O(8)	1.72(3)
U(1)-O(15)a	2.32(2) 2x	Mo(1)-O(7)	1.77(3)	Mo(3)-O(11)	1.74(3)
U(1)-O(12)b,c	2.35(3) 2x	Mo(1)-O(2)	1.86(3)	Mo(3)-O(16)	1.83(3)
U(1)-O(4)d	2.40(4)	Mo(1)-O(5)	1.95(3)	Mo(3)-O(5)	1.97(3)
$<U(1)-O_{Ur}>$	1.74	Mo(1)-O(16)h	2.19(3)	Mo(3)-O(2)g	2.23(4)
$<U(1)-\phi_{eq}>$	2.35	Mo(1)-$H_2O(17)$	2.29(2)	Mo(3)-$H_2O(14)$	2.38(2)
		$<Mo(1)-\phi>$	1.97	$<Mo(3)-\phi>$	1.98
U(2)-O(1)	1.75(3)				
U(2)-O(13)	1.84(3)	Mo(2)-O(9)	1.66(2)	O(1)···$H_2O(17)$i	2.95(4)
U(2)-O(10)e	2.35(4)	Mo(2)-O(12)	1.74(3)	O(3)···$H_2O(14)$j	2.94(4)
U(2)-O(2)f	2.33(3)	Mo(2)-O(15)f	1.93(2)	O(7)···$H_2O(6)$d	2.87(5)
U(2)-O(16)	2.36(3)	Mo(2)-O(4)	1.98(1)	O(8)···$H_2O(17)$k	2.82(4)
U(2)-O(11)e	2.40(3)	Mo(2)-O(15)d	2.19(2)	O(9)···$H_2O(14)$e	2.90(4)
U(2)-O(5)g	2.45(2)	Mo(2)-$H_2O(6)$	2.41(3)	O(13)···$H_2O(6)$l	2.85(4)
$<U(2)-O_{Ur}>$	1.80	$<Mo(2)-\phi>$	1.99		
$<U(2)-\phi_{eq}>$	2.38				

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

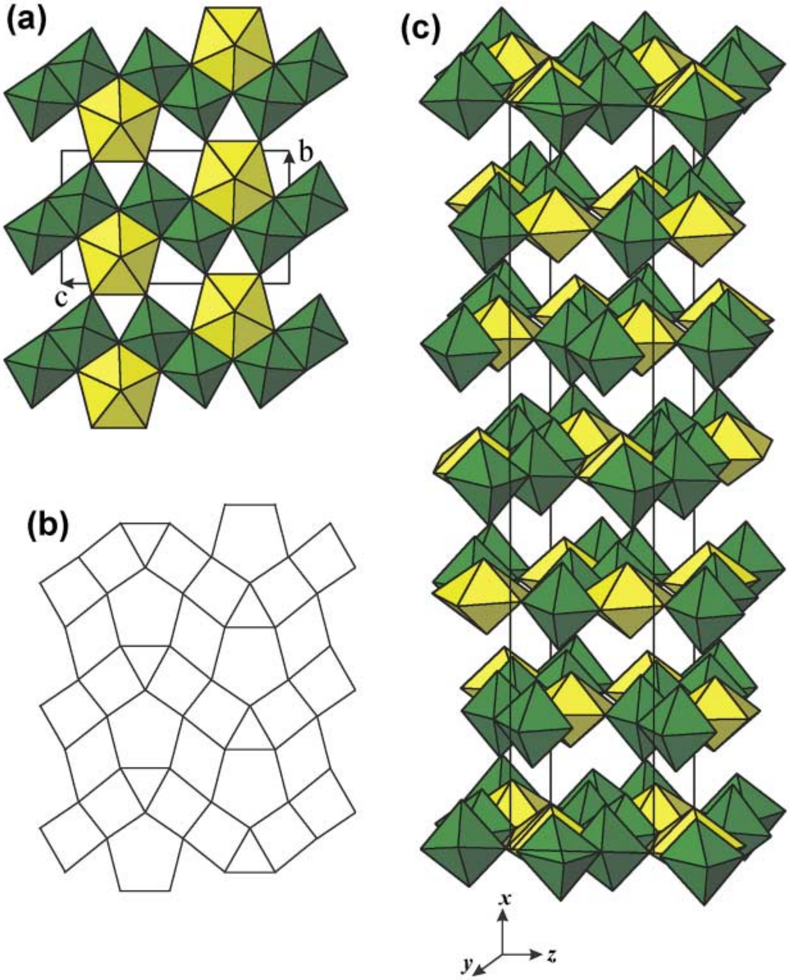

FIG. 1. (a) The sheet of uranyl and molybdate polyhedra in the structure of $[(UO_2)Mo_2O_7(H_2O)_2]$, (b) the corresponding anion-topology, derived following the method of Burns *et al.* (1996), and (c) a projection of the structure of $[(UO_2)Mo_2O_7(H_2O)_2]$. The UrO_5 and $Mo(O,H_2O)_6$ polyhedra are shown in yellow and green, respectively.

and $H_2O(14)$ groups, and the other contains the O(1) and O(8) atoms, and the $H_2O(17)$ group. The networks of hydrogen bonding within these interlayers are the same (Fig. 2).

DISCUSSION

The uranyl molybdate sheets in the structure of $[(UO_2)Mo_2O_7(H_2O)_2]$ are topologically identical to those in iriginite. The difference between the two structures involves H_2O groups located in the interlayer of iriginite that provide H bonding of adjacent sheets (Krivovichev & Burns 2000b). The distance between adjacent uranyl molybdate sheets is 6.37 Å in iriginite and 5.85 Å in $[(UO_2)Mo_2O_7(H_2O)_2]$, which is reflected in an increase of the calculated density from 4.24 for iriginite to 4.44 g/cm^3 for $[(UO_2)Mo_2O_7(H_2O)_2]$. It is noteworthy that the linear dimensions of the sheets are almost the same in both structures: 6.705 × 11.524 Å^2 in iriginite, and 6.717 × 11.513 Å^2 in $[(UO_2)Mo_2O_7(H_2O)_2]$.

As noted in Krivovichev & Burns (2000b), iriginite is probably the most common uranyl molybdate that occurs in oxidized zones of U–Mo deposits. It usually forms at a pH value in the range 1.5–5, whereas $[(UO_2)Mo_2O_7(H_2O)_2]$ was obtained under nearly neu-

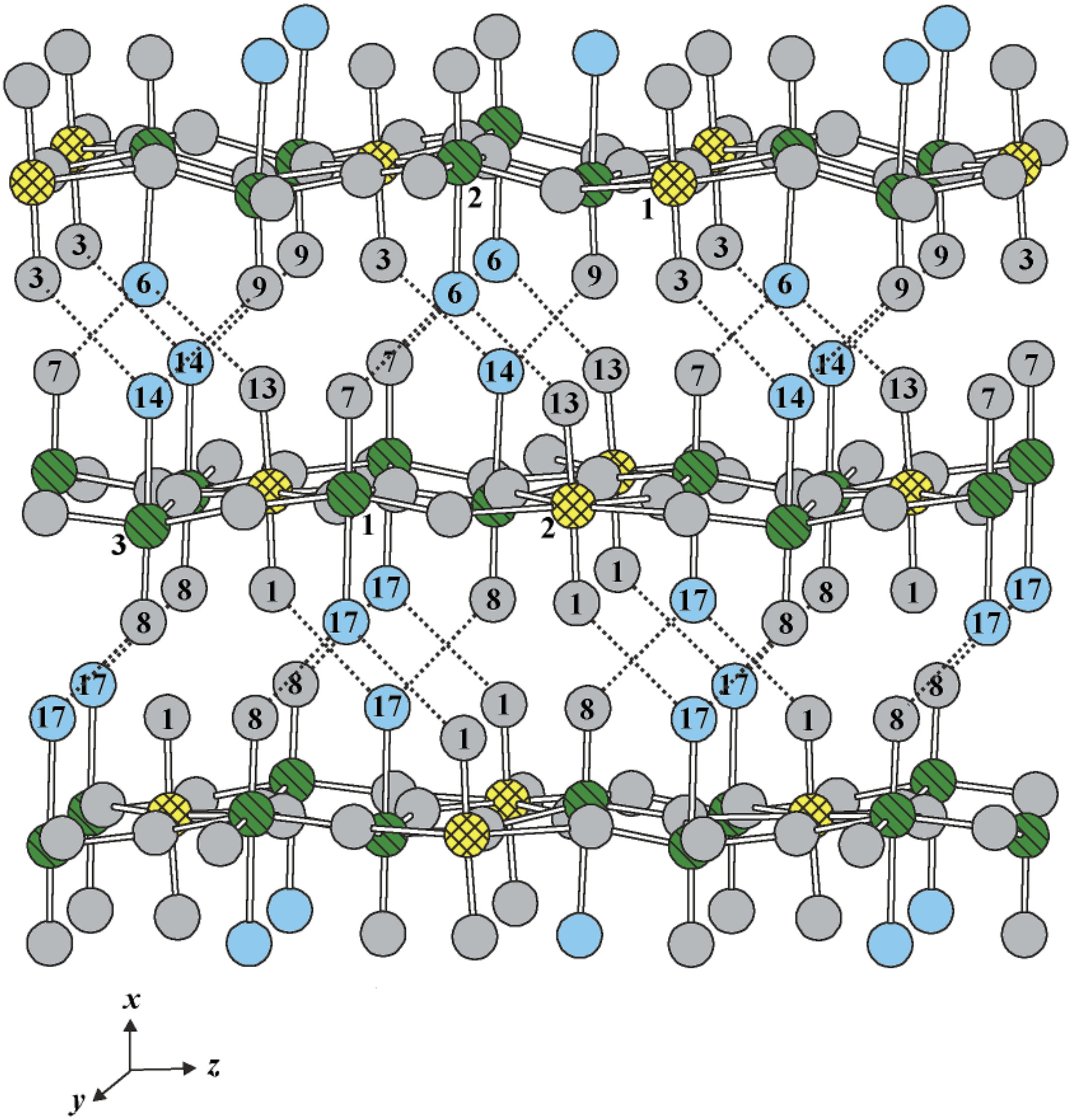

FIG. 2. The proposed network of hydrogen bonds in the structure of $[(UO_2)Mo_2O_7(H_2O)_2]$. Legend: U: yellow cross-hatched spheres, Mo: green hatched spheres, H_2O groups: blue spheres, O atoms: grey spheres. H bonds are shown as dashed lines.

tral and basic conditions. Thus, $[(UO_2)Mo_2O_7(H_2O)_2]$ may form in a neutral or basic environment, or it may be one of the phases that forms when iriginite is altered. Zhil'tsova *et al.* (1970) reported the formation of a "metastable modification" of iriginite, $[(UO_2)Mo_2O_7(H_2O)_2](H_2O)_2$, which probably contains two H_2O groups in the interlayer. The existence of low hydrates at high pH and high hydrates at low pH in the family of uranyl molybdate sheets is in agreement with general observations concerning hydrated salts in alteration zones of mineral deposits (Jambor *et al.* 2000).

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TABLE 4. BOND-VALENCE ANALYSIS FOR $[(UO_2)Mo_2O_7(H_2O)_2]$

Atom	Cation-anion bonds					Sub-total	Hydrogen bonds			total
	U(1)	U(2)	Mo(1)	Mo(2)	Mo(3)		$H_2O(6)$	$H_2O(14)$	$H_2O(17)$	
O(1)		1.78				1.78			0.14	1.92
O(2)		0.57	1.14		0.42	2.13				2.13
O(3)	$1.82^{2\downarrow}$					1.82		0.14		1.96
O(4)	0.50			$0.82^{2\downarrow}$		2.12				2.12
O(5)		0.45	0.89		0.84	2.18				2.18
$H_2O(6)$				0.26		0.26				0.26
O(7)			1.45			1.45	0.16			1.61
O(8)					1.66	1.66			0.18	1.84
O(9)				1.95		1.95		0.15		2.10
O(10)		0.55	1.45			2.00				2.00
O(11)		0.50			1.57	2.07				2.07
O(12)	$0.55^{2\downarrow}$			1.57		2.12				2.12
O(13)		1.49				1.49	0.17			1.66
$H_2O(14)$					0.28	0.28				0.28
O(15)	$0.58^{2\downarrow}$			0.94, 0.47		1.99				1.99
O(16)		0.54	0.47		1.23	2.24				2.24
$H_2O(17)$			0.36			0.36				0.36
total	6.40	5.88	5.76	6.01	6.00					

64883) that supports SVK. We thank Andrew Locock for useful comments. We thank Prof. S.K. Filatov and an anonymous referee for their comments, and Dr. E. Sokolova and Prof. R.F. Martin for their editorial work.

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