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THE CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. II. THE CRYSTAL STRUCTURE OF IRIGINITE

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ABSTRACT

The structure of synthetic iriginite, $[(UO_2)Mo_2O_7(H_2O)_2](H_2O)$, *a* 6.705(1), *b* 12.731(2), *c* 11.524(2) Å, *V* 983.6(3) Å^3, *Z* = 4, has been refined on the basis of F^2 for all unique data collected with monochromatic Mo*K*α X-radiation and a CCD-based detector. The agreement factor (*R*1) was 3.5%, calculated using 532 unique observed reflections ($|F_o| \geq 4\sigma_F$), and the goodness-of-fit (*S*) was 0.92. This study indicates that iriginite crystallizes in space group *Pbcm*, rather than $Pca2_1$ as indicated in a previous investigation. The structure contains one symmetrically distinct U^{6+} cation that is strongly bonded to two atoms of O, forming a nearly linear uranyl ion (*Ur*) coordinated by five additional atoms of O arranged at the equatorial corners of pentagonal bipyramids that are capped by the O_{Ur} atoms. The single symmetrically distinct Mo^{6+} cation is in a distorted octahedral coordination involving five atoms of O and one H_2O group. The structure consists of symmetrically identical sheets of edge-sharing $Ur\phi_5$ pentagonal bipyramids and $Mo\phi_6$ octahedra (ϕ: unspecified ligand), with composition $[(UO_2)Mo_2O_7(H_2O)_2]^0$. The sheets are linked together *via* H bonds involving interlayer H_2O groups.

Keywords: iriginite, uranyl molybdate, crystal structure.

SOMMAIRE

Nous avons affiné la structure de l'iriginite synthétique, $[(UO_2)Mo_2O_7(H_2O)_2](H_2O)$, *a* 6.705(1), *b* 12.731(2), *c* 11.524(2) Å, *V* 983.6(3) Å^3, *Z* = 4, en utilisant F^2 pour toutes les réflexions uniques mesurées avec rayonnement monochromatique Mo*K*α et un détecteur de type CCD. Le résidu *R*1 atteint est 3.5%, calculé en utilisant 532 réflexions uniques observées ($|F_o| \geq 4\sigma_F$), et le facteur de concordance *S* est de 0.92. D'après nos travaux, l'iriginite répond au groupe spatial *Pbcm*, plutôt que $Pca2_1$, comme l'indiquait une étude antérieure. La structure contient un cation U^{6+} symétriquement distinct, lié par liaisons fortes à deux atomes d'oxygène, pour former un ion uranyle presque linéaire (*Ur*), en coordinence avec cinq atomes d'oxygène additionnels disposés aux coins équatoriaux de bipyramides pentagonales dont les sommets sont les atomes O_{Ur}. Le cation Mo^{6+}, symétriquement distinct, loge dans un octaèdre difforme impliquant cinq atomes d'oxygène et un groupe H_2O. La structure contient des feuillets symétriquement identiques faits de bipyramides pentagonales $Ur\phi_5$ à arêtes partagées et d'octaèdres $Mo\phi_6$ octahedra (ϕ: ligand non spécifié), ayant une composition $[(UO_2)Mo_2O_7(H_2O)_2]^0$. Les feuillets sont rattachés l'un à l'autre par le biais de liaisons hydrogène impliquant des molécules de H_2O situées entre les feuillets.

(Traduit par la Rédaction)

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

INTRODUCTION

Iriginite is one of the most abundant secondary minerals in the oxidized zones of hydrothermal U–Mo deposits. Chernikov (1981) noted that it commonly occurs on the walls of mine shafts associated with gypsum, ilsemannite, $Mo_3O_8 \cdot nH_2O$, and uranyl sulfates. According to Getseva & Savel'eva (1956) and Epshtein (1959), it was first discovered by G.Yu. Epshtein and E.A. Osmolovskaya in 1951 in the U–Mo deposit of the Alexandrovskii mine, Udokan Range, northern Zabaikal'e, Russia (Chernikov *et al*. 1997). Iriginite was later described by Stephenson (1964) from the White River Badlands, Pennington County, South Dakota, U.S.A.

The structure of synthetic iriginite was studied by Serezhkin *et al*. (1981), who proposed space group $Pca2_1$ and reported that the structure consists of electroneutral $[(UO_2)Mo_2O_7(H_2O)_2]^0$ sheets of polymer-

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ized (UO_7) pentagonal bipyramids and distorted [$MoO_5(H_2O)$] octahedra, with the structural sheets linked by H bonding to interlayer H_2O groups. Natural iriginite was studied by Vishnev *et al.* (1991) using electron microscopy, with the results confirming the generalities of the structural model presented by Serezhkin *et al.* (1981). However, the structure reported by Serezhkin *et al.* (1981) was refined using data that had not been corrected for absorption, and several O atoms had physically unrealistic anisotropic-displacement parameters.

Mo is one of the many fission products generated during burnup of nuclear fuel in a reactor. Studies of the corrosion products that form when spent nuclear fuel is subjected to conditions similar to those of the proposed geological repository at Yucca Mountain, Nevada have revealed the formation of uranyl molybdates (Buck *et al.* 1997). A detailed understanding of the crystal chemistry of these phases is essential for the prediction of their impact on the rate of release of radionuclides under repository conditions. As part of our ongoing studies of uranyl molybdates, we have refined the structure of synthetic iriginite and present the results herein.

EXPERIMENTAL

Synthesis

Iriginite occurs only as fine-grained masses on natural specimens, necessitating the use of synthetic crystals for structure studies. A mixture of PbO, MoO_3 and $UO_2(CH_3COO)_2$•$2H_2O$ (0.045, 0.046 and 0.196 g, respectively), together with 5 mL of ultrapure water, was placed in a Teflon-lined Parr bomb. A small amount of HF (49%) was added to adjust the pH to 2.0–2.6. The reactants were heated at 200°C for 96 h and then cooled to ambient temperature. The synthetic iriginite occurs as transparent yellow plates with maximum dimensions of about 0.2 mm.

Collection of X-ray data

An inclusion-free crystal was selected for data collection on a Bruker three-circle diffractometer equipped with a SMART CCD (charge-coupled device) detector located 5 cm from the crystal. Data were collected using monochromatic Mo*K*α X-radiation with frame widths of 0.3° in ω. The unit-cell dimensions (Table 1) were refined from 4218 reflections using least-squares techniques and are similar to those reported by Serezhkin *et al.* (1981). More than a hemisphere of data was collected, and the data were integrated and corrected for Lorentz, polarization and background effects using the Bruker program SAINT. A semi-empirical absorption-correction was done on the basis of 510 intense reflections with the crystal modeled as a plate; reflections with a plate-glancing angle less than 0.3° were discarded from the dataset, which lowered the R_{INT} of the 510 intense reflections from 12.1 to 8.3%. Additional information pertinent to the data collection is given in Table 1.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR IRIGINITE

a (Å)	6.705(1)	Crystal size (mm)	0.12 x 0.03 x 0.02
b (Å)	12.731(2)	Radiation	Mo*K*α
c (Å)	11.524(2)	Total Ref.	4316
V ($Å^3$)	983.6(3)	Unique Ref.	753
Space group	*Pbcm*	Unique $\lvert F_o \rvert \geq 4\sigma_F$	532
F_{000}	1112	*R*1	0.035
μ (cm^{-1})	189.9	*S*	0.916
D_{calc} (g/cm^3)	4.241	$\Delta\rho_{min}$, $\Delta\rho_{max}$ ($eÅ^{-3}$)	-2.03, 0.97

Unit-cell contents: $4\{[(UO_2)Mo_2O_7(H_2O)_2](H_2O)\}$

$R1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for *m* observations and *n* parameters

Refinement of the structure

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.

The mean value of $| E^2 - 1 |$ of 0.989 indicated that the structure may be centrosymmetric; the systematic absences are consistent with space groups *Pbcm* and $Pca2_1$. Solutions were obtained using direct methods for each space group. The combined figure-of-merit was 4.02 for *Pbcm*, as compared to 9.68 for $Pca2_1$. Space group *Pbcm* was verified by successful refinement of the structure. The structure was refined on the basis of

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (x 10^4 $Å^2$) FOR IRIGINITE

	x	*y*	*z*	$^*U_{eq}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.7016(1)	0.49398(6)	¼	157(2)	138(4)	247(5)	85(3)	0	0	-5(4)
Mo	0.1684(2)	0.46925(9)	0.09234(8)	184(3)	138(7)	329(9)	85(5)	-3(5)	5(4)	21(5)
O(1)	0.688(2)	0.354(1)	¼	330(40)	430(110)	210(80)	350(80)	0	0	-20(70)
O(2)	0.706(2)	0.633(1)	¼	340(40)	390(110)	160(80)	470(90)	0	0	10(70)
O(3)	0.415(1)	0.4975(8)	0.1266(6)	280(20)	190(50)	490(70)	170(40)	20(50)	90(40)	0(50)
O(4)	0.146(1)	0.5098(7)	-0.0644(5)	190(20)	170(40)	270(50)	130(30)	50(40)	70(30)	0(40)
O(5)	0.055(2)	0.480(1)	¼	280(30)	270(80)	460(100)	100(50)	0	0	-60(70)
$H_2O(6)$	0.140(1)	0.6556(7)	0.1212(7)	260(20)	410(70)	160(60)	210(50)	0(40)	10(40)	-70(40)
O(7)	0.169(1)	0.3369(7)	0.0819(7)	320(30)	460(70)	310(70)	190(50)	-80(40)	20(50)	80(50)
$H_2O(8)$	0.448(2)	¾	0	500(40)	290(120)	410(110)	800(100)	150(80)	0	0

$^*U_{eq} = (1/3)\ \Sigma\Sigma\ U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF IRIGINITE

U-O(2)	1.77(1)	Mo-O(7)	1.690(9)
U-O(1)	1.79(1)	Mo-O(3)	1.736(8)
U-O(4)a, b	2.371(6) x2	Mo-O(4)	1.885(6)
U-O(5)c	2.38(1)	Mo-O(5)	1.975(5)
U-O(3),d	2.392(8) x2	Mo-O(4)e	2.148(7)
<U-O_{Ur}>	1.78	Mo-H_2O(6)	2.403(8)
<U-O_{eq}>	2.38	<Mo-O>	1.97

a = $-x+1, -y+1, z+1/2$; b = $-x+1, -y+1, -z$; c = $x+1, y, z$; d = $x, y, -z+1/2$; e = $-x, -y+1, -z$; f = $x, -y+3/2, -z$; g = $-x+1, y+1/2, z$.

TABLE 4. BOND-VALENCE* (*vu*) ANALYSIS FOR IRIGINITE

	U	Mo	Σ
O(1)	1.65		1.65
O(2)	1.71		1.71
O(3)	$0.51^{2x\downarrow}$	1.59	2.10
O(4)	$0.53^{2x\downarrow}$	1.06, 0.52	2.11
O(5)	0.52	$0.83^{2x\rightarrow}$	2.18
H_2O(6)		0.26	0.26
O(7)		1.80	1.80
H_2O(8)			0
Σ	5.96	6.06	

*values calculated using the parameters for U^{6+} from Burns *et al.* (1997) and Mo^{6+} from Brese & O'Keeffe (1991). Contributions from H atoms are not included.

F^2 using all unique data. Refinement of all atomic-positional parameters, allowing for anisotropic displacement of all atoms, and the inclusion of a refinable weighting scheme of the structure factors, resulted in a final agreement index (*R*1) of 3.5%, calculated for 532 unique observed reflections ($|F_o| \geq 4\sigma_F$) and a goodness-of-fit (*S*) of 0.92. The final atomic parameters are listed in Table 2, selected interatomic distances are in Table 3, and a bond-valence analysis is presented in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

The structure also was refined in space group $Pca2_1$, as proposed by Serezhkin *et al.* (1981), and resulted in a final *R*1 of 3.9%. The displacement ellipsoids of some of the O atoms became physically unrealistic, consistent with the structure being centrosymmetric.

RESULTS

The results of the current structure-refinement for synthetic iriginite confirm the generalities of the structural model provided by Serezhkin *et al.* (1981), with the exception of the space group. The structure contains a single symmetrically distinct U^{6+} cation that is strongly bonded to two O atoms, resulting in a nearly linear $(UO_2)^{2+}$ uranyl ion (*Ur*), as is typical for U^{6+} minerals. The uranyl ion is coordinated by five additional anions located at the equatorial positions of a pentagonal bipyramid that is capped by the O_{Ur} atoms. The <U–O_{Ur}> and <U–O_{eq}> (eq: equatorial) distances of 1.78 and 2.38 Å, respectively, are in excellent agreement with average values obtained from numerous well-refined structures (Burns *et al.* 1997).

The single symmetrically distinct Mo^{6+} site is coordinated by six ligands in a highly distorted octahedral arrangement. The four equatorial Mo–O bond lengths in the octahedron range from 1.736(8) to 2.148(7) Å. One apical position is occupied by an O atom; the Mo–O bond is strong, with a bond length of 1.690(9) Å, and the Mo^{6+} cation is shifted out of the plane defined by the equatorial ligands in the direction of this apical ligand. The other apical position corresponds to an H_2O group that is located 2.403(8) Å from the Mo^{6+} cation. The bond-valence analysis (Table 4) indicates that this bond has 0.26 *vu* associated with it, and is needed to satisfy the bonding requirements of the Mo^{6+} cation. A similar coordination polyhedron about Mo^{6+} was observed in the structures of umohoite (Krivovichev & Burns 2000) and $UMoO_5$ (D'yachenko *et al.* 1996).

The structure of iriginite consists of symmetrically identical sheets of edge-sharing $Ur\phi_5$ pentagonal bipyramids and $Mo\phi_6$ octahedra (ϕ: O, H_2O) with composition $[(UO_2)Mo_2O_7(H_2O)_2]^0$ (Fig. 1a). The corresponding sheet anion-topology, derived using the method of Burns *et al.* (1996), is shown in Figure 1b. Burns *et al.* (1996) referred to it as the iriginite anion-topology, and noted that it contains chains of pentagons and squares that share edges, as well as zigzag chains of edge-sharing squares. In the iriginite sheet, each pentagon of the underlying anion-topology is populated by a UrO_5 pentagonal bipyramid, two-thirds of the squares are populated with $Mo^{6+}\phi_6$ octahedra that occur as edge-sharing dimers, and the triangles as well as one-third of the squares are empty.

The sheets of uranyl and molybdate polyhedra are linked by H bonds involving an interlayer H_2O group (Fig. 2). The H_2O(8) group donates two H bonds that are probably accepted by O(7) anions, with donor–acceptor distances of 2.95(1) Å. The H_2O(8) anion probably accepts two H bonds donated by symmetrically distinct H_2O(6) groups that are attached to the sheets, with donor–acceptor distances of 2.77(1) Å, resulting in an approximately tetrahedral arrangement of H bonds about the H_2O(8) anion. The H_2O(6) anion is bonded to Mo^{6+}, and donates a single H bond to H_2O(8) in the interlayer. The remaining H atom associated with H_2O(6) does not appear to participate in a hydrogen bond, as there are no suitable acceptors.

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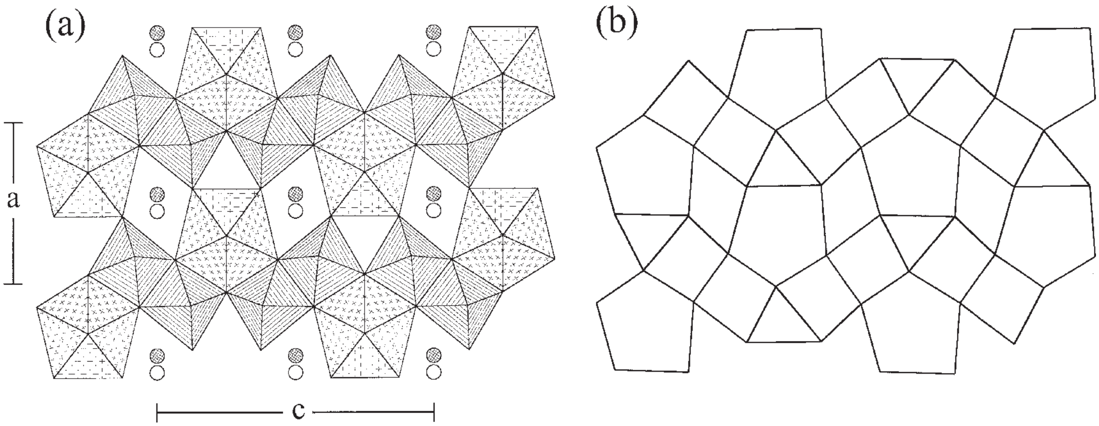

FIG. 1. The sheet of uranyl and molybdate polyhedra in the structure of iriginite. (a) Polyhedral representation; (b) anion topology derived using the method of Burns *et al.* (1996). The uranyl and molybdate polyhedra are shaded with crosses and parallel lines, respectively. The circles show the positions of H_2O groups in the interlayers, with open circles and cross-hatched circles representing H_2O groups below and above the sheet, respectively.

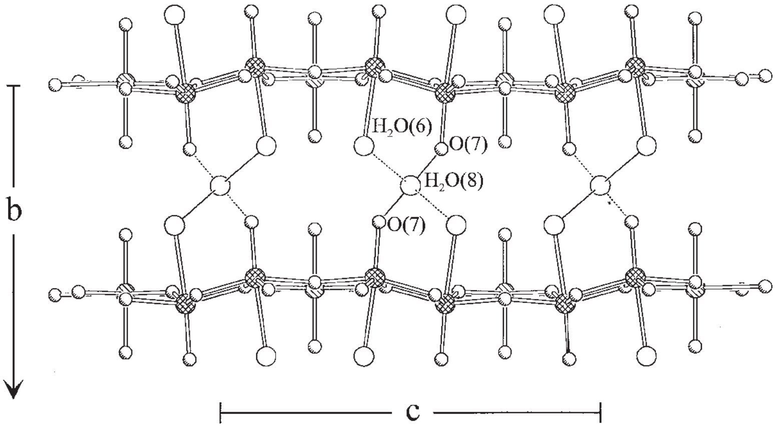

FIG. 2. The structure of iriginite projected along [100]. H_2O groups are represented by large open circles, O by smaller circles shaded in the lower left quadrant, U by circles shaded with parallel lines, and Mo by circles shaded with cross-hatching.

that supports SVK (DGE99–03354). We thank Dr. A.M. McDonald and an anonymous referee for their comments, and Dr. R.F. Martin for editing the manuscript.

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