The Canadian Mineralogist  

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

SERGEY V. KRIVOVICHEV* AND PETER C. BURNS§  
Department of Civil Engineering and Geological Sciences, University of Notre Dame,  
156 Fitzpatrick Hall, Notre Dame, Indiana 46556-0767, U.S.A.

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, \(V = 983.6(3)\) Å³, \(Z = 4\), has been refined on the basis of \(F^2\) for all unique data collected with monochromatic MoKα 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 \(Pca_2_1\) 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 \(Ur\_f5\) pentagonal bipyramids and \(Mo\_f6\) octahedra (\(f\): 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, \(V = 983.6(3)\) Å³, \(Z = 4\), en utilisant \(F^2\) pour toutes les réflexions uniques mesurées avec rayonnement monochromatique MoKα 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 \(Pca_2_1\), 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 coordination 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 \(Ur\_f5\) à arêtes partagées et d’octaèdres \(Mo\_f6\) octahédra (\(f\): 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, molybdiate 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 Epstheim (1959), it was first discovered by G.Yu. Epstheim 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 \(Pca_2_1\) and reported that the structure consists of electroneutral \[(UO_2)Mo_2O_7(H_2O)_2\]^0 sheets of polymer-
ized (UO$_2$) pentagonal bipyramids and distorted [MoO$_2$(H$_2$O)$_2$] octahedra, with the structural sheets
linked by H bonding to interlayer H$_2$O 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$_3$COO)$_2$•2H$_2$O (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 MoKα 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.

**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 $|F^2 - |F|^2|$ of 0.989 indicated that the structure may be centrosymmetric; the systematic absences are consistent with space groups Pbcm and Pca$_2_1$. 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 Pca$_2_1$. Space group Pbcm was verified by successful refinement of the structure. The structure was refined on the basis of

**TABLE 1. CRYSTALLOGRAPHIC DATA FOR IRIGINITE**

<table>
<thead>
<tr>
<th>u (Å)</th>
<th>6.705(1)</th>
<th>Crystal size (mm)</th>
<th>0.12 x 0.03 x 0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>b (Å)</td>
<td>12.752(2)</td>
<td>Radiation</td>
<td>MoKα</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.524(2)</td>
<td>Total Ref.</td>
<td>4316</td>
</tr>
<tr>
<td>ν (Å$^3$)</td>
<td>983.6(7)</td>
<td>Unique Ref.</td>
<td>753</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbcm</td>
<td>Unique/F$^2$ ≥ 4σ(F)</td>
<td>532</td>
</tr>
<tr>
<td>F$_{20}$</td>
<td>1112</td>
<td>R1</td>
<td>0.055</td>
</tr>
<tr>
<td>μ (cm$^{-1}$)</td>
<td>180.9</td>
<td>S</td>
<td>0.916</td>
</tr>
<tr>
<td>D$_{calc}$ (g/cm$^3$)</td>
<td>4.241</td>
<td>ρ$<em>{mass}$, ρ$</em>{free}$ (g/cm$^3$)</td>
<td>2.63, 0.97</td>
</tr>
<tr>
<td>Unit-cell contents:</td>
<td>4[(UO$_2$)MoO$_3$(H$_2$O)$_2$]H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_1 = \frac{\sum</td>
<td>F_0</td>
<td>-</td>
<td>F</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U$_{eq}$</th>
<th>U$_{11}$</th>
<th>U$_{22}$</th>
<th>U$_{33}$</th>
<th>U$_{23}$</th>
<th>U$_{13}$</th>
<th>U$_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.704(4)</td>
<td>0.40398(6)</td>
<td>%</td>
<td>157(2)</td>
<td>133(4)</td>
<td>247(2)</td>
<td>85(3)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mo</td>
<td>0.168(2)</td>
<td>0.46925(9)</td>
<td>0.09754(8)</td>
<td>184(3)</td>
<td>139(7)</td>
<td>379(9)</td>
<td>85(2)</td>
<td>-3(3)</td>
<td>5(4)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.681(2)</td>
<td>0.254(1)</td>
<td>%</td>
<td>330(4)</td>
<td>450(11)</td>
<td>218(8)</td>
<td>350(9)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.786(2)</td>
<td>0.637(1)</td>
<td>%</td>
<td>340(4)</td>
<td>390(11)</td>
<td>160(8)</td>
<td>470(9)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.415(1)</td>
<td>0.47057(8)</td>
<td>0.12596(8)</td>
<td>280(20)</td>
<td>291(3)</td>
<td>490(7)</td>
<td>178(9)</td>
<td>20(10)</td>
<td>90(6)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.140(1)</td>
<td>0.5109(9)</td>
<td>-0.0604(8)</td>
<td>193(20)</td>
<td>174(4)</td>
<td>276(5)</td>
<td>139(5)</td>
<td>21(4)</td>
<td>78(2)</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.055(2)</td>
<td>0.480(1)</td>
<td>%</td>
<td>280(8)</td>
<td>270(8)</td>
<td>640(109)</td>
<td>305(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(6)</td>
<td>0.401(2)</td>
<td>0.655(2)</td>
<td>0.121(7)</td>
<td>320(20)</td>
<td>174(7)</td>
<td>580(110)</td>
<td>219(8)</td>
<td>9(5)</td>
<td>10(10)</td>
</tr>
<tr>
<td>O(7)</td>
<td>0.168(1)</td>
<td>0.639(7)</td>
<td>0.083(7)</td>
<td>326(30)</td>
<td>450(7)</td>
<td>310(138)</td>
<td>800(105)</td>
<td>15(6)</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$U$_{eq}$ = (1/3) $\Sigma U_{ij}$.$\alpha_i$.$\alpha_j$.
F² 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 (R₁) of 3.5%, calculated for 532 unique observed reflections (|F₀| > 4σ(F₀)) 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 Pca₂₁, as proposed by Serezhkin et al. (1981), and resulted in a final R₁ 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 U⁶⁺ cation that is strongly bonded to two O atoms, resulting in a nearly linear (UO₂)²⁺ uranyl ion (Ur), as is typical for U⁶⁺ minerals. The uranyl ion is coordinated by five additional anions located at the equatorial positions of a pentagonal bipyramid that is capped by the Oₚ₅ atoms. The <Ur–Oₚ₅> and <Ur–O⁰ₐq> (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 Mo⁶⁺ 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 Mo⁶⁺ 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 H₂O group that is located 2.403(8) Å from the Mo⁶⁺ 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 Mo⁶⁺ cation. A similar coordination polyhedron about Mo⁶⁺ was observed in the structures of umohoite (Krivovichev & Burns 2000) and UMoO₄ (D’yachenko et al. 1996).

The structure of iriginite consists of symmetrically identical sheets of edge-sharing Ur⁵⁻ pentagonal bipyramids and Mo₆⁰ octahedra (φ: O, H₂O) with composition [(UO₂)Mo₂O₇(H₂O)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 Ur⁵⁻ pentagonal bipyramid, two-thirds of the squares are populated with Mo₆⁰ 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 H₂O group (Fig. 2). The H₂O(8) group donates two H bonds that are probably accepted by O(7) anions, with donor–acceptor distances of 2.95(1) Å. The H₂O(8) anion probably accepts two H bonds donated by symmetrically distinct H₂O(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 H₂O(8) anion. The H₂O(6) anion is bonded to Mo⁶⁺, and donates a single H bond to H₂O(8) in the interlayer. The remaining H atom associated with H₂O(6) does not appear to participate in a hydrogen bond, as there are no suitable acceptors.

ACKNOWLEDGEMENTS

This research was supported by the Environmental Management Sciences Program of the United States Department of Energy (DE–FG07–97ER14820) and by an NSF–NATO Fellowship in Science and Engineering
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.

REFERENCES


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 H2O groups in the interlayers, with open circles and cross-hatched circles representing H2O groups below and above the sheet, respectively.

Fig. 2. The structure of iriginite projected along [100]. H2O 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.
THE CRYSTAL STRUCTURE OF IRIGINITE


Received January 10, 2000, revised manuscript accepted May 21, 2000.