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# Orthorhombic Uranium(IV) Molybdenum(VI) Oxide, $UMo_2O_8$*

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**Abstract.** $M_r = 557{\cdot}8$, orthorhombic, *Pban*, $a = 20{\cdot}076\,(4)$, $b = 7{\cdot}323\,(1)$, $c = 4{\cdot}1164\,(6)$ Å, $V = 605{\cdot}2$ Å$^2$, $Z = 4$, $D_m = 6{\cdot}08\,(6)$, $D_x = 6{\cdot}12$ Mg m$^{-3}$ Mo $K\alpha$, $\lambda = 0{\cdot}70930$ Å, $\mu = 367$ cm$^{-1}$, $F(000) = 960$, $T = 298$ K, $R = 0{\cdot}049$ for 1347 reflections. The structure consists of layers of oxide-bridged uranium and molybdenum atoms connected by infinite interlayer U—O—U and Mo—O—Mo chains. The uranium atoms have pentagonal bipyramidal coordination [U—O equatorial = 2·202 (6)–2·394 (8) Å, U—O axial = 2·0584 (3) Å]; the molybdenum atoms are in a highly distorted octahedral [Mo—O = 1·684 (7)–2·432 (7) Å] arrangement. The presence of oxide ions not connected to molybdenum suggests that this structure is better formulated as a double oxide–molybdate than as a true molybdate.

**Introduction.** Processing of spent Zr-clad nuclear-fuel elements can result in undesirable insoluble residues containing zirconium, plutonium and fission-product molybdenum. Zirconium and molybdenum are thought to be present in these residues as molybdate or polymeric molybdic acid species. Losses of plutonium to insoluble residues could occur because of its association with molybdenum-containing species (Penneman, Haire & Lloyd, 1980). Little reliable structural information is available on the possible plutonium–molybdenum compounds formed under nuclear-fuel reprocessing conditions. A plutonium compound claimed to be orthorhombic and isomorphous with the mineral sedovite, $U(MoO_4)_2$, has been obtained from aqueous solutions (Penneman, Haire & Lloyd, 1980). However, a single-crystal analysis has not been reported for either the Pu or U forms.

The uranium molybdate binary oxide system was first studied using powder data by Kovba & Trunov (1964). Later, Pailleret (1967) published a single-crystal structure for an orthorhombic $UMo_2O_8$ phase different from sedovite and also different from an orthorhombic Th compound reported by Tabuteau, Pagès & Freundlich, 1972), but the high final *R* value (0·16) suggested that further work was needed. A subsequent report by Kovba (1971) described another single-crystal structure study of this phase but again the report was exceedingly sketchy (an *R* factor was not even reported).

We have succeeded in preparing crystals of this orthorhombic $UMo_2O_8$ phase by skull melting (Herrick & Behrens, 1981) and, because of its relevance to the above-mentioned plutonium compounds, have carried out a definitive single-crystal X-ray diffraction study of this phase.

**Experimental.** $D_m$ by flotation. Precession photographs revealed Laue symmetry and systematic absences consistent with *Pban*, crystal 80 × 80 × 180 μm, automated Picker diffractometer, cell refinement with eleven reflections, $2\theta > 55°$, quadrant of data $h, \pm k, l$ collected,

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graphite-monochromated Mo radiation, $\theta$–$2\theta$ technique, two standard reflections monitored every fifty reflections, corrections for absorption (transmission coefficients = 0·054–0·124), equivalent reflections averaged, heavy-atom method, 1347 unique reflections, 1157 with $I \geq 2\sigma(I)$, $4 \leq \theta \leq 35°$, refined on $F$ with isotropic extinction parameters and anomalous dispersion corrections for the scattering factors (*International Tables for X-ray Crystallography*, 1962). Details of the refinement procedure have been described previously including computer programs and weighting scheme (Ryan & Swanson, 1974; Ryan, Eller & Kubas 1976). In final difference synthesis largest feature was a peak near uranium, with height about two thirds that of an oxygen atom, $R = 0{\cdot}049$, $R_w = 0{\cdot}052$, maximum shift/standard deviation = 0·008.*

**Discussion.** The unit-cell parameters and heavy-atom positions for our determination (Table 1) roughly agree with Kovba's parameters, but Kovba's oxygen positions (which apparently were not refined) differ significantly from our more accurate values. Also, there is an apparent error in Kovba's publication in that his O(1) [our O(5)] should have been reported with $z = \frac{1}{2}$ to provide interlayer connectivity, not with $z = 0$. Bond distances and angles are given in Table 2.

The most striking feature of the orthorhombic $UMo_2O_8$ structure is the two-dimensional layered arrangement of the uranium and molybdenum atoms (Fig. 1). The molybdenum atoms are located 0·308 (3) Å from the plane of the uranium atoms at $z = 0$, and the interlayer spacing corresponds to the 4·1164 (6) Å $c$ axis.

The layers of heavy atoms are connected by U—O—U and Mo—O—Mo infinite chains. These chains are nearly perpendicular to the basal plane and the U—O(5)—U [178·4 (4)°] and Mo—O(3)—Mo [179·3 (3)°] bond angles are almost linear. The uranium–oxygen bonding along the chain is symmetrical with all U—O(5) distances being 2·0584 (3) Å. Fourier sections near $z = \frac{1}{2}$, and trial refinements with the $x$ coordinate deliberately displaced from the refined position, provided no evidence for asymmetry in U—O distances or for larger U—O—U angles [and thus larger U—O(5) distances].

The uranium atom is seven coordinate in the form of a pentagonal bipyramid. Basal coordination is accomplished by four bonds to O(6) [2·202 (6) and 2·324 (6) Å] and one to O(1)[2·394 (8) Å] to form an approximately regular pentagon. The bipyramids are edge shared to form zig-zag chains which are interconnected by a double row of molybdenum atoms. The very short axial U—O(5) distance of 2·0584 (3) Å implies some multiple bonding, since Zachariasen's bond length–bond strength formulation predicts a length of ~2·32 Å for a $U^{IV}$—$O_7$ bond of unit strength (Zachariasen, 1978).

Table 1. *Atomic coordinates* (×10⁵) *and equivalent isotropic thermal parameters* (Å² × 10⁴) *for orthorhombic uranium*(IV) *molybdenum oxide*

| | $x$ | $y$ | $z$ | $U_{eq}$ or $U$* |
|---|---|---|---|---|
| U | −1415 (2) | 25000 | 0 | 37 (2) |
| Mo | 16053 (3) | 49741 (10) | 9475 (16) | 45 (3) |
| O(1) | 63338 (40) | 25000 | 0 | 64 (12) |
| O(2) | 75000 | 45692 (12) | 0 | 98 (14) |
| O(3) | 34001 (28) | 49659 (87) | 49611 (170) | 131 (11) |
| O(4) | 32829 (47) | 25000 | 0 | 115 (15) |
| O(5) | 51559 (36) | 25000 | 50000 | 77 (14) |
| O(6) | 43670 (28) | 3723 (79) | 1069 (161) | 84 (89) |

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ for U, Mo. Oxygen atoms were refined isotropically.

Table 2. *Interatomic distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| U–U | 3·7055 (7), 4·1164 (6) | U–Mo | 3·4942 (8), 3·9666 (9) |
| U–O(1) | 2·394 (8) | Mo–O(1) | 1·967 (2) |
| U–O(5) | 2·0584 (3) (×2) | Mo–O(2) | 1·868 (2) |
| U–O(6) | 2·324 (6) (×2) | Mo–O(3) | 2·432 (7) |
| | 2·202 (6) (×2) | | 1·684 (7) |
| | | Mo–O(4) | 1·867 (1) |
| | | Mo–O(6) | 1·999 (6) |
| O(1)–U–O(5) | 89·2 (2) (×2) | O(6)–U–O(6) | 129·8 (3) |
| O(1)–U–O(6) | 64·9 (1) (×2) | | 70·1 (2) (×2) |
| | 134·9 (2) (×2) | | 160·1 (3) (×2) |
| O(5)–U–O(6) | 88·6 (2) (×2) | | |
| | 90·7 (2) (×2) | | |
| | 91·7 (2) (×2) | | |
| | 89·4 (2) (×2) | | |
| O(1)–Mo–O(2) | 93·3 (3) | O(1)–Mo–O(4) | 154·7 (1) |
| O(1)–Mo–O(3) | 78·6 (2) | O(1)–Mo–O(6) | 79·3 (3) |
| | 101·5 (2) | | |
| O(2)–Mo–O(3) | 78·2 (1) | O(3)–Mo–O(6) | 79·8 (2) |
| | 102·5 (2) | | 99·6 (3) |
| O(2)–Mo–O(4) | 90·8 (3) | O(4)–Mo–O(6) | 87·6 (3) |
| O(2)–Mo–O(6) | 157·8 (2) | | |
| O(3)–Mo–O(4) | 77·8 (2) | | |
| | 101·9 (2) | | |

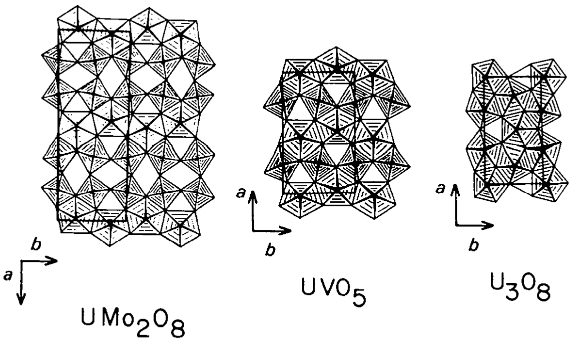

Fig. 1. View of the layer structures of $UMo_2O_8$ (this work), $UVO_5$ (Chevalier & Gasperin, 1970), and $U_3O_8$ (Loopstra, 1970*a*).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38555 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Mo—O(3)—Mo chain is not symmetry restricted to equivalent Mo—O(3) distances, and in fact the distances are drastically different, with Mo—O(3) and Mo—O(3′) bond distances of 1·684 (7) and 2·432 (7) Å. Distorted octahedral molybdenum coordination is completed by equatorial Mo—O distances of 1·868 (2)–1·999 (6) Å. This type of coordination has been observed before for molybdenum in binary oxide compounds (Magnéli, 1953; Wyckoff, 1964).

The absence of discrete molybdate tetrahedra and the existence of oxide anions not bonded to molybdenum indicate the compound discussed herein should be formulated as a double molybdenum oxide and not as the dimolybdate $U(MoO_4)_2$. This phase appears to be unique to uranium.

The $UMo_2O_8$ structure presented here has structural similarities to other uranium binary oxide structures. For example, the interlayer spacing of 4·1 Å set up by short U—O—U bridges and in-plane zig-zag chains of edge-shared pentagonal bipyramids are structural features found in $UVO_5$ and in all phases of $U_3O_8$ (Ackerman, Chang & Sorrell 1977; Shih-Hua, Kovba & Spitsyn, 1963; Chevalier & Gasperin, 1970; Andresen, 1958; Loopstra, 1964, 1970*a*, *b*, 1977). The $UVO_5$ structure (Fig. 1) especially resembles the orthorhombic uranium molybdate structure, since in $UVO_5$ zig-zag chains of uranium polyhedra are connected by a single row of vanadate octahedra. The vanadium atoms are coordinated as distorted octahedra very much like the molybdenum atoms in the orthorhombic $UMo_2O_8$ structure.

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# Orthorhombic Thorium(IV) Molybdate, $Th(MoO_4)_2$*

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**Abstract.** $M_r = 551·9$, orthorhombic, *Pbca*, $a = 10·318$ (5), $b = 9·737$ (4), $c = 14·475$ (6) Å, $V = 1454$ Å$^3$, $Z = 8$, $D_x = 5·04$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0·70930$ Å, $\mu = 244$ cm$^{-1}$, $F(000) = 1904$, $T = 298$ K, $R = 0·038$ for 3167 unique reflections. The structure is that of a true molybdate, with nearly regular molybdate tetrahedra bridging to thorium coordinated in a nearly regular square antiprismatic environment. The structure determination generally confirms but markedly improves a rough structure previously reported.

**Introduction.** Actinide molybdate formation has been suggested as a possible explanation for the troublesome formation of insoluble plutonium-containing residues in nuclear-waste processing (Penneman, Haire & Lloyd, 1980). Although crystal-structure determinations have been reported for several tetravalent actinide molybdates, in most cases the reports have been inaccurate or even incorrect (Cremers, Eller, Penneman & Herrick, 1983).

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