THE AQUEOUS SYNTHESIS OF UMoO$_6$ AND ITS SIGNIFICANCE TO NUCLEAR FUEL

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Abstract

While investigating the thermodynamics of the U-Mo-O chemical system, it became necessary to synthesize a quantity of UMoO$_6$. A novel aqueous method for the synthesis of UMoO$_6$ was explored as an alternative to conventional solid state synthesis. In this method, aqueous salts of molybdate (MoO$_4^{2-}$) and uranyl (UO$_2^{2+}$) are combined in a 1:1 ratio in order to precipitate a product that is characteristic of UMoO$_6$. One attempt resulted in the formation of a mixed U-Mo oxide: Na$_8$(UO$_2$)$_{24}$(MoO$_4$)$_{28}$. Full characterization of this novel compound, including definitive structural determination via single crystal X-ray diffraction (SC-XRD), is included herein. A second attempt formed a product resembling UMoO$_6$.

1. Background

The ability to model accurately nuclear fuel chemistry is highly valued by the nuclear industry. The fundamental bases of phase equilibrium nuclear fuel models are thermodynamic data, which are the product of many years of experimentation and computational study. These data are found by first investigating individual chemical systems and are used to predict the chemical phase equilibrium of partially burned nuclear fuel for a given environmental condition.

Research currently being completed by this group [1] investigates the thermodynamics of the individual chemical systems of Mo-O and U-Mo-O. The selection of these systems was based upon the ability of molybdenum (Mo) and uranium (U) to buffer oxygen (O$_2$). As ceramic uranium dioxide (UO$_2$) fuel undergoes fission, an excess of O$_2$ accumulates in the crystal structure and will equilibrate with its chemical surroundings. The oxidation of a nuclear fuel is important to understand and model as it affects fuel properties such as thermal conductivity of the fuel, which could lead to increased centreline temperatures in the fuel or fuel melting (in extreme cases).

An excellent visualization of the oxygen buffering ability of the Mo-O and U-Mo-O system is the Ellingham Diagram, Figure 1. The Gibbs Free Energy of a reaction ($\Delta G$) indicates the direction in which a reaction will proceed. When $\Delta G < 0$, the reaction will proceed in the forward direction. Conversely when $\Delta G > 0$, the reaction will proceed in the opposite direction written. When $\Delta G = 0$, the reaction is at equilibrium. In the case of two reactions directly competing for the same reactants, the one with the more negative $\Delta G$ will be favoured. As shown in Figure 1, the formation of molybdenum dioxide (MoO$_2$) crosses the 1:1 H$_2$:H$_2$O formation line. Below this intersection (e.g., $< 1000^\circ$C), the molybdenum oxide form is favoured and above this
intersection, the metallic form is favoured. Thus, indicating the duality of state for Mo as a function of oxygen partial pressure (or the $H_2$ to $H_2O$ ratio).

\[
\begin{align*}
H_2:O_2 &= 1:10^6 \\
H_2:O_2 &= 1:10^4 \\
H_2:O_2 &= 1:1
\end{align*}
\]

\[\text{Reducing Conditions} \]

\[\text{Oxidizing Conditions} \]

![Figure 1: Ellingham Diagram Illustrating the Range of $pO_2$ to be Tested and the Change in $\Delta G$ for the Formation of MoO$_2$ and UMoO$_6$ Based on 1 Mole of $O_2$ Gas Reacting [2].](image)

The formation of UMoO$_6$ is an even more stable reaction as the UMoO$_6$ formation line on Figure 1 lies below the MoO$_2$ formation line. The thermodynamic stability of UMoO$_6$, combined with its ability to buffer more moles of $O_2$ per mole of Mo than MoO$_2$ is of particular interest to fuel oxidation prediction by nuclear thermodynamic fuel models [3]. The first step in testing the thermodynamic values of UMoO$_6$ is to synthesize a product for experimentation.

2. **Solid State Synthesis**

A variety of methods for the synthesis of UMoO$_6$ have been developed in order to conduct experimentation as it is not available commercially. Current synthetic methods are conducted in the solid state, which involves mixing a uranium oxide powder and molybdenum trioxide powder and heating in air. Table 1 summarizes these synthetic methods. The purity of the synthesized UMoO$_6$ is evaluated using XRD, comparing the product pattern to a specific sample of UMoO$_6$ and reactant patterns. Products are sometimes contaminated with $U_3O_8$, thought to be due to the high volatility of MoO$_3$. Volatile reactants create difficulty in achieving a pure product in solid state reactions as the high temperatures required often change the initial reactant ratio and leave an excess reactant contaminant. It is believed that with an aqueous synthetic method, a higher purity product can be achieved as the reactants can be chosen in such a way as to encourage the formation of alternating U-O and Mo-O units, leaving excess reactants in solution rather than the precipitate.
Table 1: Solid State Synthesis Methods of UMoO₆.

<table>
<thead>
<tr>
<th>Method</th>
<th>U-Compound</th>
<th>Mo-Compound</th>
<th>Max Temperature (K)</th>
<th>Duration</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bharadwaj et al1</td>
<td>UO₂</td>
<td>MoO₃</td>
<td>950</td>
<td>21 h</td>
<td>[4]</td>
</tr>
<tr>
<td>Bharadwaj et al2</td>
<td>U₃O₈ᵃ</td>
<td>MoO₃</td>
<td>950</td>
<td>21 h</td>
<td>[4]</td>
</tr>
<tr>
<td>Dash et al</td>
<td>U₃O₈</td>
<td>MoO₃</td>
<td>773</td>
<td>200 h</td>
<td>[5]</td>
</tr>
<tr>
<td>Misra et alᵇ</td>
<td>UO₂</td>
<td>MoO₃</td>
<td>673</td>
<td>8 h</td>
<td>[6]</td>
</tr>
<tr>
<td>Nagai et al</td>
<td>U₃O₈</td>
<td>MoO₃</td>
<td>1043</td>
<td>2 h</td>
<td>[7]</td>
</tr>
<tr>
<td>Suleimanov et al</td>
<td>UO₃</td>
<td>MoO₃</td>
<td>823</td>
<td>48 h</td>
<td>[8]</td>
</tr>
<tr>
<td>Swaminathan et al</td>
<td>UO₂</td>
<td>MoO₃</td>
<td>873</td>
<td>48 h</td>
<td>[9]</td>
</tr>
<tr>
<td>Juenke et al</td>
<td>Unspecified U-oxide</td>
<td>Unspecified Mo-oxide</td>
<td>1073-1273</td>
<td>unspecified</td>
<td>[10]</td>
</tr>
</tbody>
</table>

ᵃ – U₃O₈ was synthesized by heating UO₂ in air for 6 h
ᵇ – 3 sequential heating phases

3. Aqueous Synthesis of UMoO₆

For this work, the aqueous synthesis of UMoO₆ was attempted through a series of wet chemistry experiments. The objective was to create UMoO₆ by combining uranyl (UO₂²⁺) and molybdate (MoO₄²⁻) salts. Variations in the method include the use of different counter-ions, temperatures, pH, and stoichiometric ratios. Herein, the results of the reaction of Na₂MoO₄ and UO₂(NO₃)₂ in a 1:1 ratio will be discussed. The theoretical reaction can be seen in Equation (1).

\[
Na₂MoO₄_{aq} + UO₂(NO₃)₂_{aq} → UMoO₆_{s} + 2NaNO₃_{aq}
\]

4. Experimental Procedure

4.1 Compound A

A solution of UO₂(NO₃)₂·6H₂O (1.0001 g, 1.9915 mmol, The British Drug Houses Ltd. in ~20 mL of distilled water) was added slowly to a stirring solution of Na₂MoO₄·2H₂O (0.4818 g, 1.9911 mmol, Anachemia, ~20 mL of distilled water) at room temperature, Equation (1). A bright yellow precipitate formed immediately. The solution was stirred for 24 h at room temperature, after which the precipitate was collected via centrifugation, washed twice with distilled water and dried overnight at 120°C (0.7527 g, 89.5% yield, based on the determined formulation Na₈(UO₂)₂₄(MoO₄)₂₈·3₈H₂O (vide infra)).

The resulting product was characterized by several techniques. Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Spectroscopy (EDX) were used to image and perform preliminary elemental analysis with a Philips XL-30CP SEM/EDX. Powder X-ray Diffraction (XRD) was conducted using a Thermo/ARL Scintag X1 X-ray diffractometer with Cu Kα radiation. Infrared Spectroscopy (IR) was conducted using a PerkinElmer Spectrum 65 FT-IR Spectrometer by mixing dry KBr with the sample and crushing to make a pellet. Thermogravimetric Analysis (TGA) was conducted using a SETARAM SETSYS Evolution 24 TGA by heating the sample to 600°C using 20 K min⁻¹ ramp rate, holding for 4 h and cooling to room temperature, all while under an ultra-high purity argon environment. Single crystal X-ray
diffraction (SC-XRD) was conducted using a Bruker-AXS SMART 1k CCD single-crystal X-ray diffractometer. The results presented are the best of several trials. A single crystal of the product was mounted on a thin glass fiber and cooled to 200 K under a stream of nitrogen gas. Information regarding collection parameters can be found in [11].

4.2 Compound B

As discussed below, compound A was found to contain Na. In an effort to drive the reaction towards UMoO₆, a replicate of compound A was synthesized as described above (0.2143 g, 0.5897 mmol) and placed in ~20 mL of a 68.5 mmol L⁻¹ solution of UO₂(NO₃)₂·6H₂O in water. The sample was refluxed for seven days at 105°C, filtered and washed twice, and allowed to dry in air for four days. SEM, EDX, XRD, and TGA were used to characterize the sample.

5. Results

5.1 Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Spectroscopy (EDX)

Using the procedure described above, compound A, a bright yellow microcrystalline product, was isolated from the aqueous solution. Examination of compound A using SEM shows small crystal formations (Figure 2), which are approximately 150 μm in length. There is a consistent plate-like appearance to each crystal resembling an elongated octagon.

![Figure 2: SEM of Compound A.](image)

EDX was conducted over a variety of spots on different crystal surfaces. As Figure 3 indicates, the elemental composition includes U, Mo, O, and Na. The homogeneity of the crystals suggests that Na is part of the crystal structure itself and not an impurity. As displayed in the Figure 3 inset, U and Mo appear in near stoichiometric ratios with a smaller amount of Na. The crystal appears oxygen-deficient as the approximate U:Mo:O ratio is 1:1:4 compared to the 1:1:6 of UMoO₆, however oxygen was calculated by difference. While EDX is a surface analysis tool, results ultimately suggest the formation of a U-Mo-Na oxide.
Examination of compound B, created by refluxing in a solution of excess UO$_2$(NO$_3$)$_2$, shows a loss of crystallinity and the formation of a powder (shown by SEM in Figure 4).

EDX was conducted over a variety of spots on compound B. As Figure 5 indicates, the elemental composition includes U, Mo, and O. However, Na was not observed in this sample. Importantly, the U:Mo ratio is approximately 1:1, as anticipated for the formation of UMoO$_6$. Oxygen, although difficult to accurately measure with EDX, was calculated as both an element and by difference, Figure 5 inset, giving a U:Mo:O ratio of 1:1:8 or 1:1:4, respectively.
5.2 Powder X-ray Diffraction (XRD)

Powder XRD analysis was performed on compound A and the results presented in Figure 6. The compound A pattern does not match the patterns of the starting reactants, U species, Mo species, or mixed U-Mo oxide species that are found in the Ref. [12] database. This concludes that either a new compound or a new crystal structure for UMoO₆ has been made.

Powder XRD analysis performed on compound B is shown in Figure 7. The pattern is visually different from compound A, indicating a change in crystal structure. This is expected, as a different crystal structure must exist if Na is no longer present in the crystal, as indicated by the EDX results in Figure 5.

* Na₂MoO₄, UO₂(NO₃)₂, MoO₃, MoO₂, various UO₃, Mo₅O₂₃, UMo₂O₈, UO₂MoO₄
5.3 **Infrared Spectroscopy (IR)**

Typical of a metal oxide, the IR spectrum of compound A is rather sparse (Figure 8). The large bowing peak around 3500 cm\(^{-1}\) indicates the presence of water in the material. The strong peaks at 1650 cm\(^{-1}\) and below 1000 cm\(^{-1}\) resemble the characteristic 1640 cm\(^{-1}\) and 965 cm\(^{-1}\) peaks of the mineral Iriginite, \((\text{UO}_2)(\text{Mo}_2\text{O}_7)\cdot3\text{H}_2\text{O}\), as well as the peaks at 1650 cm\(^{-1}\) and 944 cm\(^{-1}\) for the mineral Calcurmolite, \(\text{Ca}_2(\text{UO}_2)_3\text{Mo}_2\text{O}_{11}\cdot n\text{H}_2\text{O}\) [13]. The presence of these peaks indicates that the product is most likely not a mixture of starting materials, but rather some form of U-Mo oxide.

5.4 **Thermogravimetric Analysis (TGA)**

In order to investigate the amount of water and impurities in compound A, TGA was performed on the product. Figure 9 displays the mass loss as a function of temperature, showing that the majority of the loss occurred under 200\(^{\circ}\)C, which suggests it is associated with water loss. Figure
The above characterization methods for compound A indicate the presence of a mixed U-Mo oxide containing Na and excess water molecules. Luckily, the crystals grown from the reaction mixture were large enough to perform SC-XRD, resulting in the definitive structural determination and atomic formulation of the product being Na$_8$(UO$_2$)$_{24}$(MoO$_4$)$_{28}$ per unit cell [14]. The compound crystallizes in the orthorhombic space group $C222_1$ and displays an extended U-Mo-O network. Although there are three crystallographically distinct U atoms and four Mo atoms, all atoms display virtually identical positions in the crystal structure. Each U atom adopts a pentagonalbipyramidal geometry (Figure 13). The axial positions are occupied by...
terminal oxygen atoms (average bond lengths ~ 1.77 Å) and each equatorial oxygen atom (U-O_{av} = 2.37Å) bridges a tetrahedral Mo centre (Mo-O_{av} = 1.75Å).

Through bridging oxygen atoms, the extended solid is generated, consisting of alternating pentagonal bipyramidal uranyl and tetrahedral molybdate units. Figure 14, Figure 15, and Figure 16 show the extended structure and include the interstitial Na ions (purple).
The Na ions are incorporated in the structure by interaction with the oxygen atoms at the exterior of the highly bridged network. Although the Na ions display severe disorder and partially occupy several positions in the network, the relative stoichiometry could still be determined to include two Na\(^+\) for every six UO\(_2\)^{2+} and seven MoO\(_4\)^{2-} units, resulting in an electrically neutral formula. Although the EDX measured slightly different amounts, SC-XRD is much more accurate and considers the entire crystal, as opposed to the surface-only technique, EDX.

As shown in Figure 15 above, the 3D structure consists of void spaces. These pores most likely contain water molecules from the aqueous preparation (as concluded by IR spectroscopy). Due to the small size of the crystals and severe disorder and vibration encountered with individual solvent molecules, they were not refined during the structural determination. Incorporating the results of the TGA described earlier, and assuming the measured mass loss is due solely to loss of water, there appears to be 1.58 molecules of water per U atom, for an overall formula per unit cell of Na\(_8\)(UO\(_2\))\(_{24}\)(MoO\(_4\))\(_{28}\)·38H\(_2\)O.

The SC-XRD data were used to simulate the full XRD pattern of the product (Figure 17). The simulated XRD pattern matches very well with that obtained experimentally, indicating that the single crystal chosen for analysis is representative of the bulk material. The common peak angles are \(2\theta = 8.5, 9.4, 18.3, 18.9, 22.3, 25.0, \) and \(29.2^\circ\).
6. Discussion

The combination of results presented above conclusively demonstrates the formation of a novel compound (compound A) of formula Na₈(UO₂)₂₄(MoO₄)₂₈·3₈H₂O. To the best of our knowledge, this is the first reported single crystal structural determination of a U-Mo oxide that does not contain organic amine-based countercations. Although the synthetic procedure involves the reaction of equivalent amounts of UO₂²⁺ and MoO₄²⁻, the resulting stoichiometry of 6U:7Mo suggests that this product is formed preferentially over pure UMoO₆ under these conditions. The overall equation for this reaction is shown in Equation (2).

\[
7 \text{Na}_2\text{MoO}_4_{aq} + 6 \text{UO}_2(\text{NO}_3)_2_{aq} \rightarrow \frac{1}{4}\text{Na}_8(\text{UO}_2)_{24}(\text{MoO}_4)_{28s} + 12\text{NaNO}_3_{aq}
\]

The determining factors in the formation of compound A over UMoO₆ may be kinetic or thermodynamic in nature. Immediate precipitation of the product upon mixing may force the reaction towards compound A, preventing complete formation of the 1:1 U:Mo oxide.

In an effort to drive the reaction towards formation of the 1:1 U:Mo UMoO₆, an attempt was made to exchange the Na⁺ ions in compound A with additional UO₂²⁺ ions (compound B). XRD has confirmed a change in the crystal structure indicating a different compound has formed, and the new pattern does not reflect any of the previously published examples of UMoO₆. EDX indicates that Na has been removed from the powder as a result of the reflux in uranyl nitrate solution, resulting in a 1:1 U:Mo ratio and suggesting the formation of UMoO₆. If the compound remaining after TGA is assumed to be UMoO₆ and the mass loss entirely attributed to water, compound B is UMoO₆·2H₂O.

Further characterization is required to confirm Na removal, a 1:1 stoichiometry of Mo:U, and to better quantify the amount of oxygen in the compound. Further synthetic efforts will be geared towards mitigating premature precipitation and encouraging the exclusive formation of UMoO₆. Indeed, attempts have been made to adjust the initial stoichiometries, starting materials, reaction temperature and solvent conditions, the results of which will be presented in due course.
The compound $A$U-Mo mixed oxide, $Na_8(UO_2)_{24}(MoO_4)_{28} \cdot 38H_2O$, has been synthesized and fully characterized, representing the first single crystal study of a purely inorganic U-Mo oxide. Although the final product is not pure $UMoO_6$, the aqueous synthetic procedure described here shows great potential for the preparation of $UMoO_6$ of consistent and defined formulation. Attempts to drive the reaction towards the formation of $UMoO_6$ appear to be successful, leading to the synthesis of compound $B$ with a 1:1 U:Mo ratio and a complete absence of Na. The techniques and results presented herein forms the foundation for the synthesis of pure $UMoO_6$. The ability to prepare pure $UMoO_6$ will be a great advantage to the study of this highly important nuclear compound.

8. References


[11] Data were collected with a sequence of 0.3° 0 scans at 0, 90, 180, and 270° in . Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. Systematic absences in the diffraction data set and unit-cell parameters were consistent with orthorhombic $C-222_1$. The structure was solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on $F^2$. Na atoms were refined over several position and display partial occupancy and disorder. Interstitial water molecules were not refined.


[14] Crystallographic data: orthorhombic $C-222_1$, $a = 12.4947(6)$ Å, $b = 18.7181(10)$ Å, $c = 22.6721(11)$ Å, $5302.5(5)$ Å$^3$, $Z = 24$, empirical formula = $Mo_{1.17}Na_{0.33}O_{6.67}U$, radiation (Kα, Å) = 0.71073 Å, $D_{calcld}=3.490$ mg/m$^3$, $\mu_{calcld}=19.940$ mm$^{-1}$, $F_{000} = 4752$, $R = 0.0533$, $R^2_{p}=0.1289$, $GoF = 1.010$. 