

The Aqueous Synthesis of UMoO_6 and Its Significance for Nuclear Fuel

R.A. Barry^{*1}, J. Scott¹, I. Korobkov², J. Deveau¹ and E.C. Corcoran¹

¹ Royal Military College of Canada, Kingston, Ontario, Canada

² University of Ottawa, Ottawa, Ontario, Canada

*Aaron.Barry@rmc.ca, 11 General Crerar Crescent, Kingston, ON, K7K 7B4

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Summary

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, involving the reaction between aqueous salts of molybdate (MoO_4^{2-}) and uranyl (UO_2^{2+}) in a 1:1 ratio. One attempt resulted in the formation of a mixed U-Mo oxide: $\text{Na}_8(\text{UO}_2)_{24}(\text{MoO}_4)_{28}$. 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. 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 ΔG will be favoured. As shown in Figure 1, the formation of molybdenum dioxide (MoO_2) crosses the 1:1 $\text{H}_2:\text{H}_2\text{O}$ formation line. Below this intersection (e.g., $< 1000^\circ\text{C}$), 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 H₂ to H₂O ratio).

The formation of UMoO₆ is an even more stable reaction as the UMoO₆ formation line on Figure 1 lies below the MoO₂ formation line. The thermodynamic stability of UMoO₆, combined with its ability to buffer more moles of O₂ per mole of Mo than MoO₂ is of particular interest to fuel oxidation prediction by nuclear thermodynamic fuel models [2]. The first step in testing the thermodynamic values of UMoO₆ is to synthesize a product for experimentation.

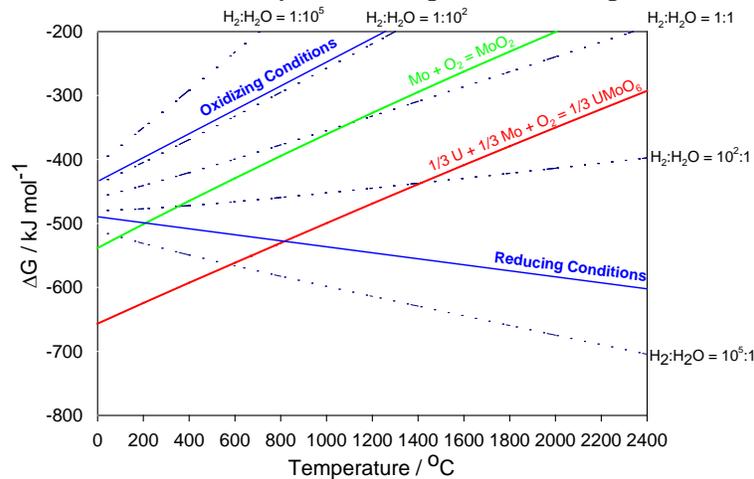


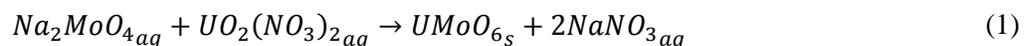
Figure 1: Ellingham Diagram Illustrating the Range of pO₂ to be Tested and the Change in ΔG for the Formation of MoO₂ and UMoO₆ Based on 1 Mole of O₂ Gas Reacting [3].

2. Solid State Synthesis

A variety of methods for the synthesis of UMoO₆ have been developed and are conducted in the solid state, which involves mixing U-oxides and MoO₃ and heating in air [4,5,6,7,8,9,10]. The purity of the synthesized UMoO₆ is evaluated using XRD, comparing the product pattern to a specific sample of UMoO₆ and the reactant patterns. Products are sometimes contaminated with U₃O₈, thought to be due to the high volatility of MoO₃, which thereby leaves an excess of reactant and results in an impure product. The potential to achieve a higher purity product may be increased using an aqueous synthesis, 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.

3. Aqueous Synthesis of UMoO₆

For this work, the aqueous synthesis of UMoO₆ was attempted 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).



4. Experimental Procedure

4.1 Compound A

A solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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 $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (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 $\text{Na}_8(\text{UO}_2)_{24}(\text{MoO}_4)_{28} \cdot 38\text{H}_2\text{O}$ (*vide infra*)).

4.2 Compound B

As discussed below, compound **A** was found to contain Na. In an effort to drive the reaction towards UMoO_6 , 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 $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 the product using SEM shows small, octagonal plate-like crystals (Figure 2), which are approximately 150 μm in length. Examination of compound **B**, created by refluxing in a solution of excess $\text{UO}_2(\text{NO}_3)_2$, shows a loss of crystallinity and the formation of a powder, Figure 3.

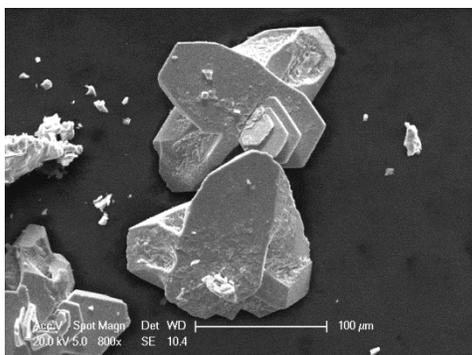


Figure 2: SEM of Compound A.

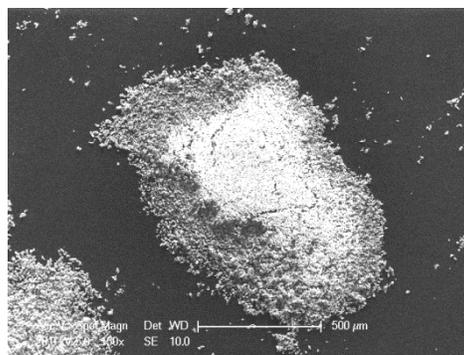


Figure 3: SEM of Compound B.

EDX was conducted over a variety of spots on compound **A**. 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 Table 1, U and Mo appear in near stoichiometric ratios with a smaller amount of Na, suggesting the formation of a U-Mo-Na oxide. The crystal appears oxygen-deficient as the approximate U:Mo:O ratio is 1:1:4, however oxygen was calculated by difference. EDX conducted on compound **B** also included the 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, Table 1, giving a U:Mo:O ratio of 1:1:8 or 1:1:4, respectively.

Table 1: Average Atom Percentage by EDX.

Element	Na	Mo	U	O
Compound A – Oxygen by Difference	4 ± 2	16 ± 4	18 ± 4	62 ± 2
Compound B - Oxygen by Difference	0	18.8 ± 0.3	17.7 ± 0.3	63.5 ± 0.1
Compound B - Oxygen as an Element	0	10.5 ± 0.1	9.7 ± 0.3	79.8 ± 0.3

5.2 Powder X-ray Diffraction (XRD)

Powder XRD analysis was performed on compound **A** and the results presented in Figure 4. 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. [11] database. This concludes that either a new compound or a new crystal structure for UMoO_6 has been made. Powder XRD analysis was also performed on compound **B**, 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 Table 1.

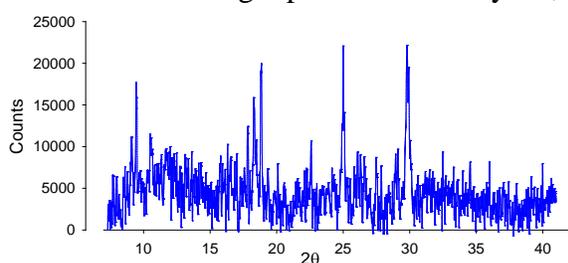


Figure 4: Powder XRD Results of Compound A.

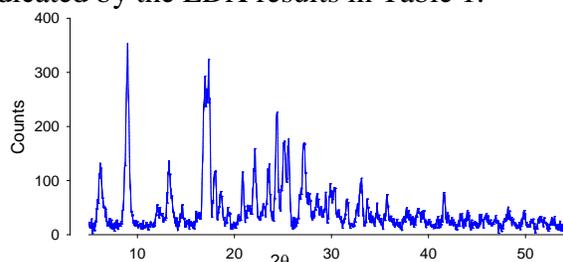


Figure 5: Powder XRD Results of Compound B.

5.3 Thermogravimetric Analysis (TGA)

In order to investigate the amount of water and impurities in the product, TGA was performed on compound **A**. The majority of the loss occurred under 200°C , which suggests it is associated with water loss. A stable mass was achieved during a 600°C temperature hold and a total mass loss of 6.76%. TGA performed on compound **B** exhibited the same trends as compound **A** and had a mass loss of 7.15 %.

5.4 Single Crystal X-ray Diffraction (SC-XRD)

The above characterization methods for compound **A** indicate the presence of a mixed U-Mo-Na oxide and excess water. 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 $\text{Na}_8(\text{UO}_2)_{24}(\text{MoO}_4)_{28}$ [12]. Compound **A** crystallizes in the orthorhombic space group $C 2 2 2_1$ 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 pentagonal bipyramidal geometry (Figure 6). The axial positions are occupied by terminal oxygen atoms ($\text{U-O}_{\text{av}} = 1.77 \text{ \AA}$) and each equatorial oxygen atom ($\text{U-O}_{\text{av}} = 2.37 \text{ \AA}$) bridges a tetrahedral Mo centre ($\text{Mo-O}_{\text{av}} = 1.75$

* Na_2MoO_4 , $\text{UO}_2(\text{NO}_3)_2$, MoO_3 , MoO_2 , various UO_3 , Mo_8O_{23} , UMo_2O_8 , UO_2MoO_4

Å). Through bridging oxygen atoms, the extended solid is generated, shown in Figure 7 with the interstitial Na ions (purple).

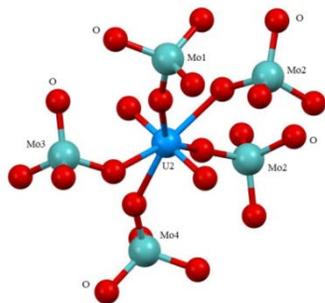


Figure 6: Partial Ball and Stick Diagram of Compound A Showing the Geometry of U (blue), Mo (teal), and O (red).

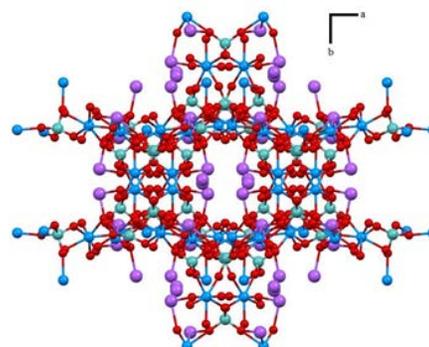


Figure 7: Partial Ball and Stick Diagram of Compound A in the *ab* Plane.

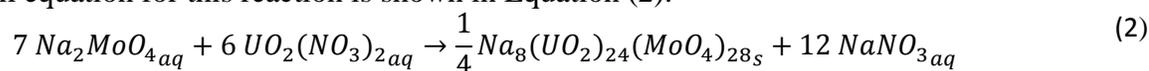
The Na ions are incorporated in the structure by interaction with the oxygen atoms at the exterior of the highly bridged network. Although the Na ions display severe disorder and partially occupy several positions in the network, the relative stoichiometry could still be determined to include two Na⁺ for every six UO₂²⁺ and seven MoO₄²⁻ units. Although the EDX measured slightly different amounts, SC-XRD is much more accurate and considers the entire crystal, as opposed to only the surface.

As shown in Figure 7 above, the 3D structure consists of void spaces, most likely containing water molecules from the aqueous preparation. Severe disorder and vibration of individual solvent molecules prevented them from being 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 Na₈(UO₂)₂₄(MoO₄)₂₈·38 H₂O.

The SC-XRD data was used to simulate the full XRD pattern of the product, displaying a very good match with that obtained experimentally. This indicates that the analysed crystal is representative of the bulk material. The common peak angles are 2θ = 8.5, 9.4, 18.3, 18.9, 22.3, 25.0, and 29.2°.

6. Discussion

The combination of results presented above conclusively demonstrate the formation of a novel compound (compound A) of formula Na₈(UO₂)₂₄(MoO₄)₂₈·38 H₂O. 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 counteranions. 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).



The determining factors in the formation of compound **A** over UMoO_6 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 UMoO_6 , an attempt was made to exchange the Na^+ ions in compound **A** with additional UO_2^{2+} 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 UMoO_6 . 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 UMoO_6 . If the compound remaining after TGA is assumed to be UMoO_6 and the mass loss entirely attributed to water, compound **B** is $\text{UMoO}_6 \cdot 2\text{H}_2\text{O}$.

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 UMoO_6 . 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.

7. Conclusion

The compound **A** U-Mo mixed oxide, $\text{Na}_8(\text{UO}_2)_{24}(\text{MoO}_4)_{28} \cdot 38\text{H}_2\text{O}$, 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

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- [12] Crystallographic data: orthorhombic $C-2\ 2\ 2$, $a = 12.4947(6)\ \text{\AA}$, $b = 18.7181(10)\ \text{\AA}$, $c = 22.6721(11)\ \text{\AA}$, $5302.5(5)\ \text{\AA}^3$, $Z = 24$, empirical formula = $\text{Mo}_{1.17}\text{Na}_{0.33}\text{O}_{6.67}\text{U}$, radiation ($K\alpha$, \AA) = $0.71073\ \text{\AA}$, $D_{\text{calcd}} = 3.490\ \text{mg/m}^3$, $\mu_{\text{calcd}} = 19.940\ \text{mm}^{-1}$, $F_{000} = 4752$, $R = 0.0533$, $R_w = 0.1289$, $\text{GoF} = 1.010$.