

Thermal Elimination of Pyridine from a Uranium Trichloride Precursor

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Renewed interest in advanced nuclear reactors, such as Molten Salt Reactors (MSRs), has spurred studies in actinide halide chemistry and property measurements. Several proposed research-scale and commercial MSR designs incorporate uranium trichloride (UCl₃) fuel. There are relatively few preparations for isolated actinide halides reported in the literature, therefore

Introduction

Pressing needs for alternatives to fossil fuel-generated energy have led to a renaissance in the area of advanced nuclear reactors, including Molten Salt Reactors (MSRs). We have been developing methods for the accurate and precise measurement of thermophysical and chemical properties of actinide-bearing salt mixtures pertinent to MSRs,^[1,2] which has driven a need for pure, isolable actinide halides. In searching the literature, we found few synthetic preparations afforded pure, isolable UCI₃. Many preparations involve the reduction of uranium(IV) chloride (UCl₄) using, for example, H₂,^[3] alkali metals,^[4] or Si^[5] at elevated temperatures (>350 °C). Some require days (>7d) of heating. The classic preparation treats UH₃^[6] with gaseous HCl^[7] however, alternatives to gaseous chloride reagents are desirable to reduce hazards. Electrochemical oxidation of uranium metal with ZnCl₂^[8] and BiCl₃,^[9,10] as examples, results in mixtures of UCl₃ in alkali metal chlorides. While the generation of these mixtures is useful for the study of their combined properties, there are some drawbacks: (1) the precise amount of generated UCl₃ in salt can be challenging to quantify, and (2) the purity of the overall mixture may be impacted by byproducts of the reaction. For these reasons, the isolation of pure UCl₃ in high yield is desirable and is our target.

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- Supporting information for this article is available on the WWW under https://doi.org/10.1002/cmtd.202300052
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novel methods for the isolation of pure material are desired. This communication describes the thermal elimination of pyridine (py) from the coordination complex UCl₃py₂ to yield gram-scale quantities of UCl₃. The purity of the UCl₃ product was determined through powder X-ray Diffractometry (pXRD) and Elemental Analysis (EA).

Facile preparations for actinide halide coordination complexes have flourished in the literature and enable the isolation of compounds that have polar ligands datively bound to the actinide metal center, (i.e., $UCI_3(L)_x$ (L=dative ligand)).^[11-15] We hypothesized that thermal scission of the dative ligand-to-metal bond and elimination of the ligand would yield desired "bare" actinide halides - in the above example, UCI₃. Identifying a molecular coordination complex that is stable and cleanly liberates the dative ligand is challenging. For example, THF is removed from UCI₃(THF)_x at 400 °C under vacuum; however, powder X-ray Diffractometry (pXRD) and combustion Elemental Analysis (EA) indicate that the elimination is incomplete and impurities are formed along with the UCI₃.^[11] In another example, the clean elimination of the seven water molecules coordinated to uranium in UCl_3 \cdot 7H₂O was observed at 260 °C, yet the aqua precursor is unstable and readily decomposes.^[16] In this communication, we report the clean thermal elimination of the pyridine ligands from the stable uranium trichloride coordination complex UCl₃py₂ yields pure UCl₃.

Results and Discussion

A detailed, reproducible synthesis of UCI_3py_4 (py = pyridine) on small (100 mg) and large scale (10 g) has recently been reported in a patent.^[17] While the reported crystal structure displays four pyridine molecules coordinated to uranium, EA results were found for 2.5 equivalents of pyridine. Disparities in the number of pyridine molecules coordinated to uranium trichloride persist in other literature reports. Santos and coworkers exchanged the THF ligand of UCl₃(THF)_x with pyridine to afford a compound they identified as UCl₃py₃.^[12] A related dimeric species, [UCl₃py₄]₂, was noted to be "vacuum sensitive" and the reported EA results yielded 7.4 equivalents of pyridine.^[14] In our hands, following the procedure in the patent, we reproducibly received EA results that matched those calculated for UCl₃py₂. Taken together, these data seemed to indicate inconsistent and possibly labile coordination of pyridine to uranium. It was also observed that upon standing in a rigorously inert glovebox $(<1 \text{ ppm O}_2/\text{H}_2\text{O})$ the surface of bulk UCl₃py₂ material changed

Chemistry-Methods 2024, e202300052 (1 of 3)



color from a dark purple-black powder to lighter shades over several months. This color change could not be attributed to decomposition as reaction chemistry was unaffected. For these combined reasons, we elevated UCl₃py₂ as a candidate for ligand elimination studies to afford pure UCl₃. We hypothesized that the compound could be treated to relatively low temperatures (<400 °C) and the pyridine ligand could be eliminated.

To test this hypothesis, approximately 0.5 g of black UCl₃py₂ powder was placed in a quartz tube and heated in a vacuum apparatus in an argon-filled glovebox (described in the Experimental Section). The furnace temperature was ramped to 300 °C over 30 minutes, reaching an internal temperature of 275 °C, then the heating element turned off and the sample was allowed to cool to ambient temperature. Assuming that UCl₃ was the sole product from this temperature treatment, a 97% yield was calculated from the collected yellow-brown material (Figure 1).

To confirm the composition of the purported UCl_3 material, it was analyzed by pXRD. As seen in Figure 2, there is an excellent match between the powder pattern obtained from



Figure 1. The UCl3 material (top) generated from heating UCl3py2 (bottom) to 300 $^\circ\text{C}.$



Figure 2. (top) The pXRD pattern for UCl₃py₂; (middle) pXRD pattern for UCl₃ generated by heating UCl₃py₂ at 300 °C; (bottom) Reference UCl₃ PDF 00-009-0067.^[18]

the experimentally obtained UCl₃ (middle) and previously reported data for this compound (bottom),^[18] with no indication of crystalline impurities within the pXRD detection limit.^[1] As further confirmation, the powder pattern for the UCl₃py₂ starting material, which has not been previously reported, was obtained (Figure 2, top spectrum) and is distinct from that obtained for UCl₃.

The EA of the UCl₃ generated from UCl₃py₂ also indicated little to no carbon, hydrogen, and nitrogen content (C=0.92, H=0.95, N=0.14, with a 0.3% limit of detection). Based on nitrogen content alone, these results would be consistent with <0.04 molecules of pyridine coordinated to uranium. For comparison, an authentic standard of UCl₃ was submitted for EA and also displayed low quantities of C and H (0.12 and 0.46%, respectively).

Finally, the robustness of this overall procedure was explored. Experiments in which the mass of UCl_3py_2 was increased to 1 g also reproducibly resulted in the clean formation of UCl_3 , as confirmed by pXRD, following the same temperature treatment. Heating UCl_3py_2 at 300 °C for extended times (2 hours) did not appear to result in any degradation, suggesting that further scale up of this procedure to multi-gram quantities is possible; this will be explored in the future.

Experimental Section

Caution: Depleted uranium (²³⁸U) is a weak α -emitter with a half-life of 4.5×10^9 years. These materials should be handled with care in radiological laboratories equipped with appropriate monitoring equipment.

All uranium materials described in this communication are air- and water-sensitive and were handled in an argon-filled NexGen Vacuum Atmospheres glovebox ($< 1 \text{ ppm } O_2$ and H_2O). The uranium trichloride pyridine complex was prepared according to the detailed procedure within a recently disclosed patent (see SI).^[17] While the patent refers to this compound as UCl₃py₄, the reported EA is consistent with 2.5 pyridine molecules coordinated to uranium and in our hands, EA results (Atlantic Microlab [Norcross, GA, USA]) reproducibly afforded two pyridine molecules calculated per uranium (calcd. C=23.9; H=2.01; N=5.57. Found, C=23.89; H=2.39; N=5.36). We therefore refer to this compound as the dipyridyl complex UCl₃py₂. pXRD data was obtained using a D2 Phaser (Bragg-Brentano geometry, Ni-filtered Cu Ka, Bruker AXS, Karlsruhe, Germany), with comparison to reference crystallographic data from the powder diffraction file (PDF-4+) database. A vacuum apparatus was used to remove the pyridine ligands from uranium trichloride (Figure 3). A description of the apparatus is as follows. A custom 2 inch x 12 inch quartz tube (ChemGlass) is fitted with a vacuum sealing assembly (MTI Corp) then inserted into a KSL-1100X muffle furnace with a 2 inch diameter hole (MTI Corp). The vacuum sealing assembly is then fitted with a vacuum hose which ultimately connects through a glovebox KF feedthrough to an external cryogenically cooled solvent trap that is under dynamic evacuation, typically reaching a pressure of -0.08 MPa. An optional graphite collar was machined in-house and can be used to stabilize the quartz tube and ensure that it stands true.





Figure 3. The vacuum apparatus used in this communication from off-theshelf components.

Conclusions

In conclusion, isolable UCl₃ can be generated from UCl₃py₂ through facile thermal elimination of the pyridine ligand, providing pure, gram-quantities. The robustness of the thermal elimination chemistry at even larger scale (multi-gram quantities of the pyridine compound) will be explored in the future. This is a simple preparation that is well-suited for synthetic laboratories, enabling studies of the chemistry and properties of UCl₃ – both in its pure state as well as in mixtures and solutions, from solid to molten temperatures. Future work will focus on scaling up this thermal elimination chemistry and examining other actinide halide coordination complexes to determine other facile pathways to pure, isolated actinide halides.

Acknowledgements

This work was funded through a Directed Research project (20210113DR) via the Los Alamos National Laboratory (LANL) Laboratory Directed Research and Development (LDRD) program. Drs. Charles Lhermitte and Jarom Chamberlain are thanked for assistance with the vacuum apparatus design and temperature measurement. The Fuels Research Laboratory (Joshua White and Shane Mann) are acknowledged for assistance in coordinating shipments and providing support. LANL is operated by Triad National Security, LLC, for the National Nuclear Security Administration of U.S. Department of Energy (Contract 89233218CNA00000).

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: molten salt reactor · uranium trichloride · uranium trichloride dipyridine

- [1] S. Parker, A. Long, C. Lhermitte, S. Vogel, M. J. Monreal, J. M. Jackson, J. Mol. Liq. 2022, 346, 118147.
- [2] S. Vogel, D. Andersson, M. J. Monreal, J. M. Jackson, S. Parker, G. Wang, P. Yang, J. Zhang, *JOM* **2021**, *73*, 3555–3563.
- [3] L. Rycerz, J. Kapala, M. Gaune-Escard, J. Mol. Liq. 2021, 342, 116963.
- [4] T. Schleid, G. Meyer, L. R. Morss, J. Less-Common Met. 1987, 132, 69-77.
- [5] S. S. Rudel, S. A. Baer, P. Woidy, T. G. Müller, H.-L. Deubner, B. Scheibe, F. Kraus, Zeitschrift für Kristallographie Crystalline Materials 2018, 233, 817–844.
- [6] J. E. Burke, C. S. Smith, J. Am. Chem. Soc. 1947, 69, 2500-2502.
- [7] J. F. Suttle, H. R. Hoekstra, Uranium(III) Chloride, in: Inorganic Syntheses, 1957, pp. 145–148.
- [8] G.-Y. Kim, T.-J. Kim, J. Jang, H.-C. Eun, S.-J. Lee, J. Radioanal. Nucl. Chem. 2018, 318, 2173–2176.
- [9] H. Lambert, T. Kerry, C. A. Sharrad, J. Radioanal. Nucl. Chem. 2018, 317, 925–932.
- [10] Y.-H. C. Sang-Eun Bae, Y. J. Park, H. J. Ahn, K. Song, *Electrochem. Solid-State Lett.* 2010, 13, F25–F27.
- [11] D. C. Moody, J. D. Odom, J. Inorg. Nucl. Chem. 1979, 41, 533-535.
- [12] I. Santos, N. Marques, A. Pires de Matos, *Radiochim. Acta* 1982, 31, 191– 192.
- [13] F. A. Hart, M. Tajik, Inorg. Chim. Acta 1983, 71, 169–173.
- [14] H. S. La Pierre, F. W. Heinemann, K. Meyer, *Chem. Commun.* **2014**, *50*, 3962–3964.
- [15] T. V. Fetrow, J. P. Grabow, J. Leddy, S. R. Daly, Inorg. Chem. 2021, 60, 7593–7601.
- [16] J. Drożdżynski, Polyhedron 1988, 7, 167-168.
- [17] J. Kiplinger, R. Beattie, J. Pagano, K. Erickson (LANL), "Metal Complexes and Methods of Making the Same," patent no. US 11,731,989 B1, August 22, 2023.
- [18] Zachariasen, U. S. A. E. C. 1955, TID 5213, 157-164.

Manuscript received: November 7, 2023 Version of record online:

RESEARCH ARTICLE

This research article describes a facile synthesis of uranium trichloride (UCl₃) from a pyridine precursor UCl₃py₂ (py = pyridine) improving accessibility to this compound. It is envisioned that this preparation will be adopted by many laboratories, enabling broader studies of its properties for molten salt technologies and other applications.



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1 – 4

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