

**Contract No:**

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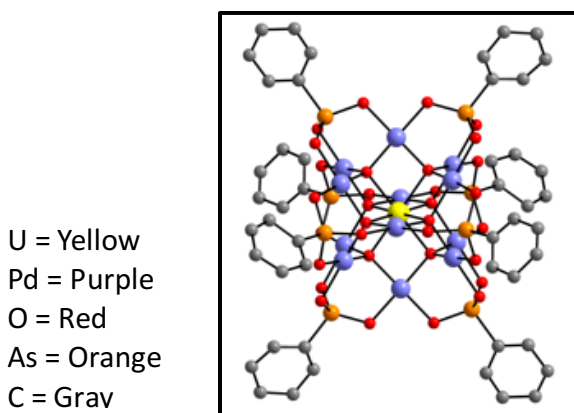
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## Synthesis and Characterization of Novel Actinide Compounds

It is important to gain new understanding of actinides in order to understand the fate of these elements in the environment and the factors that contribute to actinide-lanthanide extraction selectivity. Detailed structural, magnetic, and electronic studies of novel actinide compounds can provide useful information on bonding behavior to guide the development of novel separation and environmental remediation strategies. Development of new actinide compounds remains a relatively open area to study due to the numerous challenges faced when performing chemical synthesis with radioactive materials. In this LDRD, we sought to synthesize and characterize single crystals of novel polyoxometalates that selectively encapsulate plutonium and uranium. We were successful in preparation of  $[\text{U}^{\text{III}}\text{Pd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]^{5-}$ ; the first actinide-based polyoxopalladate (Figure 1).



**Figure 1.** Molecular structure and packing arrangement of  $[\text{U}^{\text{III}}\text{Pd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]^{5-}$ ; the first uranium-based polyoxopalladate

## Awards and Recognition

\$50 k funding was obtained through an MSIPP proposal for work aimed at developing new actinide peroxide clusters. This work is a spin-off from this LDRD and should be considered as ROI for this LDRD.

A manuscript is in preparation to describe the development and characterization of our uranium-based polyoxometalate  $[\text{U}^{\text{III}}\text{Pd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]^{5-}$

## Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

LDRD-2018-00077

LDRD Report

## SRNL Legal Signature

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Signature

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Date

## Synthesis and Characterization of Novel Actinide Compounds

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Subcontractor: N/A

Thrust Area: ES

Project Start Date: October 1, 2018

To develop new separation and environmental remediation tactics for heavy metals it is important to understand the chemical and electronic factors that distinguish lanthanides from actinides. In this LDRD, we attempted to synthesize new actinide-based polyoxometalates (POMs) using synthetic templates that have traditionally been used to develop lanthanide-based POMs. Our goal was to structurally characterize the actinide POMs so they could be compared to their lanthanide analogues. In

FY 19, we were successful in synthesis of the first uranium-based polyoxopalladate –  $[U^{III}Pd^{II}_{12}(AsPh)_8O_{32}]^{5-}$

### FY2019 Objectives

- Develop and implement a robust synthesis method for generating high-purity  $PuCl_3$
- Complete successful single-crystal syntheses of new uranium and plutonium POMs
- Use single-crystal x-ray diffractometry to elucidate the structures of newly synthesized actinide POMs
- Perform magnetic characterization of newly synthesized actinide POMs

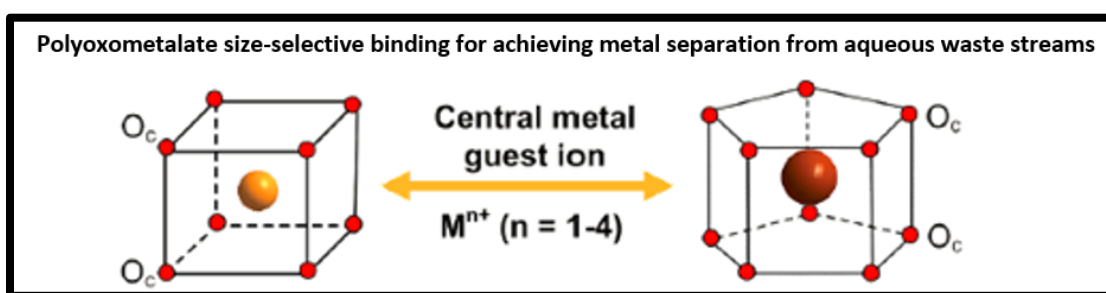
### Introduction

A crucial challenge in achieving efficient separation of nuclear waste, spent nuclear fuel, and nuclear materials interacting with water, is the difficulty in separating trivalent actinides from lanthanides due to similarities in oxidation state, ionic radii, and some chemical properties.<sup>1</sup> Therefore, it is important to improve our understanding of the coordination chemistry of f-element complexes and the chemical differences between lanthanides and actinides in order to improve our understanding of the factors that contribute to extraction selectivity and the fate of heavy elements in the environment. Currently, about 95% of actinide structures in the CCSD and ICSD databases are composed of thorium or uranium.<sup>2</sup> The lack of structural diversity in actinide chemistry is largely caused by experimental limitations due to a lack of licensing for possessing transuranic materials, limited radiological laboratory equipment, and an unfounded belief that thorium and uranium can be accurate surrogates for other actinides. These common limitations leave ample scholarly space for SRNL to conduct high throughput exploratory research involving synthesis of compounds containing uranium and transuranic elements.

Polyoxometalates (POMs) are an interesting class of compounds that can accommodate actinide ions (Figure 2). POMs have a general composition of  $[X_nM_mO_y]^{n-}$  in which X are positive-valent elements, and M are hosted metals. We believe the utility of polyoxoanions for novel actinide compound development is three-fold: (1) there is an abundance of existing POM structures in the literature; many of

which accommodate lanthanide or early-actinide ions. Therefore, these POMs could accommodate many transuranic elements while also providing the lanthanide analogs needed to directly compare bonding behavior between the Ln and Ac structures. (2) Many existing POMs encapsulate metals in well-defined coordination environments, thus making them ideal candidates for magnetic (EPR, SQUID) and spectroscopic (XPS, UV-vis, IR) characterization. (3) The well-defined coordination environments of POMs should facilitate in our construction of accurate computation models aimed at further elucidating the electronic structure and bonding behavior of new actinide compounds.

To synthesize novel uranium and plutonium POMs for this LDRD, we focused our synthetic efforts on the use of polyoxopalladates ligands, a family of metal oxide nanoclusters containing a palladium backbone that has been shown to accommodate all  $\text{Ln}^{3+}$  ions.<sup>3</sup>



**Figure 2.** Polyoxometalates can accommodate heavy metals in a variety of chemical coordinations.

## Approach

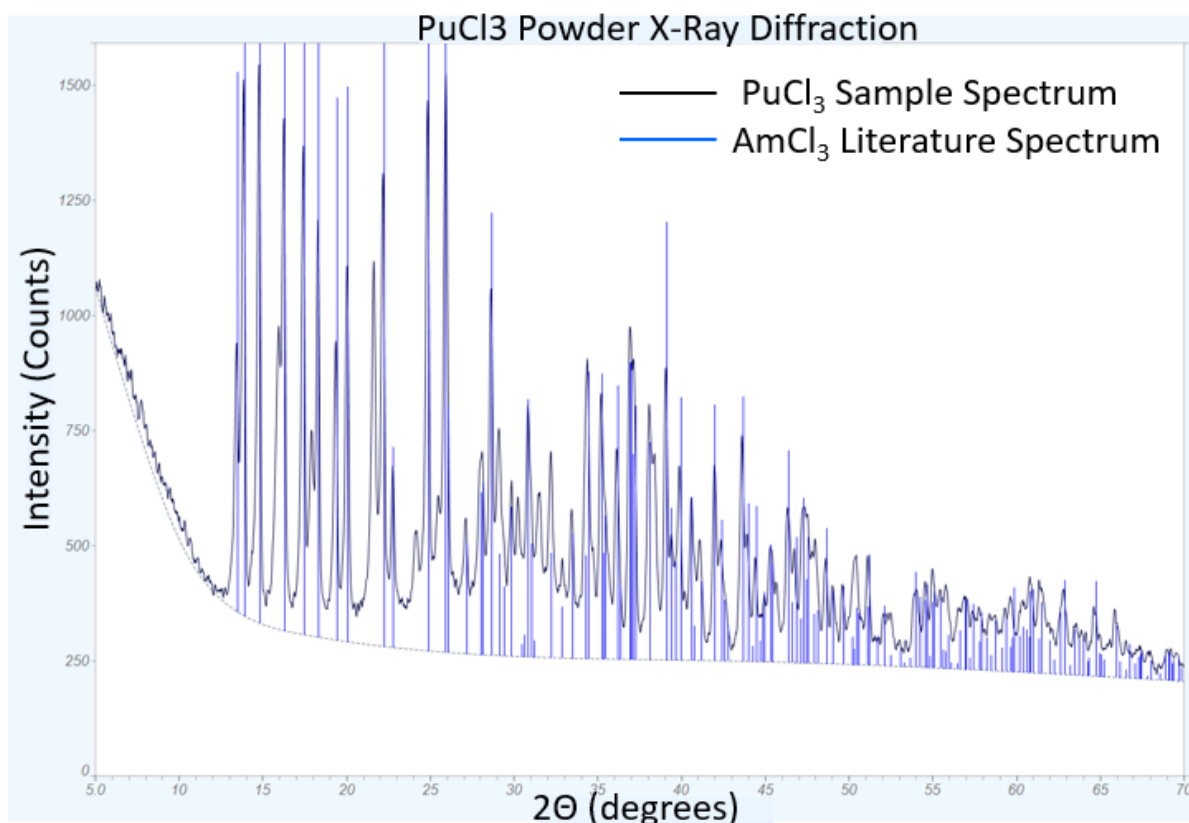
To generate new actinide compounds, we utilized existing polyoxometalate synthetic templates but substituted Pu and U as the metal cations instead of lanthanides. We narrowed our synthetic focus to a class of heteropolyoxopalladates that were recently shown to be very effective at incorporating small, medium, and also large lanthanide(III) ions into the center of the palladate ligand.<sup>3</sup> These previous results suggested that the  $\text{Pd}^{III}_{12}\text{O}_{32}$  shell can adjust to the coordination requirements of the encapsulated guest cation, which we postulated would prove useful at stabilizing U and Pu.

Typical synthesis involved a one-pot self-assembly reaction of  $\text{Pd}(\text{CH}_3\text{COO})_2$ , phenylarsonic acid, and the respective metal<sup>3+</sup> cation in 0.5 M aqueous sodium acetate solution with strict control over solution pH. Uranyl nitrate was used for uranium-based reactions while  $\text{Pu}(\text{NO}_3)_3$  was used for plutonium-based reactions. The low pH of  $\text{Pu}(\text{NO}_3)_3$  was incompatible with our reactions. Thus, at the end of FY19, we developed a robust technique for generating  $\text{PuCl}_3$ ; a water soluble, neutral inorganic salt .



**Figure 3.** Photographed inside of a radiological glovebox, crystalline product is shown from a Plutonium-Palladium POM

To generate  $\text{PuCl}_3$ , plutonium nitrate ( $\sim 0.0156$  moles) was reduced using twice the moles of ascorbic acid ( $\sim 0.0312$  moles). Plutonium<sup>3+</sup> oxalate was then precipitated according to the following reaction:  $2 \text{Pu}(\text{NO}_3)_3 + 3 \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Pu}_2(\text{C}_2\text{O}_4)_3$ . Plutonium<sup>3+</sup> oxalate was then filtered and air dried. The oxalate powder and a magnetic stirrer were then added to a round bottom flask equipped with an air reflux condenser, and a thermometer. A molar excess ( $>1$  moles  $\text{C}_3\text{Cl}_6$ : 1 mole Pu) of  $\text{C}_3\text{Cl}_6$  was added to the flask. The molar ratio was not important for the reaction as long as the ratio was  $>1$  and there was sufficient volume of  $\text{C}_3\text{Cl}_6$  to induce vigorous stirring. The solution was heated and vigorously stirred between  $180 - 190^\circ\text{C}$  for 18 hours. The solution was then cooled to room temperature and filtered. The collected solid was rinsed several times with carbon tetrachloride ( $\text{CCl}_4$ ). Successful synthesis of  $\text{PuCl}_3$  was confirmed via powder x-ray diffraction (Figure 4) and visual inspection.



**Figure 4.** Powder x-ray diffraction spectrum of synthesized  $\text{PuCl}_3$  (black) is shown with an overlay of the published  $\text{AmCl}_3$  spectrum (blue). The synthesized  $\text{PuCl}_3$  spectrum is an excellent match with  $\text{AmCl}_3$  indicating the synthesized powder is high-purity.

## Results/Discussion

In FY 18, we set up our lab for performing POM actinide synthesis work, we purified actinide precursor compounds, and we were successful in growing  $\text{Ln}^{3+}$  versions of several polyoxometalates. In FY 19, we applied our synthetic techniques towards U and Pu-based reactions. No Pu reactions were successful when using  $\text{Pu}(\text{NO}_3)_3$  as our metal source. We believe the low pH of our Pu solution was the

primary factor inhibiting growth of stable compounds. We attempted to adjust the pH of our Pu solution, but insoluble Pu hydroxide forms readily as the solution approaches neutral pH. Thus, we worked to develop a synthetic plan for generating  $\text{PuCl}_3$ ; a very soluble and neutral inorganic salt.

$\text{PuCl}_3$  was synthesized by reaction of  $\text{Pu}_2(\text{C}_2\text{O}_4)_3$  with  $\text{C}_3\text{Cl}_6$  between 180 – 190 °C for 18 hours. The light blue-green powder is very water soluble, but oxidizes within a few days if not stored under an inert environment. Unfortunately, we were not able to use our  $\text{PuCl}_3$  to synthesize Pu POMs before the end of FY 19. We were however able to synthesize the first uranium-based polyoxopalladate -  $\text{U}^{\text{III}}[\text{Pd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]_5$ . The structure of this new compound was thoroughly characterized using single crystal x-ray diffraction. The new compound has 12 palladium<sup>2+</sup> ions surrounding the central  $[\text{XO}_8]$  fragment. The oxygen atoms of the inner  $[\text{XO}_8]$  cube are coordinated to  $\text{U}^{3+}$  and three palladiums placed on a trigonal side of the cuboctahedron. Each of the twelve  $\text{Pd}^{2+}$  ions exhibits square-planar coordination. The polyanions form a hexagonal- packing framework with channels along the a axis. This structure is very similar its  $\text{Ln}^{3+}$  analogues.

## FY 2019 Accomplishments

- Successfully synthesized the first uranium-based polyoxopalladate
- Successfully synthesized  $\text{PuCl}_3$  for use with future plutonium-based reactions.
- Completed successful single-crystal syntheses of POM lanthanide analogues.

## Future Directions

- Synthesize new plutonium-based POM compounds using  $\text{PuCl}_3$
- Determine whether newly synthesized structures have a binding preference for U or Pu
- Analyze the magnetic properties of all newly synthesized compounds

## FY 2019 Publications/Presentations

Synthesis and Characterization of the First Heterooxypalladate Coordinated with Uranium  
 $\text{U}^{\text{III}}[\text{Pd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]_5$ . – *Manuscript in Preparation*.

## References

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3. M. Barsukova, N. V. Izarova, R. N. Biboum, B. Keita, L. Nadjjo, V. Ramachandran, N. S. Dalal, N. S. Antonova, J. J. Carbó, J. M. Poblet and U. Kortz, *Chemistry – A European Journal*, **2010**, 16, 9076-9085.

## Acronyms

**MSIPP** – Minority Serving Institution Partnership Program

**POM** - Polyoxometalate

## Intellectual Property

None in FY 19

*LDRD-2018-00077*

*LDRD Report*

### **Total Number of Post-Doctoral Researchers**

No post-doctoral researchers in FY 19.