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Advances in containment methods and plutonium recovery strategies that led to the structural characterization of plutonium(IV) tetrachloride tris-diphenylsulfoxide, $PuCl_4(OSPh_2)_3$

Samantha K. Cary, Kevin S. Boland, Justin N. Cross, Stosh A. Kozimor *, Brian L. Scott

Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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ABSTRACT

In an attempt to further advance the understanding of plutonium coordination chemistry, we report a robust method for recycling and obtaining plutonium aqueous stock solutions that can be used as a convenient starting material in plutonium synthesis. This approach was used to prepare and characterize plutonium(IV) tetrachloride tris-diphenylsulfoxide, $PuCl_4(OSPh_2)_3$, by single crystal X-ray diffraction. The $PuCl_4(OSPh_2)_3$ compound represents a rare example of a 7-coordinate plutonium(IV) complex. Structural characterization of $PuCl_4(OSPh_2)_3$ by X-ray diffraction utilized a new containment method for radioactive crystals. The procedure makes use of epoxy, polyimide loops, and a polyester sheath to provide a robust method for safely containing and easily handling radioactive samples. The described procedure is more user friendly than traditional containment methods that employ fragile quartz capillary tubes. Additionally, moving to polyester, instead of quartz, lowers the background scattering from the heavier silicon atoms.

1. Introduction

Advancing plutonium coordination chemistry is important for establishing a strong scientific foundation for the DOE and its laboratories to support the national nuclear agenda. However, plutonium coordination chemistry is underdeveloped in comparison to that for the main group, transition metals, and lanthanides. As a result, many well-defined fundamental concepts in plutonium chemistry are still poorly understood. As testament, Raymond [1] (among others) has previously pointed out that the number of plutonium crystal structures in the Cambridge Structural Database pale in comparison to those of the *d*-block (e.g. 43,670 for Fe versus 125 for Pu) [2]. This structural disparity exists because it is difficult to obtain plutonium and because it is challenging to safely handle the highly radioactive isotopes of plutonium. As a result, it is difficult to obtain plutonium as a useful starting material for coordination chemistry studies. Additionally, once a new compound is prepared, it is challenging to safely contain the compound for subsequent spectroscopic characterization.

Recent chemical and technological advances have provided new opportunities to overcome the aforementioned challenges. For example, there has been substantial development of plutonium separations chemistry [3–10]. Combined with recent advances in separations science [11–22] and chromatography technologies [23–29] *i.e.* commercialization of specialty resins – it is now relatively straightforward to recover/recycle plutonium from previous experiments. This provides versatile plutonium starting materials and extends the lifetime of a given plutonium sample within a laboratory by preventing it from being sent out as waste.

Another area where technological advances are dramatically impacting plutonium science is associated with single crystal X-ray diffraction. Here, more advanced detectors, sources, and modeling capabilities have enabled extremely small crystals to be analyzed by X-ray crystallography. Alongside these new developments is the emergence of new equipment that facilitates manipulating small single crystals in a safe way. These factors have significant implications on conducting single crystal measurements on highly radioactive samples. For example, these new capabilities expand the diffraction technique to crystals that diffract weakly, reduce complications during data acquisition from actinide self-absorption, and decrease hazards associated with the handling radioactive material (less sample is needed for single crystal measurements). Herein, we describe the use of a new containment method that facilitates manipulation of small and highly radioactive single crystals. Using this method we have characterized a new plutonium coordination compound by single crystal X-ray

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* Corresponding author.
E-mail address: stosh@lanl.gov (S.A. Kozimor)
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diffraction, namely $PuCl_4(OSPh_2)_3$. The sample was prepared from a well-characterized plutonium(IV) stock solution, which had been recovered/recycled from byproducts in previous experiments using robust chemical separations methods.

2. Experimental

2.1. Synthesis

2.1.1. Materials

The Ph_2SO (Fisher), HCl (Fisher), HF (Fisher), HNO_3 (Fisher), $NH_2OH{\cdot}HCl$ (Aldrich), H_3BO_3 (Aldrich), $NaNO_2$ (Aldrich), MeCN (Fisher), $(NH_4)_2SO_4$ (Baker), Rain-X™, epoxy (Grainger, clear, PC-7), and NH_4OH (Aldrich) chemicals were obtained commercially and used without further purification. All water used in these experiments was deionized and further purified using a Barnstead water purification system (18 MΩ). Experiments were carried out in a fume hood and no effort was made to exclude air and moisture. However, acetonitrile and diethyl ether solvents were dried using CaH_2 or sodium metal/benzophenone (respectively), distilled under vacuum, and then degassed by three freeze–pumpthaw cycles before use. All materials for crystallography (tips, bases, sheaths, and magnetic wand) were obtained from MiTeGen™ and used without further modification.

The plutonium starting material (MT52) was obtained as a byproduct from previous experiments in the form of a poorly characterized residue. ***Caution!*** *^{238}Pu [$t_{1/2}$ = 87.7(1) y], ^{239}Pu [$t_{1/2}$ = 24,110(30) y], ^{240}Pu [$t_{1/2}$ = 6,561(7) y], ^{241}Pu [$t_{1/2}$ = 14.325(6) y], and ^{242}Pu [$t_{1/2}$ = 3.75(2) x 10^5 y]* [30] *are serious health threats, due to their radioactive decay, as well as that of their daughters. Hence, all studies with plutonium were conducted in a radiation laboratory equipped with HEPA filtered hoods and continuous air monitors. All free-flowing solids that contained plutonium were handled in negative-pressure gloveboxes, which provided an engineering control to guard against the spread of contamination from dispersible powders.*

2.1.2. Plutonium(IV) tetrachloride starting material

The $PuCl_4(OSPh_2)_3$ samples were prepared from a poorly characterized plutonium containing residue. In a fume hood, the residue was dissolved in nitric, HNO_3 (8 M), and hydrochloric acid, HCl (6 M), and chemically purified using the following recycling procedure (Scheme 1) [31,32]. The Pu solution was evaporated to a soft dryness in a Teflon beaker. The resulting residue was dissolved in HNO_3 (8 M) and the evaporation/dissolution procedure was repeated two additional times. Subsequently, the solution was quantitatively transferred using HNO_3 (8 M) into a disposable Falcon tube (polypropylene, 50 mL). A plutonium solid, naively formulated as $Pu(OH)_4$, was precipitated from the solution by adding NH_4OH (3 mL; 14.5 M) dropwise while stirring. The precipitate was isolated, the supernatant discarded, and the solid washed with water (2×). The solid was then dissolved in concentrated hydrochloric acid, HCl (10 mL; 12 M), and diluted with water (10 mL). The oxidation state of the plutonium was reduced to +3 by the dropwise addition of a saturated aqueous solution of hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$, (1 mL). During the addition, the solution was continually stirred using a glass stir rod. After 10 min the mixture began to bubble and the Falcon tube was placed in secondary containment. The solution turned green and visibly stopped reacting after an additional 30 min. The Falcon tube was heated (75 °C; 1 h) and the color changed from green to blue/purple. Quantitative reduction of plutonium to the +3 oxidation state was confirmed by UV–Vis spectroscopy [33]. Upon addition of hydrofluoric acid, HF (5 mL, 29 M), an insoluble lilac solid, formulated as plutonium(III) trifluoride hydrate ($PuF_3{\cdot}nH_2O$), precipitated. The solid was isolated and the supernatant discarded, leaving behind a small purple pellet. The pellet was broken up with a stir rod and washed with water (5 mL, 2×). Although the PuF_3 can be difficult to dissolve, a reproducible method involved using a mixture of boric acid (H_3BO_3; saturated), HCl (concentrated), and heat. This was achieved by adding H_3BO_3 (2 mL) to the mixture while agitating the pellet with a glass stir rod. After heating the mixture (∼75 °C; 5 min), HCl (12 M, 1 mL) was added and the mixture heated for another 5 min. While maintaining the temperature near 75 °C, aliquots of H_3BO_3 (1 mL) and HCl (1 mL) were added sequentially with periodic stirring and the lilac solid completely dissolved. The solution was cooled to room temperature, and then ammonium hydroxide (NH_4OH, 15 M) was added until a solid precipitated. The solid was isolated, the supernatant discarded, and the remaining pellet was washed with water (5 mL, 2×). The solid pellet was then dissolved in HNO_3 (16 M, 0.9 mL). Water was added (1.1 mL) until the resulting solution was approximately 7.2 M in HNO_3. The resulting solution was diluted to 10 mL with HNO_3 (7.2 M). While in secondary containment, an aqueous solution of sodium nitrite, $NaNO_2$ (10 M, 1 mL), was added dropwise with constant stirring using a glass stir rod. Caution, *addition of sodium nitrite resulted in a vigorous reaction that produced red fumes and bubbling*. The solution was allowed to sit for 30 min until the reaction subsided, and the green solution was analyzed by UV–Vis spectroscopy to confirm that the plutonium was oxidized to the +4 oxidation state [34].

During this time an anion-exchange column was prepared by charging a BioRad column (20 mL), equipped with an addition funnel, with AG MP-1 anion resin (18 mL, 50–100 mesh). The resin was conditioned with water (1 × 25 mL) and then HNO_3 (7.2 M; 3 × 25 mL). Loading the plutonium solution onto the column generated a stationary green band of Pu^{IV} at the top of the column. The column was washed with HNO_3 (7.2 M, 2 × 30 mL) and then HCl (12 M, 3 × 30 mL), upon which the color of the Pu^{IV} band changed from green to red to yellow. The Pu^{IV} material was then eluted from the column with dilute HCl (50 mL of H_2O to 5 drops of HCl; 12 M). Note, upon introduction of this slightly acidic solution the plutonium band changed color again, turning from yellow to red. Concomitantly, the band immediately began moving down the resin bed. The plutonium effluent was collected in the smallest possible volume (∼5 mL). To the orange solution, HCl (12 M, 5 mL) was added until the final HCl concentration was approximately 6 M. Using an automated pipette, an aliquot of the plutonium stock solution was added to a quartz cuvette containing perchloric acid, $HClO_4$ (1 M), and the concentration of the sample was determined by UV–Vis spectroscopy ($\varepsilon_{470nm} = 56.5$ and $\varepsilon_{653nm} = 35$ L mol^{-1} - cm^{-1}) [35].

2.1.3. Plutonium(IV) tetrachloride tris-diphenylsulfoxide, $PuCl_4(OSPh_2)_3$

A aliquot from the stock solution of Pu^{IV} (1 mL; 0.0487 mol) in HCl (6 M) was boiled to a soft dryness and the resulting residue re-suspended in acetonitrile (3 mL). Separately, diphenyl sulfoxide, Ph_2SO (29.8 mg, 0.147 mol), was dissolved in acetonitrile (3 mL) and added to the plutonium solution to form a red solid. The precipitate was filtered and recrystallized in hot acetonitrile to generate red crystals that were suitable for single crystal X-ray diffraction.

2.2. Crystallographic studies

Plutonium samples were mounted for single crystal X-ray diffraction (SCXRD) as follows. First, a copper base, purchased from MiTeGen™, was assembled by epoxying the appropriate sized loop (50–300 microns) to the copper base (Fig. 1A). Excess epoxy was wiped away to ensure that proper containment was possible in