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

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ADVANCES IN CONTAINMENT METHODS AND PLUTONIUM RECOVERY STRATEGIES THAT LED TO THE STRUCTURAL CHARACTERIZATION OF PLUTONIUM(IV) TETRACHLORIDE TRIS-DIPHENYLSULFOXIDE, $\text{PuCl}_4(\text{OSPh}_2)_3$.

Samantha K. Cary,¹ Kevin S. Boland,¹ Justin N. Cross,¹ Stosh A. Kozimor,^{1,*} Brian L. Scott.¹

¹ Los Alamos National Laboratory, Los Alamos, New Mexico 87545 (U.S.A.)

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TOC

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, $\text{PuCl}_4(\text{OSPh}_2)_3$, by single crystal X-ray diffraction. The $\text{PuCl}_4(\text{OSPh}_2)_3$ compound represents a rare example of a 7 coordinate plutonium(IV) complex. Structural characterization of $\text{PuCl}_4(\text{OSPh}_2)_3$ 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 CCDC 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.^{3,4,5–8,9,10} Combined with recent advances in separations science^{11,12,13,14,15,16,17,18–20,21,22} and chromatography technologies^{23,24,25,26,27,28,29} *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 diffraction, namely $\text{PuCl}_4(\text{OSPh}_2)_3$. The sample was prepared from 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), $\text{NH}_2\text{OH}\cdot\text{HCl}$ (Aldrich), H_3BO_3 (Aldrich), NaNO_2 (Aldrich), MeCN (Fisher), $(\text{NH}_4)_2\text{SO}_4$ (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 M $\bullet$). 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-pump-thaw cycles before use. All materials for crystallography (tips, bases, sheaths) 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 [$t_{1/2} = 3.75(2) \times 10^5$ 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 $\text{PuCl}_4(\text{OSPh}_2)_3$ 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 $\text{Pu}(\text{OH})_4$, 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 (2x). 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, $\text{NH}_2\text{OH}\cdot\text{HCl}$, (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-visible spectroscopy.³³ Upon addition of hydrofluoric acid, HF (5 mL, 29 M), an insoluble lilac solid, formulated as plutonium(III) trifluoride hydrate ($\text{PuF}_3\cdot n\text{H}_2\text{O}$), 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, 2x). 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 ($\sim 75^\circ\text{C}$; 5 min), HCl (12 M, 1 mL) was added and the mixture heated for another 5 minutes. 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, 2x). 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-visible 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 x 25 mL) and then HNO_3 (7.2 M; 3 x 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 x 30 mL) and then HCl (12 M, 3 x 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, HClO₄ (1 M), and the concentration of the sample was determined by UV-visible spectroscopy ($\epsilon_{470\text{nm}} = 56.5$ and $\epsilon_{653\text{nm}} = 35 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).³⁵

2.1.3 PLUTONIUM(IV) TETRACHLORIDE TRIS-DIPHENYLSULFOXIDE, PuCl₄(OSPh₂)₃.

A aliquot from the stock solution of Pu^{IV} (0.0487 mol; 1 mL) in HCl (6 M) was boiled to a soft dryness and the resulting residue re-suspended in acetonitrile (3 mL). Separately, diphenyl sulfoxide, Ph₂SO (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 (Figure 1 A). Excess epoxy was wiped away to ensure that proper containment was possible in the next few steps. The copper base was magnetically fixed to a wand, to facilitate crystal manipulation, and a single crystal was selected using the assembly's tip (Figure 2). The crystal was then coated with epoxy. After about 5 minutes the epoxy fully dried, thereby adhering the crystal to the loop. In this scenario the epoxy serves as the first layer of containment. Next, a thin line of epoxy was applied to the middle lip of the copper base (Figure 1 B) and the loop was gently slid into a MiTeGen™ polyester sheath (Figure 1 C). Note: The sheath had been cut in half, as full-length sheaths will impact the beam

stop. Additional epoxy was painted onto the outside of the assembly where the sheath met the copper base. This assured a good seal and provided the second layer of containment. After allowing the epoxy to dry, the sheath was cleaned with ethanol and dipped into a solution of Rain-X™ Plastic Treatment to prevent icing in the cold stream. Crystals were cooled to 140 K in a liquid nitrogen gas stream on a Bruker D8 platform diffractometer. Standard peak search and indexing procedures, followed by least-square refinement yielded the cell dimensions given in (Tables 1). The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background and Lorentz and polarization effects. No corrections for crystal decay were necessary. All unique data was used in the least-squares refinements. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. Correct atomic position(s) were deduced from an E-map (SHELX); least-squares refinement and difference Fourier calculations were used to locate atoms not found in the initial solution. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms. PLATON was used to check the Crystallographic Information File (CIF) for missed symmetry and twinning.³⁶ The CIF file used in this manuscript is available through the Cambridge Crystal Data Centre (CCDC). Data collection and refinement parameters are listed in Table 1, and selected bond distances are listed in Table 2.

3. RESULTS AND DISCUSSION

3.1 SYNTHESIS OF PLUTONIUM(IV) TETRACHLORIDE TRIS-DIPHENYLSULFOXIDE,

In contrast to syntheses that involve *d*-block and *4f*-elements, there is not a commercially

available supplier of a plutonium starting material for research and development. Hence, plutonium syntheses often rely on national laboratories to provide well-characterized plutonium starting materials in the form of plutonium metal, plutonium trichloride (PuCl_3), or plutonium dioxide (PuO_2). However, there are inventories of plutonium residues left over from previous research experiments in every plutonium laboratory. If chemically purified, these poorly characterized plutonium reserves provide a convenient and valuable source of plutonium for research.³¹ We contribute here a method that has served our laboratories well in providing a convenient aqueous plutonium starting material. The procedure relied on well-established valence adjustments, precipitations, and anion exchange chromatography routinely employed in aqueous plutonium chemistry (Scheme 1).^{11,12,13,14,15,16,17,18–20,21,22,31,32}

In general, the method began by converting the unknown plutonium solution to nitric acid media. Subsequently, the plutonium oxidation state was adjusted to +3 using hydroxylamine hydrochloride, $\text{NH}_2\text{OH}\cdot\text{HCl}$. This initial valence adjustment generates a unified Pu^{III} starting point. Hence, the ingoing plutonium oxidation state associated with the residue is not important. Next, plutonium trifluoride, PuF_3 , was precipitated with hydrofluoric acid, HF. We remind the reader that PuF_3 is highly insoluble (0.157 g/L in 0.05 M HNO_3)³⁷ in comparison to many inorganic and organic salts, which are soluble in hydrofluoric acid. Hence, the fluoride precipitation step is unique in that it separates plutonium from many chemical contaminants. Upon dissolving the PuF_3 , the plutonium oxidation state was adjusted to +4 and anion exchange chromatography provided more rigorous purification.

This ion exchange chromatography step is attractive, as it provides (1) an effective method to purify plutonium (2) a convenient means for converting plutonium(IV) nitrate to other forms [*i.e.* plutonium(IV) chloride], and (3) enables small volumes of concentrated Pu^{IV} stock solutions to be collected in the column effluent. In the example presented here, after loading plutonium(IV)

nitrate on the anion column, treatment with HCl (concentrated) provided a clean method for conversion to plutonium(IV) chloride. Stripping plutonium from the column with dilute hydrochloric acid provided a plutonium(IV) chloride stock solution that could be employed for multiple experiments. As testament, here we used the solution to synthesize plutonium(IV) tetrachloride tris-diphenylsulfoxide, $\text{PuCl}_4(\text{OSPh}_2)_3$ (Scheme 2). After evaporating an aliquot of the purified Pu(IV) stock solution to a soft dryness, the Pu(IV) residue was reacted with a stoichiometric amount of diphenyl sulfoxide (OSPh_2) in acetonitrile. Under these conditions, the OSPh_2 ligand preferentially coordinated Pu^{IV} amongst the huge excess of acetonitrile, and plutonium(IV) tetrachloride tris-diphenylsulfoxide, $\text{PuCl}_4(\text{OSPh}_2)_3$ was isolated as single crystals.

3.2 PLUTONIUM SINGLE CRYSTAL CONTAINMENT STRATEGY

Until recently, many institutions, like Los Alamos National Laboratory and Lawrence Berkeley National Laboratory, have contained single crystals of highly radioactive actinides for X-ray diffraction studies using a capillary method.¹ In this procedure, a given crystal was coated in epoxy, mounted on a quartz fiber, and further encapsulated within a quartz capillary tube. While the capillary method provides robust containment for radioactive samples, the sample manipulation is complicated and capillary tubes are prone to shatter. To avoid this, the capillary tubes are often coated with acrylic (nail polish), however; this can complicate crystal centering when placed on the diffractometer, as it is difficult to see through the nail polish coating.

Herein, we present a new approach that exploits emerging crystal mounting technologies and provides a safe, physically robust, alternative to capillary mounting. The new containment strategy achieved robust containment and made use of a more practical crystal mounting apparatus. Although similar to the crystal mounting strategy of Tamain *et al.* we take a few more precautionary steps and add an additional layer of containment than previously reported.³⁸ It is

our hope that the new containment strategy appeals to the next generation of chemists working with nuclear material, who may refuse to use more traditional (and admittedly cumbersome) capillary mounting techniques. We cannot overstate the importance of establishing convenient containment methods for handling radioactive samples. By making containment procedures easy to conduct, we guard against the urge to skip safety steps.

The approach described here involves fixing the crystal to a polyimide loop with epoxy, which keeps the crystal from falling off the mount. Next, the crystal is coated in epoxy to prevent spread of contamination if the crystal shatters when being cooled. Finally, a polyester sheath provides a second layer of containment. Use of the sheath is attractive in comparison to a capillary tube for many reasons. The plastic cannot be broken like a capillary tube, which can crack or shatter when dropped or handled roughly. Additionally, the sheath has a larger inner diameter, which makes it easier to introduce the crystal into the sheath. The background scattering of the polymers compared to the quartz is also greatly reduced. Finally, the sheath is shorter than a capillary tube, which facilitates loading. We also find that dipping the entire sheath into a solution of Rain-X™ prior to introducing the assembly into the diffractometer cold stream helps guard against icing. However, if the cold stream is not properly configured (i.e. high quality dry air is not being supplied) deleterious icing still can occur.

3.3 STRUCTURE DESCRIPTIONS

The $\text{PuCl}_4(\text{OSPh}_2)_3$ compound crystalized in the triclinic space group $P\bar{1}$. The Pu^{IV} coordination environment consisted of four Cl atoms and three O atoms arranged in a 7-coordinate distorted capped trigonal prism with approximate C_{2v} -symmetry (Figure 3). Among the 125 single crystal structures currently documented in the CCSD, there are only 4 previous reports of Pu^{IV} compounds that are 7-coordinate. The low coordination number in $\text{PuCl}_4(\text{OSPh}_2)_3$

most likely resulted from steric crowding associated with the combination of large OSPh_2 ligands and the small Pu^{IV} ion. A closer look at the $\text{PuCl}_4(\text{OSPh}_2)_3$ structure revealed an average Pu–Cl bond length of $2.62 \pm 0.03 \text{ \AA}$ (error reported as standard deviation of the mean, 1σ) $\text{\AA}$. This value was slightly larger than other reported Pu–Cl bonds distances. However, the limited number of molecular Pu^{IV} compounds that contain both bulky ligands and Cl^- ligands make it difficult to make meaningful Pu–Cl bond distance comparisons. For instance, the chloride containing Pu^{IV} molecules that have been structurally characterized – namely PuCl_6^{2-} ,^{39,40,41,42,43,44} $\text{PuCl}_4(\text{OPPh}_3)_2$,⁴⁵ $\text{Pu}[\text{N}(\text{SiMe}_3)_2]_3\text{Cl}$,⁴³ $[\text{PuCl}_2(\text{NO}_3)_2][(\text{OPPh}_2)_2\text{C}_6\text{H}_4]$,⁴⁶ $\text{PuCl}_4[(\text{OPPh}_2)_2\text{C}_{12}\text{H}_6\text{O}]$,⁴⁷ and $\text{PuCl}_4(\text{DME})_2$ ⁴⁸ – have an average Pu–Cl bond distances of $2.59 \pm 0.02 \text{ \AA}$ (across all compounds). The magnitude for this cumulative Pu–Cl bond distance average is slightly shorter ($0.03 \text{ \AA}$) than our measured distances.

The three diphenylsulfoxide ligands were bound to the central Pu^{IV} ion through bent Pu–O–S interactions. For example, the Pu–O–S angles ranged from 125.92° to 150.37° . These values were substantially larger than the O–S–C and C–S–C angles within the OSPh_2 ligand, which averaged $102 \pm 2.0^\circ$. The Pu–O bond lengths averaged $2.32 \pm 0.06 \text{ \AA}$ (Table 2). These distances were quite similar to the only other Pu^{IV} sulfoxide structure, $\text{Pu}(\text{OSMe}_2)_8(\text{ClO}_4)_4$, in the CCDC, whose analogous bond Pu–O distance averaged $2.33 \pm 0.03 \text{ \AA}$.⁴⁹ Surprisingly, despite the substantially larger Pu^{IV} ionic radius ($\text{Pu}^{\text{IV}} = 0.86$; $\text{Pu}^{\text{VI}} = 0.71$),⁵⁰ both of these Pu^{IV} –O distances were slightly shorter than the average $2.38 \pm 0.04 \text{ \AA}$ PuO_2^{2+} – OSMe_2 distances in $\text{PuO}_2(\text{OSMe}_2)_5(\text{ClO}_4)_2$,⁵¹ where plutonium is in the +6 oxidation state. Understanding the origin for these unusual distances is difficult given the small sample size, *e.g.* only three plutonium dialkylsulfoxides have been structurally characterized. Overall, these results exemplify the importance of gathering more structural information on plutonium.

4. CONCLUSION

Herein, we present a robust method for preparing a plutonium(IV) stock solution from poorly characterized plutonium sources. The method was inspired by well-defined radioanalytical separations methods.^{11,12,13,14,15,16,17,18–20,21,31,32} Moreover, the resulting stock solution can be used as a convenient starting material in plutonium synthetic chemistry. As an example, we used this stock solution to prepare a new plutonium compound, $\text{PuCl}_4(\text{OSPh}_2)_3$, which was in turn characterized by single crystal X-ray diffraction. This compound represented a rare example of a 7-coordinate Pu complex, of which only four other examples have been reported. Overall, these results increase general knowledge of actinide coordination chemistry and build upon the growing number of structural studies for the transuranic elements. Additionally, we present a new single crystal containment method that can easily be used for handling radioactive samples. This approach made use of modern crystal mounting equipment and achieved robust containment for highly radioactive samples (like plutonium). Because sample manipulation was quite easy, the approach is attractive in comparison to traditional procedures, where crystals have been mounted within quartz capillary tubes. It is our hope that making crystal mounting containment strategies more convenient will guard against cavalier urges to skip safety steps when handling radioactive samples. Moreover, with the advent of new detectors, sources, and modeling technologies, we anticipate that attributes associated with the polyester sheath (large inner diameter, short length, and decreased background) combined with the ease at which crystals can be manipulated (using polymer loops and magnetic wands) will enable even smaller crystals of plutonium to be analyzed by single crystal X-ray diffraction. It is inevitable that these advances will contribute to a better understanding of plutonium and the transuranic elements.

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Figure 1. Crystals mounting assembly for transuranic samples. *A* – polypropylene sheath. *B* – crystal fixed to a polyimide loop with epoxy. *C* – lip of the copper base that is sealed to the sheath with epoxy.

Figure 2. Magnetic wand fixed to the crystal mounting assembly.

Scheme 1.

Scheme 2.

Table 1. Selected Crystallographic Information for PuCl₄(OSPh₂)₃.

Compound	PuCl ₄ (OSPh ₂) ₃
Formula Mass	990.58
Space group	$P\bar{1}$
Color	Red
Shape/Habit	Plate
Dimensions (mm)	0.06 x 0.05 x 0.03
a (Å)	10.745(4)
b (Å)	11.270(4)
c (Å)	15.890(6)
α (°)	101.002(4)
β (°)	101.491(4)
γ (°)	93.863 (4)
V (Å ³)	1839.9(11)
Z	2
T (K)	140(2)
λ (Å)	0.71073
Maximum 2θ (°)	28.426
ρ_{calc} (g/cm ³)	1.788
μ (Mo $K\alpha$) (cm ⁻¹)	22.87
$R(F)$ for $F_o^2 >$	
$2\sigma(F_o^2)^a$	0.0246
$R_w(F_o^2)^b$	0.0568
Goof	1.028
R(int)	0.029

$$^a R(F) = \Sigma \|F_{\circ} - F_{\mathfrak{c}}\| / \Sigma |F_{\circ}|$$

$$^b R_w(F_{\circ}^2) = \left[\Sigma \left[w(F_{\circ}^2 - F_{\mathfrak{c}}^2)^2 \right] / \Sigma w F_{\circ}^4 \right]^{1/2}$$

Table 2. Selected Bond Lengths (Å) for PuCl₄(OSPh₂)₃.

PuCl ₄ (OSPh ₂) ₃	
Pu–O1	2.347(2)
Pu–O2	2.353(2)
Pu–O3	2.254(2)
Pu–Cl1	2.6537(12)
Pu–Cl2	2.5941(10)
Pu–Cl3	2.6224(11)
Pu–Cl4	2.6020(10)

Figure 3. (left) Thermal ellipsoid plot of $\text{PuCl}_4(\text{OSPh}_2)_3$ with ellipsoids drawn at 50%. The hydrogen atoms were omitted. (right) The coordination environment of the Pu metal center shown with two different models (polyhedral on the top and ball and stick on the bottom).

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