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Isolation of a new polyoxometalate complex of plutonium†

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We report the synthesis, plus structural and spectroscopic characterization, of a plutonium(IV) complex with the polyoxometalate $W_5O_{18}^{6-}$. The complex was isolated as $Cs_8[Pu(W_5O_{18})_2] \cdot CsCl \cdot 6.5H_2O$, with the tetravalent actinide cation sandwiched between two lacunary polyoxotungstate anions. It represents a rare case of a POM compound with plutonium and also the first Peacock–Weakley type complex of plutonium.

Thus far, a few hundred plutonium (Pu) compounds have been synthesized and characterized, encompassing different categories of materials, from metallic phases and oxides^{1,2} to complexes with organic ligands,^{3–5} inorganic compounds,^{6–10} MOFs,^{11,12} oxo/hydroxo-clusters,^{13,14} and more. However, only a small number of Pu complexes with polyoxometalates (POM) are currently known. In fact, only two crystal structures of POM complexes with the Pu^{4+} ion^{15,16} and two crystal structures with the PuO_2^{2+} ion^{17,18} have been published to date.

Sokolova *et al.*¹⁵ reported in 2009 the first successful synthesis and structural characterization of a complex of Pu^{4+} with a POM ligand. The authors obtained $K_{12}H_4Pu(P_2W_{17}O_{61})_2 \cdot 19H_2O$, which consists of two $P_2W_{17}O_{61}^{10-}$ ligands bound to one Pu^{4+} ion. This complex belongs to the Wells–Dawson POM category. In 2016, Charushnikova *et al.*¹⁶ expanded the chemistry of Pu–POM to polyoxomolybdates, with the structural characterization of Pu^{4+} encapsulated in $Mo_{12}O_{42}^{12-}$, which belongs to the Dexter–Silverton POM category. Another major category of POMs¹⁹ is the Peacock–Weakley complexes²⁰ which typically features one cation coordinated to two $W_5O_{18}^{6-}$ (W_5) ligands (Fig. 1). However, despite the large body of literature on W_5 and on Pu chemistries, no plutonium compound with this type of POM has been reported yet.

The W_5 anion has been the subject of numerous studies due to its ability to complex a wide range of cations in aqueous

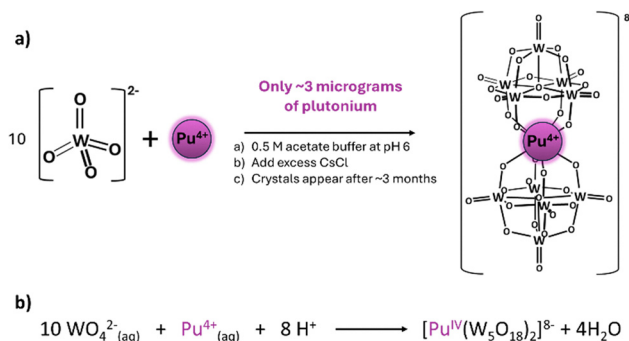


Fig. 1 Reaction scheme and equation for forming the water-soluble plutonium(IV) complex with the POM ligand $W_5O_{18}^{6-}$, formulated $[Pu(W_5O_{18})_2]^{8-}$. The complex was isolated in the solid-state as $Cs_8[Pu(W_5O_{18})_2] \cdot CsCl \cdot 6.5H_2O$.

and non-aqueous media, as well as the versatility of the compounds for a broad range of applications. For example, the W_5 complexes with lanthanides can be used as tuneable luminescent materials.²¹ The magnetic properties of W_5 compounds have also been the subject of many experimental and theoretical studies.^{22,23} Some lanthanide– W_5 complexes function as molecular nanomagnets with long coherence times, and have been proposed for quantum applications.^{24,25}

In terms of tetravalent cations, the W_5 complexes with Zr^{4+} , Ce^{4+} , Th^{4+} , U^{4+} , and Np^{4+} have been crystallized and their structures determined. $Na_8[U(W_5O_{18})_2] \cdot 30H_2O$ was first reported by Golubev *et al.*²⁶ in 1975, $Na_8[Ce(W_5O_{18})_2] \cdot 31H_2O$ by Rosu & Weakley²⁷ in 1998, $Na_8[Th(W_5O_{18})_2] \cdot 28H_2O$ by Griffith *et al.*²⁸ in 2000, $(Me_4N)_2[ZrW_5O_{18}(H_2O)_2(DMSO)]$ by Carabineiro *et al.*²⁹ in 2006, $K_4Na_3H[Np(W_5O_{18})_2] \cdot 16H_2O$ by Villars *et al.*³⁰ in 2012. We note that none of the protocols used in these prior studies would be directly transposable to plutonium chemistry due to the large amounts of materials required, with tens to hundreds of milligrams of the target element engaged in the reactions (Table S1, ESI†).

Herein, we describe efforts to overcome the radiolytic constraints associated with plutonium isotopes by leveraging a

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microscale technique that we previously used for other actinide-POM systems,^{31–34} and completed the series of tetravalent W5 complexes. Using only 3.4 micrograms of weapons-grade Pu (Fig. 1 and Table S1, ESI[†]), we managed to crystallize the compound as its caesium salt, $\text{Cs}_8[\text{Pu}(\text{W}_5\text{O}_{18})_2]\cdot\text{CsCl}\cdot 6.5\text{H}_2\text{O}$ ($\text{Cs}_8\text{Pu}(\text{W}_5)_2$).

$\text{Cs}_8\text{Pu}(\text{W}_5)_2$ was prepared by adding 1 eq. of Pu^{4+} to an aqueous solution containing ~ 50 eq. of sodium tungstate (Na_2WO_4) and buffered at pH 6 by 0.5 M sodium acetate. At the pH of the reaction, the WO_4^{2-} anions are unstable and readily undergo hydrolysis and condensation to form POMs. In the absence of cations, non-lacunary paratungstate salts can be obtained. In the presence of cations, like Pu^{4+} , the speciation is driven towards the complexation of the cation by W5 anions, resulting in a 1:2 complex, $[\text{Pu}(\text{W}_5\text{O}_{18})]^{8-}$. With subsequent addition of excess counterions (*e.g.*, alkali), the W5 complexes often precipitate or, under suitable conditions, crystallize. Upon addition of excess Cs^+ ions ($\text{Cs}:\text{W5}:\text{Pu}$ ratio $1.3 \times 10^5:10:1$), several crystals of $\text{Cs}_8\text{Pu}(\text{W}_5)_2$ were obtained (Fig. 1 and Fig. S1, ESI[†]). Due to the small scale of the reaction and low Pu and W5 concentrations (*i.e.*, $[\text{Pu}]_{\text{initial}} = 24 \mu\text{M}$, $[\text{W5}]_{\text{initial}} = 240 \mu\text{M}$), the $\text{Cs}_8\text{Pu}(\text{W}_5)_2$ crystals only appeared after about 3 months, and no by-product was co-crystallized. The synthesis was done at room temperature, in water, was one-pot, and without any complex steps like filtrations that can be detrimental to experiments with Pu.

For other elements, the obtention of some XRD-quality crystals can often be solved by scaling-up the synthesis to several milligrams of more (Table S1, ESI[†]). In the case of Pu, this kind of approach cannot be used due to its radiotoxicity. Even at the milligram scale, reactions with Pu represent a significant radiological hazard, plus logistical and financial burden. Syntheses at this scale can also result in radiolytic damage to the compound, so that scientists often resort to using longer-lived isotopes, *i.e.*, ^{242}Pu or ^{244}Pu (Half-lives = 3.73×10^5 and 8.13×10^7 years, respectively), which are only made in minute quantities for research and are highly expensive. We overcame these issues by minimizing the reaction scale, down to a few micrograms of the target element. The small scale allowed us to directly use weapons-grade Pu (*i.e.*, 94% ^{239}Pu , 6% ^{240}Pu , see ESI[†] for details), an isotope mixture that is less costly to produce and isolate than research-grade ^{242}Pu or ^{244}Pu . The reaction was done with 3.4 μg of $^{\text{WG}}\text{Pu}$, corresponding to 8.6 kBq (or 233 nCi). At this scale, the use of ^{238}Pu (Half-life = 87.7 years), which is another Pu isotope that is easier to produce than ^{242}Pu or ^{244}Pu , could also be considered knowing that 3 μg of ^{238}Pu corresponds to ~ 1.9 MBq ($\sim 50 \mu\text{Ci}$), which is still a manageable activity level. In future studies, we will leverage our microscale POM synthesis to probe isotopic effects on the properties of actinide coordination compounds.

The crystals obtained were first analyzed *via* Raman microscopy. Fig. 2 shows the solid-state spectrum of the compound. The Raman features confirmed that the crystal contained a W5 complex. The Raman spectrum of $\text{Cs}_8\text{Pu}(\text{W}_5)_2$ is readily different from that of its starting material ($\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$, Fig. S2,

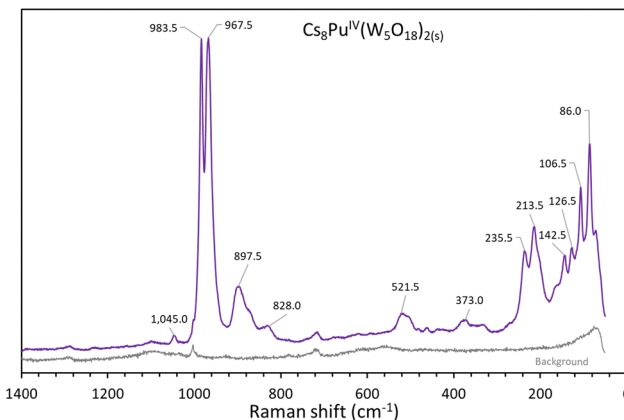


Fig. 2 Solid-state Raman spectrum of the plutonium(IV) complex with the POM ligand $\text{W}_5\text{O}_{18}^{6-}$ (purple), and background from the sample holder (grey).

ESI[†]). The Raman peaks pattern for $\text{Cs}_8\text{Pu}(\text{W}_5)_2$ is consistent with that of $\text{Na}_8[\text{Th}(\text{W}_5\text{O}_{18})_2]\cdot 28\text{H}_2\text{O}$, $\text{Na}_8[\text{Ce}(\text{W}_5\text{O}_{18})_2]\cdot 31\text{H}_2\text{O}$ and $\text{Cs}_8[\text{U}(\text{W}_5\text{O}_{18})_2]\cdot 12\text{H}_2\text{O}$ previously reported.^{28,35,36} By analogy to an experimental and TD-DFT study performed on the equivalent complex with Ce^{4+} by Roy *et al.*,³⁶ the features in the $950\text{--}1000 \text{ cm}^{-1}$ region are characteristic of terminal $\nu(\text{W}=\text{O}_t)$ stretching modes, the bands at $500\text{--}850 \text{ cm}^{-1}$ correspond to bridging $\nu(\text{W}-\text{O}-\text{W})$ and $\nu(\text{W}-\text{O}-\text{Pu})$ stretches. The multiple bands around 400 cm^{-1} correspond to the bending, rocking, and twisting modes of the complex, while the lower energy bands around 200 cm^{-1} represent Pu–O stretches.³⁶

Crystals of the sample were also analysed by solid-state UV-visible absorbance microspectrophotometry. As the crystal obtained were thin plates, their absorbance was relatively faint, but they appeared slightly red-orange under an optical microscope (Fig. 3a). This colour is often a characteristic of Pu^{4+} compounds.^{1,37} The UV-visible spectrum confirmed the presence of Pu^{4+} in the compound, with no sign of other oxidation states of Pu. The $\text{Cs}_8\text{Pu}(\text{W}_5)_2$ crystals exhibit main absorbance bands at 459, 472, 519, and 650 nm (Fig. 3b). These bands are consistent with the characteristic absorbance features observed for our reference solution of Pu^{4+} (Fig. S3, ESI[†]) and other reference spectra for the +IV oxidation state of Pu.^{1,38} As expected, the ligand field of the two POM ligands induces some minor shifts relative to aqueous $\text{Pu}(\text{IV})$. Similar shifts have been reported for Pu^{4+} complexes with donating oxygens, such as oxalates,³⁹ peroxides,⁹ or organic ligands.³

Single crystal XRD analysis definitively confirmed the isolation of a new POM complex containing Pu^{4+} . The isolated compound follows the same general speciation as the previous cases with other tetravalent metals,^{26–28,30,35} with formation of 1:2 species, *i.e.*, $[\text{Pu}(\text{W}_5\text{O}_{18})]^{8-}$. The obtained compound is fully formulated as $\text{Cs}_8[\text{Pu}(\text{W}_5\text{O}_{18})_2]\cdot\text{CsCl}\cdot 6.5\text{H}_2\text{O}$. It crystallizes in anorthic space group $P\bar{1}$, with a cell volume of $5056.8(1) \text{ \AA}^3$ (see Table S2 for full crystallographic details, ESI[†]). The asymmetric unit that describes half the unit cell is comprised of two unique $[\text{Pu}(\text{W}_5\text{O}_{18})_2]^{8-}$ complexes (Fig. 4). Cs^+ counterions then connect the $[\text{Pu}(\text{W}_5\text{O}_{18})_2]^{8-}$ units together creating an extended



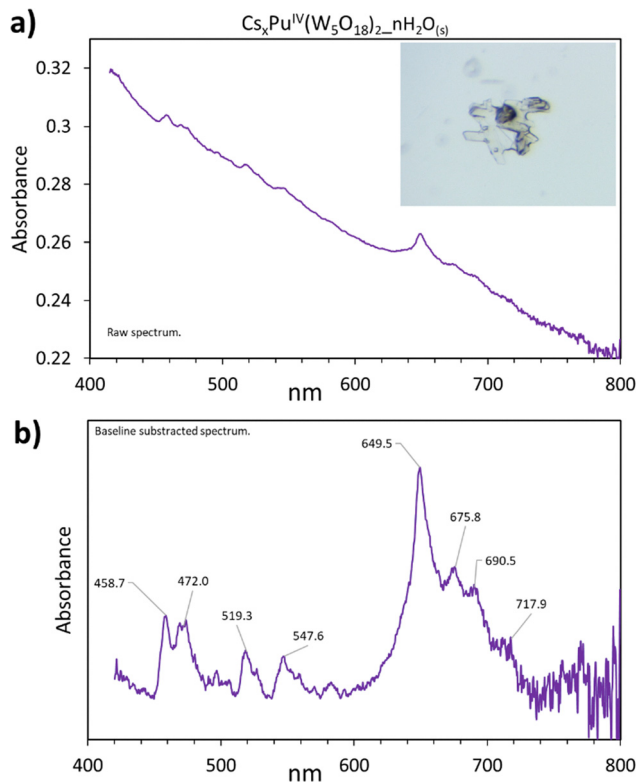


Fig. 3 Solid-state absorbance spectrum of the plutonium(IV) complex with the POM $W_5O_{18}^{6-}$. (a) Raw spectrum. Inset: A cluster of crystals used for the analysis. (b) Baseline subtracted spectrum, highlighting the transitions that correspond to Pu^{4+} .

three-dimensional network. Excess solvent water molecules and chloride ions can also be found connected throughout the Cs–Pu–W5 network (Fig. S4–S6, ESI†).

As illustrated in Fig. 4, the Cs^+ counterions are tightly packed around the Pu–POM complex. Indeed, each unique $[Pu(W_5O_{18})_2]^{8-}$ has five Cs^+ located around the equatorial plane of the complex, at 4.35–4.67 Å away from Pu^{4+} , plus a sixth one from the neighbouring complex, with Cs–Pu distance of ~ 6.7 Å (Fig. 4c). These are remarkably short distances for two cations in aqueous environment. No such interaction is seen in the previous structures reported for tetravalent complexes of W5 (Table S1, ESI†). The positions of Cs^+ in $Cs_8Pu(W_5)_2$ contrast sharply with all the equivalent structures with Th^{4+} , U^{4+} , or Np^{4+} and W5 previously reported.^{26,28,35} In a recent study from Subintoro and Carter,³⁵ the authors found alkali–U distances of 5.8–7.2 Å in $A_x[U(W_5O_{18})_2] \cdot nH_2O$, regardless of the alkali counterion ($A = Li, Na, K, Rb$, or Cs)—a difference of 1.5–2.5 Å compared to $Cs_8Pu(W_5)_2$. Interestingly, we previously observed³² a somewhat similar interaction between multiple Cs^+ counterions and the analogous complex with trivalent curium ($[Cm(W_5O_{18})_2]^{9-}$), with Cm–Cs distances of 4.48–4.54 Å. This hints that the interactions between counterions, the two POM ligands, and the central f-element maybe be specific in the case of Pu^{4+} and Cm^{3+} , with an outsized impact of the Cs^+ counterions on the overall structure. Efforts are on-going to expand the experimental dataset on transuranic–POM complexes and

to rationalize these seemingly transuranic-specific effects *via* computation.

The average Pu–O bond distance in $Cs_8Pu(W_5)_2$ is 2.378 Å, which is consistent with the oxidation state +IV of Pu. However as shown in Fig. S7 and Table S3 (ESI†), this is slightly longer than what would be extrapolated from the related complexes with Zr^{4+} , Th^{4+} , U^{4+} , and Np^{4+} . It appears that the tightly packed Cs^+ counterions in the equatorial plane of the complex lead to a slight elongation of the Pu–O bonds. Bond Valence Summation calculations reveal a calculated valency of 3.6 valence units, which is consistent with the slightly longer bond lengths measured for Pu–O resulting in a underbonded $Pu(IV)$. If the Cs counterions are positioned close to Pu^{4+} , in the equatorial plane, then we presume that the structure compensates with a slight bond elongation along the perpendicular axis (*i.e.*, stretching the complex along its long axis – Fig. 4).

In conclusion, our microscale synthesis approach allowed for the extension of the chemistry of W5 POM to plutonium, providing an important step toward better understanding actinide coordination requirements and informing ongoing efforts to develop novel actinide-based materials. The isolated compound, $Cs_8[Pu(W_5O_{18})_2] \cdot CsCl \cdot 6.5H_2O$, is the first Pu complex of the Peacock–Weakley category. The structure features elongated Pu–O bonds and closely packed Cs^+ counterions around the complex, which is different from the complexes of W5 with other tetravalent cations but reminiscent of what is observed for the analogous compound with trivalent curium. Work is underway to extend this chemistry to other cation–POM–counterions systems.

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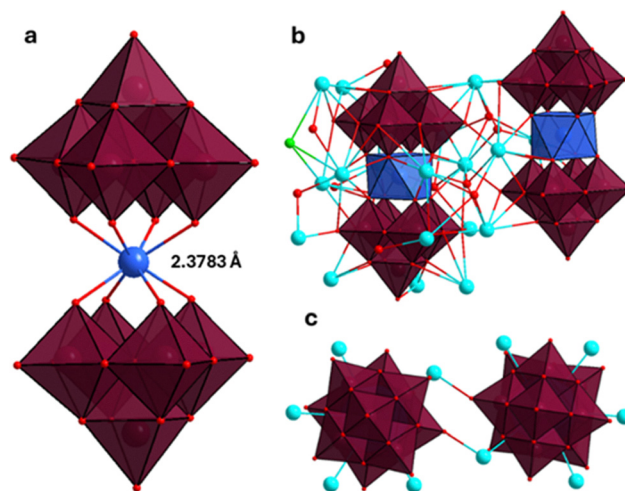


Fig. 4 Structure of the $Cs_8Pu(W_5)_2$ compound showing (a) polyhedral representation of the core complex $[Pu(W_5O_{18})_2]^{8-}$; (b) polyhedral representation with Cs, Cl, and solvent waters surrounding the asymmetric unit, and (c) top-down view showing only the equatorial Cs^+ counterions and their proximity to the Pu^{4+} cation. Colour code: Pu in blue, W in marron, Cs in cyan, Cl in green, O in red.



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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article has been included as part of the ESI† Crystallographic data for the plutonium compound has been deposited at the CCDC (Deposition number 2465152).

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