

Elucidating Trends in Synthesis and Structural Periodicity in a Series of Tetravalent Actinide-oxo Hexamers

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ELECTRONIC SUPPLEMENTAL INFORMATION

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1. CRYSTALLOGRAPHIC REFINEMENT DETAILS OF Th₆, U₆, Np₆, and Pu₆

Th₆: [Th₆O₄(OH)₄(Bz)₁₂(H₂O)₆]

A structural model consisting of one half of the hexamer per asymmetric unit was developed. There is 50/50 substitutional disorder of OH⁻/O²⁻ at the bridging oxygen sites within the cluster. Two of the benzoate groups are disordered over two orientations. The phenyl rings were constrained to be perfect hexagons. The like O-C and C-C distances were restrained to be similar (esd 0.01 Å). The disordered sites are fixed to be 50% occupancy. The other two benzoate groups are disordered across symmetry sites. The phenyl rings were constrained to be perfect hexagons. The like Th-O, O-C and C-C distances were restrained to be similar (esd 0.01). Rigid-bond restraints were imposed on displacement parameters and similar displacement amplitudes (esd 0.01) were imposed on disordered sites overlapping by less than the sum of van der Waals radii.

Several reflections were omitted from the final refinement because they were partially obscured by the shadow of the beam stop. The hydrogen atoms for water and hydroxyl groups could not be located in the difference map and thus were left off of the model. Remaining H atoms were included as riding idealized contributors. H atom U's were assigned as 1.2 times carrier U.

U₆: [U₆O₄(OH)₄(Bz)₁₂(H₂O)₄]

A structural model consisting of two halves of the target U₆ clusters and several water and ethanol solvent molecules per asymmetric unit was developed. There is substitutional disorder of all of the cluster O²⁻/OH⁻ groups. One benzoate ligand is disordered over two orientations. The like O-C and C-C distances were restrained to be similar (esd 0.01 Å). One lattice water molecule is disordered over two positions. One solvent site is substitutionally occupied by two orientations of ethanol and one water molecule. The like O-C and C-C distances were restrained to be similar (esd 0.01 Å). The cluster hydroxyl and lattice water H atoms could not be located in the difference map and thus were left off of the model. Ethanol hydroxyl H atom positions, R-OH, were optimized by rotation about R-O bonds with idealized O-H and R--H distances. Remaining H atoms were included as riding idealized contributors. Hydroxyl H atom U's were assigned as 1.5 times U of the carrier atom; remaining H atom U's were assigned as 1.2 times carrier U. Several reflections were omitted from the final refinement because they were partially obscured by the edge of the detector.

Np₆: [Np₆O₄(OH)₄(Bz)₁₂(H₂O)₄]

Refinement details for this structure are not reported as only a preliminary refinement for Np₆ was obtained.

Pu₆: [Pu₆O₄(OH)₄(Bz)₁₂(H₂O)₄]

A structural model consisting of the host plus two disordered ethanol and three disordered water solvate molecules was developed; however, positions for the idealized solvate molecules were poorly determined. Since positions for the solvate molecules were poorly determined, a second structural model was refined with contributions from the solvate molecules removed from the diffraction data using the bypass procedure in PLATON (Spek, 2015).¹ No positions for the host network differed by more than two su's between these two refined models. The electron count from the SQUEEZE model converged in good agreement with the number of solvate molecules predicted by the complete refinement. The SQUEEZE data are reported here.

There is substitutional disorder of all of the cluster O²⁻/OH⁻ groups. Two benzoate ligands are disordered over two orientations. The like O-C and C-C distances were restrained to be similar (esd 0.01 Å). Similar displacement amplitudes (esd 0.01) were imposed on disordered sites overlapping by less than the sum of van der Waals radii. H atoms were included as riding idealized contributors. H atom U's were assigned as 1.2 times carrier U.

Table S1: Crystallographic refinement details for **Th₆**, **U₆**, **Np₆**, and **Pu₆**.

Structure	Th ₆	U ₆	Np ₆ *	Pu ₆
Formula	Th ₆ C ₈₄ H ₆₀ O ₃₈	U ₆ C _{87.28} H _{69.83} O ₄₀	Np ₆ C ₈₄ H ₆₀ O ₃₆	Pu ₆ C ₈₄ H ₆₀ O ₃₆
MW (g/mol)	3069.56	3186.75	3097.32	3097.32
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	C2/m	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
λ (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	24.309(3)	15.8168(1)	15.789(4)	15.805(7)
b (Å)	17.216(2)	24.7055(1)	24.949(6)	24.801(1)
c (Å)	17.1830(1)	23.9238(1)	23.814(6)	23.813(1)
α (°)	90	90	90	90
β (°)	134.903(4)	95.234(2)	95.382(7)	95.628(1)
γ (°)	90	90	90	90
V (Å ³)	5093.5(1)	9309.5(9)	9340(4)	9289(9)
Z	2	4	4	4
ρ (g/cm ³)	2.001	2.274	2.159	2.215
μ (mm ⁻¹)	8.805	10.490	6.694	4.279
R ₁	0.0352	0.0358	0.2178	0.0554
wR ₂	0.0996	0.0643	0.5246	0.1426
GOF	1.241	1.110	1.949	1.074
CCDC	2387949	2387950	NA	2387951

*The refinement of **Np₆** is only preliminary because of poor crystal quality.

2. STRUCTURE DESCRIPTIONS OF **Th**₆, **U**₆, **Np**₆, and **Pu**₆.

The compound **Th**₆ crystallizes in the space group C2/m, Table S1. The asymmetric unit contains three unique thorium centers, four benzoate ligands, two μ_3 -oxygen atoms, and three bound aqua ligands. The thorium metal centers are bound to nine oxygen atoms and adopt a monocapped square antiprism coordination geometry with a local C_{4v} symmetry, Fig. 1. The cluster core is decorated with six aqua and twelve benzoate ligands. All benzoate ligands bridge adjacent thorium atoms (κ^2). Solvent molecules were not located during structure refinement. The experimental powder diffraction pattern of the bulk sample is consistent with the calculated diffraction pattern obtained from the single-crystal data, suggesting that the crystal used for structure determination is representative of the bulk.

A preliminary structure refinement (Table S1) was obtained for **Np**₆ which crystallizes in the space group P2₁/n. However, only the cluster core (Fig. S3) could be resolved due to weak crystal diffraction and poor data quality. Nonetheless, we believe that **Np**₆ is isomorphous with **U**₆ and **Pu**₆ based on unit cell parameters and powder X-ray diffraction data, which showed agreement between the experimental powder pattern collected for **Np**₆ and the calculated patterns of **U**₆ and **Pu**₆ (Fig. S8). Attempts were made to grow high-quality crystals through dissolution of the bulk in ethanol followed by recrystallization through slow evaporation, however this did not result in higher quality crystals.

Compounds **U**₆ and **Pu**₆ crystallize in the space group P2₁/n. The asymmetric units contain six unique U/Pu metal centers (three from each of the two crystallographically unique clusters in the unit cell), eight μ_3 -oxygens, twelve benzoate ligands, four bound aqua ligands, two unbound ethanol molecules, and two unbound water molecules (one water molecule is disordered across two parts). These solvent molecules could not be reasonably modeled for **Pu**₆. Therefore, the SQUEEZE function was applied *via* PLATON.¹ Four of the uranium/plutonium metal centers are 9-coordinate and adopt a distorted monocapped square antiprism coordination geometry, with local C₁ symmetry (Fig 2). The other two uranium metal centers are 8-coordinate and feature a square antiprism coordination geometry with D_{4d} local symmetry (Fig 2). The 9-coordinate uranium centers are bound to four μ_3 -oxygens, one aqua molecule, and four oxygens from three benzoate ligands. The 8-coordinate metal centers are coordinated by four μ_3 -oxygens and four oxygens from four benzoate ligands. The **U**₆/**Pu**₆ core is decorated with twelve benzoate and four aqua ligands. Eight benzoate ligands bridge adjacent uranium atoms (κ^2) while the remainder coordinate to a single uranium atom (κ^1).

3. THERMAL ELLIPSOID PLOTS Th_6 , U_6 , Np_6 , and Pu_6 .

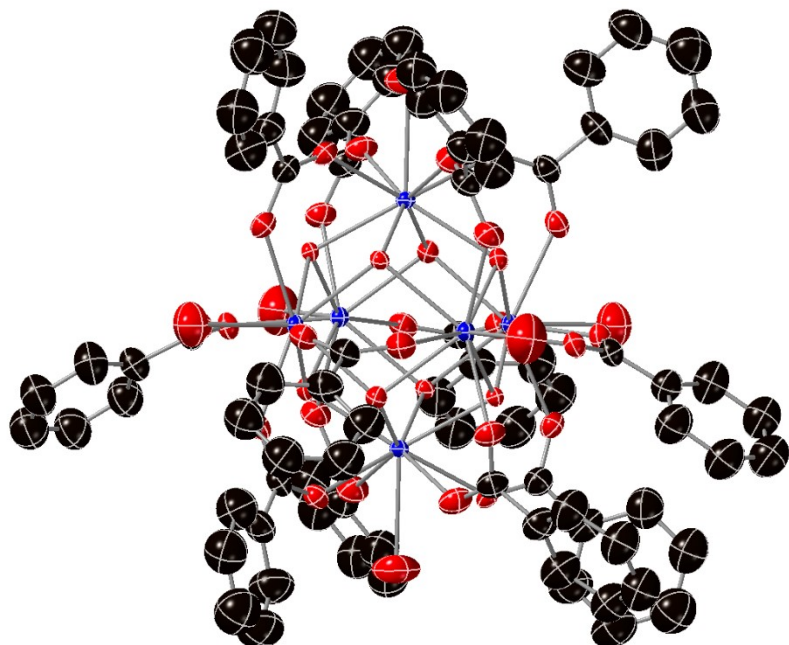


Figure S1. Thermal ellipsoid plot for Th_6 . Ellipsoids are shown at 50% probability. Disorder and hydrogens have been omitted for clarity. Th atoms are depicted in blue, oxygen atoms are red, carbon atoms are shown in black, and hydrogen atoms are omitted for clarity.

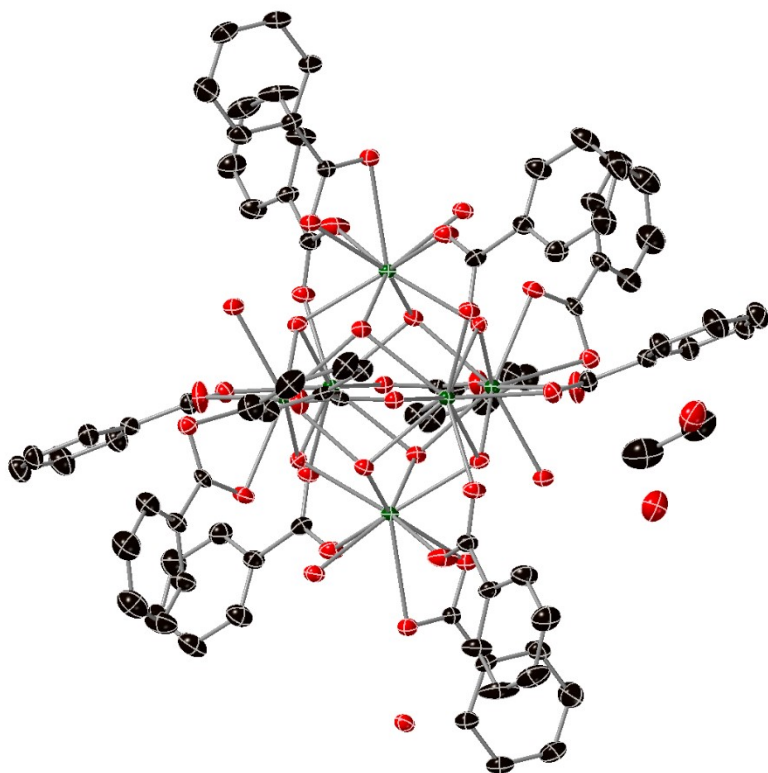


Figure S2. Thermal ellipsoid plot for U_6 . Ellipsoids are generated at 50% probability. Disorder and hydrogens have been omitted for clarity. Water and ethanol are present in the crystal structure. These lattice solvent molecules are partially occupied according to the formula provided in the previous section. U atoms are depicted in green, oxygen atoms are red, carbon atoms are shown in black, and hydrogen atoms are omitted for clarity.

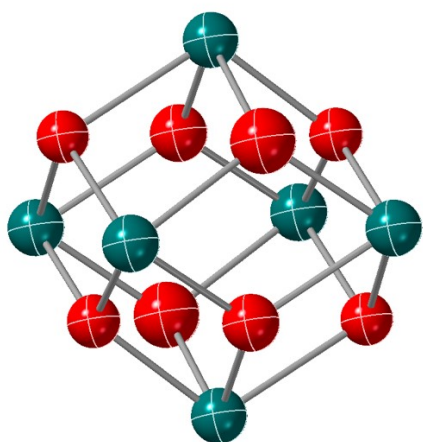


Figure S3. Cluster core of Np_6 with neptunium atoms depicted in blue and oxygen atoms are shown in red. Np atoms are depicted in light blue and oxygen atoms are red.

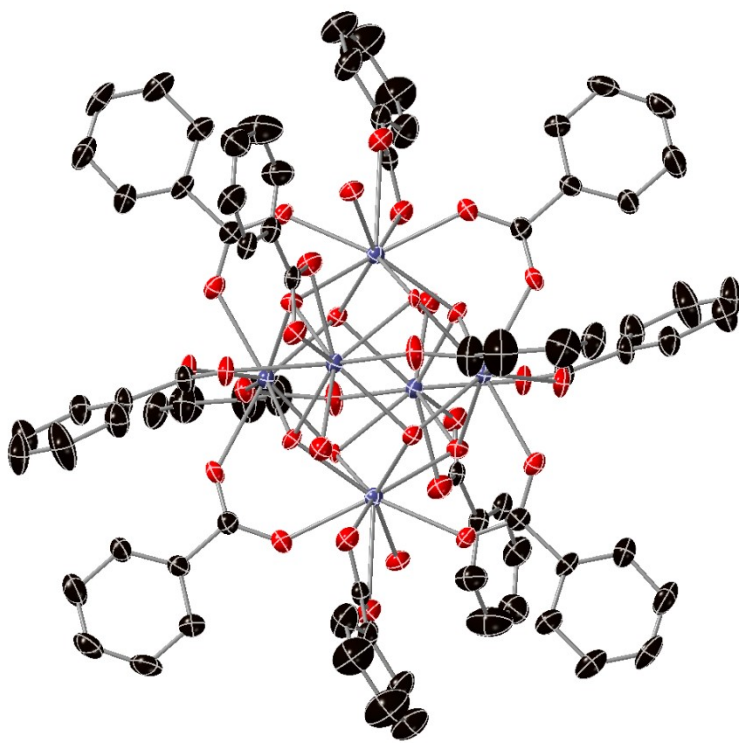


Figure S4. Thermal ellipsoid plot for **Pu₆**. Ellipsoids are generated at 50% probability. Disorder and hydrogens have been omitted for clarity. Residual electron density in the outer coordination sphere could not be resolved and was therefore squeezed from the structure. Pu atoms are depicted in blue, oxygen atoms are red, carbon atoms are shown in black, and hydrogen atoms are omitted for clarity.

4. POWDER X-RAY DIFFRACTION PATTERNS OF Th₆, U₆, and Np₆.

Powder X-Ray diffraction (PXRD) patterns were collected for **Th₆** and **U₆** in order to identify the presence of impurities prior to bulk sample measurements. For both compounds, peaks present in the experimental diffraction pattern are accounted for by the pattern calculated from the single crystal data. These results indicate that the single crystals used to collect single crystal X-ray diffraction (SCXRD) are representative of the bulk phase.

The identity of **Np₆** was confirmed by comparing an experimental PXRD pattern to the simulated pattern generated from the crystal structure of **U₆** shown in Figure S8. These patterns are in good agreement despite obvious preferred orientation and the poor crystal quality of **Np₆**.

Also shown is the experimental PXRD from the powder obtained when attempting to synthesize Th_6 in the same manner as U_6 . This pattern is in good agreement with the pattern simulated from the thorium-benzoate coordination polymer published by Loiseau et al.²

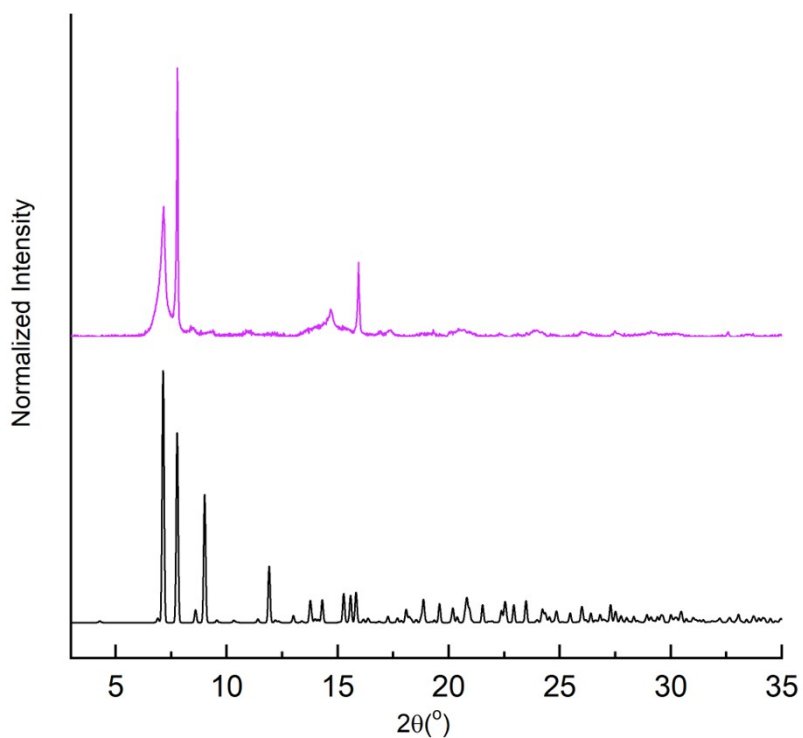


Figure S5. Powder X-ray diffraction for the previously reported thorium chain (pink) compared to the calculated diffraction pattern generated from the cif (black).

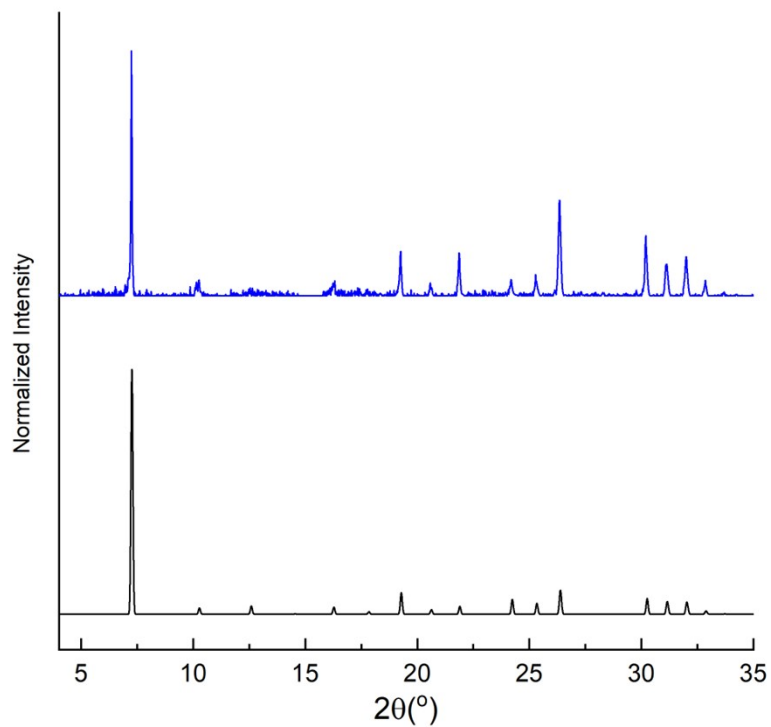


Figure S6. Powder X-ray diffraction for **Th₆** (blue) compared to the calculated diffraction pattern generated from the cif (black).

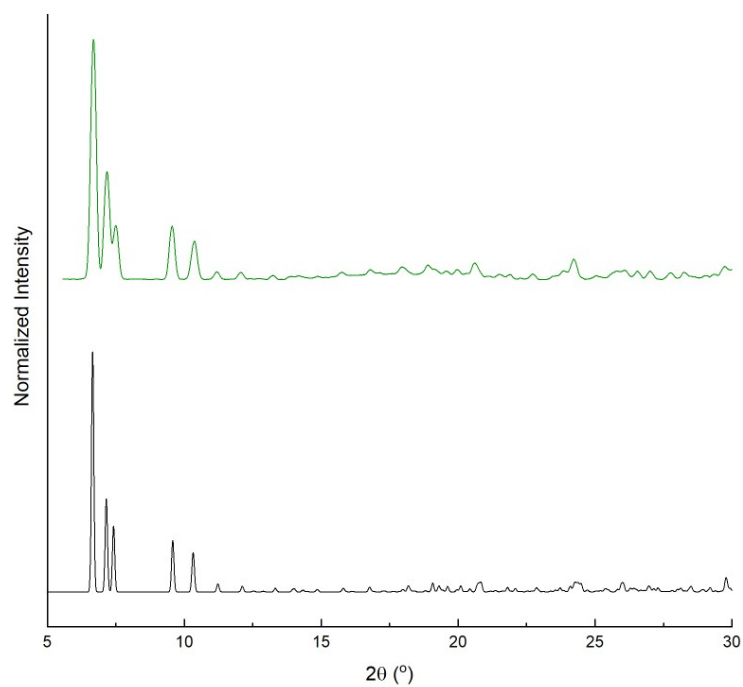


Figure S7. Powder X-ray diffraction for **U₆** (green) compared to the calculated diffraction pattern generated from the cif of **U₆** (black).

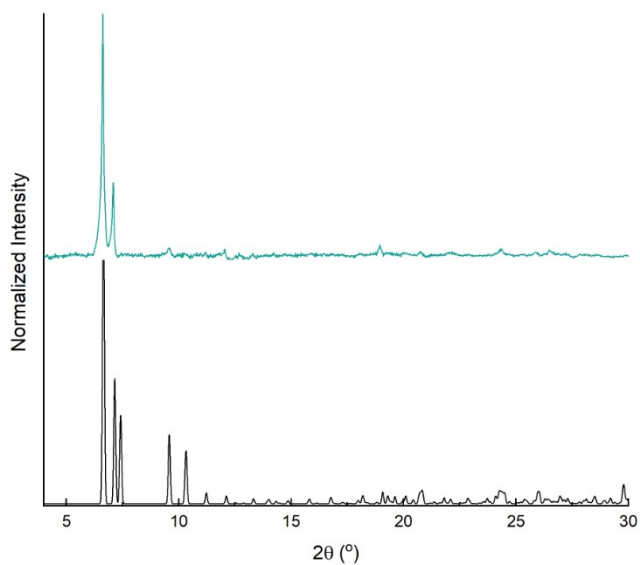


Figure S8. Powder X-ray diffraction for Np_6 (light blue) compared to the calculated diffraction pattern generated from the cif of U_6 (black). Agreement of the two patterns is consistent with formation of a Np-based hexamer.

5. RAMAN SPECTRA OF Th₆, U₆, Np₆ and Pu₆.

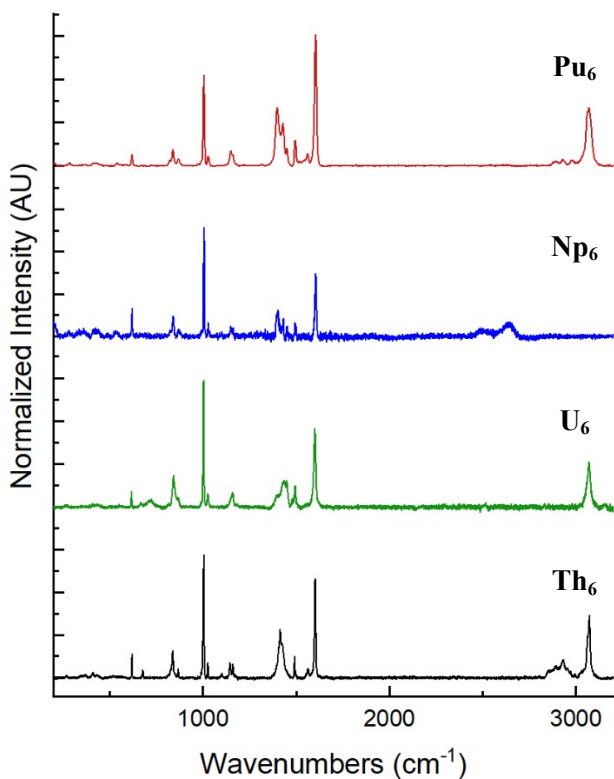


Figure S9. Raman spectra of Th₆ (black), U₆ (green), Np₆ (blue), and Pu₆ (red)

Table S2: Tentative assignment of Raman modes for Th₆, U₆, Np₆, and Pu₆.

Tentative Assignment	Th ₆	U ₆	Np ₆	Pu ₆
	619	616	620	619
μ ₃ -OH bend ³	676	722	N/A	N/A
COO ⁻ in-plane scissoring ⁴	837	842	838	837
Ring breathing in-phase ⁴	1003	1003	1006	1003
	1025	1026	1028	1028
C-C symmetric ring breathing ⁵	1145	1158	1150	1148
	1413	1414	1399	1397

	1491	1493	1493	1493
Aromatic C-C stretching (symmetric) ⁵	1560	N/A	N/A	1562
C-C stretch of benzene ring ⁴	1601	1600	1604	1604
sp ² C-H stretch ⁶	2928	N/A	N/A	2829
Aromatic C-H stretching ⁵	3072	3072	N/A	3069

Table S3: IR stretches for **Th₆**, **U₆**, **Np₆**, and **Pu₆** with assignments of select stretches.

Tentative Assignment	Th ₆	U ₆	Np ₆	Pu ₆
=C-H out of plane bending ⁶	720	705	713	712
=C-H out of plane bending ⁶	855	863	867	865
CO ₂ bend ³	943	932	937	934
	1025	1025	1025	1026
	1097	1070	1071	1071
	1160	1175	1177	1177
	1388	1396	1394	1393
C=O stretch ⁶	1551	1541	1539	1532
C=O stretch ⁶	1597	1597	1596	1595
H ₂ O bend + CO ₂ asymmetric stretch ³	1661	1677	1684	1697

sp ² C-H stretch ⁶	2928	N/A	3051	N/A
sp ² C-H stretch ⁶	3061	3064	3055	3063
H ₂ O symmetric stretch ³	3633	N/A	3629	3616

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