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(NpO_2) $_3$ (PO_4) $_2$ (Terpy)**

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COMMUNICATION

Hydrothermal synthesis and structure of organically templated layered neptunyl(VI) phosphate $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$

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A novel neptunyl(VI) phosphate compound, $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$, was synthesized by hydrothermal reaction. It crystallizes in the orthorhombic space group $Pca2_1$ with unit-cell parameters $a = 13.9944 \text{ \AA}$, $b = 12.1989 \text{ \AA}$, $c = 13.1277 \text{ \AA}$, $V = 2241.1 \text{ \AA}^3$, $Z = 4$. Related to the layered structure of the uranophane topology, it contains the first reported $(\text{Np}^{\text{VI}}\text{O}_2)_2(\text{PO}_4)_2^{2-}$ sheets, which are bonded via π - π interactions between the $\text{Np}^{\text{VI}}\text{O}_2(\text{Terpy})^{2+}$ ligands that are perpendicular to the sheets.

²³⁷Np is a byproduct in nuclear reactors, with a long half-life of 2.14×10^6 years, and contributes significantly to the potential dose of radiation over time in a deep geological repository.^[1] Managing nuclear waste and environmental contamination requires further studies of the coordination chemistry of actinides. While the crystal chemistry of uranium compounds has been more established over the last decades, neptunium compounds are less studied.^[2] Neptunium forms nearly linear neptunyl ions, $\text{Np}^{\text{V}}\text{O}_2^+$ and $\text{Np}^{\text{VI}}\text{O}_2^{2+}$. Like uranyl ions, neptunyl ions are usually coordinated by four, five, or six equatorial ligands forming bipyramids in crystal structures.^[3]

Uranyl phosphates have been extensively studied for their low solubility in aqueous environments.^[4] Neptunyl can substitute or replace uranyl due to their similar polyhedral geometries, as the bond lengths for UO_2^{2+} , NpO_2^+ , and NpO_2^{2+} are typically 1.79(4), 1.83(2), and 1.75(2) Å, respectively.^[5] Synthetic neptunyl(VI) phosphates $X[(\text{NpO}_2)(\text{PO}_4)](\text{H}_2\text{O})_3$ ($X = \text{K}^+$,

Na^+ , Rb^+ , and NH_4^+) with sheets identical to the uranyl phosphate sheets of the autunite group have been reported,^[3] along with neptunyl(V) phosphates $\text{Ba}[(\text{NpO}_2)(\text{PO}_4)](\text{H}_2\text{O})$ and $\text{Rb}_2\text{Ca}[(\text{NpO}_2)_2(\text{PO}_4)_2]$ with sheets related to the uranophane topology.^[6] The thermochemical properties of autunite-related $X[(\text{NpO}_2)(\text{PO}_4)](\text{H}_2\text{O})_3$ ($X = \text{K}^+$, Rb^+) and $X[(\text{UO}_2)(\text{PO}_4)]_m(\text{H}_2\text{O})_n$ ($X = \text{Li}^+$, Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cu^{2+} , Co^{2+}) have been studied and it has been shown that the stability of these compounds depend on the acidity of oxides of the charge balancing metal cations.^[7]

Interactions of the transuranium elements with N-donor ligands, such as pyridine and their derivatives, provide potential solutions for separating actinides from lanthanides.^[8] $\text{Np}(\text{V})$ complexes with 2,2'-bipyridine (Bipy), 2,2';6',2''-terpyridine (Terpy), 1,10-phenanthroline (Phen), have been determined by X-ray single crystal diffractometry,^[9] while $\text{Np}(\text{VI})$ complexes with pyridine and Bipy have been reported.^[10]

In this study we present a novel anhydrous neptunyl(VI) phosphate layered structure bonded to terpyridine, $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$. It has been synthesized hydrothermally at 150 °C, where brown agglomerates of plate crystals of $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ formed along with pink square-shaped crystals of $\text{K}[(\text{NpO}_2)(\text{PO}_4)](\text{H}_2\text{O})_3$,^[3] as shown in Fig. S1.[†] Its crystal structure was determined by single crystal X-ray diffraction.[‡] The experimental details of the data collection and refinement results are listed in Tables S1-S3 and Figures S2-S3. Bond-valence sum calculations (BVS) were done using bond valence parameters for Np^{6+} -O bonds and Np^{6+} -N bonds and are presented in Table S4, yielding the valence sums of 5.783, 5.811, and 5.722 for Np1, Np2, and Np3, respectively, consistent with the proposed chemical formula of $(\text{Np}^{\text{VI}}\text{O}_2)_3(\text{PO}_4)_2(\text{Terpy})$ (Terpy = $\text{C}_{15}\text{H}_{11}\text{N}_3$).

The structure of $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ consists of sheets in which the neptunyl ions ($\text{Np}^{\text{VI}}\text{O}_2^{2+}$) are coordinated in a pentagonal bipyramidal arrangement, shown in Figs. 1 and S4. The neptunium(VI) bonds strongly to two oxygen atoms (1.749(5) and 1.753(6) Å, O_{yl}) to form a nearly linear (179.0° for Np1 and 177.9° for Np2) neptunyl ion. The neptunyl ion is

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coordinated by five more oxygen atoms in the equatorial plane, where Np-O bond distances range from 2.292 – 2.512 Å, forming pentagonal bipyramids. The polyhedra share edges and form chains that are linked through phosphate tetrahedra to form a corrugated $(\text{Np}^{\text{VI}}\text{O}_2)_2(\text{PO}_4)_2^{2-}$ layer structure parallel to (010). Within the PO_4 tetrahedra, the P-O bond lengths range from 1.510 – 1.530 Å when it bonds to one oxygen of the neptunium pentagonal bipyramid, and to 1.544 – 1.554 Å when it bonds to two oxygen atoms.

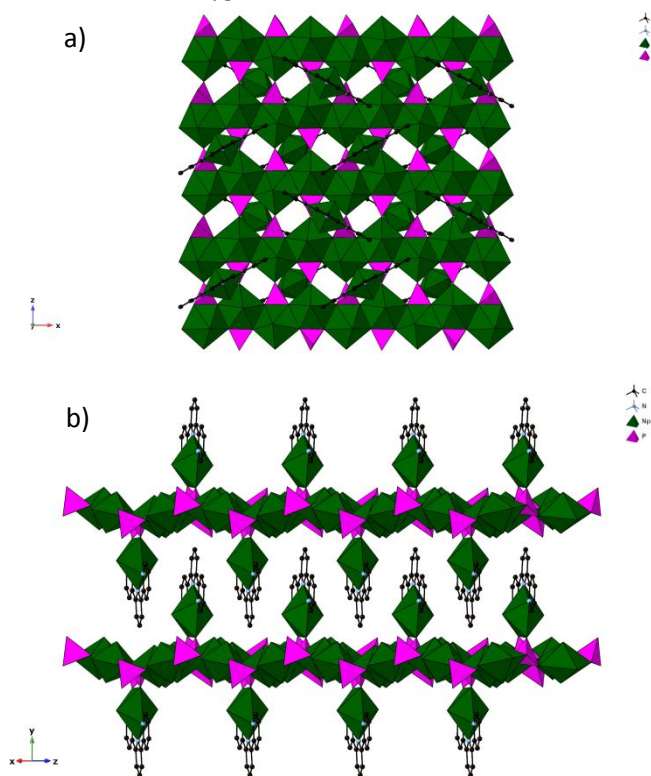
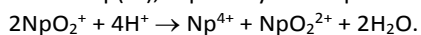


Fig. 1. Crystal structure of $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$: (a) viewed along the crystallographic b axis; (b) depiction of the layer structures of $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ inserting into each other, seen from the side of the $(\text{NpO}_2)_2(\text{PO}_4)_2^{2-}$ sheet.

The bond lengths of the neptunyl ion in $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ range from 1.749(5) to 1.753(6) Å, consistent with the average bond length for $\text{Np}^{6+}\text{-O}$ (1.75(2) Å), whereas $\text{Np}^{5+}\text{-O}$ bonds are considerably longer (1.83(2) Å).^[5a] Although the initial stock solution contained Np(V) in 1 M HCl solution, disproportionation of Np(V) through the following reaction results in Np(VI) , especially in low pH solutions,^[11]



The phosphate tetrahedra are also linked to a third neptunyl ion ($\text{Np}^{\text{VI}}\text{O}_2^{2+}$) that is bonded to terpyridine (Terpy, $\text{C}_{15}\text{H}_{11}\text{N}_3$) that is perpendicular to the sheet (Figs. 1b and 2). In Fig. 2, the coordination polyhedron of the neptunium(VI) ion is a pentagonal bipyramid. The $\text{Np}^{3(\text{VI})}$ cation is strongly bonded to two oxygen atoms (1.749(6) and 1.764(6) Å, O_{yl}) to form a nearly linear (175.4°) NpO_2^{2+} neptunyl ion. Its equatorial plane is coordinated by three nitrogen atoms of the terpyridine molecule and two oxygen atoms of the phosphate tetrahedra that are bonded to the neptunyl phosphate layers. The

distances from the neptunium atom to the equatorial atoms are different. The Np-N bond lengths lie in the range of 2.556 – 2.605 Å, which are similar to the Np-N bond reported in the $\text{Np}^{\text{V}}\text{O}_2(\text{NO}_3)(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{H}_2\text{O})$ structure;^[9b] the distances of neptunium to the oxygen atoms of the phosphate groups are 2.266 – 2.292 Å. The equatorial distances for Np(VI) complexes ranges from 2.518 – 2.630 Å for Np-N bonds, and 2.211 – 2.485 Å for Np-O bonds.^[8]

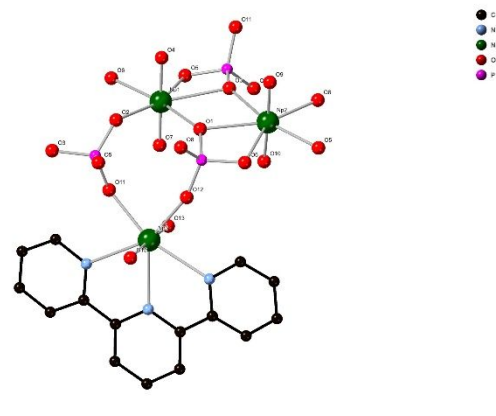


Fig. 2. Ball-and-stick drawings of the crystal structure of $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$. The H atoms are omitted from the image.

The $(\text{NpO}_2)_2(\text{PO}_4)_2^{2-}$ sheets are linked through π - π interactions between the $\text{NpO}_2(\text{Terpy})^{2+}$ ligands in the interlayers, as shown in Fig. 3, where the $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ layers insert into each other like a pair of combs (see Fig. 1b). The neighboring terpyridine coordinate with each other in an offset face to face stacking manner, with a vertical distance of 3.39 Å and the distance from center to center of 3.68 Å, which is consistent with π - π interactions.^[12]

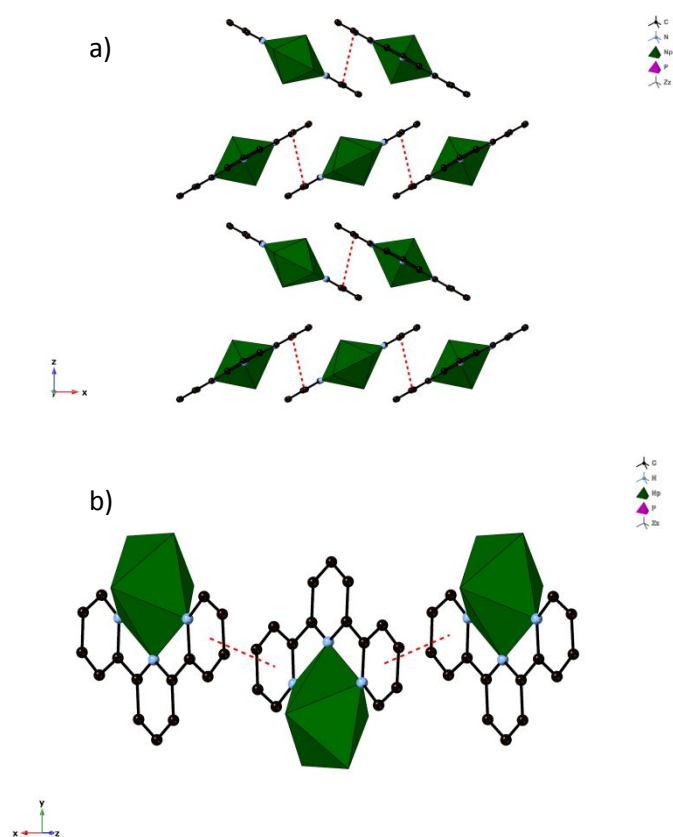


Fig. 3. Depiction of π - π interactions between the $\text{NpO}_2(\text{Terpy})^{2+}$ in the interlayers of $(\text{NpO}_2)_3(\text{PO}_4)_2^{2-}$ sheets: (a) viewed along the crystallographic b axis; (b) showing the π - π interactions between the neighboring terpyridines.

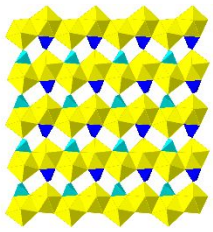
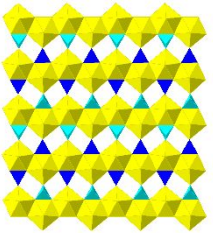
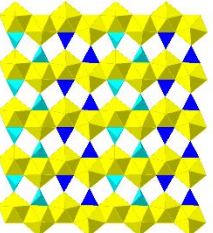
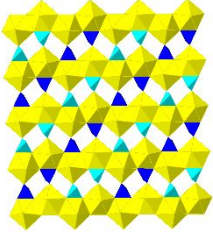
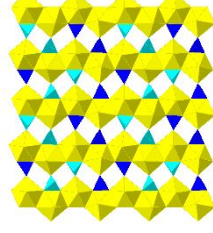
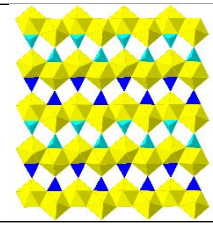
The sheet structures of $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ is related to the sheet of $(\text{NpO}_2)_2(\text{PO}_4)_2^{2-}$ that is similar to those of the uranophane $\text{Ca}[(\text{UO}_2)_2(\text{HSiO}_4)_2](\text{H}_2\text{O})_5$ group of uranyl silicate minerals.^[13] There are three known Np(V) compounds that contain sheets based on the uranophane anion topology: $\text{Cs}[(\text{NpO}_2)(\text{CrO}_4)](\text{H}_2\text{O})$, $\text{Ba}[(\text{NpO}_2)(\text{PO}_4)](\text{H}_2\text{O})$, and $\text{Rb}_2\text{Ca}[(\text{NpO}_2)(\text{PO}_4)]_2$.^[6]

Many uranyl compounds contain sheets based upon the uranophane anion topology, differing in the orientation of the silicate or phosphate tetrahedra. The uranophane sheet anion topology contains two perpendicular chains: one containing edge-sharing squares and triangles (S-T chain) and one containing edge-sharing pentagons and triangles (P-T chain). Table 1 lists selected uranyl and neptunyl compounds with sheets based on the uranophane topology, grouped by the XO_4 ($\text{X} = \text{Si}, \text{P}, \text{Cr}$) orientation along the S-T chain, in our work along the $[001]$ direction. Six variants are observed, where the tetrahedral orientations are distinguished by coloring the 'up' and 'down' tetrahedra differently. The uranophane anion-topology is basis for many sheets and framework structures containing hexavalent U or Np, deriving from its simplicity and flexibility in polymerization through various interlayer cations or ligands.^[14]

Unfortunately, $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ crystals as synthesized in this work was not a pure form to be separated for further characterization. On the other hand, we have tried to crystallize an isostructural $(\text{UO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ compound using similar method.^[56] We were able to synthesize powders of $(\text{UO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ that were characterized by powder X-ray diffraction (Fig. S5), which are comparable to the PXRD patterns of $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ calculated from its single X-ray diffraction data. All peaks of the $(\text{UO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ pattern are shifted slightly to lower 2θ angles, as U(VI) is slightly bigger than the Np(VI) ion. Furthermore, we have utilized EDS, IR, UV-vis, and Raman techniques to investigate the $(\text{UO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ compound, as shown in Figs S6-S10 and Tables S5-S6. Although no crystals of $(\text{UO}_2)_3(\text{PO}_4)_2(\text{Terpy})$ have been made, its characterization shows that the powder $(\text{U}^{\text{VI}}\text{O}_2)_3(\text{PO}_4)_2(\text{Terpy})$ is isostructural to $(\text{Np}^{\text{VI}}\text{O}_2)_3(\text{PO}_4)_2(\text{Terpy})$.

In conclusion, we report the synthesis of a novel neptunyl(VI) phosphate compound, $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$, and its isostructural $(\text{UO}_2)_3(\text{PO}_4)_2(\text{Terpy})$, which are based on sheets with the uranophane topology. The $(\text{NpO}_2)_2(\text{PO}_4)_2^{2-}$ sheets are bonded via π - π interactions between the $\text{Np}^{\text{VI}}\text{O}_2(\text{Terpy})^{2+}$ ligands perpendicular to the sheets.

Table 1. List of selected uranyl and neptunyl compounds with sheets based on uranophane anion-topology.

Tetrahedra orientation along S-T chain (U: upward; D: downward)	Uranophane-type anion-sheets differing in the orientations of XO ₄ tetrahedra (cyan: upward; blue: downward)	Name	Formula	Reference
UDUDUDUD UDUDUDUD UDUDUDUD UDUDUDUD		α -uranophane	$\text{Ca}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2(\text{H}_2\text{O})_5$	[13]
		Boltwoodite	$(\text{K}_{0.56}\text{Na}_{0.42})[(\text{UO}_2)(\text{SiO}_3\text{OH})](\text{H}_2\text{O})_1$	[15]
		Cuprosklodowskite	$\text{Cu}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2(\text{H}_2\text{O})_6$	[16]
		Sklodowskite	$\text{Mg}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2(\text{H}_2\text{O})_6$	[17]
		Kasolite	$\text{Pb}[(\text{UO}_2)(\text{SiO}_4)]\text{H}_2\text{O}$	[18]
			$\text{Ba}[(\text{Np}^{\text{V}}\text{O}_2)(\text{PO}_4)]\text{H}_2\text{O}$	[6a]
			$\text{Cs}[(\text{Np}^{\text{V}}\text{O}_2)(\text{CrO}_4)]\text{H}_2\text{O}$	[19]
UDUDUDUD DUDUDUDU UDUDUDUD DUDUDUDU		Oursinite	$\text{Co}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2(\text{H}_2\text{O})_6$	[20]
			$(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_4$	[21]
UUDDUUDD UUDDUUDD UUDDUUDD UUDDUUDD		β -uranophane	$\text{Ca}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2(\text{H}_2\text{O})_5$	[22]
UUDDUUDD DDUUDDUU UUDDUUDD DDUUDDUU			$\text{Be}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_3$	[23]
			$(\text{NHEt}_3)[(\text{UO}_2)_2(\text{PO}_4)(\text{HPO}_4)]$	[24]
			$[(\text{C}_2\text{H}_5)_2\text{NH}_2]_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4$	[25]
UUDDUUDD DUUDDUUD UUDDUUDD DUUDDUUD			$\text{A}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$	[26]
			$(\text{Np}^{\text{VI}}\text{O}_2)_3(\text{PO}_4)_2(\text{Terpy})$ (Terpy = $\text{C}_{15}\text{H}_{11}\text{N}_3$)	This work.
UUUUUUUU DDDDDDDD UUUUUUUU DDDDDDDD			$\text{Rb}_2\text{Ca}[(\text{Np}^{\text{V}}\text{O}_2)(\text{PO}_4)]_2$	[6b]

Note: A = Cs, Rb, K.

Acknowledgements

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Conflicts of interest

The authors declare no known competing financial interests.

Notes and references

‡ $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$: **CAUTION**: ^{237}Np presents a serious health risk due to its emission of alpha radiation. It decays to short-lived ^{233}Pa that emits strong beta radiation. All studies were done in laboratories at the University of Notre Dame that have appropriate equipment and personnel for working with such materials. A stock solution of 100 mM of $\text{Np}(\text{V})$ dissolved in 1 M HCl was prepared. Reagents of KCl (Fisher), 2,2':6',2''-Terpyridine (Sigma-Aldrich), were used as received. Apatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, from the Liscombe deposit, was used as the phosphate source. 250 μL of 100 mM $\text{Np}(\text{V})$ stock solution, 750 μL of 18 M Ω H_2O , 0.01 g of apatite, 0.01 g of KCl , and 2 mg of 2,2':6',2''-terpyridine, were added to a 7 mL Teflon cup with a screw-top lid. Two of each Teflon cups with loaded reagents were put in 125 mL Teflon-lined Parr reaction vessels with 40 mL of ultrapure water to provide counter-pressure when heating. The reaction vessels were heated in an oven at 150 $^\circ\text{C}$ for two weeks and allowed to cool slowly to room temperature afterwards.

§ Structural data for $(\text{NpO}_2)_3(\text{PO}_4)_2(\text{Terpy})$: A total of 25503 reflections were collected representing a full reciprocal sphere from a yellow plate grain with dimensions $0.02 \times 0.02 \times 0.002$ mm³, Orthorhombic, $\text{Pca}2_1$, $a = 13.9944(8)$ Å, $b = 12.1989(7)$, $c = 13.1277(8)$ Å, $V = 2241.1(2)$ Å³, $Z = 4$, $\rho = 3.647$ g cm⁻³, and $\mu(\text{Mo K}\alpha) = 14.031$ mm⁻¹ were measured on a Bruker Apex2 CCD diffractometer at 298 K. An absorption correction was applied using SADABS. The structure was solved by direct methods and all calculations were performed using the Bruker SHELXL-2014/7 package. The final refinement cycles converged with $R_1 = 0.0176$, $wR_2 = 0.0453$, $\text{GOF} = 1.07$ for 5463 $I > 2\sigma(I)$, $\Delta\rho_{\text{max,min}} = +2.03 / -1.29$ e Å⁻³. CCDC 2246550 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing da-ta_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

§§ $(\text{UO}_2)_3(\text{PO}_4)_2(\text{Terpy})$: Similar method was used to synthesize $(\text{UO}_2)_3(\text{PO}_4)_2(\text{Terpy})$. A stock solution of 125 mM of $\text{U}(\text{VI})$ dissolved in 1M HCl was prepared by dissolving $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ in HCl . 200 μL of 125 mM $\text{U}(\text{VI})$ stock solution, 800 μL of 18 M Ω H_2O , 0.01 g of apatite, and 0.01 g of KCl , and 2 mg of 2,2':6',2''-terpyridine, were added to a 7 mL Teflon cup with a screw-top lid. The Teflon cups were put into Parr reaction vessels, heated in an oven at 160 $^\circ\text{C}$ for two weeks and allowed to cool slowly to room temperature afterwards.

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- The data supporting this article have been included as part of the Supplementary Information.
- Crystallographic data for [compound number] has been deposited at the CCDC under **2246550** and can be obtained from https://www.ccdc.cam.ac.uk/data_request/cif.