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Unexpected Actinyl Cation-Directed Structural Variation in Neptunyl(VI) A-Type Tri-lacunary Heteropolyoxotungstate Complexes

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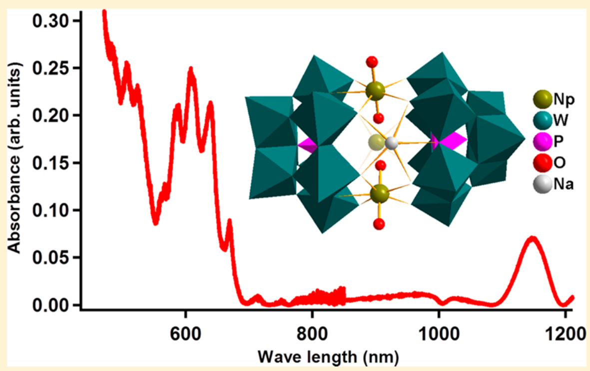
Supporting Information

ABSTRACT: A-type tri-lacunary heteropolyoxotungstate anions (e.g., $[PW_9O_{34}]^{9-}$, $[AsW_9O_{34}]^{9-}$, $[SiW_9O_{34}]^{10-}$, and $[GeW_9O_{34}]^{10-}$) are multidentate oxygen donor ligands that readily form sandwich complexes with actinyl cations ($\{UO_2\}^{2+}$, $\{NpO_2\}^{+}$, $\{NpO_2\}^{2+}$, and $\{PuO_2\}^{2+}$) in near-neutral/slightly alkaline aqueous solutions. Two or three actinyl cations are sandwiched between two tri-lacunary anions, with additional cations (Na^+, K^+, or NH_4^+) also often held within the cluster. Studies thus far have indicated that it is these additional +1 cations, rather than the specific actinyl cation, that direct the structural variation in the complexes formed. We now report the structural characterization of the neptunyl(VI) cluster complex $(NH_4)_{13}[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 12H_2O$. The anion in this complex, $[Na(NpO_2)_2(PW_9O_{34})_2]^{13-}$, contains one Na^+ cation and two $\{NpO_2\}^{2+}$ cations held between two $[PW_9O_{34}]^{9-}$ anions, with an additional partial occupancy NH_4^+ or $\{NpO_2\}^{2+}$ cation also present. In the analogous uranium(VI) system, under similar reaction conditions that include an excess of NH_4Cl in the parent solution, it was previously shown that $[(NH_4)_2(U^{VI}O_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$ is the dominant species in both solution and the crystallized salt. Spectroscopic studies provide further proof of differences in the observed chemistry for the $\{NpO_2\}^{2+}/[PW_9O_{34}]^{9-}$ and $\{UO_2\}^{2+}/[PW_9O_{34}]^{9-}$ systems, both in solution and in solid state complexes crystallized from comparable salt solutions. This work reveals that varying the actinide element (Np vs U) can indeed measurably impact structure and complex stability in the cluster chemistry of actinyl(VI) cations with A-type tri-lacunary heteropolyoxotungstate anions.



■ INTRODUCTION

Basic research into the chemistry of the actinide elements underpins many aspects of the nuclear fuel cycle, including uranium processing, spent nuclear fuel reprocessing, long-term storage of nuclear waste, and environmental cleanup of legacy facilities. The chemistry of the +V and +VI oxidation states for U, Np, Pu, and Am is dominated by the linear dioxo actinyl moieties, $\{An^{VI}O_2\}^{2+}$ and $\{An^{V}O_2\}^{+}$, and these species play an important role in many applied/environmental processes.[1] Because of the low radiotoxicity of natural and depleted uranium, and relative ease of performing quantum chemical calculations on closed shell $5f^0$ actinide ions, our understanding of the chemistry of uranyl(VI) has improved greatly in recent decades.[2] In the past few years, synthetic advances have also led to a rapid growth in research into uranyl(V), $\{UO_2\}^{+}$, an unstable species under most common chemical environments.[3] Significantly greater radiological hazards are encountered when working with the transuranic elements, resulting in fewer experimental studies and thus a less complete understanding of the chemistry of the Np, Pu, and Am (vs U) actinyl moieties. With this in mind, researchers have looked to probe coordination environments that allow for the direct comparison of uranyl(VI) species with well-characterized structural and spectroscopic properties of analogous transuranic actinyl systems.[4]

Heteropolyoxotungstate anions are effective complexants for actinide cations, often stabilizing unusual oxidation states and producing a wide range of structural motifs.[5] The study of the interaction of actinyl cations with A-type tri-lacunary heteropolyoxotungstate anions is a prominent subset of such research efforts. These anions are formed from the partial base degradation of Keggin anions (e.g., $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ to $[\alpha\text{-}PW_9O_{34}]^{9-}$) and possess six formally unsaturated terminal oxygen atoms that can readily coordinate to other metal centers.[6] Two such ligands can complex two or three actinyl cations in sandwich structures in which the equatorial plane of the actinyl moiety is coordinated by two terminal oxygen atoms of one tri-lacunary anion and two terminal oxygen atoms and a bridging oxygen atom of a second tri-lacunary anion (see Figure 1). This coordination environment has now been observed for $\{UO_2\}^{2+}$, $\{NpO_2\}^{2+}$, $\{NpO_2\}^{+}$, and $\{PuO_2\}^{2+}$.[7−14]

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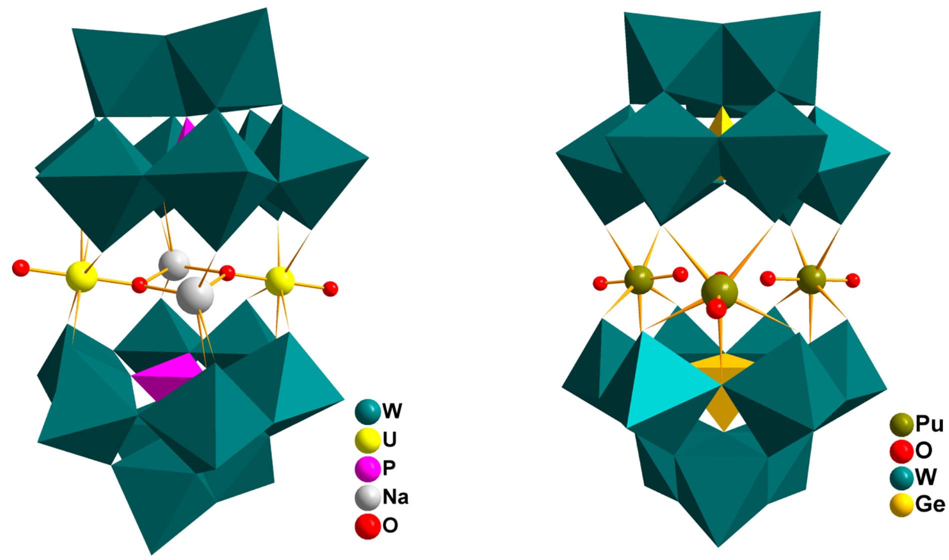

Figure 1. Examples of 2:2 and 3:2 actinyl complexes with tri-lacunary heteropolyoxotungstate anions: $[Na_2(UO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$ and $[K_3(PuO_2)_3(A\text{-}GeW_9O_{34})_2]^{11-}$ (externally coordinated K^+ cations removed for the sake of clarity).[7,8]

Table 1. Actinyl Complexes with A-Type Tri-lacunary Heteropolyoxotungstate Anions

	+1 cations trapped in the cluster		
actinyl moiety	two	one[a]	none[b]
uranyl(VI)	$[Na_2(UO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$, $[Na_2(UO_2)_2(A\text{-}SiW_9O_{34})_2]^{14-}$, $[Na_2(UO_2)_2(A\text{-}GeW_9O_{34})_2]^{14-}$	$[(NH_4)_2(UO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$, $[(NH_4)_2(UO_2)_2(A\text{-}AsW_9O_{34})_2]^{12-}$, $[K_2(UO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$, $[K_2(UO_2)_2(A\text{-}AsW_9O_{34})_2]^{12-}$	$[(UO_2)_3(A\text{-}AsW_9O_{34})_2]^{12-}$
neptunyl(VI)	$[Na_2(NpO_2)_2(A\text{-}GeW_9O_{34})_2]^{14-}$		
neptunyl(V)	$[Na_2(NpO_2)_2(A\text{-}PW_9O_{34})_2]^{14-}$		
plutonyl(VI)			$[K_3(PuO_2)_3(A\text{-}GeW_9O_{34})_2]^{11-}$

[a]Only one of the two +1 cations associated with the formula is actually trapped in the cluster, and the two complexes containing K^+ have not been structurally characterized. [b]None of the K^+ cations associated with the plutonyl(VI) complex are trapped inside the cluster.

In actinyl tri-lacunary heteropolyoxotungstate complexes, the type of salt (NaCl, NH_4Cl, KCl, or KNO_3) used to crystallize the complex has been shown to play a key role in directing structure type. If a sufficient excess of Na^+ was present, the hydrated sodium salts that crystallize contain two actinyl cations and two sodium cations encapsulated between two tri-lacunary anions $\{[Na_2(U^{VI}O_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$, $[Na_2(U^{VI}O_2)_2(A\text{-}SiW_9O_{34})_2]^{14-}$, $[Na_2(U^{VI}O_2)_2(A\text{-}GeW_9O_{34})_2]^{14-}$ (α and β isomers), and $[Na_2(Np^{V}O_2)_2(A\text{-}PW_9O_{34})_2]^{14-}\}$.[7,9,11,13] Significantly less excess Na^+ was required to crystallize $[Na_2(Np^{VI}O_2)_2(A\text{-}GeW_9O_{34})_2]^{14-}$,[14] but in all these complexes with encapsulated Na^+, each of the two sandwiched actinyl cations was bonded by a bridging oxygen of a different tri-lacunary anion. If excess K^+ was used, the crystallized products resulted in the formation of complexes containing three actinyl cations coordinated to two tri-lacunary anions, as seen in both $[(U^{VI}O_2)_3(A\text{-}AsW_9O_{34})_2]^{12-}$ and $[K_3(Pu^{VI}O_2)_3(A\text{-}GeW_9O_{34})_2]^{11-}$ (see Figure 1).[8,10] In the latter case, there were no K^+ cations actually trapped within the center of the anionic clusters. With excess NH_4Cl, the hydrated ammonium salt of $[(NH_4)_2(U^{VI}O_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$ crystallized with one ammonium cation trapped in the sandwich complex and one on the surface of the cluster. Two fully coordinated uranyl cations (~100% occupancy) and a "vacant" site partially occupied (5%) by a third uranyl were encapsulated in the center of the cluster.[7] Similarly, for the $[(NH_4)_2(U^{VI}O_2)_2(A\text{-}AsW_9O_{34})_2]^{12-}$ anion, one NH_4^+ is believed to be coordinated inside the sandwich complex, but evidence of a third partial occupancy $\{U^{VI}O_2\}^{2+}$ cation was not discussed.[12] K^+ analogues of these $\{UO_2\}^{2+}$-PW_9 and $\{UO_2\}^{2+}$-AsW_9 complexes were also prepared, and partial crystal structures and strong spectroscopic evidence indicated that one K^+ cation is incorporated in the center of the cluster.[7,12] In the complexes with three encapsulated actinyl cations, and those with two encapsulated actinyl cations and one encapsulated monopositive cation (NH_4^+ or K^+), the actinyl moieties bond to the bridging oxygens of the same tri-lacunary anion. Table 1 lists all the structurally characterized actinyl complexes with A-type tri-lacunary anions.

This work explores whether the dominant role that cations (Na^+, K^+, and NH_4^+) play in directing structure in actinyl tri-lacunary heteropolyoxotungstate complexes extends beyond known U^{VI}, Np^{V}, Np^{VI}, and Pu^{VI} chemistry, with a focus on previously unreported Np^{VI} chemistry. Because of the stability of $\{Np^{V}O_2\}^{+}$ under most aqueous environments, solution chemistry studies have tended to focus on this species. However, the chemistry of Np^{IV} and $\{Np^{VI}O_2\}^{2+}$ can also be significant in a range of environmental, waste treatment, and spent nuclear fuel processing scenarios.[1b,15] Previously, it has been shown that complexation of both $[A\text{-}PW_9O_{34}]^{9-}$ ("PW_9") and $[A\text{-}GeW_9O_{34}]^{10-}$ ("GeW_9") to $\{Np^{VI}O_2\}^{2+}$ results in a dramatic change in the vis/near-infrared (nIR) absorption spectrum of this actinide cation (cf. hydrated $\{Np^{VI}O_2\}^{2+}$) and sensitization of Np^{VI} luminescence.[14] We now report further

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investigations into the complexation of $\{Np^{VI}O_2\}^{2+}$ by A-type tri-lacunary anions, focusing in more detail on the reaction between $[PW_9O_{34}]^{9-}$ and $\{NpO_2\}^{2+}$ and contrasting the chemistry of $\{Np^{VI}O_2\}^{2+}$ with previously reported $\{U^{VI}O_2\}^{2+}$ structural chemistry. This work will reveal that Np^{VI} chemistry does not always mimic U^{VI} chemistry, even with a heteropolyoxometalate ligand system that provides such a well-defined coordination environment.

■ EXPERIMENTAL SECTION

Caution! *^{237}Np (and daughter isotopes) are radioactive, and any chemical manipulations with this isotope should be conducted only in an appropriate radiological laboratory while following all necessary controls and regulations.*

General. $\{Np^{VI}O_2\}^{2+}$ stocks in dilute HCl were generated from an initial sample of NpO_2. Dissolution of NpO_2 in 8 M HNO_3 with gentle heat and a few drops of 5% HF led to the formation of $\{Np^{VI}O_2\}^{2+}$, with partial reduction to $\{Np^{V}O_2\}^{+}$ and Np^{IV} over time. Pure $\{NpO_2\}^{2+}$ could be generated by ozonolysis followed by addition of base (NH_4OH) to precipitate solid neptunyl(VI) hydroxide species. These Np^{VI} solids could in turn be washed with H_2O prior to dissolution in HCl. Oxidation state purity and neptunium concentration were confirmed by vis/nIR spectroscopy, with assays in 2 M $HClO_4$ yielding the characteristic $[NpO_2(OH_2)_5]^{2+}$ bands, including the 1223 nm transition, with <1% Np^{V} oxidation state impurity.[16] $Na_8H[A\text{-}\beta\text{-}PW_9O_{34}]\cdot 20H_2O$ ($[PW_9O_{34}]^{9-}$, PW_9) was prepared in accordance with the literature method.[17] Solution state vis/nIR spectra were recorded on a Cary 6000i spectrometer using both 1 cm and 2 mm path length cells specially adapted for work with high-specific activity radionuclides. Solid state vis/nIR spectra were recorded on either a Cary 6000i or a Cary 5 spectrometer with diffuse reflectance attachment in specially adapted glass sample holders, sealed with Teflon plugs. The IR spectrum was recorded as a nujol mull between KBr plates on a Nicolet 6700 FT-IR instrument. The Raman spectrum was recorded on a DXR Smart Raman, Thermo Scientific, with a 780 nm HP laser using a sample previously prepared for diffuse reflectance measurements. The $^{31}P\{^1H\}$ NMR spectrum was recorded on a Bruker Avance 300 MHz spectrometer at 121.5 MHz, relative to external H_3PO_4 (85%). The sample was contained in a sealed PTFE NMR tube that was itself contained in a standard 5 mm glass NMR tube filled with a few drops of D_2O.

Synthesis. Detailed synthetic methodology for the synthesis of $\{NpO_2\}^{2+}$ tri-lacunary complexes has been described elsewhere.[14] In general excess "PW_9" was added to $\{NpO_2\}^{2+}$ in dilute HCl and the pH increased above pH 7 using dilute NaOH (aqueous) to ensure complete complexation (defined as complex **1**). Addition of excess KCl led to precipitation of an apple green complex, defined as "NpO_2^{2+}−PW_9−KCl" (**2**), which could be dissolved in H_2O and recrystallized by vapor diffusion with MeCN. While crystalline products could readily be obtained using this procedure, none proved to be suitable for X-ray diffraction. Reactions were initially undertaken with 3−4 mg of Np^{VI}, but the reaction was also scaled up to 15−20 mg of $\{NpO_2\}^{2+}$. In this reaction, a portion of the solution prior to KCl addition was used for ^{31}P NMR and quantitative vis/nIR analysis (i.e., a bulk solution of complex **1**). Addition of excess KCl to the remaining solution led to the formation of the "NpO_2^{2+}−PW_9−KCl" (**2**) with the reaction workup as described previously.

In contrast, addition of excess NH_4Cl to the $\{NpO_2\}^{2+}$−PW_9 complex in solution (**1**) led to the formation of a salt that was still soluble in the reaction solution. Vapor diffusion of the clear green solution with MeCN produced crystals suitable for single-crystal X-ray diffraction, and $(NH_4)_{13}[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 12H_2O$ (**3**) was subsequently structurally characterized.

Single-Crystal X-ray Diffraction. Crystal data for $(NH_4)_{13}[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 12H_2O$ (**3**) were collected on a Bruker D8 instrument with an APEX II CCD detector. Chemical formula = $H_{66}N_{13}NaNp_2O_{84}P_2W_{18}$, Mw = 5460.89, triclinic space group, $P\bar{1}$, a = 12.8871(11) Å, b = 16.0745(14) Å, c = 21.5515(19) Å, α = 99.1340(10)°, β = 95.0050(10)°, γ = 105.8640(10)°, V = 4199.7(6) Å^3, T = 141(2) K, Z = 2, Mo Kα radiation (λ = 0.71073 Å), μ = 27.153 mm^{-1}, green-yellow needle with crystal dimensions = 0.22 mm × 0.10 mm × 0.08 mm, ρ_{calcd} = 4.318 g cm^{-3}. Intensity data of 42194 reflections were collected in the range $-15 \le h \ge 15$, $-19 \le k \ge 19$, $-26 \le l \ge 26$, R_1 = 0.0886 (for 11406 reflections with $I \ge 2\sigma I$), wR_2 = 0.1194 (all data), GOF = 1.210.

■ RESULTS AND DISCUSSION

$Na_8H[A\text{-}\beta\text{-}PW_9O_{34}]\cdot 20H_2O$ ($[PW_9O_{34}]^{9-}$, PW_9) was added to $\{NpO_2\}^{2+}$ in a dilute HCl aqueous solution, followed by the adjustment of the pH to >7. A deep green solution was obtained with vis/nIR solution spectra characteristic of formation of the complex between A-type tri-lacunary anions and $\{NpO_2\}^{2+}$ (**1**).[14] Addition of excess KCl led to precipitation of a complex containing almost all the Np^{VI} present in solution, which could be then be dissolved in distilled H_2O and recrystallized via MeCN vapor diffusion. Throughout the rest of this paper, we will refer to the products from this reaction between Np^{VI} and PW_9 in KCl as Np^{VI}−PW_9−KCl, complex **2** (as previously described in the Experimental Section). In contrast, addition of an excess of NH_4Cl to the $\{NpO_2\}^{2+}$−PW_9 solution at near-neutral pH yielded a more soluble complex. This solution containing $\{NpO_2\}^{2+}$−PW_9−NH_4Cl yielded deep green crystals of $(NH_4)_{13}[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 7H_2O$ (**3**).

Single-crystal X-ray diffraction analysis of **1** revealed two $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ ligands sandwiching two $\{NpO_2\}^{2+}$ moieties and a sodium cation {i.e., $[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{13-}$}, as well as a partial occupancy (0.8) ammonium cation. In addition, there is a third partial occupancy (0.2) $\{NpO_2\}^{2+}$ moiety trapped within the cluster that takes the place of the trapped ammonium cation (see Figure 2). In the presence of the third

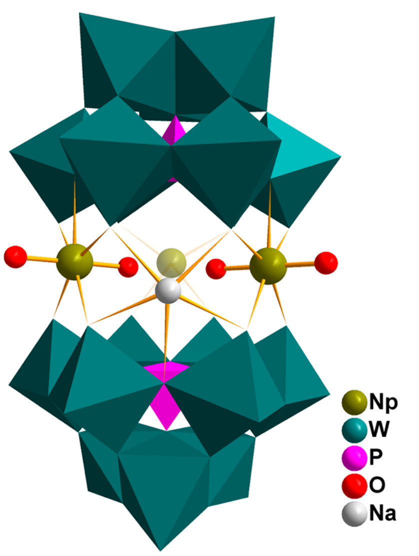

Figure 2. Combined ball and stick and polyhedral representation of $[Na(Np^{VI}O_2)_2(PW_9O_{34})_2]^{13-}$, showing the 0.2 occupancy Np of an additional $\{NpO_2\}^{2+}$ moiety as a partially transparent structure (rather than the 0.8 occupancy NH_4^{+}) .

partial occupancy Np, the overall charge of the salt can be balanced by substituting two ammonium cations with two lattice waters {i.e., $(NH_4)_{11}[Na(NpO_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 14H_2O$}. Such small changes normally cannot be observed through X-ray diffraction in a disordered structure. This anion represents a further structural variation in the observed

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complexation of actinyl cations by A-type tri-lacunary heteropolyoxotungstate anions.

As with previously reported actinyl A-type tri-lacunary heteropolyoxotungstate complexes,[7−14] the Np atoms in $[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{13-}$ are seven-coordinate, with the linear $O{=}Np{=}O^{2+}$ core coordinated by two terminal oxygens of one $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ ligand and two terminal oxygens and one bridging oxygen of a second $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ ligand. In this structure, the Np atoms are coordinated to bridging oxygen atoms of the same $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ ligand. Again, as observed previously, the distortion from pentagonal bipyramidal geometry is caused by the geometric constraints imposed by coordination to three oxygen atoms from one ligand and two oxygen atoms from the other. The longer An−O bond length observed for the oxygen atom that bridges two tungsten atoms versus the terminal oxygen atoms bound to only one tungsten atom has also been well-documented.[7−14] Only the Np−O bond lengths and O−Np−O bond angles for the two full occupancy Np atoms will be discussed in detail. These observed structural parameters for $[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{13-}$ are very similar to the Np−O bond lengths and O−Np−O bond angles in $[Na_2(NpO_2)_2(A\text{-}\alpha\text{-}GeW_9O_{34})_2]^{14-}$,[14] yielding additional evidence that changes in overall structure have a limited impact on the local actinide coordination environment in actinyl−A-type tri-lacunary heterpolyoxotungstate complexes (see Table 2). Finally, the

Table 2. Comparison of the Neptunium Coordination Environment in $[Na(Np^{VI}O_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{13-}$ (3) (only the full occupancy inequivalent Np atoms) and $[Na_2(Np^{VI}O_2)_2(A\text{-}\alpha\text{-}GeW_9O_{34})_2]^{14-11}$

	$[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{13-}$ (Np1 and Np2 data)	$[Na_2(NpO_2)_2(A\text{-}\alpha\text{-}GeW_9O_{34})_2]^{14-}$
	Bond Lengths (Å)	
Np−O (neptunyl)	1.725(14), 1.758(15), 1.751(14), 1.798(15)	1.77(2), 1.82(3)
Np−O (W−O, terminal)	2.306(13), 2.321(11), 2.335(13), 2.365(14), 2.292(14), 2.297(14), 2.305(14), 2.378(16)	2.25(3), 2.32(3), 2.36(3), 2.39(3)
Np−O (W_2−O, bridging)	2.552(13), 2.552(14)	2.47(3)
	Bond Angles (deg)	
O=Np=O (neptunyl)	179.0(7), 177.2(7)	176.3(12)
O−Np−O (equatorial)	62.4(5), 62.1(5), 72.6(5), 79.1(5), 85.0(5), 61.5(4), 63.3(4), 72.9(4), 77.8(4), 85.2(4)	63.7(9), 64.6(10), 74.9(11), 79.6(9), 81.4(10)

Np−O bond lengths in $[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{13-}$ are within the range previously observed for seven-coordinate neptunyl(VI) compounds with oxygen donor ligands. The average $Np{-}O_{axial}$ bond length [1.76(3) Å] is comparable to the 1.705(17)−1.751(5) Å range observed for $2NpO_2SO_4\cdot H_2SO_4\cdot 4H_2O$, $NpO_2(IO_3)_2\cdot 0.5KCl\cdot 3.25H_2O$, $[NpO_2\{(OOC)_2C_6H_4\}H_2O]\cdot {}^1/_3H_2O$, $K_2[(NpO_2)_2(CrO_4)_3(H_2O)]\cdot 3H_2O$, and $[(NpO_2)(CrO_4)(H_2O)]\cdot 4H_2O$.[18−22] In addition, the average $Np{-}O_{equatorial}$ bond lengths in these five compounds are 2.40(3), 2.39(3), 2.41(5), 2.37(6), and 2.38(3) Å, respectively. Again, these values are comparable to the average $Np{-}O_{equatorial}$ bond length of 2.37(9) Å for $[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{13-}$.[18−22] Perhaps the most unusual structural feature of $[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{13-}$ is the incorporation of Na^+ into the cluster, despite the addition of excess NH_4^+ prior to crystallization. A previous solution state ^{31}P NMR competition study has shown that K^+ and NH_4^+ cations can readily displace Na^+ in $[Na_2(UO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$,[7] and Na^+ cations have not previously been observed encapsulated within actinyl−A-type tri-lacunary heteropolyoxotungstate complexes crystallized in the presence of either excess K^+ or NH_4^+.[8,10,13] We therefore turned to additional spectroscopic characterization as a means to probe any further differences in the chemical interactions between PW_9 and $\{NpO_2\}^{2+}$ and $\{UO_2\}^{2+}$.

The complexation of $\{NpO_2\}^{2+}$ by A-type tri-lacunary heteropolyoxotungstate anions yields very distinctive electronic absorption spectra, as indicated previously.[14] The spectrum of $[NpO_2(OH)_5]^{2+}$ in perchloric acid and the spectrum of the solution complex formed between $\{NpO_2\}^{2+}$ and "PW_9" (**1**) are compared in Figure 3. It should be noted that PW_9 was present as the sodium salt, introducing Na^+ into the reaction solution, while the presence of some NH_4^+ from the preparation of Np^{VI} cannot be discounted. Nevertheless, while the exact structure of the Np^{VI}−PW_9−monopositive cation complex (**2**) in solution cannot be determined, it is reasonable to assume two or three $\{NpO_2\}^{2+}$ cations sandwiched by two PW_9 anions with seven-coordinate Np in distorted D_{5h} symmetry. The UV/vis/nIR absorption spectrum of $[NpO_2(OH)_5]^{2+}$ (between 350 and 1300 nm, 28600−7700 cm^{-1}) contains three main spectral features: (i) a band at 1223 nm (8177 cm^{-1}) likely resulting from an intra-5f transition, (ii) two transitions in the visible region at 476 and 555 nm (21000 and 18000 cm^{-1}, respectively), and (iii) high-energy $O_{equatorial} \rightarrow$ Np charge transfer transitions (<400 nm, >25000 cm^{-1}).[16,23] Upon complexation by tri-lacunary heteropolyoxotungstate anions, the 1223 nm (8177 cm^{-1}) 5f−5f Np^{VI} transition shifts to a higher energy, in this case to 1137 nm (8795 cm^{-1}), and its intensity decreases. This blue shift is consistent with previous studies, in which an even greater increase in energy, to 1120 nm (8929 cm^{-1}), and concomitant drop in intensity have recently been observed upon complexation of nitrate to $\{NpO_2\}^{2+}$ in 14.5 M HNO_3.[24] At the greatest extreme, this 5f−5f transition for $\{NpO_2\}^{2+}$ dramatically decreases in intensity in the presence of both excess acetate and carbonate, although the reason for this decrease was not discussed.[25,26]

Turning to the UV/vis region of the absorption spectrum of **1**, we found substitution of H_2O by "PW_9" equatorial ligands shifts the O → Np charge transfer transition to a lower energy (∼550 nm, 18200 cm^{-1}). The most notable feature in the spectrum of the complex is the progression of transitions around 600 nm, the most intense peak occurring at 609 nm (16400 cm^{-1}). The progression has a splitting energy of ∼700 cm^{-1}, comparable to the energy of O=Np=O ν_1 in the ground state (*vide infra*). Denning reported the assignment of both LMCT and 5f−5f transitions in this region for both $Cs_2NpO_2Cl_4$ and $CsNpO_2(NO_3)_3$, with the LMCT transitions exhibiting much more prominent progressions in multiple quanta of ν_1.[27] In analogy with the $\{UO_2\}^{2+}$ moiety,[28] the prominence of such progressions is indicative of changes in the $An{-}O_{axial}$ bond strength and/or length upon excitation from the ground state to a LMCT state. Comparable vibronic bands at similar energies are also observed for $[NpO_2(CO_3)_3]^{4-}$,[26,29] $\{NpO_2\}^{2+}$ in DMSO,[30] and NpO_2Cl_2 in THF.[4h] Similar spectral features are also observed in the visible region for the complexation of $\{NpO_2\}^{2+}$ with $[SiW_{11}O_{39}]^{8-}$, as previously reported,[5q] although this structurally distinct mono-lacunary hetropolyoxotungstate anion must form a complex with the

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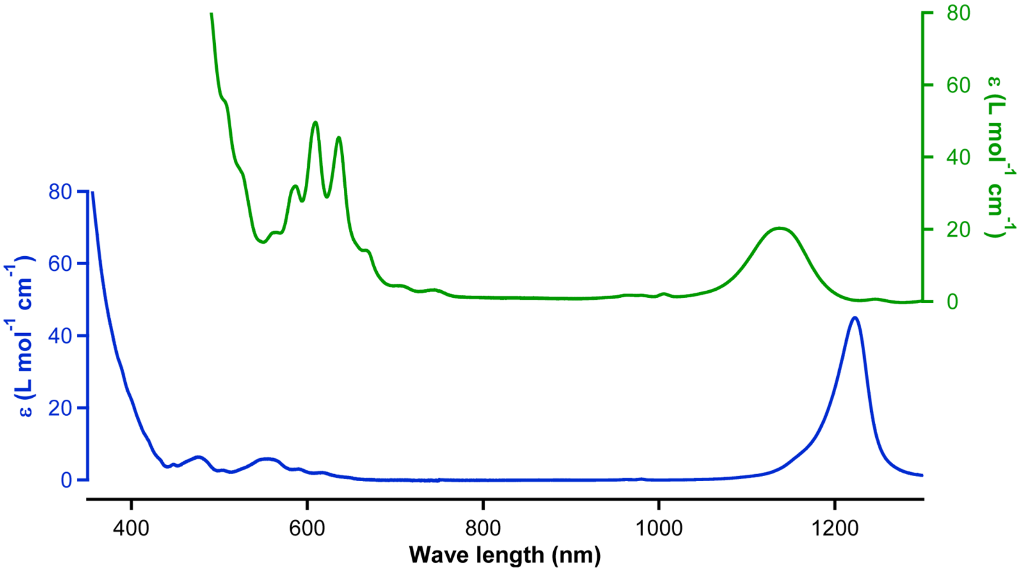

Figure 3. Vis/nIR absorption spectra of $[NpO_2(OH_2)_5]^{2+}$ (5 mmol/L) in 2 M $HClO_4$ (left axis) and (b) the reaction between $\{NpO_2\}^{2+}$ (11 mmol/L) and A-$[PW_9O_{34}]^{9-}$ (1:2 molar ratio) at pH 7.5 (right axis) (**1**). The molar absorptivity values for **1** are calculated on the basis of the $\{NpO_2\}^{2+}$ concentration and the assumption of complete complexation with formation of a single species in solution.

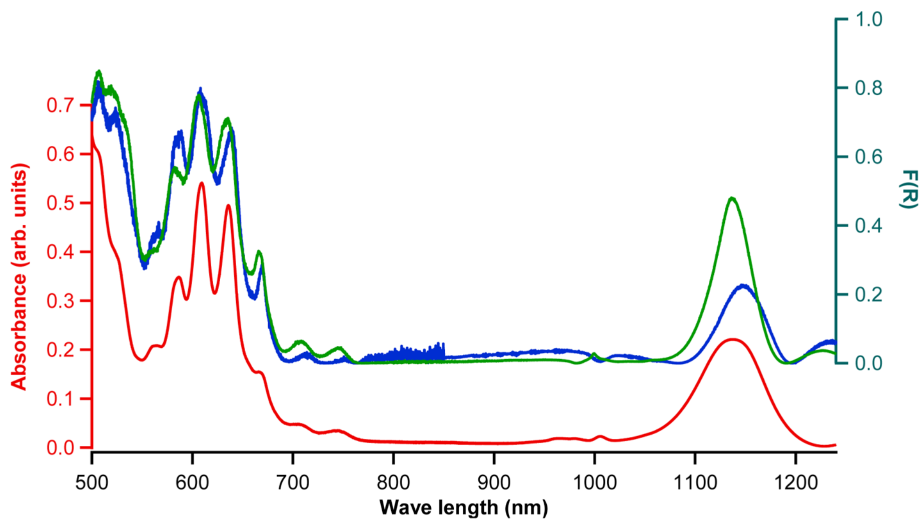

Figure 4. Vis/nIR absorption spectrum of $\{NpO_2\}^{2+}$ and PW_9 in a pH 7.5 aqueous solution (**1**) (red, left axis) and vis/nIR diffuse reflectance spectra of both the crystalline product prepared from the addition of excess KCl to the complex formed between $\{NpO_2\}^{2+}$ and A-$[PW_9O_{34}]^{9-}$ (**2**) (green trace, right axis) and $(NH_4)_{13}[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 12H_2O$ (**3**) (blue trace, right axis). The trace of **3** was offset from the trace of **2** by 3.2-fold on the *y*-axis to allow for direct comparison.

neptunyl moiety in a manner different from that of the tri-lacunary anions discussed in this work.

Figure 4 compares the diffuse reflectance spectra of crystalline $(NH_4)_{13}[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 12H_2O$ (**3**) and Np^{VI}–PW_9–KCl (**2**) with the previously discussed solution spectrum of $\{NpO_2\}^{2+}$ with PW_9 (**1**). While subtle variations are observed in the relative intensities of the transitions observed in the visible region (550–700 nm), more significant differences in both relative intensities and peak energies are observed for the main 5f–5f transition in the nIR region of the spectra. The energy of this transition is almost identical for both the solution spectrum of $\{NpO_2\}^{2+}$ and PW_9 (**1**) and the solid spectrum of Np^{VI}–PW_9–KCl (**2**), observed at 1138 nm (8787 cm^{-1}) and 1136 nm (8803 cm^{-1}), respectively. This could be indicative of very similar anionic cluster structures for these solution state and solid state species. In contrast, the 5f–5f transition energy is significantly different for $(NH_4)_{13}[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 12H_2O$ (**3**) (1147 nm, 8718 cm^{-1}), indicating that the structure observed for $[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{13-}$ (with partial occupancy $\{NpO_2\}^{2+}/NH_4^+$) is not replicated in either **1** or **2**.

During the course of the vis/nIR studies, it should also be noted that a trace $\{NpO_2\}^+$ impurity was useful in determining complete complexation of $\{NpO_2\}^{2+}$ with tri-lacunary hetero-polyoxotungstate anions. The dominant $\{NpO_2\}^+$ 5f–5f transition comes at 980 nm (10200 cm^{-1}) for $[NpO_2(OH_2)_5]^+$ and decreases in energy upon complexation by "PW_9".[13] By following the disappearance of this 980 nm transition and the appearance of a transition around 1000–1010 nm (10000–9900 cm^{-1}), we can assume all the $\{NpO_2\}^+$ can be complexed by A-type tri-lacunary anions. Typically, $\{NpO_2\}^{2+}$ forms stronger complexes with equatorial ligands

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than $\{NpO_2\}^{+}$,[1b,e] and thus by inference, complete complexation of Np^{V} is indicative of complete complexation of Np^{VI}. This is clearly seen in the solid state diffuse reflectance spectrum of the Np^{VI}–PW_9–KCl complex (**2**) (see Figure 1 of the Supporting Information). Also, the presence of a lower Np oxidation state, Np^{V}, makes it highly unlikely that the distinctive Np^{VI} spectroscopic features described here are actually due to the presence of Np^{VII}. Np^{VII} is stabilized in only highly oxidizing environments.[31]

Using a sample of the same $\{NpO_2\}^{2+}$ and PW_9 solution from which the vis/nIR spectrum shown in Figure 3 was obtained (**1**) (i.e., with Na^{+} being the dominant cation in solution), we recorded the ^{31}P NMR spectrum. Unfortunately, the results were inconclusive (see Figure 2 of the Supporting Information). However, the solid state vibrational spectra (IR/Raman) of Np^{VI}–PW_9–KCl (**2**) crystallized from that same parent solution (**1**) were more informative and are shown in Figure 5. Focusing first on the IR spectrum, we found

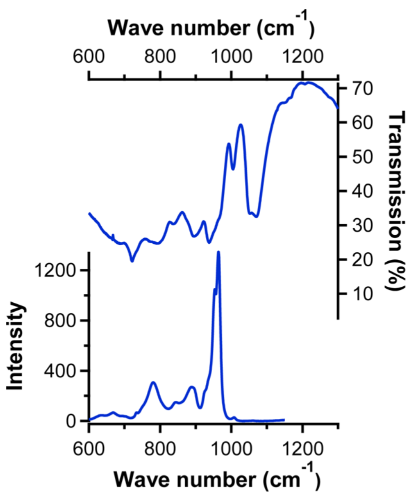

Figure 5. Raman (left axis) and IR (right axis) spectra of the crystalline Np^{VI}–PW_9–KCl complex (**2**).

complexation could not be probed by monitoring the changes in the $\{NpO_2\}^{2+}$ asymmetric stretch {observed previously at 964 and 919 cm^{-1} for $[NpO_2(H_2O)_5]^{2+}$ and $Cs_2Np^{VI}O_2Cl_4$, respectively}.[32,33] This region is obscured by the large W–O stretching range (700–1010 cm^{-1}) of the ligand.[34] The P–O asymmetric stretch is split into two overlapping bands at 1070 and 1051 cm^{-1}, comparable to the bands at 1063 and 1057 cm^{-1}, respectively, observed for $Na_{14}[Na_2(Np^{V}O_2)_2(A\text{-}PW_9O_{34})_2]\cdot 15H_2O$.[35] Taken as a fingerprint, the IR spectrum of **2** between 600 and 1100 cm^{-1} is almost identical to that of $Na_{12}[Na_2(UO_2)_2(A\text{-}PW_9O_{34})_2]\cdot 42H_2O$, in which two Na^{+} cations and two $\{UO_2\}^{2+}$ moieties are encapsulated by two "PW_9" ligands (a 2:2:2 complex), and is distinct from the previously reported spectrum of $K_{12}[K_2(UO_2)_2(A\text{-}PW_9O_{34})_2]\cdot xH_2O$.[7] This indicates that $[K_2(NpO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$ is not crystallized from solution in the presence of K^{+}, and this is therefore not the anion in **2**. Rather, the solid state product could contain $[Na_2(NpO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$.

The Raman spectrum of Np^{VI}–PW_9–KCl (**2**) contains transitions at 964 and 953 cm^{-1} that are assigned to $\nu_s(W\text{–}O_t)$ and $\nu_{as}(W\text{–}O_t)$, respectively, and 889 and 850 cm^{-1} that are assigned to $\nu_{as}(W\text{–}O_b)$.[34] This leaves a peak at 781 cm^{-1} that is assigned to the $\nu_1\{NpO_2\}^{2+}$ symmetric stretch and comes at an energy significantly lower than that previously observed for $Cs_2NpO_2Cl_4$ (802 cm^{-1}), $Na_{14}[Na_2(Np^{VI}O_2)_2(GeW_9O_{34})_2]\cdot 36H_2O$ (814 cm^{-1}), $[Np^{VI}O_2(H_2O)_5]^{2+}$ (856 cm^{-1}), or $NpO_2(IO_3)(H_2O)$ (872 cm^{-1}).[14,21,33,36] This comparatively low-energy transition could be indicative of weaker neptunyl(VI) bonds in this complex, with an even lower-energy $\nu_1\{NpO_2\}^{2+}$ transition also recently reported for $[Co(NH_3)_6]_2[NpO_2(OH)_4]_3\cdot H_2O$ (741 cm^{-1}).[37] This $\nu_1\{NpO_2\}^{2+}$ symmetric stretch is comparable to the average vibronic splitting of the bands in the visible diffuse reflectance spectrum of **2**, ~700 cm^{-1} (Figure 4).

■ CONCLUSIONS

Many studies have indicated the differences in redox and complex stability between actinyl cations of different elements (U, Np, Pu, and Am) and oxidation states (V and VI). To date, reports of actinyl complexation by A-type tri-lacunary heteropolyoxotungstate anions ($[PW_9O_{34}]^{9-}$, $[AsW_9O_{34}]^{9-}$, $[GeW_9O_{34}]^{10-}$, and $[SiW_9O_{34}]^{10-}$) have shown almost identical coordination environments around the actinide. In fact, the presence of different counter cations (Na^{+}, K^{+}, and NH_4^{+}) has been the key factor in determining subtle (but significant) structural variation, not the variation in actinyl cation ($\{UO_2\}^{2+}$, $\{NpO_2\}^{+}$, $\{NpO_2\}^{2+}$, or $\{PuO_2\}^{2+}$). Thus, previous studies involving $\{UO_2\}^{2+}$ lead to the expectation that the reaction between $Na_8H[A\text{-}\beta\text{-}PW_9O_{34}]\cdot 20H_2O$ and $\{NpO_2\}^{2+}(aq)$ would produce $[Na_2(NpO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$ in an aqueous solution, and $[(X)_2(NpO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$ after addition of XCl (where X = K or NH_4). However, in this study, after the addition of NH_4Cl, a complex still containing trapped Na^{+}, $(NH_4)_{13}[Na(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 12H_2O$ (**3**), was structurally characterized. Clearly, $\{NpO_2\}^{2+}$ is exhibiting behavior different from that of $\{UO_2\}^{2+}$ in this ligand environment, trapping Na^{+} more effectively in the anionic clusters formed. Complementary spectroscopic studies, notably UV/vis/nIR and IR, provide evidence of other subtle differences in PW_9–$\{NpO_2\}^{2+}$ versus PW_9–$\{UO_2\}^{2+}$ anionic cluster structures in the presence of PW_9 and $K^{+}/NH_4^{+}/Na^{+}$. Therefore, even in the presence of coordinating heteropolyoxotungstate anions that trap actinyl cations in nearly identical seven-coordinate distorted pentagonal bipyramidal geometries, switching from one actinide element to another (U to Np) can lead to different structures. This work thus provides further evidence that understanding actinyl chemistry requires experimental studies for all the actinyl (VI/V) cations, not just uranyl(VI).

■ ASSOCIATED CONTENT

Supporting Information

Additional figures and references and two CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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