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2.2.2-Cryptand Complexes of Neptunium(III) and Plutonium(III)

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New coordination environments are reported for Np(III) and Pu(III) based on pilot studies of U(III) in 2.2.2-cryptand (crypt). The U(III)-in-crypt complex, [U(crypt)₂][I], obtained from the reaction between U₄I₃ and crypt, is treated with Me₃SiOTf (OTf = O₃SCF₃) in benzene to form the [U(crypt)(OTf)₂][OTf] complex. Similarly, the isomorphous Np(III) and Pu(III) complexes were obtained by addition of crypt to AnI₃(THF)₄. All three An(III)-in-crypt complexes (1-An; An = U, Np, Pu) contain an encapsulated actinide in a THF-soluble complex. Absorption spectroscopy and DFT calculations are consistent with 5f³ U(III), 5f⁴ Np(III), and 5f⁵ Pu(III) electron configurations.

Expanding the coordination chemistry of the transuranium metals can achieve a better understanding of the chemistry of the actinide series.¹ The limited availability of transuranium isotopes to basic research laboratories coupled with their radiological hazards limits the reaction scales and scientific breadth. In contrast, thorium and uranium chemistry is better developed than the rest of the actinide series.^{1d, 2} The number of Np and Pu structures in the Cambridge Structural Database together is less than 7% the number of uranium structures.³ Defining new coordination environments for the transuranium elements by X-ray crystallography is facilitated by high yield reactions that generate single crystals in a short time period. Ideally, reactions will originate from readily available

transuranium starting materials, and they must be conducted within the bounds of certain practical/safety restrictions that can limit solvent and reagent choice. Described here is such a reaction system using the 2.2.2-cryptand (crypt) ligand, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

The crypt ligand is a polydentate bicyclic molecule with six oxygen and two nitrogen donor atoms.⁴ It has been used extensively to encapsulate many types of metal ions,⁴⁻⁵ but it is mostly known for its high affinity for potassium and other alkali and alkaline earth metals. Recently, crypt has been used with Ln(II) ions⁶ (Ln = lanthanide), but the application of this ligand system to the coordination chemistry of the actinides has been less studied.^{6h,7} Spectroscopic and elemental analytical data on U(IV) and U(VI) crypt complexes have been reported in the literature as early as 1976,^{6h, 7a, 7d-f} but the first X-ray crystal structures of uranium crypt complexes were only recently reported in 2018 on the U(III) complexes [U(crypt)₂][I], [U(crypt)(OH₂)][I]₂, and [U(crypt)I(OH₂)][I][BPh₄].^{7c} Additional crystallographic data were subsequently reported on [U(crypt)(MeCN)I][I]₂ and [U(crypt)(OH₂)₂][I]₃·2MeCN.^{7b} X-ray crystallographic data on [U(crypt)I][I]₂ also have been obtained as part of this study (see Supporting Information).

Although these iodide complexes established the structural details of U(III)-in-crypt, they were only soluble in DMF and MeCN, which limited the utility of this encapsulating ligand environment for developing further actinide reaction chemistry. The closest encapsulating ligands in Np and Pu literature involved 18-crown-6 (crown).⁸ However, these typically featured high-valent actinyl AnO₂ⁿ⁺ centers or counter-anions such as [ClO₄]⁻ that diminished the solubility necessary for more extensive investigation of reactivity.^{8b} However, studies of Ln-in-crypt complexes revealed that triflate counter-anions were useful in increasing the solubility of 4f element crypt compounds.^{6g, 7b} In addition, triflates were used as ancillary ligands for an electrochemical study of the effect of crypt on redox potentials of in situ generated putative Cf complexes.^{6g}

We describe the isolation of a THF-soluble U(III)-in-crypt triflate complex that can be generated and crystallized quickly on a small scale such that the synthesis is viable for analogous Np(III) and Pu(III) complexes. This has provided Np and Pu in the polydentate coordination environment of crypt for the first time. Previous

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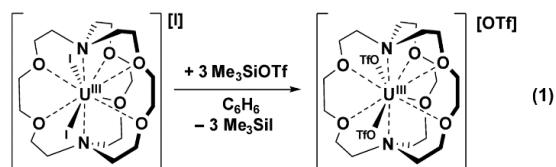
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attempts to synthesize a THF soluble U(III)-in-crypt complex involved the reaction of a solution of KOTf with the THF-insoluble brown-green complex $[\text{U}(\text{crypt})_2][\text{I}]$.^{7c} This generated a green solution that upon workup was found to be $[\text{U}(\text{crypt})(\text{OTf})_2][\text{OTf}]$, **1-U**. While this method provided a route to yield single crystals of **1-U**, it was difficult to isolate analytically pure material and the crystals grew slowly. As such, this route was not optimal for Np and Pu analogs and an alternative synthesis using Me_3SiOTf as the triflate ligand source was explored.



In an inert atmosphere argon glovebox, Me_3SiOTf reacts with $[\text{U}(\text{crypt})_2][\text{I}]$ as a suspension in benzene to form a green oil that, upon workup and recrystallization from THF/ Et_2O , quickly gives pure single crystals of green **1-U**, eq 1, in 66% yield on a 100 mg scale. Various small-scale (11 mg) recrystallizations of crude **1-U** were examined but the THF/ Et_2O combinations provided the best single crystals and thus optimal conditions for Np and Pu.

Indeed, these small-scale optimizations were then successfully extended to Np and Pu using $[\text{An}(\text{THF})_4]$ starting materials that were obtained by converting $[\text{AnCl}_4(\text{DME})_2]$ to $[\text{An}(\text{THF})_4]$.⁹ In an inert atmosphere, negative pressure helium atmosphere glovebox, a 15 mg sample of orange-colored $[\text{Np}(\text{THF})_4]$ reacts with crypt in THF to form a yellow suspension that is presumed to be the analog of $[\text{U}(\text{crypt})_2][\text{I}]$ in eq 1. A suspension of this yellow material in benzene reacts with Me_3SiOTf to form a yellow powder that dissolves in THF, eq 2. Recrystallization from THF/ Et_2O produced pale blue plates of $[\text{Np}(\text{crypt})(\text{OTf})_2][\text{OTf}]$, **1-Np**, identified by X-ray crystallography, in 79% yield based on the $[\text{Np}(\text{THF})_4]$ starting material, Figure 1.

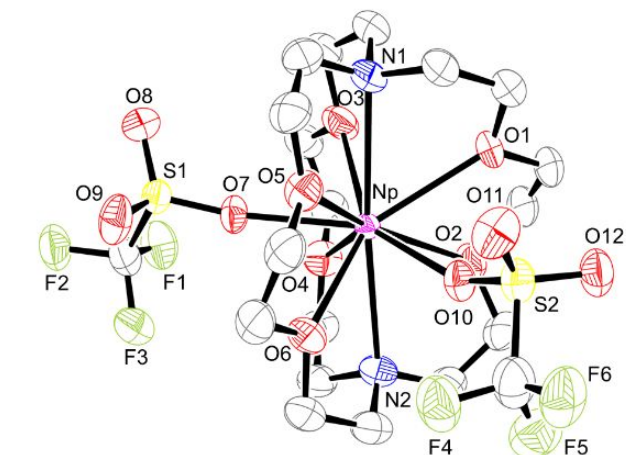
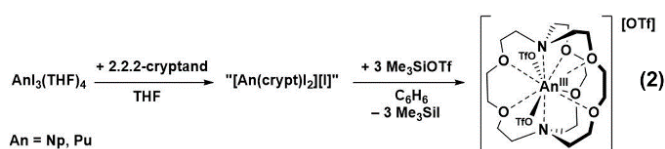


Figure 1. Representation of **1-Np** with atomic displacement parameters drawn at the 30% probability level. Hydrogen atoms and are omitted for clarity, as is the non-coordinating triflate anion. **1-U** is isomorphous.

Similarly, 25 mg of the cream-colored $[\text{Pu}(\text{THF})_4]$ reacted with crypt in THF to form a cream-colored precipitate that then reacts with Me_3SiOTf in benzene to form $[\text{Pu}(\text{crypt})(\text{OTf})_2][\text{OTf}]$, **1-Pu**, as pale lilac plates in 14% yield, Figure 2, eq 2. The lower yield for Pu is probably due the difficulties in obtaining single crystals of **1-Pu** of X-ray diffraction quality, which required multiple recrystallizations.

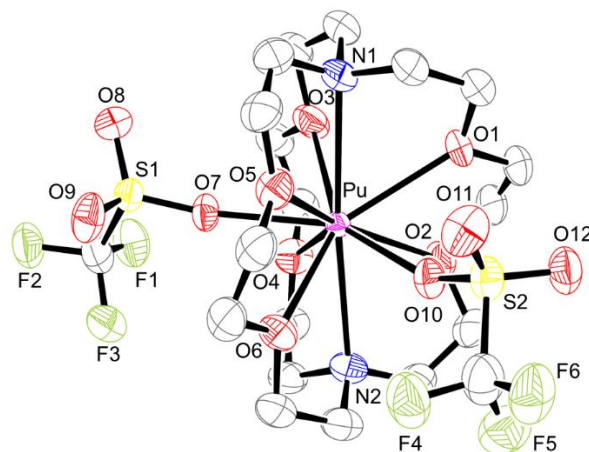


Figure 2. Representation of **1-Pu** with atomic displacement parameters drawn at the 30% probability level. Hydrogen atoms are omitted for clarity, as is the non-coordinating triflate anion.

Structural data on **1-U**, **1-Np**, and **1-Pu** are presented in Table 1. The complexes crystallize in the $P\bar{1}$ space group and are isomorphous. Each structure contains an $[\text{An}(\text{crypt})(\text{OTf})_2]^{1+}$ cation that approximates to a 10-coordinate tetra-capped trigonal prism with the nitrogen donors capping both trigonal faces and the triflate oxygens capping two of the rectangular faces. A third triflate anion is present and well separated from the $[\text{An}(\text{crypt})(\text{OTf})_2]^{1+}$ cations. There are three formula units within the asymmetric unit that give a wide range of distances in Table 1. Hence, for **1-Pu** as a representative example, the Pu–O(OTf) range (2.439(9)–2.512(9) Å) is for six bond distances. These Pu–O distances to the triflate anions are shorter than the range of Pu–O(crypt) distances (2.565(12)–2.677(13) Å) to the neutral oxygen donor sites of the crypt. The range of Pu–N(crypt) distances in **1-Pu** (2.731(14)–2.83(2) Å) is the largest of the **1-An** series, containing both the shortest and longest An–N bonds.

Table 1. Selected bond distances [Å] in $[\text{An}(\text{crypt})(\text{OTf})_2][\text{OTf}]$, **1-An**.

	An–O(OTf)	An–O(crypt)	An–N(crypt)
1-U	2.454(4) – 2.518(4)	2.566(4) – 2.677(4)	2.754(5) – 2.809(5)
1-Np	2.427(9) – 2.512(9)	2.570(11) – 2.659(13)	2.734(14) – 2.775(17)
1-Pu	2.439(9) – 2.512(9)	2.565(12) – 2.677(13)	2.731(14) – 2.834(17)

There is some overlap between the bond distance ranges in **1-An**, but the small differences from **1-U** to **1-Np** to **1-Pu** are reasonable based on the small decreases in ionic radii from U to Np to Pu.¹⁰ There is no clear evidence of the expected trend of bond shortening due to increased charge density from U^{3+} to Np^{3+} to Pu^{3+} .

This could simply be due to the magnitude of error values in our data associated with the individual metal-ligand distances to relatively light O and N atoms, along with the wide spread of values precluding useful comparison of average values (large standard deviation). Higher resolution data may have revealed a trend. Unfortunately, the paucity single-crystal X-ray structural data across homologous trivalent series, extending from U–Pu, with neutral O-donor ligands provides limited contextualization of the **1-An** data. However, the trivalent halide series $[\text{AnI}_3(\text{THF})_4]$ (An = U, Np, Pu), where there is just a single molecule per asymmetric unit, do show An–O_(THF) bond length shortening from U to Np to Pu, though also exhibiting a wide range of values for each metal (e.g. An–O bond lengths for An = U, 2.502(5)–2.563(5) Å; Np, 2.481(5)–2.550(5) Å; Pu, 2.445(3)–2.521(4) Å) but with 3 σ overlap between the shortest U–O and Np–O distances.¹¹ The nine-coordinate tricapped trigonal prismatic $[\text{An}(\text{H}_2\text{O})_9]^{3+}$ structures have An–O_(prismatic) distances that decrease more consistently than the An–O_(capping) distances, but still with some An–O distances exhibiting overlap (between next-neighbor elements) applying a 3 σ error analysis confidence level of statistical significance.¹² These comparisons highlight the difficulty in unambiguously observing decreasing An³⁺-ligand (An = U, Np, Pu) distances with relatively light atom donors.

The ¹⁹F NMR resonances of **1-U** (–79.93 ppm), **1-Np** (–82.22 ppm), and **1-Pu** (–79.77 ppm) in THF-*d*₈ all show a single resonance that indicates that the triflate anions are equivalent in solution presumably due to rapid exchange on the NMR timescale. They are only slightly shifted from that of KOTf at –79.54 ppm. Similarly, the ¹H NMR spectra of **1-Np** and **1-Pu** each show just a single set of three resonances assigned to the crypt ligand: **1-Np**, 10.85, 6.12, and 1.14 ppm; **1-Pu**, 4.29, 4.05, and 3.23 ppm, indicating that in solution it is in a symmetric environment in contrast to the solid-state structures that contain two coordinated OTf anions, and thus don't C₃ symmetry. These ¹H NMR resonances are shifted slightly from the values for free crypt at 3.60, 3.52, and 2.57 ppm. These small shifts are consistent with other NMR spectra of Np(III) and Pu(III).^{9, 13} The room temperature ¹H NMR spectrum of **1-U** in THF-*d*₈ has a single discernible broad signal at –8.25 ppm within a window of 300 ppm to –150 ppm. This differs from the ¹H NMR spectrum of $[\text{U}(\text{crypt})_2][\text{I}]$ in MeCN-*d*₃ which contains resonances at 8.39, 6.86 and 5.97 ppm. The broad resonance of **1-U** splits into several broad resonances at 260 K, but a clearly resolved three-line spectrum was not obtained down to 245 K.

The experimental solution UV-vis-NIR spectra of the **1-An** compounds are shown in Figure 3 (black lines) alongside TDDFT simulated spectra (see below). Each complex has numerous weak transitions at low energy in the f-f transition region (ca. 7,000–

15,000 cm^{–1}; 700–1400 nm) and large absorptions at energies over 20,000 cm^{–1} (500 nm) that extend into the UV region which are plausibly charge transfer bands or 5f→6d transitions. Electronic structure calculations on the $[\text{An}(\text{crypt})(\text{OTf})_2]^{1+}$ complexes were carried out at the density functional level of theory using the TPSSH¹⁴ functional with Grimme's D3 dispersion correction¹⁵ in C₁ symmetry to evaluate the ground state nature of these complexes and their UV-visible spectra. All calculations were carried out with the TURBOMOLE program suite, Version V-7.5.¹⁶ The calculations indicated quartet 5f³, quintet 5f⁴, and sextet 5f⁵ ground state configurations for $[\text{U}(\text{crypt})(\text{OTf})_2]^{1+}$, $[\text{Np}(\text{crypt})(\text{OTf})_2]^{1+}$, and $[\text{Pu}(\text{crypt})(\text{OTf})_2]^{1+}$, respectively. The calculated average An–O and An–N bond distances are within 0.02 Å of the experimental values in $[\text{An}(\text{crypt})(\text{OTf})_2][\text{OTf}]$.

TDDFT calculations of the simulated UV-vis-NIR spectra are shown in Figure 3 (green lines). For all three complexes $[\text{U}(\text{crypt})(\text{OTf})_2]^{1+}$, $[\text{Np}(\text{crypt})(\text{OTf})_2]^{1+}$, and $[\text{Pu}(\text{crypt})(\text{OTf})_2]^{1+}$, the calculations indicate that there are very weak 5f→5f transitions in the 7,000–20,000 cm^{–1} region and intense 5f→6d transitions at energies over 20,000 cm^{–1}. Although scalar relativistic DFT calculations do not provide accurate estimates of intensity and splitting patterns of these 5f→5f transitions, the overall match of the UV-visible spectra in the 5f→6d region and the absence of 6d→7p transitions (characteristic of divalent actinide compounds with 6d¹ ground states)¹⁷ supports the assignment of 5fⁿ ground states with no 6d occupation. The onset of 5f→6d transitions occurs at higher energies in the order U < Np < Pu, in keeping with the increasing stabilization of the 5f manifold relative to the 6d orbitals as the actinide series is traversed from U to Np to Pu. Since TDDFT excitation calculations are susceptible to spurious charge transfer excitations from weakly bound anions, the spectra also were modelled with triflate-free cations $[\text{An}(\text{crypt})]^{3+}$. However, the $[\text{An}(\text{crypt})(\text{OTf})_2]^{1+}$ calculations provided the better match, and are shown here, but the calculations for $[\text{An}(\text{crypt})]^{3+}$ are included in the Supporting Information for comparison.

In summary, the coordination chemistry of 2.2.2-cryptand has been expanded to Np(III) and Pu(III) through methods initially found to be successful for U(III). The U(III)-in-crypt complex, $[\text{U}(\text{crypt})_2][\text{I}]$, reacts with Me₃SiOTf to generate $[\text{U}(\text{crypt})(\text{OTf})_2][\text{OTf}]$. Using analogous procedures, crystallographically characterizable $[\text{An}(\text{crypt})(\text{OTf})_2][\text{OTf}]$ complexes of Np and Pu could be prepared and isolated. The transuranic complexes are isomorphous with the U analog and all are THF-soluble. The solubility provides the opportunity to use this encapsulating coordination environment for further development of transuranium chemistry. DFT calculations reveal 5fⁿ ground-state electronic configurations in accord with that expected for trivalent ions. TDDFT performed on $[\text{An}(\text{crypt})(\text{OTf})_2]^{1+}$ show UV-vis-NIR

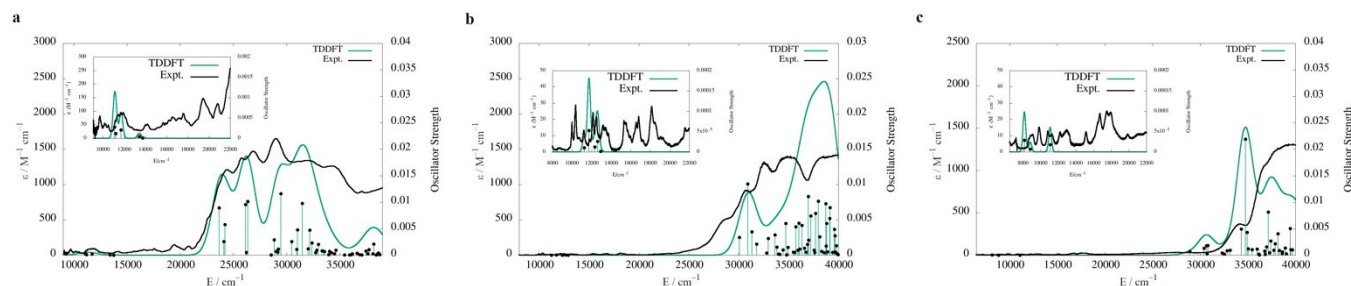


Figure 3. Black lines show solution UV-Vis-NIR spectra of a) $[\text{U}(\text{crypt})(\text{OTf})_2][\text{OTf}]$ (**1-U**) (5 mM), b) **1-Np** (1.89 mM), and c) **1-Pu** (2.05 mM) in THF at ambient temperature. Green lines show simulated UV-Vis-NIR spectra of a) $[\text{U}(\text{crypt})(\text{OTf})_2]^{1+}$, b) $[\text{Np}(\text{crypt})(\text{OTf})_2]^{1+}$, and c) $[\text{Pu}(\text{crypt})(\text{OTf})_2]^{1+}$ with computed TDDFT oscillator

strengths shown as vertical lines. The experimental spectrum is shown in black for comparison. A Gaussian line broadening of 0.10 eV was applied. The computed intensities were scaled (see SI for details) to ease comparison with the experiment spectrum.

features that agree well with the experimental spectra for all three metals. These combined theoretical/experimental results reveal a clear and simple physical manifestation of increased 5f-6d energetic separation across the series from U to Np to Pu whereby the onset of 5f→6d transitions occurs at higher energies for Pu, than U. The degree to which this affects the chemical reactivity of these molecules is an area of ongoing research

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