

## Electronic Supplementary Information

# Synthesis and characterization of $\text{NpCl}_4(\text{DME})_2$ and $\text{PuCl}_4(\text{DME})_2$ neutral transuranic An(IV) starting materials

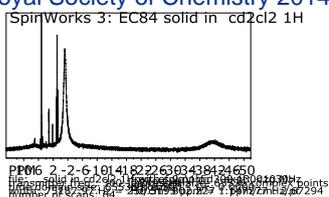
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**Additional Experimental Details:** *Caution! All plutonium chemistry (weapons grade isotopic composition, obtained from internal sources at Los Alamos National Laboratory) and neptunium chemistry (using the  $^{237}\text{Np}$  isotope) was conducted inside specialist radiological facilities designed for the safe handling and manipulation of high specific-activity  $\alpha$ -particle emitting radionuclides.*

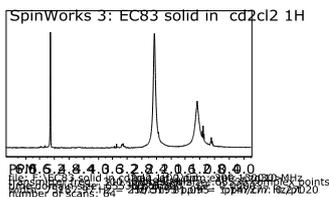
*Synthetic note for 1:* As outlined in the experimental write-up in the communication, an oxidation state pure Np(IV) solution was obtained through addition of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  as a reductant to a Np/HCl acidic stock solution that contained a mixture of IV and VI oxidation states. Although not fully understood, we found that isolation of **1** in the stated yield was best facilitated when employing the minimum amount of reductant necessary to condition the stock solution to pure Np(IV), which was usually just over 2 equiv based upon the amount of Np(V) present. In cases where a large excess of reductant was utilized to attempt to expedite the process, subsequent work-up of the reaction solution and isolation of the product was problematic. It was also determined that addition of excess  $\text{Me}_3\text{SiCl}$  was important for product isolation to proceed smoothly. In cases where the above two conditions were not met, formation of a pink viscous oil could occur which thwarted subsequent product isolation efforts.

Solution electronic absorption spectra were collected in quartz cuvettes at room temperature using a Varian Cary 6000i UV-vis-NIR spectrophotometer with a 0.3 nm spectral bandwidth. Generally, 2 to 4 milligrams of compound were dissolved in approximately 0.75 to 1.5 mL of solvent. Solid diffuse reflectance spectra were collected using a Varian Cary 6000i with installed Internal Diffuse Reflectance Accessory. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer.  $^1\text{H}$  NMR spectra were referenced using the residual protio solvent peaks as internal standards).  $^{31}\text{P}\{1\text{H}\}$  NMR spectra were referenced to external 85%  $\text{H}_3\text{PO}_4$ . All solvents used were dried over a mixture of 3 Å and 4 Å sieves whilst being stored inside a helium atmosphere drybox.

**Single-crystal X-ray Diffraction Collection Details.** Pu and Np containing single crystals were coated in paratone-N oil and mounted inside a 0.5 mm capillary tube, which was sealed with hot capillary wax. The sealed capillary was coated with a thin film of acrylic in ethyl acetate (Hard as Nails<sup>®</sup>) to provide structural integrity and additional containment. The capillary was placed on a Bruker Platform diffractometer with 1k CCD, and cooled to 140 K using a Bruker Kryoflex cryostat. The instrument was equipped with a sealed, graphite monochromatized  $\text{MoK}\alpha$  X-ray source ( $\lambda = 0.71073$  Å). Data collection and initial indexing and cell refinement were handled using SMART software (version 5.632, 2005, Bruker AXS, Inc., Madison, Wisconsin 53719). Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software (version 6.45, 2003, Bruker AXS, Inc., Madison, Wisconsin 53719). The data were corrected for absorption using the SADABS program (version 2.05, 2002, George Sheldrick, University of Göttingen, Germany). Decay of reflection intensity was monitored *via* analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. Hydrogen atoms were idealized. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, and materials for publication were performed using SHELXTL Version 6.10, 2001, Bruker AXS, Inc., Madison, Wisconsin 53719).



**Figure S1.**  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2$  solution. The two broad resonances are attributed to coordinated DME. All the other resonances are readily attributed to residual protio solvent resonances.



**Figure S2.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_2\text{Cl}_2$  solution. The two broad resonances are attributed to coordinated DME. All the other resonances are readily attributed to residual protio solvent resonances.



