Divergent Stabilities of Tetravalent Cerium, Uranium, and Neptunium Imidophosphorane Complexes

Kaitlyn S. Otte,+[a] Julie E. Niklas,+[a] Chad M. Studvick,[c] Andrew C. Boggiano,[a] John Bacsa,[a] Ivan A. Popov,*[c] and Henry S. La Pierre*[a][b]

[a]   Ms. K. S. Otte, Dr. J. E. Niklas, Mr. A. C. Boggiano, Dr. J. Bacsa, Prof. H. S. La Pierre
        School of Chemistry and Biochemistry
        Georgia Institute of Technology
        Atlanta, Georgia 30332-0400, United States
        E-mail: la_pierre@chemistry.gatech.edu
[b]   Prof. H. S. La Pierre
        Nuclear and Radiological Engineering Program
        Georgia Institute of Technology
        Atlanta, Georgia 30332-0400, United States
[c]   Mr. C. M. Studvick, Prof. I. A. Popov
        Department of Chemistry
        The University of Akron
        Akron, Ohio 44325-3601, United States
        E-mail: ipopov@uakron.edu

        Supporting information for this article is given via a link at the end of the document.

Abstract: The study of the redox chemistry of mid-actinides (U – Pu) has historically relied on cerium as a model, due to the accessibility of trivalent and tetravalent oxidation states for these ions. Recently, dramatic shifts of lanthanide 4+/3+ non-aqueous redox couples have been established within a homoleptic imidophosphorane ligand framework. Herein we extend the chemistry of the imidophosphorane ligand (NPC = [N=P^{t}Bu(pyrr)$_2$]$^-$; pyrr = pyrrolidinyl) to tetrahomoleptic NPC complexes of neptunium and cerium (**1-M, 2-M**, M = Np, Ce) and present comparative structural, electrochemical, and theoretical studies of these complexes. Large cathodic shifts in the M$^{4+/3+}$ (M = Ce, U, Np) couples underpin the stabilization of higher metal oxidation states owing to the strongly donating nature of the NPC ligands, providing access to the U$^{5+/4+}$, U$^{6+/5+}$, and to an unprecedented, well-behaved Np$^{5+/4+}$ redox couple. The differences in the chemical redox properties of the U $vs.$ Ce and Np complexes are rationalized based on their redox potentials, degree of structural rearrangement upon reduction/oxidation, relative molecular orbital energies, and orbital composition analyses employing density functional theory.

Introduction

Ligand development has proved an invaluable tool in actinide chemistry and has afforded the isolation of many elusive oxidation states in actinide complexes. The accessible low oxidation states of the actinides have been redefined by novel coordination complexes which move the redox potentials of these unique species (Np^{2+}, Pu^{2+}, and U$^{2+,1+}$) into the solvent window.[1] A complementary ligand design approach has led to the development of ligand systems that induce substantial cathodic shifts of the metal redox couples and stabilize high-valent f-element complexes.[2] Due in no small part to the difficulty of working with radioactive elements with the exclusion of air, a detailed analysis of the ligand field effects on redox properties of transuranic complexes is absent, and there is limited data to compare to the studies of uranium redox chemistry.[3] Developing an understanding of the factors that govern actinide redox behaviors, especially in non-aqueous solutions, is critical in informing synthetic strategies to enable the characterization of unusual transuranic molecules.

Previously, we have demonstrated dramatic shifts in the Ce$^{4+/3+}$ couple to its most negative reported potentials through the use of imidophosphorane ("NP") ligands,[2f, 4] and have built on this redox control to stabilize high-valent actinides.[5] Herein we present the effects of a homoleptic NPC (NPC = [N=P^{t}Bu(pyrr)$_2$]$^-$; pyrr = pyrrolidinyl; where C indicates an alkyl substituent) ligand field on the redox properties of mid-valent actinides (U, Np) and Ce, and reveal the anomalous behavior of U and Np, particularly the remarkable inaccessibility of U^{3+}, a uniquely reducing Np^{3+} complex, and electrochemical access to the Np$^{5+/4+}$ couple. The NPC ligand facilitates greater stabilization of the higher-valent complexes than the previous iterations of NP ligands. These results demonstrate the effect of ligand architecture on redox properties and the resultant remapping of the accessible oxidation states of the mid-actinides in this homoleptic ligand field.
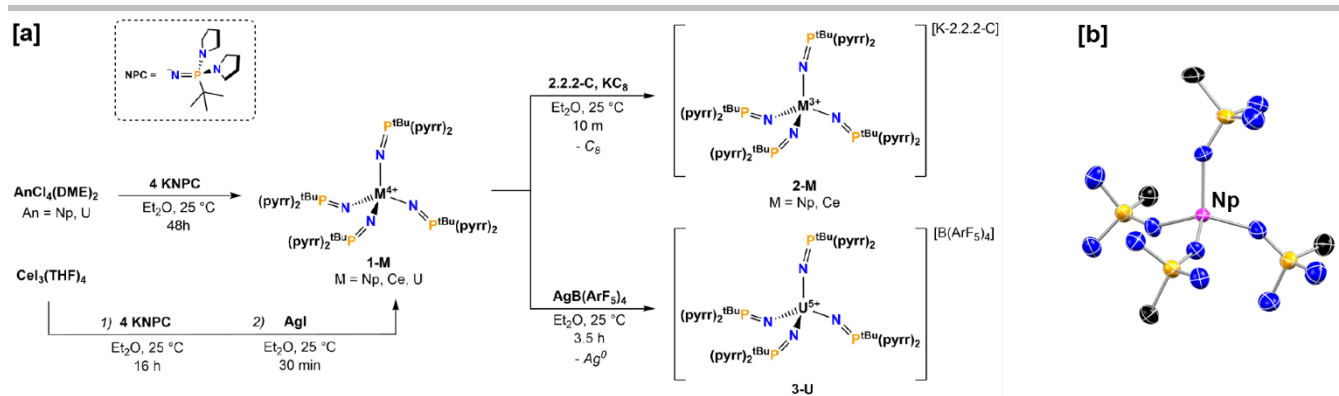
Figure 1. [a] Schematic of the synthesis of **1-Np**, **1-U**, **1-Ce**, **2-Np**, and **2-Ce**. **[b]** Truncated crystal structure (all H atoms and all C except quaternary ^{t}Bu removed for clarity) of **1-Np** with thermal ellipsoids (pink, Np; blue, N; black, C; orange, P) shown at 50%. Core structure is representative of all complexes.

Results and Discussion

We prepared a family of neutral, homoleptic, tetravalent U, Np, and Ce complexes supported by the NPC ligand, **1-U**,[5a] **1-Np**, and **1-Ce**, (**Figure 1**). **1-Ce** and **1-Np** can be reduced to their trivalent states with the resultant complexes (**2-Ce** and **2-Np**) supported by an outer sphere 2.2.2-cryptand, potassium cation, ([K(2.2.2-C)]$^{1+}$). Attempted reductions of **1-U** resulted in no reaction, and the use of U^{3+} starting materials yielded large crops of tetravalent **1-U** as the only isolable product after workup (see SI for further synthetic details). Complex **1-U** can be oxidized with AgB(ArF$_5$)$_4$ in THF to yield the tetrahedral U^{5+} complex, **3-U** (τ_4 = 0.95) (Figure S47). Further oxidation cannot be achieved with AgB(ArF$_5$)$_4$ (see SI for further synthetic details). The core structures of these homoleptic complexes are consistent across all oxidation states (**Figure 1**, **Table 1**, and Figures S43-S47). [6] **1-Np** and **1-Ce** are tetrahedral and isotypic with the previously reported **1-U** (average τ_4 = 0.95(3), Np; 0.94(4), Ce).[5a] Bond metrics across the three complexes are comparable and selected metrics are reported in **Table 1**. For trivalent **2-Np** and **2-Ce**, which crystallize as one [M^{3+}(NPC)$_4$] anion and one [K(2.2.2-C)] cation per asymmetric unit, the elongation of M–N distances are observed, consistent with one-electron reduction and an increase of the metal ionic radii. The pyrrolidinyl N-atom pyramidalization was examined for these complexes using the sum of angles (ΣN°), where ΣN° = 360° corresponds to planar N (more donating) and ΣN° ≤ 345° represents a significantly pyramidalized N atom (less donating). In NPC complexes, the two pyrrolidine substituents on each ligand are crystallographically unique and typically present divergent degrees of pyramidalization – two values are expected for each independent ligand. We note that **1-Ce/Np** follows the same trend observed for **1-U** (Figure S48), where these atoms' collective geometry remains largely planar. The trivalent species **2-Ce/Np**, however, each contains three ligands with one planar and one pyramidalized pyrrolidinyl N atom, and the fourth ligand consists exclusively of planar (Np) or near-planar (Ce) pyrrolidinyl N-atoms (**Table 1**). N-atom pyramidalization in this ligand set is therefore a reporter of metal oxidation state and differences in electronic structure.[5a, 7] When geometry and ligand field are conserved in these species, the more electron-deficient, higher-oxidation state complexes feature more planar N (indicating a more highly-electron-donating ligand), and more electron-rich complexes show increased pyramidalization, consistent with a less electron-donating ligand.

Table 1. Selected bond metrics of M^{n+}(NPC)$_4$ complexes (n = 3-5)

Complex	Distance (Å)		
	M—N	**P=N$_{im}$**	**ΣN°$_{planar}$/ ΣN°$_{pyram}$**
1-Ce	2.157(24)	1.531(1)	359.6(4)/342(6)
1-Np	2.156(22)	1.533(2)	358(2)/351(1)
1-U	2.167(25)	1.538(2)	357(2)/352(2)
2-Ce	2.315(23)	1.540(18)	359.6(4)/342(6)[a]
2-Np	2.291(10)	1.530(4)	359.7(4)/337(2)[a]
3-U	2.101(24)	1.565(12)	359.6(4)/345(2)

[a] For three ligands. Aver. ΣN° for fourth ligand = 358.8(5) (Np), and 353(3) (Ce).

Calculated bond metrics show good agreement for these complexes and are within 0.1% and 1.6% for M–N and N=P bonds (Tables S11-12). Density functional theory (DFT) corroborates the increasing effects of pyramidalization on reduction, particularly in the smaller ΣN°$_{pyram}$ values calculated for **2-M** relative to **1-M**, albeit to a lesser extent: Δ=8.7-11.2° (exp.) *vs.* Δ=3.0-3.5° (theor.). Mulliken spin density confirms metal-based reductions for all considered complexes, with metal centers acquiring 0.93-1.03 |e| upon reduction (Table S14). The electron gain is accompanied by the elongation of the M−N bond distances by ~0.11-0.13 Å (exp.)/0.13-0.16 Å (theor.), consistent with the (Ce/Np)$^{4+/3+}$ effective ionic radii.[8] This assignment also agrees with the presence of the additional metal f-dominant molecular orbital (MO) in **2-M** compared to **1-M** (Table S15). It is positioned as one of the highest occupied molecular orbitals (HOMOs) in **2-M**, which are appreciably separated from the frontier ligand-dominant occupied MOs by ~ 1.6-3.0 eV (**Table 2**, Figure S50).

Cyclic voltammetry studies of **1-M** (M = Ce, U, Np) were performed in 0.05 M [N(^{n}Bu)$_4$][BPh$_4$] in THF and referenced to Fc$^{+/0}$ (see SI for special considerations; all literature values discussed are vs Fc$^{+/0}$). Notably, only the reduction of **1-Ce** is observed electrochemically. Calculated potentials show that the electrochemical reductions of **1-Np** and **1-U** are shifted cathodically outside of the accessible solvent window. Most deviations between experimental and calculated redox potentials are within 0.05-0.16 V (**Figure 2**, **Table 3**), in accordance with the expected calculation errors.[9] The theoretical E$_{1/2}$ for the U$^{6+/5+}$ couple is overestimated by 0.29 V, underlining the challenge of implicit solvent models to account for the increased polarization that could compensate for the high charge of the most oxidized U^{6+} complex in a low dielectric solvent. The calculated

Table 2. α-MO energy levels € and orbital contribution from the metal (M) and ligand (L) for the $M^{n+}(NPC)_4$ complexes (M = Ce, Np, U; n = 3-6) calculated in THF. MO diagrams and additional orbital contributions are shown in Figures S50-S53 and Tables S15-S16.

	2-Ce	1-Ce	[1-U]⁻	1-U	3-U	[1-U]²⁺	2-Np	1-Np	[1-Np]⁺
LUMO	0.93	-1.08	1.08	0.02	-1.96	-3.17	1.08	-0.54	-2.73
M	71.0%	92.7%	23.5%	96.1%	97.6%	96.6%	22.2%	97.4%	96.8%
L	29.0%	7.3%	76.5%	3.9%	2.4%	3.4%	77.8%	2.6%	3.2%
HOMO	-3.06	-5.49	-1.52	-3.90	-5.97	-6.91	-2.55	-5.11	-6.17
M	98.2%	3.0%	96.7%	96.6%	84.3%	2.1%	97.7%	58.2%	5.0%
L	1.8%	97.0%	3.3%	3.4%	5.7%	97.9%	2.3%	41.8%	95.0%

vertical/adiabatic detachment energies (VDE/ADE) and vertical/adiabatic electron affinities (VEA/AEA) benchmark the degree of structural rearrangement associated with the redox processes (vertical, none; adiabatic, total). For **1-Ce**, the appreciable absolute differences ([VDE–ADE], 0.90 V and [VEA–AEA], 0.79 V) indicate substantial structural rearrangement, suggesting the irreversibility of the couple. In contrast, the [VDE–ADE] and [VEA–AEA] differences are much smaller for the quasi-reversible $Np^{5+/4+}$ (0.42 V and 0.49 V), $U^{5+/4+}$ (0.39 V and 0.50 V), and $U^{6+/5+}$ (0.31 V and 0.51 V) waves, indicating smaller structural changes.

The $Ce^{4+/3+}$ couple shares the same features as previously characterized imidophosphorane complexes,[2d, 2f] and is electrochemically irreversible. The reduction of **1-Ce** occurs at
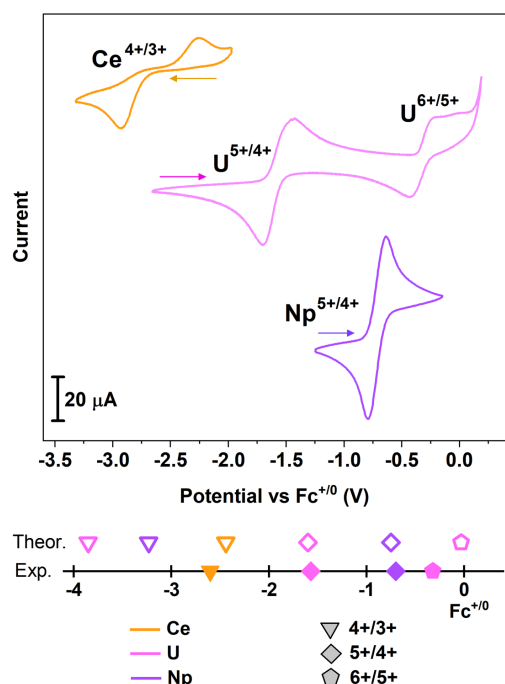
Figure 2. Cyclic voltammograms of **1-Ce**, **1-U**, and **1-Np** (~3 mM; 0.05 M TBABPh₄ in THF), and comparison of experimental and theoretical E₁/₂ values.

Table 3. Experimental and theoretical redox potentials (V vs Fc⁰/⁺)

	E₁/₂ (V)		Eₚₐ (V)			Eₚc (V)		
	Exp.	Theor.	Exp.	VDE	ADE	Exp.	VEA	AEA
Ce⁴⁺/Ce³⁺	-2.60	-2.44	-2.28	-1.49	-2.39	-2.91	-3.19	-2.4
Np⁴⁺/Np³⁺		-3.23		-2.50	-3.15		-3.68	-3.22
Np⁵⁺/Np⁴⁺	-0.70	-0.75	-0.62	-0.33	-0.75	-0.77	-1.24	-0.75
U⁴⁺/U³⁺		-3.85		-3.40	-3.85		-4.23	-3.85
U⁵⁺/U⁴⁺	-1.57	-1.72	-1.47	-1.47	-1.71	-1.67	-2.21	-1.71
U⁶⁺/U⁵⁺	-0.32	-0.03	-0.22	+0.28	-0.03	-0.42	-0.54	-0.03

E_{pc} = -2.91 V (E_{pa} = -2.28 V; ΔE_p = 0.63 V), rendering it the most negatively shifted $Ce^{4+/3+}$ couple reported, highlighting the stabilization afforded by this ligand. Reduction of **1-U** is not observed chemically or electrochemically, and the calculated $E_{1/2}$ of -3.85 V (AEA = -3.85; VEA = -4.23 V) places this event far outside of the solvent window, similar to $[U(pyNO)_4]$.[2a] This predicted potential is far more negative than reported $U^{4+/3+}$ couples for trivalent and tetravalent organouranium complexes (-0.94 V to -1.46 V, and -1.41 V to –2.23 V, respectively),[10] and is approximately 2.0 V more negative than that of $[U(N(TMS)_2)_4]$ (-2.05 V).[11] Remarkably, the reduction potential for **1-U** surpasses even those reported for $U^{3+/2+}$ couples (~ -2.45 V to -3.11 V).[1b, 10d] Both the $U^{5+/4+}$ and $U^{6+/5+}$ couples ($E_{1/2}$ = -1.57 V, -0.32 V, respectively) are observed for **1-U** and are quasireversible. Few comparable systems exist in which both of these couples are accessible—this generally requires higher coordination numbers and/or metal ligand multiple bonds (MLMBs).[2c, 12] Tetravalent **1-U** features redox couples that are markedly similar to those reported for pentavalent imido ($U^{6+/5+}$ = -0.42 V)[12a] and organouranium imido/ketimido complexes ($U^{5+/4+}$ = -1.21 V to -1.84 V; $U^{6+/5+}$ = +0.36 V to -0.34 V)[2c] which are stabilized significantly by covalent MLMB interactions. The readily accessible $U^{6+/5+}$ couple in **1-U** represents a highly-stabilized hexavalent state comparable to those of higher-valent, higher-coordinate, and MLMB complexes (-0.23 V to -1.51 V).[12b-d] Relative to similar complexes with monoanionic donors, including $U(NCyTMS)_4$ (-0.37 V), and $U[N(TMS)_2]_4$, (+0.49 V), the $U^{5+/4+}$ couple in **1-U** is cathodically shifted by ~-1.2 V and -2.1 V, respectively, though solvent and electrolyte differences complicate direct comparisons.[11, 13] The stabilization of the pentavalent state in [**1-U**]⁺ is confirmed synthetically, as the species **3-U** is chemically isolated as a tetrahomoleptic $[B(ArF_5)_4]^{1-}$ salt (Figure S47) featuring the expected contracted U−N distances relative to **1-U**.[5a, 13a] We note that isolable (pseudo)tetrahedral U^{5+} are quite rare.[13a] Additionally, comparison between **1-U** and $[U(N=P^tBu(pip)_2)_4]$ (pip = piperidinyl), reveals more cathodic redox potentials for **1-U** (Figure S31), further supporting the higher electron-donating capacity of $[N=P^tBu(pyrr)_2]^-$.[5a]

Strikingly, **1-Np** can be chemically reduced to **2-Np** unlike **1-U**, but the $Np^{4+/3+}$ couple is not electrochemically observable, with a calculated potential modestly outside the solvent window ($E_{1/2}$ = -3.23 V), consistent with previous theoretical analyses.[14] Experimentally determined nonaqueous $Np^{4+/3+}$ couples are scarce, but range from -0.68 V to -1.38 V for organoneptunium species,[10a, 15] and -1.85 V for $(Tren^{TIPS})Np^{4+}Cl$.[16] Trivalent **2-Np**

is an exceptionally potent reductant which readily reduces Teflon, and the deep brown crystalline material partially decomposes within a few days at -35 °C to the characteristic magenta crystals of **1-Np**. The $Np^{5+/4+}$ couple, however, is accessible ($E_{1/2}$ = -0.70, ΔE_p = 150 mV), and is shifted anodically from that of **1-U**, consistent with the expected trend in redox potentials across the actinide series.[17] This data agrees exceptionally well with the calculated $E_{1/2}$ potential (-0.75 V). This result is important, as there are currently no known Np^{5+} complexes that are not supported by MLMB interactions.[16, 18] Non-actinyl Np^{5+} complexes are notoriously difficult to stabilize, which significantly restricts the isolation and study of such molecular compounds.[16, 18] We also note that nonaqueous electrochemical measurements of transuranic species are still rare,[10a, 14-15, 16, 19] and this is to our knowledge the first non-aqueous measurement of a well-defined $Np^{5+/4+}$ couple. Recently, the irreversible oxidation of $(Tren^{TIPS})Np^{4+}Cl$ was putatively assigned at +0.86 V.[16] Given the trends observed with this ligand to cathodically shift redox potentials, non-actinyl Np^{5+} compounds are rational targets for NPC ligand systems.

The differences in redox behavior of **1-U/[1-U]⁻** *vs.* **1/2-(Np/Ce)** were further rationalized based on the MO compositions and their energy diagrams. The lowest unoccupied MOs (LUMOs) of the tetravalent species are all f-dominant (**Table 2**), consistent with metal-centered reductions of **1-M** (Table S14). However, significant differences are noted in their positions for **1-(Np/Ce)** *vs.* **1-U**. The LUMO of **1-U** (+0.02 eV) resides appreciably higher in energy, *i.e.*, by +1.10 eV and +0.56 eV from that of **1-Ce** and **1-Np** (**Table 2**, Figure S50). Qualitatively,[20] the relative positions of the LUMOs clearly indicate the following order in the capacity of these species to be reduced: **1-Ce>1-Np>1-U**. While the NPC ligand brings the U 5f-dominant LUMO level too high in energy in **1-U**, making trivalent **[1-U]⁻** inaccessible, the electron donating nature of this ligand provides ample support to higher oxidation states, up to U^{6+} inclusively. In the U^{5+} compound, **3-U**, the HOMO 5f-dominant orbital is decreased in energy by 2.07 eV (**Table 2**); however, it is still sufficiently separated from the frontier ligand-dominant MOs (-5.97 eV *vs.* -6.21 eV) to facilitate a subsequent metal-based oxidation to produce the U^{6+} species, **[1-U]²⁺** (Table S14).

Conclusion

This work reports the synthesis, electrochemical, and DFT studies of homoleptic NPC complexes of cerium, neptunium, and uranium. The cathodically shifted $M^{4+/3+}$ redox potentials afforded by this NPC ligand are rationalized by their relative LUMO energy values, which can therefore be instrumental in guiding the synthesis of similar f-element complexes. Stabilization of higher-valent actinides is particularly evident from the isolation of pentavalent **3-U**, and access to both the $U^{6+/5+}$ and $Np^{5+/4+}$ redox couples. The typically modest redox potentials of neptunium often place it at the fulcrum of thermodynamic dominance of the 4+ oxidation state in the early actinides and of the 3+ state in the mid-to-late actinides.[17, 21] The NPC ligand field not only pushes the $Np^{4+/3+}$ couple out of the electrochemical window, strongly

favoring Np^{4+} over Np^{3+}, but also brings the Np^{5+} oxidation state into the accessible anodic region. This homoleptic ligand field, in effect, shifts the conventional redox stabilities of the mid-actinides to redefine the readily accessible oxidation states.

Supporting Information

Acknowledgments

[1] a) M. R. MacDonald, M. E. Fieser, J. E. Bates, J. W. Ziller, F. Furche, W. J. Evans, *J. Am. Chem. Soc.* **2013**, *135*, 13310-13313; b) H. S. La Pierre, H. Kameo, D. P. Halter, F. W. Heinemann, K. Meyer, *Angew. Chem., Int. Ed.* **2014**, *53*, 7154-7157; c) C. J. Windorff, G. P. Chen, J. N. Cross, W. J. Evans, F. Furche, A. J. Gaunt, M. T. Janicke, S. A. Kozimor, B. L. Scott, *J Am Chem Soc* **2017**, *139*, 3970-3973; d) J. Su, C. J. Windorff, E. R. Batista, W. J. Evans, A. J. Gaunt, M. T. Janicke, S. A. Kozimor, B. L. Scott, D. H. Woen, P. Yang, *J. Am. Chem. Soc.* **2018**, *140*, 7425-7428; e) J.-N. Tian, M. Zheng, L. Li, G. Schreckenbach, Y.-R. Guo, Q.-J. Pan, *New J. Chem.* **2019**, *43*, 1469-1477; f) H.-B. Zhao, M. Zheng, G. Schreckenbach, Q.-J. Pan, *Dalton Trans.* **2018**, *47*, 2148-2151; g) A. J. Ryan, M. A. Angadol, J. W. Ziller, W. J. Evans, *Chem. Commun.* **2019**, *55*, 2325-2327; h) S. A. Moehring, W. J. Evans, *Chem. Eur. J.* **2020**, *26*, 1530-1534; i) S. Niu, H.-X. Cai, H.-B. Zhao, L. Li, Q.-J. Pan, *RSC Adv.* **2020**, *10*, 26880-26887; j) M. A. Boreen, J. Arnold, *Dalton Transactions* **2020**, *49*, 15124-15138; k) M. D. Straub, E. T. Ouellette, M. A. Boreen, R. D. Britt, K. Chakarawet, I. Douair, C. A. Gould, L. Maron, I. Del Rosal, D. Villarreal, S. G. Minasian, J. Arnold, *J. Am. Chem. Soc.* **2021**, *143*, 19748-19760; l) L. Barluzzi, S. R. Giblin, A. Mansikkamäki, R. A. Layfield, *J. Am. Chem. Soc.* **2022**, *144*, 18229-18233.

[2] a) A. McSkimming, J. Su, T. Cheisson, M. R. Gau, P. J. Carroll, E. R. Batista, P. Yang, E. J. Schelter, *Inorg. Chem.* **2018**, *57*, 4387-4394; b) J. A. Bogart, A. J. Lewis, S. A. Medling, N. A. Piro, P. J. Carroll, C. H. Booth, E. J. Schelter, *Inorg. Chem.* **2013**, *52*, 11600-11607; c) C. R. Graves, A. E. Vaughn, E. J. Schelter, B. L. Scott, J. D. Thompson, D. E. Morris, J. L. Kiplinger, *Inorg. Chem.* **2008**, *47*, 11879-11891; d) N. T. Rice, J. Su, T. P. Gompa, D. R. Russo, J. Telser, L. Palatinus, J.

Bacsa, P. Yang, E. R. Batista, H. S. La Pierre, *Inorg. Chem.* **2019**, *58*, 5289-5304; e) N. T. Rice, I. A. Popov, D. R. Russo, J. Bacsa, E. R. Batista, P. Yang, J. Telser, H. S. La Pierre, *J. Am. Chem. Soc.* **2019**, *141*, 13222-13233; f) N. T. Rice, I. A. Popov, D. R. Russo, T. P. Gompa, A. Ramanathan, J. Bacsa, E. R. Batista, P. Yang, H. S. La Pierre, *Chem. Sci.* **2020**, *11*, 6149-6159; g) N. T. Rice, I. A. Popov, R. K. Carlson, S. M. Greer, A. C. Boggiano, B. W. Stein, J. Bacsa, E. R. Batista, P. Yang, H. S. La Pierre, *Dalton Trans.* **2022**, *51*, 6696-6706; h) C. T. Palumbo, I. Zivkovic, R. Scopelliti, M. Mazzanti, *J. Am. Chem. Soc.* **2019**, *141*, 9827-9831; i) A. R. Willauer, C. T. Palumbo, F. Fadaei-Tirani, I. Zivkovic, I. Douair, L. Maron, M. Mazzanti, *J. Am. Chem. Soc.* **2020**, *142*, 5538-5542; j) A. R. Willauer, C. T. Palumbo, R. Scopelliti, I. Zivkovic, I. Douair, L. Maron, M. Mazzanti, *Angew. Chem. Int. Ed.* **2020**, *59*, 3549-3553; k) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Science* **2012**, *337*, 717-720.

[3] J. Riedhammer, D. P. Halter, K. Meyer, *Chemical Reviews* **2023**.

[4] N. T. Rice, J. Su, T. P. Gompa, D. R. Russo, J. Telser, L. Palatinus, J. Bacsa, P. Yang, E. R. Batista, H. S. La Pierre, *Inorg. Chem.* **2019**, *58*, 5289-5304.

[5] a) J. E. Niklas, C. M. Studvick, J. Bacsa, I. A. Popov, H. S. La Pierre, *Inorganic Chemistry* **2023**, *62*, 2304-2316; b) N. T. Rice, K. McCabe, J. Bacsa, L. Maron, H. S. La Pierre, *J. Am. Chem. Soc.* **2142**, 7368-7373.

[6] CCDC Deposition Numbers of Complexes: 1-Np, 2246290; 2-Np, 2246291; 1-Ce, 2246292; 2-Ce, 2246293; 3-U, 2246294. These supplementary crystallographic data (CIFs) for this paper are deposited to the CCDC and can 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.

[7] M. L. Clarke, G. L. Holliday, A. M. Z. Slawin, J. D. Woollins, *Journal of the Chemical Society, Dalton Transactions* **2002**, 1093-1103.

[8] R. D. Shannon, *Acta Crystallographica Section A* **1976**, *32*, 751-767.

[9] L. E. Roy, E. Jakubikova, M. G. Guthrie, E. R. Batista, *The Journal of Physical Chemistry A* **2009**, *113*, 6745-6750.

[10] a) D. C. Sonnenberger, J. G. Gaudiello, *Inorganic Chemistry* **1988**, *27*, 2747-2748; b) D. E. Morris, R. E. Da Re, K. C. Jantunen, I. Castro-Rodriguez, J. L. Kiplinger, *Organometallics* **2004**, *23*, 5142-5153; c) M. A. Boreen, D. J. Lussier, B. A. Skeel, T. D. Lohrey, F. A. Watt, D. K. Shuh, J. R. Long, S. Hohloch, J. Arnold, *Inorg. Chem.* **2019**, *58*, 16629-16641; d) J. C. Wedal, J. M. Barlow, J. W. Ziller, J. Y. Yang, W. J. Evans, *Chemical Science* **2021**, *12*, 8501-8511.

[11] A. J. Lewis, U. J. Williams, P. J. Carroll, E. J. Schelter, *Inorganic Chemistry* **2013**, *52*, 7326-7328.

[12] a) C. J. Burns, W. H. Smith, J. C. Huffman, A. P. Sattelberger, *J. Am. Chem. Soc.* **1990**, *112*, 3237-3239; b) S. T. Löffler, J. Hümmer, A. Scheurer, F. W. Heinemann, K. Meyer, *Chemical Science* **2022**; c) K. C. Mullane, A. J. Lewis, H. Yin, P. J. Carroll, E. J. Schelter, *Inorganic Chemistry* **2014**, *53*, 9129-9139; d) J. K. Gibson, W. A. de Jong, *Experimental and Theoretical Approaches to Actinide Chemistry*, Wiley, **2018**.

[13] a) A. M. Tondreau, T. J. Duignan, B. W. Stein, V. E. Fleischauer, J. Autschbach, E. R. Batista, J. M. Boncella, M. G. Ferrier, S. A. Kozimor, V. Mocko, M. L. Neidig, S. K. Cary, P. Yang, *Inorg. Chem.* **2018**, *57*, 8106-8115; b) F. Ossola, P. Zanella, P. Ugo, R. Seeber, *Inorganica Chimica Acta* **1988**, *147*, 123-126; c) P. Waldschmidt, J. Riedhammer, D. R. Hartline, F. W. Heinemann, K. Meyer, *Inorganic Chemistry* **2023**.

[14] J. Su, T. Cheisson, A. McSkimming, C. A. P. Goodwin, Ida M. DiMucci, T. Albrecht-Schönzart, B. L. Scott, E. R. Batista, A. J. Gaunt, S. A. Kozimor, P. Yang, E. J. Schelter, *Chemical Science* **2021**, *12*, 13343-13359.

[15] a) S. L. Staun, L. M. Stevens, D. E. Smiles, C. A. P. Goodwin, B. S. Billow, B. L. Scott, G. Wu, A. M. Tondreau, A. J. Gaunt, T. W. Hayton, *Inorganic Chemistry* **2021**, *60*, 2740-2748; b) D. C. Sonnenberger, J. Gaudiello, *Journal of the Less Common Metals* **1986**, *126*, 411-414.

[16] M. S. Dutkiewicz, C. A. P. Goodwin, M. Perfetti, A. J. Gaunt, J.-C. Griveau, E. Colineau, A. Kovács, A. J. Wooles, R. Caciuffo, O. Walter, S. T. Liddle, *Nature Chemistry* **2022**, *14*, 342-349.

[17] P. L. Arnold, M. S. Dutkiewicz, O. Walter, *Chemical Reviews* **2017**, *117*, 11460-11475.

[18] a) J. L. Brown, E. R. Batista, J. M. Boncella, A. J. Gaunt, S. D. Reilly, B. L. Scott, N. C. Tomson, *Journal of the American Chemical Society* **2015**, *137*, 9583-9586; b) D. L. Clark, S. S. Hecker, G. D. Jarvinen, M. P. Neu, *The Chemistry of the Actinide and Transactinide Elements, Vol. 2*, Springer, Dordrecht, **2010**.

[19] a) B. E. Klamm, C. J. Windorff, C. Celis-Barros, M. J. Beltran-Leiva, J. M. Sperling, T. E. Albrecht-Schönzart, *Inorg. Chem.* **2020**, *59*, 18035-18047; b) J. C. Wedal, J. Murillo, J. W. Ziller, B. L. Scott, A. J. Gaunt, W. J. Evans, *Inorganic Chemistry* **2022**; c) F. D. White, M. L. Marsh, in *Handbook on the Physics and Chemistry of Rare Earths, Vol. 55* (Eds.: J.-C. G. Bünzli, V. K. Pecharsky), Elsevier, **2019**, pp. 123-158; d) N. B. Beck, Z. Bai, J. P. Brannon, D. G. Martinez, D. Grödler, B. N. Long, T. N. Poe, B. M. Rotermund, T. E. Albrecht-Schönzart, J. M. Sperling, *Inorganic Chemistry* **2022**, *61*, 17730-17737.

[20] a) W.-L. Li, J. Su, T. Jian, G. V. Lopez, H.-S. Hu, G.-J. Cao, J. Li, L.-S. Wang, *The Journal of Chemical Physics* **2014**, *140*, 094306; b) M. Amati, S. Stoia, E. J. Baerends, *Journal of Chemical Theory and Computation* **2020**, *16*, 443-452; c) T. Koopmans, *Physica* **1934**, *1*, 104-113.

[21] a) M. S. Dutkiewicz, C. Apostolidis, O. Walter, P. L. Arnold, *Chemical Science* **2017**, *8*, 2553-2561; b) L. R. Morss, in *Handbook on the Physics and Chemistry of Rare Earths, Vol. 18*, Elsevier, **1994**, pp. 239-291.

[22] a) M. Schlosser, J. Hartmann, *Angewandte Chemie International Edition in English* **1973**, *12*, 508-509; b) J. J. K. S. A. Johnson, P. E. Fanwick, S. C. Bart, *Organometallics* **2015**, *34*, 2889-2895; c) H. C. E. Mannerskantz, G. W. Parshall, G. Wilkinson, *Journal of the Chemical Society (Resumed)* **1963**, 3137-3164; d) J. L. Kiplinger, D. E. Morris, B. L. Scott, C. J. Burns, *Organometallics* **2002**, *21*, 5978-5982; e) T. P. Gompa, N. T. Rice, D. R. Russo, L. M. Aguirre Quintana, B. J. Yik, J. Bacsa, H. S. La Pierre, *Dalton Transactions* **2019**, *48*, 8030-8033; f) M. T. J. C. A. P. Goodwin, B. L. Scott, A. J. Gaunt, *Journal of the American Chemical Society* **2021**, 20680-20696; g) B. W. Stein, S. A. Kozimor, V. Mocko, in *Plutonium Handbook: Nuclear science and materials science* (Ed.: D. L. Clark), American Nuclear Society, **2019**.

[23] B. W. Stein, S. A. Kozimor, V. Mocko, in *Plutonium Handbook: Nuclear science and materials science* (Ed.: D. L. Clark), American Nuclear Society, **2019**.

[24] a) L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J Appl Crystallogr* **2015**, *48*, 3-10; b) Bruker, V8.40B ed., Bruker AXS Inc., Madison, Wisconsin, USA.

[25] G. Sheldrick, *Acta crystallographica. Section A, Foundations and advances* **2015**, *71*, 3-8.

[26] O. Dolomanov, L. Bourhis, R. Gildea, J. Howard, H. Puschmann, *J. Appl. Cryst. J. Appl. Cryst* **2009**, *42*, 339-341.

[27] C. Groom, I. Bruno, M. Lightfoot, S. Ward, *Acta Crystallographica Section B Structural Science, Crystal Engineering and Materials* **2016**, *72*, 171-179.

[28] J. P. Perdew, M. Ernzerhof, K. Burke, *The Journal of Chemical Physics* **1996**, *105*, 9982-9985.

[29] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K.

5

Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Wallingford, CT, **2016**.

[30] X. Cao, M. Dolg, H. Stoll, *The Journal of Chemical Physics* **2003**, *118*, 487-496.

[31] X. Cao, M. Dolg, *Journal of Molecular Structure: THEOCHEM* **2004**, *673*, 203-209.

[32] X. Cao, M. Dolg, *The Journal of Chemical Physics* **2001**, *115*, 7348-7355.

[33] M. Dolg, H. Stoll, H. Preuss, *The Journal of Chemical Physics* **1989**, *90*, 1730-1734.

[34] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *The Journal of Chemical Physics* **1980**, *72*, 650-654.

[35] a) E. Cancès, B. Mennucci, J. Tomasi, *The Journal of Chemical Physics* **1997**, *107*, 3032-3041; b) B. Mennucci, E. Cancès, J. Tomasi, *The Journal of Physical Chemistry B* **1997**, *101*, 10506-10517; c) E. Cancès, B. Mennucci, *Journal of Mathematical Chemistry* **1998**, *23*, 309-326.

[36] a) P. J. Hay, W. R. Wadt, *The Journal of Chemical Physics* **1985**, *82*, 299-310; b) L. E. Roy, P. J. Hay, R. L. Martin, *Journal of Chemical Theory and Computation* **2008**, *4*, 1029-1031.

[37] L. Skripnikov, Chemissian v4.67.

Entry for the Table of Contents