

Supporting information

Aqueous chemistry of Ce(IV): estimations using actinide analogues

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Table S1. Calculated mean and structural standard deviations for the An-O and Ce-O bond distances (in Å) in the $[M(H_2O)_{10-n}]^{4+} \cdot (H_2O)_n$ ($n = 0-2$) clusters (M=Ce, Th-Pu). The actinide values are taken from Banik et al.⁴² in the main text.

	$[M(H_2O)_{10}]^{4+}$	$[M(H_2O)_9]^{4+} \cdot H_2O$	$[M(H_2O)_8]^{4+} \cdot (H_2O)_2$
Ce-O	2.470±0.033	2.419±0.036	2.376±0.021
Th-O	2.551±0.020	2.506±0.031	2.466±0.018
Pa-O	2.518±0.026	2.471±0.034	2.429±0.016
U-O	2.491±0.043	2.443±0.039	2.400±0.022
Np-O	2.472±0.033	2.425±0.039	2.383±0.025
Pu-O	2.454±0.023	2.406±0.032	2.361±0.020

Table S2. Relative free energies, of the $[M(H_2O)_{10}]^{4+}$, $[M(H_2O)_9]^{4+} \cdot H_2O$, and $[M(H_2O)_8]^{4+} \cdot (H_2O)_2$ clusters for M=Ce (this work), and M=Th-Pu, without (ΔG) and with (ΔG^{corr}) the hydrogen bond correction of -6.97 kJ/mol, per hydrogen bonds. The actinide values are taken from Banik et al.⁴² in the main text.

	$[M(H_2O)_8]^{4+} \cdot (H_2O)_2$		$[M(H_2O)_9]^{4+} \cdot H_2O$		$[M(H_2O)_{10}]^{4+}$	
	ΔG	ΔG^{corr}	ΔG	ΔG^{corr}	ΔG	ΔG^{corr}
Ce	15.6	1.6	0.0	0.0	33.6	47.6
Th	25.2	11.3	0.0	0.0	3.7	17.6
Pa	18.4	4.5	0.0	0.0	16.7	30.7
U	16.6	2.7	0.0	0.0	23.9	37.8
Np	17.8	3.9	0.0	0.0	26.0	40.0
Pu	15.1	1.2	0.0	0.0	32.9	46.9

Table S3. Difference from the formal metal valence d and f populations, QTAIM charge ($Q(M)$) and the electron density (ρ_b), Laplacian ($\nabla^2 \rho_b$), and the energy density (H_b) at the Ce-O and An-O bond critical points. The actinide values are taken from Banik et al.⁴² in the main text.

	n(f)	n(d)	$Q(M)$	ρ_b [e^-/bohr^3]	$\nabla^2 \rho_b$ [e^-/bohr^5]	H_b [au]
Ce	0.28	0.90	3.28	0.056	0.211	-0.0048
Th	0.48	0.64	3.41	0.051	0.194	-0.0033
Pa	0.18	0.69	3.44	0.052	0.223	-0.0026
U	0.21	0.78	3.29	0.055	0.226	-0.0044
Np	0.21	0.72	3.31	0.057	0.239	-0.0045
Pu	0.26	0.73	3.29	0.058	0.248	-0.0049

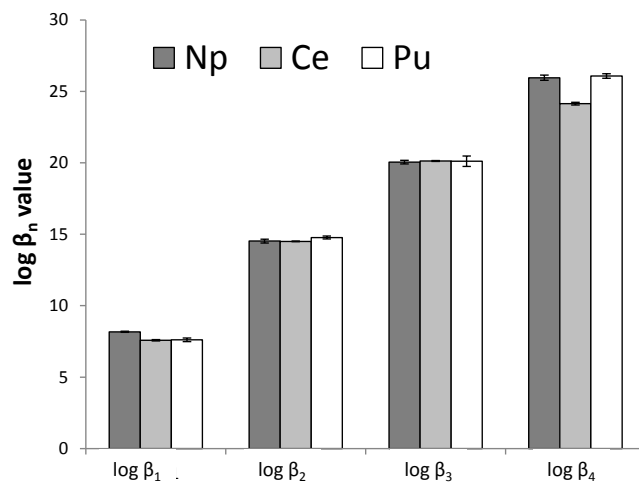


Figure S1. Comparison between $\log \beta_n$ values for the reactions $M^{4+} + nF^- = MF_n^{(4-n)}$, where $M = Ce, Np$ or Pu .