Supporting information for:

Actinyl-cation interactions: Experimental and theoretical assessment of Np(VI) and U(VI) tetrachloro systems.

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I. Crystal Structure Information

Table S1. Select Crystallographic parameters for, **LiNp**, **NaNp**, and **KNp**.

	LiNp	**NaNp**	**KNp**
Empirical formula	$C_{16}H_{32}Cl_4Li_2NpO_{10}$	$C_{24}H_{52}Cl_4Na_2NpO_{16}$	$C_{24}H_{49}Cl_4K_2NpO_{14.50}$
Formula weight	777.00	1021.43	1026.63
Space group	*Fmmm*	$P2_1/n$	$P2_1/c$
a	13.115(8)	14.117(3)	10.0239(17)
b	13.371(7)	9.517(2)	9.9861(17)
c	14.838(10)	14.336(3)	19.349(3)
α	90	90	90
β	90	101.388(8)	95.187(7)
γ	90	90	90
V	2602(3)	1888.2(7)	1928.9(6)
Z	4	2	2
ρ (g/cm^3)	1.902	1.797	1.768
μ (mm^{-1})	4.447	3.122	3.244
F(000)	1372	1014	1016
θ range for data collection (°)	2.253 to 26.442	2.260 to 28.346	2.938 to 28.351
Limiting indices	-16<*h*<16 -16<*k*<16 -18<*l*<18	-18<*h*<18 -12<*k*<12 -19<*l*<19	-13<*h*<13 -13<*k*<12 -25<*l*<25
Reflections collected / unique	11439/766	33982 / 4677	37361 / 4764
R_{int}	0.0494	0.0653	0.0545
Data / restraints / parameters	766 / 0 / 78	4677 / 0 / 318	4764 / 3 / 311
GOF on F^2	1.07	1.10	0.99
Final R indices [I>2σ(I)]	R_1 = 0.0419 wR_2 = 0.1088	R_1 = 0.0204 wR_2 = 0.0439	R_1 = 0.0175 wR_2 = 0.0392
R indices (all data)	R_1 = 0.0419 wR_2 = 0.1088	R_1 = 0.0284 wR_2 = 0.0468	R_1 = 0.0244 wR_2 = 0.0409
Largest diff. peak and hole	2.26 and -1.67	0.832 and -0.999	0.665 and -0.785

Table S2. Select bond lengths (Å) and angles (°) for **LiNp.**

Np(1)-O(1)	1.776 (12)	Li(1)-O(1)	1.92(3)
Np(1)-O(1)	1.776 (12)	Li(1)-O(2A)	2.03(2)
Np(1)-Cl(1)	2.626(3)	Li(1)- O(2A)	2.03(2)
Np(1)-Cl(1)	2.626(3)	Li(1)- O(2B)	2.08(1)
Np(1)-Cl(1)	2.626(3)	Li(1)- O(2B)	2.08(1)
Np(1)-Cl(1)	2.626(3)		
O(1)-Np(1)-O(1)	180.0		
O(1)-Np(1)-C1(1)	91.3(6)		
O(1)-Np(1)-C1(1)	88.7(6)		

Table S3. Select bond lengths (Å) and angles (°) for **NaNp**.

Np(1)-O(1)	1.757(2)	C(1)-O(7)	1.417(3)
Np(1)-O(1)[a]	1.757(2)	C(1)-C(2)	1.500(3)
Np(1)-Cl(1)	2.6637(7)	O(2)-C(2)	1.423(3)
Np(1)-Cl(1)[a]	2.6637(7)	O(2)-C(3)	1.427(3)
Np(1)-Cl(2)	2.6675(8)	O(3)-C(4)	1.431(3)
Np(1)-Cl(2)[a]	2.6676(8)	O(3)-C(5)	1.436(3)
O(1)[a]-Np(1)-O(1)	180.0	C(3)-C(4)	1.497(4)
O(1)-Np(1)-Cl(1)	90.85(6)	O(4)-C(7)	1.423(3)
O(1)-Np(1)-Cl(2)	89.58(6)	O(4)-C(6)	1.431(3)
		O(5)-C(8)	1.420(3)
Na(1)-O(8)[b]	2.355(2)	O(5)-C(9)	1.429(3)
Na(1)-O(3)	2.486(2)	C(5)-C(6)	1.499(3)
Na(1)-O(7)[b]	2.550(2)	O(6)-C(10)	1.428(3)
Na(1)-O(2)[b]	2.563(2)	O(6)-C(11)	1.431(3)
Na(1)-O(5)[b]	2.586(2)	C(7)-C(8)	1.503(4)
Na(1)-O(4)[b]	2.646(2)	O(7)-C(12)	1.426(3)
Na(1)-O(6)[b]	2.880(2)	C(9)-C(10)	1.498(4)
Na(1)-O(3)[b]	2.972(2)	C(11)-C(12)	1.507(4)

a:-x+1,-y+1,-z; b:-x+1,-y+1,-z+1.

Table S4. Select bond lengths (Å) and angles (°) for **KNp**.

Np(1)-O(1)	1.7662(13)	O(2)-C(1)	1.424(2)
Np(1)-O(1)[a]	1.7662(13)	O(2)-C(12)	1.426(2)
Np(1)-Cl(1)	2.6513(5)	O(3)-C(2)	1.424(2)
Np(1)-Cl(1)[a]	2.6513(5)	O(3)-C(3)	1.426(2)
Np(1)-Cl(2)	2.6614(6)	O(4)-C(5)	1.423(2)
Np(1)-Cl(2)[a]	2.6614(6)	O(4)-C(4)	1.425(2)
O(1)[a]-Np(1)-O(1)	180.0	O(5)-C(7)	1.425(2)
O(1)-Np(1)-Cl(1)	88.34(5)	O(5)-C(6)	1.426(2)
O(1)-Np(1)-Cl(2)	89.52(5)	O(6)-C(8)	1.420(2)
		O(6)-C(9)	1.423(2)
K(1)-O(6)	2.8553(14)	O(7)-C(11)	1.423(2)
K(1)-O(2)	2.8626(15)	O(7)-C(10)	1.425(2)
K(1)-O(4)	2.8706(14)	C(1)-C(2)	1.504(3)
K(1)-O(3)	2.8881(14)	C(3)-C(4)	1.504(3)
K(1)-O(5)	2.9110(15)	C(5)-C(6)	1.500(3)
K(1)-O(7)	3.0387(14)	C(7)-C(8)	1.499(3)
K(1)-Cl(2)	3.2550(8)	C(9)-C(10)	1.499(3)
K(1)-Cl(1)	3.3179(8)	C(11)-C(12)	1.493(3)

a: -x,-y+1,-z+1.

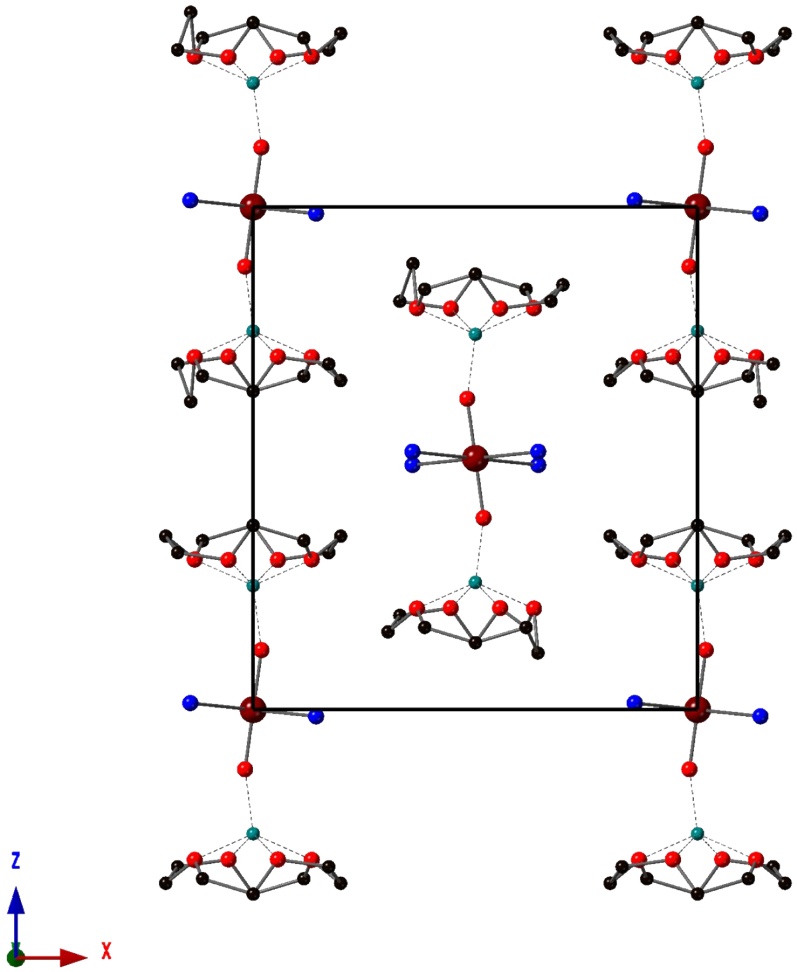


Figure S1. Crystalline packing for **LiNp**. The Np, Cl, Li, O, C atoms are depicted as maroon, blue, teal, red, and black spheres, respectively. H atoms have been removed from the image for clarity.

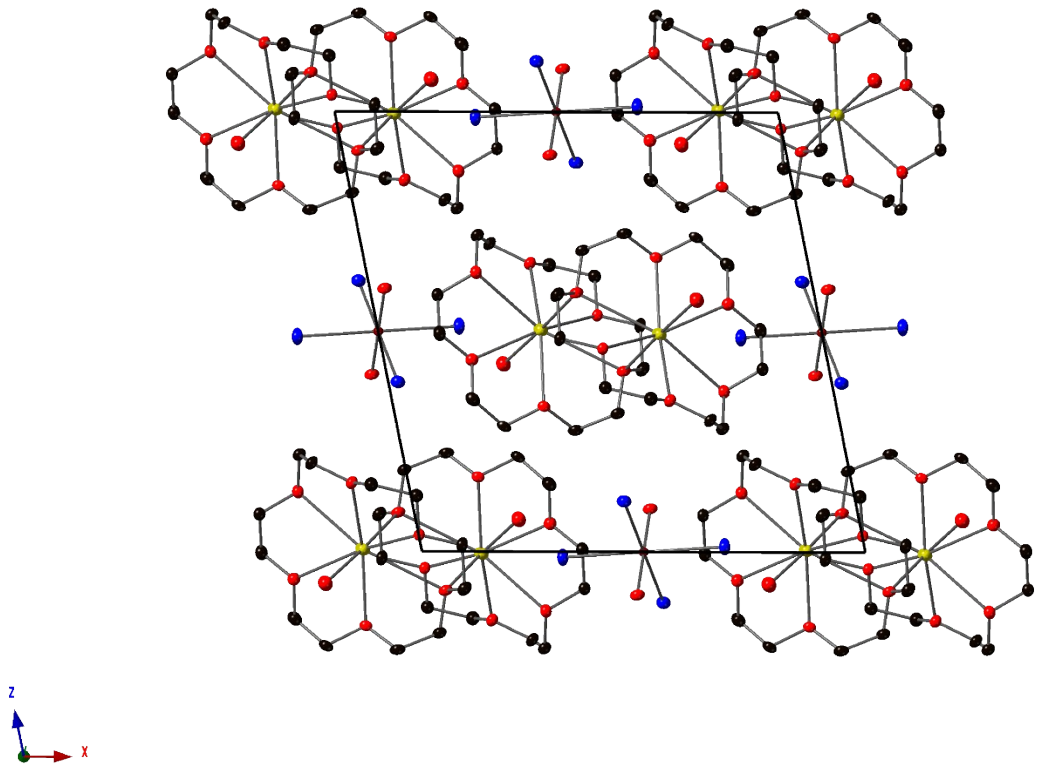


Figure S2. Crystalline packing for **NaNp1**. The Np, Cl, Na, O, C atoms are depicted as maroon, blue, yellow, red, and black ellipsoids, respectively. H atoms have been removed from the image for clarity.

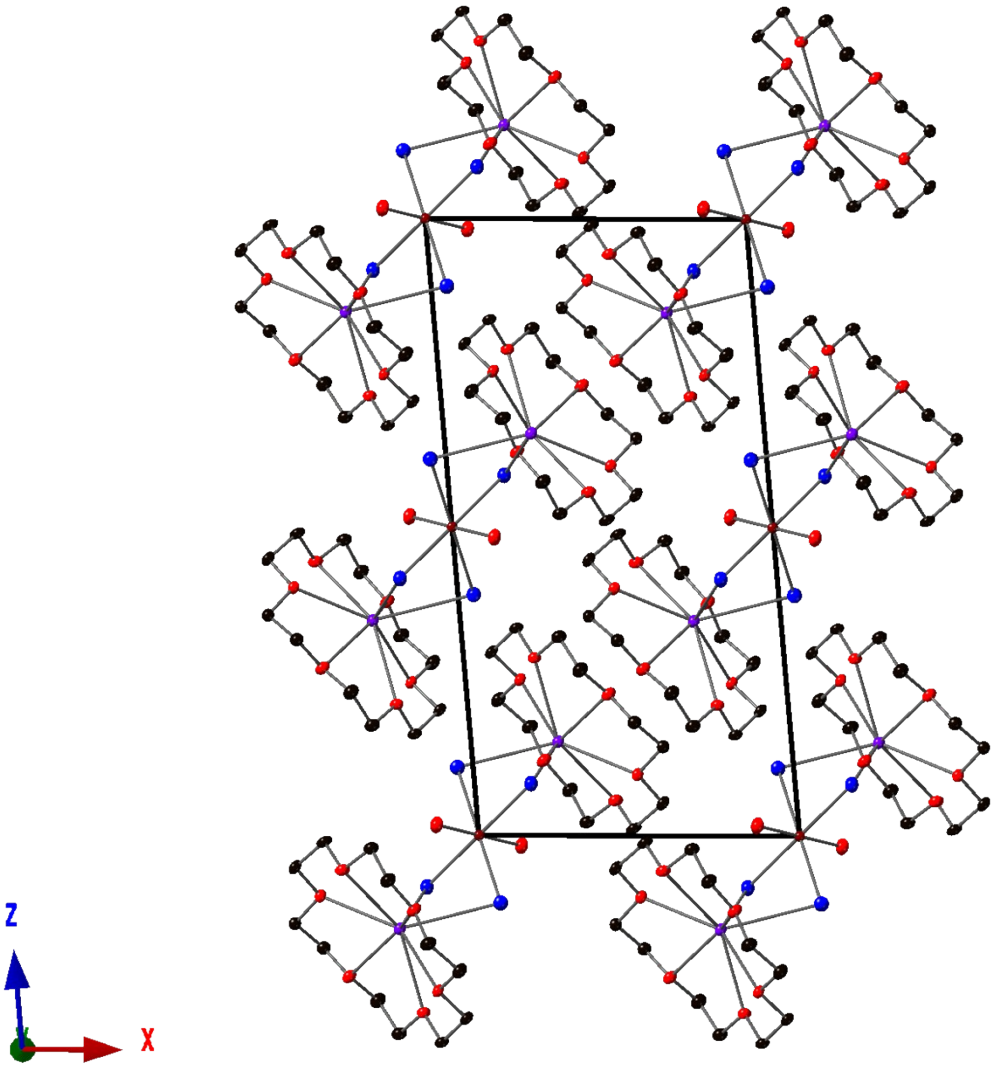
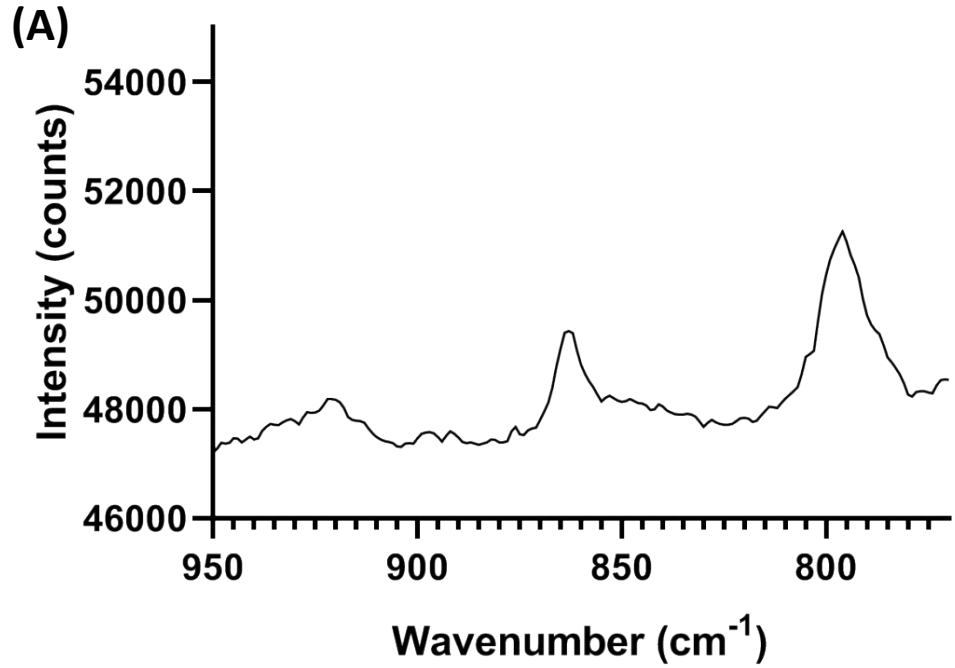
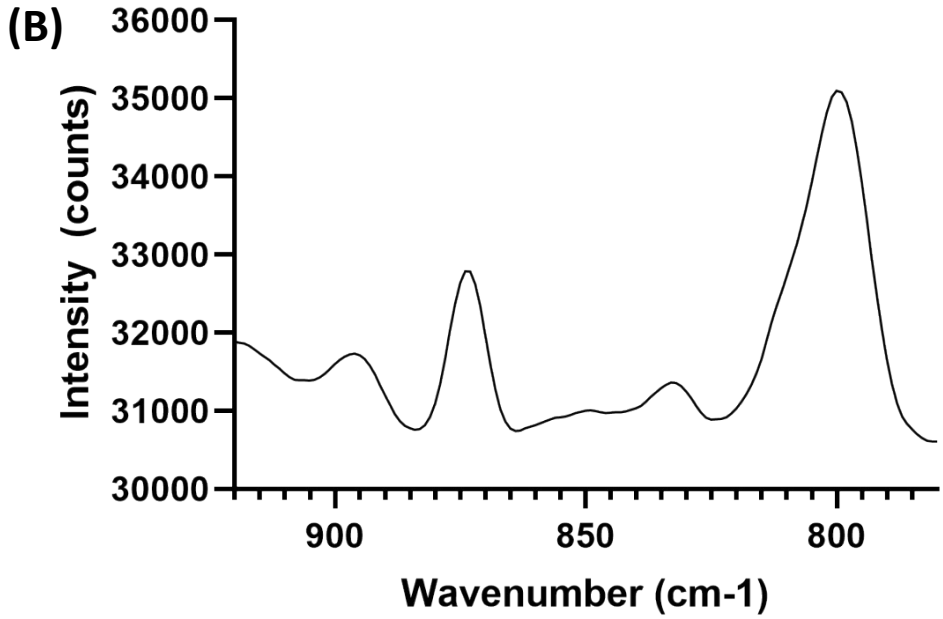


Figure S3. Extended topology for **KNp1**. The Np, K, O, Cl, C atoms are depicted as maroon, purple, red, blue, and black ellipsoids, respectively. The H atoms have been removed for clarity.

II. Raman Spectroscopy





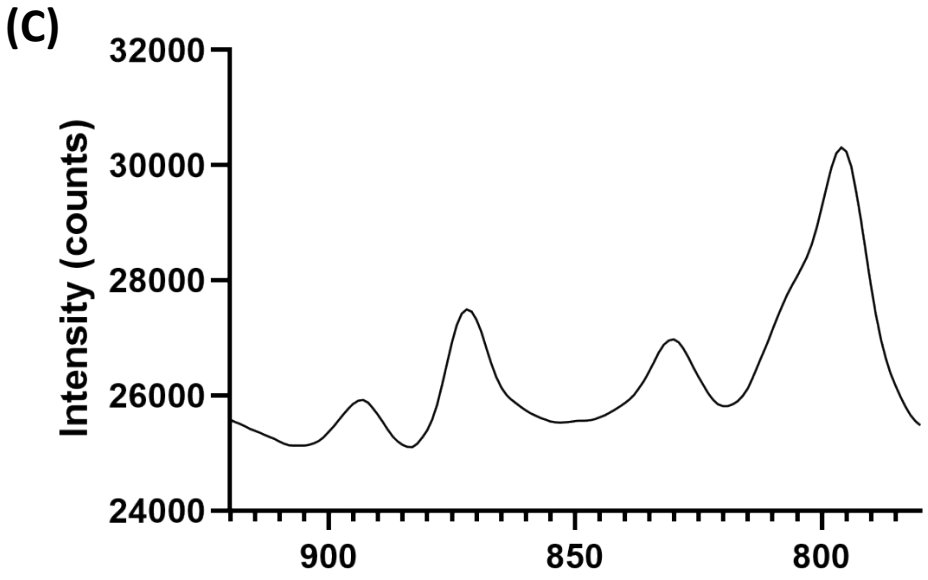
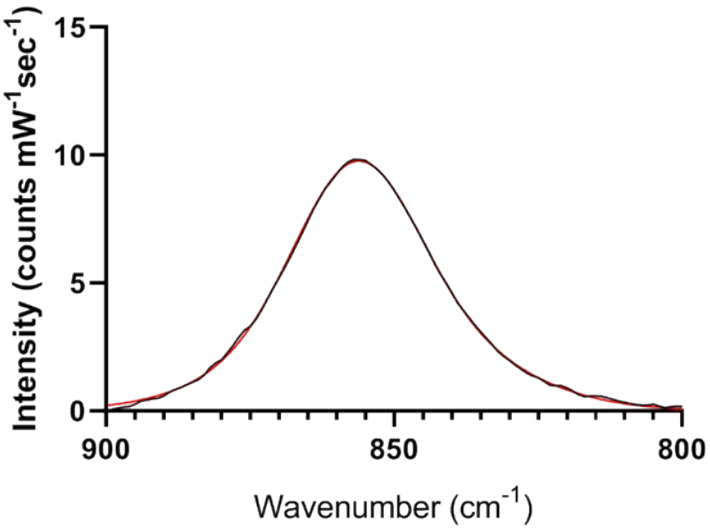
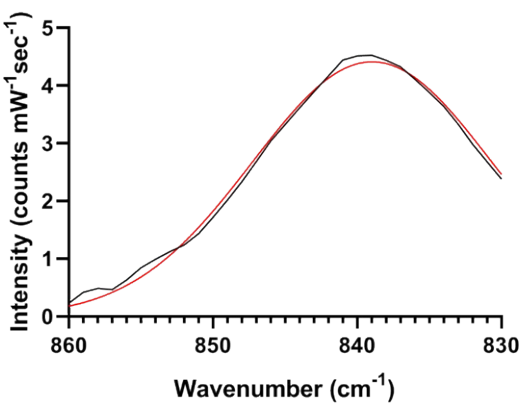


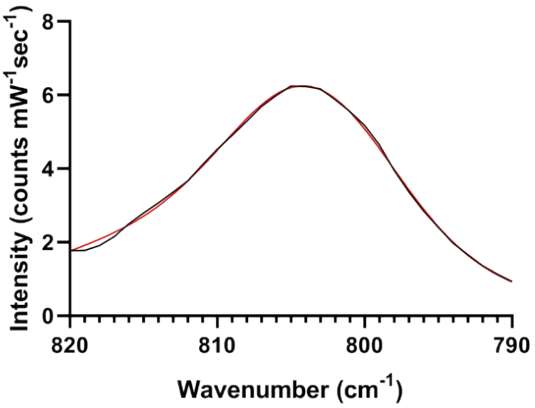
Figure S4. Solid state spectra for the **LiNp**, **NaNp**, and **KNp** compounds.



Simpler model	Gaussian
Probability it is correct	<0.01%
Alternative model	Sum of two Gaussians
Probability it is correct	>99.99%
Ratio of probabilities	
Preferred model	Sum of two Gaussians
Sum of two Gaussians	
Best-fit values	
Amplitude1	5.947
Mean1	856.5
SD1	10.31
Amplitude2	3.855
Mean2	853.7
SD2	19.10
Goodness of Fit	
Degrees of Freedom	95
R squared	0.9995
Sum of Squares	0.5490

Figure S5. Peak fitting parameters for the Np(VI) stock solution in 1 M HCl





Gaussian	
Best-fit values	
Amplitude	4.412
Mean	839.0
SD	8.302
Goodness of Fit	
Degrees of Freedom	34
R squared	0.9958
Sum of Squares	0.3400

Sum of two Gaussians	
Best-fit values	
Amplitude1	3.909
Mean1	803.6
SD1	5.417
Amplitude2	2.566
Mean2	809.1
SD2	12.20

Figure S6. Peak fitting parameters for the Np(VI) stock solution with Li^+ concentration of 13.3 M.

III. DFT methodology

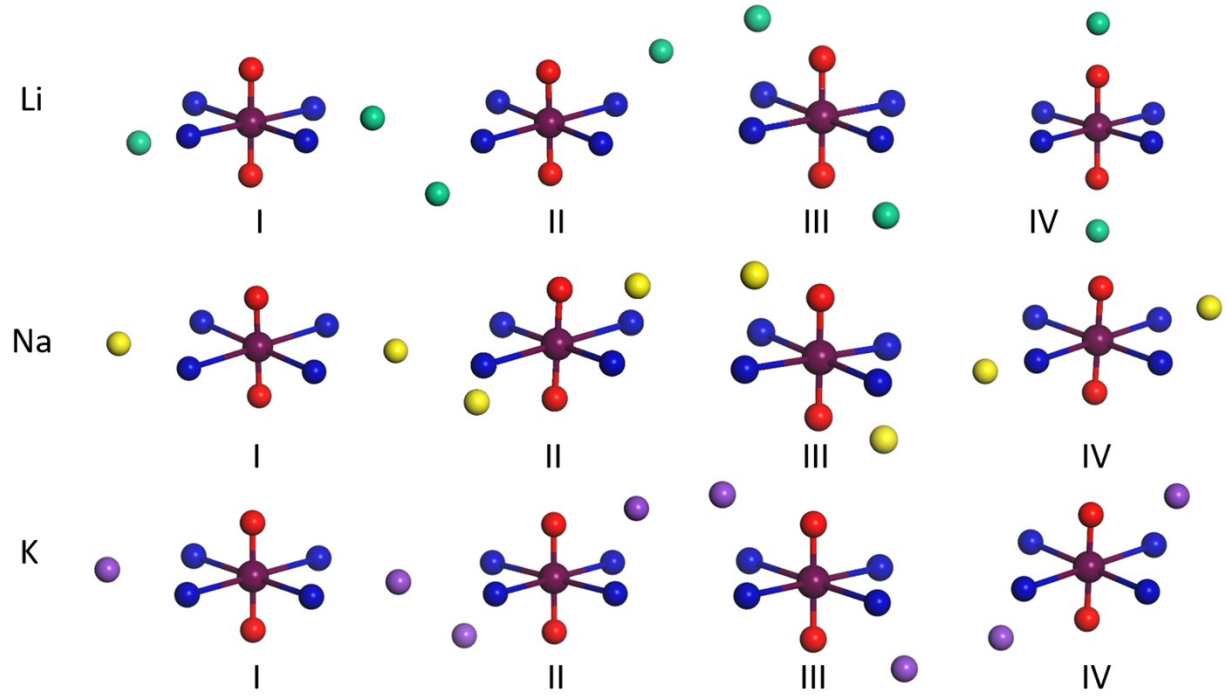


Figure S7. DFT-optimized structures of **DFT-NaNp, DFT-LiNp, DFT-KNp** for the four structure types (I-IV), where Cl, O, Np, Na, Li, and K are represented by blue, red, maroon, yellow, turquoise, and purple, respectively.

Table S5. Selected average bond lengths from the optimized **DFT-NaNp, DFT-LiNp,** and **DFT-KNp** structures.

	Np=O (Å)	Np-Cl (Å)
Li-I	1.756	2.696
Li-II	1.756	2.700
Li-III	1.763	2.686
Li-IV	1.798	2.632
Na-I	1.756	2.711
Na-II	1.771	2.684
Na-III	1.773	2.656
Na-IV	1.754	2.695
K-I	1.758	2.695
K-II	1.762	2.684
K-III	1.768	2.671
K-IV	1.767	2.672

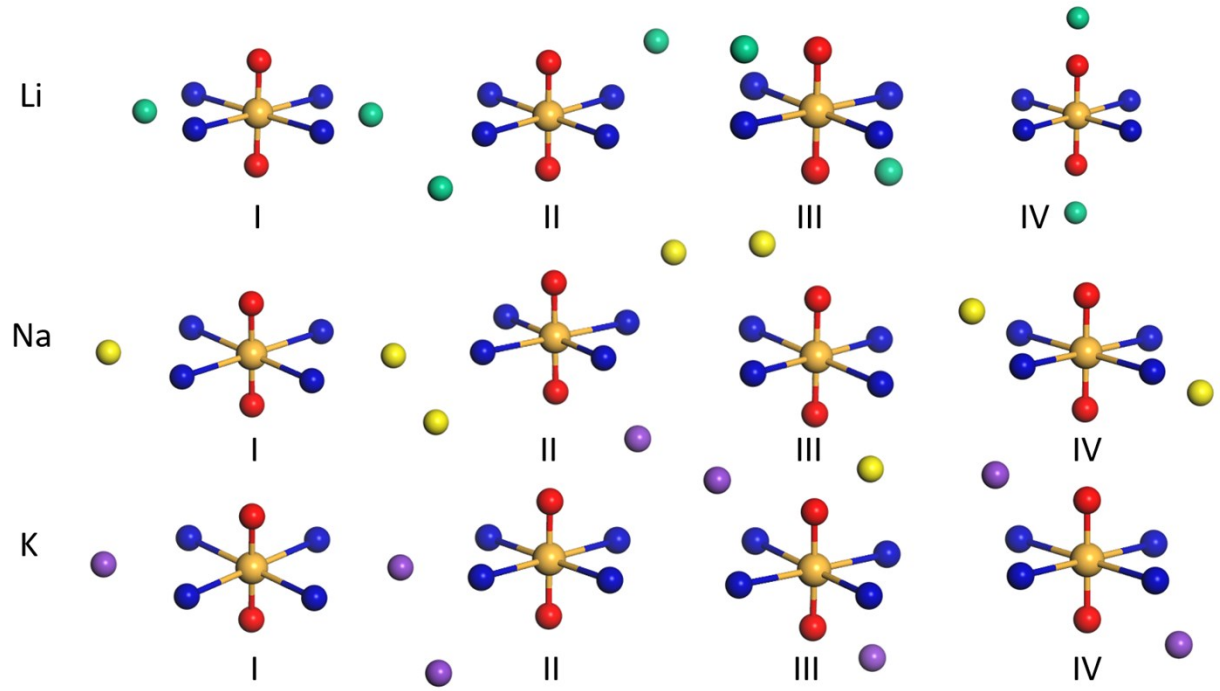


Figure S8. DFT-optimized structures of **DFT-NaU, DFT-LiU, DFT-KU** for the four structure types (I-IV), where Cl, O, U, Na, Li, and K are represented by blue, red, orange, yellow, turquoise, and purple, respectively.

Table S6. Selected average bond lengths from the optimized **DFT-NaU, DFT-LiU,** and **DFT-KU** structures.

	U=O (Å)	U-Cl (Å)
Li-I	1.776	2.724
Li-II	1.777	2.715
Li-III	1.785	2.702
Li-IV	1.819	2.646
Na-I	1.776	2.728
Na-II	1.779	2.706
Na-III	1.795	2.687
Na-IV	1.774	2.712
K-I	1.779	2.711
K-II	1.783	2.700
K-III	1.789	2.688
K-IV	1.787	2.688