Synthesis, characterization, and Density Functional Theory investigation of $(CH_6N_3)_2[NpO_2Cl_3]$ and $Rb[NpO_2Cl_2(H_2O)]$ chain structures

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Supporting Information

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1. Preparation of Np(v) stock

Approximately 300 mg of ^{237}Np was reprocessed from precipitates from previous experiments. These Np precipitates were dissolved in 50 mL of 4.0 M HNO_3 solution and ozonation was performed for 45 min at 1 L/min flow rate resulting in a yellow Np(VI) solution. ^{237}Np from the resulting solution was extracted with 15 mL aliquots of 30% TBP in dodecane. ^{237}Np in organic layer was back extracted to 0.1 M HCl solution by slow addition $NaNO_2$ until the organic layer turns colorless. Purified ^{237}Np was precipitated with a minimal amount of sat. NaOH resulting in a light gray precipitate. The precipitate was separated by centrifuging at 5000 rpm for 5 minutes. The supernatant was removed and the precipitate was washed with distilled water three times. To make the stock solution, the final purified precipitate was dissolved in a minimum amount of 2 M HCl solution. The ^{237}Np concentration was determined to be 0.27 M with liquid scintillation counting.

2. Crystallography

2.1 Thermal ellipsoid plots generated through CheckCIF

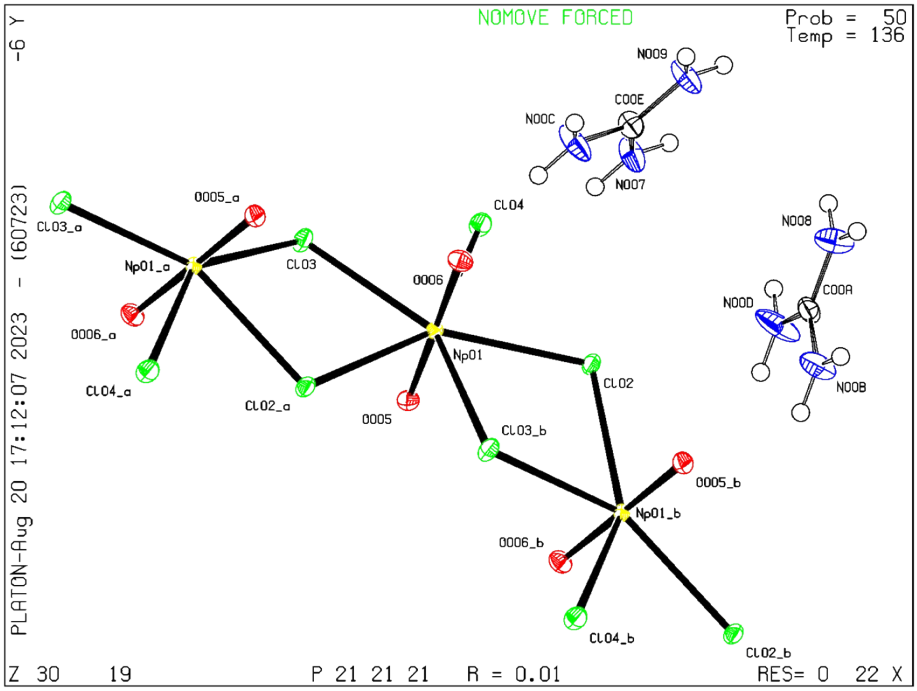

Figure S1: The Thermal ellipsoid plot of Np-Gua generated through CheckCIF.

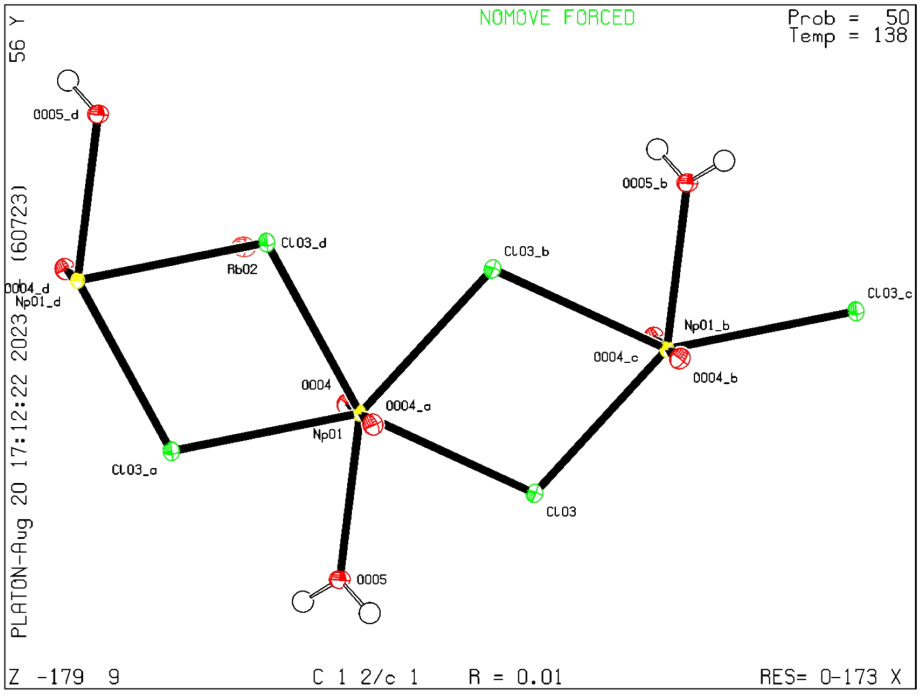

Figure S2: The Thermal ellipsoid plot of Np-Rb generated through CheckCIF.

2.2 Crystallographic bond lengths

Table S1: Selected crystallographic bond lengths of Np-Gua.

Atoms	Bond Lengths (Å)
Np01 Cl02[1]	2.8693(7)
Np01 Cl02	2.8577(6)
Np01 Cl03	2.8477(7)
Np01 Cl03[2]	2.8568(7)
Np01 Cl04	2.8355(7)
Np01 O005	1.823(2)
Np01 O006	1.8128(19)
[1]-1/2+X,1/2-Y,1-Z; [2]1/2+X,1/2-Y,1-Z	

Table S2: Selected crystallographic bond lengths of Np-Rb

Atoms	Bond Lengths (Å)
Np01 Cl03[4]	2.8231(5)
Np01 Cl03[5]	2.8587(5)
Np01 Cl03[6]	2.8587(5)
Np01 Cl03	2.8232(5)
Np01 O004[4]	1.8265(15)
Np01 O004	1.8265(15)
Np01 O005	2.452(2)
[4]1-X,+Y,1/2-Z; [5]1/2-X,3/2-Y,-Z; [6]1/2+X,3/2-Y,1/2+Z	

2.3 Crystallographic bond angles

Table S3: Selected crystallographic bond angles of Np-Gua.

Atoms	Bond angel (°)
Cl02 Np01 Cl02[1]	142.620(15)
Cl03 Np01 Cl02	145.14(2)
Cl03[2] Np01 Cl02[1]	71.93(2)
Cl03[2] Np01 Cl02	71.55(2)
Cl03 Np01 Cl02[1]	71.51(2)
Cl03 Np01 Cl03[2]	143.269(17)
Cl04 Np01 Cl02	72.53(2)
Cl04 Np01 Cl02[1]	144.18(2)
Cl04 Np01 Cl03[2]	143.86(2)
Cl04 Np01 Cl03	72.81(2)
O005 Np01 Cl02[1]	86.80(7)
O005 Np01 Cl02	86.46(7)
O005 Np01 Cl03	89.92(7)
O005 Np01 Cl03[2]	91.51(7)

O005 Np01 Cl04	90.13(7)
O006 Np01 Cl02	93.93(8)
O006 Np01 Cl02[1]	92.86(7)
O006 Np01 Cl03[2]	88.57(7)
O006 Np01 Cl03	89.79(8)
O006 Np01 Cl04	90.04(6)
O006 Np01 O005	179.61(11)
Np01 Cl02 Np01[2]	105.36(2)
Np01 Cl03 Np01[1]	105.96(2)

[1]-1/2+X,1/2-Y,1-Z; [2]1/2+X,1/2-Y,1-Z

Table S4: Selected crystallographic bond angles of Np-Rb.

Atoms	Bond angel (°)
Cl03 Np01 Cl03[4]	72.288(17)
Cl03[5] Np01 Cl03[6]	72.289(17)
Cl03 Np01 Cl03[6]	143.628(12)
Cl03[6] Np01 Cl03[4]	71.35(2)
Cl03[5] Np01 Cl03[4]	143.629(12)
Cl03[5] Np01 Cl03	144.08(2)
O004[5] Np01 Cl03[6]	91.40(5)
O004 Np01 Cl03	90.79(5)
O004[5] Np01 Cl03[4]	89.32(5)
O004 Np01 Cl03[5]	88.94(5)
O004 Np01 Cl03[4]	91.41(5)
O004[5] Np01 Cl03[5]	90.79(5)
O004 Np01 Cl03[6]	89.32(5)
O004[5] Np01 Cl03	88.94(5)
O004 Np01 O004[5]	179.10(9)
O004[5] Np01 O005	89.55(5)
O004 Np01 O005	89.55(5)
O005 Np01 Cl03[6]	144.326(10)
O005 Np01 Cl03	72.041(11)
O005 Np01 Cl03[5]	72.040(11)
O005 Np01 Cl03[4]	144.326(10)
Np01 Cl03 Np01[4]	107.713(17)

[4]1/2-X,3/2-Y,-Z; [5]1-X,+Y,1/2-Z; [6]1/2+X,3/2-Y,1/2+Z

3. Computational details

3.1 Periodic Density Functional Theory calculations

3.1.1 Periodic Density Functional Theory calculations details

Table S1: K-grid used in periodic DFT calculations

Compound	K grid
Np-Gua	5x4x3
Np-Rb	5x4x6

Table S5: Comparison of experimental and calculated lattice parameters of Np-Gua

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Experimental	8.6197(3)	9.7216(4)	14.5517(6)	90	90	90
Theoretical	8.7103	9.8516	14.2635	90	90	90
Percent Error	1.05 %	1.34 %	-1.98 %	0 %	0 %	0 %

Table S6: Comparison of experimental and calculated lattice parameters of Np-Rb

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Experimental	8.4988(4)	11.3956(5)	7.4459(6)	90	114.205(1)	90
Theoretical	8.5810	11.4890	7.5237	90	115.011	90
Percent Error	0.97 %	0.82 %	-1.04 %	0 %	0.71 %	0 %

3.1.2 Periodic Density Functional Theory calculated bond lengths.

Table S7: The periodic DFT calculated bond lengths of Np-Gua and Np-Rb

Structure	Average Np=O bond length (Å)	Average terminal Np-Cl bond length (Å)	Average bridging Np-Cl bond length (Å)	Average Np-OH_2 bond length (Å)
Np-Gua	1.832	2.864	2.884	-
Np-Rb	1.826	-	2.841	2.322

3.1.3 Bond Order (BO) calculation

The bond order between A and j atoms ($^{B_{A,j}}$) is defined as following equation.[1-4]

$$B_{A,j} = 2\oint\oint \frac{\rho^{\rightarrow avg}_{A}(r_A) \cdot \rho^{\rightarrow avg}_{j}(r'_j)}{\rho^{\rightarrow avg}(\vec{r}) \cdot \rho^{\rightarrow avg}(\vec{r'})} \rho(\vec{r}) \rho^{DX_{hole}}(\vec{r},\vec{r'})\, d^3\vec{r}'\, d^3\vec{r} \qquad \text{SI Eq 1}$$

$\rho^{\rightarrow avg}(\vec{r})$ = spherically average electron density at r

$\rho^{\rightarrow avg}_{A}(r_A)$ = spherically average electron density of atom A at r_A distance from A,

$\rho(\vec{r})$ = electron density at r

$\rho^{DX_{hole}}(\vec{r},\vec{r'})$ = the dressed exchange holes

The above equation describing the bond order is taken from previous work by Manz *et al*.[1-4] For more details on the bond order determination we encourage readers to refer to the cited works.

Table S8: The periodic DFT calculated bond order of neptunyl units of Np-Gua, Np-Rb and Np-Cs.

Structure	Average Np=O bond BO	Average terminal Np-Cl bond BO	Average bridging Np-Cl bond BO	Average Np-OH_2 bond BO
Np-Gua	1.425	0.285	0.295	-
Np-Rb	1.47	-	0.295	0.30
Np-Cs	1.53	0.40	-	-

3.2 Molecular Density Functional Theory calculations

3.2.1 XYZ coordinates of optimized molecular DFT optimized structures in aqueous media

Table S9: The xyz coordinates of optimized $[NpO_2Cl_2(H_2O)_2]^-$

O	28.47500	21.53470	2.11970
O	28.47830	21.53480	-1.48260
O	28.27250	18.91710	0.21660
H	27.29790	18.93700	0.18420
O	31.09270	21.74500	0.41710
H	31.06910	22.71980	0.44460
Cl	25.72680	20.70060	0.30660
Cl	29.30700	24.28650	0.32710

H	28.55850	18.52960	-0.62010
H	31.48260	21.46500	1.25480
Np	28.45140	21.56000	0.31850

Table S10: The xyz coordinates of optimized $[NpO_2Cl_2(H_2O)_3]^-$

Np	-5.35950	-0.96440	0.10060
O	-5.42440	0.83500	-0.05630
O	-7.99750	-0.97800	0.06070
O	-5.33270	-2.75030	0.36850
O	-6.53050	-0.79390	2.43380
H	-7.07350	-0.00870	2.57470
H	-5.90310	-0.82490	3.16710
H	-8.39520	-1.72530	0.52400
H	-8.04540	-1.18200	-0.89280
O	-3.68180	-0.64030	2.15320
H	-2.91430	-0.77690	1.56210
H	-3.61790	0.27800	2.44520
Cl	-2.56540	-1.03800	-0.64490
Cl	-6.49030	-1.32060	-2.54230

Table S11: The xyz coordinates of optimized $[NpO_2Cl_3(H_2O)]^{2-}$

O	28.42450	21.28730	2.12560
O	28.38650	21.53250	-1.48550
O	31.00380	21.74300	0.30370
H	30.89530	22.70860	0.41760
Cl	25.57820	21.77870	0.36150
Cl	29.21030	24.19630	0.49480
H	31.45330	21.42750	1.09730
Np	28.36550	21.40430	0.31940
Cl	28.09260	18.58750	0.12250

Table S12: The xyz coordinates of optimized $[NpO_2Cl_3(H_2O)_2]^{2-}$

Np	-5.33490	-0.89990	0.22010
O	-5.59400	0.88800	0.15020
O	-7.92440	-1.31900	-0.28600
O	-5.14410	-2.69650	0.22520
O	-6.02270	-1.01790	-2.35150
H	-6.36340	-1.88850	-2.58980
H	-5.08720	-0.99380	-2.63820
H	-8.33620	-0.56470	-0.72460
H	-8.15060	-1.24770	0.66380
Cl	-3.11840	-0.66160	-1.71580
Cl	-7.08920	-1.09520	2.58050
Cl	-3.29270	-0.62490	2.17350

Table S13: The xyz coordinates of optimized $[NpO_2Cl_4]^{3-}$

O	28.37580	21.59410	2.12310
O	28.38420	21.66000	-1.48930
Cl	25.53520	21.64650	0.30950
Cl	28.39690	24.47080	0.37360
Cl	31.22490	21.60770	0.32440
Cl	28.36310	18.78340	0.26030
Np	28.38000	21.62710	0.31690

Table S14: The xyz coordinates of optimized $[NpO_2Cl_4(H_2O)]^{3-}$

Np	-5.35950	-0.83120	0.26340
O	-5.55110	0.95810	0.14000
O	-5.17230	-2.62200	0.34740
O	-5.87330	-0.84180	-2.37020
H	-6.63840	-1.43990	-2.34810
H	-5.08100	-1.31590	-2.66660
Cl	-3.00720	-0.89290	-1.59120
Cl	-6.79800	-0.81070	2.74960
Cl	-3.17280	-0.47070	2.09390
Cl	-8.19510	-1.42040	-0.62970

Table S15: The xyz coordinates of optimized $[(NpO_2)_2Cl_7]^{-5}$

Cl	8.02760	34.71010	14.29170
Cl	4.57140	34.96040	13.66460
Np	6.13610	37.15900	14.80410
Cl	3.41160	38.19570	14.63630
Cl	6.30300	39.85600	15.92670
O	5.81990	36.51350	16.46240
O	6.50260	37.78530	13.14740
Np	10.67500	35.83380	14.31300
Cl	12.10260	33.73980	12.99900
O	10.35950	36.61910	12.71170
O	10.98050	35.04440	15.91460
Cl	13.03230	37.41670	14.60100
Cl	9.04920	37.76350	15.64680

Table S16: The xyz coordinates of optimized $[(NpO_2)_2Cl_8]^{-6}$

Cl	7.91770	34.79130	14.56450
Cl	4.48840	34.88220	13.77630
Np	6.05810	37.14660	14.80740
Cl	3.30150	38.16730	14.57300
Cl	6.20290	39.97000	15.63620
O	5.69820	36.64730	16.50420
O	6.42840	37.64200	13.11170
Np	10.72680	35.79020	14.24390
Cl	13.44880	35.23530	13.24390
Cl	10.63020	33.05510	13.20340

O	10.27460	36.44710	12.62500
O	11.17050	35.13230	15.86600
Cl	12.24870	38.24180	14.80750
Cl	8.87980	37.73320	15.5867

Table S17: The xyz coordinates of optimized $[(NpO2)_2Cl_6(H_2O)_2]^{4-}$

Cl	6.13670	29.69110	1.17270
H	7.11630	34.67270	1.43960
Cl	5.73490	33.36880	0.35110
O	6.55070	32.16230	3.47310
Cl	8.95510	29.69950	3.55550
O	8.84870	31.70780	0.72190
H	7.94310	34.96920	2.74390
Np	7.69290	31.90870	2.09730
O	7.98210	34.54860	1.87680
O	11.20650	30.71570	6.05660
H	12.48220	27.98280	4.23270
Cl	14.18230	29.27080	4.80590
O	12.05610	30.75040	2.54380
H	11.15780	27.80590	3.40220
Cl	9.82110	33.00930	3.84690
Cl	13.39540	32.96100	4.75410
Np	11.63750	30.75830	4.30050
O	11.51220	28.09950	4.24990

Table S18: The xyz coordinates of optimized $[(NpO2)_3Cl_8(H_2O)_3]^{5-}$

Cl	6.20970	29.66540	0.85680
H	6.68220	34.63400	1.85000
Cl	5.22300	33.29000	0.92070
O	7.01140	31.75090	3.41490
Cl	9.59200	29.70740	2.34740
O	8.44130	32.12650	0.12050
H	7.81250	34.83890	2.92010
Np	7.71800	31.91410	1.76300
O	7.64370	34.55350	2.01490
O	10.50010	30.71140	5.48240
H	12.04590	27.91930	4.84220
Cl	13.70010	29.64430	5.86610
O	12.82020	30.94550	2.72940
H	10.83100	27.90800	3.86810
Cl	10.15810	33.08970	3.03900
H	15.24250	34.83930	5.39050
Cl	12.95940	33.02530	5.49180
O	15.13050	31.93740	8.05500
Np	11.65620	30.85270	4.10680
O	11.73820	28.22030	3.97740
Cl	17.29430	29.63850	6.81350
O	16.04650	31.84860	4.56430

H	16.53030	34.60500	6.27350
Np	15.59900	31.86980	6.31050
O	15.55640	34.52700	6.24740
Cl	18.17070	33.28580	6.82910

Table S19: The xyz coordinates of optimized $[(NpO2)_3Cl_{10}]^{7-}$

Cl	7.91710	34.78050	14.49410
Cl	4.42210	34.86300	13.99050
Np	6.03240	37.14740	14.82180
Cl	3.28420	38.17640	14.55470
Cl	6.22120	39.99500	15.57840
O	5.74050	36.70660	16.55100
O	6.34290	37.56930	13.09280
Np	10.66110	35.75210	14.23010
Cl	17.44350	35.81320	14.59240
Cl	13.53770	35.29780	13.37760
Cl	10.72820	33.11400	13.03220
O	10.30170	36.45440	12.60390
O	11.04890	35.05460	15.85250
Np	15.00300	37.26590	14.91040
Cl	12.31320	38.19720	14.89940
Cl	8.92330	37.77330	15.47080
Cl	16.06250	39.41040	16.44990
O	14.68360	36.34760	16.43560
O	15.32380	38.17800	13.38210

3.2.2 Selected bond lengths of molecular DFT optimized structures in aqueous media

Table S20: Selected bond lengths of molecular DFT optimized monomeric structures in aqueous media

Structure	**Average Np=O bond length (Å)**	**Average Np-Cl bond length (Å)**	**Average Np-OH_2 bond length (Å)**
$[NpO_2Cl_2(H_2O)_2]^-$	1.801	2.858	2.651
$[NpO_2Cl_2(H_2O)_3]^-$	1.807	2.895	2.642
$[NpO_2Cl_3(H_2O)]^{2-}$	1.811	2.857	2.660
$[NpO_2Cl_3(H_2O)_2]^2$	1.808	2.913	2.669
$[NpO_2Cl_4]^{3-}$	1.806	2.845	-
$[NpO_2Cl_4(H_2O)]^{3-}$	1.803	2.943	2.683

Table S21: Selected bond lengths of molecular DFT optimized dimeric and trimeric structures in aqueous media

Structure	**Average Np=O bond**	**Average terminal Np-Cl**	**Average bridging Np-Cl**	**Average Np-OH_2 bond**

	length (Å)	bond length (Å)	bond length (Å)	length (Å)
$[(NpO_2)_2Cl_7]^{-5}$	1.811*, 1.808	2.855*, 2.925	2.865*, 3.114	-
$[(NpO_2)_2Cl_8]^{-6}$	1.805	2.943	3.998	-
$[(NpO2)_2Cl_6(H_2O)_2]^{4-}$	1.807	2.935	2.962	2.664
$[(NpO2)_3Cl_{10}]^{7-}$	1.809*,1.808	2.852*, 2.928	2.870*, 2.999	-
$[(NpO2)_3Cl_8(H_2O)_3]^{5-}$	1.805	2.914	2.948	2.655

*Np center with equatorial coordination number of 4

4. Non-covalent interactions analysis

Table S22: The full list of hydrogen bonding interactions in the unit cell of Np-Gua

Hydrogen atom	H accepter	Interaction distance (Å)	Bond order	Hydrogen atom	H accepter	Interaction distance (Å)	Bond order
49 H	16 Cl	2.237	0.114	71 H	20 O	2.314	0.047
50 H	15 Cl	2.237	0.114	72 H	19 O	2.314	0.047
51 H	14 Cl	2.237	0.114	73 H	6 Cl	2.614	0.054
52 H	13 Cl	2.237	0.114	73 H	14 Cl	2.744	0.036
53 H	5 Cl	2.986	0.025	74 H	5 Cl	2.6144	0.054
53 H	13 Cl	2.335	0.094	74 H	13 Cl	2.744	0.036
54 H	6 Cl	2.986	0.025	75 H	8 Cl	2.614	0.054
54 H	14 Cl	2.335	0.094	75 H	16 Cl	2.744	0.036
55 H	7 Cl	2.986	0.025	76 H	15 Cl	2.744	0.036
55 H	15 Cl	2.335	0.094	76 H	7 Cl	2.614	0.054
56 H	16 Cl	2.33	0.094	77 H	20 O	1.993	0.092
56 H	8 Cl	2.986	0.025	78 H	19 O	1.993	0.092
57 H	6 Cl	2.420	0.082	79 H	18 O	1.993	0.092
57 H	23 O	2.474	0.032	80 H	17 O	1.993	0.092
58 H	5 Cl	2.420	0.082	81 H	21 O	1.847	0.136
58 H	24 O	2.474	0.032	82 H	22 O	1.847	0.136
59 H	8 Cl	2.420	0.082	83 H	23 O	1.847	0.136
59 H	21 O	2.474	0.032	84 H	24 O	1.847	0.136
60 H	7 Cl	2.42	0.082	85 H	18 O	1.884	0.123
60 H	22 O	2.474	0.032	86 H	17 O	1.884	0.123
61 H	16 Cl	2.329	0.089	87 H	20 O	1.884	0.123
62 H	15 Cl	2.329	0.089	88 H	19 O	1.884	0.123
63 H	14 Cl	2.329	0.089	89 H	16 Cl	2.401	0.076
64 H	13 Cl	2.329	0.089	90 H	15 Cl	2.401	0.076
65 H	12 Cl	2.678	0.048	91 H	14 Cl	2.401	0.076
66 H	11 Cl	2.678	0.048	92 H	13 Cl	2.401	0.076
67 H	10 Cl	2.678	0.048	93 H	9 Cl	2.383	0.090
68 H	9 Cl	2.678	0.048	94 H	10 Cl	2.383	0.090
69 H	18 O	2.314	0.047	95 H	11 Cl	2.383	0.090

70 H	17 O	2.314	0.047	96 H	12 Cl	2.3835	0.090

Table S23: The full list of cation interactions in the unit cell of Np-Rb

Rb^+ atom	accepter	Interaction distance (Å)	Bond order	Rb^+ atom	accepter	Interaction distance (Å)	Bond order
5 Rb	16 Cl	3.318	0.094	7 Rb	9 Cl	3.294	0.096
5 Rb	17 O	2.992	0.065	7 Rb	12 Cl	3.318	0.094
5 Rb	22 O	3.126	0.060	7 Rb	20 O	3.126	0.061
5 Rb	24 O	3.126	0.060	7 Rb	10 Cl	3.318	0.094
5 Rb	13 Cl	3.294	0.096	7 Rb	11 Cl	3.294	0.096
5 Rb	14 Cl	3.318	0.094	7 Rb	18 O	3.126	0.061
5 Rb	15 Cl	3.294	0.096	7 Rb	21 O	2.992	0.065
5 Rb	19 O	2.992	0.065	7 Rb	23 O	2.992	0.065
6 Rb	15 Cl	3.318	0.094	8 Rb	12 Cl	3.294	0.096
6 Rb	18 O	2.992	0.065	8 Rb	17 O	3.126	0.061
6 Rb	21 O	3.126	0.060	8 Rb	22 O	2.992	0.065
6 Rb	23 O	3.126	0.060	8 Rb	9 Cl	3.318	0.094
6 Rb	13 Cl	3.318	0.094	8 Rb	10 Cl	3.294	0.096
6 Rb	14 Cl	3.294	0.096	8 Rb	11 Cl	3.318	0.094
6 Rb	16 Cl	3.294	0.096	8 Rb	19 O	3.126	0.061
6 Rb	20 O	2.992	0.065	8 Rb	24 O	2.992	0.065

Table S24: The full list of hydrogen bonding interactions in the unit cell of Np-Rb

Hydrogen atom	H accepter	Interaction distance (Å)	Bond order
29 H	18 O	1.942	0.109
30 H	17 O	1.942	0.109
31 H	20 O	1.942	0.109
32 H	19 O	1.942	0.109
33 H	22 O	1.942	0.109
34 H	21 O	1.942	0.109
35 H	24 O	1.942	0.109
36 H	23 O	1.942	0.109

5. Vibrational analysis

4.1 Fitted Raman spectra

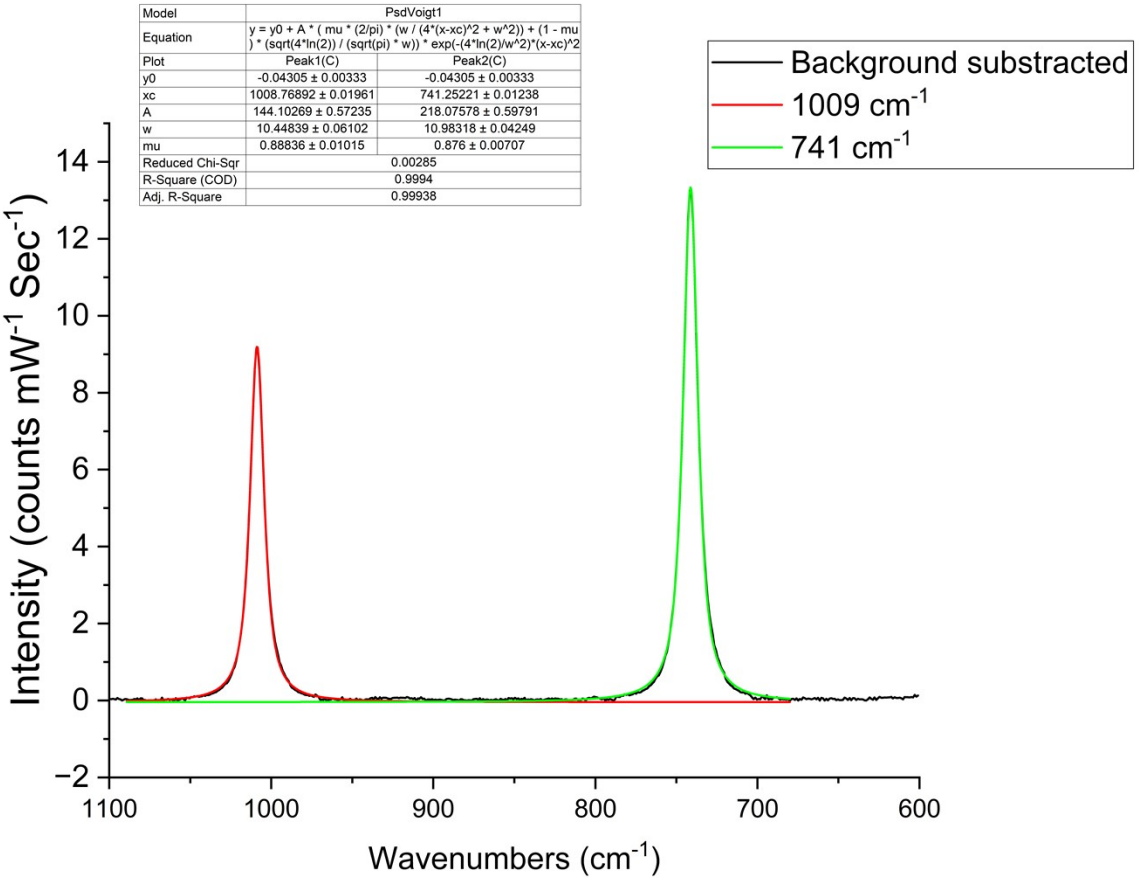

Figure S3: Fitted Raman spectrum of Np-Gua in the spectral window of 1100-600 cm^{-1} with fitting parameters.

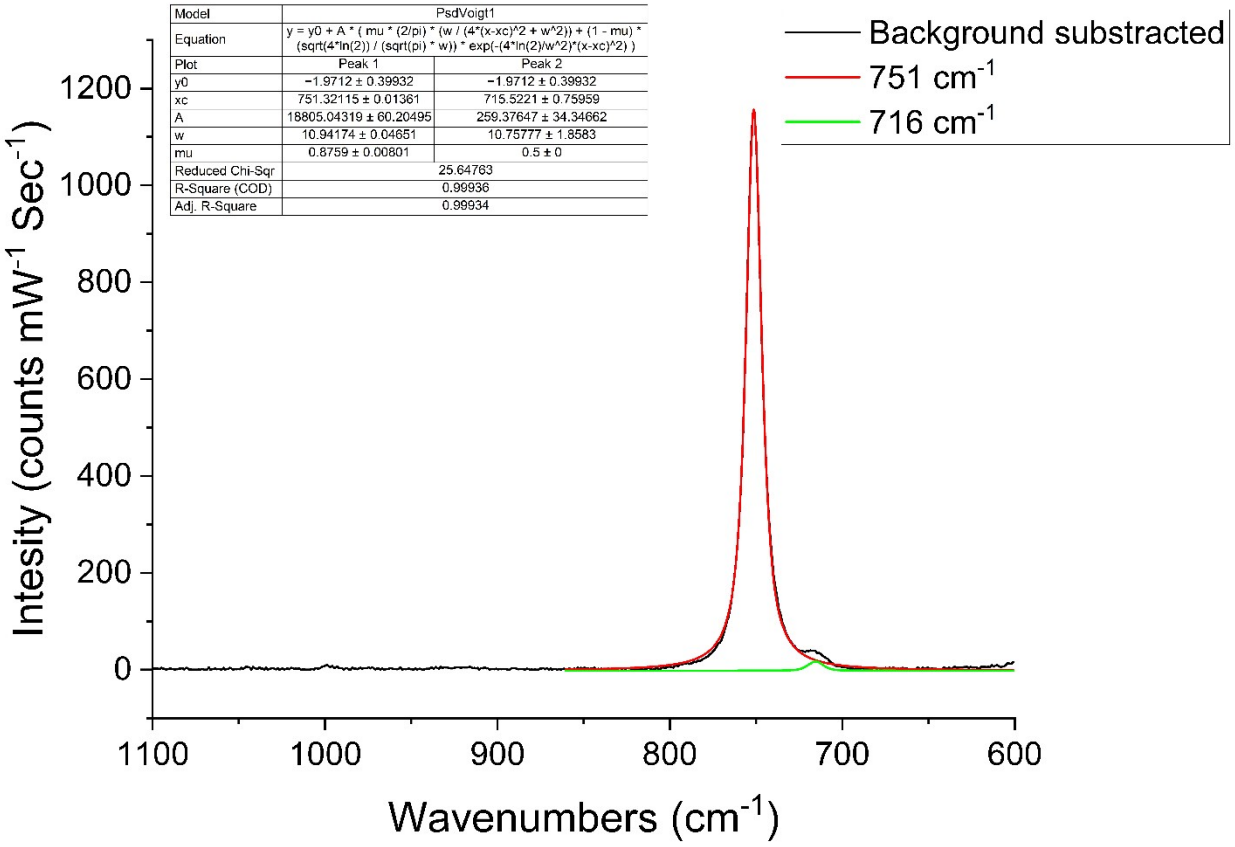

Figure S4: Fitted Raman spectrum of Np-Rb in the spectral window of 1100-600 cm^{-1} with fitting parameters.

4.2 Calculated vibrational modes

Table S25: The calculated vibrational modes of $[(NpO_2)_2Cl_8]^{6-}$. Red font is used to identify the neptunyl symmetric and asymmetrical stretches.

Mode #	Frequency (cm^{-1})	Mode #	Frequency (cm^{-1})	Mode #	Frequency (cm^{-1})
1	33.57	13	115.07	25	195.91
2	35.58	14	117.96	26	201.39
3	37.46	15	120.4	27	203.66
4	51.83	16	128.1	28	207.94
5	56.01	17	134.17	29	277.32
6	74.16	18	135.01	30	281.06
7	80.38	19	148.12	31	281.76
8	84.81	20	148.84	32	284.26
9	91.57	21	161.19	33	765.36
10	94.52	22	168.67	34	770.38
11	100.04	23	187.28	35	796
12	109.19	24	192.86	36	798.19

Table S26: The calculated vibrational modes of $[(NpO_2)_2Cl_6(H_2O)_2]^{4-}$. Red font is used to identify the neptunyl symmetric and asymmetrical stretches.

Mode #	Frequency (cm^{-1})	Mode #	Frequency (cm^{-1})	Mode #	Frequency (cm^{-1})
1	34.18	17	157.04	33	278.65
2	35.61	18	162.27	34	296.28
3	45.81	19	169.84	35	432.73
4	50.74	20	170.60	36	436.52
5	57.94	21	173.50	37	645.50
6	59.72	22	177.87	38	646.35
7	70.98	23	180.88	39	776.10
8	76.77	24	185.02	40	780.55
9	80.03	25	190.60	41	809.99
10	88.48	26	197.17	42	812.26
11	92.86	27	232.06	43	1550.34
12	99.10	28	233.05	44	1553.25
13	108.55	29	252.15	45	3528.15
14	114.08	30	256.89	46	3545.21
15	130.04	31	260.59	47	3822.44
16	150.32	32	270.80	48	3823.60

Table S27: The calculated vibrational modes of Guanidinium cation

Mode #	Frequency (cm^{-1})	Mode #	Frequency (cm^{-1})	Mode #	Frequency (cm^{-1})
1	209.00	9	728.95	17	1677.21
2	242.78	10	1028.30	18	1703.22
3	259.05	11	1047.37	19	3591.13
4	297.55	12	1123.16	20	3594.41
5	519.09	13	1131.33	21	3607.02
6	526.79	14	1597.12	22	3706.01
7	576.37	15	1598.03	23	3708.70
8	579.10	16	1676.38	24	3711.15

6. Insight into chain formation

Table S28: Possible formation reactions that may be involved in the formation of **Np-Gua**.

Step		Possible Reactions	ΔH (kJ/mol)
1	I	$2[NpO_2Cl_3(H_2O)]^{2-}_{(aq)} + HCl_{(aq)} \rightarrow [(NpO2)_2Cl_7]^{5-}_{(aq)} + H_3O^+_{(aq)} + H_2O_{(aq)}$	-94.00
	II	$[NpO_2Cl_4(H_2O)]^{3-}_{(aq)} + [NpO_2Cl_3(H_2O)]^{2-}_{(aq)} \rightarrow [(NpO2)_2Cl_7]^{5-}_{(aq)} + 2H_2O_{(aq)}$	-46.17
	III	$[NpO_2Cl_4]^{3-}_{(aq)} + [NpO_2Cl_3(H_2O)]^{2-}_{(aq)} \rightarrow [(NpO2)_2Cl_7]^{5-}_{(aq)} + H_2O_{(aq)}$	-44.63
	IV	$2[NpO_2Cl_3(H_2O)_2]^{2-}_{(aq)} + HCl_{(aq)} \rightarrow [(NpO2)_2Cl_7]^{5-}_{(aq)} + H_3O^+_{(aq)} + 3H_2O_{(aq)}$	-34.50
	V	$[NpO_2Cl_4(H_2O)]^{3-}_{(aq)} + [NpO_2Cl_3(H_2O)_2]^{2-}_{(aq)} \rightarrow [(NpO2)_2Cl_7]^{5-}_{(aq)} + 3H_2O_{(aq)}$	-16.42
	VI	$[NpO_2Cl_4]^{3-}_{(aq)} + [NpO_2Cl_3(H_2O)_2]^{2-}_{(aq)} \rightarrow [(NpO2)_2Cl_7]^{5-}_{(aq)} + 2H_2O_{(aq)}$	-14.88
	VII	$[NpO_2Cl_4]^{3-}_{(aq)} + [NpO_2Cl_4(H_2O)]^{3-}_{(aq)} + H_3O^+_{(aq)} \rightarrow [(NpO2)_2Cl_7]^{5-}_{(aq)} + HCl_{(aq)} + 2H_2O_{(aq)}$	> 0
	VIII	$6[NpO_2Cl_4(H_2O)]^{3-}_{(aq)} + H_3O^+_{(aq)} \rightarrow [(NpO2)_2Cl_7]^{5-}_{(aq)} + HCl_{(aq)} + 3H_2O_{(aq)}$	> 0
	IX	$[NpO_2Cl_4]^{3-}_{(aq)} + [NpO_2Cl_4]^{3-}_{(aq)} + H_3O^+_{(aq)} \rightarrow [(NpO2)_2Cl_7]^{5-}_{(aq)} + HCl_{(aq)} + H_2O_{(aq)}$	> 0
2	I	$[(NpO2)_2Cl_7]^{5-}_{(aq)} + [NpO_2Cl_3(H_2O)]^{2-}_{(aq)} \rightarrow [(NpO2)_3Cl_{10}]^{7-}_{(aq)} + H_2O_{(aq)}$	-23.47
	II	$[(NpO2)_2Cl_7]^{5-}_{(aq))} + [NpO_2Cl_3(H_2O)_2]^{2-}_{(aq)} \rightarrow [(NpO2)_3Cl_{10}]^{7-}_{(aq)} + 2H_2O_{(aq)}$	> 0
	III	$[(NpO2)_2Cl_7]^{5-}_{(aq)} + [NpO_2Cl_4(H_2O)]^{2-}_{(aq)} + H_3O^+_{(aq)} \rightarrow [(NpO2)_3Cl_{10}]^{7-}_{(aq)} + HCl_{(aq)} + 2H_2O_{(aq)}$	> 0
	IV	$[(NpO2)_2Cl_7]^{5-}_{(aq)} + [NpO_2Cl_4]^{3-}_{(aq))} + H_3O^+_{(aq)} \rightarrow [(NpO2)_3Cl_{10}]^{7-}_{(aq)} + HCl_{(aq)} + H_2O_{(aq)}$	> 0

Table S29: Possible formation reactions that may be involved in the formation of Np-Rb.

Step		Possible Reactions	ΔH (kJ/mol)
1	I	$2[NpO_2Cl_3(H_2O)]^{2-}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)}$	-34.27
	II	$[NpO_2Cl_3(H_2O)]^{2-}_{(aq)} + [NpO_2Cl_2(H_2O)_2]^{-}_{(aq)} + HCl_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + H_3O^{+}_{(aq)}$	-8.19
	III	$[NpO_2Cl_3(H_2O)]^{2-}_{(aq)} + [NpO_2Cl_3(H_2O)_2]^{2-}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + H_2O_{(aq)}$	-4.52
	IV	$2[NpO_2Cl_3(H_2O)_2]^{2-}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + 2H_2O_{(aq)}$	> 0
	V	$2[NpO_2Cl_2(H_2O)_2]^{-}_{(aq)} + 2HCl_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + 2H_3O^{+}_{(aq)}$	> 0
	VI	$[NpO_2Cl_3(H_2O)]^{2-}_{(aq)} + [NpO_2Cl_2(H_2O)_3]^{-}_{(aq)} + HCl_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + H_3O^{+}_{(aq)} + H_2O_{(aq)}$	> 0
	VII	$2[NpO_2Cl_2(H_2O)_3]^{-}_{(aq)} + 2HCl_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + 2H_3O^{+}_{(aq)} ++ 2H_2O_{(aq)}$	> 0
	VIII	$[NpO_2Cl_4(H_2O)]^{3-}_{(aq)} + [NpO_2Cl_2(H_2O)_2]^{-}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + H_2O_{(aq)}$	> 0
	IX	$[NpO_2Cl_4]^{3-}_{(aq)} + [NpO_2Cl_2(H_2O)_2]^{-}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)}$	> 0
	X	$[NpO_2Cl_4(H_2O)]^{3-}_{(aq)} + [NpO_2Cl_2(H_2O)_3]^{-}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + 2H_2O_{(aq)}$	> 0
	XI	$[NpO_2Cl_4]^{3-}_{(aq)} + [NpO_2Cl_2(H_2O)_3]^{-}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + H_2O_{(aq)}$	> 0
	XII	$[NpO_2Cl_3(H_2O)]^{2-}_{(aq)} + [NpO_2Cl_4(H_2O)]^{2-}_{(aq)} + H_3O^{+}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + HCl_{(aq)} + H_2O_{(aq)}$	> 0
	XII	$2[NpO_2Cl_4(H_2O)]^{2-}_{(aq)} + 2H_3O^{+}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + 2HCl_{(aq)} + 2H_2O_{(aq)}$	> 0
	XIV	$[NpO_2Cl_4(H_2O)]^{2-}_{(aq)} + [NpO_2Cl_4]^{3-}_{(aq)} + 2H_3O^{+}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + 2HCl_{(aq)} + H_2O_{(aq)}$	> 0
	XV	$2[NpO_2Cl_4]^{3-}_{(aq} + 2H_3O^{+}_{(aq)} \rightarrow [(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + 2HCl_{(aq)}$	> 0
2	I	$[(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + [NpO_2Cl_3(H_2O)]^{2-}_{(aq)} + H_3O^{+}_{(aq)} \rightarrow [(NpO2)_3Cl_8(H_2O)_3]^{5-}_{(aq)} + H_2O_{(aq)} + HCl_{(aq)}$	-56.66
	II	$[(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + [NpO_2Cl_2(H_2O)_2]^{-}_{(aq)} \rightarrow [(NpO2)_3Cl_8(H_2O)_3]^{5-}_{(aq)} + H_2O_{(aq)}$	-30.58
	III	$[(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + [NpO_2Cl_3(H_2O)_2]^{2-}_{(aq)} + H_3O^{+}_{(aq)} \rightarrow [(NpO2)_3Cl_8(H_2O)_3]^{5-}_{(aq)} + 2H_2O_{(aq)} + HCl_{(aq)}$	-26.91
	IV	$[(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + [NpO_2Cl_2(H_2O)_3]^{-}_{(aq)} \rightarrow [(NpO2)_3Cl_8(H_2O)_3]^{5-}_{(aq)} + 2H_2O_{(aq)}$	-14.59
	V	$[(NpO2)_2Cl_6(H_2O)_2]^{4-}_{(aq)} + [NpO_2Cl_4(H_2O)]^{3-}_{(aq)} + 2H_3O^{+}_{(aq)} \rightarrow [(NpO2)_3Cl_8(H_2O)_3]^{5-}_{(aq)} +$	> 0

	VI	$2HCl_{(aq)} + 2H_2O_{(aq)}$ $[(NpO2)_2Cl_6(H_2O)_2]^{4-}{}_{(aq)} + [NpO_2Cl_4]^{3-}{}_{(aq)} + 2H_3O^+{}_{(aq)} \rightarrow [(NpO2)_3Cl_8(H_2O)_3]^{5-}{}_{(aq)} + 2HCl_{(aq)} + H_2O_{(aq)}$	> 0

7. References

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