Supplementary information for

Unveiling the Covalency of Versatile Pu(III)–N bonds in a Unique Plutonium(III) Complex

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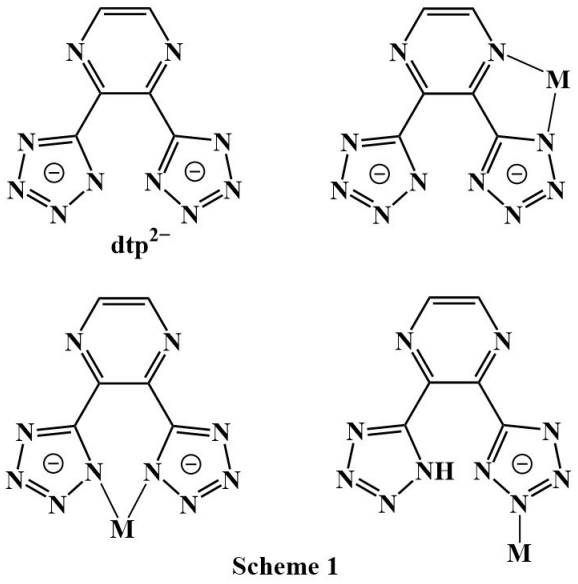
Contents

Section S1. Coordination modes of 2,3-di-1H-tetrazolate-5-ylpyrazine (dtp^{2-}) in Pu_dtp



Scheme 1

Figure S1.1. Structures of the ligands dtp^{2-} and its coordination modes in Pu_dtp.

Section S2. Images of reaction and crystals

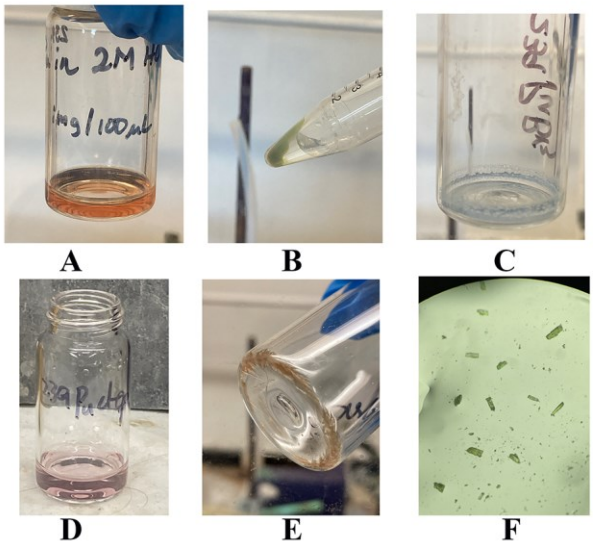


Figure S2.1. A. Stock solution of $^{239}Pu^{n+}$ (1 mg/0.1mL). B. Pellet of $^{239}Pu(OH)_4$ after centrifugation. C. $^{239}PuBr_3 \cdot nH_2O$. D. Reaction picture. E. Crystals of **Pu_dtp** grown from aqueous solution. F. Crystals of **Pu_dtp** used for single-crystal X-ray diffraction and solid-state UV-vis-NIR spectroscopy.

Section S3. Additional crystal structures of Pu_dtp

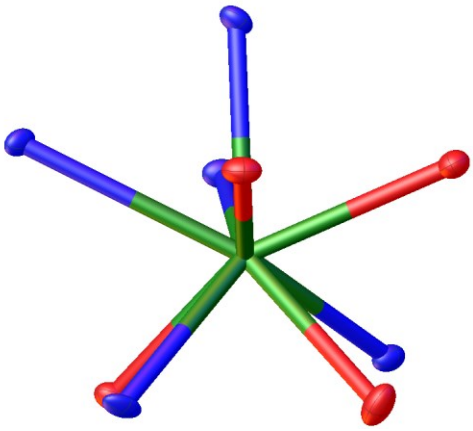


Figure S3.1 A view of the local coordination environment (spherical capped square antiprismatic geometry with a deviation value of 0.928, from the analysis via SHAPE software[1,2]) of the Pu^{3+} cation within **Pu_dtp** from OLEX2.

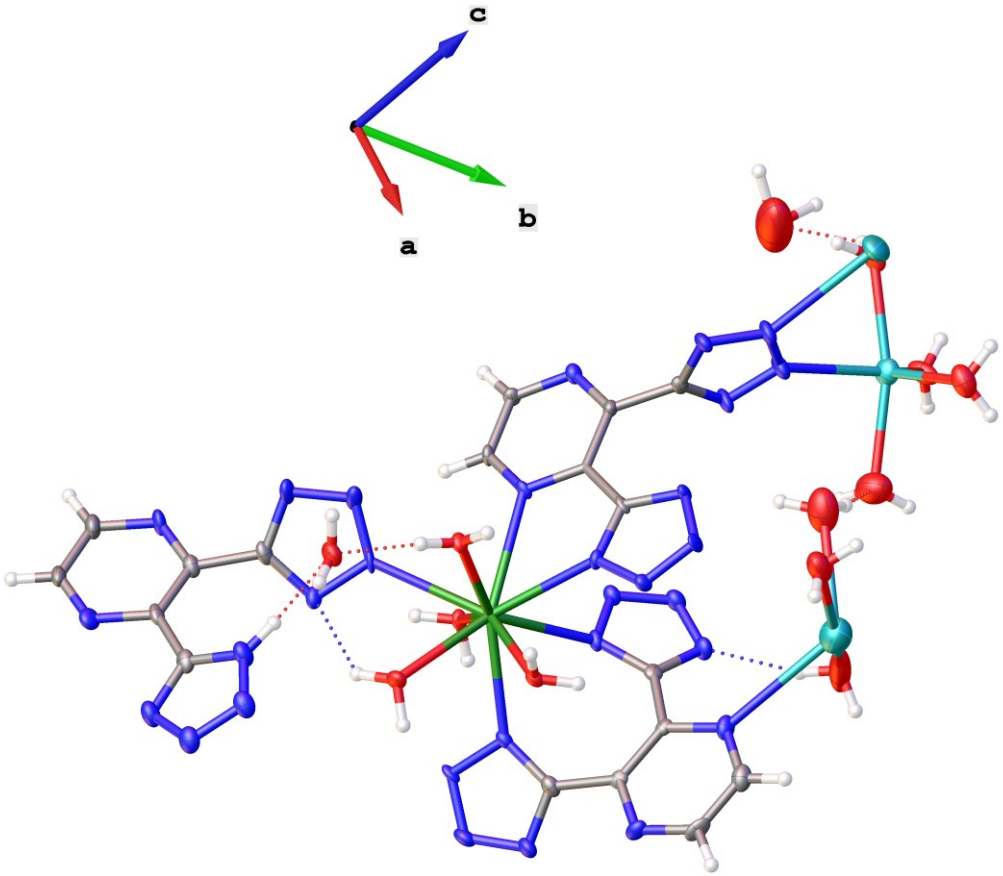


Figure S3.2. Thermal ellipsoid plot of **Pu_dtp** asymmetrical unit from OLEX2. The thermal ellipsoid probability is 50% at 100 K and Na^+ ions, hydrogen atoms and non-coordinating H_2O molecules are shown.

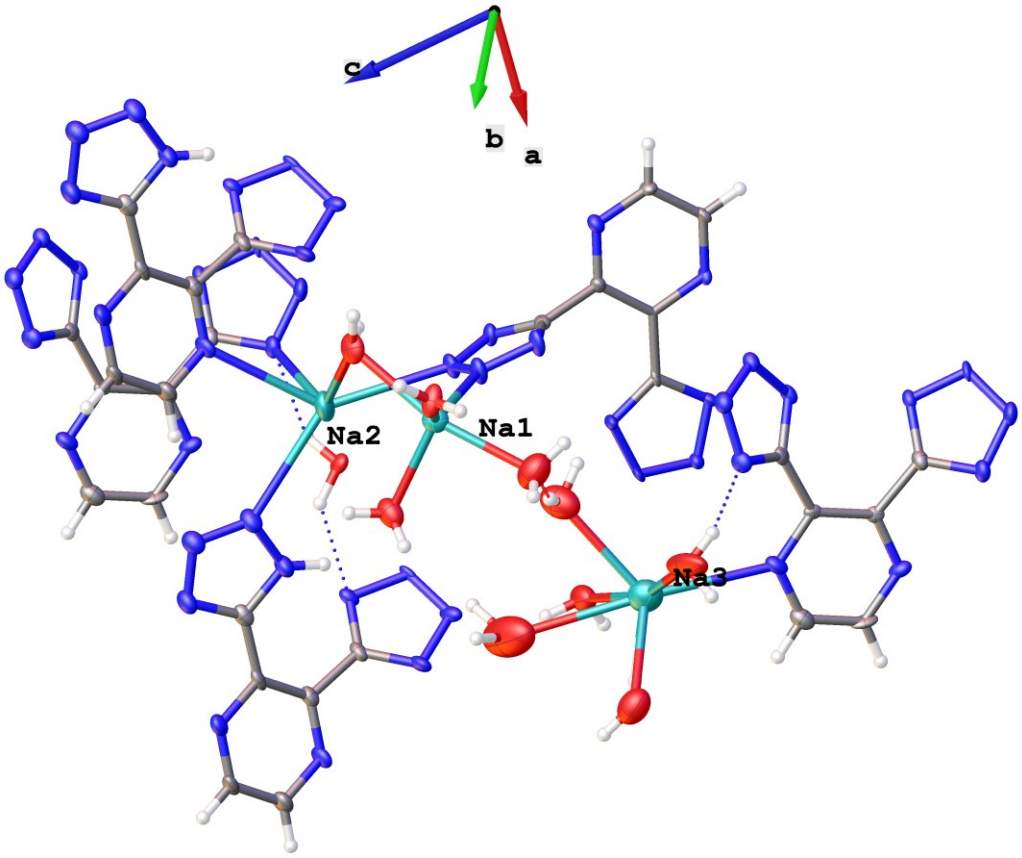


Figure S3.3. Thermal ellipsoid plot of **Pu_dtp** from OLEX2, shown the coordination environment of Na^+ ions. The thermal ellipsoid probability is 50% at 100 K and Na^+ ions, hydrogen atoms and non-coordinating H_2O molecules are shown. Na1 is fully occupied and coordinated with four water molecules and one nitrogen from dtp^{2-} anions. Na2 is coordinated with one water molecule and four nitrogen atoms from two dtp^{2-} anions and two $Hdtp^-$ anions. Na1 and Na2 are linked from bidentate tetrazolate of one dtp^{2-} anion. Na3 is coordinated with five water molecules and one nitrogen from pyrizinyl of dtp^{2-} anion. Na3 is linked to Na1 through a Na3–$H_2O\cdots H_2O$–Na1.

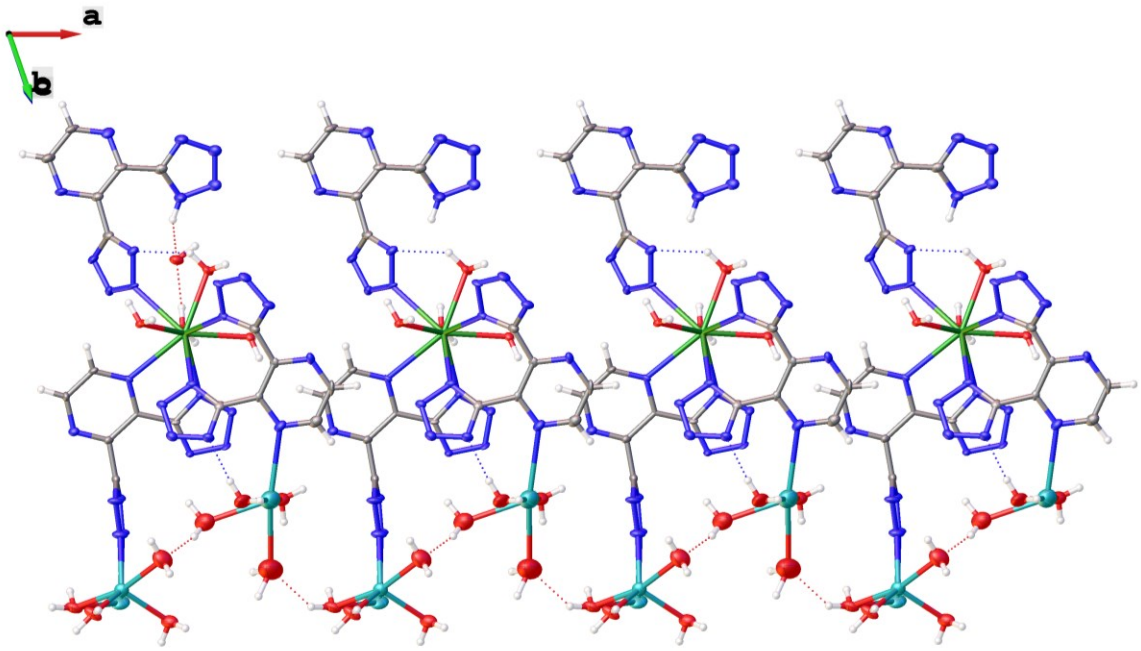


Figure S3.4. Thermal ellipsoid plot of **Pu_dtp** from OLEX2, shown that the $[Pu(Hdtp)(dtp)_2(H_2O)_4]^{2-}$ anions are linked by hydrogen frameworks through metal chain of $[Na_2(H_2O)_8]^{2+}$ units with the direction shown upper left corner forming a chain.

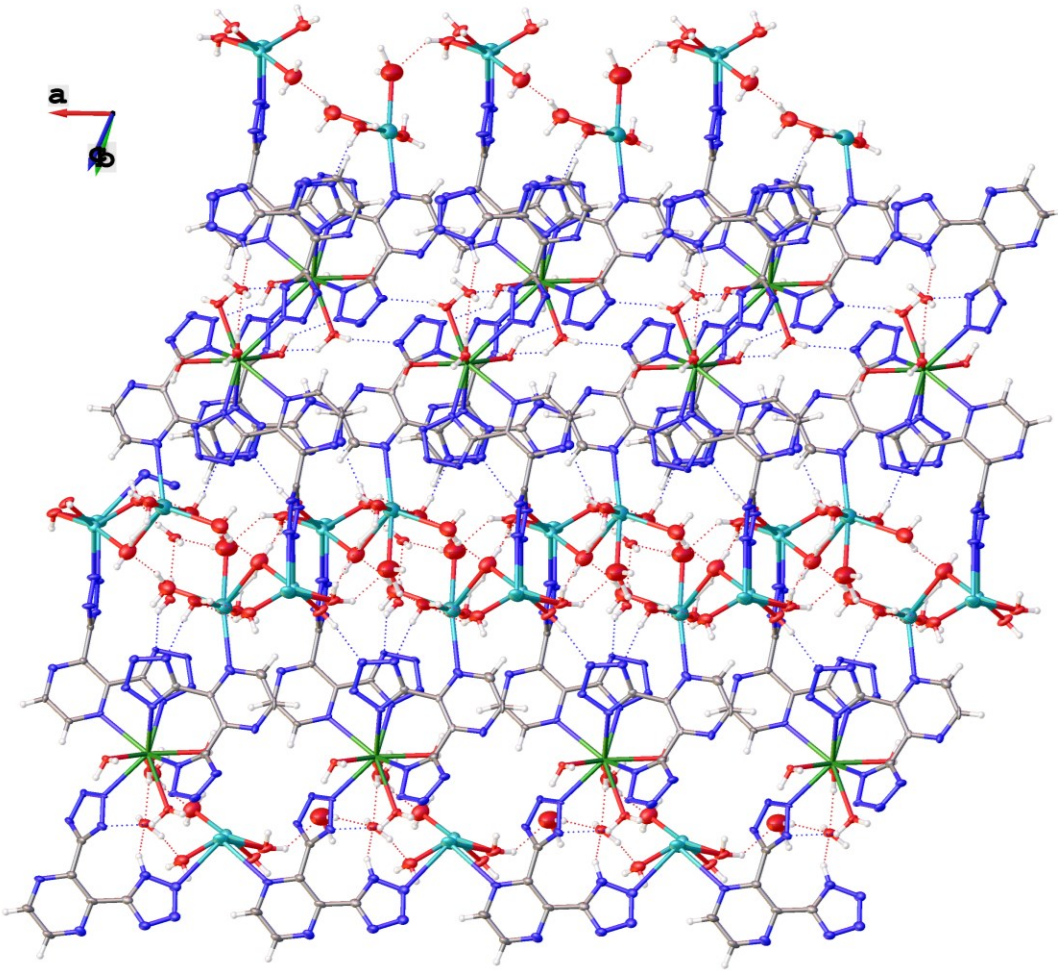


Figure S3.5 A view of the extended structures within **Pu_dtp** from OLEX2. From this direction (shown upper left corner). The chains formed from $[Pu(Hdtp)(dtp)_2(H_2O)_4]^{2-}$ and $[Na_2(H_2O)_8]^{2+}$ are linked together by the hydrogen bonds between water molecules and nitrogen atoms from ligands forming a pseudo-2D layer.

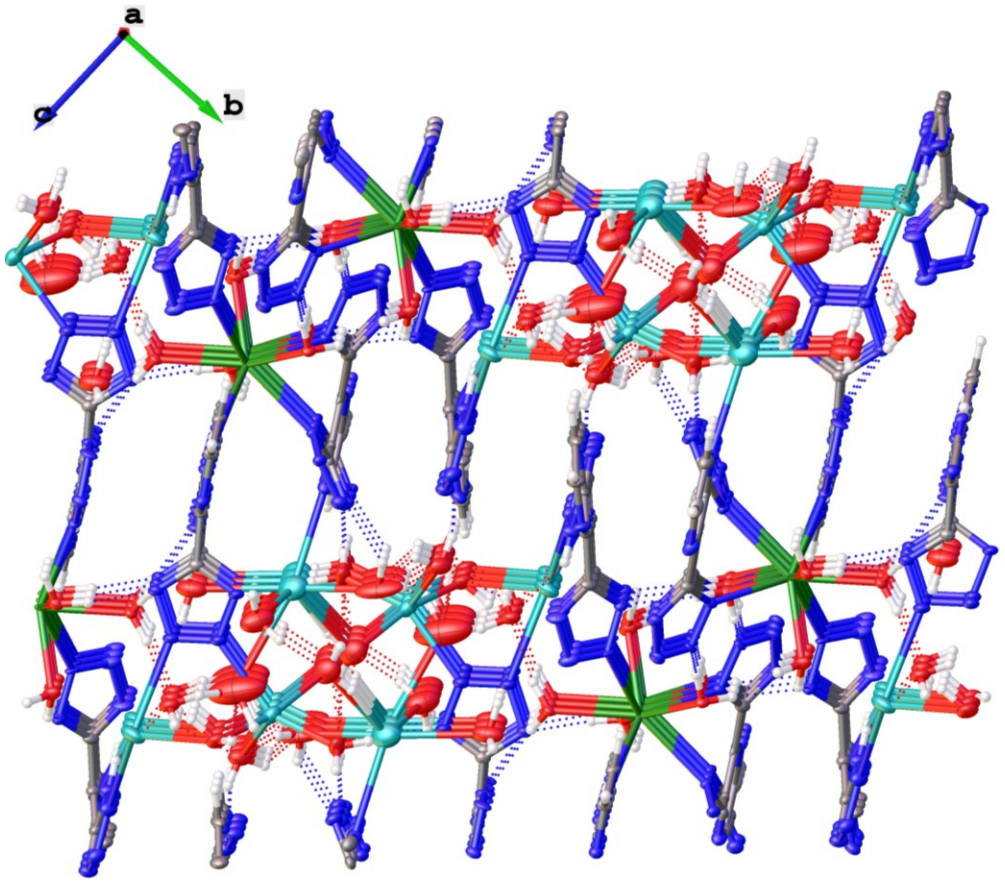


Figure S3.6 A view of the extended structures within **Pu_dtp** from OLEX2. From this direction (shown upper left corner). The neighboring layers shown in **Figure S3.5** are connected through hydrogen bonds of $H_2O\cdots N$ from tetrazolate and $Na–H_2O\cdots H_2O–Na$ to constitute a pseudo-3D framework.

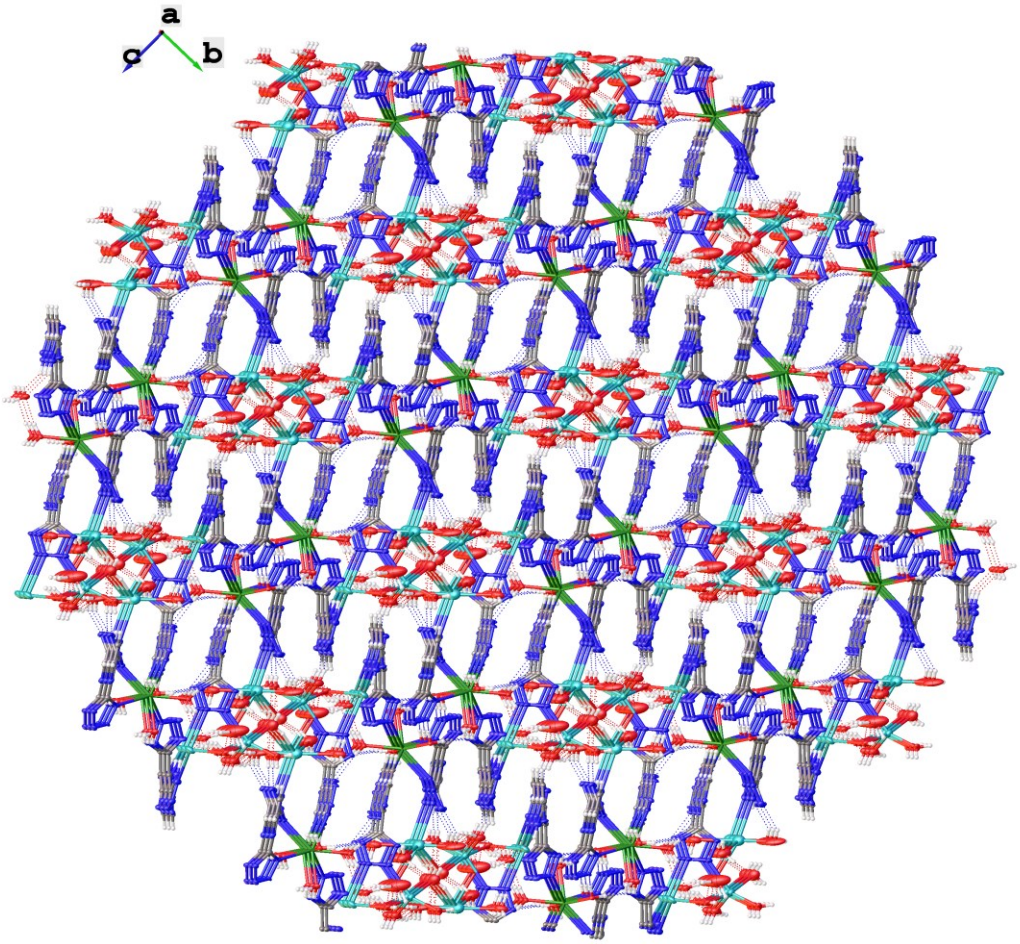


Figure S3.7 A view of the extended structures within **Pu_dtp** from OLEX2. The hydrogen bonds details are also shown in section S4.

Section S4. Crystallographic data for Pu_dtp

Table S4.1. Crystal data and structure refinement for **Pu_dtp**.

Identification code	Pu_dtp
Empirical formula	$C_{18}H_{33}N_{30}Na_2O_{13}Pu$
Formula weight/g/mol	1165.72
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	9.5590(5)
b/Å	14.5429(8)
c/Å	14.7750(8)
α/°	88.144(2)
β/°	74.108(2)
γ/°	79.653(2)
Volume/Å^3	1943.02(18)
Z	2
ρ_{calc}/g/cm^3	2.013
μ/mm^{-1}	1.822
F(000)	1150.0
Crystal size/mm^3	0.15 × 0.034 × 0.01
Radiation	Mo K_α (λ = 0.71073 Å)
2θ range for data collection/°	4.004 to 54.968
Index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-19 \le l \le 19$
Reflections collected	23016
Independent reflections	8912 [R_{int} = 0.0522, R_{sigma} = 0.0646]
Data/restraints/parameters	8912/4/601
Goodness-of-fit on F^2	1.180
Final R indexes [I≥2σ (I)]	R_1 = 0.0560, ωR_2 = 0.1144
Final R indexes [all data]	R_1 = 0.0650, ωR_2 = 0.1178
Largest diff. peak/hole/eÅ^{-3}	4.04/−4.80

R_1, = $\sum||F_c|-|F_c|/\sum|F_o|$. $\omega R_2 = [\sum\{\omega(F_o^2 - F_c^2)^2/\sum\omega(F_o^2)^2\}]^{1/2}$

Table S4.2. Bond Lengths for **Pu_dtp**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pu1	O2	2.470(5)	N15	N14	1.308(9)
Pu1	O3	2.496(5)	N25	C14	1.335(11)
Pu1	O1	2.468(5)	N25	C15	1.335(10)
Pu1	N3	2.596(6)	N25	Na2[1]	2.865(11)
Pu1	N5	2.756(6)	C12	C11	1.486(10)
Pu1	N2	2.586(6)	N26	C17	1.358(10)
Pu1	O4	2.498(5)	N26	C16	1.325(11)
Pu1	N4	2.671(6)	N29	N30	1.343(10)
Pu1	N1	2.572(6)	N29	N28	1.317(10)
N3	N19	1.354(8)	N29	Na2[2]	2.883(11)
N3	C12	1.336(10)	C8	C11	1.401(10)
N13	N12	1.356(9)	C8	C7	1.478(10)
N13	C6	1.326(10)	N12	N11	1.292(10)

N19	N20	1.308(9)	N12	Na2	2.801(10)
N5	C3	1.333(9)	C6	N10	1.331(10)
N5	C2	1.355(8)	C6	C5	1.476(10)
N2	C7	1.345(10)	C1	C2	1.433(10)
N2	N14	1.352(9)	N23	C13	1.335(10)
N18	C11	1.337(10)	O11	Na1	2.340(8)
N18	C10	1.336(11)	N11	N10	1.351(9)
N21	N7	1.315(8)	N11	Na1	2.482(8)
N21	N1	1.351(8)	O6	Na7	2.818(15)
N9	C4	1.349(9)	C3	C4	1.391(10)
N9	C5	1.330(10)	N30	C18	1.343(10)
N24	N4	1.356(8)	N27	N28	1.334(10)
N24	C13	1.335(10)	N27	C18	1.339(11)
N20	N6	1.348(10)	C14	C13	1.488(10)
N4	N22	1.319(10)	C14	C17	1.398(11)
N6	C12	1.345(10)	C5	C2	1.434(9)
N17	C8	1.354(9)	C10	C9	1.382(12)
N17	C9	1.318(11)	C17	C18	1.467(12)
N17	Na7	2.883(13)	C16	C15	1.394(12)
N8	N7	1.344(9)	O10	Na1	2.350(9)
N8	C1	1.335(9)	O10	$Na7^{3}$	2.807(14)
N22	N23	1.345(9)	O9	Na7	2.683(14)
N16	N15	1.343(10)	O8	Na7	2.600(18)
N16	C7	1.330(10)	Na2	O13	2.952(12)
N1	C1	1.335(9)	Na1	O13	2.326(8)
O12	Na1	2.282(7)	O15	$Na7^{4}$	2.995(19)

Table S4.3. Bond Angles for **Pu_dtp**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O2	Pu1	O3	146.04(18)	N18	C11	C8	121.3(7)
O2	Pu1	N3	74.95(19)	C8	C11	C12	125.7(7)
O2	Pu1	N5	77.07(18)	N13	N12	Na2	140.2(6)
O2	Pu1	N2	71.04(19)	N11	N12	N13	109.6(6)
O2	Pu1	O4	100.93(18)	N11	N12	Na2	109.3(5)
O2	Pu1	N4	68.63(19)	N13	C6	N10	111.9(7)
O2	Pu1	N1	124.90(18)	N13	C6	C5	127.3(7)
O3	Pu1	N3	71.22(19)	N10	C6	C5	120.4(7)
O3	Pu1	N5	129.35(17)	N8	C1	C2	128.1(6)
O3	Pu1	N2	91.88(19)	N1	C1	N8	111.8(7)
O3	Pu1	O4	71.55(18)	N1	C1	C2	120.1(6)
O3	Pu1	N4	130.71(18)	N2	C7	C8	127.4(7)
O3	Pu1	N1	69.05(18)	N16	C7	N2	111.2(7)
O1	Pu1	O2	134.74(18)	N16	C7	C8	121.4(7)
O1	Pu1	O3	77.51(18)	C13	N23	N22	104.8(7)
O1	Pu1	N3	142.40(19)	N15	N14	N2	109.1(6)
O1	Pu1	N5	77.16(18)	N12	N11	N10	109.7(6)
O1	Pu1	N2	137.23(18)	N12	N11	Na1	127.6(5)

O1	Pu1	O4	78.59(18)	N10	N11	Na1	122.8(5)
O1	Pu1	N4	70.11(18)	N5	C3	C4	122.1(7)
O1	Pu1	N1	70.85(18)	C6	N10	N11	104.4(7)
N3	Pu1	N5	139.60(19)	N29	N30	C18	104.9(7)
N3	Pu1	N4	116.64(19)	N9	C4	C3	121.1(7)
N2	Pu1	N3	65.2(2)	N28	N27	C18	104.1(7)
N2	Pu1	N5	78.4(2)	N25	C14	C13	113.4(7)
N2	Pu1	N4	136.8(2)	N25	C14	C17	121.2(7)
O4	Pu1	N3	72.18(19)	C17	C14	C13	125.1(7)
O4	Pu1	N5	142.25(18)	N9	C5	C6	114.4(7)
O4	Pu1	N2	137.3(2)	N9	C5	C2	122.5(6)
O4	Pu1	N4	66.43(19)	C2	C5	C6	123.0(6)
O4	Pu1	N1	134.1(2)	N29	N28	N27	110.8(7)
N4	Pu1	N5	78.27(19)	N24	C13	N23	112.3(7)
N1	Pu1	N3	114.74(19)	N24	C13	C14	127.3(7)
N1	Pu1	N5	61.41(19)	N23	C13	C14	120.4(7)
N1	Pu1	N2	66.7(2)	N18	C10	C9	121.0(7)
N1	Pu1	N4	128.6(2)	N17	C9	C10	122.2(8)
N19	N3	Pu1	118.9(5)	N26	C17	C14	120.2(8)
C12	N3	Pu1	134.6(5)	N26	C17	C18	113.1(7)
C12	N3	N19	104.8(6)	C14	C17	C18	126.5(7)
C6	N13	N12	104.4(6)	N26	C16	C15	122.5(7)
N20	N19	N3	109.3(6)	Na1	O10	$Na7^{3}$	111.4(4)
C3	N5	Pu1	124.2(5)	N25	C15	C16	120.0(8)
C3	N5	C2	118.4(6)	N30	C18	C17	126.6(7)
C2	N5	Pu1	116.6(4)	N27	C18	N30	111.7(8)
C7	N2	Pu1	133.1(5)	N27	C18	C17	121.3(7)
C7	N2	N14	104.7(6)	N5	C2	C1	117.4(6)
N14	N2	Pu1	116.5(5)	N5	C2	C5	118.6(6)
C10	N18	C11	117.7(7)	C1	C2	C5	124.0(6)
N7	N21	N1	108.3(6)	$N25^{1}$	Na2	$N29^{2}$	85.4(3)
C5	N9	C4	117.2(7)	$N25^{1}$	Na2	O13	78.5(3)
C13	N24	N4	104.1(6)	$N29^{2}$	Na2	O13	124.5(4)
N19	N20	N6	109.9(6)	N12	Na2	$N25^{1}$	136.0(4)
N24	N4	Pu1	123.4(5)	N12	Na2	$N29^{2}$	138.6(4)
N22	N4	Pu1	125.7(5)	N12	Na2	O13	76.0(3)
N22	N4	N24	109.6(6)	O12	Na1	O11	120.3(3)
C12	N6	N20	104.5(6)	O12	Na1	N11	139.2(3)
C8	N17	Na7	136.6(6)	O12	Na1	O10	90.2(3)
C9	N17	C8	117.8(7)	O12	Na1	O13	91.0(3)
C9	N17	Na7	105.1(6)	O11	Na1	N11	100.5(3)
C1	N8	N7	104.1(6)	O11	Na1	O10	90.7(3)
N4	N22	N23	109.3(6)	O10	Na1	N11	87.4(3)
C7	N16	N15	105.1(6)	O13	Na1	O11	100.3(3)
N21	N7	N8	110.6(6)	O13	Na1	N11	82.9(3)
N21	N1	Pu1	130.8(5)	O13	Na1	O10	166.5(3)
C1	N1	Pu1	122.5(5)	Na1	O13	Na2	91.3(3)
C1	N1	N21	105.2(6)	N17	Na7	$O15^{4}$	165.3(6)
N14	N15	N16	109.9(6)	O6	Na7	N17	106.5(4)

C14	N25	C15	118.6(7)	O6	Na7	O15[4]	59.7(4)
C14	N25	Na2[1]	128.8(5)	O10[3]	Na7	N17	111.5(4)
C15	N25	Na2[1]	108.1(6)	O10[3]	Na7	O6	116.1(5)
N3	C12	N6	111.4(7)	O10[3]	Na7	O15[4]	73.7(4)
N3	C12	C11	129.6(7)	O9	Na7	N17	120.0(4)
N6	C12	C11	118.9(7)	O9	Na7	O6	80.3(4)
C16	N26	C17	117.4(7)	O9	Na7	O10[3]	118.1(5)
N30	N29	Na2[2]	112.2(5)	O9	Na7	O15[4]	65.2(4)
N28	N29	N30	108.5(7)	O8	Na7	N17	77.7(4)
N28	N29	Na2[2]	139.2(6)	O8	Na7	O6	165.4(5)
N17	C8	C11	120.0(7)	O8	Na7	O10[3]	73.8(4)
N17	C8	C7	113.3(7)	O8	Na7	O9	85.6(5)
C11	C8	C7	126.5(7)	O8	Na7	O15[4]	117.0(5)
N18	C11	C12	113.0(7)				

Table S4.4. Hydrogen Bonds for **Pu_dtp**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2A	N19[1]	0.88	2.13	2.860(8)	139.7
O3	H3A	N13[2]	0.87	1.97	2.828(9)	168.1
O1	H1A	O5	0.87	1.86	2.719(8)	169.0
O4	H4A	N24	0.92	2.11	2.851(9)	135.9
O4	H4B	N6[3]	0.92	2.14	2.864(9)	134.5
O12	H12A	N15[4]	0.87	1.93	2.792(9)	172.3
O12	H12B	N10[4]	0.87	1.99	2.853(9)	169.1
O11	H11A	O8[5]	0.88	2.12	2.829(13)	136.9
O11	H11B	N28[6]	0.88	2.05	2.888(10)	158.8
N30	H30	O5	0.88	2.12	2.856(9)	140.2
O10	H10A	Na7[5]	0.88	2.00	2.807(14)	151.5
O10	H10B	O12[4]	0.88	2.01	2.837(12)	155.6
O13	H13A	O15	0.91	2.05	2.774(16)	135.5

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

Section S5. Spectra of Pu_dtp and $[Pu(H_2O)_9]^{3+}$

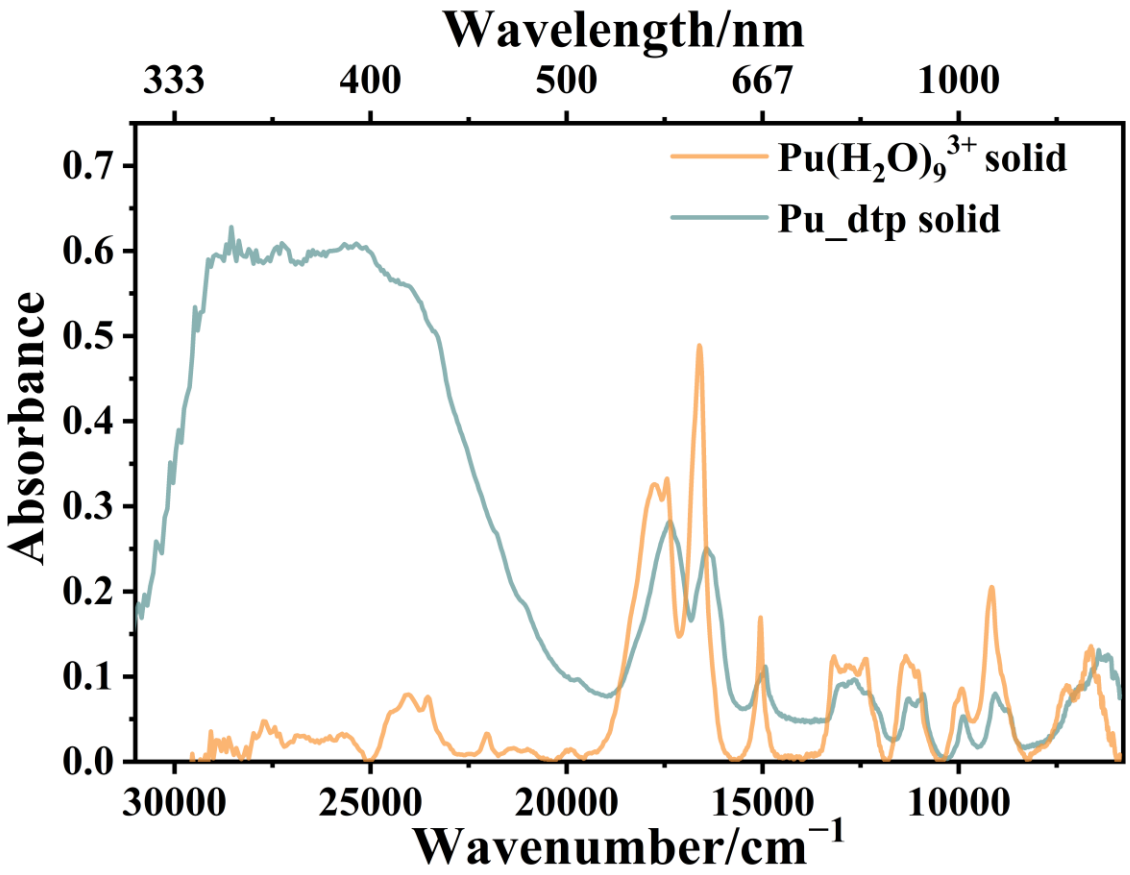


Figure S5.1 Solid state UV-vis-NIR spectra of **Pu_dtp** (blue) and $[Pu(H_2O)_9]^{3+}$,[3] (brown) at room temperature.

Section S6. The Quantum Theory of Atoms in Molecules (QTAIM)

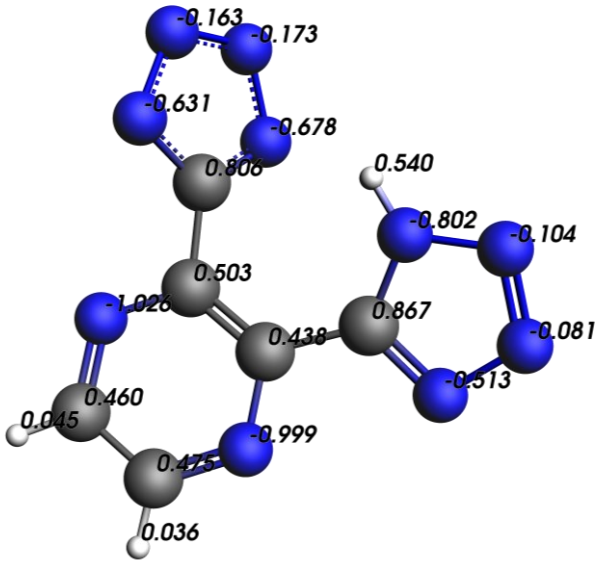


Figure S6.1 The Quantum Theory of Atoms in Molecules (QTAIM) change of $Hdtp^{-}$ before coordinating with Pu^{3+}.

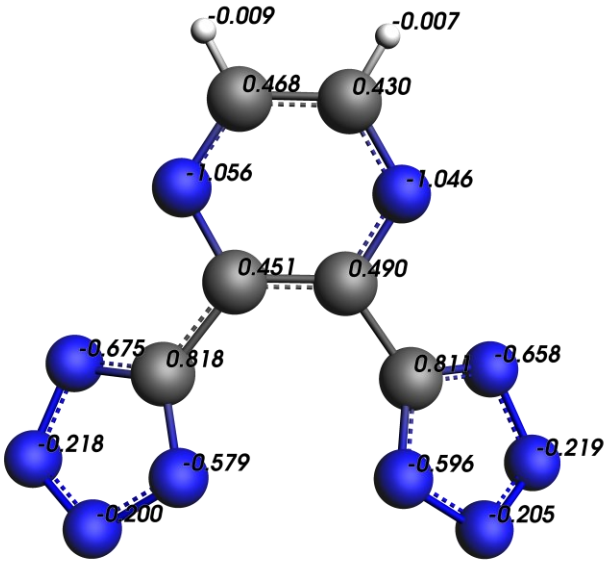


Figure S6.2 The Quantum Theory of Atoms in Molecules (QTAIM) change of dtp^{2-} before coordinating with Pu^{3+}. This dtp^{2-} is coordinated with Pu^{3+} through two nitrogen atoms from all tetrazolate.

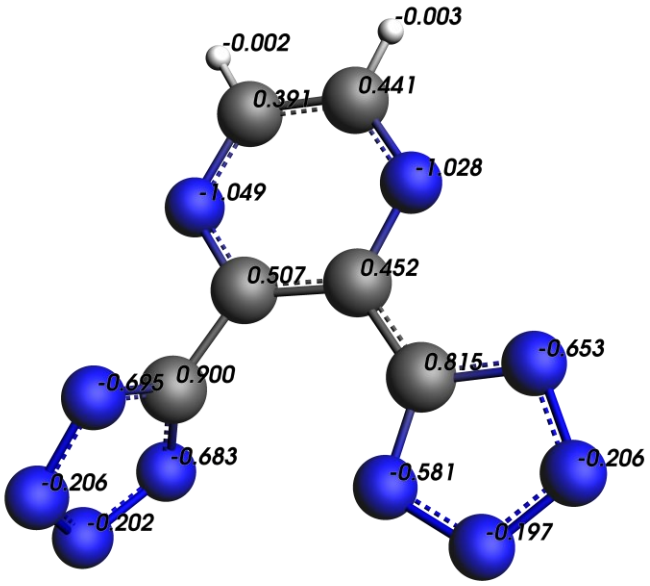
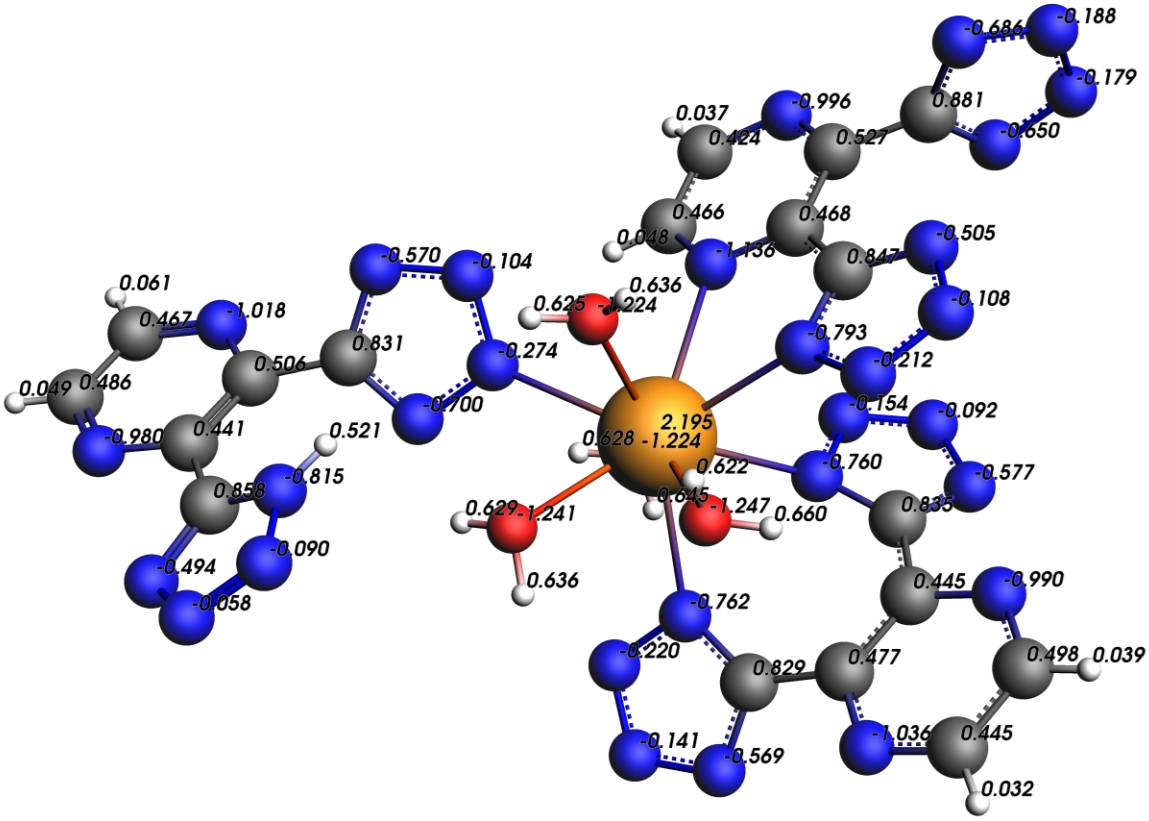


Figure S6.3 The Quantum Theory of Atoms in Molecules (QTAIM) change of dtp^{2-} before coordinating with Pu^{3+}. This dtp^{2-} is coordinated with Pu^{3+} through two nitrogen atoms from tetrazolate and pyrizinyl.



S6.4 The Quantum Theory of Atoms in Molecules (QTAIM) change of **Pu_dtp**.

Table S6.1. Bond length of Pu−H_2O and Pu−N in **Pu1** at 100 K and QTAIM metrics (including the electron density, ρ(r) in e·Å^{-3}, potential (V), kinetic (G), and total (H) energy densities in kJ·mol^{-1}·Å^{-3}, bond degree, H(r)/ρ(r), delocalization indices, δ(r), and localization indices, λ(M), integrated oxidation state, OS, calculated from the equation OS(M) = Z(M) − λ(M), at the BCP of and **Pu_dtp**.

Experiment	Pu−O1	Pu−O2	Nd−O3	Nd−O4
Calculation	Pu−O8	Pu−O2	Nd−O5	Nd−O16
Distance	2.468(5)	2.471(5)	2.496(5)	2.499(5)
Cal distance	2.443	2.498	2.548	2.573
ρ(r)	0.34	0.34	0.32	0.32
V(r)	−993.20	−925.25	−923.02	−1016.92
G(r)	954.67	909.15	902.07	1004.13
H(r)	−38.54	−16.10	−20.96	−12.79
H(r)/*ρ*(r)	−114.50	−50.53	−65.67	−38.04
δ(r)	0.2517	0.2802	0.2616	0.2619

Section S7. Natural localized molecular orbitals (NLMO)

Table S7.1. Wiberg bond indices (WBI). (Corresponding atoms numbers within crystal structures are shown in Section S1)

Bond	WBI
M–O1	0.2285
M–O2	0.2503
M–O3	0.2352
M–O4	0.2260
M–O Average	**0.2350**
M–N1	0.3236
M–N2	0.3095
M–N3	0.2979
M–N4	0.2518
M–N5	0.2273
M–N Average	**0.2820**

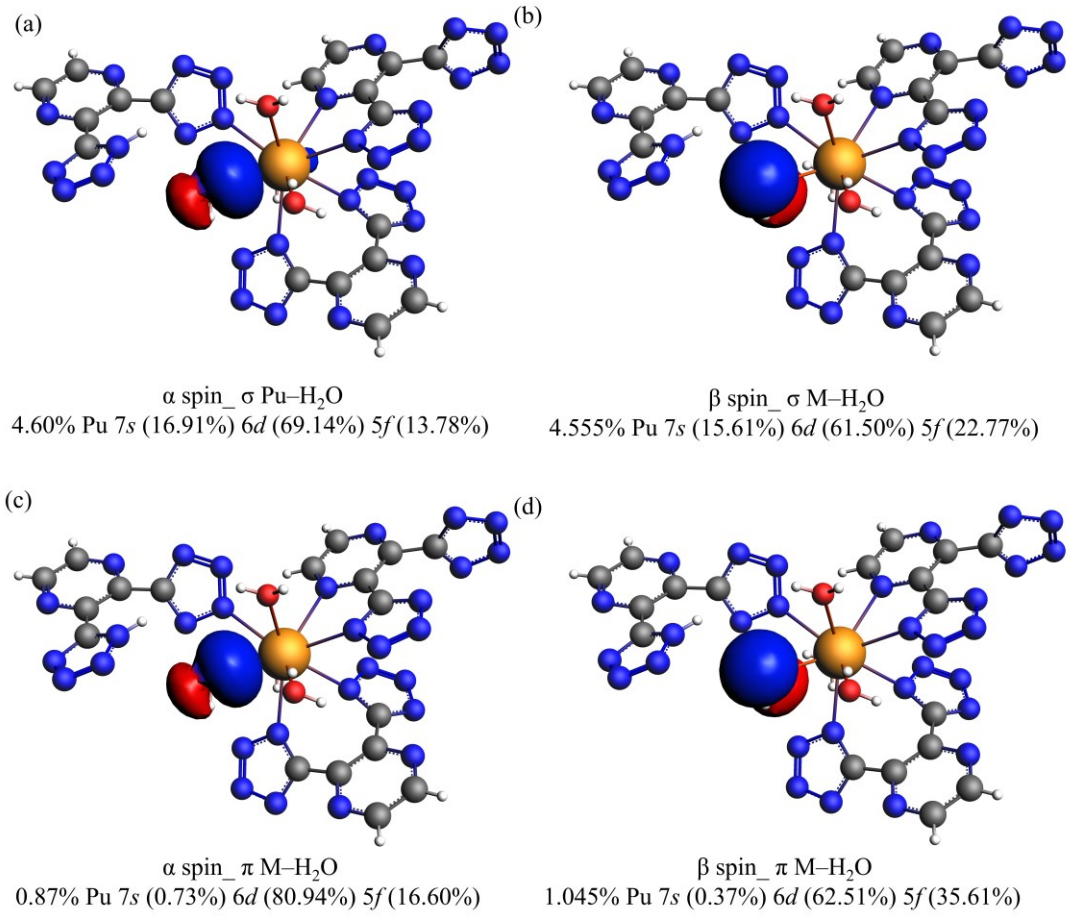


Figure S7.1. Selected NLMOs of α and β spins for Pu–O1 in **Pu_dtp**, showing Pu contributions to the NLMOs along with their hybrid contributions.

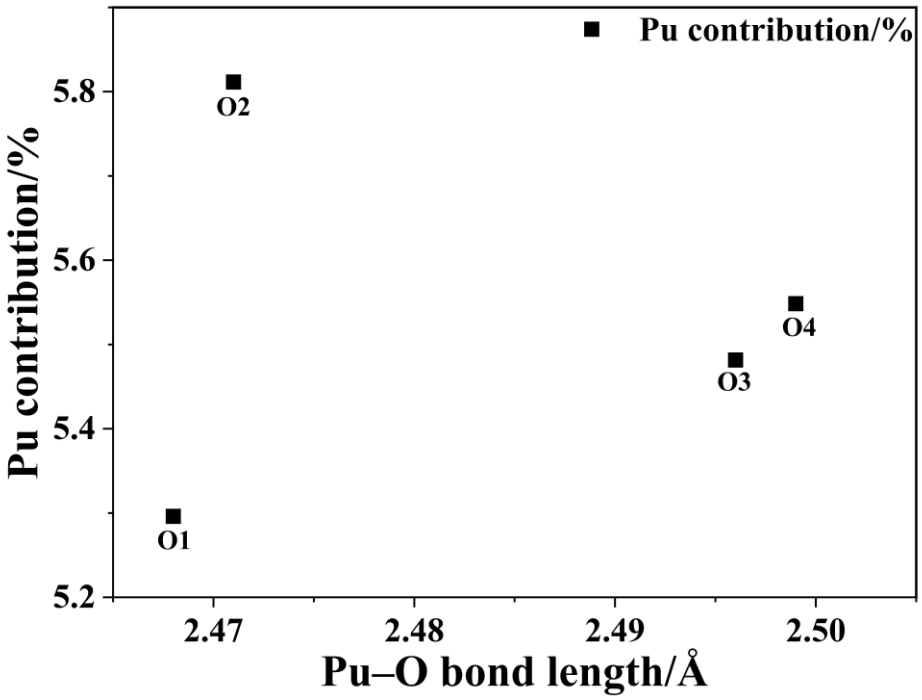


Figure S7.2. Plutonium contribution to selected NLMOs of average α + β spin Pu–H_2O in **Pu_dtp**.

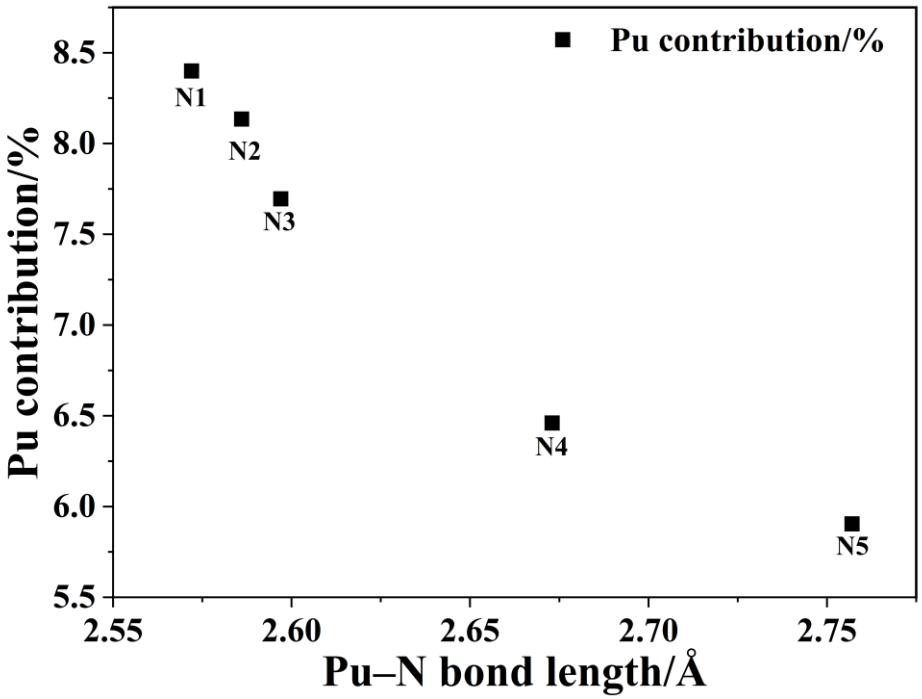


Figure S7.3. Plutonium contribution to selected NLMOs of average α + β spin Pu–N in **Pu_dtp**.

Table S7.2. The corresponding atomic numbers between experiment and calculation and experimental Pu−L bond length for **Pu_dtp**.

Experimental label	Calculation label	Experimental Distance with Pu^{3+}	Computational Distance with Pu^{3+}
O1	O4	2.468(5)	2.4679
O2	O2	2.471(5)	2.4708
O3	O3	2.496(5)	2.4955
O4	O5	2.499(5)	2.4989
N1	N38	2.572(6)	2.5716
N2	N25	2.586(6)	2.5862
N3	N21	2.597(6)	2.5967
N4	N31	2.673(6)	2.6728
N5	N24	2.757(6)	2.7567

Table S7.3. Selected NLMOs of α spin Pu–H_2O in **Pu_dtp**, showing metal contributions to the NLMOs along with their hybrid contributions (Atoms numbers are from the NLMO calculation, and respective atom numbers are shown in **Table S7.2**). In general, H_2O acts as a σ-donor ligand through the lone pair on oxygen (mainly from its sp^3 hybrid orbital). The lone pairs on oxygen in H_2O are in sp^3 hybrid orbitals, making them poorly suited for π interactions with metal *d*- and *f*-orbitals.

101. (1.00000) 98.9498% LP (1) O 2 0.915% Pu 1 s(0.23%)p 9.35(2.14%)d99.99(85.42%) f53.46(12.22%) 98.950% O 2 s(12.54%)p 6.96(87.25%)d 0.02(0.20%) f 0.00(0.02%)
102. (1.00000) 94.6809% LP (2) O 2 4.970% Pu 1 s(16.56%)p 0.01(0.18%)d 3.84(63.56%) f 1.19(19.70%) 94.691% O 2 s(29.30%)p 2.41(70.57%)d 0.00(0.12%) f 0.00(0.01%)
103. (1.00000) 99.1775% LP (1) O 3 0.666% Pu 1 s(1.25%)p 1.04(1.30%)d66.88(83.87%) f10.82(13.57%) 99.178% O 3 s(14.02%)p 6.12(85.80%)d 0.01(0.16%) f 0.00(0.02%)

104. (1.00000) 94.9142% LP (2) O 3 4.804% Pu 1 s(16.57%)p 0.01(0.15%)d 3.99(66.05%) f 1.04(17.23%) 0.046% O 2 s(26.04%)p 2.65(69.15%)d 0.18(4.79%) f 0.00(0.02%) 94.926% O 3 s(25.89%)p 2.86(74.00%)d 0.00(0.11%) f 0.00(0.01%)
105. (1.00000) 98.8184% LP (1) O 4 1.056% Pu 1 s(0.48%)p 4.87(2.36%)d99.99(74.85%) f46.05(22.30%) 98.819% O 4 s(4.37%)p21.83(95.43%)d 0.04(0.17%) f 0.01(0.03%)
106. (1.00000) 95.8522% LP (2) O 4 3.929% Pu 1 s(18.87%)p 0.01(0.28%)d 4.13(77.97%) f 0.15(2.87%) 0.030% O 2 s(20.77%)p 3.71(77.06%)d 0.10(2.14%) f 0.00(0.03%) 95.859% O 4 s(36.43%)p 1.74(63.50%)d 0.00(0.06%) f 0.00(0.01%)
107. (1.00000) 99.0362% LP (1) O 5 0.838% Pu 1 s(0.94%)p 1.22(1.15%)d84.98(79.60%) f19.55(18.31%) 99.037% O 5 s(12.30%)p 7.12(87.56%)d 0.01(0.13%) f 0.00(0.01%)
108. (1.00000) 95.0849% LP (2) O 5 4.682% Pu 1 s(15.62%)p 0.00(0.08%)d 4.42(68.99%) f 0.98(15.31%) 0.022% O 2 s(43.11%)p 1.29(55.58%)d 0.03(1.26%) f 0.00(0.05%) 95.094% O 5 s(33.73%)p 1.96(66.20%)d 0.00(0.07%) f 0.00(0.01%)
109. (1.00000) 89.3434% LP (1) N 21 8.270% Pu 1 s(12.52%)p 0.01(0.09%)d 5.03(62.93%) f 1.95(24.46%) 89.350% N 21 s(38.63%)p 1.59(61.34%)d 0.00(0.02%) f 0.00(0.00%)
112. (1.00000) 90.7652% LP (1) N 24 5.889% Pu 1 s(14.11%)p 0.01(0.12%)d 5.72(80.67%) f 0.36(5.10%) 90.767% N 24 s(29.58%)p 2.38(70.38%)d 0.00(0.04%) f 0.00(0.00%)

113. (1.00000) 89.0543% LP (1) N 25 8.568% Pu 1 s(9.30%)p 0.01(0.13%)d 7.73(71.91%) f 2.01(18.66%) 89.068% N 25 s(39.18%)p 1.55(60.79%)d 0.00(0.03%) f 0.00(0.00%)
119. (1.00000) 90.9318% LP (1) N 31 6.756% Pu 1 s(16.14%)p 0.01(0.09%)d 4.34(70.09%) f 0.85(13.68%) 90.941% N 31 s(44.72%)p 1.24(55.25%)d 0.00(0.03%) f 0.00(0.00%)
129. (1.00000) 89.0259% LP (1) N 38 8.771% Pu 1 s(12.23%)p 0.01(0.07%)d 5.83(71.32%) f 1.34(16.38%) 89.040% N 38 s(38.20%)p 1.62(61.78%)d 0.00(0.02% f 0.00(0.00%)

Table S7.4. Selected natural localized molecular orbitals (NLMOs) of β spin Pu–H_2O in **Pu_dtp**, showing metal contributions to the NLMOs along with their hybrid contributions (Atoms numbers are from the NLMO calculation.).

96. (1.00000) 98.7587% LP (1) O 2 1.122% Pu 1 s(0.22%)p 8.31(1.84%)d99.99(63.36%) f99.99(34.58%) 98.759% O 2 s(12.93%)p 6.71(86.85%)d 0.02(0.20%) f 0.00(0.01%)
97. (1.00000) 95.1083% LP (2) O 2 4.616% Pu 1 s(15.75%)p 0.01(0.14%)d 3.89(61.22%) f 1.45(22.90%) 95.122% O 2 s(28.93%)p 2.45(70.95%)d 0.00(0.12%) f 0.00(0.01%)
98. (1.00000) 98.9560% LP (1) O 3 0.899% Pu 1 s(0.27%)p 3.98(1.07%)d99.99(60.34%) f99.99(38.33%) 98.956% O 3 s(11.66%)p 7.56(88.16%)d 0.01(0.16%) f 0.00(0.02%)
99. (1.00000) 95.1581% LP (2) O 3 4.594% Pu 1 s(15.75%)p 0.01(0.10%)d 3.88(61.09%) f 1.46(23.06%) 0.049% O 2 s(24.03%)p 2.97(71.38%)d 0.19(4.54%) f 0.00(0.04%) 95.171% O 3 s(28.38%)p 2.52(71.51%)d 0.00(0.11%) f 0.00(0.01%)

100. (1.00000) 98.6718% LP (1) O 4
1.209% Pu 1 s(0.38%)p 5.21(1.96%)d99.99(62.87%)
f92.29(34.79%)
98.672% O 4 s(4.76%)p19.96(95.04%)d 0.04(0.17%)
f 0.01(0.03%)

101. (1.00000) 95.3194% LP (2) O 4
4.403% Pu 1 s(16.94%)p 0.01(0.22%)d 3.52(59.61%)
f 1.37(23.23%)
0.017% O 2 s(18.10%)p 4.27(77.26%)d 0.25(4.54%)
f 0.01(0.09%)
0.031% O 3 s(16.66%)p 4.94(82.36%)d 0.05(0.86%)
f 0.01(0.12%)
95.328% O 4 s(35.77%)p 1.79(64.16%)d 0.00(0.06%)
f 0.00(0.01%)

102. (1.00000) 98.9045% LP (1) O 5
0.968% Pu 1 s(0.61%)p 1.84(1.13%)d99.99(63.48%)
f56.64(34.77%)
98.905% O 5 s(11.03%)p 8.05(88.82%)d 0.01(0.13%)
f 0.00(0.01%)

103. (1.00000) 95.1840% LP (2) O 5
4.609% Pu 1 s(14.00%)p 0.00(0.05%)d 4.58(64.08%)
f 1.56(21.87%)
0.019% O 2 s(42.33%)p 1.32(55.81%)d 0.04(1.80%)
f 0.00(0.06%)
0.019% O 4 s(46.59%)p 1.06(49.39%)d 0.08(3.77%)
f 0.01(0.25%)
95.194% O 5 s(34.92%)p 1.86(65.01%)d 0.00(0.07%)
f 0.00(0.01%)

104. (1.00000) 90.6313% LP (1) N 21
7.123% Pu 1 s(14.41%)p 0.00(0.07%)d 4.45(64.09%)
f 1.49(21.43%)
90.636% N 21 s(38.83%)p 1.57(61.14%)d 0.00(0.03%)
f 0.00(0.00%)

107. (1.00000) 90.8242% LP (1) N 24
5.919% Pu 1 s(12.68%)p 0.01(0.08%)d 5.32(67.49%)
f 1.56(19.75%)
90.826% N 24 s(29.76%)p 2.36(70.20%)d 0.00(0.04%)
f 0.00(0.00%)

108. (1.00000) 90.0570% LP (1) N 25 7.695% Pu 1 s(11.07%)p 0.01(0.12%)d 5.98(66.19%) f 2.04(22.62%) 90.069% N 25 s(39.28%)p 1.55(60.69%)d 0.00(0.03%) f 0.00(0.00%)
114. (1.00000) 91.4744% LP (1) N 31 6.161% Pu 1 s(15.35%)p 0.00(0.05%)d 4.37(67.02%) f 1.15(17.58%) 91.481% N 31 s(44.93%)p 1.22(55.04%)d 0.00(0.03%) f 0.00(0.00%)
124. (1.00000) 89.9698% LP (1) N 38 8.025% Pu 1 s(12.24%)p 0.00(0.06%)d 5.49(67.24%) f 1.67(20.46%) 89.977% N 38 s(38.42%)p 1.60(61.56%)d 0.00(0.02%) f 0.00(0.00%)

Section S8. Energy Decomposition Analysis (EDA)

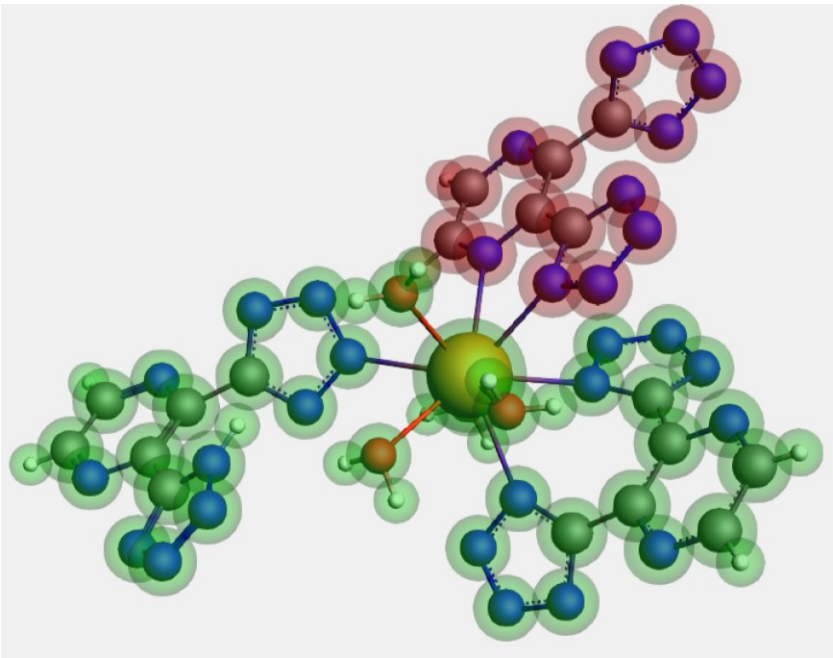


Figure S8.1. EDA of Pu−N1/N5, $[Pu(Hdtp)(dtp)(H_2O)_4]$ + dtp^{2-} → $[Pu(Hdtp)(dtp)_2(H_2O)_4]^{2-}$.

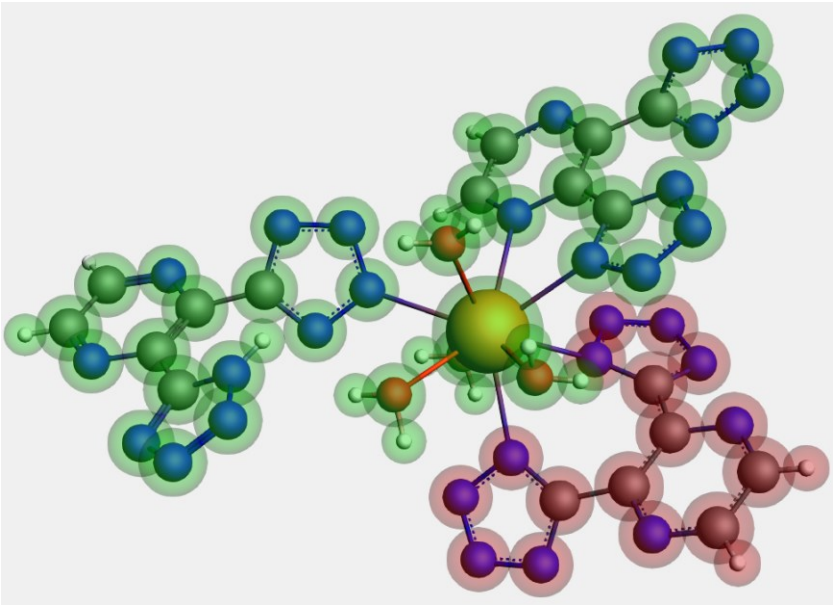


Figure S8.2. EDA of Pu−N2/N3, $[Pu(Hdtp)(dtp)(H_2O)_4]$ + dtp^{2-} → $[Pu(Hdtp)(dtp)_2(H_2O)_4]^{2-}$,

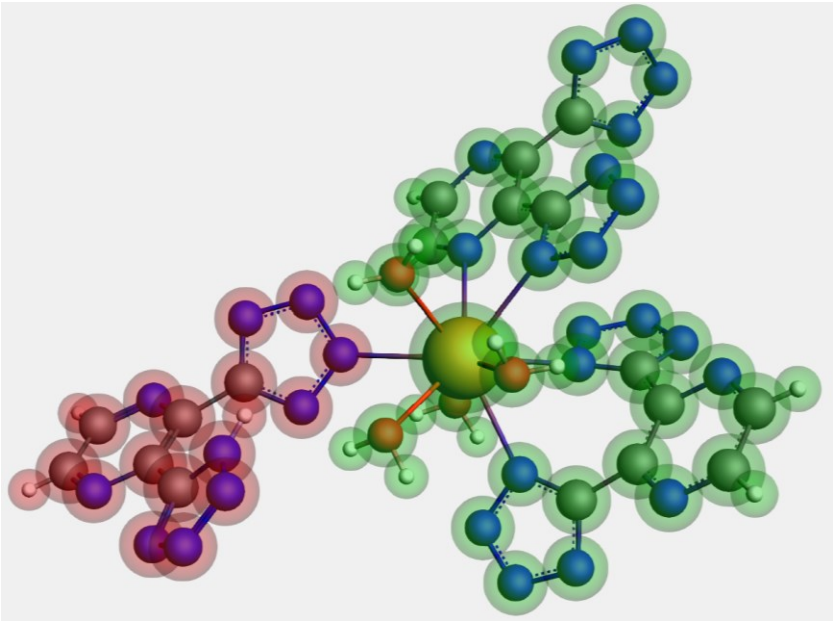


Figure S8.3. EDA of Pu–N4, $[Pu(dtp)_2(H_2O)_4]^{-}$ + $Hdtp^{-}$ → $[Pu(Hdtp)(dtp)_2(H_2O)_4]^{2-}$.

Section S9. Cartesian coordinates for $[Pu(Hdtp)(dtp)_2(H_2O)_4]^{2-}$

Pu	12.4049	6.9039	2.7771
O	10.6614	7.9034	1.3398
H	10.2448	7.2721	0.8898
H	11.0350	8.3996	0.7157
O	14.8538	6.6587	3.1940
H	14.9886	6.0545	3.8114
H	15.1690	7.3968	3.5421
O	12.4936	4.9764	4.3164
H	12.4949	4.1530	4.0368
H	12.9941	4.9678	5.0272
N	13.7019	8.0538	0.8454
N	10.1524	9.1562	8.9383
N	13.4747	7.6501	-0.4277
N	10.3749	7.4500	4.5594
N	12.5469	9.4800	2.9510
O	13.2871	5.1133	1.2759
H	12.6249	4.7570	0.7374
H	13.8823	5.4485	0.6524
N	16.8769	9.4830	1.6538
N	14.2241	8.0368	5.6733
N	8.3933	8.4570	6.2572
N	10.5324	4.5013	0.8582
N	14.3940	8.1504	-1.2105
N	10.5679	5.0977	2.0772
N	15.2663	8.8815	-0.4873
N	15.7931	10.7426	3.8731
N	12.6984	8.8586	7.0074
N	9.7620	4.4578	2.9041
N	13.0963	11.4420	3.8007
N	14.0158	8.7022	6.7886
N	13.0243	7.7331	5.1319
N	11.7650	11.2806	3.8674
N	7.9632	2.2757	-0.0568
C	14.7992	8.8119	0.7729
N	9.6908	0.7422	-1.5927
N	13.6445	1.8845	-0.0199
C	14.9928	10.1320	2.9681
C	15.5553	9.4894	1.8570
N	10.2284	10.3287	9.6174
C	9.9495	9.5176	7.6795
C	12.1215	8.2417	5.9731
C	13.5522	10.3276	3.2323
N	9.1802	3.4336	2.2534
N	11.4320	10.1178	3.3687
N	10.0619	11.3147	8.7990
C	9.0780	7.3003	4.2866
H	8.8256	6.8573	3.4857
N	9.8664	10.8390	7.5487

N	12.3817	2.1961	0.3168
H	12.1064	2.6065	1.0446
C	8.0841	7.7730	5.1362
H	7.1723	7.6106	4.9249
N	12.3808	1.1652	-1.6481
C	9.2816	2.4779	-0.0014
C	9.6831	8.6354	6.5272
N	13.6293	1.2859	-1.1935
C	9.6816	3.4856	1.0173
C	17.6468	10.1008	2.5546
H	18.5890	10.1129	2.4356
C	17.0926	10.7221	3.6586
H	17.6685	11.1499	4.2817
C	10.1660	1.7045	-0.7587
C	8.3777	0.5859	-1.6552
H	8.0233	-0.0590	-2.2570
C	7.4963	1.3289	-0.8752
H	6.5624	1.1637	-0.9257
C	11.6320	1.7464	-0.7033
C	10.7227	8.1080	5.6917

Section S10. Reference

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