Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Highvalent actinyl (AnO_2; An=U, Np and Pu) complexation with TEtraQuinoline (TEQ) ligand – A DFT study

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Table S1. Geometric and electronic properties of actinyl cations in gas-phase computed at PBE/TZ2P level of theory

	Bond length (in Å)	NBO	Bond angle (in °)	Mulliken charge		NPA charge		Spin density		An's valence orbital occupancy			
	An=O1/2	An=O1/2	∠O1=An=O2	An	O1/O2 (avg.)	An	O1/O2 (avg.)	An	O1/O2 (avg.)	7s	5f	6d	7p
$[UO_2]^{+}$	1.771	1.022	180.0	2.524	-0.262	2.034	-0.517	1.088	-0.044	0.050	3.010	0.930	-
$[NpO_2]^{+}$	1.765	1.008	180.0	1.857	-0.428	1.895	-0.448	2.201	-0.101	0.040	4.190	0.890	-
$[PuO_2]^{+}$	1.734	0.998	180.0	1.804	-0.402	1.719	-0.360	3.315	-0.158	0.040	5.400	0.860	-
$[UO_2]^{2+}$	1.716	2.283	180.0	2.554	-0.277	2.465	-0.233	0.000	0.000	0.050	2.520	1.020	0.010
$[NpO_2]^{2+}$	1.713	1.117	180.0	2.457	-0.228	2.311	-0.155	1.125	-0.063	0.040	2.730	0.960	-
$[PuO_2]^{2+}$	1.684	1.098	180.0	2.388	-0.194	2.128	-0.064	2.249	-0.125	0.040	4.940	0.930	0.010
$[NpO_2]^{3+}$	1.705	1.253	149.5	2.982	0.009	2.739	0.131	0.000	0.000	0.010	1.700	0.450	-
$[PuO_2]^{3+}$	1.715	1.190	152.0	2.855	0.072	2.576	0.212	1.339	-0.169	0.010	1.650	0.410	-

Table S2. Cavity size (in Å) of the TEQ after and before complexation with actinyl. The cavity size computed at PBE/TZ2P and PBE-D3(BJ)/TZ2P are provided on either side of "/", respectively

	Actinyl-TEQ complexes		TEQ	
	N1-N3	N2-N4	N1-N3	N2-N4
$[UO_2L]^+$	4.806 / 4.800	4.827 / 4.829	4.515 / 4.492	4.452 / 4.433
$[NpO_2L]^+$	4.802 / 4.800	4.814 / 4.813		
$[PuO_2L]^+$	4.793 / 4.783	4.813 / 4.810		
$[UO_2L]^{2+}$	4.751 / 4.749	4.789 / 4.784		
$[NpO_2L]^{2+}$	4.727 / 4.722	4.763 / 4.765		
$[PuO_2L]^{2+}$	4.728 / 4.719	4.751 / 4.744		
$[NpO_2L]^{3+}$	4.660 / 4.653	4.713 / 4.714		
$[PuO_2L]^{3+}$	4.723 / 4.717	4.720 / 4.718		

Table S3. Torsion angle (°) in TEQ and its complexes computed with PBE and PBE-D3(BJ) functionals in gas-phase

Complex	N1-C1-C2-C3	N2-C1-C2-C3	N3-C1-C2-C3	N4-C1-C2-C3
TEQ	71.8 / 74.5	69.2 / 72.0	71.1 / 72.8	71.8 / 75.2
$[UO_2L]^+$	77.1 / 82.1	52.1 / 52.5	77.2 / 78.2	55.2 / 55.4
$[NpO_2L]^+$	71.5 / 71.6	60.0 / 60.0	62.2 / 62.3	59.0 / 59.1
$[PuO_2L]^+$	61.3 / 61.5	62.5 / 62.4	61.0 / 61.2	66.1 / 66.3
$[UO_2L]^{2+}$	65.1 / 64.7	56.7 / 57.6	62.9 / 62.8	61.4 / 61.8
$[NpO_2L]^{2+}$	64.0 / 65.1	57.5 / 56.5	62.4 / 63.3	61.5 / 61.0
$[PuO_2L]^{2+}$	64.8 / 65.0	56.9 / 56.1	63.0 / 62.6	59.3 / 61.6
$[NpO_2L]^{3+}$	62.0 / 63.0	57.9 / 56.6	60.0 / 60.6	62.0 / 61.8
$[PuO_2L]^{3+}$	59.8 / 60.5	60.0 / 59.8	58.3 / 58.1	61.6 / 62.0

Table S4. Computed bond lengths (in Å) of the actinyl-TEQ complexes in gas-phase at PBE-D3(BJ)/TZ2P level of theory

Complex	An-N1	An-N2	An-N3	An-N4	An=O1	An=O2
$[UO_2L]^{+}$	2.395	2.411	2.406	2.419	1.811	1.813
$[NpO_2L]^{+}$	2.407	2.361	2.399	2.455	1.801	1.802
$[PuO_2L]^{+}$	2.395	2.407	2.397	2.403	1.790	1.787
$[UO_2L]^{2+}$	2.375	2.394	2.375	2.395	1.795	1.796
$[NpO_2L]^{2+}$	2.360	2.384	2.363	2.386	1.776	1.777
$[PuO_2L]^{2+}$	2.346	2.377	2.373	2.374	1.763	1.765
$[NpO_2L]^{3+}$	2.327	2.359	2.328	2.361	1.769	1.771
$[PuO_2L]^{3+}$	2.360	2.351	2.359	2.372	1.758	1.760

Table S5. Computed bond angles (in °) of the actinyl-TEQ complexes in gas-phase using PBE and PBE-D3(BJ) functionals

	Angles between adjacent N atoms (cis)				∠O1=An=O2	Angles between opposite N atoms (trans)	
Complex	**∠N1-An-N2**	**∠N2-An-N3**	**∠N3-An-N4**	**∠N4-An-N5**		**∠N1-An-N3**	**∠N2-An-N4**
$[UO_2L]^{+}$	85.4 / 85.0	93.8 / 95.9	85.0 / 85.3	95.9 / 93.9	179.5 / 179.3	177.2 / 178.0	177.8 / 177.2
$[NpO_2L]^{+}$	94.5 / 94.5	90.5 / 90.5	89.2 / 89.2	86.0 / 86.1	179.1 / 179.2	174.6 / 174.6	175.7 / 175.7
$[PuO_2L]^{+}$	90.2 / 90.3	89.7 / 89.8	89.6 / 89.4	90.5 / 90.5	179.9 / 179.9	173.1 / 173.1	179.2 / 179.2
$[UO_2L]^{2+}$	92.5 / 91.9	88.0 / 88.6	90.8 / 90.6	88.8 / 89.1	179.8 / 179.8	178.1 / 177.8	174.8 / 175.2
$[NpO_2L]^{2+}$	91.9 / 92.4	88.4 / 88.1	90.8 / 91.0	89.1 / 88.7	179.8 / 179.9	178.5 / 178.0	174.0 / 174.7
$[PuO_2L]^{2+}$	92.8 / 92.8	88.8 / 87.3	91.0 / 90.6	87.5 / 89.5	179.7 / 179.8	177.7 / 178.1	173.9 / 173.9
$[NpO_2L]^{3+}$	92.0 / 92.3	88.5 / 88.2	90.5 / 90.7	89.3 / 89.0	179.7 / 179.8	177.3 / 177.0	173.7 / 174.1
$[PuO_2L]^{3+}$	91.2 / 91.5	90.0 / 89.9	89.9 / 89.6	89.2 / 89.3	179.6 / 179.6	176.6 / 176.5	174.6 / 174.8

Table S6. O=An=O vibration frequencies (cm^{-1}) in actinyl cations and their TEQ complexes calculated at PBE/TZ2P and PBE-D3(BJ)/TZ2P level of theories (given on the respective sides of /)

	Actinyl cations			Actinyl-TEQ complexes	
	ν_{sym}	ν_{asym}		ν_{sym}	ν_{asym}
$[UO_2]^+$	906.7 / 906.8	984.1 / 984.2	**$[UO_2L]^+$**	800.7 / 803.0	894.0 / 895.9
$[NpO_2]^+$	888.1 / 917.3	980.2 / 998.7	**$[NpO_2L]^+$**	780.6 / 782.3	881.7 / 883.5
$[PuO_2]^+$	891.8 / 892.1	989.6 / 989.9	**$[PuO_2L]^+$**	772.3 / 773.7	877.7 / 879.3
$[UO_2]^{2+}$	998.8 / 998.1	1101.0 / 1100.3	**$[UO_2L]^{2+}$**	836.0 / 837.2	926.6 / 927.6
$[NpO_2]^{2+}$	966.5 / 967.2	1083.1 / 1083.9	**$[NpO_2L]^{2+}$**	828.7 / 830.0	928.4 / 929.7
$[PuO_2]^{2+}$	977.4 / 888.4	1096.8 / 1008.1	**$[PuO_2L]^{2+}$**	809.5 / 812.4	926.3 / 928.5
$[NpO_2]^{3+}$	931.0 / 930.6	1030.9 / 1030.5	**$[NpO_2L]^{3+}$**	840.1 / 841.8	949.1 / 950.9
$[PuO_2]^{3+}$	862.8 / 865.9	969.5 / 973.1	**$[PuO_2L]^{3+}$**	821.1 / 821.5	938.5 / 939.0

Table S7. Wiberg bond index calculated by the Natural Bond Orbital (NBO) analysis of actinyl-TEQ complexes in gas phase at PBE/TZ2P level of theory

Complex	An-N1	An-N2	An-N3	An-N4	An=O1	An=O2
$[UO_2L]^+$	0.236	0.231	0.233	0.229	1.054	1.058
$[NpO_2L]^+$	0.223	0.194	0.212	0.210	1.033	1.036
$[PuO_2L]^+$	0.194	0.186	0.194	0.186	1.010	1.005
$[UO_2L]^{2+}$	0.551	0.513	0.548	0.511	2.168	2.162
$[NpO_2L]^{2+}$	0.267	0.250	0.268	0.250	1.073	1.077
$[PuO_2L]^{2+}$	0.244	0.229	0.241	0.238	1.045	1.049
$[NpO_2L]^{3+}$	0.325	0.287	0.325	0.288	1.101	1.109
$[PuO_2L]^{3+}$	0.250	0.247	0.253	0.247	1.054	1.058

Table S8. Mulliken charges on interacting atoms of actinyl-TEQ complexes computed at PBE/TZ2P level of theory

Complex	An	N1	N2	N3	N4	O1	O2
$[UO_2L]^+$	1.828	-0.488	-0.515	-0.483	-0.518	-0.585	-0.580
$[NpO_2L]^+$	1.743	-0.472	-0.488	-0.496	-0.491	-0.584	-0.580
$[PuO_2L]^+$	1.786	-0.493	-0.481	-0.490	-0.484	-0.576	-0.581
$[UO_2L]^{2+}$	1.961	-0.534	-0.518	-0.521	-0.521	-0.546	-0.541
$[NpO_2L]^{2+}$	1.887	-0.515	-0.503	-0.506	-0.505	-0.530	-0.525
$[PuO_2L]^{2+}$	1.939	-0.504	-0.507	-0.503	-0.503	-0.521	-0.513
$[NpO_2L]^{3+}$	1.953	-0.523	-0.503	-0.511	-0.505	-0.496	-0.485
$[PuO_2L]^{3+}$	1.970	-0.507	-0.509	-0.504	-0.502	-0.505	-0.493

Table S9. Spin density and orbital population of the actinyl's valence orbital on complexation with TEQ computed through NPA in gas-phase at Hybrid: PBE0-D3(BJ)/TZ2P/SR-ZORA

Complex	NPA Spin density			An's valence orbital occupancy in complex			
	An	Assigned OS	O1/O2 (avg.)	7s	5f	6d	7p
$[UO_2L]^+$	0.712	V	-0.032	0.16	2.89	1.50	0.02
$[NpO_2L]^+$	2.122	V	-0.103	0.15	4.21	1.39	0.02
$[PuO_2L]^+$	3.284	V	-0.177	0.15	5.35	1.34	0.02
$[UO_2L]^{2+}$	0.000	VI	0.000	0.17	2.65	1.58	0.02
$[NpO_2L]^{2+}$	1.136	VI	-0.072	0.18	3.94	1.54	0.02
$[PuO_2L]^{2+}$	2.468	VI	-0.163	0.17	5.17	1.50	0.02
$[NpO_2L]^{3+}$	0.000	VII	0.000	0.18	3.98	1.62	0.02
$[PuO_2L]^{3+}$	2.338	VII → VI	-0.158	0.18	4.11	1.50	0.02

Table S10. Thermodynamic parameters (in kcal/mol) for the formation of actinyl-TEQ complexes computed at PBE-D3(BJ)/TZ2P level of theory

Complex	Gas phase				DCE medium			
	ΔG	ΔH	ΔE	-TΔS	ΔG	ΔH	ΔE	-TΔS
$[UO_2L]^+$	-116.21	-129.85	-130.46	13.64	-36.64	-47.32	-48.57	10.68
$[NpO_2L]^+$	-115.17	-128.27	-129.15	13.10	-45.86	-51.26	-64.79	11.34
$[PuO_2L]^+$	-108.97	-120.35	-122.15	11.38	-34.34	-47.05	-48.33	12.71
$[UO_2L]^{2+}$	-288.06	-302.66	-304.61	14.60	-74.55	-88.39	-90.18	13.85
$[NpO_2L]^{2+}$	-291.47	-306.24	-308.27	14.77	-84.31	-98.39	-100.24	14.08
$[PuO_2L]^{2+}$	-306.19	-319.80	-321.76	13.61	-102.00	-115.01	-116.58	13.02
$[NpO_2L]^{3+}$	-624.24	-637.81	-640.64	13.56	-198.24	-214.44	-215.92	16.20
$[PuO_2L]^{3+}$	-636.88	-651.36	-653.4	14.48	-218.09	-230.29	-232.75	12.20

Table S11. Energy decomposition analysis (EDA) of actinyl-TEQ complexes. Actinyl versus TEQ, with energy contributions given in kcal/mol computed at PBE-D3(BJ)/TZ2P level of theory in gas phase

Fragments	$\Delta E_{el\text{-}stat}$	ΔE_{orb}	ΔE_{steric}	ΔE_{Pauli}	ΔE_{int}	ΔE_{disp}
$[UO_2]^+$ vs L	-221.68	-188.84	54.87	276.55	-145.33	-11.35
$[NpO_2]^+$ vs L	-222.32	-169.94	41.14	263.47	-139.61	-10.82
$[PuO_2]^+$ vs L	-216.28	-159.95	33.75	250.03	-138.28	-12.08
$[UO_2]^{2+}$ vs L	-288.61	-332.27	8.51	297.12	-334.99	-11.24
$[NpO_2]^{2+}$ vs L	-288.49	-324.91	5.95	294.44	-329.72	-10.76
$[PuO_2]^{2+}$ vs L	-284.01	-317.85	-0.46	283.55	-330.36	-12.05
$[NpO_2]^{3+}$ vs L	-359.86	-633.44	-32.57	327.29	-676.73	-10.72
$[PuO_2]^{3+}$ vs L	-343.25	-625.34	-47.11	296.14	-684.46	-12.01

Table S12. EDA of actinyl-TEQ complexes (in kcal/mol) computed at PBE0-D3(BJ)/TZ2P level of theory in gas phase

Fragments	$\Delta E_{el\text{-}stat}$	ΔE_{orb}	ΔE_{steric}	ΔE_{Pauli}	ΔE_{int}	ΔE_{disp}
$[UO_2]^+$ vs L	-218.20	-172.44	42.23	260.44	-142.47	-12.27
$[NpO_2]^+$ vs L	-220.15	-164.89	28.37	248.52	-147.31	-11.69
$[PuO_2]^+$ vs L	-214.48	-148.72	22.70	237.18	-139.49	-13.47
$[UO_2]^{2+}$ vs L	-289.67	-321.59	-5.07	284.60	-337.81	-12.11
$[NpO_2]^{2+}$ vs L	-289.63	-319.82	-9.67	279.97	-341.10	-11.62
$[PuO_2]^{2+}$ vs L	-285.34	-318.68	-14.79	270.55	-346.54	-13.07
$[NpO_2]^{3+}$ vs L	-362.93	-595.26	-48.30	314.62	-654.26	-11.57
$[PuO_2]^{3+}$ vs L	-343.88	-653.18	-53.82	290.06	-720.02	-13.01

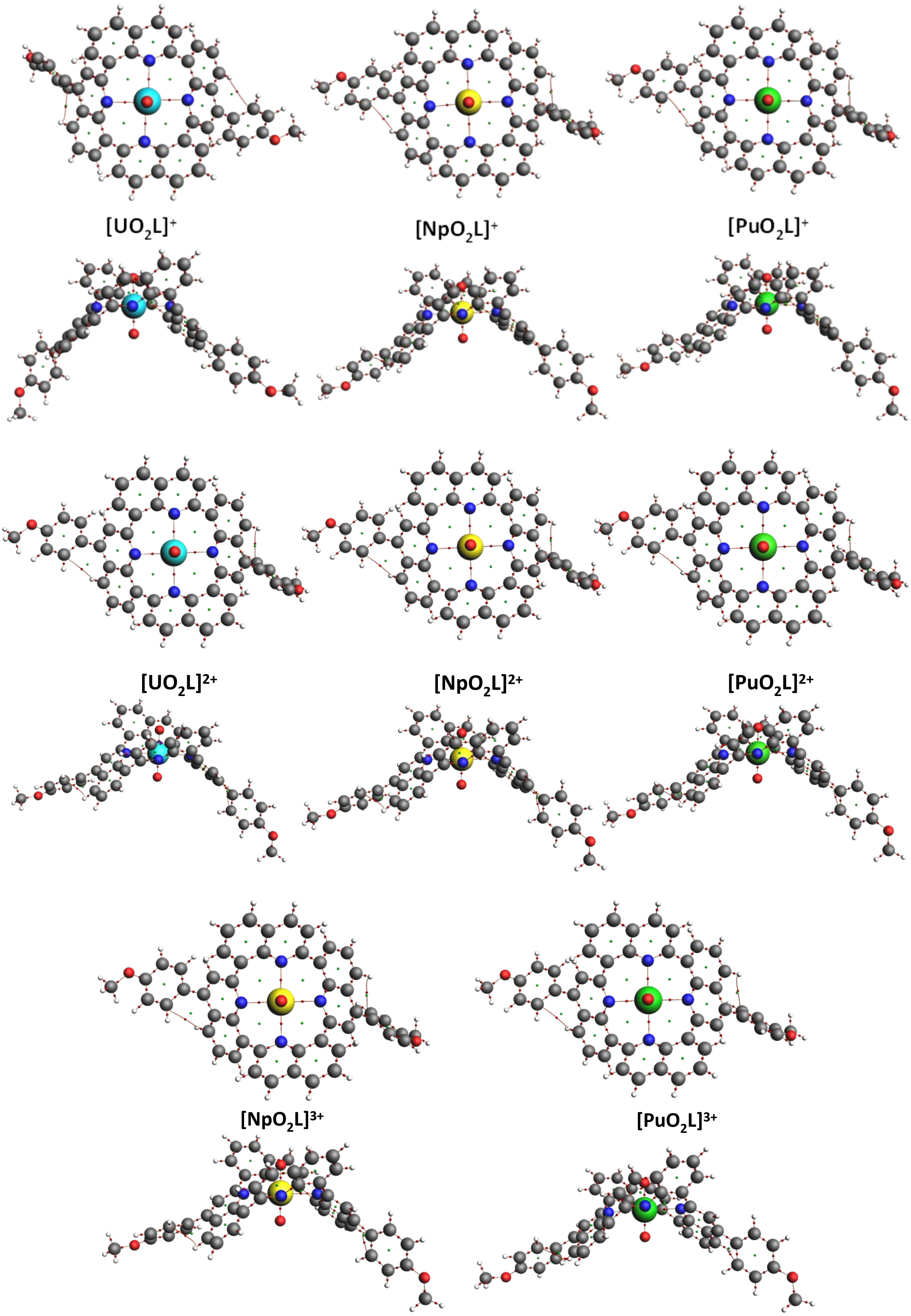

Figure S1. QTAIM topology of the actinyl-TEQ complexes representing the bond paths and electron densities (ρ) at the BCPs.