Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Table S1. Electronic and geometric structure of $OsCl_5(H_2O)^-$ (Figure S3). Multiplicity M; bond lengths ROsCl(1), ROsCl(2), ROsCl(3), ROsCl(4), ROsCl(5), RCl_5-H_1, RCl_3-H_2, ROs-O, RO-H_1, RO-H_2; bond angles ∠Cl(1)OsCl(2), ∠Cl(1)OsCl(3), ∠Cl(1)OsCl(4), ∠Cl(1)OsCl(5), ∠Cl(4)OsCl(2), ∠Cl(2)OsCl(5); atom charges q_{Os}, $q_{Cl(1)}$, $q_{Cl(2)}$, $q_{Cl(3)}$, $q_{Cl(4)}$, $q_{Cl(5)}$

	Methods	M	ROsCl(1)	ROsCl(2) ROsCl(3) ROsCl(4) ROsCl(5)	RCl_5-H_1 RCl_3-H_2	ROs-O	RO-H_1 RO-H_2	∠H_1OH_2	∠Cl(1)OsCl(2) ∠Cl(1)OsCl(3) ∠Cl(1)OsCl(4) ∠Cl(1)OsCl(5)	∠Cl(4)OsCl(2) ∠Cl(3)OsCl(5)	∠Cl(4)OsCl(3) ∠Cl(2)OsCl(5)	q_{Os}	$q_{cl(2)}$, $q_{cl(3)}$, $q_{cl(4)}$, $q_{cl(5)}$,	$q_{cl(1)}$	q_O	q_{H1} q_{H2}	E_0, Hartree
gas																	
1	ROHF/IMCP-SR1	3	2.284	2.380 2.426 2.380 2.426	2.608 2.595	2.189	0.952 0.952	107.037	95.431 96.014 95.280 95.895	90.622 89.029	89.027 89.098	0.786	-0.428 -0.476 -0.427 -0.477	-0.333	0.002	0.176 0.175	-157.0766
2	ROHF/IMCP-SR1	5	2.493	2.356 2.380 2.356 2.380	2.792 2.792	4.485	0.947	103.318	99.533 99.044 99.533 99.044	88.773 88.388	88.434 88.434	0.999	-0.357 -0.387 -0.357 -0.387	-0.488	-0.364	0.170	-157.0837
3	CASSCF(8,6)/IMCP-SR1	3	2.362	2.406 2.431 2.373 2.415	2.864 2.729	2.252	0.949 0.950	107.521	92.868 94.017 93.155 94.056	90.382 89.310	89.942 89.501	0.822	-0.453 -0.480 -0.402 -0.463	-0.300	-0.070	0.179 0.179	-157.1161
4	CASSCF(6,6)/IMCP-SR1	5	2.492	2.377 2.401 2.378 2.402	2.788 2.785	4.508	0.947 0.946	103.312	100.092 99.667 99.760 99.451	88.141 88.700	88.221 88.376	1.019	-0.355 -0.397 -0.350 -0.397	-0.496	-0.365	0.171	-157.0999
5	ROHF/SBKJC	3	2.335	2.432 2.432 2.433 2.433	2.815 2.815	2.115	0.965 0.965	117.481	93.491 93.491 96.909 96.935	89.590 89.571	89.577 89.582	-0.155	-0.246 -0.245 -0.263 -0.263	-0.102	-0.607	0.441 0.441	-180.9040
6	ROHF/SBKJC	5	2.498	2.392 2.408 2.392 2.409	2.869 2.879	4.927	0.968 0.968	107.732	99.91 98.87 99.99 99.02	88.655 88.373	88.411 88.380	0.053	-0.160 -0.203 -0.160 -0.204	-0.325	-0.648	0.323 0.324	-180.9032
7	CASSCF(10,8)/SBKJC	3	2.335	2.432 2.433 2.433 2.433	2.815 2.815	2.115	0.965 0.965	117.481	93.477 93.485 96.928 96.920	89.597 89.568	89.571 89.586	-0.155	-0.246 -0.245 -0.263 -0.263	-0.102	-0.607	0.441 0.441	-180.9040
8	CASSCF(10,8)/SBKJC	5	2.496	2.392 2.409 2.392 2.409	2.869 2.879	4.927	0.968 0.968	107.745	99.934 98.896 100.019 99.041	88.651 88.366	88.374 88.400	0.052	-0.160 -0.204 -0.160 -0.204	-0.323	-0.648	0.323 0.324	-180.9033
water																	
9	ROHF/IMCP-SR1/PCM (water)	3	2.306	2.395 2.401 2.399 2.404	3.182 2.885	2.122	0.954 0.954	108.739	94.215 94.309 92.317 92.780	90.078 89.891	89.666 89.607	0.755	-0.458 -0.463 -0.465 -0.468	-0.342	-0.077	0.262 0.256	-157.1675
10	ROHF/IMCP-SR1/PCM (water)	5	2.593	2.369 2.373	3.281 3.292	2.590	0.950 0.950	105.571	94.884 94.944	89.845 89.578	89.386 89.517	1.041	-0.391 -0.394	-0.625	-0.284	0.219 0.219	-157.1643

				2.369 2.373					94.707 95.081				-0.390 -0.394				
11	ROHF/IMCP-SR1/PCM (water)	5	2.618	2.385 2.399 2.385 2.400	2.905 2.922	4.495	0.947	0.947	90.160 90.430 90.208 90.445	92.308 87.882	89.914 89.890	1.194	-0.394 -0.396 -0.394 -0.396	-0.599	-0.401	0.193 0.193	-157.1639
12	CASSCF(6,6)/IMCP-SR1/PCM (water)	3	2.378	2.416 2.421 2.391 2.393	3.350 3.047	2.166	0.952 0.952	108.478	91.922 92.152 91.522 91.475	90.155 90.086	89.778 89.768	0.789	-0.472 -0.476 -0.433 -0.433	-0.328	-0.142	0.249 0.245	-157.2061
13	CASSCF(6,6)/IMCP-SR1/PCM (water)	5	2.617	2.409 2.417 2.408 2.417	2.898 2.908	4.482	0.947 0.947	104.675	90.547 90.683 90.568 90.676	92.328 87.942	89.810 89.894	1.222	-0.403 -0.395 -0.402 -0.397	-0.610	-0.401	0.193	-157.1813
14	ROHF/SBKJC/PCM (water)	3	2.392	2.397 2.397 2.423 2.425	3.005 3.013	2.073	0.969 0.969	112.765	91.499 91.274 91.661 91.705	89.998 89.898	89.967 89.975	-0.179	-0.198 -0.197 -0.262 -0.265	-0.224	-0.622	0.474 0.473	-181.0064
15	ROHF/SBKJC/PCM (water)	5	2.374	2.647 2.648 2.388 2.388	3.012 3.024	2.128	0.971 0.971	111.901	94.150 94.665 92.520 92.519	89.681 89.808	89.973 89.764	0.186	-0.511 -0.511 -0.163 -0.164	-0.140	-0.648	0.475 0.476	-180.9830
16	CASSCF(10,8)/SBKJC/PCM (water)	3	2.412	2.391 2.388 2.609 2.607	2.905 2.935	2.189	0.971 0.971	112.696	90.971 90.927 100.729 97.107	89.886 89.085	90.688 89.753	0.170	-0.131 -0.128 -0.481 -0.480	-0.217	-0.654	0.460 0.460	-181.0006
17	CASSCF(10,8)/SBKJC/PCM (water)	5	2.396	2.621 2.618 2.403 2.411	2.861 2.866	2.187	0.971 0.971	112.823	100.981 99.793 89.541 90.312	90.242 89.958	89.854 89.999	0.216	-0.491 -0.489 -0.157 -0.185	-0.158	-0.654	0.459 0.459	-181.0148

Table S2. Electronic and geometric structure of $OsCl_5(OH)^{2-}$ (Figure S4). Multiplicity M; bond lengths ROsCl(1), ROsCl(2), ROsCl(3), ROsCl(4), ROsCl(5), RCl_5-H, ROs-O, RO-H_1, RO-H_2; bond angles ∠Cl(1)OsCl(2), ∠Cl(1)OsCl(3), ∠Cl(1)OsCl(4), ∠Cl(1)OsCl(5), ∠Cl(4)OsCl(2), ∠Cl(2)OsCl(5); atom charges q_{Os}, $q_{Cl(1)}$, $q_{Cl(2)}$, $q_{Cl(3)}$, $q_{Cl(4)}$, $q_{Cl(5)}$

	Methods	M	ROsCl(1)	ROsCl(2) ROsCl(3) ROsCl(4) ROsCl(5)	ROs-O	RCl-H	RO-H	∠$OOsCl_2$ ∠$OOsCl_3$ ∠$OOsCl_4$ ∠$OOsCl_5$	∠Cl_1OsCl_2 ∠Cl_1OsCl_3 ∠Cl_1OsCl_4 ∠Cl_1OsCl_5	∠OsOH	∠Cl_4OsCl_2 ∠Cl_3OsCl_5	∠Cl_4OsCl_3 ∠Cl_2OsCl_5	q_{Os}	$q_{cl(2)}$, $q_{cl(3)}$, $q_{cl(4)}$, $q_{cl(5)}$,	$q_{cl(1)}$	q_O	q_H	E_0, Hartree
gas																		
1	ROHF/IMCP-SR1	3	2.505	2.425 2.463 2.413 2.413	1.967	2.643	0.945	88.436 87.410 89.992 89.964	91.255 92.899 90.018 90.034	107.174	90.646 89.337	89.367 90.649	0.917	-0.527 -0.559 -0.503 -0.503	-0.612	-0.346	0.132	-156.4411
2	ROHF/IMCP-SR1	5	2.429	2.438 2.438 2.681 2.856	1.922	2.533	0.950	90.224 90.301 90.197 79.612	89.611 89.617 93.860 96.331	106.471	91.781 88.345	91.719 88.305	1.101	-0.507 -0.507 -0.688 -0.745	-0.521	-0.300	0.167	-156.4419
3	CASSCF(6,6)/IMCP-SR1	3	2.458	2.455 2.454 2.431 2.474	1.935	2.618	0.945	89.781 89.913 89.056 86.885	90.154 90.136 91.961 92.097	108.057	90.435 89.610	90.391 89.544	0.913	-0.555 -0.555 -0.515 -0.545	-0.569	-0.325	0.151	-156.4560
4	CASSCF(6,6) /IMCP-SR1	5	2.429	2.681 2.854 2.438 2.438	1.922	2.535	0.950	90.213 79.701 90.247 90.253	93.821 96.265 89.622 89.634	106.481	91.744 88.326	88.325 91.748	1.101	-0.688 -0.744 -0.507 -0.507	-0.521	-0.300	0.167	-156.4419
5	ROHF/SBKJC	3	2.508	2.421 2.455 2.465 2.466	2.011	2.801	0.965	89.151 88.279 88.976 88.984	91.309 91.262 91.014 91.015	113.401	90.621 89.325	89.347 90.617	0.085	-0.286 -0.326 -0.355 -0.355	-0.425	-0.645	0.307	-180.2804
6	ROHF/SBKJC	5	2.438	2.538 2.591 2.639 2.641	1.924	2.776	0.965	89.256 85.998 89.862 89.607	91.786 92.960 90.206 90.262	116.692	91.696 88.167	88.379 91.722	0.488	-0.417 -0.462 -0.509 -0.510	-0.312	-0.631	0.352	-180.2908
7	CASSCF(10,8)/ SBKJC	3	2.508	2.421 2.455 2.465 2.465	2.011	2.801	0.965	89.151 88.279 88.976 88.984	91.309 91.262 91.014 91.015	113.401	90.621 89.325	90.617 89.347	0.085	-0.286 -0.326 -0.355 -0.355	-0.425	-0.645	0.307	-180.2805
8	CASSCF(10,8)/ SBKJC	5	2.450	2.698 2.878 2.466 2.465	1.931	2.700	0.967	91.334 80.372 90.203 90.157	92.867 95.427 89.677 89.711	114.872	91.710 88.341	88.308 91.741	0.455	-0.574 -0.672 -0.295 -0.295	-0.333	-0.645	0.359	-180.3058
water																		
9	ROHF/IMCP-SR1/PCM (water)	3	2.498	2.431 2.424 2.394 2.402	1.965	2.705	0.947	88.309 88.485 90.478 90.584	91.388 91.822 89.692 89.248	110.070	89.752 90.446	89.128 90.734	0.825	-0.525 -0.515 -0.473 -0.481	-0.604	-0.409	0.182	-156.7228
10	ROHF/IMCP-SR1/PCM (water)	5	2.414	2.429 2.429 2.692 2.723	1.921	2.746	0.951	90.538 90.644 87.907 85.243	89.392 89.396 94.053 92.798	111.667	90.524 89.646	90.428 89.546	1.011	-0.487 -0.488 -0.704 -0.708	-0.490	-0.344	0.211	-156.7172

11	CASSCF(6,6)/IMCP-SR1/PCM (water)	3	2.456	2.440 2.440 2.429 2.442	1.931	2.722	0.948	90.261 90.329 88.708 88.589	89.772 89.637 91.184 91.519	112.007	89.975 90.330	89.708 90.015	0.815	-0.537 -0.538 -0.504 -0.506	-0.554	-0.380	0.204	-156.7378
12	CASSCF(6,6)/IMCP-SR1/PCM (water)	5	2.416	2.431 2.431 2.694 2.727	1.921	2.729	0.951	90.395 90.407 88.394 84.749	89.615 89.575 92.975 93.882	111.632	90.264 89.969	90.088 89.776	1.014	-0.488 -0.488 -0.704 -0.709	-0.490	-0.346	0.212	-156.7173
13	ROHF/SBKJC	3	2.43235	2.41791 2.43306 2.43310 2.43386	1.92379	2.92878	0.96887	87.555 91.147 90.340 90.320	91.270 90.028 89.497 89.845	120.018	90.013 89.889	90.115 89.998	-0.087	-0.315 -0.321 -0.327 -0.328	-0.327	-0.684	0.391	-180.5768
14	ROHF/SBKJC	5	2.412	2.616 2.656 2.458 2.459	1.917	3.074	0.970	87.958 91.202 89.880 90.137	91.200 89.642 90.026 89.976	121.121	91.174 89.273	89.383 56.479	0.281	-0.531 -0.549 -0.321 -0.323	-0.275	-0.690	0.409	-180.5662
15	CASSCF(10,8)/ SBKJC/PCM (water)	3	2.421	2.422 2.439 2.436 2.436	1.942	2.931	0.968	86.929 90.733 90.502 90.479	91.826 90.512 89.327 89.697	119.885	90.072 89.839	90.160 89.968	-0.129	-0.331 -0.340 -0.322 -0.323	-0.227	-0.707	0.380	-180.6055
16	CASSCF(10,8)/ SBKJC/PCM (water)	5	2.412	2.616 2.656 2.458 2.459	1.917	3.074	0.9704	87.958 91.202 89.880 90.137	91.200 89.642 90.026 89.976	121.121	91.174 89.273	89.383 90.170	0.280	-0.530 -0.549 -0.321 -0.323	-0.275	-0.690	0.409	-180.5663

Table S3. Energies and orbiltal populations of $OsCl_5(H_2O)^-$ and $OsCl_5(OH)^{2-}$ in triplet state as a result of CASSCF(6,6)/IMCP-SR1 gas phase calculations (GAMESS-US package).

	State	Energy, eV	Delta Energy of transition $T1 \rightarrow T_i$, eV (nm)	Orbitals population					
				HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1
				A	A	A	A	A	A
$OsCl_5(H_2O)^-$									
1	T1	-4275.35	0	1.92	1.9	0.98	0.97	0.04	0.03
2	T2	-4271.36	3.97 (312)	1.93	1.88	0.62	0.38	0.07	0.94
3	T3	-4270.98	4.37 (284)	1.87	1.81	0.47	0.65	0.31	0.61
4	T4	-4270.70	4.65 (267)	1.84	1.12	1.32	1.23	0.08	0.17
5	T5	-4270.14	5.21 (238)	1.87	1.13	1.15	1.3	0.28	0.03
6	Q1	-4269.82	5.53 (224)	1.79	1.09	0.97	0.97	0.94	0.04
7	T6	-4269.75	5.60 (221)	1.77	1.82	0.61	0.69	0.67	0.16
8	T7	-4269.39	5.95 (208)	1.87	1.65	0.73	0.69	0.74	0.04
$OsCl_5(OH)^{2-}$									
9	T1	-4256.73	0	1.88	1.75	0.92	0.97	0.26	0.05
10	T2	-4252.92	3.81 (325)	1.89	1.78	0.19	0.94	0.97	0.05
11	T3	-4252.30	4.44 (279)	1.85	1.77	0.94	0.16	1.05	0.06
12	T4	-4250.65	6.08 (204)	1.84	1.65	0.92	0.11	0.25	0.97
13	T5	-4250.26	6.48 (191)	1.85	1.67	0.13	0.97	0.16	0.96
14	Q1	-4249.73	6.70 (185)	1.03	1.78	0.97	0.96	1.05	0.03
15	T6	-4249.71	7.02 (177)	0.98	1.71	1.74	0.98	0.32	0.03
16	T7	-4249.58	7.15 (173)	1.05	1.67	0.97	1.82	0.25	0.03

Table S4. Energies and orbiltal populations of $OsCl_5(H_2O)^-$ and $OsCl_5(OH)^{2-}$ in quintet state as a result of CASSCF(6,6)/IMCP-SR1 gas phase calculations (GAMESS-US package).

	State	Energy, eV	Delta Energy of transition $Q1 \rightarrow Q_i$, eV (nm)	Orbitals population					
				HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO
				A	A	A	A	A	A
$OsCl_5(H_2O)^-$									
1	Q1	-4257.01	0	1.83	1.10	0.99	0.99	0.98	0.05
2	Q2	-4250.38	6.62 (187)	1.32	1.50	0.97	1.08	0.72	0.35
3	Q3	-4250.29	6.71 (185)	1.06	1.13	1.59	1.03	0.91	0.14
4	Q4	-4250.27	6.73 (184)	1.36	1.26	1.22	0.99	0.62	0.46
5	Q5	-4250.20	6.80 (182)	1.09	1.01	1.01	1.76	0.88	0.17
6	Q6	-4249.62	7.38 (168)	0.99	0.98	1.05	0.97	1.88	0.05
7	Q7	-4248.92	8.08 (153)	1.51	0.44	0.98	1.00	1.00	1.00
8	Q8	-4248.43	8.57 (144)	1.58	1.01	0.93	0.44	0.92	0.98
$OsCl_5(OH)^{2-}$									
9	Q1	4274.91	0	1.68	0.35	0.99	0.87	0.98	1.04
10	Q2	4271.45	3.46 (358)	1.77	1.05	1.01	0.75	0.26	1.1
11	Q3	4270.30	4.60 (270)	1.65	1.08	0.79	0.98	0.99	0.46
12	Q4	4270.17	4.7 (264)	1.72	0.99	0.75	0.58	0.84	1.08
13	Q5	4270.17	4.74 (262)	1.65	1.01	0.57	0.88	0.92	0.95
14	Sp1 (M=7)	4269.12	5.79 (214)	1	1	1	1	1	1
15	Q6	4268.9947	5.91 (210)	1.09	0.19	1.13	0.88	0.98	1.66
16	Q7	4268.2216	6.69 (185)	1.02	0.36	0.98	1.35	1.23	0.97

Table S5. Energies and orbiltal populations of $OsCl_5(H_2O)^-$ and $OsCl_5(OH)^{2-}$ in triplet state as a result of CASSCF(6,6)/IMCP-SR1/PCM aqueous phase calculations (GAMESS-US package).

	State	Energy, eV	Delta Energy of transition Q1→Q_i , eV (nm)	Orbitals population					
				HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1
				A	A	A	A	A	A
$OsCl_5(H_2O)^-$									
1	T1	-4277.80	0	1.92	1.91	0.97	0.97	0.04	0.01
2	T2	-4273.81	3.98 (312)	1.93	1.92	0.77	0.21	0.07	0.93
3	T3	-4273.42	4.37 (284)	1.92	1.91	0.25	0.78	0.28	0.69
4	T4	-4272.93	4.87 (255)	1.43	1.57	1.52	1.11	0.14	0.08
5	T5	-4272.44	5.35 (232)	1.37	1.64	1.06	1.37	0.26	0.01
6	T6	-4272.11	5.69 (218)	1.92	1.71	0.5	0.85	0.63	0.17
7	Q1	-4271.89	5.91 (210)	1.46	1.46	0.97	0.97	0.93	0.04
8	T7	-4271.72	6.08 (204)	1.53	1.86	0.93	0.86	0.53	0.04
$OsCl_5(OH)^{2-}$									
9	T1	-4265.06	0	1.98	1.98	0.99	1.00	0.02	0.01
10	T2	-4264.58	0.48 (2579)	1.97	0.99	1.96	0.99	0.03	0.01
11	T3	-4264.29	0.76 (1621)	1.97	1.00	0.98	1.97	0.02	0.00
12	Q1	-4260.6	4.46 (278)	1.97	0.98	0.98	0.98	0.48	0.51
13	Q2	-4259.3	5.76 (215)	2.00	1.00	1.00	1.00	0.52	0.48
14	T4	-4258.98	6.07 (204)	1.98	0.99	0.99	0.99	0.63	0.37
15	T5	-4258.89	6.17 (201)	1.96	0.98	1.82	0.14	0.33	0.68
16	T6	-4258.71	6.34 (196)	1.97	1.79	0.98	0.19	0.35	0.66

Table S6. Energies and orbiltal populations of $OsCl_5(H_2O)^-$ and $OsCl_5(OH)^{2-}$ in quintet state as a result of CASSCF(6,6)/IMCP-SR1 aqueous phase calculations (GAMESS-US package).

	State	Energy, eV	Delta Energy of transition Q1→Q_i , eV (nm)	Orbitals population					
				HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO
				A	A	A	A	A	A
$OsCl_5(H_2O)^-$									
1	Q1	-4277.12	0	1.66	0.37	0.98	0.88	0.98	1.04
2	Q2	-4273.45	3.67 (338)	1.75	1.08	1.00	0.75	0.25	1.10
3	Q3	-4272.47	4.65 (267)	1.60	1.09	0.88	0.99	0.99	0.39
4	Q4	-4272.03	5.09 (243)	1.68	1.03	0.67	0.64	0.86	1.07
5	Q5	-4272.01	5.11 (242)	1.63	1.00	0.58	0.80	0.92	1.05
6	Q6	-4271.42	5.71 (217)	1.00	1.00	1.00	1.00	1.00	1.00
7	Sp1	-4271.21	5.91 (210)	1.11	0.19	1.09	0.88	0.98	1.67
8	Q7	-4270.48	6.64 (187)	1.08	0.33	1.42	1.07	1.02	1.01
$OsCl_5(OH)^{2-}$									
9	Q1	-4264.5	0	2.00	1.00	1.00	1.00	1.00	0.00
10	Q2	-4257.37	7.13 (174)	1.00	1.98	1.00	1.00	1.00	0.01
11	Q3	-4257.17	7.32 (169.3)	0.99	0.99	1.39	1.58	1.00	0.01
12	Q4	-4257.16	7.34 (169.0)	1.00	1.01	1.55	1.41	1.01	0.01
13	Q5	-4257.02	7.47 (166)	1.00	1.00	1.01	1.00	1.97	0.01
14	Q6	-4246.52	17.97 (69)	1.98	1.00	0.99	1.00	0.01	1.00
15	Q7	-4244.64	19.85 (62.5)	1.41	0.89	0.71	0.95	0.99	0.99
16	Sp1	-4244.53	19.96 (62.1)	1.00	1.00	1.00	1.00	1.00	1.00

Table S7. Energies and orbiltal populations of $OsCl_5(H_2O)^-$ and $OsCl_5(OH)^{2-}$ in triplet state as a result of SBKJC gas phase calculations (FireFly package).

	State	Energy, eV	Energy of transition 1→i, eV (nm)	XMC-QDPT2	XMC-QDPT2 energy of transition 1→i, eV (nm)	f	Orbitals population									
							HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4
							A	A	A	A	A	A	A	A	A	A
$OsCl_5(H_2O)^-$																
1	T1	-4922.65	0	-4934.74	0	-	2.0	1.98	1.97	1.01	1.00	0.02	0.01	0.01	0.01	0
2	T2	-4916.96	5.69 (218)	-4934.67	0.07 (17714)	1.32E-6	2.0	1.99	1.98	1.00	1.00	0.01	0.07	0.01	0	0
3	T3	-4916.78	5.87 (211)	-4934.6	0.14 (8857)	0.00029	2.0	1.98	1.97	1.01	1.01	0.01	0.01	0.01	0	0
4	T4	-4916.36	6.29 (197)	-4934.5	0.24 (5167)	1.29E-5	2.0	1.95	1.94	1.04	1.02	0.03	0.01	0.01	0.01	0
5	T5	-4916.08	6.57 (189)	-4934.37	0.37 (3351)	0.00094	2.0	1.97	1.96	1.01	1.01	0.03	0.02	0.01	0.01	0
6	T6	-4915.39	7.26 (171)	-4933.57	1.17 (1060)	3.397E-5	2.0	1.96	1.96	1.02	1.00	0.04	0.01	0.01	0.01	0
7	T7	-4915.13	7.52 (165)	-4932.11	2.63 (471)	0.00011	2.0	1.99	1.03	1.00	0.97	0.91	0.09	0	0	0
8	T8	-4914.44	8.21 (151)	-4932.05	2.69 (461)	9.79E-5	1.99	1.97	1.65	1.00	0.88	0.38	0.12	0.01	0	0
9	T9	-4914.16	8.49 (146)	-4932.03	2.71 (458)	2.65E-6	2.0	1.99	1.10	1.01	0.89	0.70	0.30	0	0	0
10	Q1	-4913.39	9.26 (134)	-4931.98	2.76 (449)	9.63E-6	1.99	1.97	1.82	0.99	0.95	0.22	0.06	0	0	0
11	T10	-4913.27	9.38 (132)	-4931.93	2.81 (441)	4.00E-5	2.0	1.99	1.29	0.97	0.88	0.74	0.13	0	0	0
12	Q2	-4912.78	9.87 (126)	-4931.91	2.83 (438)	0.00014	2.0	1.9	1.14	0.95	0.91	0.84	0.16	0	0	0
13	T11	-4912.76	9.89 (125)	-4931.9	2.84 (437)	4.92E-5	2.0	1.99	1.42	1.01	0.86	0.57	0.14	0	0	0
14	T12	-4912.46	10.19 (122)	-4931.88	2.87 (432)	5.295E-6	2.0	1.99	1.59	0.99	0.95	0.42	0.06	0	0	0
15	T13	-4912.05	10.6 (117)	-4931.79	2.95 (420)	6.355E-5	1.99	1.99	1.09	0.98	0.93	0.63	0.37	0	0	0
16	Q3	-4912.01	10.64 (117)	-4931.78	2.97 (418)	0.00018	2.0	1.99	1.10	0.99	0.91	0.77	0.23	0.00	0	0
17	T14	-4911.94	10.71(116)	-4931.63	3.11 (399)	0.00028	1.99	1.98	1.07	0.99	0.95	0.86	0.15	0.00	0	0
18	T15	-4911.88	10.77 (115)	-4931.49	3.25 (382)	5.02E-5	1.99	1.99	1.05	1.02	0.97	0.92	0.05	0.00	0	0
19	T16	-4911.83	10.82 (114.60)	-4931.35	3.39 (366)	0.00014	1.95	1.87	1.69	0.99	0.86	0.46	0.18	0.01	0	0
20	Q4	-4911.81	10.84 (114.39)	-4931.22	3.52 (352)	0.00030	1.96	1.83	1.54	0.99	0.77	0.64	0.27	0.01	0	0
21	T17	-4911.74	10.91 (114)	-4931.03	3.7 (335)	0.00071	1.99	1.97	1.53	0.93	0.86	0.49	0.22	0	0	0
22	T18	-4911.48	11.17 (111)	-4930.82	3.92 (316)	1.31E-6	1.99	1.98	1.72	0.93	0.93	0.31	0.14	0	0	0
$OsCl_5(OH)^{2-}$																
1	T1	-4905.69	0	-4920.92	0	-	1.97	1.85	1.77	1.15	1.01	0.21	0.02	0.01	0.01	0.01
2	T2	-4899.26	6.43 (193)	-4918.32	2.61 (476)	0.00078	1.99	1.97	1.94	1.03	1.00	0.06	0.03	0	0	0
3	T3	-4899.18	6.51 (191)	-4917.92	3.00 (413)	0.0006	1.99	1.97	1.96	1.01	1.00	0.03	0.03	0.01	0	0
4	T4	-4899.12	6.57 (189)	-4917.49	3.44 (361)	0.032	1.96	1.94	1.88	1.07	1.02	0.07	0.05	0.01	0	0.37

5	T5	-4898.9	6.79 (183)	-4915.73	5.19 (239)	0.00024	1.97	1.96	1.17	1.01	0.96	0.85	0.07	0.01	0	0
6	T6	-4898.85	6.83 (181)	-4915.67	5.25 (236)	0.0016	1.97	1.96	1.79	1.02	0.96	0.25	0.04	0.01	0.01	0
7	T7	-4898.8	6.89 (180)	-4915.54	5.38 (230)	0.00064	1.97	1.95	1.34	1.05	0.84	0.76	0.09	0.01	0	0
8	Q1	-4898.16	7.52 (165)	-4915.32	5.61 (221)	0.0027	1.97	1.97	1.43	1.08	0.83	0.53	0.17	0.01	0	0
9	T8	-4897.82	7.87 (158)	-4915.27	5.66 (219.1)	1.18E-5	1.98	1.97	1.36	0.90	0.80	0.75	0.23	0.01	0	0
10	T9	-4897.79	7.90 (157)	-4915.26	5.67 (218.7)	0.0005	1.97	1.97	1.39	1.04	0.62	0.59	0.40	0.01	0	0
11	Q2	-4897.68	8.00 (155)	-4915.08	5.85 (212)	0.00092	1.97	1.96	1.04	1.01	0.99	0.94	0.06	0.01	0	0
12	T10	-4897.54	8.14 (152)	-4914.89	6.03 (206)	0.00034	1.97	1.92	1.53	0.90	0.82	0.66	0.18	0.01	0	0
13	T11	-4897.4	8.29 (150)	-4914.84	6.08 (204)	0.0021	1.97	1.95	1.53	1.00	0.72	0.52	0.29	0.01	0	0
14	T12	-4897.12	8.57 (145)	-4914.74	6.19 (200)	0.0067	1.97	1.90	1.50	0.99	0.79	0.66	0.17	0.01	0	0
15	T13	-4896.69	9.00 (138)	-4914.7	6.22 (199)	0.0045	1.982	1.9	1.36	1.09	0.84	0.58	0.16	0.01	0	00
16	T14	-4896.5	9.19 (135)	-4914.51	6.42 (193)	0.006	1.968	1.83	1.3	1.15	0.83	0.58	0.32	0.01	0	0
17	T15	-4896.44	9.25 (134)	-4914.44	6.48 (191)	0.0054	1.97	1.8924	1.44	1.05	0.72	0.66	0.26	0.01	0	0
18	Q3	-4896.3	9.39 (132)	-4914.22	6.70 (185)	0.018	1.98	1.8379	1.18	1.10	0.99	0.82	0.07	0.01	0	0
19	T16	-4896.16	9.53 (130)	-4914.13	6.79 (183)	0.0003	1.98	1.9627	1.31	0.98	0.95	0.68	0.13	0.01	0	0
20	T17	-4896	9.68 (128)	-4913.42	7.51 (165)	0.0057	1.97	1.9310	1.21	1.00	0.89	0.74	0.25	0.01	0	0
21	T18	-4895.96	9.72 (128)	-4913.37	7.55 (164)	0.0013	1.97	1.93	1.61	0.91	0.89	0.5071	0.17	0.01	0	0
22	T19	-4895.8	9.88 (125)	-4907.9	13.02 (95)	0.063	1.96	1.62	1.57	1.38	1.00	0.4401	0.02	0.01	0.01	0.01

Table S8. Energies and orbiltal populations of $OsCl_5(H_2O)^-$ and $OsCl_5(OH)^{2-}$ in triplet state as a result of SBKJC aqueous phase calculations (FireFly package).

	State	Energy, eV	Energy of transition T1→Ti, Q1→Qi eV (nm)	XMC-QDPT2	XMC-QDPT2 energy of transition 1→i, eV (nm)	f	Orbitals population									
							HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4
							A	A	A	A	A	A	A	A	A	A
$OsCl_5(H_2O)^-$																
1	T1	-4925.38	0	-4937.59	0	-	1.99	1.99	1.97	1.01	0.99	0.03	0.02	0	0	0
2	T2	-4925.04	0.35 (3543)	-4937.35	0.24 (5157)	2.02E-6	1.99	1.99	1.97	1.01	1.00	0.02	0.02	0	0	0
3	T3	-4924.94	0.44 (2818)	-4937.22	0.38 (3290)	5.58E-6	2.00	1.99	1.97	1.00	1.00	0.02	0.01	0	0	0
4	Q1	-4924.52	-	-4935.47	-	0.0027	2.00	1.99	1.19	1.00	1.00	0.80	0.02	0	0	0
5	T4	-4922.63	2.76 (449)	-4934.91	2.68 (462)	2.37E-5	1.99	1.99	1.17	1.00	0.95	0.83	0.07	0	0	0
6	T5	-4922.31	3.07 (404)	-4934.84	2.76 (449)	6.68E-5	1.99	1.99	1.33	1.02	0.94	0.65	0.08	0	0	0
7	T6	-4922.17	3.21 (386)	-4934.78	2.82 (440)	7.96E-5	1.99	1.99	1.36	1.00	0.99	0.64	0.02	0	0	0
8	T7	-4922.14	3.24 (383)	-4934.76	2.84 (437)	3.99E-5	1.99	1.99	1.14	0.99	0.88	0.86	0.14	0	0	0
9	T8	-4922.09	3.29 (377)	-4934.73	2.87 (433)	0.00059	1.99	1.99	1.04	0.99	0.97	0.96	0.05	0	0	0
10	T9	-4922.07	3.32 (373)	-4934.33	3.26 (380)	0.00013	1.99	1.99	1.29	1.00	0.70	0.68	0.33	0	0	0
11	T10	-4920.82	4.57 (271)	-4934.29	3.30 (376)	0.00079	1.99	1.99	1.11	1.00	0.89	0.83	0.18	0	0	0
12	T11	-4920.71	4.68 (265)	-4934.25	3.35 (370)	1.44E-5	1.99	1.99	1.44	1.02	0.69	0.53	0.33	0	0	0
13	T12	-4920.61	4.77 (260)	-4934.17	3.42 (362)	7.60E-6	1.99	1.99	1.67	1.01	0.85	0.31	0.17	0	0	0
14	Q2	-4919.69	4.83 (257)	-4933.84	1.63 (761)	9.04E-5	1.99	1.99	1.22	1.00	0.82	0.76	0.21	0	0	0
15	T13	-4919.65	5.73 (216)	-4933.79	3.80 (326)	0.00019	1.99	1.99	1.35	0.97	0.72	0.64	0.34	0	0	0
16	T14	-4919.44	5.94 (209)	-4933.67	3.92 (316.2)	0.00040	1.99	1.99	1.33	0.97	0.89	0.64	0.19	0	0	0
17	T15	-4919.39	5.99 (207)	-4933.67	3.93 (315.8)	0.0021	1.99	1.99	1.03	0.99	0.97	0.96	0.04	0	0	0
18	T16	-4919.32	6.07 (204)	-4933.49	4.10 (302)	0.00014	1.99	1.99	1.61	0.93	0.87	0.38	0.22	0	0	0
19	T17	-4919.28	6.10 (203)	-4932.96	4.64 (267)	9.24E-5	1.99	1.99	1.38	0.93	0.87	0.60	0.23	0	0	0
20	T18	-4919.23	6.15 (202)	-4932.75	4.85 (256)	7.541E-5	1.99	1.99	1.85	1.01	0.99	0.13	0.03	0	0	0
21	Q3	-4918.92	5.6 (221)	-4932.48	2.99 (415)	1.17E-5	1.99	1.99	1.44	0.90	0.60	0.54	0.52	0	0	0
22	Q4	-4918.86	5.66 (219)	-4932.21	3.26 (380)	3.16E-6	1.99	1.99	1.61	0.97	0.71	0.37	0.35	0	0	0
$OsCl_5(OH)^{2-}$																
1	T1	-4914.53	0	-4918.25	0	-	1.99	1.96	1.94	1.02	0.98	0.07	0.04	0.01	0	0
2	T2	-4909.88	4.65 (267)	-4917.9	0.35 (3517)	0.00027	1.97	1.94	1.88	1.03	0.93	0.17	0.07	0.01	0.01	0
3	T3	-4909.75	4.78 (259)	-4916	2.26 (550)	0.00017	1.99	1.98	1.98	1.00	1.00	0.02	0.01	0.00	0	00
4	T4	-4908.64	5.89 (210)	-4914.71	3.54 (350)	0.0059	1.94	1.93	1.85	0.98	0.90	0.26	0.13	0.00	0.01	0

5	T5	-4908.51	6.02 (206)	-4914.59	3.66 (339)	0.00399	1.97	1.94	1.75	0.96	0.87	0.33	0.16	0.00	0.01	0
6	T6	-4908.3	6.23 (199)	-4914.29	3.97 (313)	0.017	1.96	1.71	1.61	1.30	0.92	0.39	0.09	0.01	0.01	0
7	T7	-4908.27	6.26 (198)	-4914.12	4.13 (300)	0.0034	1.94	1.86	1.59	1.23	0.69	0.50	0.16	0.01	0.01	0
8	T8	-4908.03	6.50 (190.9)	-4913.99	4.26 (291)	0.014	1.99	1.95	1.80	1.01	0.88	0.33	0.03	0.01	0.01	0
9	T9	-4908.02	6.51 (190.6)	-4913.53	4.73 (262)	0.00021	2.00	1.99	1.97	1.01	1.00	0.02	0.01	0	0	0
10	Q1	-4906.93	-	-4913.39	-	0.0564	2.00	1.71	1.67	1.31	1.26	0.05	0.02	0.01	0.01	0
11	Q2	-4906.56	0.37 (3351)	-4912.45	0.94 (1319)	0.0076	2.00	1.95	1.90	1.07	1.01	0.06	0.02	0	0	0
12	T10	-4906.01	8.52 (146)	-4912.14	6.12 (203)	0.01669	2.00	1.94	1.29	0.96	0.84	0.82	0.18	0.01	0	0
13	T11	-4905.85	8.68 (143)	-4911.89	6.36 (195)	0.00598	2.00	1.75	1.31	1.17	1.03	0.66	0.14	0.01	0	0
14	Q3	-4905.79	1.14 (1088)	-4911.74	1.65 (752)	0.0082	2.00	1.72	1.56	1.31	1.00	0.32	0.09	0.01	0	0
15	T12	-4905.73	8.80 (141)	-4911.52	6.73 (184)	0.00046	2.00	1.92	1.24	1.12	0.89	0.76	0.09	0.01	0	0
16	T13	-4905.46	9.07 (137)	-4910.85	7.40 (168)	0.0043	2.00	1.95	1.07	1.02	0.99	0.83	0.14	0.01	0	0
17	T14	-4905.09	9.43 (131)	-4910.7	7.56 (164)	0.00819	2.00	1.93	1.20	1.07	0.83	0.66	0.32	0.01	0	0
18	T15	-4904.98	9.55 (130)	-4910.59	7.66 (162)	0.00171	2.00	1.94	1.14	1.12	0.80	0.77	0.24	0.01	0	0
19	T16	-4904.89	9.64 (129)	-4910.5	7.75 (160)	0.03042	2.00	1.88	1.30	1.09	0.95	0.65	0.17	0.01	0	0
20	T17	-4904.8	9.73 (127)	-4910.05	8.21 (151)	0.003105	2.00	1.96	1.05	1.02	0.98	0.97	0.03	0	0	0
21	T18	-4904.4	10.12 (122)	-4909.4	8.86 (140)	0.007593	2.00	1.94	1.29	1.02	0.86	0.72	0.17	0.01	0	0
22	T19	-4904.05	10.48 (118)	-4899.16	19.10 (65)	0.24251	2.00	1.90	1.40	1.10	0.98	0.59	0.04	0.01	0	0

Table S9. Energies and orbiltal populations of $OsCl_5(H_2O)^-$ and $OsCl_5(OH)^{2-}$ in quintet state as a result of SBKJC gas phase calculations (FireFly package).

	State	Energy, eV	Energy of transition 1→i, eV (nm)	XMC-QDPT2	XMC-QDPT2 energy of transition 1→i, eV (nm)	f	Orbitals population									
							HOMO-5	HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
							A	A	A	A	A	A	A	A	A	A
$OsCl_5(H_2O)^-$																
1	Q1	-4922.63	0	-4935.35	0	-	1.99	1.99	1.00	1.00	1.00	1.00	0.01	0.01	0	0
2	Q2	-4918.81	3.82 (325)	-4932.38	2.97 (418)	9.06E-5	1.97	1.94	1.03	1.00	1.00	0.96	0.08	0.01	0	0
3	Q3	-4917.38	5.25 (236)	-4932.17	3.19 (389)	0.019	1.78	1.65	1.23	1.18	1.00	0.93	0.22	0.01	0	0
4	Q4	-4917.37	5.26 (236)	-4932.05	3.30 (376)	0.036	1.89	1.57	1.09	1.04	1.00	0.80	0.59	0.01	0	0
5	Sp1	-4917.36	-	-4931.79	-	0.028	1.92	1.77	1.16	1.05	1.00	0.91	0.17	0.01	0	0
6	Q5	-4917.36	5.28 (234.9)	-4931.69	3.66 (339)	0.0021	2.00	1.97	1.00	1.00	1.00	1.00	0.02	0	0	0
7	Sp2	-4917.33	5.3 (234)	-4931.67	3.68 (337)	0.0071	1.95	1.91	1.07	1.04	1.00	0.98	0.05	0.01	0	0
8	Q6	-4917.07	5.56 (223)	-4931.62	3.73 (332)	0.0032	1.93	1.90	1.08	1.05	1.00	0.98	0.04	0.01	0	0
9	Q7	-4917	5.63 (220)	-4931.45	3.90 (318)	0.014	1.87	1.85	1.12	1.10	1.01	1.00	0.03	0.01	0	0
10	Q8	-4916.89	5.75 (216)	-4931.13	4.22 (294)	0.016	1.86	1.52	1.13	1.00	1.00	0.85	0.62	0.01	0	0
11	Q9	-4916.86	5.78 (215)	-4930.88	4.47 (277)	0.0031	1.99	1.96	1.01	1.00	1.00	1.00	0.04	0.01	0	0
12	Q10	-4916.84	5.8 (214)	-4930.70	4.65 (267)	0.0040	1.88	1.80	1.12	1.00	1.00	0.99	0.20	0.01	0	0
13	Q11	-4916.82	5.81 (213.4)	-4930.20	5.15 (241)	0.00045	1.98	1.86	1.01	1.00	1.00	0.99	0.15	0.01	0	0
14	Q12	-4916.81	5.82 (213.1)	-4929.51	5.84 (212)	0.00042	1.96	1.26	1.03	1.01	1.00	0.97	0.76	0.01	0	0
15	Q13	-4916.81	5.82 (213.1)	-4928.94	6.41 (193)	0.0057	1.93	1.26	1.03	1.01	0.99	0.97	0.80	0	0	0
16	Q14	-4916.78	5.86 (212)	-4928.75	6.60 (188)	0.0037	2.00	1.02	1.01	1.00	1.00	0.99	0.98	0	0	0
17	Q15	-4916.65	5.98 (207)	-4928.66	6.70 (185)	0.0020	1.98	1.64	1.13	1.02	1.00	0.88	0.35	0	0	0
18	Q16	-4915.6	7.03 (176)	-4928.58	6.77 (183)	0.00013	2.00	1.70	1.01	1.00	1.00	0.99	0.30	0	0	0
19	Q17	-4915.57	7.06 (176)	-4928.45	6.90 (180)	0.00019	2.00	1.21	1.01	1.00	1.00	0.98	0.80	0	0	0
20	Q18	-4915.06	7.57 (164)	-4928.38	6.97 (178)	0.00018	1.99	1.19	1.03	1.00	0.99	0.98	0.81	0	0	0
21	Q19	-4915.03	7.6 (163)	-4928.36	6.99 (177)	0.00041	1.99	1.41	1.03	1.01	1.00	0.96	0.59	0	0	0
22	Q20	-4914.83	7.8 (325)	-4927.80	7.55 (164)	0.0013	1.98	1.15	1.02	1.01	0.99	0.99	0.84	0	0	0
$OsCl_5(OH)^{2-}$																
1	Q1	-4906.37	0	-4919.13	0.00	-	1.94	1.55	1.24	1.02	0.99	0.83	0.40	0.01	0.01	0
2	Q2	-4900.1	6.27 (198)	-4917.70	1.43 (867)	0.0046	1.98	1.98	1.01	1.00	1.00	1.00	0.02	0.01	0	0
3	Q3	-4899.82	6.56 (189)	-4916.43	2.70 (459)	0.023	1.91	1.68	1.16	1.02	1.00	0.83	0.38	0.01	0.01	0
4	Q4	-4899.79	6.58 (188)	-4914.81	4.31 (288)	0.0019	1.89	1.66	1.17	1.03	0.98	0.94	0.31	0.01	0	0

5	Q5	-4899.6	6.77 (183.1)	-4914.62	4.51 (275)	0.00094	1.96	1.80	1.16	1.01	1.00	0.88	0.19	0.01	0	0
6	Q6	-4899.6	6.78 (183.0)	-4914.45	4.67 (266)	0.032	1.96	1.76	1.19	1.00	1.00	0.81	0.26	0.01	0.01	0
7	Q7	-4899.43	6.94 (179)	-4914.24	4.88 (254)	0.0089	1.80	1.62	1.36	1.10	1.00	0.88	0.23	0.01	0.01	0
8	Q8	-4899.14	7.24 (171.4)	-4914.01	5.12 (242)	0.0024	1.92	1.90	1.08	1.06	1.00	0.99	0.03	0.01	0	0
9	Q9	-4899.13	7.25 (171.1)	-4913.53	5.60 (221)	0.018	1.76	1.71	1.06	1.02	0.92	0.82	0.70	0.01	0.01	0
10	Q10	-4899.09	7.28 (170)	-4913.46	5.67 (219)	0.021	1.86	1.65	1.10	1.05	0.97	0.75	0.60	0.01	0.01	0
11	Q11	-4898.72	7.65 (162)	-4913.28	5.84 (212)	0.003	1.83	1.76	1.21	1.09	1.01	0.96	0.14	0.01	0.01	0
12	Sp1	-4898.52	-	-4913.22	-	0.003	1.82	1.70	1.18	1.14	1.03	1.00	0.12	0.01	0	0
13	Sp2	-4898.26	-	-4912.92	-	0.0004	1.71	1.54	1.20	1.08	0.99	0.81	0.65	0.01	0.01	0
14	Q12	-4897.74	8.63 (144)	-4912.08	7.05 (176)	0.0078	1.69	1.44	1.26	1.10	0.8	0.84	0.68	0.01	0.01	0
15	Q13	-4897.15	9.22 (135)	-4911.73	7.39 (168)	0.016	1.90	1.39	1.12	1.07	1.00	0.84	0.67	0.01	0	0
16	Q14	-4897.06	9.31 (133)	-4911.53	7.59 (163)	0.0028	1.94	1.45	1.07	1.07	1.01	0.88	0.57	0.01	0	0
17	Q15	-4896.81	9.57 (130)	-4911.44	7.69 (161)	0.002	1.98	1.23	1.04	1.02	1.02	0.99	0.71	0	0	0
18	Q16	-4896.39	9.98 (124)	-4911.27	7.85 (158)	0.03	1.98	1.34	1.04	1.01	0.99	0.92	0.71	0.01	0	0
19	Q17	-4896.3	10.07 (123)	-4911.09	8.04 ()154	0.0019	1.97	1.533	1.09	1.03	0.99	0.92	0.46	0	0	0
20	Q18	-4896.21	10.17 (122)	-4910.92	8.21 (151)	0.019	1.91	1.36	1.14	1.08	0.95	0.89	0.65	0.01	0.01	0
21	Q19	-4896.16	10.21 (121)	-4910.31	8.81 (141)	0.01	1.71	1.32	1.27	1.21	1.00	0.84	0.64	0.01	0.01	0
22	Q20	-4896.16	10.21 (121)	-4909.49	9.64 (129)	0.03	1.90	1.80	1.14	1.02	0.98	0.93	0.22	0.01	0	0

Table S10. Energies and orbiltal populations of $OsCl_5(H_2O)^-$ and $OsCl_5(OH)^{2-}$ in quintet state as a result of SBKJC aqueous phase calculations (FireFly package).

	State	Energy, eV	Energy of transition 1→i, eV (nm)	XMC-QDPT2	XMC-QDPT2 energy of transition 1→i, eV (nm)	f	Orbitals population									
							HOMO-5	HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
							A	A	A	A	A	A	A	A	A	A
$OsCl_5(OH)^{2-}$																
1	Q1	-4913.46	0	-4924.76	0	-	2.00	2.00	1.00	1.00	1.00	1.00	0	0	0	0
2	Q2	-4907.33	6.13 (202)	-4923.47	1.29 (961)	3.28E-5	1.99	1.99	1.01	1.00	1.00	0.99	0.02	0	0	0
3	Q3	-4907.12	6.34 (196)	-4922.32	2.44 (508)	0.0032	1.99	1.96	1.02	1.00	1.00	0.99	0.02	0	0	0
4	Q4	-4906.96	6.50 (191)	-4922.13	2.63 (471)	0.0017	2.00	1.97	1.00	1.00	1.00	1.00	0.02	0	0	0
5	Q5	-4906.9	6.57 (189)	-4921.97	2.79 (444)	0.00014	2.00	1.98	1.01	1.00	1.00	1.00	0.02	0	0	0
6	Q6	-4906.29	7.17 (173)	-4921.91	2.85 (435)	0.0058	1.99	1.97	1.01	1.01	1.00	1.00	0.01	0	0	0
7	Q7	-4905.7	7.76 (160)	-4921.7	3.06 (405)	9.20E-6	2.00	1.99	1.00	1.00	1.00	1.00	0.01	0	0	0
8	Q8	-4905.04	8.41 (147)	-4921.6	3.16 (392)	7.60E-6	2.00	1.97	1.01	1.00	1.00	0.99	0.02	0	0	0
9	Q9	-4904.72	8.75 (142)	-4921.55	3.21 (386)	3.63E-5	1.97	1.94	1.01	1.01	1.00	0.98	0.08	0	0	0
10	Sp1	-4904.04	-	-4921.27	-	0.00032	2.00	1.23	1.00	1.00	1.00	1.00	0.77	0	0	0
11	Q10	-4903.71	9.75 (127)	-4921.18	3.58 (346)	0.0043	1.99	1.38	1.00	1.00	1.00	1.00	0.62	0	0	0
12	Q11	-4903.48	9.98 (124)	-4920.61	4.15 (299)	0.0024	1.89	1.80	1.06	1.00	1.00	0.95	0.30	0	0	0
13	Q12	-4903.37	10.10 (123)	-4920.5	4.26 (291)	3.00E-5	1.97	1.90	1.06	1.00	1.00	0.98	0.08	0	0	0
14	Q13	-4903.27	10.19 (122)	-4920.27	4.49 (276)	0.00034	1.99	1.91	1.03	1.00	1.00	0.99	0.08	0	0	0
15	Q14	-4902.61	10.85 (114.3)	-4920.21	4.55 (273)	0.0046	1.96	1.70	1.11	1.01	0.99	0.90	0.34	0	0	0
16	Q15	-4902.6	10.86 (114.2)	-4920.2	4.56 (272)	0.048	2.00	1.78	1.07	1.01	1.00	1.00	0.14	0	0	0
17	Q16	-4902.55	10.91 (113.7)	-4920.1	4.66 (266)	6.02E-5	1.78	1.71	1.04	1.03	0.98	0.83	0.62	0	0	0
18	Q17	-4901.94	11.52 (108)	-4919.97	4.79 (259)	4.976E-8	1.97	1.85	1.08	1.03	1.00	0.94	0.12	0	0	0
19	Q18	-4901.68	11.78 (105.3)	-4919.94	4.82 (257)	5.25E-6	2.00	1.89	1.04	1.00	1.00	0.96	0.11	0	0	0
20	Q19	-4901.62	11.84 (104.7)	-4919	5.76 (215)	7.53E-5	1.80	1.57	1.19	1.11	1.00	0.98	0.33	0	0	0
21	Q20	-4901.55	11.91 (104)	-4918.87	5.89 (211)	0.00081	1.89	1.12	1.09	1.02	1.00	0.98	0.90	0	0	0
22	Q21	-4901.25	12.21 (102)	-4918.69	6.07 (204)	0.0031	1.96	1.16	1.04	1.02	1.00	0.97	0.84	0	0	0

Table S11. Electronic and geometric structure of H_2O and H_3O^+. Multiplicity M; bond lengths RH-Cl, RO-H(1), RO-H(2); bond angles ∠ H(1)OH(2); atom charges q_O, q_{Cl}, $q_{H(1)}$, $q_{H(2)}$; total energy E_0.

	Structure	RO-H(1), Å RO-H(2), Å RO-H(3), Å	∠H(1)OH(2) ∠H(1)OH(3) ∠H(2)OH(3)	q_O	$q_{H(1)}$, $q_{H(2)}$ $q_{H(3)}$	E_{TOTAL}, Hartree	E_{TOTAL}, eV
ROHF/IMCP-SR1 (gas)							
1	H_2O	0.944 0.944 -	105.541 - -	-0.313	0.156 0.156 -	-16.9635	-461.60
2	H_3O^+	0.962 0.962 0.962	120.026 119.987 119.987	0.033	0.322 0.322 0.322	-17.2371	-469.05
ROHF/IMCP-SR1/PCM (water)							
3	H_2O	0.948 0.948 -	104.999 - -	-0.400	0.200 0.200 -	-16.9745	-461.90
4	H_3O^+	1.051 1.051 1.063	123.200 118.400 118.400	0.039	0.321 0.322 0.318	-17.3666	-472.57
ROHF/SBKJC (gas)							
5	H_2O	0.967 0.967 -	110.089 - -	-0.606	0.303 0.303 -	-16.8193	-457.68
6	H_3O^+	0.979 0.979 0.979	120.000 120.000 120.000	-0.485	0.495 0.495 0.495	-17.0998	-465.31
ROHF/SBKJC (water)							
7	H_2O	1.002 1.001 -	105.401 - -	-0.708	0.354 0.354 -	-16.8308	-457.99
8	H_3O^+	0.96497 0.96471 0.96447	121.134 118.755 120.102	-0.451	0.484 0.485 0.482	-17.2323	-468.92

Table S12. The thermochemical characteristics of photoaquatation products and H_2O and H_3O^+ calculated at 298 K. Multiplicity M; energy E, enthalpy H, Gibbs free energy G, entropy S, logarithm of statistical sum $\ln Q_i$.

	Method	M	E, eV	H, eV	G, eV	S, eV/K	ln Q_{el}	ln Q_{TRANS}	ln Q_{rot}	ln Q_{vib}
$OsCl_5(H_2O)^-$										
1	ROHF/IMCP-SR1	3	1.196088	1.221587	-0.1963	0.00475559	1.098612	19.508270	14.194569	7.752374
2	ROHF/IMCP-SR1	5	1.174373	1.199872	-0.778	0.0066337	1.609438	19.508270	13.631587	31.047479
3	ROHF/SBKJC	3	1.181855	1.207311	-0.18417	0.00466709	1.098612	19.508270	14.218236	7.133274
4	ROHF/SBKJC	5	1.150852	1.176308	-0.16073	0.00448447	1.609438	19.508270	14.218251	5.982369
$OsCl_5(OH)^{2-}$										
5	ROHF/IMCP-SR1	3	0.826331	0.85183	-0.51974	0.00460018	1.098612	19.504336	14.216528	6.780932
6	ROHF/IMCP-SR1	5	0.837081	0.86258	-0.62814	0.00499991	1.609438	19.504336	14.337747	9.360135
7	ROHF/SBKJC	3	0.849766	0.875265	-0.51458	0.0046615	1.098612	19.504336	14.213988	7.113717
8	ROHF/SBKJC	5	0.841983	0.867439	-0.58777	0.00488084	1.609438	19.504336	14.315425	8.438571
H_2O										
9	ROHF/IMCP-SR1	1	0.684517	0.709973	0.115455	0.00199404	0.000000	14.915558	4.418084	0.000228
10	ROHF/SBKJC	1	0.623156	0.648612	0.049923	0.00200801	0.000000	14.915558	4.581707	0.000210
H_3O^+										
11	ROHF/IMCP-SR1	1	0.9976	1.023056	0.406909	0.00206662	0.000000	14.997230	5.181022	0.000781
12	ROHF/SBKJC	1	1.012134	1.037633	0.420626	0.00206942	0.000000	14.997230	5.194453	0.003968

Figure S1. Scheme of $Os^{IV}Cl_6^{2-}$ structure.

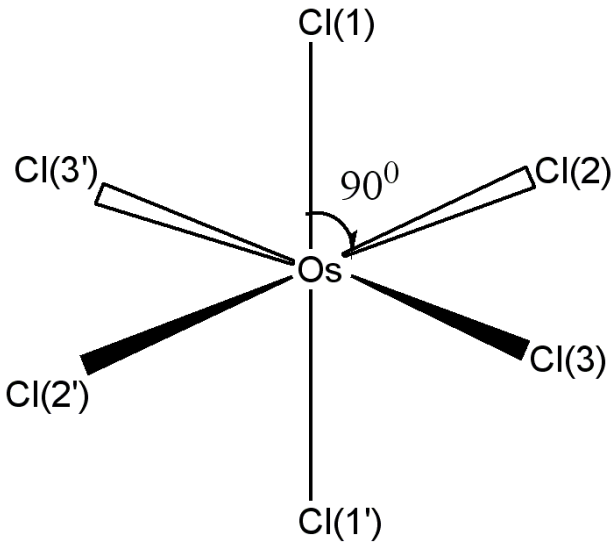


Figure S2a. Scheme of $OsCl_5^{2-}$ (Planar) structure.

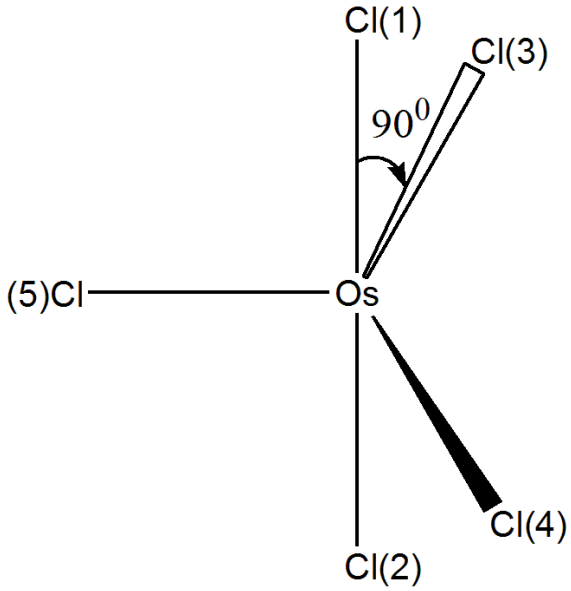


Figure S2b. Scheme of $OsCl_5^{2-}$ (Axial) structure.

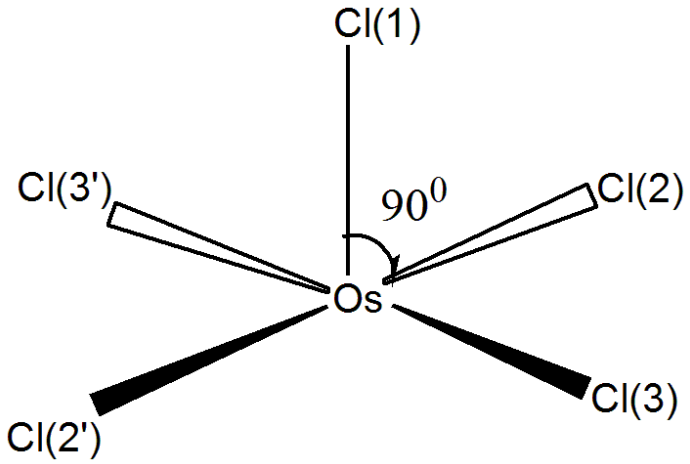
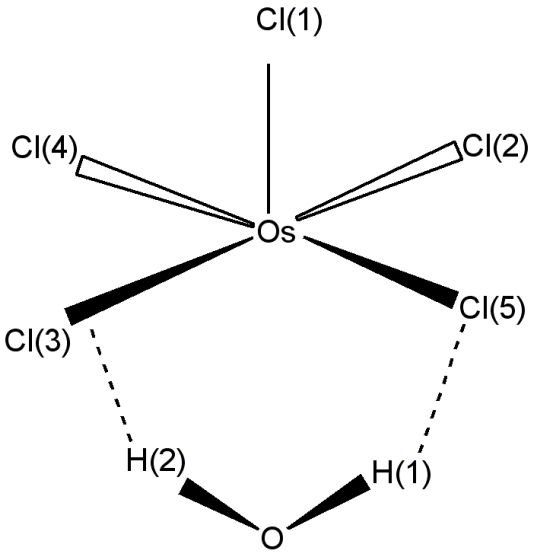


Figure S3. Scheme of structure of $OsCl_5(H_2O)^-$



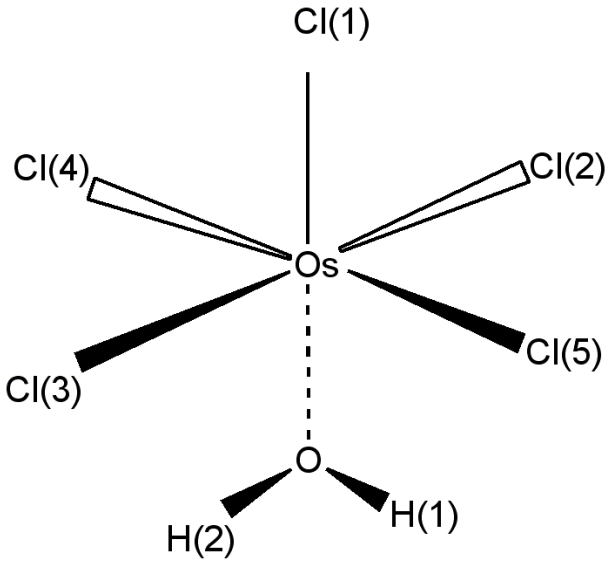


Figure S4. Scheme of structure of $OsCl_5(OH)^{2-}$