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Supporting Information

to paper of Marina V. Rogozina, Vladislav V. Yudanov, Roman G. Fedunov, Ivan P. Pozdnyakov, Alexey A. Melnikov, Sergey V. Chekalin, and Evgeni M. Glebov

"Short-Lived Intermediates in Photochemistry of $OsCl_6^{2-}$ Complex in Aqueous Solutions"

(Photochemical & Photopbiological Sciences, 2017)

Table S1. Electronic and geometric structure of $Os^{IV}Cl_6^{2-}$ (Figure S1). Multiplicity M; bond lengths ROsCl(1), ROsCl(2), ROsCl(3); bond angles ∠Cl(2)OsCl(3); atom charges q_{Os}, $q_{Cl(1)}$, $q_{Cl(2)}$; total energy E_0.

	Methods	M	ROsCl(1), Å	ROsCl(2), Å	ROsCl(3), Å	∠Cl(2)OsCl(3)	q_{Os}	$q_{cl(1)}$	$q_{cl(2)}$	$q_{cl(3)}$	E_0, Hartree
	Calculations in GAMESS										
1	UHF/IMCP-NR1	3	2.478	2.462	2.462	89.718	1.238	-0.550	-0.534	-0.534	-153.3726
2	RHF/IMCP-NR1	1	2.413	2.464	2.464	88.338	1.215	-0.504	-0.552	-0.552	-153.3083
3	ROHF/IMCP-NR1	3	2.431	2.467	2.467	90	1.245	-0.517	-0.553	-0.553	-153.3656
4	CASSCF(6, 6)/IMCP-NR1	1	2.416	2.464	2.464	88.106	1.201	-0.509	-0.545	-0.545	-153.3128
5	CASSCF(10, 8)/IMCP-NR1	3	2.434	2.470	2.476	90	1.213	-0.562	-0.517	-0.527	-153.3779
6	UHF/IMCP-SR1	3	2.405	2.440	2.440	90	1.007	-0.471	-0.516	-0.516	-154.9780
7	RHF/IMCP-SR1	1	2.477	2.383	2.383	89.957	0.972	-0.574	-0.456	-0.456	-154.9101
8	ROHF/IMCP-SR1	3	2.434	2.418	2.418	89.954	1.011	-0.516	-0.495	-0.495	-154.9729
9	ROHF/IMCP-SR1	5	2.728	2.402	2.401	90	1.214	-0.701	-0.453	-0.453	-154.9616
10	CASSCF(6, 6)/IMCP-SR1	1	2.477	2.383	2.383	89.983	0.972	-0.574	-0.456	-0.456	-154.9101
11	CASSCF(10, 8)/IMCP-SR1	3	2.442	2.477	2.401	90.015	0.977	-0.530	-0.485	-0.473	-155.0107
12	UHF/IMCP-SR1/PCM (water)	3	2.429	2.412	2.4090	90±0.07	0.893	-0.500	-0.475	-0.472	-155.2502
13	RHF/IMCP-SR1/PCM (water)	1	2.466	2.372	2.370	90±0.03	0.858	-0.568	-0.431	-0.430	-155.1835
14	ROHF/IMCP-SR1/PCM (water)	3	2.422	2.404	2.409	90±0.015	0.897	-0.500	-0.476	-0.472	-155.2449
15	ROHF/IMCP-SR1/PCM (water)	5	2.687	2.392	2.396	90±0.6	1.106	-0.698	-0.428	-0.427	-155.2312
16	CASSCF(6, 6)/IMCP-SR1/PCM(water)	1	2.466	2.372	2.370	90±0.02	0.842	-0.550	-0.435	-0.436	-155.1887
17	CASSCF(10, 8)/IMCP-SR1 (water)	3	2.430	2.391	2.469	90±0.01	0.864	-0.515	-0.462	-0.454	-155.2828
18	UHF/Def2-TZVP	3	2.371	2.413	2.413	90	2.136	-0.676	-0.696	-0.696	-2847.1946
19	RHF/Def2-TZVP	1	2.457	2.356	2.355	90	2.136	-0.725	-0.672	-0.672	-2847.1273
20	ROHF/Def2-TZVP	3	2.370	2.411	2.411	90	2.151	-0.679	-0.698	-0.698	-2847.18695
21	CASSCF(10, 8)/Def2-TZVP	3	2.367	2.411	2.411	90	2.151	-0.679	-0.698	-0.698	-2847.18696

	Methods	M	ROsCl(1), Å	ROsCl(2), Å	ROsCl(3), Å	∠Cl(2)OsCl(3)	q_{Os}	$q_{cl(1)}$	$q_{cl(2)}$	$q_{cl(3)}$	E_0, Hartree
	Calculations in FireFly										
22	UHF/ SBKJC	3	2.463	2.450	2.449	90±0.02	-0.110	-0.333	-0.306	-0.306	-178.7606
23	RHF/ SBKJC	1	2.496	2.414	2.414	90±0.002	-0.174	-0.401	-0.256	-0.256	-178.6906
24	ROHF/ SBKJC	3	2.428	2.460	2.460	90±0.02	-0.123	-0.275	-0.332	-0.332	-178.7546
25	ROHF/ SBKJC	5	2.728	2.433	2.433	90±0.015	0.197	-0.573	-0.262	-0.263	-178.7465
26	CASSCF(10, 8)/ SBKJC	3	2.429	2.461	2.46	90±0.01	-0.114	-0.276	-0.333	-0.333	-178.7594
27	UHF/ SBKJC/PCM (water)	3	2.399	2.428	2.422	90±0.4	-0.352	-0.231	-0.298	-0.292	-179.0280
28	RHF/ SBKJC/PCM (water)	1	2.414	2.405	2.406	90±0.35	-0.396	-0.276	-0.264	-0.262	-178.9650
29	ROHF/ SBKJC/PCM (water)	3	2.394	2.425	2.420	90±0.01	-0.366	-0.228	-0.297	-0.292	-179.0225
30	ROHF/ SBKJC/PCM (water)	5	2.653	2.411	2.401	90±0.1	-0.019	-0.544	-0.218	-0.228	-179.0106
31	CASSCF(10, 8)/ SBKJC/PCM (water)	3	2.396	2.426	2.421	90±0.01	0.357	-0.230	-0.298	-0.294	-179.0272

Table S2. Energies and orbiltal populations of $Os^{IV}Cl_6^{2-}$ as a result of CASSCF(10,8)/IMCP-SR1 gas phase calculations (GAMESS-US package). Symmetry of orbitals corresponds to irreducible representations of D_{2h} group.

State	Energy, eV	Energy of transition 1→i, eV (nm)	Orbitals population									
			HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4
			A_g	B_u	B_g	B_g	A_g	A_g	A_g	A_g	A_g	B_u
T1	-4218.05	0	1.912	1.928	0.97	0.97	1.939	0.039	0	0	0	0
Q1	-4216.38	1.68 (737)	1.916	1.943	0.971	0.971	0.998	0.872	0.1	0	0	0
S0	-4215.32	2.74 (453)	-	-	2	2	2	0	0	0	-	-
T2	-4214.95	3.10 (399)	1.877	1.919	0.959	0.959	0.983	0.897	0.081	0	0	0
T3	-4214.19	3.87 (321)	1.907	1.942	1.5	0.442	0.998	0.922	0.056	0	0	0
T4	-4214.11	3.95 (314)	1.894	1.926	0.965	0.96	0.991	0.877	0.089	0	0	0
Q2	-4214.05	4.01 (310)	1.83	1.9	0.95	0.95	0.973	0.151	0.791	0.023	0.032	0
T5	-4214.03	4.03 (307)	1.905	1.934	0.967	0.967	0.985	0.902	0.077	0	0	0
T6	-4213.20	4.86 (255)	1.822	1.923	0.524	1.523	0.977	0.601	0.306	0.009	0.008	0
T7	-4212.45	5.61 (221)	1.848	1.899	0.954	0.954	0.978	0.1	0.837	0.025	0.035	0
Q3	-4211.86	6.21 (200)	1	1.908	0.96	0.96	1.892	0.93	0.018	0	0	0.012
T8	-4211.77	6.29 (197)	1.856	1.903	0.959	0.959	0.982	0.134	0.819	0.024	0.033	0
T9	-4211.76	6.30 (197)	1.241	1.864	1.394	1.717	1.018	0.15	0.238	0.005	0.007	0
S1	-4197.10	20.96 (59)	-	-	0	1.986	1.986	1.979	0	0.006	-	-

Table S3. Energies and orbiltal populations of $Os^{IV}Cl_6^{2-}$ 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
T1	-4864.16	0	-4874.66	0	0	2	2	1.96	1.00	1.00	0.03	0.01	0	0	0
T2	-4864.13	0.03 (40000)	-4874.59	0.03 (41333)	2.57E-09	2	2	1.98	1.00	1.00	0.01	0.01	0	0	0
T3	-4864.13	0.03 (36471)	-4874.57	0.09 (14588)	1.87E-09	2	2	1.98	1.00	1.00	0.01	0.01	0	0	0
Q1	-4863.37	0.80 (1558)	-4873.33	1.33 (3942)	-	2	2	1	1	1	1	0	0	0	0
Q2	-4863.19	0.98(1268)	4873.16	1.50 (827)	-	2	2	1	1	1	1	0	0	0	0
T4	-4861.81	2.35 (527)	-4871.89	2.77 (447)	3.30E-08	2	2	1.03	1.00	1.00	0.96	0.01	0	0	0
T5	-4861.68	2.49 (499)	-4871.62	3.04 (408)	4.40E-09	2	2	1.00	1.00	0.99	0.86	0.14	0	0	0
T6	-4861.44	2.722 (456)	-4871.41	3.247 (382)	4.26E-08	2	2	1.75	0.96	0.94	0.29	0.06	0	0	0
T7	-4861.44	2.724 (455)	-4871.40	3.254 (381)	1.70E-08	2	2	1.71	0.96	0.94	0.33	0.07	0	0	0
T8	-4861.39	2.78 (447)	-4871.29	3.37 (367)	1.71E-09	2	2	1.79	0.99	0.99	0.21	0.02	0	0	0
T9	-4861.36	2.80 (442)	-4871.27	3.39 (366)	3.23E-08	2	2	1.78	0.99	0.99	0.22	0.02	0	0	0
T10	-4861.28	2.887 (430)	-4871.21	3.45 (359)	1.69E-07	2	2	1.6	1.01	0.81	0.39	0.13	0	0	0
T11	-4861.28	2.888 (429)	-4871.20	3.46 (358)	3.17E-07	2	2	1.61	1.01	0.89	0.37	0.11	0	0	0
T12	-4861.21	2.95 (420)	-4871.13	3.53 (351)	5.49E-09	2	2	1.14	1	0.86	0.74	0.26	0	0	0
T13	-4861.17	2.99 (415)	-4871.10	3.56 (348)	2.44E-08	2	2	1.0	0.99	0.98	0.76	0.26	0	0	0
T14	-4860.97	3.19 (388)	-4870.93	3.73 (332)	8.73E-09	2	2	1.07	0.99	0.92	0.72	0.29	0	0	0
T15	-4860.93	3.24 (383)	-4870.82	3.84 (323)	4.35E-08	2	2	1.01	1.00	0.98	0.83	0.19	0	0	0
T16	-4860.01	4.15 (299)	-4870.36	4.30 (288)	3.58E-08	2	1.99	1.78	1.96	0.92	0.22	0.12	0	0	0
T17	-4859.99	4.17 (297)	-4870.32	4.34 (286)	1.99E-06	2	2	1.8	0.96	0.93	0.19	0.12	0	0	0
Q3	-4859.91	4.25 (292)	-4869.59	5.075 (244.3)	-	2	2	1	1	1	1	0	0	0	0
Q4	-4859.89	4.27 (290)	-4869.58	5.078 (244.2)	-	2	2	1	1	1	1	0	0	0	0
T18	-4859.88	4.28 (289.5)	-4870.25	4.41 (281)	4.04E-08	2	2	1.04	0.95	0.87	0.82	0.32	0	0	0
T19	-	-	-4869.94	4.7137 (263)	1.54E-07	2	2	1.02	0.97	0.94	0.82	0.25	0	0	0
T20	-	-	-4869.60	5.0605 (245)	6.22E-09	2	2	1.63	0.99	0.90	0.33	0.14	0	0	0
T21	-	-	-4869.59	5.0638 (245)	4.67E-09	2	2	1.63	0.99	0.90	0.33	0.14	0	0	0
T22	-	-	4868.87	5.7865 (214)	1.11E-06	2	2	1.69	1.01	0.99	0.28	0.04	0	0	0

Table S4. Energies and orbiltal populations of $Os^{IV}Cl_6^{2-}$ as a result of CASSCF(10,8)/IMCP-SR1/PCM aqueous phase calculations (GAMESS-US package).

State	Energy, eV	Energy of transition 1→i, eV (nm)	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
T1	-4225.46	0	1.91	1.93	0.97	0.97	1.94	0.04	0	0	0	0
T2	-4225.15	0.31 (4013)	1.88	1.93	1.94	0.97	1	0.04	0	0	0	0
T3	-4225.13	0.34 (3702)	1.89	1.93	0.97	1.94	1	0.04	0	0	0	0
Q1	-4223.67	1.79 (692)	1.92	1.94	0.97	0.97	1	0.88	0.1	0	0	0
S0	-4222.90	2.56 (484)	-	-	1,99	2	2	0	0	0,01	-	-
T4	-4222.27	3.20 (388)	1.87	1.92	0.96	0.96	0.98	0.9	0.08	0	0	0
T5	-4221.501	3.96 (313)	1.89	1.92	1.28	0.64	0.99	0.9	0.07	0	0	0
T6	-4221.497	3.97 (312.7)	1.89	1.91	1.18	0.74	0.97	0.88	0.08	0	0	0
T7	-4221.46	4.00 (309)	1.89	1.93	1.46	0.97	0.51	0.9	0.08	0	0	0
T8	-4221.42	4.05 (306)	1.89	1.92	0.96	0.96	0.99	0.88	0.09	0	0	0
T9	-4221.33	4.13 (300)	1.9	1.93	0.97	0.97	0.98	0.9	0.07	0	0	0
T10	-4221.23	4.23 (293)	1.87	0.97	0.98	1.94	1.93	0.08	0	0.01	0.01	0.01
Q2	-4221.06	4.40 (282)	1.83	1.9	0.95	0.95	0.97	0.14	0.79	0.03	0.04	0
T11	-4220.78	4.68 (265)	1.87	0.97	1.91	1	1.9	0.1	0	0.01	0	0.01
T12	-4220.58	4.88 (254)	1.59	1.89	0.96	1.3	1.24	0.61	0.06	0	0	0
T13	-4220.47	5.00 (249)	1.8	1.92	0.53	1.54	0.98	0.63	0.26	0.01	0.01	0
Q3	-4220.35	5.12 (242.2)	1.9	0.95	0.95	0.95	1.9	0.92	0.01	0	0.01	0
T14	-4220.33	5.13 (241.7)	1.86	0.97	1.8	1.8	1.13	0.22	0	0	0	0
T15	-4220.30	5.17 (240)	1.69	1.9	0.8	0.97	1.56	0.66	0.09	0	0	0
Q3	-4220.01	5.46 (227.3)	1.87	0.95	1.9	0.95	0.98	0.93	0	0	0.02	0
Q4	-4219.99	5.47 (226.8)	1.86	0.94	0.94	1.89	0.97	0.89	0.05	0	0	0
T16	-4219.91	5.56 (223)	1.31	1.86	0.98	1.55	1.62	0.3	0.07	0.01	0.01	0
T17	-4219.62	5.84 (212)	1.86	0.94	1.06	1.06	1.78	0.83	0.02	0	0.01	0
T18	-4219.48	5.99 (207)	1.85	1.9	0.95	0.95	0.98	0.1	0.83	0.03	0.04	0
T19	-4219.44	6.03 (206)	1.23	1.84	1.57	1.01	1.72	0.27	0.04	0.01	0	0
T20	-4219.38	6.08 (204)	1.85	0.95	0.97	1.89	0.99	0.87	0.08	0	0	0
T21	-4219.33	6.135 (202)	1.88	0.96	1.92	0.96	0.99	0.95	0.01	0	0.01	0
Q5	-4219.18	6.28 (197)	1	1.91	0.96	0.96	1.89	0.93	0.02	0	0	0.01
T22	-4219.09	6.37 (195)	1.06	1.84	1.7	1.76	1.05	0.17	0.06	0	0	0
Q6	-4218.91	6.55 (189)	0.99	1.94	0.97	1.95	0.97	0.9	0.06	0	0	0.01
Q7	-4218.86	6.60 (188)	0.98	1.93	1.94	0.97	0.97	0.95	0.01	0	0	0.01
T23	-4218.79	6.68 (186)	1.85	1.89	0.95	0.95	0.98	0.13	0.81	0.03	0.04	0
T24	-4218.71	6.75 (184)	1.86	1.89	0.25	0.95	1.67	0.16	0.76	0.02	0.04	0
S1	-4217.04	8.42 (147)	-	-	1,21	1,99	1,77	0,62	0,35	0,03	-	-

Table S5. Energies and orbiltal populations of $Os^{IV}Cl_6^{2-}$ 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 T1→T_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
T1	-4871.59	0	-4881.54	0	-	2	2	1.97	1.00	1.00	0.01	0.01	0	0	0
T2	-4871.37	0.22 (5936)	-4881.53	0.02 (62000)	4.91E-12	2	2	1.98	1.00	1.00	0.01	0.01	0	0	0
T3	-4871.36	0.23 (5391)	-4881.40	0.14 (8857)	6.51E-10	2	2	1.98	1.00	1.00	0.01	0	0	0	0
Q1	-4870.30	1.29 (961)	-4879.99	1.56 (795)	-	2	2	1	1	1	1	0	0	0	0
Q2	-4869.91	1.68 (738)	-4879.88	1.66 (745)	-	2	1.99	1	1	1	1	0	0	0	0
T4	-4868.63	2.96 (419)	-4878.74	2.80 (443)	9.96E-9	2	2	1.00	1.00	1.00	0.95	0.05	0	0	0
T5	-4868.38	3.21 (386)	-4878.62	2.93 (423)	1.30E-8	2	2	1.01	1.00	0.99	0.76	0.24	0	0	0
T6	-4868.31	3.28 (378)	-4878.58	2.97 (418)	6.71E-8	1.99	1.99	1.11	1.0	0.9	0.76	0.24	0	0	0
T7	-4868.26	3.33 (376)	-4878.56	2.99 (415)	8.03E-8	1.99	1.99	1.22	1.05	0.74	0.60	0.40	0	0	0
T8	-4868.25	3.34 (371)	-4878.52	3.03 (409)	7.49E-9	2	1.99	1.42	0.86	0.83	0.73	0.17	0	0	0
T9	-4868.11	3.48 (356)	-4878.48	3.07 (404)	8.92E-10	2	1.99	1.44	0.99	0.90	0.58	0.10	0	0	0
T10	-4868.01	3.58 (346)	-4878.38	3.16 (392)	7.55E-8	1.99	1.99	1.01	1.00	0.98	0.73	0.28	0	0	0
T11	-4868.00	3.59 (345)	-4878.34	3.20 (388)	6.82E-9	2	1.99	1.42	1.00	0.89	0.59	0.12	0	0	0
T12	-4867.98	3.60 (344)	-4878.32	3.23 (384)	1.62E-8	1.99	1.99	1.24	1.01	0.76	0.76	0.23	0	0	0
T13	-4867.96	3.63 (342)	-4878.3	3.24 (382)	8.55E-9	2	1.99	1.28	1.01	0.73	0.70	0.29	0	0	0
T14	-4867.69	4.74 (262)	-4878.22	3.32 (373)	5.51E-8	1.99	1.99	1.04	0.99	0.98	0.73	0.28	0	0	0
T15	-4867.53	4.06 (305)	-4877.96	3.59 (345)	6.08E-9	2	2	1.02	0.99	0.98	0.98	0.03	0	0	0
Q3	-4866.85	4.74 (261)	-4877.06	4.48 (277)	-	1.99	1.93	1.01	1.00	1.00	1.00	0.08	0	0	0
T16	-4866.84	4.75 (261.6)	-4877.67	3.87 (320)	1.68E-7	1.99	1.99	1.17	1.93	0.84	0.70	0.38	0	0	0
T17	-4866.77	4.82 (257)	-4877.53	4.02 (308)	9.40E-8	1.99	1.99	1.17	0.98	0.83	0.78	0.27	0	0	0
T18	-4866.66	4.93 (252)	-4876.94	4.61 (269)	9.96E-9	1.99	1.99	1.34	0.87	0.85	0.68	0.27	0	0	0
Q4	-4866.57	5.02 (247)	4877.04	4.5 (276)	-	1.99	1.93	1.01	1.00	1.00	1.00	0.07	0	0	0
T19	-	-	-4876.89	4.66 (266)	1.64E-9	1.99	1.99	1.35	0.92	0.86	0.68	0.20	0	0	0
T20	-	-	-4876.81	4.73 (262)	3.64E-10	2	1.99	1.47	0.96	0.86	0.52	0.20	0	0	0
T21	-	-	-4876.52	5.03 (247)	6.46E-9	1.99	1.99	1.33	0.97	0.90	0.67	0.15	0	0	0
T22	-	-	-4875.78	5.76 (215)	1.71E-9	1.99	1.96	1.60	1.01	0.99	0.39	0.05	0	0	0

Table S6a. Electronic and geometric structure of $OsCl_5^-$ (Planar, Fig. 2Sa) as a result of calculations (GAMESS-US package). Multiplicity M; bond lengths ROsCl(1), ROsCl(2); bond angles ∠Cl(1)OsCl, ∠Cl(3)OsCl(4), ∠Cl(4)OsCl(5), ∠Cl(5)OsCl(3); atom charges q_{Os}, $q_{Cl(1)}$, $q_{Cl(2)}$, $q_{Cl(3)}$, $q_{Cl(4)}$, $q_{Cl(5)}$; total energy E_0.

Planar structure										
	Methods	M	ROsCl(1), Å	ROsCl(3), Å	∠Cl(1)OsCl	∠Cl(3)OsCl(4) ∠Cl(4)OsCl(5) ∠Cl(5)OsCl(3)	q_{Os}	$q_{cl(1)}$ $q_{cl(2)}$	$q_{cl(3)}$ $q_{cl(4)}$ $q_{cl(5)}$	E_0, Hartree
Gas										
1	UHF/IMCP-SR1	3	2.379	2.340 2.417 2.340	90 89.831 89.831	120	0.870	-0.402	-0.316 -0.316 -0.434	-140.0751
2	RHF/IMCP-SR1	1	2.431	2.248	90	120	0.801	-0.486	-0.276	-140.04997
3	ROHF/IMCP-SR1	3	2.385	2.307 2.307 2.395	90.309 89.691 90.000	120	0.866	-0.416	-0.307 -0.308 -0.419	-140.0665
4	ROHF/IMCP-SR1	5	2.342	2.434	90	120	-0.568	-0.032	-0.121 -0.121 -0.126	-140.1072
5	CASSCF(6,6)/IMCP-SR1	1	2.429	2.249	90	120	0.776	-0.461	-0.285	-140.0655
6	CASSCF(6,6)/IMCP-SR1	3	2.397	2.339 2.339 2.291	89.453 93.258 89.449	99.775 99.802 160.423	0.851	-0.271	-0.385 -0.405	-140.0965
7	CASSCF(6,6)/IMCP-SR1	5								
Water										
8	UHF/IMCP-SR1/PCM (water)	3	2.386 2.377	2.328 2.428 2.328	89.681 89.681 90.000	120	0.855	-0.423 -0.416	-0.281 -0.281 -0.454	-140.1461
9	RHF/ IMCP-SR1/PCM (water)	1	2.436	2.242	90.094 90.031 89.874	120.192 120.192 119.615	0.797	-0.514	-0.258 -0.255 -0.255	-140.1250
10	ROHF IMCP-SR1/PCM (water)	3	2.383 2.387	2.396 2.299 2.299	90.292 90.006 90	120	0.856	-0.427	-0.288 -0.287 -0.424	-140.1377

11	ROHF/ IMCP-SR1/PCM (water)	5	2.342 2.333	2.435 2.430 2.430	90	120	0.973	-0.341 -0.335	-0.435 -0.431	-140.1766
12	CASSCF(8,10)/ IMCP-SR1/PCM (water)	1	-	-	-	-	-	-	-	-
13	CASSCF(8,10)/ IMCP-SR1/PCM (water)	3	2.397	2.351 2.315 2.303	88.773 90.226 90.743	122.840 103.567 133.594	0.851	-0.427 -0.427	-0.311 -0.373 -0.313	-140.1553
14	CASSCF(8,10)/ IMCP-SR1/PCM (water)	5								

Table S6b. Electronic and geometric structure of $OsCl_5^-$ (Axial, Fig. 2Sb) as a result of calculations (GAMESS-US package). Multiplicity M; bond lengths ROsCl(1), ROsCl(2); bond angles ∠Cl(1)OsCl, ∠Cl(3)OsCl(4), ∠Cl(4)OsCl(5), ∠Cl(5)OsCl(3); atom charges q_{Os}, $q_{Cl(1)}$, $q_{Cl(2)}$, $q_{Cl(3)}$, $q_{Cl(4)}$, $q_{Cl(5)}$; total energy E_0.

Axial structure													
	Methods	M	ROsCl(1), Å	ROsCl(2), Å	ROsCl(3), Å	∠Cl(1)OsCl	∠Cl(2)OsCl(3)	∠Cl(2)OsCl(3')	q_{Os}	$q_{cl(1)}$	$q_{cl(2)}$	$q_{cl(3)}$	E_0, Hartree
Gas													
1	UHF/IMCP-SR1	3	5.306	2.418	2.372	89.526 89.776 90.380 89.776	90.001	89.998	0.000	0.901	-0.456	-0.456	-140.1022
2	RHF/IMCP-SR1	1	2.333	2.346	2.346	93.712	89.760	120	0.827	-0.312	-0.379	-0.379	-140.0302
3	ROHF/IMCP-SR1	3	2.289	2.393	2.338	95.804 99.872	89.481	89.47	0.872	-0.260	-0.429	-0.377	-140.0848
4	ROHF/IMCP-SR1	5	2.502	2.366	2.368	98.938 99.718	88.497	88.497	0.998	-0.501	-0.373	-0.375	-140.1094
5	CASSCF((6,6)/)/IMCP-SR1	1	2.333	2.346	2.346	93.746 93.693	89.767	89.77	0.827	-0.312	-0.379	-0.379	-140.0303
6	CASSCF(6,6))/IMCP-SR1	3	2.289	2.393	2.338	99.981 93.005 99.937 93.000	89.473 89.491	89.481 89.473	0.872	-0.260	-0.429	-0.377	-140.0848
7	CASSCF(6,6)/IMCP-SR1	5	2.502	2.366	2.368	99.499 99.173	88.490	88.499	0.988	-0.501	-0.374	-0.375	-140.1094
Water													
8	UHF/IMCP-SR1/PCM (water)	3	2.369	2.399 2.368	2.419	90.161 92.193 90.161 88.850	90.552	89.445	1.017	-0.212	-0.478	-0.416 -0.432	-140.1822
9	RHF/IMCP-SR1/PCM (water)	1	2.358	2.365	2.370	89.478 91.527 89.885 89.887	88.825 91.180	91.181 88.819	0.976	-0.376	-0.401	-0.398	-140.1184
10	ROHF/IMCP-SR1/PCM (water)	3	2.295	2.392	2.345	92.337 100.822 94.482 100.211	89.466 88.653	89.334 90.080	0.956	-0.281	-0.383 -0.390	-0.445 -0.456	-140.1670

11	ROHF/IMCP-SR1/PCM (water)	5	2.541	2.363 2.359	2.379 2.377	96.626 100.435 95.018 101.677	88.744 88.673	89.190 88.934	1.090	-0.561	-0.390	-0.376	-140.1893
12	CASSCF(6,6))/IMCP-SR1/PCM (water)	3	2.299	2.354 2.345	2.409 2.393	100.232 92.346 100.898 94.543	89.298 90.086	89.432 88.661	0.964	-0.289	-0.390	-0.446 -0.457	-140.1707
13	CASSCF(6,6)/ IMCP-SR1/PCM (water)	5	2.542	2.377 2.379	2.363 2.360	100.416 95.170 101.666 96.526	89.174 88.951	88.726 88.676	1.096	-0.269	-0.374	-0.389	-140.1893

Table S7. Electronic and geometric structure of $OsCl_5^-$ (Axial, Fig. S2b) as a result of FireFly calculations. Multiplicity M; bond lengths ROsCl(1), ROsCl(2), ROsCl(3); bond angles ∠Cl(1)OsCl, ∠Cl(2)OsCl(3), ∠Cl(4)OsCl(3), ∠Cl(2)OsCl(3'); atom charges q_{Os}, $q_{Cl(1)}$, $q_{Cl(2)}$, $q_{Cl(3)}$,; total energy E_0.

	Methods	M	ROsCl(1), Å	ROsCl(2), Å	ROsCl(3), Å	∠Cl(1)OsCl	∠Cl(2)OsCl(3)	∠Cl(2)OsCl(3')	q_{Os}	$q_{cl(1)}$	$q_{cl(2)}$	$q_{cl(3)}$	E_0, Hartree
gas													
1	ROHF/IMCP-SR1	3	2.301	2.399	2.399	99.071 99.081 99.072 99.082	88.568 88.571	88.583 88.574	-0.133	-0.018	-0.212	-0.212	-164.0361
2	ROHF/IMCP-SR1	5	2.505	2.400	2.400	99.544 99.309 99.649 99.430	88.449 88.449	88.430 88.452	0.061	-0.343	-0.179	-0.180	-164.0725
3	CASSCF(10,8)/IMCP-SR1	3	2.394	2.414	2.414	94.867 94.854 94.856 94.841	89.817 89.817	89.371 89.354	-0.071	-0.014	-0.229	-0.228	-164.1052
4	CASSCF(10,8) /IMCP-SR1	5	2.509	2.410	2.414	98.355 101.040 98.397 101.003	88.408 88.411	88.416 88.382	0.097	-0.357	-0.177	-0.193	-164.1040
water													
5	ROHF/IMCP-SR1	3	2.320	2.393	2.393	91.485 92.676 91.266 91.317	89.576 90.271	90.361 89.599	0.066	-0.021	-0.262	-0.258 -0.263	-164.1325
6	ROHF/IMCP-SR1	5	2.596	2.390	2.393	94.548 92.602 93.423 92.670	88.991 90.710	90.698 88.870	0.300	-0.473	-0.204	-0.206 -0.212	-164.1628
7	CASSCF(10,8)/IMCP-SR1	3	2.397	2.425 2.420	2.390 2.392	89.627 89.958 90.317 91.620	89.931 90.090	90.129 89.852	0.093	-0.034	-0.301 -0.290	-0.235 -0.233	-164.1988
8	CASSCF(10,8)/IMCP-SR1	5	2.624	2.392	2.396	90.390 90.443 91.323 91.671	90.186 89.830	89.664 90.276	0.334	-0.506	-0.201 -0.203	-0.210 -0.213	-164.1937

Table S8. Energies and orbiltal populations of $Os^{IV}Cl_5^-$ (M = 3) 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
T1	-4465.532	0	-4472.92	0		1.97	1.96	1.92	1.00	1.00	0.1	0.04	0.01	0	0
T2	-4465.394	0.13 (895)	-4472.91	0,01 (104)	6.07E-11	1.97	1.96	1.92	1.00	1.00	0.08	0.04	0.01	0	0
T3	-4465.186	0.34 (358)	-4472.69	0,22 (539)	1.30E-5	1.97	1.96	1.92	1.00	1.00	0.09	0.04	0.01	0	0
Q1	-4464.033	1.49 (827)	-4471.99	0,92 (134)	1.1E-3	1.99	1.96	1.01	1.00	1.00	1.00	0.04	0	0	0
Q2	-4463.398	2.13 (580)	-4471.33	1,58 (780)	6.64E-5	1.98	1.96	1.60	1.00	0.99	0.41	0.05	0.01	0	0
T4	-4462.87	2.66 (465)	-4471.31	1,60 (770)	2.13E-7	1.99	1.96	1.54	1.0	0.99	0.46	0.05	0.01	0	0
T5	-4461.999	3.53 (350)	-4471.31	1,61 (768)	8.13E-4	1.98	1.96	1.01	1.00	0.99	0.98	0.07	0	0	0
T6	-4461.96	3.57 (347)	-4471.27	1,65 (750)	8.31E-4	1.98	1.96	1.00	1.00	1.00	0.99	0.05	0	0	0
T7	-4461.856	3.67 (337)	-4471.26	1,66 (746)	3.46E-4	1.99	1.96	1.01	1.00	0.99	0.99	0.05	0	0	0
T8	-4461.851	3.68 (336)	-4470.63	2,29 (541)	2.40E-4	1.96	1.88	1.44	1.12	0.99	0.50	0.09	0.01	0	0
T9	-4461.826	3.70 (334)	-4470.58	2,33 (530)	1.14E-3	1.96	1.01	1.00	0.99	0.93	0.13	0	0	0	0
T10	-4461.566	3.96 (312)	-4470.48	2,44 (508)	2.72E-8	1.96	1.96	1.35	1.14	1.00	0.47	0.10	0.47	0.1	0
T11	-4461.506	4.02 (308)	-4470.08	2,83 (436)	4.35E-6	1.96	1.93	1.75	0.95	0.92	0.34	0.14	0	0	0
T12	-4461.48	4.05 (306)	-4470.02	2,90 (427)	8.39E-3	1.96	1.92	1.69	0.96	0.93	0.39	0.14	0	0	0
T13	-4461.422	4.10 (301)	-4469.94	2,98 (416)	1.43E-3	1.99	1.91	1.00	1.00	1.00	1.00	0.10	0	0	0
Q3	-4461.378	4.15 (298)	-4469.55	3,37 (367)	2.27E-6	1.99	1.89	1.77	1.03	0.96	0.23	0.12	0.01	0	0
Q4	-4461.255	4.27 (289)	-4469.54	3,37 (367)	1.02E-7	1.99	1.91	1.78	1.02	0.97	0.19	0.12	0.01	0	0
Q5	-4461.147	4.38 (282)	-4469.31	3,60 (343)	1.27E-3	1.99	1.91	1.00	1.00	0.99	0.98	0.11	0	0	0
T14	-4461.124	4.40 (281)	-4469.29	3,62 (341)	7.92E-4	1.98	1.91	1.01	1.00	1.00	0.98	0.10	0	0	0
T15	-4460.967	4.56 (271)	-4469.21	3,70 (334)	2.59E-3	1.98	1.89	1.01	1.01	0.96	0.93	0.21	0	0	0
T16	-4460.956	4.57 (270)	-4469.13	3,79 (327)	9.94E-3	1.96	1.86	1.64	1.05	1.00	0.41	0.06	0.01	0	0
T17	-4460.885	4.64 (266)	-4468.65	4,26 (290)	4.86E-3	1.98	1.94	1.94	1.02	1.01	0.05	0.05	0.01	0.01	0

Table S9. Energies and orbiltal populations of $Os^{IV}Cl_5^-$ (M = 5) as a result of SBKJC gas phase calculations (FireFly package). Quintet and septet states are marked as Q and Sp correspondingly.

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
Q1	-4465.5	0	-4475.03	0		1.96	1.95	1.03	1.01	1.00	0.99	0.06	0.01	0	0
Q2	-4461.89	3.60 (343)	-4472.49	2.54 (487)	5.02E-5	1.96	1.85	1.09	1.00	1.00	0.92	0.17	0.01	0	0
Q3	-4461.813	3.68 (336)	-4472.16	2.86 (432)	3.87E-4	1.93	1.81	1.16	1.01	0.99	0.85	0.25	0	0	0
Q4	-4460.853	4.64 (266)	-4471.03	4.00 (309)	1.73E-8	1.98	1.78	1.01	1.00	1.00	1.00	0.23	0	0	0
Q5	-4460.72	4.77 (259)	-4470.23	4.80 (257)	2.90E-3	1.97	1.96	1.01	1.01	1.00	0.98	0.07	0	0	0
Q6	-4459.826	5.67 (218)	-4470.18	4.85 (255)	3.37E-3	1.97	1.96	1.01	1.01	1.00	0.97	0.07	0	0	0
Q7	-4459.771	5.72 (216)	-4469.01	6.02 (205)	5.69E-4	1.98	1.96	1.02	1.00	1.00	0.98	0.05	0.01	0	0
Q8	-4459.495	6.00 (206)	-4468.87	6.16 (201)	1.77E-3	1.67	1.64	1.34	1.27	1.00	1.00	0.07	0.01	0	0
Sp1	-4459.461	6.03 (205)	-4468.68	6.35 (195)	4.08E-6	1.99	1.98	1.00	1.00	1.00	1.00	0.02	0.01	0	0
Sp2	-4459.455	6.04 (205)	-4468.58	6.45 (192)	9.44E-4	1.65	1.62	1.34	1.32	1.01	1.00	0.05	0.01	0	0
Q9	-4459.13	6.36 (194)	-4468.55	6.47 (191)	1.50E-3	1.98	1.92	1.03	1.01	1.00	0.99	0.06	0.01	0	0
Q10	-4459.003	6.49 (190)	-4468.15	6.88 (180)	1.97E-7	1.98	1.94	1.00	1.00	1.00	1.00	0.08	0	0	0
Q11	-4458.674	6.82 (181)	-4467.63	7.40 (167)	3.07E-3	1.98	1.91	1.01	1.01	1.00	1.00	0.08	0	0	0
Q12	-4458.472	7.02 (176)	-4467.30	7.73 (160)	7.17E-5	1.87	1.80	1.13	1.13	1.00	0.98	0.08	0.01	0	0
Q13	-4458.078	7.42 (167)	-4467.28	7.75 (159)	7.78E-6	1.94	1.31	1.05	1.00	1.00	1.00	0.69	0	0	0
Q14	-4458.014	7.48 (165)	-4467.12	7.91 (156)	4.00E-5	1.73	1.69	1.27	1.25	1.00	0.98	0.08	0	0	0
Q15	-4457.484	8.01 (154)	-4467.06	7.97 (155)	1.31E-5	1.73	1.68	1.26	1.25	1.00	0.99	0.07	0	0	0
Q16	-4457.427	8.07 (153)	-4466.99	8.04 (154)	4.60E-7	1.99	1.05	1.00	1.00	1.00	1.00	0.95	0	0	0
Q17	-4457.425	8.07 (153)	-4466.98	8.05 (153)	3.51E-4	1.87	1.82	1.13	1.13	1.00	0.99	0.06	0	0	0
Q18	-4457.177	8.32 (148)	-4466.76	8.27 (149)	3.43E-5	1.99	1.06	1.04	1.01	1.00	0.99	0.90	0	0	0
Q19	-4457.145	8.35 (148)	-4466.51	8.52 (145)	1.28E-6	2.00	1.84	1.00	1.00	1.00	0.99	0.16	0	0	0
Q20	-4457.132	8.36 (148)	-4462.39	12.6 (98)	3.97E-4	1.84	1.62	1.08	1.04	1.02	0.98	0.42	0	0	0

Table S10. Energies and orbiltal populations of $Os^{IV}Cl_5^-$ (M = 3) 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-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
T1	-4468.079	0	-4475.26	0	0	1.97	1.96	1.92	1.00	1.00	0.09	0.04	0.01	0	0
T2	-4465.644	2.43 (509)	-4475.08	0.18 (678)	2.01E-6	1.97	1.96	1.93	1.00	1.00	0.07	0.04	0.01	0	0
T3	-4465.603	2.47 (500)	-4474.94	0.31 (388)	1.29E-5	1.97	1.96	1.93	1.00	1.00	0.09	0.04	0.01	0	0
Q1	-4464.126	3.95 (313)	-4473.57	1.68 (734)	1.36E-3	1.98	1.96	1.02	1.00	1.00	0.97	0.05	0	0	0
T4	-4464.087	3.99 (310)	-4473.11	2.14 (577)	1.12E-4	1.96	1.95	1.38	1.03	0.97	0.65	0.05	0.01	0	0
Q2	-4463.996	4.08 (303)	-4473.04	2.21 (559)	1.13E-3	1.98	1.95	1.24	1.02	0.99	0.76	0.06	0	0	0
T5	-4463.979	4.10 (302)	-4473	2.26 (548)	3.12E-5	1.99	1.96	1.44	1.00	0.99	0.55	0.05	0.01	0	0
T6	-4463.65	4.42 (279)	-4472.97	2.28 (541)	2.11E-4	1.98	1.96	1.03	1.00	0.98	0.97	0.06	0	0	0
T7	-4463.4	4.67 (264)	-4472.96	2.30 (538)	1.19E-3	1.98	1.96	1.02	1.00	0.99	0.97	0.06	0	0	0
Q3	-4463.394	4.68 (264)	-4472.36	2.89 (427)	3.02E-2	1.96	1.82	1.29	1.03	0.95	0.79	0.14	0.01	0	0
T8	-4462.978	5.10 (243)	-4472.31	2.94 (420)	1.62E-3	1.96	1.94	1.46	1.00	0.93	0.58	1.12	0.01	0	0
T9	-4462.834	5.24 (236)	-4472.22	3.03 (408)	1.31E-5	1.97	1.94	1.47	0.98	0.87	0.55	0.21	0.01	0	0
T10	-4462.695	5.38 (230)	-4472.16	3.09 (400)	3.38E-5	1.99	1.92	1.00	1.00	0.99	0.98	0.11	0	0	0
T11	-4462.536	5.54 (223)	-4472.08	3.18 (389)	9.61E-5	1.98	1.88	1.78	1.01	0.89	0.30	0.14	0.01	0	0
T12	-4462.297	5.78 (214)	-4471.85	3.40 (364)	1.51E-4	1.94	1.92	1.90	0.96	0.95	0.18	0.14	0.01	0	0
T13	-4462.232	5.84 (212)	-4471.68	3.57 (346)	1.08E-5	1.98	1.92	1.73	1.01	0.9	0.26	0.19	0.01	0	0
T14	-4462.124	5.95 (208)	-4471.53	3.73 (332)	2.72E-5	1.99	1.92	1.08	1.00	0.98	0.92	0.10	0	0	0
T15	-4462.038	6.04 (205)	-4471.5	3.76 (329)	3.61E-5	1.99	1.92	1.03	1.00	0.99	0.97	0.10	0	0	0
T16	-4461.979	6.10 (203)	-4470.91	4.35 (284)	4.59E-3	1.98	1.81	1.50	1.02	0.96	0.54	0.17	0.01	0	0
T17	-4461.912	6.16 (201)	-4470.88	4.37 (283)	3.58E-3	1.98	1.66	1.64	1.17	1.13	0.25	0.16	0.01	0	0
T18	-4461.741	6.33 (195)	-4470.64	4.62 (268)	2.03E-3	1.97	1.80	1.35	1.29	1.01	0.39	0.18	0.01	0	0
T19	-4461.675	6.40 (193)	-4470.01	5.24 (236)	2.90E-3	1.97	1.67	1.46	1.25	1.16	0.34	0.13	0.01	0	0

Table S11. The total energies of the free ion Os^{4+}, E_{tot} and multiplicity, M using the GAMESS and FireFly packages (ROHF/IMCP-SR1) in gas phase.

	Gamess-US	FireFly
M	E_{tot}, Hartree	E_{tot}, Hartree
1	-62.0182308154	-86.9546637532
3	-62.0705485195	-87.0079831896
5	-62.1745721143	-87.1146248235
7	-60.5680946266	-85.5225780401

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

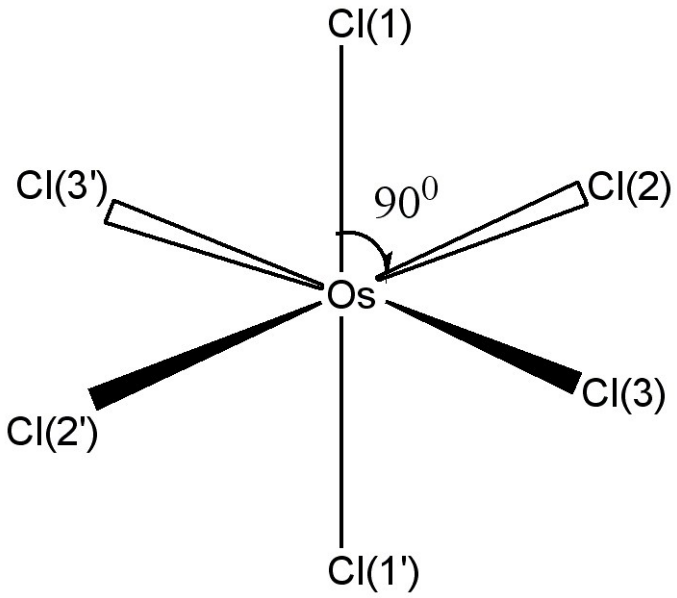


Figure S2. Active orbitals, which symmetry and populations are given in Tables S2.

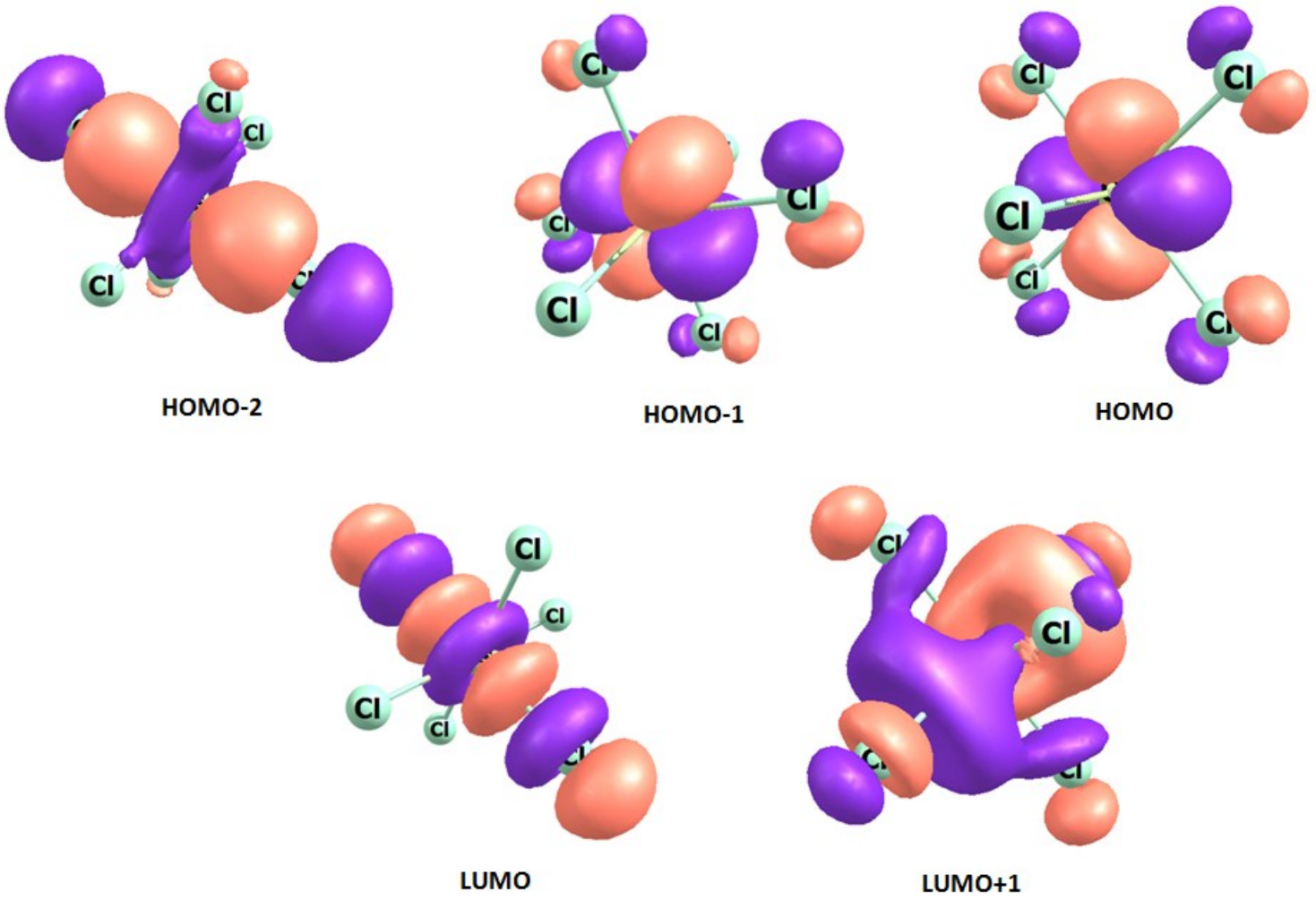


Figure S3a. Scheme of $Os^{IV}Cl_5^-$ (Planar) structure.

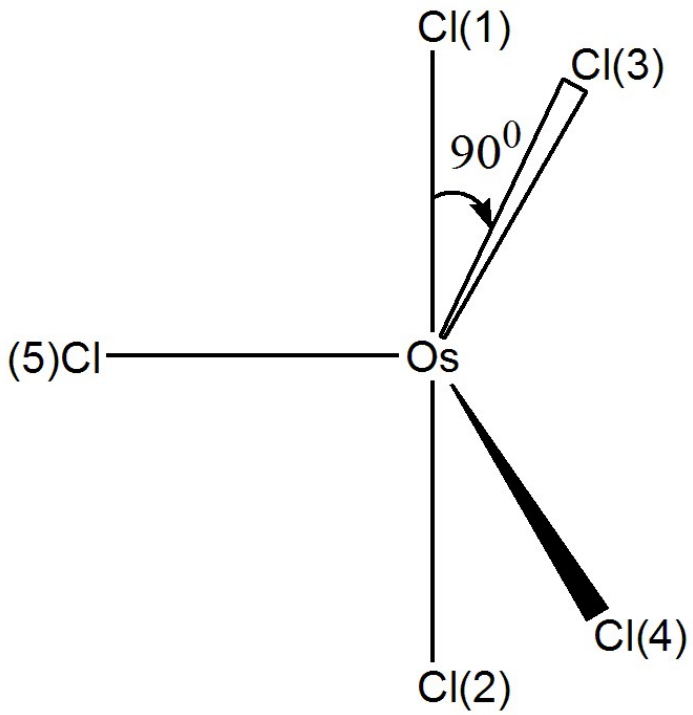
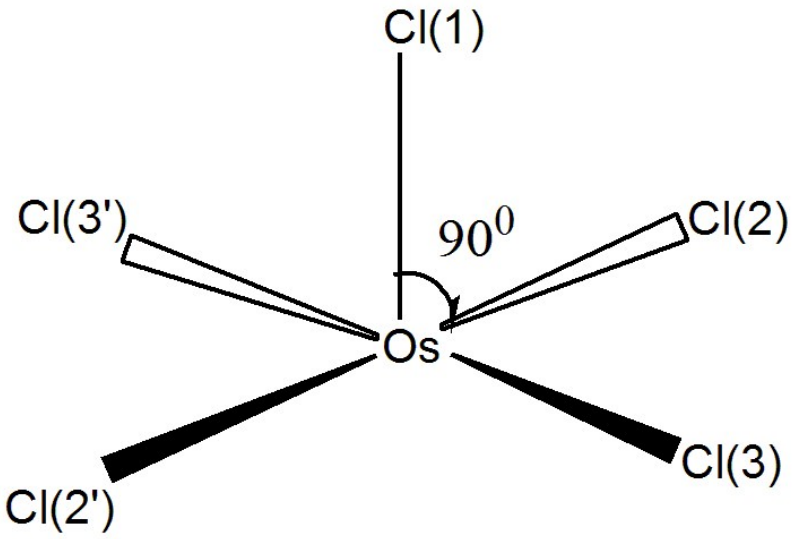


Figure S3b. Scheme of $Os^{IV}Cl_5^-$ (Axial) structure.



Species Associated Differential Spectra (SADS)

The kinetic curves obtained in the experiments on the ultrafast pump-probe spectroscopy were globally fitted using a triexponential function (S1) (biexponential fit did not give a satisfactory description).

$$\Delta A(\lambda,t) = A_1(\lambda)e^{-k_1 t} + A_2(\lambda)e^{-k_2 t} + A_3(\lambda)e^{-k_3 t} \qquad \text{(S1)}$$

When the kinetic curves are fitted using the triexponential function (S1), the sequential decay of the transient absorption $A \rightarrow B \rightarrow C \rightarrow$ (ground state + products) is proposed. The species associated difference spectra (SADS) of the individual components were calculated by means of the formulae (S2-S4) derived in [36].

$$S_A(\lambda) = A_1(\lambda) + A_2(\lambda) + A_3(\lambda) \qquad \text{(S2)}$$

$$S_B(\lambda) = A_2(\lambda)\frac{k_1 - k_2}{k_1} + A_3(\lambda)\frac{k_1 - k_3}{k_1} \qquad \text{(S3)}$$

$$S_C(\lambda) = A_3(\lambda)\frac{(k_1 - k_3)(k_2 - k_3)}{k_1 k_2} \qquad \text{(S4)}$$