Effects of a strong π-accepting ancillary ligand on the water oxidation activity of weakly coupled binuclear ruthenium catalysts

Tiago A. Matias*,[a] Francisca N. Rein,[b] Reginaldo C. Rocha,[b] André Luiz Barboza Formiga,[c] Henrique E. Toma,[a] Koiti Araki*[a]

[a] Department of Chemistry, Institute of Chemistry, University of São Paulo, Av. Lineu Prestes 748, São Paulo, SP 05508-000, Brazil.

[b] Los Alamos National Laboratory, Los Alamos, New Mexico, NM 87545, USA.

[c] Institute of Chemistry, University of Campinas – UNICAMP, P.O. Box 6154, Campinas, SP 13083-970, Brazil.

E-mail: tiagomatias@usp.br; koiaraki@iq.usp.br

Electronic supplementary information (ESI)

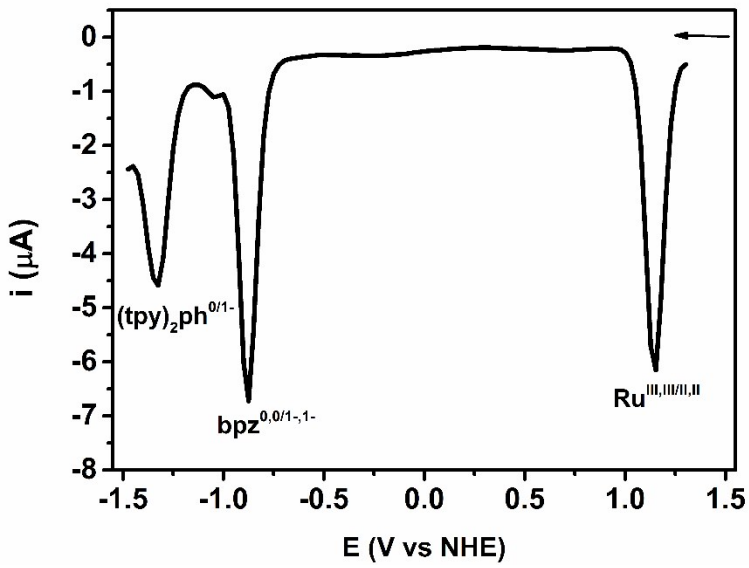
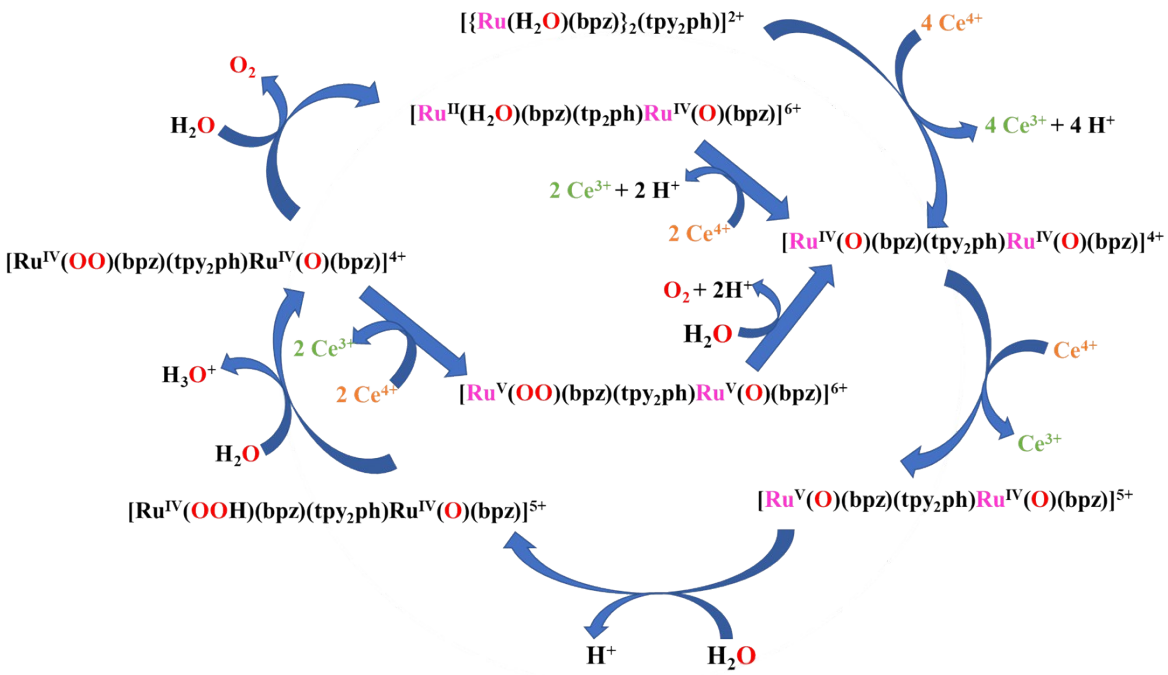


Figure S1: Differential pulse voltammogram of a 1.0 mM solution of $[\{RuCl(bpz)\}_2(tpy_2ph)](PF_6)_2$ in DMF (0.10 M Bu_4NClO_4; ν = 10 mV s^{-1}).



Scheme S1: Proposed catalytic mechanism for $[\{Ru(H_2O)(bpz)\}_2(tpy_2ph)]^{4+}$.

Table S1. Cartesian coordinates for the complex $[\{Ru^{V}(O)(bpy)\}_2(tpy_2ph))]^{6+}$ obtained by BP86/SDD.

	x	y	z
Ru	6.684818	0.123225	-2.477071
O	6.400569	1.506975	-3.564251
Ru	-6.687368	0.131895	-2.492099
O	-6.411830	1.502426	-3.597756
C	6.672127	-2.195574	-0.372390
N	7.354352	-1.591573	-1.355122
C	8.576694	-2.041729	-1.730648
C	9.149510	-3.151360	-1.093579
C	8.444447	-3.789589	-0.066360
C	7.185226	-3.306092	0.302262
N	8.532440	-0.243837	-3.331687
C	9.033380	0.507296	-4.334866
C	10.281248	0.235161	-4.884404
C	11.019761	-0.844946	-4.376257
H	8.417310	1.337788	-4.696098
H	10.664435	0.859470	-5.696491
H	11.056851	-2.461363	-2.936862
H	10.134898	-3.517874	-1.392344
H	6.600514	-3.774257	1.099064
H	5.689062	-1.799211	-0.099762
C	10.489134	-1.617907	-3.337678
C	9.228846	-1.301554	-2.818281
N	7.166797	1.399944	-0.881471
C	8.381081	1.941141	-0.729687
C	8.652072	2.800012	0.338777
C	7.629494	3.093283	1.247624
C	6.362801	2.527660	1.065097
C	6.147326	1.677679	-0.024921
C	4.869173	1.044658	-0.359774
N	4.912145	0.285806	-1.474124
C	3.835934	-0.372500	-1.953985
C	2.612708	-0.272394	-1.288061
C	2.504934	0.508231	-0.113932
C	3.668469	1.169891	0.343422
C	4.110326	-1.150020	-3.165416
N	5.392212	-1.080957	-3.614129
C	5.783622	-1.710071	-4.728292
C	4.884528	-2.487322	-5.463344
C	3.561133	-2.590794	-5.021097
C	3.167959	-1.915367	-3.860485
H	9.163595	1.692813	-1.453364
H	9.655893	3.220940	0.446363
H	7.813200	3.763592	2.093026
H	5.547919	2.752178	1.759024

H	3.632322	1.807972	1.229903
H	1.749999	-0.822562	-1.671963
H	2.136125	-1.977362	-3.503487
H	2.834920	-3.190975	-5.577982
H	5.232199	-3.000691	-6.364440
H	6.824633	-1.612142	-5.051719
C	1.224918	0.636375	0.608993
C	-1.220100	0.919007	1.989341
H	-2.158898	1.017620	2.543342
C	-0.002686	0.498787	-0.069137
H	0.000884	0.329911	-1.150192
C	-0.010524	1.035651	2.679125
H	-0.013892	1.224683	3.757095
C	1.202924	0.907419	1.998909
H	2.138192	0.996153	2.560450
C	-6.656912	-2.156135	-0.353730
N	-7.343397	-1.571926	-1.345257
C	-8.565000	-2.032927	-1.709580
C	-9.132559	-3.132826	-1.050890
C	-8.423647	-3.749310	-0.013101
C	-7.164980	-3.255372	0.343061
N	-8.534408	-0.258371	-3.337099
C	-9.041558	0.473245	-4.351261
C	-10.286190	0.181178	-4.898045
C	-11.015134	-0.898674	-4.375351
H	-8.432877	1.303750	-4.724765
H	-10.674427	0.789785	-5.719615
H	-11.039474	-2.493094	-2.911644
H	-10.117606	-3.507668	-1.340193
H	-6.577107	-3.706195	1.147508
H	-5.673964	-1.752795	-0.091009
C	-10.479025	-1.650536	-3.324486
C	-9.222328	-1.314571	-2.808294
N	-7.172144	1.420090	-0.907631
C	-8.386231	1.961942	-0.757430
C	-8.657354	2.825446	0.307384
C	-7.635132	3.122287	1.215084
C	-6.368359	2.556279	1.034398
C	-6.152258	1.702427	-0.052441
C	-4.872607	1.069980	-0.384905
N	-4.913723	0.308684	-1.497621
C	-3.837416	-0.352114	-1.974121
C	-2.615605	-0.252014	-1.305968
C	-2.509555	0.529215	-0.131551
C	-3.672771	1.195851	0.320124
C	-4.112441	-1.138155	-3.180951
N	-5.396035	-1.079451	-3.626167

C	-5.786982	-1.719429	-4.734184
C	-4.886439	-2.497238	-5.466553
C	-3.561038	-2.590163	-5.027806
C	-3.167988	-1.903568	-3.873870
H	-9.169285	1.710382	-1.479400
H	-9.661140	3.246626	0.413518
H	-7.819224	3.794934	2.058381
H	-5.554202	2.783501	1.728163
H	-3.636905	1.834574	1.206381
H	-1.752453	-0.805601	-1.683964
H	-2.134797	-1.957485	-3.519795
H	-2.833032	-3.190533	-5.582147
H	-5.233868	-3.018836	-6.363005
H	-6.829437	-1.627438	-5.055049
C	-1.233687	0.648118	0.599343
H	-11.997209	-1.155007	-4.784578
H	-8.855041	-4.608180	0.510072
H	12.005098	-1.085523	-4.787301
H	8.879093	-4.657361	0.439167

Table S2. Cartesian coordinates for the complex $[\{Ru^{V}(O)(bpz)\}_2(tpy_2ph)]^{6+}$ obtained by BP86/SDD.

	x	y	z
Ru	6.621207	0.137155	-2.490948
O	6.198678	1.479289	-3.565830
Ru	-6.609878	0.076499	-2.525372
O	-6.166600	1.335154	-3.689094
C	6.897851	-2.273915	-0.461874
N	7.485440	-1.561485	-1.423212
C	8.753317	-1.839068	-1.802535
C	9.447025	-2.881360	-1.150418
N	8.837160	-3.585929	-0.220368
C	7.597405	-3.326974	0.154005
N	8.534639	-0.023968	-3.355892
C	8.974623	0.764744	-4.344304
C	10.260531	0.563365	-4.869007
N	11.028965	-0.390318	-4.368429
H	8.320238	1.561326	-4.714509
H	10.633734	1.207240	-5.676577
H	11.262153	-1.998577	-3.056507
H	10.493170	-3.108613	-1.400230
H	7.109956	-3.942420	0.921985
H	5.867325	-2.050229	-0.167325
C	10.603020	-1.197256	-3.419408
C	9.315843	-1.019838	-2.868247
N	7.112553	1.415454	-0.890780

C	8.292476	2.025615	-0.732485
C	8.527709	2.876192	0.351400
C	7.502775	3.088462	1.279353
C	6.269860	2.452714	1.096371
C	6.090781	1.616499	-0.011220
C	4.839419	0.919773	-0.331379
N	4.897211	0.167971	-1.448449
C	3.851491	-0.544314	-1.923700
C	2.632615	-0.502276	-1.243503
C	2.504892	0.274013	-0.068158
C	3.641494	0.983243	0.386982
C	4.154447	-1.314362	-3.137142
N	5.428263	-1.191746	-3.602871
C	5.834300	-1.829291	-4.705396
C	4.964929	-2.660328	-5.418198
C	3.651539	-2.812865	-4.961312
C	3.240363	-2.133851	-3.808631
H	9.080183	1.842351	-1.469099
H	9.505916	3.353973	0.456956
H	7.657797	3.747180	2.139388
H	5.453673	2.610619	1.806775
H	3.582929	1.612494	1.278491
H	1.790100	-1.091278	-1.614640
H	2.216552	-2.238493	-3.438900
H	2.947513	-3.455917	-5.498444
H	5.325390	-3.175340	-6.313234
H	6.867598	-1.690651	-5.039777
C	1.223643	0.367005	0.656354
C	-1.219845	0.638992	2.041432
H	-2.162331	0.739315	2.589111
C	-0.000851	0.225442	-0.024716
H	0.002138	0.061764	-1.106748
C	-0.013082	0.744964	2.736324
H	-0.017761	0.924094	3.815818
C	1.199505	0.625925	2.054566
H	2.135726	0.715154	2.614567
C	-6.929957	-2.169043	-0.319966
N	-7.503088	-1.523751	-1.335983
C	-8.775466	-1.807267	-1.695536
C	-9.487696	-2.784535	-0.967388
N	-8.892497	-3.424149	0.017558
C	-7.649616	-3.156962	0.375434
N	-8.524226	-0.118919	-3.381396
C	-8.948061	0.597744	-4.429904
C	-10.234771	0.375781	-4.944202
N	-11.020326	-0.523396	-4.374159
H	-8.279817	1.353308	-4.856959

H	-10.595067	0.960159	-5.801377
H	-11.285331	-2.020160	-2.942278
H	-10.536364	-3.014319	-1.203572
H	-7.174794	-3.717415	1.191883
H	-5.895654	-1.942206	-0.041353
C	-10.611129	-1.260784	-3.363131
C	-9.322495	-1.062515	-2.822342
N	-7.078611	1.470836	-1.018435
C	-8.242263	2.122385	-0.913586
C	-8.464926	3.045033	0.112439
C	-7.444225	3.286429	1.038050
C	-6.227014	2.608590	0.908919
C	-6.059296	1.701333	-0.143154
C	-4.821685	0.958943	-0.409916
N	-4.887557	0.144726	-1.482035
C	-3.854622	-0.616351	-1.906683
C	-2.638404	-0.557134	-1.222748
C	-2.505211	0.278973	-0.090444
C	-3.628737	1.036400	0.315918
C	-4.168296	-1.455976	-3.070077
N	-5.439355	-1.342237	-3.545390
C	-5.853808	-2.039695	-4.607637
C	-4.997090	-2.927333	-5.265426
C	-3.687547	-3.073729	-4.795687
C	-3.267121	-2.331457	-3.686189
H	-9.026781	1.914368	-1.647223
H	-9.430449	3.554978	0.176304
H	-7.590322	4.000648	1.854216
H	-5.413229	2.790121	1.616351
H	-3.562877	1.710800	1.173633
H	-1.803847	-1.181140	-1.553051
H	-2.246231	-2.430587	-3.307120
H	-2.993145	-3.760253	-5.289873
H	-5.364665	-3.490294	-6.128124
H	-6.884052	-1.905070	-4.952947
C	-1.229992	0.375502	0.644392

Table S3. Kohn-Sham orbitals obtained by $[\{Ru^{V}(O)(bpy)\}_2(tpy_2ph)]^{6+}$ obtained by BP86/SDD. The frontier orbitals of each set are in boldface.

alpha		**Contribution / %**			**beta**		**Contribution / %**		
#	**E / eV**	**Ru**	**O**	**L**	**#**	**E / eV**	**Ru**	**O**	**L**
170	-0.2905	8.2	5	86.7	170	-0.2874	2.1	0.5	97.3
171	-0.2904	8.1	4.9	87	171	-0.2873	2.2	0.5	97.3
172	-0.2884	3.8	2.4	93.8	172	-0.2806	0.2	1.3	98.5
173	-0.2882	8.7	5.8	85.5	**173**	**-0.2764**	**5.9**	**2.6**	**91.6**
174	-0.2874	29.2	19.3	51.6	**174**	**-0.2745**	**65.6**	**0**	**34.3**
175	-0.286	27.6	17.3	55.1	175	-0.2743	62.8	0.2	37
176	-0.278	52	25	22.9	176	-0.2186	40.3	33.4	26.3
177	-0.2777	52.3	25.2	22.6	177	-0.218	40.4	33	26.6
178	-0.2759	35.9	16.1	48	178	-0.2166	47.4	37.5	15
179	**-0.2719**	**30.4**	**12**	**57.7**	179	-0.2163	47.4	37.5	15.1
180	**-0.1797**	**5**	**0.4**	**94.7**	180	-0.1754	11	2.5	86.4
181	-0.1795	4.5	0.4	95	181	-0.1752	10.8	2.5	86.8
182	-0.1674	4	0.2	95.8	182	-0.1642	1.4	0.1	98.6
183	-0.1673	2.7	0.2	97.1	183	-0.1641	1.3	0.1	98.6
184	-0.1672	38.6	0.4	61	184	-0.1621	5.6	1	93.5
185	-0.1666	38.7	0.4	60.9	185	-0.162	5.7	1	93.3
186	-0.165	1.6	0	98.4	186	-0.1495	39	0.3	60.7
187	-0.1649	2.8	0	97.3	187	-0.1488	39	0.3	60.7
188	-0.1351	1.1	0	98.8	188	-0.1336	1	0.1	98.9
189	-0.1348	0.8	0	99.1	189	-0.1329	1.3	0.1	98.7
190	-0.1346	0.8	0	99.1	190	-0.1328	1.2	0.1	98.7

Table S4. Kohn-Sham orbitals obtained by $[\{Ru^{V}(O)(bpz)\}_2(tpy_2ph)]^{6+}$ obtained by BP86/SDD. The frontier orbitals of each set are in boldface.

alpha		**Contribution / %**			**beta**		**Contribution / %**		
#	**E / eV**	**Ru**	**O**	**L**	**#**	**E / eV**	**Ru**	**O**	**L**
170	-0.2919	1	0.6	98.3	170	-0.2829	5.7	0.4	93.9
171	-0.2919	1	0.6	98.3	171	-0.2806	25.7	0.8	73.6
172	-0.2897	3.6	3.3	93.2	172	-0.2805	23.8	0.5	75.6
173	-0.2889	7.6	7.3	85.1	**173**	**-0.2789**	**5**	**1.7**	**93.3**
174	-0.2873	2.7	2	95.4	**174**	**-0.2777**	**36.3**	**0.3**	**63.3**
175	-0.2869	3	2.4	94.7	175	-0.2773	33.8	0.8	65.4
176	-0.2687	52.2	24.7	23.1	176	-0.2128	40.1	31.6	28.4
177	-0.268	53.8	25.3	20.9	177	-0.2123	40.3	31.2	28.5
178	-0.2672	55.1	26.4	18.5	178	-0.2111	43.3	32	24.7
179	**-0.2665**	**51.7**	**24**	**24.4**	179	-0.211	43.3	31.8	24.9
180	**-0.1909**	**4.4**	**0.4**	**95.1**	180	-0.1865	9.7	4	86.4
181	-0.1909	4.4	0.4	95.2	181	-0.1865	9.7	4	86.4
182	-0.1793	5.6	0.5	94	182	-0.1731	14.3	3.7	82
183	-0.1784	5.9	0.5	93.6	183	-0.1729	14.5	3.8	81.7
184	-0.1647	1.4	0.1	98.5	184	-0.1621	3.1	0.5	96.4
185	-0.1646	1.4	0.1	98.4	185	-0.162	3.2	0.5	96.4
186	-0.1562	8.2	0.2	91.6	186	-0.1536	2.1	0.2	97.8
187	-0.1562	8	0.2	91.8	187	-0.1536	2.1	0.2	97.7
188	-0.154	3.2	0.1	96.7	188	-0.1515	2.6	0.7	96.7
189	-0.154	2.8	0.1	97	189	-0.1515	2.5	0.7	96.8
190	-0.1522	35.3	0.2	64.5	190	-0.1377	36.6	0.2	63.2

Table S5. Mulliken and Löwdin (in parentheses) spin populations on the $Ru^{V}O^{3+}$ fragment for the complexes $[Ru^{V}(O)(L)(tpy_2ph)Ru^{V}(O)(L)]^{6+}$ obtained by BP86/SDD and BP86/B3LYP/SDD.

	L = bpy	**L = bpz**
BP86		
Ru	1.63 (1.57)	1.41 (1.35)
O	0.99 (0.98)	0.97 (0.96)
BP86/B3LYP		
Ru	1.67 (1.67)	1.70 (1.64)
O	1.13 (1.11)	1.14 (1.11)