Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Quantum Chemical Characterization of the Generation of High-Valent Oxoruthenium Species of Keggin Typical Polyoxometalate: Electronic Structure and Bonding Feature

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The POM complex ^{2}**1** has been characterized as energy minima at the B3LYP/6-31g(d) level (LANL2DZ basis sets on the metal atom) using the GAUSSIAN 03 because of its robust and fast frequency calculation routine.

Diagonal vibrational polarizability:

251.3415578 254.4072359 275.3065415

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scatteringactivities (A**4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

		1			2			3		
		A			A			A		
Frequencies --		30.1380			65.4955			67.2312		
Red. masses --		66.7285			60.1798			72.0437		
Frc consts --		0.0357			0.1521			0.1919		
IR Inten --		0.0477			0.0011			0.0055		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	8	-0.01	-0.02	-0.01	0.01	0.02	-0.04	0.00	0.00	0.03
2	15	0.00	-0.01	0.00	0.00	0.01	0.00	-0.01	0.00	-0.02
3	8	0.00	0.01	0.00	0.00	0.05	0.00	0.06	0.00	-0.07
4	8	0.00	0.00	0.00	0.00	-0.06	0.00	-0.08	0.00	-0.07
5	44	0.00	-0.12	0.00	0.00	-0.06	0.00	-0.02	0.00	-0.12
6	8	0.05	-0.06	0.06	0.05	-0.01	-0.06	-0.07	-0.04	-0.09
7	74	0.11	0.07	0.07	-0.02	-0.16	-0.06	-0.15	-0.04	-0.03
8	8	0.06	-0.02	0.03	0.12	-0.05	-0.03	-0.05	0.03	0.07
9	74	-0.03	-0.04	-0.15	-0.04	0.01	0.01	0.03	0.00	0.23
10	8	-0.01	-0.02	0.03	0.06	0.17	-0.07	0.07	-0.05	0.06
11	74	-0.13	-0.09	0.07	0.06	0.14	-0.13	0.13	0.03	-0.02
12	8	0.00	0.04	0.06	0.12	0.09	-0.08	-0.01	0.00	0.01
13	8	0.01	-0.02	0.01	-0.01	0.02	0.04	0.00	0.00	0.03
14	8	0.00	0.01	0.00	0.00	0.17	0.00	0.14	0.00	0.01
15	74	0.13	-0.09	-0.07	-0.07	0.14	0.13	0.14	-0.02	-0.02
16	8	0.01	0.10	-0.03	-0.05	0.10	0.02	0.03	-0.01	-0.10
17	74	0.00	0.19	0.00	0.00	-0.07	0.00	-0.04	0.01	-0.17
18	8	-0.01	0.10	0.03	0.05	0.10	-0.02	0.03	0.01	-0.11
19	8	0.00	0.04	-0.06	-0.12	0.09	0.07	-0.01	0.01	0.01
20	74	-0.10	0.07	-0.07	0.03	-0.16	0.06	-0.14	0.03	-0.03
21	8	-0.05	-0.06	-0.06	-0.04	-0.01	0.06	-0.07	0.05	-0.09
22	8	-0.13	0.09	-0.10	0.01	-0.12	0.08	-0.13	0.02	-0.01
23	8	-0.06	-0.02	-0.03	-0.11	-0.05	0.02	-0.05	-0.03	0.08
24	74	0.03	-0.04	0.14	0.03	0.01	-0.01	0.04	-0.01	0.23
25	8	0.01	-0.03	-0.04	-0.11	0.04	-0.08	0.04	-0.02	0.07
26	74	0.08	0.11	-0.08	0.04	0.19	-0.05	0.16	0.04	-0.04
27	8	0.00	0.01	0.00	0.00	-0.02	0.00	0.24	0.00	0.03
28	74	-0.08	0.11	0.08	-0.04	0.19	0.05	0.16	-0.03	-0.04

29	8	-0.01	-0.03	0.04	0.11	0.05	0.08	0.05	0.02	0.07
30	8	0.00	0.06	0.00	0.00	-0.05	0.00	-0.16	0.00	0.01
31	8	0.12	-0.07	-0.09	-0.08	0.17	0.10	0.14	-0.02	-0.03
32	8	0.01	-0.02	-0.03	-0.06	0.17	0.06	0.06	0.05	0.07
33	8	0.01	-0.04	0.13	-0.03	0.02	-0.05	0.03	-0.01	0.21
34	8	-0.07	-0.05	-0.04	-0.11	-0.06	-0.11	-0.05	0.00	0.07
35	74	-0.13	-0.10	-0.08	-0.01	-0.12	-0.07	-0.16	-0.01	-0.02
36	8	-0.05	-0.03	-0.08	-0.05	-0.13	-0.09	-0.03	-0.01	0.01
37	8	-0.15	-0.10	-0.09	-0.03	-0.14	-0.08	-0.14	0.00	0.00
38	8	-0.04	0.06	-0.02	0.00	-0.05	-0.08	-0.04	-0.01	-0.11
39	8	0.00	-0.04	0.00	0.00	-0.13	0.00	-0.16	0.00	0.08
40	74	0.13	-0.10	0.08	0.01	-0.12	0.07	-0.15	0.01	-0.01
41	8	0.05	-0.03	0.08	0.05	-0.13	0.09	-0.02	0.00	0.01
42	8	0.09	0.09	-0.10	0.02	0.11	-0.08	0.12	0.01	-0.01
43	8	-0.01	-0.10	-0.07	-0.04	-0.10	-0.01	0.05	0.05	-0.12
44	8	0.00	0.21	0.00	0.00	-0.03	0.00	-0.03	0.00	-0.17
45	8	0.04	0.06	0.03	0.00	-0.05	0.08	-0.03	0.00	-0.11
46	8	-0.12	-0.06	0.08	0.08	0.17	-0.10	0.14	0.03	-0.03
47	8	0.14	0.09	0.09	0.00	-0.12	-0.08	-0.13	-0.02	-0.01
48	8	0.01	-0.10	0.07	0.04	-0.09	0.01	0.05	-0.04	-0.12
49	8	0.15	-0.10	0.09	0.03	-0.14	0.08	-0.12	-0.01	0.00
50	8	0.07	-0.04	0.04	0.11	-0.06	0.11	-0.05	-0.02	0.06
51	8	-0.01	-0.04	-0.13	0.03	0.02	0.05	0.03	0.00	0.21
52	8	-0.09	0.09	0.10	-0.02	0.12	0.09	0.13	-0.01	-0.01
53	8	0.00	-0.26	0.00	0.00	-0.11	0.00	-0.01	0.01	-0.12
54	1	0.02	-0.25	0.05	0.03	-0.13	0.01	-0.01	0.00	-0.13
55	1	-0.02	-0.25	-0.05	-0.03	-0.13	-0.01	-0.01	0.01	-0.13

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Table S1. The Calculated Total Bonding Energies and Expectation Values of All Mono-Ruthenium Substituted Keggin-Type POMs in Different Spin States

Complex	d-electron	Energy (Kcal mol^{-1})	Exact value	Expectation value
$^{1}\mathbf{1}^{1e}_{reduced}$	d^6	-10196.34	-	-
$^{2}\mathbf{1}$	d^5	-10346.25	0.75000	0.75540
$^{2}\mathbf{1(Si)}$	d^5	-10238.53	0.75000	0.75321
$^{1}\mathbf{1}^{1e}_{oxidized}$	d^4	-10403.22	-	-
$^{3}\mathbf{1}^{1e}_{oxidized}$		-10413.84	2.00000	2.00706
$^{5}\mathbf{1}^{1e}_{oxidized}$		-10402.07	6.00000	6.01085
$^{1}\mathbf{1}^{1e1H+}_{oxidized}$	d^4	-10246.03	-	-
$^{3}\mathbf{1}^{1e1H+}_{oxidized}$		-10260.32	2.00000	2.00647
$^{5}\mathbf{1}^{1e1H+}_{oxidized}$		-10232.42	6.00000	6.01180
$^{1}\mathbf{1}^{1e2H+}_{oxidized}$	d^4	-10002.95	-	-
$^{3}\mathbf{1}^{1e2H+}_{oxidized}$		-10027.05	2.00000	2.01138
$^{5}\mathbf{1}^{1e2H+}_{oxidized}$		-10003.65	6.00000	6.01090
$^{2}\mathbf{1}^{2e2H+}_{oxidized}$	d^3	-10157.50	0.75000	0.76937
$^{4}\mathbf{1}^{2e2H+}_{oxidized}$		-10159.60	3.75000	3.75943
$^{1}\mathbf{1}^{3e2H+}_{oxidized}$	d^2	-10214.91	-	-
$^{3}\mathbf{1}^{3e2H+}_{oxidized}$		-10218.30	2.00000	2.00796
$^{5}\mathbf{1}^{3e2H+}_{oxidized}$		-10190.38	6.00000	6.01607

Table S2. Energy decomposition analysis (EDA) of ruthenium(III) complex $^{2}\mathbf{1}$ at BP86/TZP calculations (Energy contributions for Ru^{III}-OH_2 bond in kcal mol^{-1}).

System	ΔE_{int}	ΔE_{Pauli}	ΔE_{elsat}	ΔE_{orb}	ΔE_{prep}	$\Delta E_{prep}(Ru^{III})$	$\Delta E_{prep}(H_2O)$	$\Delta E(=-D_e)$
$^{2}\mathbf{1}$	-25.94	79.77	-68.62	-37.09	6.55	5.80	0.75	-19.39

As shown in Table S2, the EDAs show that Ru-OH_2 bond has the low orbital interaction energy, ΔE_{orb}, and high electronstatic interaction energy, ΔE_{elsa}, and thus it displays high ionic character. Because the bonding contribution of electrostatic attractions ΔE_{elstat} to Ru-OH_2 bond has been largely cancelled by the repulsive term ΔE_{Pauli}, the interaction energy between the H_2O molecule and POM fragment are relative small, -19.4 kcal mol^{-1}.

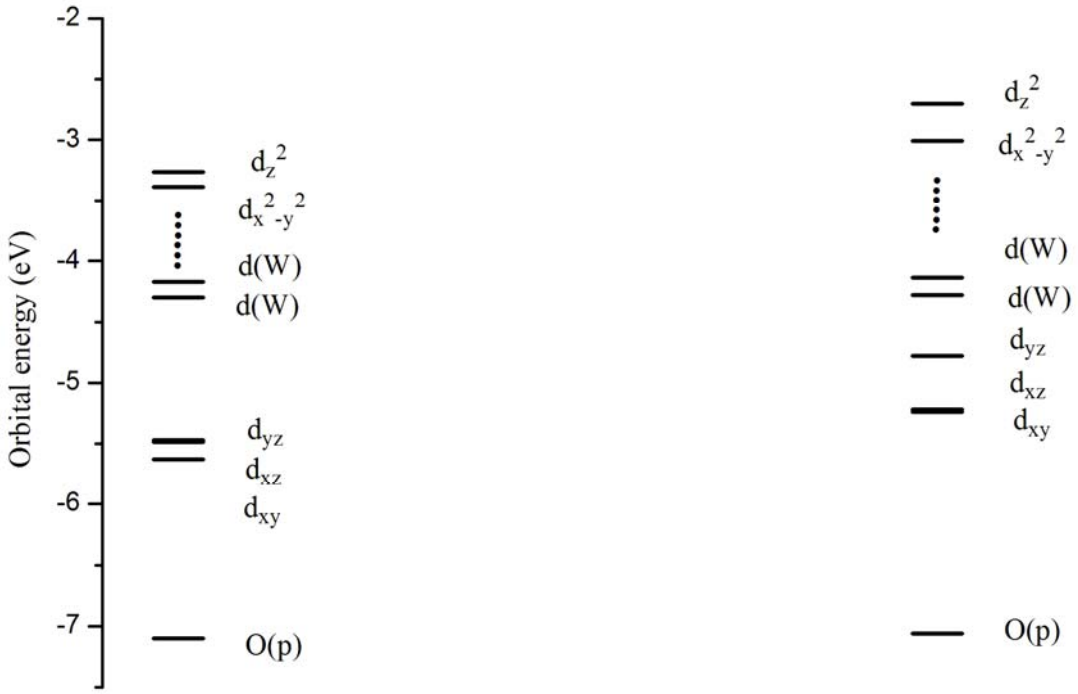

Fig S1. The metal-based d orbital energy level diagram for aquaruthenium(III) POM complexes in ground state obtained by the BP86/TZP calculations in acetonitrile (the dense d-W orbitals of POM ligand are not listed overall here)

The optimized geometry of $^{1}\mathbf{1}^{\mathbf{1e}}_{\mathbf{reduced}}$ in ground state

O	-0.013638	-0.015394	-0.015397
P	-0.010526	-0.016816	1.538962
O	1.448881	-0.021203	2.076843
O	-0.715032	-1.333611	2.049610
Ru	-2.742652	-1.721984	1.688406
O	-2.766174	-2.163762	3.713259
W	-1.096618	-1.950720	4.503572
O	-1.468974	-0.016185	4.669689
W	-1.111691	1.845474	4.416526
O	0.769581	1.339689	4.638038
W	2.147067	0.015861	4.453049
O	0.789244	-1.282236	4.675203
O	-0.775710	1.228034	2.067803
O	3.236012	-1.302292	3.506099
W	3.158996	-1.746052	1.609539
O	3.981386	0.017514	1.322056
W	3.167270	1.751701	1.589661
O	3.210033	1.353982	3.487102
O	1.759914	-2.967246	1.959245
W	-0.081686	-3.693639	1.613469
O	-1.892791	-3.562717	1.382131
O	0.209171	-5.410553	1.462406
O	0.267512	-3.013360	-0.186668
W	0.986729	-1.745334	-1.442458
O	-0.749996	-1.318692	-2.143146
W	-2.082901	-0.031179	-1.450868
O	-2.651845	1.441504	-0.257205
W	-3.165594	1.876686	1.550981
O	-2.754188	2.159031	3.476619
O	-0.324797	-3.455330	3.577445
O	4.551974	-2.783557	1.442662
O	2.488667	-1.637393	-0.191705
O	1.613768	-2.792160	-2.686355
O	1.575849	0.003367	-2.111272
W	0.978647	1.733057	-1.477325
O	-0.746709	1.354044	-2.136281
O	1.616166	2.794378	-2.706538
O	2.466367	1.661976	-0.193086
O	0.226822	2.983210	-0.195582
W	-0.091820	3.628521	1.603528
O	-1.959964	3.482673	1.319773

O	-3.262855	-0.006738	-2.747174
O	-2.749619	-1.233557	-0.275828
O	4.537339	2.817938	1.419401
O	1.717322	2.969681	1.936769
O	2.922924	0.042573	6.015814
O	-1.383210	-2.563603	6.110550
O	-3.610153	0.126627	1.922991
O	0.167434	5.346326	1.449602
O	-0.417590	3.439733	3.496710
O	-1.490452	2.509051	5.983390
O	-4.727861	2.646538	1.399315
O	-5.004632	-2.053226	2.137487
H	-4.558578	-2.235809	3.008661
H	-4.925426	-1.052998	2.092126

The optimized geometry of ^{2}**1** in ground state

O	-0.052878	-0.046231	0.012459
P	-0.019345	-0.018716	1.563334
O	1.445645	-0.017457	2.076534
O	-0.717547	-1.323579	2.124723
Ru	-2.720903	-1.715220	1.660170
O	-2.696232	-2.133096	3.640234
W	-1.067775	-1.928567	4.515156
O	-1.463981	-0.005909	4.705305
W	-1.093797	1.847729	4.435675
O	0.772937	1.337306	4.634272
W	2.164395	0.016107	4.443204
O	0.795789	-1.284506	4.678926
O	-0.778281	1.231844	2.080350
O	3.236040	-1.300170	3.492859
W	3.161571	-1.733880	1.594427
O	3.974563	0.022644	1.306971
W	3.163515	1.752950	1.590521
O	3.214135	1.359979	3.479314
O	1.752497	-2.965060	1.950852
W	-0.065495	-3.686450	1.666894
O	-1.894726	-3.536411	1.360507
O	0.211457	-5.393794	1.502065
O	0.243058	-3.007809	-0.161398
W	0.953715	-1.764531	-1.421482
O	-0.793522	-1.331433	-2.121370
W	-2.083493	0.003204	-1.468500
O	-2.712435	1.368471	-0.234558

W	-3.156302	1.883728	1.588627
O	-2.762023	2.130588	3.497054
O	-0.341525	-3.480421	3.584844
O	4.541875	-2.770477	1.419233
O	2.465394	-1.639961	-0.197390
O	1.565918	-2.810740	-2.661968
O	1.521398	-0.014000	-2.107606
W	0.982129	1.718794	-1.464030
O	-0.780645	1.331592	-2.119280
O	1.595363	2.772137	-2.698097
O	2.452423	1.657363	-0.202044
O	0.194062	2.953630	-0.195628
W	-0.098676	3.610892	1.601093
O	-1.988158	3.451897	1.317700
O	-3.253676	0.034941	-2.755059
O	-2.797471	-1.284865	-0.313845
O	4.519642	2.819133	1.408914
O	1.705403	2.968297	1.924681
O	2.938941	0.043649	5.995588
O	-1.403471	-2.556582	6.100098
O	-3.585612	0.094551	1.925734
O	0.142693	5.320064	1.430819
O	-0.441413	3.438062	3.489956
O	-1.461963	2.524283	5.989673
O	-4.725925	2.618930	1.442750
O	-4.848615	-2.006530	1.092401
H	-4.956653	-1.067521	1.417314
H	-4.517228	-1.837951	0.164575

The optimized geometry of ^{2}**1(Si)** in ground state

O	-0.048677	-0.041116	-0.081187
Si	-0.009219	-0.012275	1.562289
O	1.546075	-0.004824	2.102921
O	-0.733295	-1.395921	2.161894
Ru	-2.720528	-1.738758	1.675041
O	-2.720500	-2.161996	3.656972
W	-1.063620	-1.929614	4.480829
O	-1.465194	-0.007745	4.669324
W	-1.094505	1.848549	4.397325
O	0.775741	1.339622	4.594283
W	2.169287	0.019169	4.404627
O	0.802731	-1.287416	4.643999
O	-0.817216	1.310503	2.110730

O	3.286062	-1.311697	3.517795
W	3.148642	-1.700120	1.608663
O	4.034818	0.025824	1.308152
W	3.148970	1.721947	1.602933
O	3.265262	1.377875	3.503340
O	1.741297	-2.935727	1.967188
W	-0.079490	-3.657106	1.680201
O	-1.916567	-3.572870	1.367826
O	0.232905	-5.368199	1.496040
O	0.224051	-2.977940	-0.148147
W	0.937440	-1.731744	-1.409146
O	-0.800634	-1.349004	-2.174305
W	-2.044402	-0.001834	-1.454483
O	-2.673003	1.364284	-0.219194
W	-3.117221	1.881570	1.605516
O	-2.798253	2.164280	3.526314
O	-0.347561	-3.525637	3.610345
O	4.522201	-2.762380	1.411633
O	2.450653	-1.605336	-0.184788
O	1.568577	-2.805725	-2.633979
O	1.536805	-0.014284	-2.160930
W	0.962656	1.687629	-1.452923
O	-0.788370	1.343429	-2.173691
O	1.593909	2.774285	-2.665697
O	2.434884	1.623149	-0.190752
O	0.169598	2.919758	-0.182803
W	-0.116282	3.581039	1.615670
O	-2.015492	3.498634	1.322163
O	-3.248676	0.033944	-2.726112
O	-2.757367	-1.294299	-0.297789
O	4.490320	2.821792	1.395250
O	1.686789	2.937723	1.941100
O	2.920451	0.051021	5.982174
O	-1.380695	-2.534382	6.091121
O	-3.545058	0.088484	1.946975
O	0.158585	5.294596	1.420038
O	-0.453641	3.485877	3.515555
O	-1.447083	2.503918	5.977876
O	-4.707538	2.595930	1.434942
O	-4.918882	-1.896933	1.000190
H	-4.903881	-0.964435	1.368193
H	-4.464896	-1.731929	0.121432

The optimized geometry of $^{3}\mathbf{1}^{\mathbf{1e}}_{\mathbf{oxidized}}$ in ground state

O	-0.079569	-0.048990	0.006635
P	-0.030620	0.006943	1.549034
O	1.421262	-0.035340	2.070593
O	-0.770133	-1.277956	2.134999
Ru	-2.713178	-1.736192	1.653460
O	-2.720403	-2.151104	3.636993
W	-1.093636	-1.908548	4.530134
O	-1.486366	-0.001806	4.715744
W	-1.092470	1.857158	4.451842
O	0.759682	1.328796	4.634586
W	2.150436	0.002331	4.440015
O	0.768933	-1.293554	4.671092
O	-0.769414	1.263260	2.068998
O	3.211555	-1.319361	3.481396
W	3.170912	-1.729451	1.587917
O	3.965406	0.012366	1.299469
W	3.157484	1.749640	1.589319
O	3.195826	1.340002	3.470751
O	1.743847	-2.995420	1.947544
W	-0.036778	-3.664799	1.671715
O	-1.936663	-3.478023	1.354050
O	0.193801	-5.367188	1.500400
O	0.199890	-2.985707	-0.146774
W	0.944565	-1.761378	-1.428414
O	-0.810643	-1.339109	-2.130851
W	-2.086331	-0.009618	-1.489436
O	-2.707514	1.322753	-0.214926
W	-3.100271	1.895155	1.593373
O	-2.764710	2.115065	3.501650
O	-0.380765	-3.460810	3.559385
O	4.539356	-2.766108	1.409954
O	2.440503	-1.661086	-0.189604
O	1.550475	-2.818826	-2.650686
O	1.503115	-0.020083	-2.102795
W	0.964167	1.720094	-1.459451
O	-0.799570	1.323660	-2.120864
O	1.576622	2.769284	-2.685345
O	2.428293	1.651439	-0.192342
O	0.173255	2.949954	-0.187790
W	-0.085101	3.616276	1.607589
O	-2.012710	3.458859	1.316845
O	-3.264800	0.039565	-2.754404

O	-2.830609	-1.322494	-0.338928
O	4.510167	2.805518	1.406962
O	1.703031	2.980156	1.929180
O	2.921048	0.021849	5.984661
O	-1.429889	-2.546304	6.100986
O	-3.434783	0.027230	1.964107
O	0.145823	5.317599	1.431625
O	-0.462517	3.443131	3.488644
O	-1.457737	2.531640	5.997957
O	-4.709690	2.516996	1.448801
O	-4.739829	-2.192688	1.005676
H	-5.147819	-1.372608	1.365932
H	-4.382312	-1.884005	0.103527

The optimized geometry of $^{3}\mathbf{1}^{\mathbf{1e1H^{+}}}_{\mathbf{oxidized}}$ in ground state

O	-0.047651	-0.033600	0.008310
P	-0.019644	-0.003224	1.560039
O	1.446341	-0.022677	2.074687
O	-0.763795	-1.274555	2.116376
Ru	-2.828211	-1.775945	1.638643
O	-2.747076	-2.157676	3.634404
W	-1.116519	-1.899014	4.493607
O	-1.486149	0.012776	4.689032
W	-1.077277	1.873907	4.443498
O	0.771891	1.336411	4.641765
W	2.151473	-0.002997	4.439431
O	0.768565	-1.281783	4.656473
O	-0.742836	1.273651	2.073726
O	3.229733	-1.319176	3.494055
W	3.167265	-1.732449	1.595832
O	3.979259	0.010646	1.310084
W	3.159597	1.747703	1.591703
O	3.206617	1.342028	3.480219
O	1.740526	-2.964004	1.952421
W	-0.065060	-3.645516	1.654579
O	-1.926154	-3.500185	1.352099
O	0.197045	-5.352735	1.491610
O	0.224058	-2.982185	-0.161786
W	0.965130	-1.746368	-1.434255
O	-0.785850	-1.333273	-2.127855
W	-2.089882	-0.022400	-1.458254
O	-2.676251	1.357091	-0.228046
W	-3.097961	1.870552	1.597965

O	-2.744399	2.148646	3.506515
O	-0.378555	-3.451123	3.559576
O	4.538734	-2.779931	1.422449
O	2.464045	-1.653786	-0.193113
O	1.576020	-2.804657	-2.664379
O	1.537660	-0.012752	-2.107096
W	0.968743	1.726352	-1.464600
O	-0.769344	1.328652	-2.121083
O	1.594829	2.776011	-2.695058
O	2.445917	1.648546	-0.189845
O	0.208075	2.974435	-0.195276
W	-0.083413	3.624865	1.603499
O	-1.976397	3.468832	1.318593
O	-3.246458	0.041452	-2.755190
O	-2.826230	-1.293710	-0.328461
O	4.522088	2.805591	1.412508
O	1.716040	2.979043	1.933411
O	2.920442	0.011950	5.994322
O	-1.432417	-2.525582	6.081773
O	-3.436014	0.063839	1.940567
O	0.160661	5.333487	1.434428
O	-0.430523	3.459750	3.498948
O	-1.442535	2.541246	6.001330
O	-4.688409	2.552597	1.445775
O	-4.625718	-2.469269	1.322972
H	-4.749417	-2.228252	0.376569

The optimized geometry of $^{3}\mathbf{1}^{\mathbf{1e2H+}}_{\mathbf{oxidized}}$ in ground state

O	-0.049852	-0.091087	0.006226
P	-0.020142	-0.025216	1.563498
O	1.458287	-0.061531	2.056745
O	-0.792861	-1.246302	2.149456
O	-0.691667	1.308473	2.038167
Ru	0.005051	3.435773	1.495615
O	0.293259	5.184016	1.259386
O	-0.368037	3.500543	3.507912
W	-0.993584	2.025691	4.411441
O	-1.337531	2.679675	5.992346
O	-2.027623	3.468492	1.251067
W	-3.056421	1.985673	1.605466
O	-2.730831	2.133700	3.525898
O	0.344924	2.882903	-0.428816
W	1.010080	1.582885	-1.516443

O	1.658710	2.481321	-2.866887
O	1.950505	2.913616	1.753809
W	3.204419	1.625235	1.465246
O	4.674296	2.539458	1.230156
O	0.832012	1.318088	4.618473
W	2.197850	-0.006505	4.400257
O	2.989603	0.016899	5.952305
O	-1.455728	0.091123	4.689167
W	-1.099979	-1.757625	4.547974
O	-1.468497	-2.358287	6.143432
O	0.765823	-1.298556	4.693577
O	3.303050	1.202469	3.396439
O	3.166432	-1.460456	3.513947
W	3.110485	-1.896175	1.627106
O	4.424459	-3.034326	1.492056
O	-2.808964	-2.017755	3.644244
W	-3.167130	-1.797444	1.740208
O	-2.756135	-1.367757	-0.093241
W	-2.067228	-0.091871	-1.397796
O	-0.912393	-1.540688	-2.031530
W	0.879090	-1.939481	-1.408551
O	2.360814	-1.908625	-0.160692
O	-0.542317	-3.410500	3.646881
W	-0.209833	-3.661879	1.754403
O	1.595551	-3.069880	2.039156
O	-2.118328	-3.441215	1.505551
O	-3.433399	0.052937	2.001714
O	-4.791707	-2.422390	1.629173
O	0.048869	-3.100332	-0.064044
O	-0.039628	-5.394336	1.653710
O	-4.676589	2.615119	1.450144
O	-2.700138	1.248587	-0.184113
O	-0.797465	1.122108	-2.176741
O	-3.313586	-0.109317	-2.615383
O	2.544978	1.340434	-0.343725
O	1.453335	-0.299957	-2.148843
O	3.965750	-0.251457	1.266566
O	1.415773	-3.092303	-2.601525

The optimized geometry of $^{4}\mathbf{1}^{2e2H^{+}}_{\mathbf{oxidized}}$ in ground state

O	-0.044826	-0.091990	0.004543
P	-0.013396	-0.032575	1.558678
O	1.461542	-0.062444	2.052302

O	-0.788324	-1.247869	2.146274
O	-0.693501	1.296174	2.039797
Ru	-0.005616	3.393910	1.503972
O	0.296356	5.138912	1.258159
O	-0.342923	3.505160	3.465244
W	-0.985533	2.003609	4.408771
O	-1.317971	2.684175	5.969761
O	-1.979517	3.473262	1.239617
W	-3.051215	1.963322	1.599364
O	-2.696213	2.200992	3.499531
O	0.307046	2.870685	-0.399469
W	1.001822	1.566991	-1.526101
O	1.639880	2.490370	-2.851530
O	1.911307	2.901299	1.781335
W	3.211545	1.609654	1.476625
O	4.654000	2.548382	1.242872
O	0.838396	1.341940	4.602359
W	2.202779	-0.002368	4.402410
O	2.982550	0.025992	5.950267
O	-1.458582	0.117184	4.678831
W	-1.100574	-1.755169	4.541657
O	-1.467108	-2.338251	6.133254
O	0.758124	-1.268000	4.692076
O	3.298356	1.225895	3.399654
O	3.173121	-1.435461	3.513130
W	3.099321	-1.886959	1.627459
O	4.411862	-3.011521	1.489011
O	-2.809360	-1.992291	3.644199
W	-3.160939	-1.795201	1.741765
O	-2.757540	-1.337598	-0.086377
W	-2.068117	-0.087271	-1.403523
O	-0.910206	-1.516067	-2.038125
W	0.874400	-1.930319	-1.397946
O	2.358734	-1.886060	-0.159290
O	-0.545405	-3.397809	3.651273
W	-0.211918	-3.648613	1.756487
O	1.595505	-3.055460	2.039840
O	-2.123292	-3.428606	1.507296
O	-3.424251	0.079099	2.006914
O	-4.781688	-2.402148	1.630480
O	0.048242	-3.085810	-0.064055
O	-0.040970	-5.371209	1.654529
O	-4.649098	2.619930	1.437872
O	-2.683486	1.272355	-0.186073

O	-0.802604	1.145342	-2.173881
O	-3.314055	-0.100594	-2.608593
O	2.512320	1.414856	-0.320794
O	1.453493	-0.271875	-2.142047
O	3.959528	-0.223520	1.263771
O	1.414681	-3.068993	-2.588788

The optimized geometry of $^{3}\mathbf{1}^{\mathbf{3e2H^{+}}}_{\mathbf{oxidized}}$ in ground state

O	-0.049165	-0.069050	0.001464
P	-0.008963	-0.024557	1.553476
O	1.467917	-0.077656	2.043256
O	-0.788676	-1.233807	2.137882
O	-0.673554	1.309080	2.039854
Ru	0.019775	3.471466	1.493839
O	0.321960	5.166779	1.272000
O	-0.343868	3.552551	3.455929
W	-0.959458	2.029717	4.402636
O	-1.297348	2.710880	5.952903
O	-1.870754	3.421796	1.228052
W	-3.039848	1.898248	1.612733
O	-2.672308	2.219586	3.482921
O	0.299755	2.942848	-0.410488
W	0.964402	1.598348	-1.538229
O	1.616394	2.515069	-2.849895
O	1.735453	2.798646	1.846523
W	3.204520	1.524605	1.472453
O	4.548671	2.586388	1.250548
O	0.847255	1.364047	4.603757
W	2.197710	-0.000084	4.415012
O	2.978533	0.034011	5.953119
O	-1.449691	0.143603	4.661344
W	-1.109291	-1.729132	4.531155
O	-1.476454	-2.302864	6.116772
O	0.763765	-1.253218	4.686762
O	3.272712	1.251912	3.394206
O	3.197047	-1.404962	3.503734
W	3.092708	-1.914666	1.642024
O	4.411311	-3.017154	1.494395
O	-2.813130	-1.981468	3.629470
W	-3.164914	-1.828538	1.732130
O	-2.766461	-1.327690	-0.080976
W	-2.069279	-0.094053	-1.408406
O	-0.899211	-1.501409	-2.034953

W	0.889754	-1.897548	-1.388336
O	2.377129	-1.852241	-0.142833
O	-0.542505	-3.374026	3.640948
W	-0.209729	-3.642394	1.758722
O	1.622605	-3.070666	2.051388
O	-2.123298	-3.435529	1.496588
O	-3.458733	0.078170	2.009562
O	-4.776532	-2.433630	1.618005
O	0.072862	-3.054664	-0.048707
O	-0.039487	-5.355743	1.652136
O	-4.589409	2.638740	1.431728
O	-2.669268	1.271528	-0.180072
O	-0.818124	1.169072	-2.175806
O	-3.313777	-0.105835	-2.603445
O	2.461658	1.451377	-0.293615
O	1.455067	-0.228483	-2.126737
O	3.988925	-0.200536	1.258854
O	1.438961	-3.025111	-2.573437