An Experimental and Computational Study of a new Wheel-shaped $\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ Polyoxometalate

Pere Miró,[a] Jie Ling,[b] Jie Qiu,[b] Peter C. Burns,[b,c,*] Laura Gagliardi[a,*] and Christopher J. Cramer[a,*]

[a] Department of Chemistry and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, Minne-sota 55455 (USA) [b] Department of Civil Engineering and Geological Sciences , University of Notre Dame, Notre Dame, Indiana 46556 (USA) [c] Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556 (USA)

Supporting Information

Table S1. Cartesian coordinates (in Å) for the $\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ species.

U	4.159715	-2.805178	0.000000
U	0.349498	-5.005008	0.000000
U	-4.509213	-2.199830	0.000000
U	-4.509213	2.199830	0.000000
U	4.159715	2.805178	0.000000
U	0.349498	5.005008	0.000000
W	-3.146434	-5.449783	0.000000
W	-3.962841	-3.593843	3.408171
W	-1.130939	-5.228843	3.408171
W	5.093780	-1.634999	3.408171
W	5.093780	1.634999	3.408171
W	-1.130939	-5.228843	-3.408171
W	-3.146434	5.449783	0.000000
W	-1.130939	5.228843	3.408171
W	-3.962841	3.593843	3.408171
W	6.292867	0.000000	0.000000
W	-3.962841	-3.593843	-3.408171
W	-1.130939	5.228843	-3.408171
W	-3.962841	3.593843	-3.408171
W	5.093780	-1.634999	-3.408171
W	5.093780	1.634999	-3.408171
O	-2.744036	-1.697022	0.000000
O	4.012707	2.814071	2.376586
O	-0.097646	-3.224916	0.000000
O	6.638661	-2.642638	3.585912
O	-6.327537	-2.694043	0.000000
O	-4.443410	2.068071	2.376586
O	-1.979183	-3.428046	-3.001301
O	0.430703	-4.882141	2.376586
O	-4.018013	-4.290034	-1.241009
O	-0.097646	3.224916	0.000000
O	-1.706272	-5.624718	-1.241009
O	-1.030739	-7.070568	3.585912
O	-4.018013	4.290034	-1.241009
O	-1.979183	3.428046	3.001301
O	2.608155	-4.517457	-0.730052
O	-3.141302	-5.440894	-3.739637
O	-4.018013	4.290034	1.241009
O	5.724285	1.334684	-1.241009
O	-4.443410	-2.068071	-2.376586
O	-4.443410	-2.068071	2.376586
O	-1.030739	-7.070568	-3.585912
O	0.830659	-6.826830	0.000000
O	6.282603	0.000000	3.739637
O	-1.706272	5.624718	1.241009
O	-1.979183	-3.428046	3.001301
O	5.496878	-4.132787	0.000000
O	-4.018013	-4.290034	1.241009

0	4.370143	1.929938	5.064510
0	8.104967	0.000000	0.000000
0	-0.513696	4.749624	5.064510
0	-6.327537	2.694043	0.000000
0	-3.856447	2.819686	5.064510
0	0.430703	4.882141	2.376586
0	-4.443410	2.068071	-2.376586
0	5.724285	1.334684	1.241009
0	2.841683	1.527894	0.000000
0	-1.706272	-5.624718	1.241009
0	-5.607922	-4.427930	3.585912
0	5.724285	-1.334684	1.241009
0	5.724285	-1.334684	-1.241009
0	-3.856447	-2.819686	5.064510
0	-0.513696	-4.749624	5.064510
0	4.370143	-1.929938	5.064510
0	-5.216310	0.000000	0.730052
0	6.282603	0.000000	-3.739637
0	-0.513696	-4.749624	-5.064510
0	-1.030739	7.070568	3.585912
0	2.608155	4.517457	0.730052
0	6.638661	2.642638	3.585912
0	0.830659	6.826830	0.000000
0	2.841683	-1.527894	0.000000
0	4.012707	-2.814071	-2.376586
0	-5.607922	4.427930	3.585912
0	3.958366	0.000000	-3.001301
0	-1.979183	3.428046	-3.001301
0	-5.607922	-4.427930	-3.585912
0	-3.856447	-2.819686	-5.064510
0	-4.052484	7.019108	0.000000
0	6.638661	-2.642638	-3.585912
0	-2.744036	1.697022	0.000000
0	4.012707	2.814071	-2.376586
0	0.430703	-4.882141	-2.376586
0	-1.706272	5.624718	-1.241009
0	0.430703	4.882141	-2.376586
0	5.496878	4.132787	0.000000
0	-5.607922	4.427930	-3.585912
0	-3.856447	2.819686	-5.064510
0	6.638661	2.642638	-3.585912
0	-3.141302	5.440894	-3.739637
0	2.608155	4.517457	-0.730052
0	-1.030739	7.070568	-3.585912
0	-4.052484	-7.019108	0.000000
0	-3.141302	5.440894	3.739637
0	-5.216310	0.000000	-0.730052
0	-3.141302	-5.440894	3.739637
0	2.608155	-4.517457	0.730052
0	3.958366	0.000000	3.001301
0	4.012707	-2.814071	2.376586

O	-0.513696	4.749624	-5.064510
O	4.370143	-1.929938	-5.064510
O	4.370143	1.929938	-5.064510

Table S2. Cartesian coordinates (in Å) for the $H_{18}\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ species.

U	-4.129542	2.879185	0.000000
U	-0.428676	5.015880	0.000000
U	4.558218	2.136696	0.000000
U	4.558218	-2.136696	0.000000
U	-4.129542	-2.879185	0.000000
U	-0.428676	-5.015880	0.000000
W	3.067799	5.313584	0.000000
W	4.152110	3.847533	3.444423
W	1.256007	5.519599	3.444423
W	-5.408117	1.672066	3.444423
W	-5.408117	-1.672066	3.444423
W	1.256007	5.519599	-3.444423
W	3.067799	-5.313584	0.000000
W	1.256007	-5.519599	3.444423
W	4.152110	-3.847533	3.444423
W	-6.135598	0.000000	0.000000
W	4.152110	3.847533	-3.444423
W	1.256007	-5.519599	-3.444423
W	4.152110	-3.847533	-3.444423
W	-5.408117	1.672066	-3.444423
W	-5.408117	-1.672066	-3.444423
O	2.799989	1.644267	0.000000
O	-4.026727	-2.852671	2.490549
O	0.023983	3.246995	0.000000
O	-6.829587	2.741372	3.400655
O	6.300368	2.705243	0.000000
O	4.483849	-2.060912	2.490549
O	1.968074	3.408804	-3.095231
O	-0.457122	4.913583	2.490549
O	3.930234	4.134434	-1.256851
O	0.023983	-3.246995	0.000000
O	1.615408	5.470899	-1.256851
O	1.040696	7.285281	3.400655
O	3.930234	-4.134434	-1.256851
O	1.968074	-3.408804	3.095231
O	-2.652648	4.594521	-0.726786
O	3.201264	5.544752	-3.704841
O	3.930234	-4.134434	1.256851
O	-5.545642	-1.336465	-1.256851
O	4.483849	2.060912	-2.490549
O	4.483849	2.060912	2.490549
O	1.040696	7.285281	-3.400655
O	-0.807375	6.808901	0.000000
O	-6.402528	0.000000	3.704841
O	1.615408	-5.470899	1.256851
O	1.968074	3.408804	3.095231

0	-5.492994	4.103657	0.000000
0	3.930234	4.134434	1.256851
0	-4.721051	-1.970009	5.053700
0	-7.898543	0.000000	0.000000
0	0.654447	-5.073555	5.053700
0	6.300368	-2.705243	0.000000
0	4.066603	-3.103545	5.053700
0	-0.457122	-4.913583	2.490549
0	4.483849	-2.060912	-2.490549
0	-5.545642	-1.336465	1.256851
0	-2.823972	-1.602728	0.000000
0	1.615408	5.470899	1.256851
0	5.788891	4.543910	3.400655
0	-5.545642	1.336465	1.256851
0	-5.545642	1.336465	-1.256851
0	4.066603	3.103545	5.053700
0	0.654447	5.073555	5.053700
0	-4.721051	1.970009	5.053700
0	5.305296	0.000000	0.726786
0	-6.402528	0.000000	-3.704841
0	0.654447	5.073555	-5.053700
0	1.040696	-7.285281	3.400655
0	-2.652648	-4.594521	0.726786
0	-6.829587	-2.741372	3.400655
0	-0.807375	-6.808901	0.000000
0	-2.823972	1.602728	0.000000
0	-4.026727	2.852671	-2.490549
0	5.788891	-4.543910	3.400655
0	-3.936148	0.000000	-3.095231
0	1.968074	-3.408804	-3.095231
0	5.788891	4.543910	-3.400655
0	4.066603	3.103545	-5.053700
0	3.949271	-6.840339	0.000000
0	-6.829587	2.741372	-3.400655
0	2.799989	-1.644267	0.000000
0	-4.026727	-2.852671	-2.490549
0	-0.457122	4.913583	-2.490549
0	1.615408	-5.470899	-1.256851
0	-0.457122	-4.913583	-2.490549
0	-5.492994	-4.103657	0.000000
0	5.788891	-4.543910	-3.400655
0	4.066603	-3.103545	-5.053700
0	-6.829587	-2.741372	-3.400655
0	3.201264	-5.544752	-3.704841
0	-2.652648	-4.594521	-0.726786
0	1.040696	-7.285281	-3.400655
0	3.949271	6.840339	0.000000
0	3.201264	-5.544752	3.704841
0	5.305296	0.000000	-0.726786
0	3.201264	5.544752	3.704841
0	-2.652648	4.594521	0.726786

O	-3.936148	0.000000	3.095231
O	-4.026727	2.852671	2.490549
O	0.654447	-5.073555	-5.053700
O	-4.721051	1.970009	-5.053700
O	-4.721051	-1.970009	-5.053700
H	-3.649670	0.000000	2.160541
H	-3.649670	0.000000	-2.160541
H	-3.572366	-3.479402	-3.081396
H	-1.227067	-4.833461	-3.081396
H	-3.572366	-3.479402	3.081396
H	-1.227067	-4.833461	3.081396
H	-3.572366	3.479402	-3.081396
H	-3.572366	3.479402	3.081396
H	-1.227067	4.833461	3.081396
H	-1.227067	4.833461	-3.081396
H	1.824835	3.160707	-2.160541
H	1.824835	3.160707	2.160541
H	4.799434	1.354059	3.081396
H	4.799434	1.354059	-3.081396
H	4.799434	-1.354059	3.081396
H	4.799434	-1.354059	-3.081396
H	1.824835	-3.160707	-2.160541
H	1.824835	-3.160707	2.160541

Table S3. Cartesian coordinates (in Å) for the $Na_3\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{27-}$ species.

U	4.574314	2.356147	0.000000
U	4.574314	-2.356147	0.000000
U	-0.246674	-5.139546	0.000000
U	-4.327640	-2.783399	0.000000
U	-0.246674	5.139546	0.000000
U	-4.327640	2.783399	0.000000
W	3.252304	-5.633156	0.000000
W	1.224939	-5.384269	3.395565
W	4.050445	-3.752963	3.395565
W	4.050445	3.752963	3.395565
W	1.224939	5.384269	3.395565
W	4.050445	-3.752963	-3.395565
W	-6.504608	0.000000	0.000000
W	-5.275383	1.631307	3.395565
W	-5.275383	-1.631307	3.395565
W	3.252304	5.633156	0.000000
W	1.224939	-5.384269	-3.395565
W	-5.275383	1.631307	-3.395565
W	-5.275383	-1.631307	-3.395565
W	4.050445	3.752963	-3.395565
W	1.224939	5.384269	-3.395565
O	0.424385	-3.430157	0.000000
O	-0.338541	5.048989	2.343354
O	2.758411	-2.082606	0.000000
O	5.694574	4.575950	3.605760
O	-0.922998	-6.896699	0.000000
O	-4.203283	-2.817680	2.343354
O	2.079154	-3.601200	-2.950733
O	4.541823	-2.231310	2.343354
O	1.808860	-5.832762	-1.240179
O	-3.182795	1.347551	0.000000
O	4.146890	-4.482900	-1.240179
O	5.694574	-4.575950	3.605760
O	-5.955750	-1.349862	-1.240179
O	-4.158308	0.000000	2.950733
O	4.803103	0.000000	-0.731736
O	3.228979	-5.592755	-3.756239
O	-5.955750	-1.349862	1.240179
O	1.808860	5.832762	-1.240179
O	-0.338541	-5.048989	-2.343354
O	-0.338541	-5.048989	2.343354
O	5.694574	-4.575950	-3.605760
O	6.434215	-2.649010	0.000000

0	3.228979	5.592755	3.756239
0	-5.955750	1.349862	1.240179
0	2.079154	-3.601200	2.950733
0	6.434215	2.649010	0.000000
0	1.808860	-5.832762	1.240179
0	0.591555	4.865564	5.030420
0	4.156905	7.199971	0.000000
0	-4.509480	1.920480	5.030420
0	-5.511218	-4.247689	0.000000
0	-4.509480	-1.920480	5.030420
0	-4.203283	2.817680	2.343354
0	-4.203283	-2.817680	-2.343354
0	1.808860	5.832762	1.240179
0	0.424385	3.430157	0.000000
0	4.146890	-4.482900	1.240179
0	1.115602	-7.219621	3.605760
0	4.146890	4.482900	1.240179
0	4.146890	4.482900	-1.240179
0	0.591555	-4.865564	5.030420
0	3.917925	-2.945084	5.030420
0	3.917925	2.945084	5.030420
0	-2.401552	-4.159609	0.731736
0	3.228979	5.592755	-3.756239
0	3.917925	-2.945084	-5.030420
0	-6.810176	2.643671	3.605760
0	-2.401552	4.159609	0.731736
0	1.115602	7.219621	3.605760
0	-5.511218	4.247689	0.000000
0	2.758411	2.082606	0.000000
0	4.541823	2.231310	-2.343354
0	-6.810176	-2.643671	3.605760
0	2.079154	3.601200	-2.950733
0	-4.158308	0.000000	-2.950733
0	1.115602	-7.219621	-3.605760
0	0.591555	-4.865564	-5.030420
0	-8.313810	0.000000	0.000000
0	5.694574	4.575950	-3.605760
0	-3.182795	-1.347551	0.000000
0	-0.338541	5.048989	-2.343354
0	4.541823	-2.231310	-2.343354
0	-5.955750	1.349862	-1.240179
0	-4.203283	2.817680	-2.343354
0	-0.922998	6.896699	0.000000
0	-6.810176	-2.643671	-3.605760
0	-4.509480	-1.920480	-5.030420
0	1.115602	7.219621	-3.605760
0	-6.457957	0.000000	-3.756239
0	-2.401552	4.159609	-0.731736
0	-6.810176	2.643671	-3.605760
0	4.156905	-7.199971	0.000000
0	-6.457957	0.000000	3.756239

O	-2.401552	-4.159609	-0.731736
O	3.228979	-5.592755	3.756239
O	4.803103	0.000000	0.731736
O	2.079154	3.601200	2.950733
O	4.541823	2.231310	2.343354
O	-4.509480	1.920480	-5.030420
O	3.917925	2.945084	-5.030420
O	0.591555	4.865564	-5.030420
Na	-1.020902	-1.768254	0.000000
Na	-1.020902	1.768254	0.000000
Na	2.041804	0.000000	0.000000

Figure S1. Electrostatic potential plot for the $\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ species. Colour code: blue ≈-1.70, green ≈-2.08 and red ≈-2.46.

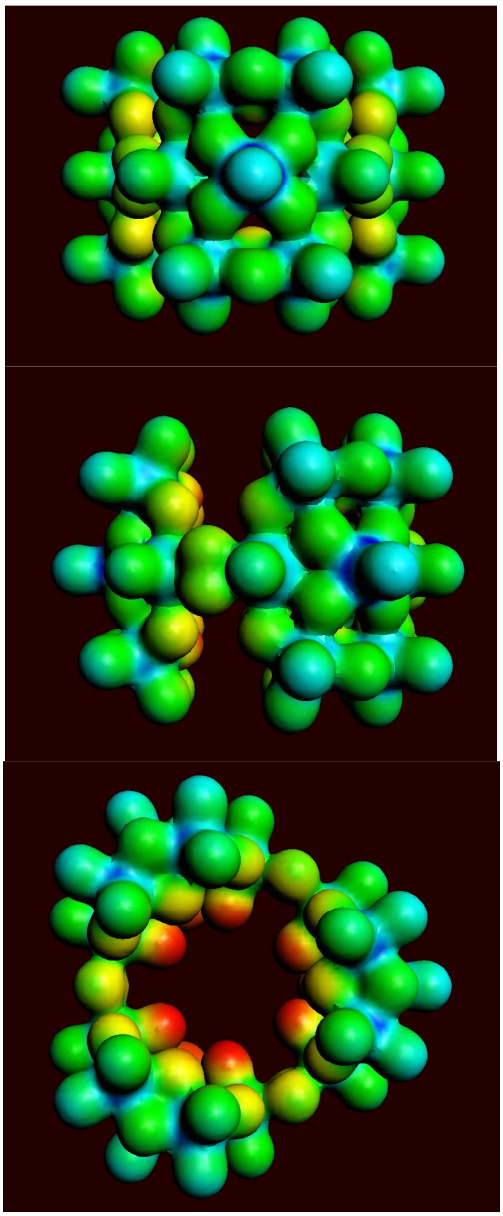


Figure S2. Electrostatic potential plot for the $H_{18}\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ species. Color code: blue ≈-0.21, green ≈-0.57 and red ≈-0.92.

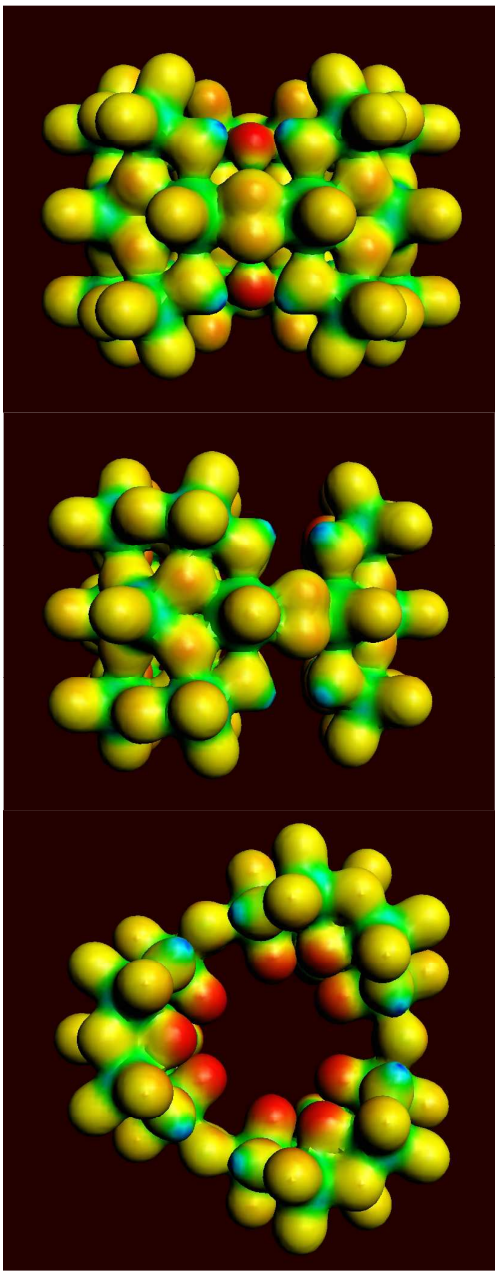
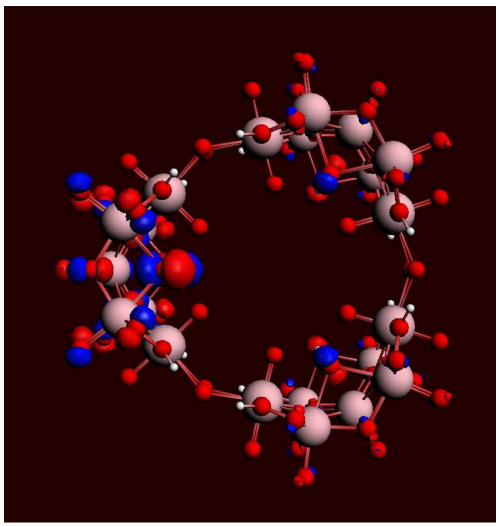
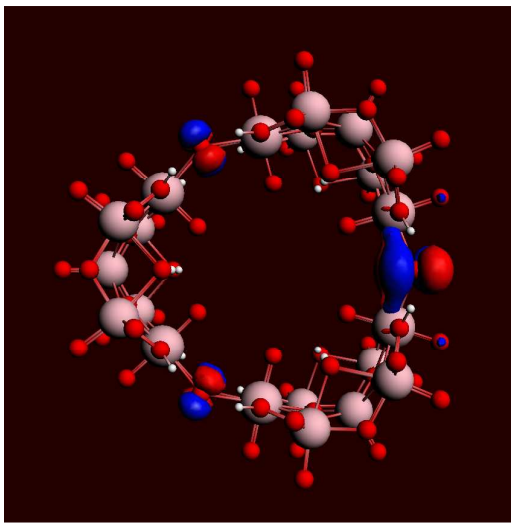


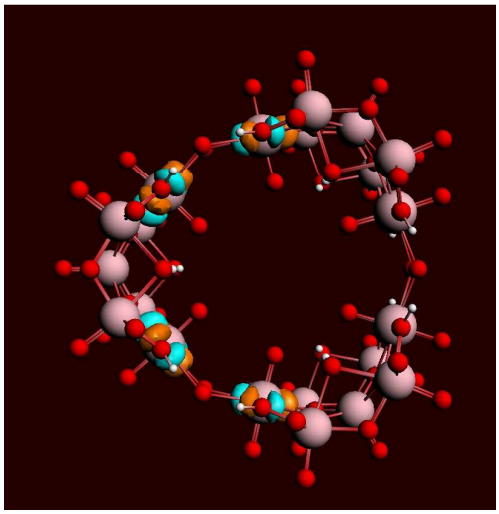
Figure S3. Selected molecular orbitals for the $H_{18}\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ species.



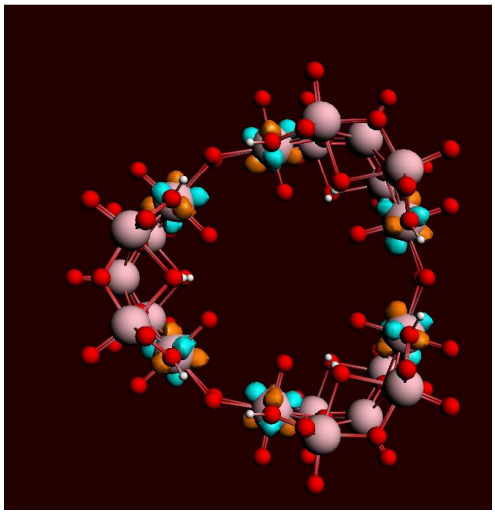
HOMO-3



HOMO

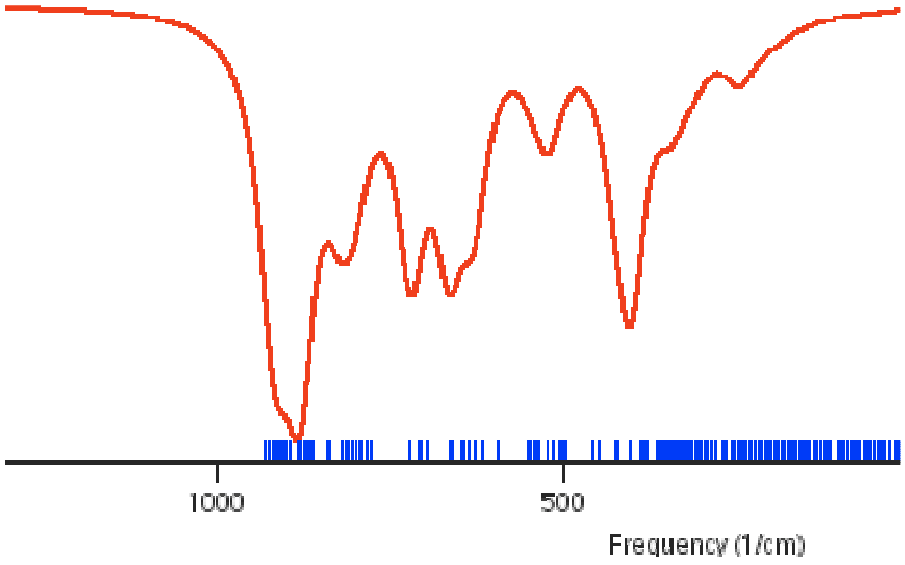


LUMO



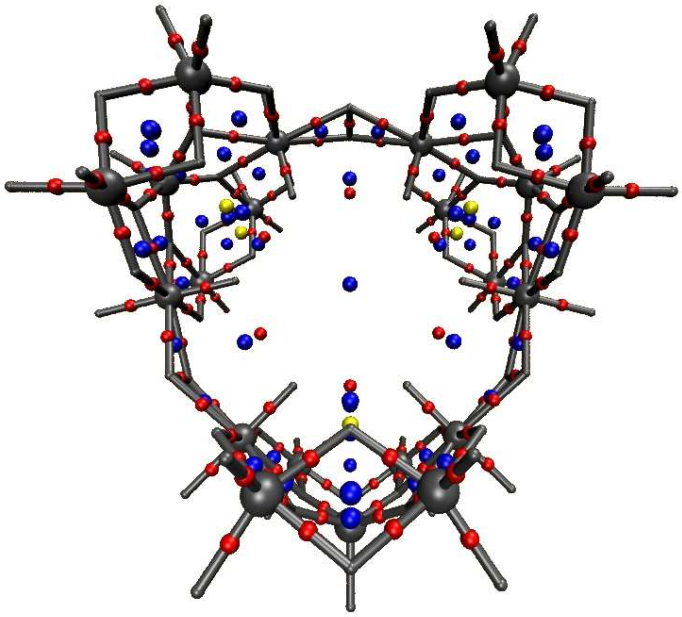
LUMO+21

Figure S4. IR spectra for the $H_{18}\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ species.



Frequency (cm^{-1})	Intensity (km/mole)	Assignment
404	1462	O_2 peroxide
425	997	tricoordinated oxo U-W-W
524	583	OH (W-OH-U) bridge
548	101	OH (W-OH-W) bridge + O (W-O-W) bridge OH (W-OH-U) bridge
629	1626	OH (W-OH-W) bridge
642	106	OH (W-OH-W) bridge
666	2152	OH (W-OH-W) bridge
721	1302	OH (W-OH-W) bridge + O (W-O-W) bridge
784	110	UO_2
801	167	OH (W-OH-U) bridge
806	365	OH (W-OH-U) bridge
821	582	OH (W-OH-W) bridge
873	321	$W{=}O_{terminal}$ + small cont. OH (W-OH-U) bridge
886	1192	$W{=}O_{terminal}$ + small cont. OH (W-OH-U) bridge
914	1712	$W{=}O_{terminal}$ + small cont. OH (W-OH-U) bridge
925	627	$W{=}O_{terminal}$ + small O-O peroxide contribution

Figure S5. Topological analysis of the electron density of the $\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ species. Critical point code: red (3,-1), blue (3,+1) and yellow (3,+3).



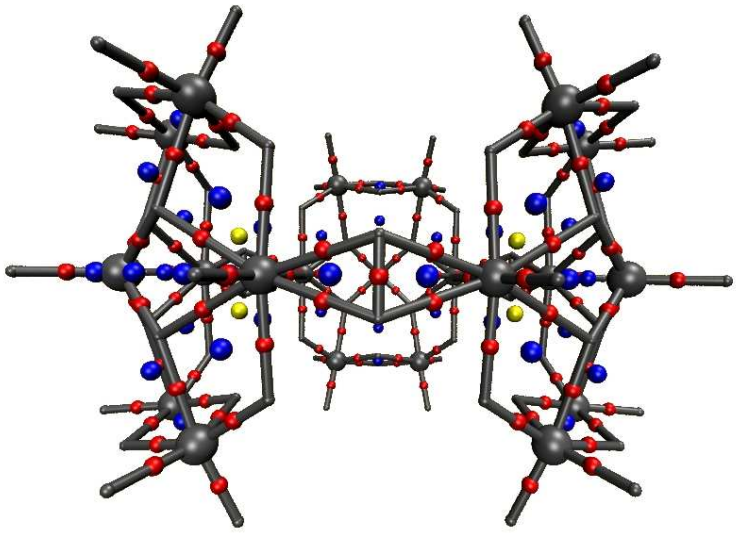


Table S4. Theoretical bond critical point properties for the $H_{18}\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ species. All values are expressed in atomic units.

Type	Location	ρ_b	$\nabla^2\rho_b$	G_b	V_b	E_b
Ring Critical Point	O_{uranyl}-O_{uranyl}	0.004200	0.015116	0.002929	-0.002078	0.000851
Bond Critical Point	O_{uranyl}-O_{uranyl}	0.004427	0.016481	0.003111	-0.002101	0.001010
Ring Critical Point	U-$(O_{peroxide})_2$	0.053501	0.283972	0.073120	-0.075246	-0.002126
Bond Critical Point	U-$O_{peroxide}$	0.069645	0.217782	0.066932	-0.079420	-0.012488
Bond Critical Point	$O_{peroxide}$-$O_{peroxide}$	0.270351	0.179379	0.214222	-0.383599	-0.169377

Figure S6. Electronic structure of $\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$. Only selected orbitals are presented for clarity. In parenthesis orbital symmetries. Energies in eV.

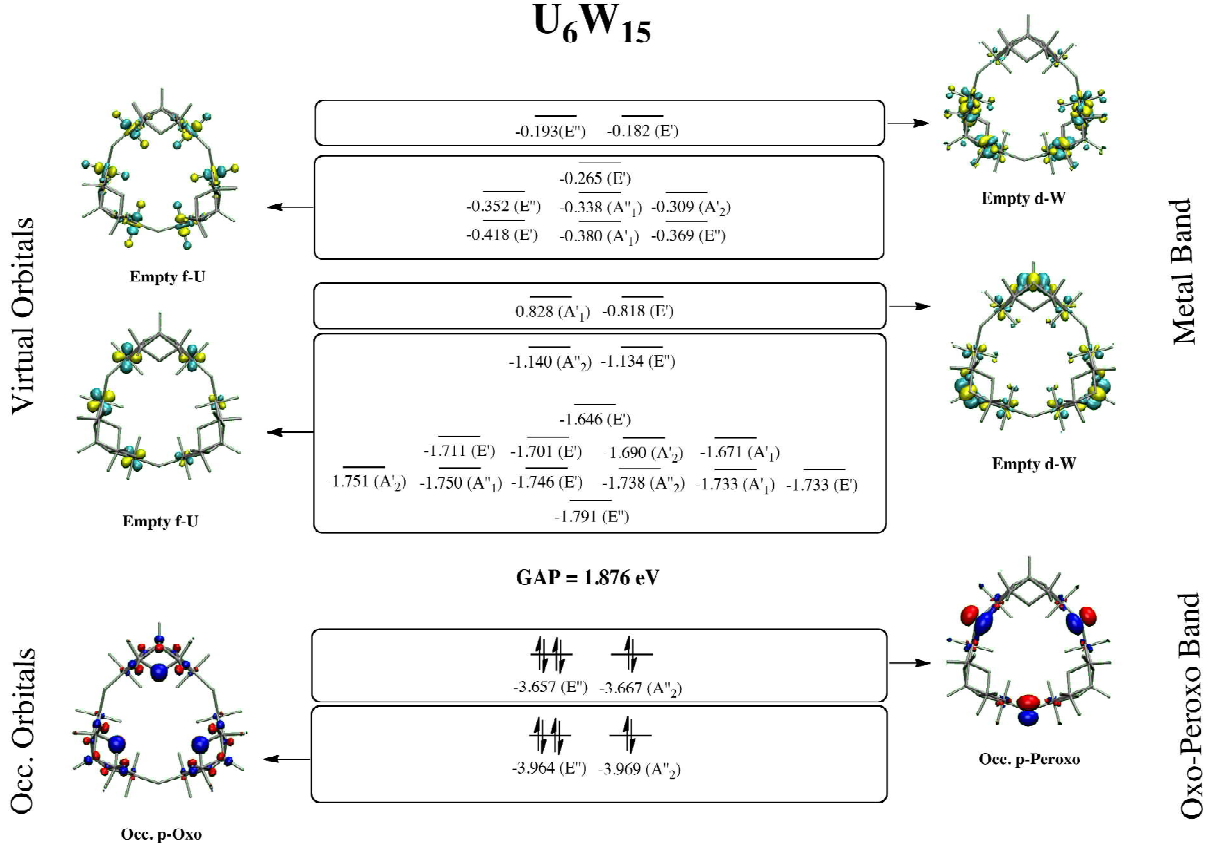


Figure S7. Fragment interactions in the electronic structure of $\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$. $[(UO_2)_2(O_2)]^{2+}$ fragment (left), $\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ (centre) and $[W_5O_{21}]^{12-}$ fragment (right). Only HOMO and LUMO for each fragment and selected orbitals in the

$\{[W_5O_{21}]_3[(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ are presented for clarity. In parenthesis orbital symmetries. Energies in eV.

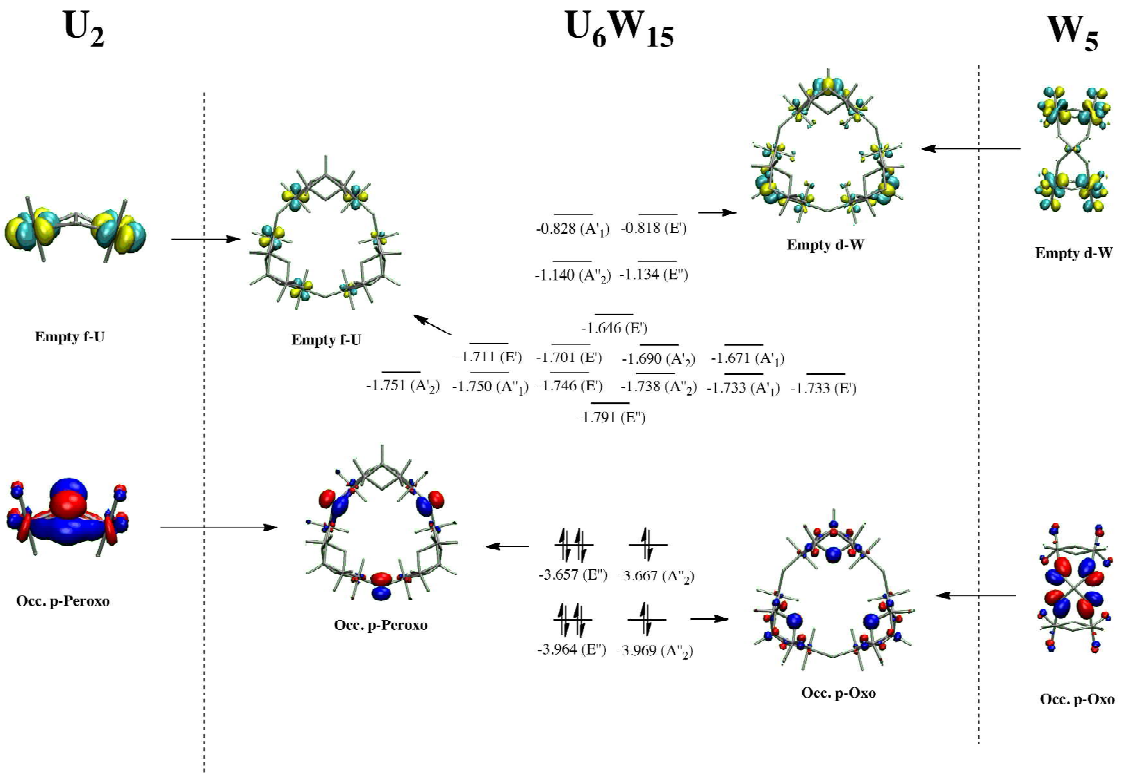
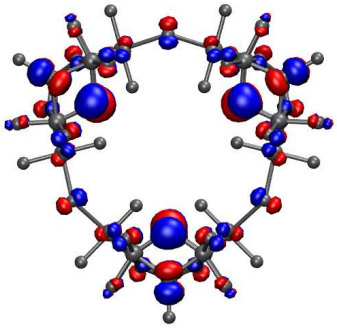
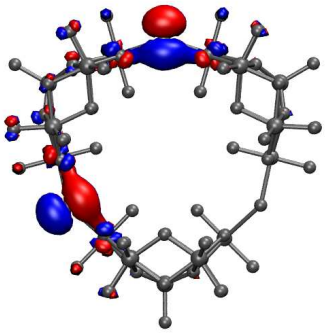


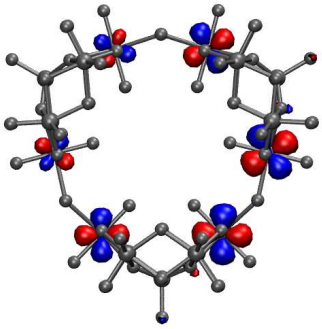
Figure S8. Selected molecular orbitals of $\{[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ at LB94 level of theory.



HOMO-3

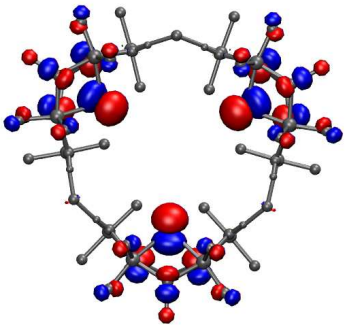


HOMO

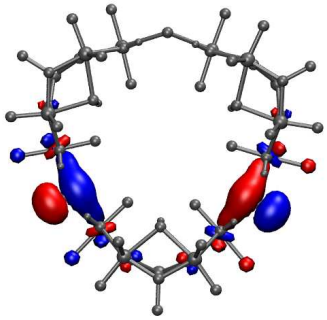


LUMO

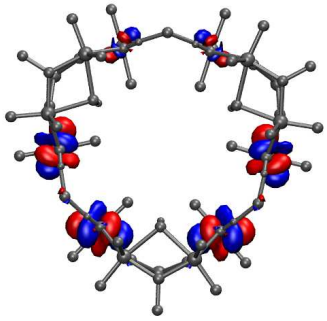
Figure S9. Selected molecular orbitals of $\{H_{18}[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ at LB94 level of theory.



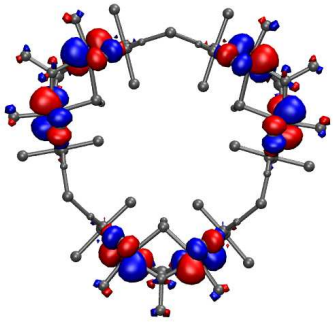
HOMO-3



HOMO

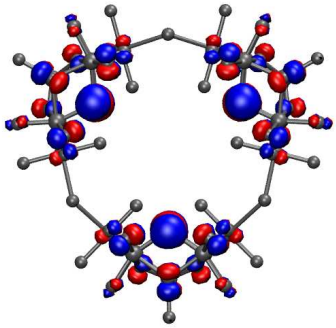


LUMO

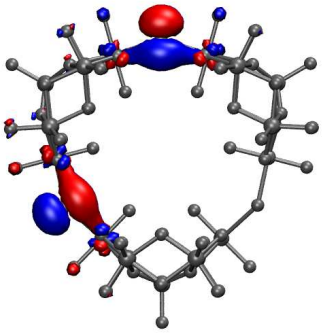


LUMO+21

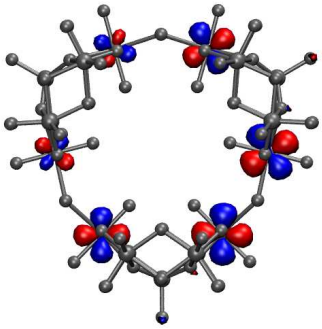
Figure S10. Selected molecular orbitals of $\{[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ at PBE level of theory.



HOMO-3

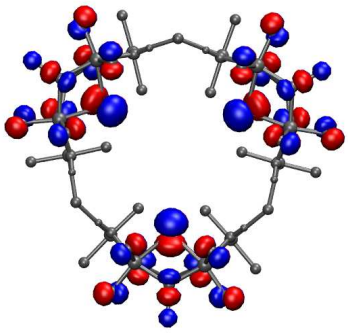


HOMO

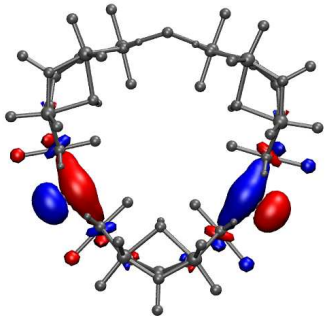


LUMO

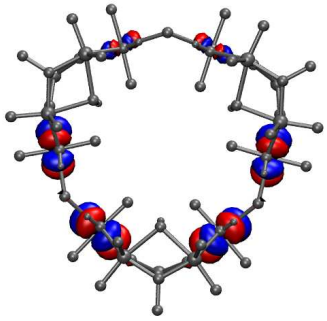
Figure S11. Selected molecular orbitals of $\{H_{18}[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ at PBE level of theory.



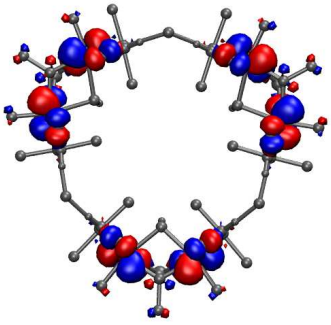
HOMO-3



HOMO

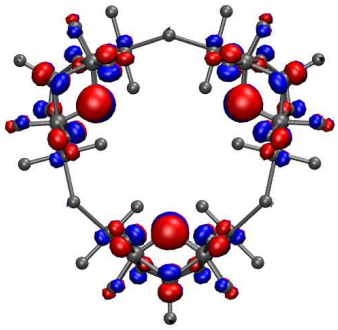


LUMO

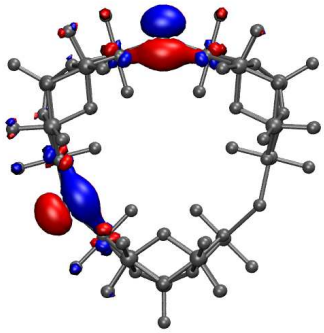


LUMO+21

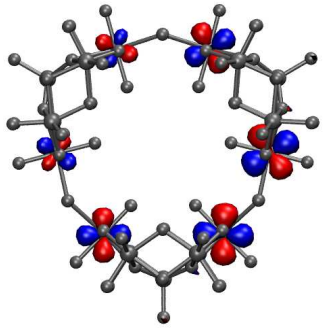
Figure S12. Selected molecular orbitals of $\{[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ at M06-L level of theory.



HOMO-3

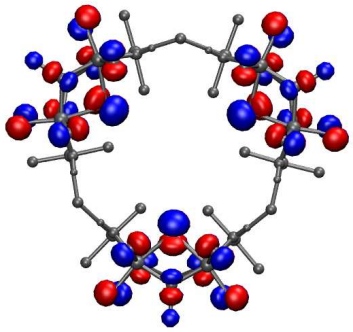


HOMO

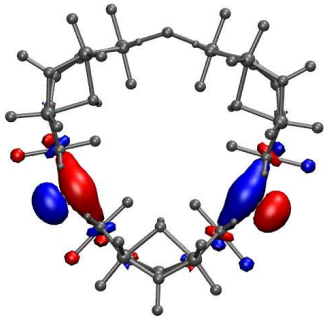


LUMO

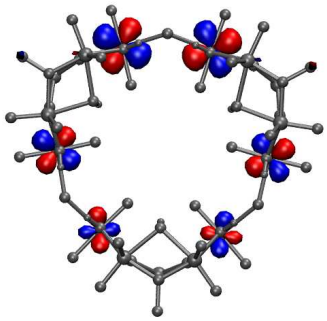
Figure S13. Selected molecular orbitals of $\{H_{18}[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ at M06-L level of theory.



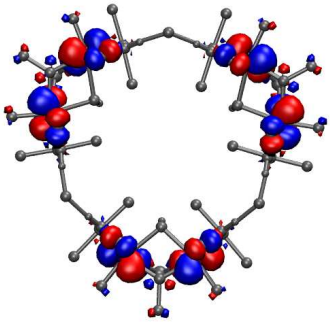
HOMO-3



HOMO



LUMO



LUMO+21

Table S5. Cartesian coordinates of $\{[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ optimized at M06-L level of theory.

U	4.078660	-2.728883	0.000000
U	0.323952	-4.896664	0.000000
U	-4.402612	-2.167781	0.000000
U	-4.402612	2.167781	0.000000
U	4.078660	2.728883	0.000000
U	0.323952	4.896664	0.000000
O	-2.667699	-1.679458	0.000000
O	-0.120604	-3.150024	0.000000
O	-6.189935	-2.640176	0.000000
O	-0.120604	3.150024	0.000000
O	2.562650	-4.438639	-0.724883
O	0.808508	-6.680729	0.000000
O	5.381427	-4.040553	0.000000
O	-6.189935	2.640176	0.000000
O	2.788303	1.470566	0.000000
O	-5.125299	0.000000	0.724883
O	2.562650	4.438639	0.724883
O	0.808508	6.680729	0.000000
O	2.788303	-1.470566	0.000000
O	-2.667699	1.679458	0.000000
O	5.381427	4.040553	0.000000
O	2.562650	4.438639	-0.724883
O	-5.125299	0.000000	-0.724883
O	2.562650	-4.438639	0.724883
W	-3.109423	-5.385678	0.000000
O	-3.952458	-4.239949	-1.225418
O	-1.695675	-5.542904	-1.225418
O	-3.952458	-4.239949	1.225418
O	-1.695675	-5.542904	1.225418
O	-3.999898	-6.928027	0.000000
W	-1.121208	-5.169191	-3.396829
W	-1.121208	-5.169191	3.396829
O	-1.957589	-3.390644	-2.992488
O	-3.105137	-5.378254	-3.705665
O	-0.993409	-6.981951	-3.520296
O	-0.563651	-4.725935	-5.044100
O	0.408473	-4.784691	-2.407944
O	0.408473	-4.784691	2.407944
O	-0.993409	-6.981951	3.520296
O	-1.957589	-3.390644	2.992488
O	-0.563651	-4.725935	5.044100
O	-3.105137	-5.378254	3.705665
W	-3.916047	-3.555590	-3.396829
W	-3.916047	-3.555590	3.396829
O	-4.347900	-2.038597	-2.407944
O	-5.549842	-4.351293	-3.520296
O	-3.810954	-2.851104	-5.044100
O	-4.347900	-2.038597	2.407944
O	-5.549842	-4.351293	3.520296
O	-3.810954	-2.851104	5.044100
O	3.939427	-2.746093	-2.407944

W	5.037255	-1.613601	-3.396829
O	6.210273	0.000000	-3.705665
O	3.915178	0.000000	-2.992488
O	6.543251	-2.630658	-3.520296
O	4.374606	-1.874831	-5.044100
W	5.037255	1.613601	-3.396829
O	3.939427	2.746093	-2.407944
O	6.543251	2.630658	-3.520296
O	4.374606	1.874831	-5.044100
O	5.648133	1.302955	-1.225418
W	6.218845	0.000000	0.000000
O	7.999797	0.000000	0.000000
O	5.648133	1.302955	1.225418
O	5.648133	-1.302955	1.225418
O	5.648133	-1.302955	-1.225418
W	5.037255	1.613601	3.396829
O	3.939427	2.746093	2.407944
O	6.210273	0.000000	3.705665
O	4.374606	1.874831	5.044100
O	6.543251	2.630658	3.520296
O	3.915178	0.000000	2.992488
W	5.037255	-1.613601	3.396829
O	6.543251	-2.630658	3.520296
O	4.374606	-1.874831	5.044100
O	3.939427	-2.746093	2.407944
O	0.408473	4.784691	-2.407944
W	-1.121208	5.169191	-3.396829
O	-1.957589	3.390644	-2.992488
O	-3.105137	5.378254	-3.705665
O	-0.993409	6.981951	-3.520296
O	-0.563651	4.725935	-5.044100
W	-3.916047	3.555590	-3.396829
O	-4.347900	2.038597	-2.407944
O	-5.549842	4.351293	-3.520296
O	-3.810954	2.851104	-5.044100
O	-3.952458	4.239949	-1.225418
W	-3.109423	5.385678	0.000000
O	-3.952458	4.239949	1.225418
O	-1.695675	5.542904	1.225418
O	-3.999898	6.928027	0.000000
O	-1.695675	5.542904	-1.225418
W	-3.916047	3.555590	3.396829
O	-4.347900	2.038597	2.407944
O	-1.957589	3.390644	2.992488
O	-3.810954	2.851104	5.044100
O	-5.549842	4.351293	3.520296
O	-3.105137	5.378254	3.705665
W	-1.121208	5.169191	3.396829
O	-0.563651	4.725935	5.044100
O	0.408473	4.784691	2.407944
O	-0.993409	6.981951	3.520296

Table S6. Cartesian coordinates of $\{H_{18}[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ optimized at M06-L level of theory.

U	-4.167349	2.818091	0.000000
U	-0.356864	5.018075	0.000000
U	4.524213	2.199984	0.000000
U	4.524213	-2.199984	0.000000
U	-4.167349	-2.818091	0.000000
U	-0.356864	-5.018075	0.000000
W	3.139653	5.438038	0.000000
W	4.247774	4.046687	3.412886
W	1.380647	5.702024	3.412886
W	-5.628421	1.655337	3.412886
W	-5.628421	-1.655337	3.412886
W	1.380647	5.702024	-3.412886
W	3.139653	-5.438038	0.000000
W	1.380647	-5.702024	3.412886
W	4.247774	-4.046687	3.412886
W	-6.279305	0.000000	0.000000
W	4.247774	4.046687	-3.412886
W	1.380647	-5.702024	-3.412886
W	4.247774	-4.046687	-3.412886
W	-5.628421	1.655337	-3.412886
W	-5.628421	-1.655337	-3.412886
O	2.769059	1.810590	0.000000
O	-4.197170	-2.774867	2.490800
O	0.183487	3.303370	0.000000
O	-6.998493	2.734755	3.306409
O	6.272139	2.629858	0.000000
O	4.501690	-2.247423	2.490800
O	2.079389	3.601608	-3.138691
O	-0.304520	5.022289	2.490800
O	3.986943	4.271489	-1.241714
O	0.183487	-3.303370	0.000000
O	1.705747	5.588539	-1.241714
O	1.130879	7.428250	3.306409
O	3.986943	-4.271489	-1.241714
O	2.079389	-3.601608	3.138691
O	-2.543898	4.406161	-0.729311
O	3.308769	5.730956	-3.628162
O	3.986943	-4.271489	1.241714
O	-5.692690	-1.317050	-1.241714
O	4.501690	2.247423	-2.490800
O	4.501690	2.247423	2.490800
O	1.130879	7.428250	-3.306409
O	-0.858546	6.746760	0.000000
O	-6.617538	0.000000	3.628162
O	1.705747	-5.588539	1.241714
O	2.079389	3.601608	3.138691
O	-5.413593	4.116903	0.000000
O	3.986943	4.271489	1.241714

O	-5.016923	-1.932955	5.022491
O	-8.014300	0.000000	0.000000
O	0.834473	-5.311260	5.022491
O	6.272139	-2.629858	0.000000
O	4.182450	-3.378305	5.022491
O	-0.304520	-5.022289	2.490800
O	4.501690	-2.247423	-2.490800
O	-5.692690	-1.317050	1.241714
O	-2.952546	-1.492780	0.000000
O	1.705747	5.588539	1.241714
O	5.867613	4.693495	3.306409
O	-5.692690	1.317050	1.241714
O	-5.692690	1.317050	-1.241714
O	4.182450	3.378305	5.022491
O	0.834473	5.311260	5.022491
O	-5.016923	1.932955	5.022491
O	5.087796	0.000000	0.729311
O	-6.617538	0.000000	-3.628162
O	0.834473	5.311260	-5.022491
O	1.130879	-7.428250	3.306409
O	-2.543898	-4.406161	0.729311
O	-6.998493	-2.734755	3.306409
O	-0.858546	-6.746760	0.000000
O	-2.952546	1.492780	0.000000
O	-4.197170	2.774867	-2.490800
O	5.867613	-4.693495	3.306409
O	-4.158778	0.000000	-3.138691
O	2.079389	-3.601608	-3.138691
O	5.867613	4.693495	-3.306409
O	4.182450	3.378305	-5.022491
O	4.007150	-6.940588	0.000000
O	-6.998493	2.734755	-3.306409
O	2.769059	-1.810590	0.000000
O	-4.197170	-2.774867	-2.490800
O	-0.304520	5.022289	-2.490800
O	1.705747	-5.588539	-1.241714
O	-0.304520	-5.022289	-2.490800
O	-5.413593	-4.116903	0.000000
O	5.867613	-4.693495	-3.306409
O	4.182450	-3.378305	-5.022491
O	-6.998493	-2.734755	-3.306409
O	3.308769	-5.730956	-3.628162
O	-2.543898	-4.406161	-0.729311
O	1.130879	-7.428250	-3.306409
O	4.007150	6.940588	0.000000
O	3.308769	-5.730956	3.628162
O	5.087796	0.000000	-0.729311
O	3.308769	5.730956	3.628162
O	-2.543898	4.406161	0.729311
O	-4.158778	0.000000	3.138691
O	-4.197170	2.774867	2.490800

O	0.834473	-5.311260	-5.022491
O	-5.016923	1.932955	-5.022491
O	-5.016923	-1.932955	-5.022491
H	-3.825976	0.000000	2.230644
H	-3.825976	0.000000	-2.230644
H	-3.635419	-3.285679	-3.084438
H	-1.027772	-4.791204	-3.084438
H	-3.635419	-3.285679	3.084438
H	-1.027772	-4.791204	3.084438
H	-3.635419	3.285679	-3.084438
H	-3.635419	3.285679	3.084438
H	-1.027772	4.791204	3.084438
H	-1.027772	4.791204	-3.084438
H	1.912988	3.313392	-2.230644
H	1.912988	3.313392	2.230644
H	4.663191	1.505525	3.084438
H	4.663191	1.505525	-3.084438
H	4.663191	-1.505525	3.084438
H	4.663191	-1.505525	-3.084438
H	1.912988	-3.313392	-2.230644
H	1.912988	-3.313392	2.230644

Table S7. Charges of $\{[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ at LB94 level of theory.

Atom	Mulliken	MDC-q
U	3.0027	3.577991
U	3.0027	3.577991
U	3.0027	3.577991
U	3.0027	3.577991
U	3.0027	3.577991
U	3.0027	3.577991
O	-0.8585	-0.976287
O	-0.8585	-0.976287
O	-0.9819	-1.139092
O	-0.8585	-0.976287
O	-0.7781	-0.839829
O	-0.9819	-1.139092
O	-0.9819	-1.139092
O	-0.9819	-1.139092
O	-0.8585	-0.976287
O	-0.7781	-0.839829
O	-0.7781	-0.839829
O	-0.9819	-1.139092
O	-0.8585	-0.976287
O	-0.8585	-0.976287
O	-0.9819	-1.139092
O	-0.7781	-0.839829
O	-0.7781	-0.839829
O	-0.7781	-0.839829
W	2.6387	2.380741
O	-1.2056	-1.133517
O	-1.2056	-1.133517
O	-1.2056	-1.133517
O	-1.2056	-1.133517
O	-1.0827	-0.965553
W	2.6384	2.355125
W	2.6384	2.355125
O	-1.1661	-1.005319
O	-1.1913	-1.124632
O	-1.1072	-1.087680
O	-1.0851	-1.080203
O	-1.1428	-1.153938
O	-1.1428	-1.153938
O	-1.1072	-1.087680
O	-1.1661	-1.005319
O	-1.0851	-1.080203
O	-1.1913	-1.124632
W	2.6384	2.355125
W	2.6384	2.355125
O	-1.1428	-1.153938

O	-1.1072	-1.087680
O	-1.0851	-1.080203
O	-1.1428	-1.153938
O	-1.1072	-1.087680
O	-1.0851	-1.080203
O	-1.1428	-1.153938
W	2.6384	2.355125
O	-1.1913	-1.124632
O	-1.1661	-1.005319
O	-1.1072	-1.087680
O	-1.0851	-1.080203
W	2.6384	2.355125
O	-1.1428	-1.153938
O	-1.1072	-1.087680
O	-1.0851	-1.080203
O	-1.2056	-1.133517
W	2.6387	2.380741
O	-1.0827	-0.965553
O	-1.2056	-1.133517
O	-1.2056	-1.133517
O	-1.2056	-1.133517
W	2.6384	2.355125
O	-1.1428	-1.153938
O	-1.1913	-1.124632
O	-1.0851	-1.080203
O	-1.1072	-1.087680
O	-1.1661	-1.005319
W	2.6384	2.355125
O	-1.1072	-1.087680
O	-1.0851	-1.080203
O	-1.1428	-1.153938
O	-1.1428	-1.153938
W	2.6384	2.355125
O	-1.1661	-1.005319
O	-1.1913	-1.124632
O	-1.1072	-1.087680
O	-1.0851	-1.080203
W	2.6384	2.355125
O	-1.1428	-1.153938
O	-1.1072	-1.087680
O	-1.0851	-1.080203
O	-1.2056	-1.133517
W	2.6387	2.380741
O	-1.2056	-1.133517
O	-1.2056	-1.133517
O	-1.0827	-0.965553
O	-1.2056	-1.133517
W	2.6384	2.355125
O	-1.1428	-1.153938
O	-1.1661	-1.005319
O	-1.0851	-1.080203

O	-1.1072	-1.087680
O	-1.1913	-1.124632
W	2.6384	2.355125
O	-1.0851	-1.080203
O	-1.1428	-1.153938
O	-1.1072	-1.087680

Table S8. Charges of $\{H_{18}[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ at LB94 level of theory.

Atom	Mulliken	MDC-q
U	3.1368	3.529820
U	3.1368	3.529820
U	3.1368	3.529820
U	3.1368	3.529820
U	3.1368	3.529820
U	3.1368	3.529820
W	2.7694	2.363599
W	2.7890	2.301287
W	2.7890	2.301287
W	2.7890	2.301287
W	2.7890	2.301287
W	2.7890	2.301287
W	2.7694	2.363599
W	2.7890	2.301287
W	2.7890	2.301287
W	2.7694	2.363599
W	2.7890	2.301287
W	2.7890	2.301287
W	2.7890	2.301287
W	2.7890	2.301287
W	2.7890	2.301287
O	-0.7965	-0.882014
O	-1.0356	-1.240632
O	-0.7965	-0.882014
O	-0.8929	-0.799949
O	-0.8270	-0.888600
O	-1.0356	-1.240632
O	-1.0724	-0.984222
O	-1.0356	-1.240632
O	-1.2379	-1.143278
O	-0.7965	-0.882014
O	-1.2379	-1.143278
O	-0.8929	-0.799949
O	-1.2379	-1.143278
O	-1.0724	-0.984222
O	-0.7553	-0.838405
O	-1.1155	-0.990103
O	-1.2379	-1.143278
O	-1.2379	-1.143278
O	-1.0356	-1.240632
O	-1.0356	-1.240632
O	-0.8929	-0.799949

0	-0.8270	-0.888600
0	-1.1155	-0.990103
0	-1.2379	-1.143278
0	-1.0724	-0.984222
0	-0.8270	-0.888600
0	-1.2379	-1.143278
0	-0.8895	-0.793499
0	-0.9140	-0.723746
0	-0.8895	-0.793499
0	-0.8270	-0.888600
0	-0.8895	-0.793499
0	-1.0356	-1.240632
0	-1.0356	-1.240632
0	-1.2379	-1.143278
0	-0.7965	-0.882014
0	-1.2379	-1.143278
0	-0.8929	-0.799949
0	-1.2379	-1.143278
0	-1.2379	-1.143278
0	-0.8895	-0.793499
0	-0.8895	-0.793499
0	-0.8895	-0.793499
0	-0.7553	-0.838405
0	-1.1155	-0.990103
0	-0.8895	-0.793499
0	-0.8929	-0.799949
0	-0.7553	-0.838405
0	-0.8929	-0.799949
0	-0.8270	-0.888600
0	-0.7965	-0.882014
0	-1.0356	-1.240632
0	-0.8929	-0.799949
0	-1.0724	-0.984222
0	-1.0724	-0.984222
0	-0.8929	-0.799949
0	-0.8895	-0.793499
0	-0.9140	-0.723746
0	-0.8929	-0.799949
0	-0.7965	-0.882014
0	-1.0356	-1.240632
0	-1.0356	-1.240632
0	-1.2379	-1.143278
0	-1.0356	-1.240632
0	-0.8270	-0.888600
0	-0.8929	-0.799949
0	-0.8895	-0.793499
0	-0.8929	-0.799949
0	-1.1155	-0.990103
0	-0.7553	-0.838405
0	-0.8929	-0.799949
0	-0.9140	-0.723746

O	-1.1155	-0.990103
O	-0.7553	-0.838405
O	-1.1155	-0.990103
O	-0.7553	-0.838405
O	-1.0724	-0.984222
O	-1.0356	-1.240632
O	-0.8895	-0.793499
O	-0.8895	-0.793499
O	-0.8895	-0.793499
H	0.3850	0.487944
H	0.3850	0.487944
H	0.3256	0.548899
H	0.3256	0.548899
H	0.3256	0.548899
H	0.3256	0.548899
H	0.3256	0.548899
H	0.3256	0.548899
H	0.3256	0.548899
H	0.3256	0.548899
H	0.3850	0.487944
H	0.3850	0.487944
H	0.3256	0.548899
H	0.3256	0.548899
H	0.3256	0.548899
H	0.3256	0.548899
H	0.3850	0.487944
H	0.3850	0.487944

Table S9. Charges of $\{[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ at PBE level of theory.

Atom	Mulliken	MDC-q
U	2.2551	2.877352
U	2.2551	2.877352
U	2.2551	2.877352
U	2.2551	2.877352
U	2.2551	2.877352
U	2.2551	2.877352
O	-0.7725	-0.842998
O	-0.7725	-0.842998
O	-0.8807	-1.010422
O	-0.7725	-0.842998
O	-0.6038	-0.702276
O	-0.8807	-1.010422
O	-0.8807	-1.010422
O	-0.8807	-1.010422
O	-0.7725	-0.842998
O	-0.6038	-0.702276
O	-0.6038	-0.702276
O	-0.8807	-1.010422
O	-0.7725	-0.842998
O	-0.7725	-0.842998
O	-0.8807	-1.010422
O	-0.6038	-0.702276
O	-0.6038	-0.702276
O	-0.6038	-0.702276
W	2.4913	2.111989
O	-1.0470	-0.972270
O	-1.0470	-0.972270
O	-1.0470	-0.972270
O	-1.0470	-0.972270
O	-1.0053	-0.900019
W	2.2467	1.974490
W	2.2467	1.974490
O	-1.0391	-0.868319
O	-1.0626	-1.008476
O	-1.0326	-1.025574
O	-0.9953	-1.005549
O	-0.9914	-0.996519
O	-0.9914	-0.996519
O	-1.0326	-1.025574

O	-1.0391	-0.868319
O	-0.9953	-1.005549
O	-1.0626	-1.008476
W	2.2467	1.974490
W	2.2467	1.974490
O	-0.9914	-0.996519
O	-1.0326	-1.025574
O	-0.9953	-1.005549
O	-0.9914	-0.996519
O	-1.0326	-1.025574
O	-0.9953	-1.005549
O	-0.9914	-0.996519
W	2.2467	1.974490
O	-1.0626	-1.008476
O	-1.0391	-0.868319
O	-1.0326	-1.025574
O	-0.9953	-1.005549
W	2.2467	1.974490
O	-0.9914	-0.996519
O	-1.0326	-1.025574
O	-0.9953	-1.005549
O	-1.0470	-0.972270
W	2.4913	2.111989
O	-1.0053	-0.900019
O	-1.0470	-0.972270
O	-1.0470	-0.972270
O	-1.0470	-0.972270
W	2.2467	1.974490
O	-0.9914	-0.996519
O	-1.0626	-1.008476
O	-0.9953	-1.005549
O	-1.0326	-1.025574
O	-1.0391	-0.868319
W	2.2467	1.974490
O	-1.0326	-1.025574
O	-0.9953	-1.005549
O	-0.9914	-0.996519
O	-0.9914	-0.996519
W	2.2467	1.974490
O	-1.0391	-0.868319
O	-1.0626	-1.008476
O	-1.0326	-1.025574
O	-0.9953	-1.005549
W	2.2467	1.974490
O	-0.9914	-0.996519
O	-1.0326	-1.025574
O	-0.9953	-1.005549
O	-1.0470	-0.972270
W	2.4913	2.111989
O	-1.0470	-0.972270
O	-1.0470	-0.972270

O	-1.0053	-0.900019
O	-1.0470	-0.972270
W	2.2467	1.974490
O	-0.9914	-0.996519
O	-1.0391	-0.868319
O	-0.9953	-1.005549
O	-1.0326	-1.025574
O	-1.0626	-1.008476
W	2.2467	1.974490
O	-0.9953	-1.005549
O	-0.9914	-0.996519
O	-1.0326	-1.025574

Table S10. Charges of $\{H_{18}[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ at PBE level of theory.

Atom	Mulliken	MDC-q
U	2.4719	2.914515
U	2.4719	2.914515
U	2.4719	2.914515
U	2.4719	2.914515
U	2.4719	2.914515
U	2.4719	2.914515
W	2.6630	2.151626
W	2.4388	1.985457
W	2.4388	1.985457
W	2.4388	1.985457
W	2.4388	1.985457
W	2.4388	1.985457
W	2.6630	2.151626
W	2.4388	1.985457
W	2.4388	1.985457
W	2.6630	2.151626
W	2.4388	1.985457
W	2.4388	1.985457
W	2.4388	1.985457
W	2.4388	1.985457
W	2.4388	1.985457
O	-0.7090	-0.758274
O	-0.8472	-1.053669
O	-0.7090	-0.758274
O	-0.8364	-0.738443
O	-0.7379	-0.758247
O	-0.8472	-1.053669
O	-0.9095	-0.797274
O	-0.8472	-1.053669
O	-1.0879	-1.022134
O	-0.7090	-0.758274
O	-1.0879	-1.022134
O	-0.8364	-0.738443
O	-1.0879	-1.022134
O	-0.9095	-0.797274
O	-0.5921	-0.718022

0	-1.0011	-0.881712
0	-1.0879	-1.022134
0	-1.0879	-1.022134
0	-0.8472	-1.053669
0	-0.8472	-1.053669
0	-0.8364	-0.738443
0	-0.7379	-0.758247
0	-1.0011	-0.881712
0	-1.0879	-1.022134
0	-0.9095	-0.797274
0	-0.7379	-0.758247
0	-1.0879	-1.022134
0	-0.8274	-0.740985
0	-0.8535	-0.672116
0	-0.8274	-0.740985
0	-0.7379	-0.758247
0	-0.8274	-0.740985
0	-0.8472	-1.053669
0	-0.8472	-1.053669
0	-1.0879	-1.022134
0	-0.7090	-0.758274
0	-1.0879	-1.022134
0	-0.8364	-0.738443
0	-1.0879	-1.022134
0	-1.0879	-1.022134
0	-0.8274	-0.740985
0	-0.8274	-0.740985
0	-0.8274	-0.740985
0	-0.5921	-0.718022
0	-1.0011	-0.881712
0	-0.8274	-0.740985
0	-0.8364	-0.738443
0	-0.5921	-0.718022
0	-0.8364	-0.738443
0	-0.7379	-0.758247
0	-0.7090	-0.758274
0	-0.8472	-1.053669
0	-0.8364	-0.738443
0	-0.9095	-0.797274
0	-0.9095	-0.797274
0	-0.8364	-0.738443
0	-0.8274	-0.740985
0	-0.8535	-0.672116
0	-0.8364	-0.738443
0	-0.7090	-0.758274
0	-0.8472	-1.053669
0	-0.8472	-1.053669
0	-1.0879	-1.022134
0	-0.8472	-1.053669
0	-0.7379	-0.758247
0	-0.8364	-0.738443

O	-0.8274	-0.740985
O	-0.8364	-0.738443
O	-1.0011	-0.881712
O	-0.5921	-0.718022
O	-0.8364	-0.738443
O	-0.8535	-0.672116
O	-1.0011	-0.881712
O	-0.5921	-0.718022
O	-1.0011	-0.881712
O	-0.5921	-0.718022
O	-0.9095	-0.797274
O	-0.8472	-1.053669
O	-0.8274	-0.740985
O	-0.8274	-0.740985
O	-0.8274	-0.740985
H	0.3483	0.376749
H	0.3483	0.376749
H	0.2724	0.511029
H	0.2724	0.511029
H	0.2724	0.511029
H	0.2724	0.511029
H	0.2724	0.511029
H	0.2724	0.511029
H	0.2724	0.511029
H	0.2724	0.511029
H	0.3483	0.376749
H	0.3483	0.376749
H	0.2724	0.511029
H	0.2724	0.511029
H	0.2724	0.511029
H	0.2724	0.511029
H	0.3483	0.376749
H	0.3483	0.376749

Table S11. Charges of $\{[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{30-}$ at M06-L level of theory.

Atom	Mulliken	MDC-q
U	2.4457	3.109666
U	2.4457	3.109666
U	2.4457	3.109666
U	2.4457	3.109666
U	2.4457	3.109666
U	2.4457	3.109666
O	-0.7928	-0.872782
O	-0.7928	-0.872782
O	-0.9111	-1.012250
O	-0.7928	-0.872782
O	-0.6090	-0.757569
O	-0.9111	-1.012250
O	-0.9111	-1.012250
O	-0.9111	-1.012250
O	-0.7928	-0.872782
O	-0.6090	-0.757569
O	-0.6090	-0.757569
O	-0.9111	-1.012250
O	-0.7928	-0.872782
O	-0.7928	-0.872782
O	-0.9111	-1.012250
O	-0.6090	-0.757569
O	-0.6090	-0.757569
O	-0.6090	-0.757569
W	2.7636	2.233018
O	-1.1325	-1.044810
O	-1.1325	-1.044810
O	-1.1325	-1.044810
O	-1.1325	-1.044810
O	-1.0626	-0.902392
W	2.5877	2.176909
W	2.5877	2.176909
O	-1.1556	-0.969125

O	-1.1788	-1.071206
O	-1.1187	-1.076284
O	-1.0853	-1.035060
O	-1.0757	-1.066779
O	-1.0757	-1.066779
O	-1.1187	-1.076284
O	-1.1556	-0.969125
O	-1.0853	-1.035060
O	-1.1788	-1.071206
W	2.5877	2.176909
W	2.5877	2.176909
O	-1.0757	-1.066779
O	-1.1187	-1.076284
O	-1.0853	-1.035060
O	-1.0757	-1.066779
O	-1.1187	-1.076284
O	-1.0853	-1.035060
O	-1.0757	-1.066779
W	2.5877	2.176909
O	-1.1788	-1.071206
O	-1.1556	-0.969125
O	-1.1187	-1.076284
O	-1.0853	-1.035060
W	2.5877	2.176909
O	-1.0757	-1.066779
O	-1.1187	-1.076284
O	-1.0853	-1.035060
O	-1.1325	-1.044810
W	2.7636	2.233018
O	-1.0626	-0.902392
O	-1.1325	-1.044810
O	-1.1325	-1.044810
O	-1.1325	-1.044810
W	2.5877	2.176909
O	-1.0757	-1.066779
O	-1.1788	-1.071206
O	-1.0853	-1.035060
O	-1.1187	-1.076284
O	-1.1556	-0.969125
W	2.5877	2.176909
O	-1.1187	-1.076284
O	-1.0853	-1.035060
O	-1.0757	-1.066779
O	-1.0757	-1.066779
W	2.5877	2.176909
O	-1.1556	-0.969125
O	-1.1788	-1.071206
O	-1.1187	-1.076284
O	-1.0853	-1.035060
W	2.5877	2.176909
O	-1.0757	-1.066779

O	-1.1187	-1.076284
O	-1.0853	-1.035060
O	-1.1325	-1.044810
W	2.7636	2.233018
O	-1.1325	-1.044810
O	-1.1325	-1.044810
O	-1.0626	-0.902392
O	-1.1325	-1.044810
W	2.5877	2.176909
O	-1.0757	-1.066779
O	-1.1556	-0.969125
O	-1.0853	-1.035060
O	-1.1187	-1.076284
O	-1.1788	-1.071206
W	2.5877	2.176909
O	-1.0853	-1.035060
O	-1.0757	-1.066779
O	-1.1187	-1.076284

Table S12. Charges of $\{H_{18}[(W_5O_{21})_3][(U^{VI}O_2)_2(\mu\text{-}O_2)]_3\}^{12-}$ at M06-L level of theory.

Atom	Mulliken	MDC-q
U	2.5980	3.211002
U	2.5980	3.211002
U	2.5980	3.211002
U	2.5980	3.211002
U	2.5980	3.211002
U	2.5980	3.211002
W	2.9511	2.248540
W	2.7329	2.152285
W	2.7329	2.152285
W	2.7329	2.152285
W	2.7329	2.152285
W	2.7329	2.152285
W	2.9511	2.248540
W	2.7329	2.152285
W	2.7329	2.152285
W	2.9511	2.248540
W	2.7329	2.152285
W	2.7329	2.152285
W	2.7329	2.152285
W	2.7329	2.152285
W	2.7329	2.152285
O	-0.7278	-0.812804
O	-0.8504	-1.111774
O	-0.7278	-0.812804
O	-0.9175	-0.776948
O	-0.7734	-0.752904
O	-0.8504	-1.111774
O	-0.9326	-0.875854
O	-0.8504	-1.111774
O	-1.1718	-1.117797

0	-0.7278	-0.812804
0	-1.1718	-1.117797
0	-0.9175	-0.776948
0	-1.1718	-1.117797
0	-0.9326	-0.875854
0	-0.5960	-0.818061
0	-1.1313	-0.944145
0	-1.1718	-1.117797
0	-1.1718	-1.117797
0	-0.8504	-1.111774
0	-0.8504	-1.111774
0	-0.9175	-0.776948
0	-0.7734	-0.752904
0	-1.1313	-0.944145
0	-1.1718	-1.117797
0	-0.9326	-0.875854
0	-0.7734	-0.752904
0	-1.1718	-1.117797
0	-0.9117	-0.767882
0	-0.9084	-0.667398
0	-0.9117	-0.767882
0	-0.7734	-0.752904
0	-0.9117	-0.767882
0	-0.8504	-1.111774
0	-0.8504	-1.111774
0	-1.1718	-1.117797
0	-0.7278	-0.812804
0	-1.1718	-1.117797
0	-0.9175	-0.776948
0	-1.1718	-1.117797
0	-1.1718	-1.117797
0	-0.9117	-0.767882
0	-0.9117	-0.767882
0	-0.9117	-0.767882
0	-0.5960	-0.818061
0	-1.1313	-0.944145
0	-0.9117	-0.767882
0	-0.9175	-0.776948
0	-0.5960	-0.818061
0	-0.9175	-0.776948
0	-0.7734	-0.752904
0	-0.7278	-0.812804
0	-0.8504	-1.111774
0	-0.9175	-0.776948
0	-0.9326	-0.875854
0	-0.9326	-0.875854
0	-0.9175	-0.776948
0	-0.9117	-0.767882
0	-0.9084	-0.667398
0	-0.9175	-0.776948
0	-0.7278	-0.812804

O	-0.8504	-1.111774
O	-0.8504	-1.111774
O	-1.1718	-1.117797
O	-0.8504	-1.111774
O	-0.7734	-0.752904
O	-0.9175	-0.776948
O	-0.9117	-0.767882
O	-0.9175	-0.776948
O	-1.1313	-0.944145
O	-0.5960	-0.818061
O	-0.9175	-0.776948
O	-0.9084	-0.667398
O	-1.1313	-0.944145
O	-0.5960	-0.818061
O	-1.1313	-0.944145
O	-0.5960	-0.818061
O	-0.9326	-0.875854
O	-0.8504	-1.111774
O	-0.9117	-0.767882
O	-0.9117	-0.767882
O	-0.9117	-0.767882
H	0.3244	0.432636
H	0.3244	0.432636
H	0.2273	0.506896
H	0.2273	0.506896
H	0.2273	0.506896
H	0.2273	0.506896
H	0.2273	0.506896
H	0.2273	0.506896
H	0.2273	0.506896
H	0.2273	0.506896
H	0.3244	0.432636
H	0.3244	0.432636
H	0.2273	0.506896
H	0.2273	0.506896
H	0.2273	0.506896
H	0.2273	0.506896
H	0.3244	0.432636
H	0.3244	0.432636