Electronic Supplementary Material (ESI) for Dalton Transactions

Exploring the Rotational Isomerism in Non–Classical Wells–Dawson Anions $\{W_{18}X\}$: A Combined Theoretical and Mass Spectrometry Study

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Table S1. Relative energies in kcal mol^{-1} with respect to the most stable isomer for $[W_{18}O_{54}(XO_4)_2]^{q-}$ where X= As, P, S and M=W, compared to $[W_{18}O_{54}]$ box. Highlighted in grey the observed isomers.

Isomer	Symmetry	[a]$[W_{18}O_{54}]$	[b]$[W_{18}O_{54}(AsO_4)_2]^{6-}$	[b]$[W_{18}O_{54}(PO_4)_2]^{6-}$	[b]$[W_{18}O_{54}(SO_4)_2]^{4-}$
α	D_{3h}	0.3	1.1	0.0	0.0
β	C_{3v}	3.3	2.4	5.2	3.6
γ	D_{3h}	0.0	0.6	5.4	3.7
α*	D_{3d}	3.3	16.5	22.1	16.7
β*	C_{3v}	0.1	6.5	12.6	7.0
γ*	D_{3d}	3.3	0.0	7.5	1.9

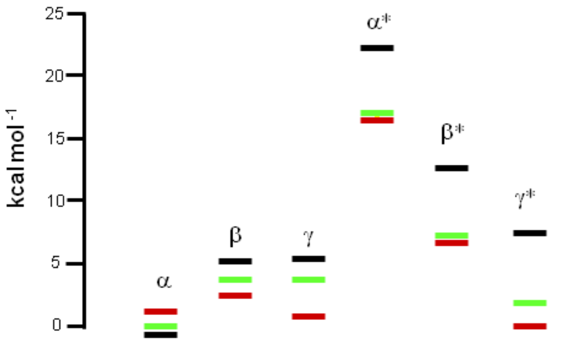

Fig. S1 Graphical representation of relative energies with respect to the most stable isomer for $[W_{18}O_{54}(XO_4)_2]^{q-}$ where X= As (red), P (black) and S (green).

Table S2. Common isonuclear species assigned from the fragmentation of α isomer $((n\text{-}C_3H_7)_4N)_4[\alpha\text{-}H_4W_{19}O_{62}]^{2-}$ (*m/z* 2617.4) and γ* isomer $((n\text{-}C_3H_7)_4N)_4[\gamma^*\text{-}H_4W_{19}O_{62}]^{2-}$ (*m/z* 2617.4). The isonuclear fragments are the same for both Wells-Dawson isomers.

m/z	Peak Assignment	α isomer	γ* isomer
355.9	$[W_3O_{10}]^{2-}$	·····	·····
471.9	$[W_4O_{13}]^{2-}$	✓	✓
480.9	$[W_2O_6(OH)]^{-}$	·····	·····
587.8	$[W_5O_{16}]^{2-}$	✓	✓
696.5	$[W_3O_8(OH)]^{-}$	·····	·····
702.8	$[W_6O_{19}]^{2-}$	✓	✓
712.8	$[W_3O_9(OH)]^{-}$	·····	·····
819.8	$[W_7O_{22}]^{2-}$	✓	✓
935.7	$[W_8O_{25}]^{2-}$	✓	✓
1051.7	$[W_9O_{28}]^{2-}$	✓	✓
1166.7	$[W_{10}O_{31}]^{2-}$	·····	·····
1282.6	$[W_{11}O_{34}]^{2-}$	✓	✓
1398.6	$[W_{12}O_{37}]^{2-}$	·····	·····
1514.6	$[W_{13}O_{40}]^{2-}$	✓	✓
1630.5	$[W_{14}O_{43}]^{2-}$	✓	✓
1746.5	$[W_{15}O_{46}]^{2-}$	✓	✓
1862.5	$[W_{16}O_{49}]^{2-}$	✓	✓
1978.5	$[W_{17}O_{52}]^{2-}$	✓	✓
2094.4	$[W_{18}O_{55}]^{2-}$	✓	✓
2210.4	$[W_{19}O_{58}]^{2-}$	✓	✓

Table S3 Plenary cluster fragments observed in the fragmentation of α isomer $((n\text{-}C_3H_7)_4N)_4[H_3W_{19}O_{62}]^{3-}$ triply-charged peak: *m/z* = 1744.6 which fragments with a collision energy equal to 60 eV.

m/z	Peak Assignment
897.8	$[H_5W_{19}O_{62}]^{5-}$
935.2	$((n\text{-}C_3H_7)_4N)_1[H_4W_{19}O_{62}]^{5-}$
1139.2	$Na_3[H_3W_{19}O_{62}]^{5-}$
1168.8	$((n\text{-}C_3H_7)_4N)_1[H_5W_{19}O_{62}]^{4-}$
1179.8	$((n\text{-}C_3H_7)_4N)_1Na_2[H_3W_{19}O_{62}]^{4-}$
1215.6	$((n\text{-}C_3H_7)_4N)_2[H_4W_{19}O_{62}]^{4-}$
1261.6	$((n\text{-}C_3H_7)_4N)_3[H_3W_{19}O_{62}]^{4-}$
1620.7	$((n\text{-}C_3H_7)_4N)_2[H_5W_{19}O_{62}]^{3-}$
1676.5	$((n\text{-}C_3H_7)_4N)_3[H_2W_{19}O_{61}]^{3-}$
1682.5	$((n\text{-}C_3H_7)_4N)_3[H_4W_{19}O_{62}]^{3-}$
1744.6	$((n\text{-}C_3H_7)_4N)_4[H_3W_{19}O_{62}]^{3-}$
2524.2	$((n\text{-}C_3H_7)_4N)_3[H_5W_{19}O_{62}]^{2-}$
2617.3	$((n\text{-}C_3H_7)_4N)_4[H_4W_{19}O_{62}]^{2-}$
2709.9	$((n\text{-}C_3H_7)_4N)_5[H_3W_{19}O_{62}]^{2-}$

Table S4. Plenary cluster fragments observed in the fragmentation of γ^* isomer $((n\text{-}C_3H_7)_4N)_4[H_3W_{19}O_{62}]^{3-}$ triply-charged peak: *m/z* = 1744.6 which fragments with a collision energy equal to 75 eV.

m/z	Peak Assignment
897.8	$[H_5W_{19}O_{62}]^{5-}$
935.2	$((n\text{-}C_3H_7)_4N)_1[H_4W_{19}O_{62}]^{5-}$
1139.2	$Na_3[H_3W_{19}O_{62}]^{5-}$
1168.8	$((n\text{-}C_3H_7)_4N)_1[H_5W_{19}O_{62}]^{4-}$
1179.8	$((n\text{-}C_3H_7)_4N)_1Na_2[H_3W_{19}O_{62}]^{4-}$
1215.6	$((n\text{-}C_3H_7)_4N)_2[H_4W_{19}O_{62}]^{4-}$
1620.7	$((n\text{-}C_3H_7)_4N)_2[H_5W_{19}O_{62}]^{3-}$
1676.5	$((n\text{-}C_3H_7)_4N)_3[H_2W_{19}O_{61}]^{3-}$
1682.5	$((n\text{-}C_3H_7)_4N)_3[H_4W_{19}O_{62}]^{3-}$
1744.6	$((n\text{-}C_3H_7)_4N)_4[H_3W_{19}O_{62}]^{3-}$
2524.2	$((n\text{-}C_3H_7)_4N)_3[H_5W_{19}O_{62}]^{2-}$
2617.3	$((n\text{-}C_3H_7)_4N)_4[H_4W_{19}O_{62}]^{2-}$
2709.9	$((n\text{-}C_3H_7)_4N)_5[H_3W_{19}O_{62}]^{2-}$

The ESI-MS of both isomers show the same plenary cluster heteropolyanions.

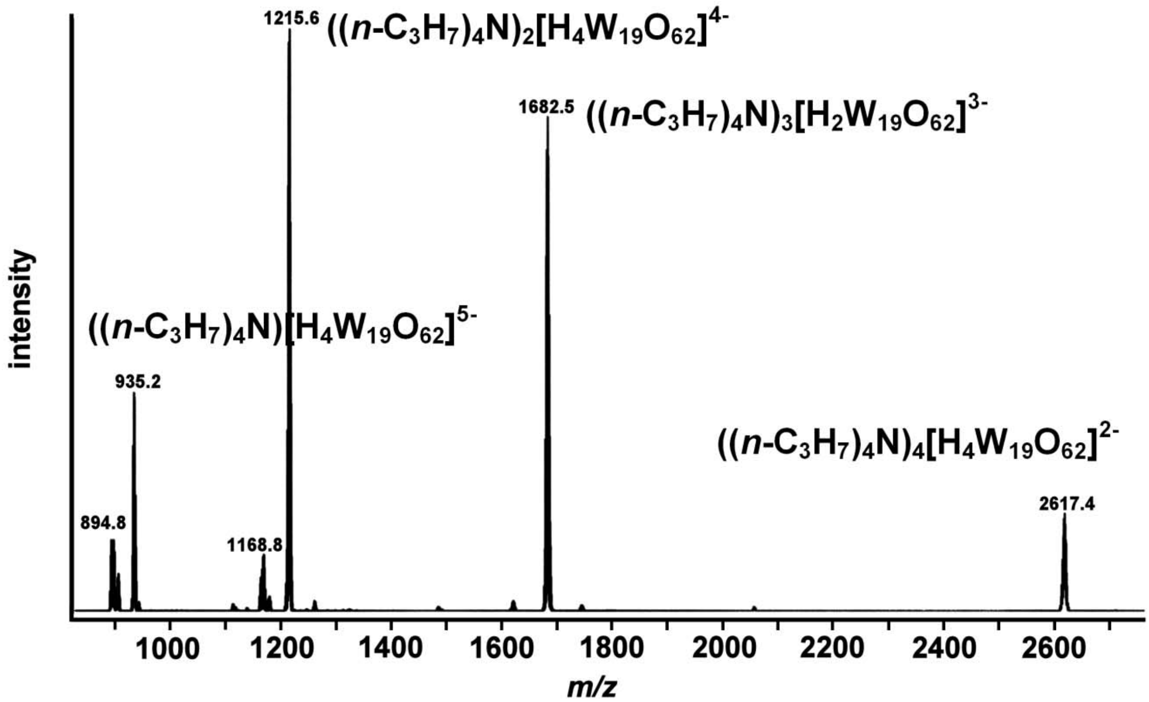

Figure S2. CID ESI-MS data of ((*n*-$C_3H_7)_4N)_6[\alpha\text{-}H_4W_{18}O_{56}(W^{VI}O_6)]\cdot 6CH_3CN$ in acetonitrile showing the plenary cluster fragments observed, from doubly-charged peak ((*n*-$C_3H_7)_4N)_4[H_4W_{19}O_{62}]^{2-}$ (*m/z* 2617.4) to $[H_5W_{19}O_{62}]^{5-}$ (*m/z* 897.8).

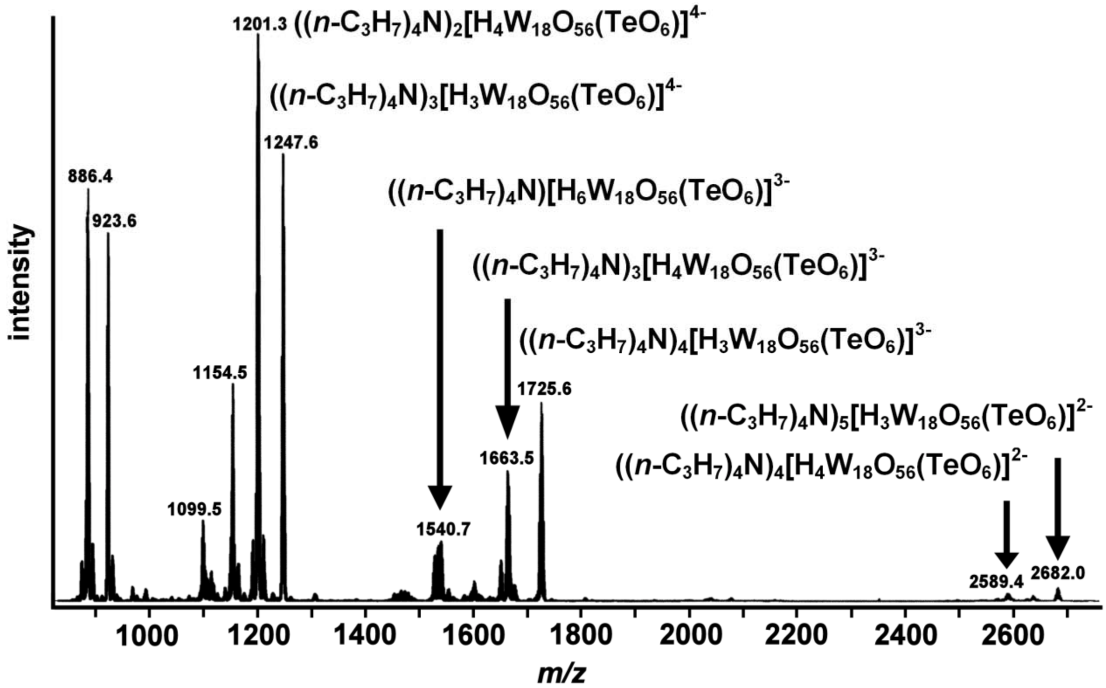

Figure S3 CID ESI-MS data of ((*n*-$C_3H_7)_4N)_7[\gamma^*\text{-}H_3W_{18}O_{56}(Te^{VI}O_6)]\cdot 4CH_3CN$ in acetonitrile showing the plenary cluster fragments observed, from doubly-charged peak ((*n*-$C_3H_7)_4N)_5[H_3W_{18}O_{56}(Te^{VI}O_6)]^{2-}$ (*m/z* 2681.9) to $[H_5W_{18}O_{56}(Te^{VI}O_6)]^{5-}$ (*m/z* 886.4).

Table S5. Plenary and isonuclear cluster fragments observed in the fragmentation of β* isomer $((n\text{-}C_3H_7)_4N)_4[\beta^*\text{-}H_2W_{18}O_{56}(IO_6)]^{3-}$ triply-charged peak: *m/z* = 1725.3 which fragments with a collision energy equal to 17 eV. Importantly, no peaks can be assigned to $[H_4W_{19}O_{62}]^{6-}$

m/z	Peak Assignment
471.9	$[W_4O_{13}]^{2-}$
587.8	$[W_5O_{16}]^{2-}$
703.8	$[W_6O_{19}]^{2-}$
819.8	$[W_7O_{22}]^{2-}$
886.3	$[H_4W_{18}O_{56}(IO_6)]^{5-}$
923.4	$((n\text{-}C_3H_7)_4N)_1[H_3W_{18}O_{56}(IO_6)]^{5-}$
935.8	$[W_8O_{25}]^{2-}$
1051.7	$[W_9O_{28}]^{2-}$
1154.5	$((n\text{-}C_3H_7)_4N)_1[H_4W_{18}O_{56}(IO_6)]^{4-}$
1200.8	$((n\text{-}C_3H_7)_4N)_2[H_3W_{18}O_{56}(IO_6)]^{4-}$
1247.1	$((n\text{-}C_3H_7)_4N)_3[H_2W_{18}O_{56}(IO_6)]^{4-}$
1282.7	$[W_{11}O_{34}]^{2-}$
1514.6	$[W_{13}O_{40}]^{2-}$
1533.7	$((n\text{-}C_3H_7)_4N)[H_3W_{18}O_{55}(IO_6)]^{3-}$
1595.4	$((n\text{-}C_3H_7)_4N)_2[H_2W_{18}O_{55}(IO_6)]^{3-}$
1663.2	$((n\text{-}C_3H_7)_4N)_3[H_3W_{18}O_{56}(IO_6)]^{3-}$
1676.5	$((n\text{-}C_3H_7)_4N)_3[H_2W_{19}O_{61}]^{3-}$
1725.3	$((n\text{-}C_3H_7)_4N)_4[H_2W_{18}O_{56}(IO_6)]^{3-}$
1746.5	$[W_{15}O_{46}]^{2-}$
1862.5	$[W_{16}O_{49}]^{2-}$
1978.5	$[W_{17}O_{52}]^{2}$
2094.4	$[W_{18}O_{55}]^{2}$
2587.9	$((n\text{-}C_3H_7)_4N)_4[H_3W_{18}O_{56}(IO_6)]^{2-}$
2681.0	$((n\text{-}C_3H_7)_4N)_5[H_2W_{18}O_{56}(IO_6)]^{2-}$

Table S6. Plenary cluster fragments observed from the fragmentation of doubly−charged peak $((n\text{-}C_3H_7)_4N)_4[\alpha\text{-}H_4W_{19}O_{62}]^{2-}$ (*m/z* 2617.4).

m/z	Peak Assignment
897.8	$[H_5W_{19}O_{62}]^{5-}$
935.2	$((n\text{-}C_3H_7)_4N)[H_4W_{19}O_{62}]^{5-}$
1139.2	$Na_3[H_3W_{19}O_{62}]^{5-}$
1168.8	$((n\text{-}C_3H_7)_4N)[H_5W_{19}O_{62}]^{4-}$
1179.8	$((n\text{-}C_3H_7)_4N)Na_2[H_3W_{19}O_{62}]^{4-}$
1215.6	$((n\text{-}C_3H_7)_4N)_2[H_4W_{19}O_{62}]^{4-}$
1261.6	$((n\text{-}C_3H_7)_4N)_3[H_3W_{19}O_{62}]^{4-}$
1620.7	$((n\text{-}C_3H_7)_4N)_2[H_5W_{19}O_{62}]^{3-}$
1676.5	$((n\text{-}C_3H_7)_4N)_3[H_2W_{19}O_{61}]^{3-}$
1682.5	$((n\text{-}C_3H_7)_4N)_3[H_4W_{19}O_{62}]^{3-}$
1744.6	$((n\text{-}C_3H_7)_4N)_4[H_3W_{19}O_{62}]^{3-}$
2524.2	$((n\text{-}C_3H_7)_4N)_3[H_5W_{19}O_{62}]^{2-}$
2617.3	$((n\text{-}C_3H_7)_4N)_4[H_4W_{19}O_{62}]^{2-}$
2709.9	$((n\text{-}C_3H_7)_4N)_5[H_3W_{19}O_{62}]^{2-}$

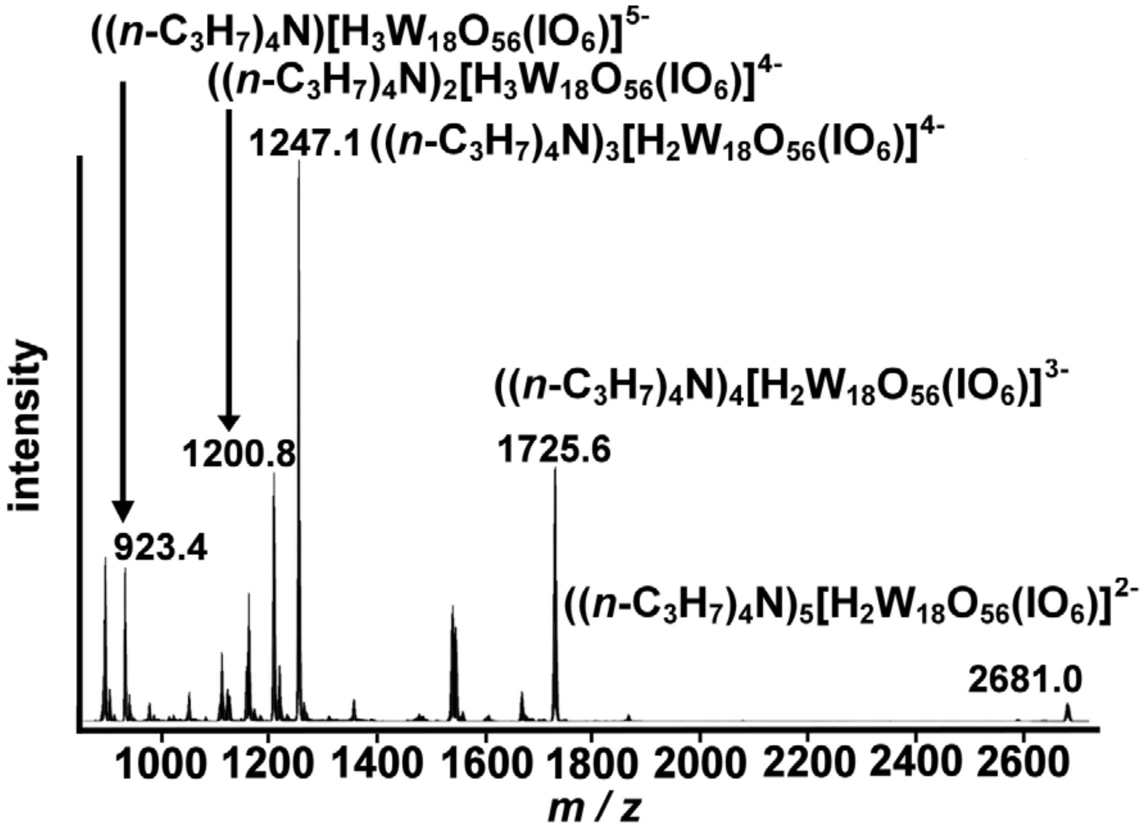

Fig. S4 ESI-MS data of $((n\text{-}C_3H_7)_4N)_6[\beta^*\text{-}H_3W_{18}O_{56}(I^{VII}O_6)]$ in acetonitrile showing the plenary cluster fragments observed, from doubly−charged peak $((n\text{-}C_3H_7)_4N)_5[H_2W_{18}O_{56}(IO_6)]^{2-}$ (*m/z* 2681.0) to $((n\text{-}C_3H_7)_4N)_1[H_3W_{18}O_{56}(IO_6)]^{5-}$ (*m/z* 923.4).

Table S7. Summary of both the plenary and isonuclear cluster fragments observed in the fragmentation of γ^* isomer ((*n*-$C_3H_7)_4N)_4[\gamma^*-H_3W_{18}O_{56}(Te^{VI}O_6)]^{3-}$ triply-charged peak: *m/z* = 1725.54 which fragments with a collision energy equal to 15 eV. Importantly, only one minor peak can be assigned to $[H_4W_{19}O_{62}]^{6-}$ and there are fewer isonuclear species than in the $\{W_{19}\}$ Wells–Dawsons: none above $[W_{13}O_{40}]^{2-}$.

m/z	Peak Assignment
471.9	$[W_4O_{13}]^{2-}$
587.8	$[W_5O_{16}]^{2-}$
703.8	$[W_6O_{19}]^{2-}$
819.8	$[W_7O_{22}]^{2-}$
886.8	$[H_5W_{18}O_{56}(Te^{VI}O_6)]^{5-}$
923.8	$((n\text{-}C_3H_7)_4N)_1[H_4W_{18}O_{56}(Te^{VI}O_6)]^{5-}$
935.7	$[W_8O_{25}]^{2-}$
1051.7	$[W_9O_{28}]^{2-}$
1155.0	$((n\text{-}C_3H_7)_4N)_1[H_4W_{18}O_{56}(Te^{VI}O_6)]^{4-}$
1166.7	$[W_{10}O_{31}]^{2-}$
1201.3	$((n\text{-}C_3H_7)_4N)_2[H_4W_{18}O_{56}(Te^{VI}O_6)]^{4-}$
1247.6	$((n\text{-}C_3H_7)_4N)_3[H_3W_{18}O_{56}(Te^{VI}O_6)]^{4-}$
1282.7	$[W_{11}O_{34}]^{2-}$
1478.6	$[H_7W_{18}O_{56}(Te^{VI}O_6)]^{3-}$
1514.6	$[W_{13}O_{40}]^{2-}$
1540.1	$((n\text{-}C_3H_7)_4N)_1[H_6W_{18}O_{56}(Te^{VI}O_6)]^{3-}$
1602.1	$((n\text{-}C_3H_7)_4N)_2[H_5W_{18}O_5(Te^{VI}O_6)_6]^{3-}$
1663.8	$((n\text{-}C_3H_7)_4N)_3[H_4W_{18}O_{56}(Te^{VI}O_6)]^{3-}$
1676.5	$((n\text{-}C_3H_7)_4N)_3[H_2W_{19}O_{61}]^{3-}$
1725.54	$((n\text{-}C_3H_7)_4N)_4[H_3W_{18}O_{56}(Te^{VI}O_6)]^{3-}$
2588.8	$((n\text{-}C_3H_7)_4N)_4[H_4W_{18}O_{56}(Te^{VI}O_6)]^{2-}$
2681.9	$((n\text{-}C_3H_7)_4N)_5[H_3W_{18}O_{56}(Te^{VI}O_6)]^{2-}$

Table S8 Binding Energy (BE) for the observed isomers and the correction applied to obtain the Corrected Binding Energy.

Isomers	DFT (eV)			
	BE	Correction	Corrected BE	ΔE_{BE}
$\gamma^*-[W_{18}O_{56}(TeO_6)]^{10-}$	–609.54	–150.6	–458.9	12
$\beta^*-[W_{18}O_{56}(IO_6)]^{9-}$	–619.29	–150.6	–468.6	3
$\alpha-[W_{18}O_{56}(WO_6)]^{10-}$	–624.00	–153.5	–470.5	1
$\gamma^*-[W_{18}O_{56}(WO_6)]^{10-}$	–624.74	–153.5	–471.2	0