Inversed Stability Order in Keggin Polyoxothiometalate Isomers: A DFT Study of 12-Electron Reduced α, β, γ, δ, and ε $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ Anions

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Table S1. Total electronic energies (au) the five most stable $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ isomers, ε-$[(NbO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$ and $[(C_9H_3O_6)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$ at the GGA-PW91/DNP level (opt =optimization, sp = single-point).

Anions	E_{ainon}/opt	E_{host}/sp	E_{guest}/sp	E_{eval}[a]	*FIE*/(kcal/mol)[b]
α-MoO_4^{2-}/D_{2d}	–7783.687886	–7413.828017	–369.444535	–7414.243351	–260.6
α-MoO_4^{2-}/T_d	–7783.685075	–7413.824901	–369.444534	–7414.240541	–260.8
β-MoO_4^{2-}/C_{3v}	–7783.690581	–7413.833617	–369.444768	–7414.245814	–258.7
γ-MoO_4^{2-}/C_{2v}	–7783.701781	–7413.839870	–369.443535	–7414.258246	–262.5
δ-MoO_4^{2-}/C_{3v}	–7783.783151	–7413.921412	–369.4445483	–7414.338603	–261.8
ε-MoO_4^{2-}/C_{2v}	–7783.889654	–7414.040203	–369.4445392	–7414.445115	–254.1
ε-MoO_4^{2-}/T_d	–7783.887559	–7414.038246	–369.4445444	–7414.443015	–254.0
ε-NbO_4^{3-}/D_{2d}	–7772.667474	–7413.988054	–357.8805465	–7414.786927	–501.3
ε-NbO_4^{3-}/T_d	–7772.665466	–7413.984649	–357.8805463	–7414.784921	–502.2
$C_9H_3O_6^{3-}/D_{3h}$	–8210.798727	–7414.1503541	–796.1509037	–7414.647823	–312.2

a) $E_{eval} = E_{host} + FIE$. b) $FIE = E_{ainon}/\text{opt} - [E_{host}/\text{sp} + E_{guest}/\text{sp}]$.

Table S2. Mayer indexes for a series of polyoxothiometalate anions.

Anions	X–O_i	Mo–O_i	Mo–O_t	Mo–S	Mo–O(H)	Mo–Mo[a]
α-MoO_4^{2-}/D_{2d}	1.397	0.144	2.165	1.182	0.572	-
β-MoO_4^{2-}/C_{3v}	1.381	0.120-0.181	2.162-2.163	1.167-1.281	0.560-0.609	-
γ-MoO_4^{2-}/C_{2v}	1.411	0.131-0.273	2.129-2.163	1.110-1.344	0.549-0.640	0.682
δ-MoO_4^{2-}/C_{3v}	1.427	0.166-0.173	2.128-2.147	1.180-1.221	0.561-0.578	0.691
ε-MoO_4^{2-}/C_{2v}	1.401	0.152	2.128	1.187	0.556	0.689
ε-NbO_4^{3-}/D_{2d}	1.163	0.229	2.102	1.176	0.548	0.687
$C_9H_3O_6^{3-}$/D_{3h}	-	0.385	2.106	1.160	0.489-0.600	0.680

a) The short Mo–Mo inside the [$Mo_2(\mu$-$S)_2O_2$] fragment.

Table S3. Mulliken charges for a series of polyoxothiometalate anions (X is the central heteroatom).

Isomers	X	Mo	XO_4^{2-}	O_i	O_b	O_t	S
α-MoO_4^{2-}/D_{2d}	1.687	0.677	–0.941	–0.657	–0.610	–0.466	–0.073
β-MoO_4^{2-}/C_{3v}	1.642	0.617-0.693	–0.986	–0.657	–0.611~–0.617	–0.453~–0.473	–0.115-0.078
γ-MoO_4^{2-}/C_{2v}	1.647	0.559-0.579	–0.913	–0.640	–0.556~–0.576	–0.472~–0.492	–0.075-0.065
δ-MoO_4^{2-}/C_{3v}	1.637	0.555-0.706	–0.927	–0.641	–0.568~–0.574	–0.474~–0.481	–0.097-0.052
ε-MoO_4^{2-}/C_{2v}	1.675	0.703	–0.889	–0.641	–0.566	–0.474	–0.087
ε-NbO_4^{3-}/D_{2d}	1.822	0.709	–1.206	–0.757	–0.564	–0.488	–0.141
$C_9H_3O_6^{3-}$/D_{3h}	-	0.797~0.867	-	–0.532	–0.593	–0.464	–0.259

Table S4. Total electronic energies (au), relative energy (kcal/mol), bond length (Å) and Mayer

indexes of short Mo^{VI}–Mo^{VI} inside the $[Mo_2(\mu\text{-}O)_2O_2]$ fragment for five Keggin-typed $[PMo_{12}O_{40}]^{3-}$ isomers.

Isomers	Mo–Mo		E_t (au)	[a]ΔE_t (kcal/mol)
	Bond-length	Mayer Index		
α/T_d	-	-	–4173.886828	0.0
β/C_{3v}	-	-	–4173.881428	3.4
γ/C_{2v}	3.017	0.104	–4173.867956	11.8
δ/C_{3v}	2.996	0.111	–4173.835831	32.0
ε/T_d	2.962	0.120	–4173.792048	59.5

a) Defined as E_t of the others subtracts that of α isomer.

Table S5. Total electronic energies (au), relative energy (kcal/mol), bond length (Å) and Mayer indexes of short Mo^{V}–Mo^{V} inside the $[Mo_2(\mu\text{-}O)_2O_2]$ fragment for five reduced Keggin-typed $[PMo_{12}O_{28}(OH)_{12}]^{3-}$ isomers.

Isomers	Mo–Mo		E_t (au)	[a]ΔE_t (kcal/mol)
	Bond-length	Mayer Index		
α/T_d	-	-	-4180.90358	0.0
β/C_{3v}	-	-	-4180.93514	19.8
γ/C_{2v}	2.601	0.739	-4180.95005	29.2
δ/C_{3v}	2.584	0.749	-4180.99863	59.6
ε/T_d	2.564	0.742	-4181.01815	71.9

b) Defined as E_t of the others subtracts that of α isomer.