Structural and Electronic Properties of Hetero-Transition-Metal Keggin Anions: A DFT Study of α/β - $[\text{XW}_{12}\text{O}_{40}]^{n-}$ ($\text{X} = \text{Cr}^{\text{VI}}, \text{V}^{\text{V}}, \text{Ti}^{\text{IV}}, \text{Fe}^{\text{III}}, \text{Co}^{\text{III}}, \text{Ni}^{\text{III}}, \text{Co}^{\text{II}}$ and Zn^{II}) Relative Stability

Fu-Qiang Zhang, Xian-Ming Zhang, Hai-Shun Wu, Haijun Jiao

Figure S1. Ball-and-stick representations of α - and β -isomers of Keggin anions. The structures can be viewed as assembly of two caps (Site I, III) and one belt (Site II).

Figure S2. Four kinds of W–W distances (Å) as functions of X for β - $[\text{XW}_{12}\text{O}_{40}]^{n-}$ ($\text{X} = \text{Cr}^{\text{VI}}, \text{V}^{\text{V}}, \text{Ti}^{\text{IV}}, \text{Fe}^{\text{III}}, \text{Co}^{\text{III}}, \text{Ni}^{\text{III}}, \text{Co}^{\text{II}}$ and Zn^{II}). $\text{W}^{\text{I}}-\text{W}^{\text{I}}$, $\text{W}^{\text{I}}-\text{W}^{\text{II}}$, $\text{W}^{\text{II}}-\text{W}^{\text{III}}$, $\text{W}^{\text{III}}-\text{W}^{\text{III}}$ denote the W–W distances inside Site I, between Site I and II, between Site II and III and inside Site III as shown in Figure S1, respectively.

Figure S3. Qualitative molecular-orbital diagram of the $\beta-[V^V W_{12}O_{40}]^{3-}$ showing the contributions of the VO_4^{3-} and $W_{12}O_{36}$ fragments. $\beta-[Cr^{VI} W_{12}O_{40}]^{2-}$ has the similar diagram.

$\beta\text{-Ti}^{\text{IV}}\text{W}_{12}$

$\beta\text{-Fe}^{\text{III}}\text{W}_{12}$

$\beta\text{-Co}^{\text{III}}\text{W}_{12}$

$\beta\text{-Co}^{\text{II}}\text{W}_{12}$

$\beta\text{-Ni}^{\text{III}}\text{W}_{12}$

$\beta\text{-Zn}^{\text{II}}\text{W}_{12}$

Figure S4. Spatial representation of the frontier orbitals of $\beta\text{-[XW}_{12}\text{O}_{40}]^{\text{n-}}$ ($\text{X} = \text{Ti}^{\text{IV}}, \text{Fe}^{\text{III}}, \text{Co}^{\text{III}}, \text{Ni}^{\text{III}}, \text{Co}^{\text{II}}$ and Zn^{II}).

Table S1. The W–O–W angles (degree) for a series of α/β -Keggin anions. $W-O-W_{\text{intra}}^{\text{I}}$, $W^{\text{I}}-O-W_{\text{inter}}^{\text{II}}$, $W-O-W_{\text{intra}}^{\text{II}}/W-O-W_{\text{inter}}^{\text{II}}$, $W^{\text{II}}-O-W_{\text{intra}}^{\text{III}}$, $W-O-W_{\text{inter}}^{\text{III}}$ denote the W–O–W angle inside Site I, between Site I and II, inside Site II, between Site II and III and inside Site III in Figure S1, respectively (averaged value for $\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}^{5-}$ are given). In α isomers, all intratriad W–O–W are identical while all intertriad W–O–W are identical.

X		$W-O-W_{\text{intra}}^{\text{II}}$	$W-O-W_{\text{inter}}^{\text{II}}$	$W-O-W_{\text{intra}}^{\text{I}}$	$W^{\text{I}}-O-W_{\text{inter}}^{\text{II}}$	$W^{\text{II}}-O-W_{\text{intra}}^{\text{III}}$	$W-O-W_{\text{inter}}^{\text{III}}$
Cr^{VI}	α	128.1	153.2				
	β	124.7	161.6	128.0	148.2	128.0	153.2
V^{V}	α	124.8	152.9				
	β	118.5	160.0	124.8	147.5	124.6	153.0
Ti^{IV}	α	120.6	153.1				
	β	118.0	160.6	121.9	147.1	120.5	153.2
Fe^{III}	α	117.1	152.6				
	β	115.6	159.3	117.7	146.4	117.4	152.5
Co^{III}	α	117.4	152.2				
	β	115.7	158.8	117.7	146.2	117.6	152.1
Ni^{III}	α	117.6	152.2				
	β	116.0	158.6	117.9	146.1	118.0	152.1
Co^{II}	α	114.3	152.3				
	β	113.1	158.7	114.6	146.0	114.5	152.1
Zn^{II}	α	114.2	152.4				
	β	113.1	158.8	114.6	146.0	114.3	152.2

Table S2. The distances of W–W (in Å) for a series of β -Keggin anions. $W^{\text{I}}-W^{\text{I}}$, $W^{\text{I}}-W^{\text{II}}$, $W^{\text{II}}-W^{\text{III}}$, $W^{\text{III}}-W^{\text{III}}$ denote the W–W distances inside Site I, between Site I and II, between Site II and III and inside Site III in Figure S1, respectively (averaged value for $\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}^{5-}$ are given).

X	$W^{\text{I}}-W^{\text{I}}$	$W^{\text{I}}-W^{\text{II}}$	$W^{\text{II}}-W^{\text{III}}$	$W^{\text{III}}-W^{\text{III}}$
Cr^{VI}	3.446	3.679	3.449	3.704
V^{V}	3.401	3.670	3.354	3.710
Ti^{IV}	3.349	3.675	3.346	3.717
Fe^{III}	3.306	3.669	3.304	3.711
Co^{III}	3.305	3.665	3.305	3.706
Ni^{III}	3.306	3.662	3.310	3.702
Co^{II}	3.265	3.669	3.265	3.711
Zn^{II}	3.266	3.671	3.263	3.712

Table S3. Spin densities (α - β) for the open-shell Keggin anions (O_i is the interior oxygen atoms)

Anions	type	X	O_i	Total
$Fe^{III}W_{12}$	α	4.065	0.178	4.777
	β	4.075	0.176	4.779
$Co^{III}W_{12}$	α	2.949	0.206	3.773
	β	2.957	0.205	3.777
$Ni^{III}W_{12}$	α	1.933	0.216	2.797
	β	1.934	0.217	2.802
$Co^{II}W_{12}$	α	2.604	0.056	2.828
	β	2.618	0.057	2.846

Table S4. Total electronic energies (au) of a series of Keggin anions, $W_{12}O_{36}$ ^a and XO_4 at the GGA-PW91/DND level. The optimizations of XO_4^{n-} ($X = Fe^{III}$, $Co^{III/II}$, Ni^{III} and Zn^{II}) are not converged at the same theoretical level. (opt = optimization, sp = single-point)

X	Isomers	Anion/opt	$W_{12}O_{36}/sp$	XO_4/sp	XO_4/opt
Cr^{VI}	α	-195153.18911	-193796.89749	-1355.83753	-1355.84207
	β	-195153.18383	-193796.88935	-1355.83807	-1355.84207
V^V	α	-195054.77103	-193796.86236	-1257.01396	-1257.02790
	β	-195054.76689	-193796.85359	-1257.01542	-1257.02790
Ti^{IV}	α	-194962.47401	-193796.80793	-1164.21510	-1164.24803
	β	-194962.47273	-193796.80285	-1164.21784	-1164.24803
Fe^{III}	α	-195369.50368	-193796.74252	-1570.58245	-
	β	-195369.50152	-193796.74411	-1570.58648	-
Co^{III}	α	-195488.50057	-193796.74386	-1689.56780	-
	β	-195488.49771	-193796.74399	-1689.57111	-
Ni^{III}	α	-195614.54808	-193796.74539	-1815.59969	-
	β	-195614.54404	-193796.74595	-1815.60225	-
Co^{II}	α	-195488.19173	-193796.67425	-1688.54535	-
	β	-195488.18759	-193796.67533	-1688.55024	-
Zn^{II}	α	-195892.78431	-193796.67381	-2093.14829	-
	β	-195892.78178	-193796.67470	-2093.15496	-

a) Free $E(W_{12}O_{36}/T_d, opt) = -193796.939655$ au and $E(W_{12}O_{36}/C_{3v}, opt) = -193796.953430$ au.

Table S5. The fragment interaction energy (*FIE*, kcal/mol) and deformation energy of the $W_{12}O_{36}$ ($DE_{W_{12}O_{36}}$, kcal/mol) and XO_4 (DE_{XO_4} , kcal/mol)

X	^a <i>FIE</i>		^b $DE_{W_{12}O_{36}}$ (DE_{XO_4})	
	α	β	α	β
Cr ^{VI}	-284.95	-286.40	35.10(2.85)	31.57(2.51)
V ^V	-561.44	-563.43	57.15(8.75)	54.01(7.83)
Ti ^{IV}	-910.50	-911.17	91.30(20.66)	85.85(18.94)
Fe ^{III}	-1367.16	-1362.28	132.35	122.71
Co ^{III}	-1373.56	-1369.61	131.51	122.78
Ni ^{III}	-1382.40	-1377.91	130.55	121.55
Co ^{II}	-1865.04	-1858.70	175.19	165.87
Zn ^{II}	-1858.82	-1852.48	175.46	166.26

a) $FIE = E(\text{anion}) - [E(W_{12}O_{36}, \text{single-point}) + E(XO_4, \text{single-point})]$. b) $DE_{W_{12}O_{36}} = E(W_{12}O_{36}/\beta, \text{single-point}) - E(W_{12}O_{36}/\alpha, \text{single-point})$ and $DE_{XO_4} = E(XO_4/\beta, \text{single-point}) - E(XO_4/\alpha, \text{single-point})$.

Table S6. The relative energies (kcal/mol) of the $W_{12}O_{36}$ isomers obtained by (β - α) (the ΔE_{free} is 8.64 kcal/mol)

X	ΔFIE^a	ΔDE^b	ΔE_t^c	$\Delta DE_{W_{12}O_{36}}^d$	$\Delta DE_{XO_4}^e$
Cr ^{VI}	-1.45	-3.87	3.31	-3.53	-0.34
V ^V	-1.99	-4.06	2.60	-3.14	-0.92
Ti ^{IV}	-0.67	-7.17	0.80	-5.45	-1.72
Fe ^{III}	4.88	-12.17	1.36	-9.64	-2.53
Co ^{III}	3.95	-10.81	1.79	-8.73	-2.08
Ni ^{III}	4.49	-10.61	2.54	-9.00	-1.61
Co ^{II}	6.34	-12.39	2.60	-9.32	-3.07
Zn ^{II}	6.33	-13.39	1.59	-9.20	-4.19

a) $\Delta FIE = FIE(\beta) - FIE(\alpha)$. b) $\Delta DE = \Delta DE_{W_{12}O_{36}} + \Delta DE_{XO_4}$. c) $\Delta E_t = E(\text{anion}, \beta) - E(\text{anion}, \alpha)$. d) $\Delta DE_{W_{12}O_{36}} = DE_{W_{12}O_{36}}(\beta) - DE_{W_{12}O_{36}}(\alpha)$. f) $\Delta DE_{XO_4} = E_{XO_4}(\beta, \text{single-point}) - E_{XO_4}(\alpha, \text{single-point})$.