Supporting Information

\[\text{[MW}_{12}\text{O}_{44}]\text{ cluster: unprecedented central heteroatoms atomically dispersed in eight coordination state bridging 1:12 polyoxometalate family of Keggin and Silverton} \]

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Experimental

\textbf{Synthesis of (NH}_4\textsubscript{10}H}_4[\text{NiW}_{12}\text{O}_{44}]\)

\((\text{NH}_4)\text{10H}_4\text{W}_{12}\text{O}_{42}\) (3.060 g, 1 mmol) was dissolved in 35 mL \(\text{H}_2\text{O}\) then the solution was acidized by \(\text{HNO}_3\) to \(\text{pH} 2.5\) and refluxing for 1h. The 15ml 1M Glycine-hydrochloric acid buffer was added to provide precise and stable \(\text{pH}\) control at 2.5, and \(\text{Ni(NO}_3)_2\) (0.18g 1mmol) was added, the solution was kept at 80 \(\text{°C}\) for 0.5h. Then the solution was evaporated to dryness. The title compound could be obtained as pale blue crystalline products with the yield about 80% based on \(\text{W}\). Suitable single crystals for X-ray diffraction were grown by slow evaporation. Crystal
data and structure refinement: \((\text{NH}_4)_{10}\text{H}_4[\text{NiW}_{12}\text{O}_{44}]\): \(Im-3m\), \(a=17.6345\ \text{Å}\), \(V=5483.9\ \text{Å}^3\), \(Z=2\), 517 reflections measured, \(R_1=0.0649\), \(wR_2=0.1645\).

**Synthesis of \((\text{NC}_{16}\text{H}_{36})_{4}(\text{NH}_4)_{10}[\text{NiW}_{12}\text{O}_{44}]\)**

\((\text{NC}_{16}\text{H}_{36})_{4}(\text{NH}_4)_{10}[\text{NiW}_{12}\text{O}_{44}]\) was obtained by cation exchange: \((\text{NH}_4)_{10}\text{H}_4[\text{NiW}_{12}\text{O}_{44}]\) (0.788g, 0.25 mmol) was dissolved in 15 mL H2O then 5ml \((\text{NC}_{16}\text{H}_{36})\text{Br}\) aqueous was added (0.322, 1mmol), through vigorous stir The title compound was formed and separated by filtration as pale blue precipitate.

C64H184N14O44NiW12, Mr =4118.98. C: N: Ni: W=63.86:13.73:1:12.04. IR (cm\(^{-1}\)): 3849, 3746, 2954, 2874, 1636, 1471, 1382, 1157, 1068, 960, 890, 806. UV-Vis (H2O, nm): \(\lambda_{LMCT}=263\), \(\lambda_{d-d}=630\).

**Synthesis of \((\text{NH}_4)_{10}\text{H}_4[\text{CoW}_{12}\text{O}_{44}]\) and \((\text{NC}_{16}\text{H}_{36})_{4}(\text{NH}_4)_{10}[\text{CoW}_{12}\text{O}_{44}]\)**

The synthesis process is similar to the synthesis of compound 1 while used \(\text{Co(NO}_3)_2\) instead of \(\text{Ni(NO}_3)_2\). \((\text{NH}_4)_{10}\text{H}_4[\text{CoW}_{12}\text{O}_{44}]\) could be obtained as pale pink crystalline products with the yield about 78% based on W. Crystal data and structure refinement:

\((\text{NH}_4)_{10}\text{H}_4[\text{CoW}_{12}\text{O}_{44}]\): \(Im-3m\), \(a=17.555\ \text{Å}\), \(V=5410.1\ \text{Å}^3\), Z=2, 515 reflections measured, \(R_1=0.0585\), \(wR_2=0.1946\).

C64H184N14O44CoW12, Mr =4119.22. C: N: Co: W=64.36:14.21:1:11.94. IR (cm\(^{-1}\)): 3849, 3741, 3432, 2963, 2874, 1641, 1471, 1373, 1152, 1064, 951, 890, 815. UV-Vis (H2O, nm): \(\lambda_{LMCT}=263\), \(\lambda_{d-d}=523\).

**Synthesis of \((\text{NH}_4)_{9}\text{H}_4[\text{FeW}_{12}\text{O}_{44}]\) and \((\text{NC}_{16}\text{H}_{36})_{4}(\text{NH}_4)_{9}[\text{FeW}_{12}\text{O}_{44}]\)**

The synthesis process is similar to the synthesis of compound 1 while used \(\text{Fe(NO}_3)_3\) instead of \(\text{Ni(NO}_3)_2\). \((\text{NH}_4)_{9}\text{H}_4[\text{FeW}_{12}\text{O}_{44}]\) could be obtained as white crystalline products with the yield about 81% based on W. Crystal data and structure refinement:

\((\text{NH}_4)_{9}\text{H}_4[\text{FeW}_{12}\text{O}_{44}]\): \(Im-3m\), \(a=17.5944\ \text{Å}\), \(V=5446.6\ \text{Å}^3\), Z=2, 516 reflections measured, \(R_1=0.1002\), \(wR_2=0.2166\).

C64H180N13O44FeW12, Mr =4098.10. C: N: Fe: W=63.86:13.32:1:11.96. IR (cm\(^{-1}\)): 3854, 3741, 3437, 2958, 2874, 1641, 1476, 1378, 1158, 1064, 956, 890, 810. UV-Vis (H2O, nm): \(\lambda_{LMCT}=263\).

**Synthesis of \((\text{NH}_4)_{10}\text{H}_6[\text{W}_{12}\text{O}_{44}]\)**
(NH₄)₁₀H₂[W₁₂O₄₂] (3.060 g, 1 mmol) was dissolved in 35 mL H₂O then the solution was acidized by HNO₃ to pH 2.5 and refluxing for 1h. Then the solution was evaporated to dryness. The title compound could be obtained as white crystalline products. Suitable single crystals for X-ray diffraction were grown by slow evaporation. Crystal data and structure refinement: (NH₄)₁₀H₂[W₁₂O₄₂]: I-43m, a=17.6345 Å, V=5483.9 Å³, Z=2, 857 reflections measured, R₁=0.0889, wR₂=0.2290.

**XAFS analysis**

The EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, the χ(k) data of were Fourier transformed to real (R) space using a hanning windows (dk=1.0 Å⁻¹) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of Demeter software packages.

The following EXAFS equation was used:

\[
χ(k) = \sum_j N_j F_j(k) \exp(-2k^2\sigma_j^2) \exp(-\frac{2}{\lambda(k)}\exp[2k R_j + \phi_j(k)]]
\]

S₀² is the amplitude reduction factor, F_j(k) is the effective curved-wave backscattering amplitude, N_j is the number of neighbors in the j⁰ atomic shell, R_j is the distance between the X-ray absorbing central atom and the atoms in the j⁰ atomic shell (backscatterer), λ is the mean free path in Å, φ_j(k) is the phase shift (including the phase shift for each shell and the total central atom phase shift), σ_j is the Debye-Waller parameter of the j⁰ atomic shell (variation of distances around the average R_j). The functions F_j(k), λ and φ_j(k) were calculated with the ab initio code FEFF. The additional details for EXAFS simulations are given below.

The coordination numbers of model samples were fixed as the nominal values. The obtained S₀² was fixed in the subsequent fitting. While the internal atomic distances R, Debye-Waller factor σ², and the edge-energy shift ΔE₀ were allowed to run freely.
**Figure S1a.** ORTEP drawings of cluster anions of [CoW$_{12}$O$_{44}$] (a) and [FeW$_{12}$O$_{44}$] (b). Thermal ellipsoids are drawn at the 30% probability level through symmetric operation of minimum asymmetric unit of MWO$_3$.

**Figure S1b.** The formation of [NiW$_{12}$O$_{44}$] nanocluster from the minimum asymmetric unit of NiWO$_3$ (the grey fragment) through color symmetric operation.

The color symmetric operation code is list as following:

'x, y, z'

'-x, -y, z'
'z, -y, x'

'x+1/2, y+1/2, z+1/2'

'-x+1/2, -y+1/2, z+1/2'

'-x+1/2, y+1/2, -z+1/2'

'x+1/2, -y+1/2, -z+1/2'

'z+1/2, x+1/2, y+1/2'

'z+1/2, -x+1/2, -y+1/2'

'-z+1/2, -x+1/2, y+1/2'

'-z+1/2, x+1/2, -y+1/2'

'y+1/2, z+1/2, x+1/2'

'-y+1/2, z+1/2, -x+1/2'

'y+1/2, -z+1/2, -x+1/2'

'-y+1/2, -z+1/2, x+1/2'

'y+1/2, x+1/2, z+1/2'

'-y+1/2, -x+1/2, z+1/2'

'y+1/2, -x+1/2, -z+1/2'

'-y+1/2, x+1/2, -z+1/2'

'x+1/2, y+1/2, z+1/2'

'-x+1/2, z+1/2, y+1/2'

'-x+1/2, z+1/2, -y+1/2'

'-x+1/2, -z+1/2, y+1/2'

'-x+1/2, -z+1/2, -y+1/2'

'x+1/2, -z+1/2, -y+1/2'
Figure S2a. ORTEP drawings of cluster anions of \([\text{W}_{12}\text{O}_{44}]^{16-}\). Thermal ellipsoids are drawn at the 30% probability level through symmetric operation of minimum asymmetric unit of WO₅.
**Figure S2b.** The formation of $[\text{W}_{12}\text{O}_{44}]^{16-}$ nanocluster from the minimum asymmetric unit of WO$_5$ (the grey fragment) through Color symmetric operation.

The color symmetric operation code is list as following:

- 'x, y, z'
- '-x, -y, z'
- '-x, y, -z'
- 'x, -y, -z'
- 'z, x, y'
- 'z, -x, -y'
- '-z, -x, y'
- '-z, x, -y'
- 'y, z, x'
- '-y, z, -x'
'y, -z, -x'
'-y, -z, x'
y, x, z'
'-y, -x, z'
y, -x, -z'
'-y, x, -z'
x, z, y'
'-x, z, -y'
'-x, -z, y'
x, -z, -y'
z, y, x'
'-z, -y, x'
'-z, y, -x'
'-z, -y, x'
x+1/2, y+1/2, z+1/2'
'-x+1/2, -y+1/2, z+1/2'
'-x+1/2, y+1/2, -z+1/2'
x+1/2, -y+1/2, -z+1/2'
'z+1/2, x+1/2, y+1/2'
'z+1/2, -x+1/2, -y+1/2'
'-z+1/2, -x+1/2, y+1/2'
'-z+1/2, -x+1/2, y+1/2'
-z+1/2, x+1/2, -y+1/2
'y+1/2, z+1/2, x+1/2'
'-y+1/2, z+1/2, -x+1/2'
'y+1/2, -z+1/2, -x+1/2'
'-y+1/2, -z+1/2, x+1/2'
'y+1/2, x+1/2, z+1/2'
'-y+1/2, -x+1/2, z+1/2'
'y+1/2, -x+1/2, -z+1/2'
'-y+1/2, x+1/2, -z+1/2'
'x+1/2, z+1/2, y+1/2'
'-x+1/2, z+1/2, -y+1/2'
'-x+1/2, -z+1/2, y+1/2'
'x+1/2, -z+1/2, -y+1/2'
'z+1/2, y+1/2, x+1/2'
'z+1/2, -y+1/2, -x+1/2'
'-z+1/2, y+1/2, -x+1/2'
'-z+1/2, -y+1/2, x+1/2'
**Figure S3.** Polyhedron of 1:12 heteropolyoxometalates with different central heteroatom configuration: tetrahedron for Keggin, hexahedron for [MW_{12}O_{44}]; icosahedron for Silverton.

6 WO₆ octahedrons surrounded around the central heteroatom polyhedron in approximate plane defined as equatorial position; (ii) each 3 WO₆ octahedrons in the up and down plane defined as polar position.
Figure S4. UV/Vis spectra of [MW₁₂O₄₄] clusters: (a) LMCT absorption and (b) d-d transition absorption spectra.
Figure S5a. The FT-IR spectrum of (NC$_{16}$H$_{36}$)$_4$(NH$_4$)$_{10}$[NiW$_{12}$O$_{44}$].

Figure S5b. The FT-IR spectrum of (NC$_{18}$H$_{36}$)$_4$(NH$_4$)$_{10}$[CoW$_{12}$O$_{44}$].
**Figure S5c.** The FT-IR spectrum of (NC\textsubscript{16}H\textsubscript{36})\textsubscript{4}(NH\textsubscript{4})\textsubscript{9}[FeW\textsubscript{12}O\textsubscript{44}].

**Figure S6a.** TGA analysis of (NC\textsubscript{16}H\textsubscript{36})\textsubscript{4}(NH\textsubscript{4})\textsubscript{10}[NiW\textsubscript{12}O\textsubscript{44}].
Figure S6b. TGA analysis of (NC16H36)4(NH4)10[CoW12O44].

Figure S6c. TGA analysis of (NC16H36)4(NH4)9[FeW12O44].
Figure S7a. The simulated and experimental powder XRD pattern of [CoW_{12}O_{44}] and the simulated powder XRD pattern of [CoW_{12}O_{40}] respectively.

Figure S7b. The simulated and experimental powder XRD pattern of [NiW_{12}O_{44}] (a) and [FeW_{12}O_{44}] (b) respectively.