Electronic Supplementary Information

Unprecedented β-Keggin Cluster Incorporating Two \([\text{Mo}^{IV}_3\text{O}_4]\) Cluster Units Concomitant with \(\text{MoO}_2\) Nucleophilic Addition

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Crystallographic Analysis

The intensity data were collected on a Saturn70 CCD diffractometer for \(1\), with graphite-monochromated \(\text{MoK}\alpha\) radiation \((\lambda = 0.71073 \ \text{Å})\) at room temperature. All absorption corrections were performed by using the multi-scan program. The structure were solved by direct methods and refined by full-matrix least squares on \(F^2\) with the SHELXTL-97 program. CCDC-923715 (1) contain the supplementary crystallographic data for this paper, these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

BVS calculation results of \([\text{H}_4\text{Mo}^{IV}_6\text{Mo}^{VI}_7\text{O}_{36}\text{py}_6]^{2-}\) (1a)

\[
\begin{align*}
\text{Mo1} &= 4.39 & \text{Mo2} &= 4.42 & \text{Mo3} &= 4.33 & \text{Mo4} &= 4.36 & \text{Mo5} &= 4.30 & \text{Mo6} &= 4.45 \\
\text{Mo7} &= 5.94 & \text{Mo8} &= 5.93 & \text{Mo9} &= 5.86 & \text{Mo10} &= 5.92 & \text{Mo11} &= 5.92 & \text{Mo12} &= 5.91 \\
\text{Mo13} &= 5.76
\end{align*}
\]

\[
\begin{align*}
\text{O1} &= 2.17 & \text{O2} &= 2.22 & \text{O3} &= 1.24 & \text{O4} &= 1.25 & \text{O5} &= 1.73 & \text{O6} &= 1.74 & \text{O7} &= 1.78 \\
\text{O8} &= 2.09 & \text{O9} &= 1.71 & \text{O10} &= 2.00 & \text{O11} &= 1.95 & \text{O12} &= 1.85 & \text{O13} &= 1.81 & \text{O14} &= 1.83 \\
\text{O15} &= 1.90 & \text{O16} &= 1.93 & \text{O17} &= 1.69 & \text{O18} &= 1.82 & \text{O19} &= 1.89 & \text{O20} &= 1.20 & \text{O21} &= 1.77 \\
\text{O22} &= 1.80 & \text{O23} &= 1.90 & \text{O24} &= 2.00 & \text{O25} &= 2.05 & \text{O26} &= 1.85 & \text{O27} &= 1.80 & \text{O28} &= 1.56 \\
\text{O29} &= 1.86 & \text{O30} &= 1.81 & \text{O31} &= 1.83 & \text{O32} &= 1.24 & \text{O33} &= 1.73 & \text{O34} &= 1.62 & \text{O35} &= 1.64 \\
\text{O36} &= 1.73
\end{align*}
\]
Fig. S1 Mass spectrum of [H₄Mo⁴⁺₆Mo⁶⁺O₅₆py₆]·H₂py₃·2H₂O (I)

NL: 7.40 E4
RT: 3.05; AV: 1
+ ESI Full ms [200.00-3000.00]
Fig. S  (1a) simulated (red lines) and measured MS spectrum of \(\text{[H}_6\text{[Mo}^{IV}_6\text{Mo}^{VI}_7\text{O}_{34}\text{py}_6]}\)\(^+\) (1b) simulated (red lines) and measured MS spectrum of \(\text{[H}•\text{I]}\)\(^+\)
ESI mass spectrum of 1 was recorded in positive ion mode in a solution of pyridine. Signal of the 4+ species at m/z 567.8 corresponds to \{H_6[Mo^{IV}_6Mo^{VI}_7O_{34}py_6]\}^{4+}, which results from a loss of two H$_2$O from [H$_4$Mo$_4^{IV}_6$Mo$_7^{VI}O_{36}py_6]^{2-}$ (1a) concomitant with six additional protons to achieve a charge of 4+. Similar loss of H$_2$O resulting from protonated oxygen has also been observed in MS of other polyoxometalates.\textsuperscript{15-17} Signal at 2577.7 corresponds to \{H•1\}$^+$ as a consequence of the low solubility and ionization of 1 in the pyridine solution.

Reference

\textbf{Fig. S2} IR spectrum of 1.