

A mixed-valent nonanuclear $[\text{Mn}_5^{\text{II}}\text{Mn}_4^{\text{III}}]$ molecular cluster with cubic topology of highest symmetry as a bifunctional electrocatalyst for efficient water splitting

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The development of inexpensive and efficient bifunctional electrocatalysts for water splitting is very important but still a challenging task. In the present research, a mixed-valent molecular cluster, $[\text{Mn}_9\text{L}_4(\mu_2\text{-O})_4(\mu_3\text{-Cl})_2]$ (**1**; 5Mn^{II} , 4Mn^{III}) possessing cubic *lad* symmetry has been synthesized as an efficient bifunctional water-splitting electrocatalyst for the first time. This synthesis is achieved by adopting a molecular library approach that utilizes an inorganic metal salt, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and a multidentate organic linker, H_3L as building blocks ($\text{H}_3\text{L} = N,N'$ -bis[2-carboxybenzomethyl]- N,N' -bis[2-pyridylmethyl]-1,3-diaminopropan-2-ol). The organic linker is so flexible and the inclination towards cubic symmetry is so high that this cluster is readily formed through subcomponent self-assembly. Structural investigation reveals that the metallic hub of **1** consists of a central $[\text{Mn}^{\text{II}}(\mu_2\text{-O})_4(\mu_3\text{-Cl})_2]$ backbone that connects four Mn^{II} and four Mn^{III} ions, located at eight vertices of a body-centered cubic (BCC) structure, *via* the μ_2 -oxido and μ_3 -chlorido groups. A total of 24 discrete $[\text{Mn}_9]$ cluster units are packed together in the unit cell through a number of intramolecular $\pi \cdots \pi$ stacking interactions among the adjoining benzoate and pyridyl moieties, forming aesthetically attractive 3D polyhedral topologies with essentially large unit cell dimensions, and a cell volume of $113\,112(9) \text{ \AA}^3$. When working as both a hydrogen evolution reaction (HER) and an oxygen evolution reaction (OER) catalyst, **1** exhibits excellent activity with overpotential values of $209 \text{ mV}_{\text{HER}}$ and $410 \text{ mV}_{\text{OER}}$ to attain a current density of 10 mA cm^{-2} , and the Tafel slopes of $180 \text{ mV dec}_{\text{HER}}^{-1}$ and $113.54 \text{ mV dec}_{\text{OER}}^{-1}$. The chronoamperometric studies reveal the commendable stability of **1**, accompanied by minimal degradation of current density which is the key yardstick for HER and OER activities. The mechanistic insight obtained from DFT calculations on the intermediate species show that the $\text{Mn}^{\text{II}}\text{-O}_{\text{oxido}}\text{-Mn}^{\text{III}}$ linkage is the active site for the formation of H_2 and O_2 .

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