

Electrocatalytic properties of $\{\text{Mo}_3\text{S}_4\}$ -based complexes with regard to the hydrogen evolution reaction and application to PEM water electrolysis

Joumada Al Cheikh,^a Rosa Zakari,^{a,b} Amit C. Bhosale,^{a,c,†} Angel Villagra,^a Nathalie Leclerc,^b Sébastien Floquet,^b Prakash C. Ghosh,^c Alireza Ranjbari,^a Emmanuel Cadot,^b Pierre Millet^a, and Loïc Assaud^a

^a Equipe de Recherche et d'Innovation en Electrochimie pour l'énergie (ERIEE), Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO), UMR CNRS 8182, Université Paris-Saclay, 91405 Orsay, France.

^b ILV, CNRS, Université de Versailles Saint Quentin, Université Paris-Saclay, Avenue des Etats Unis, 78035 Versailles France.

^c Department of Energy Science and Engineering, IIT Bombay, Mumbai – 400076, India.

† Present address: Department of Hydro and Renewable Energy, Indian Institute of Technology Roorkee, Uttarakhand, India.

Supplementary information

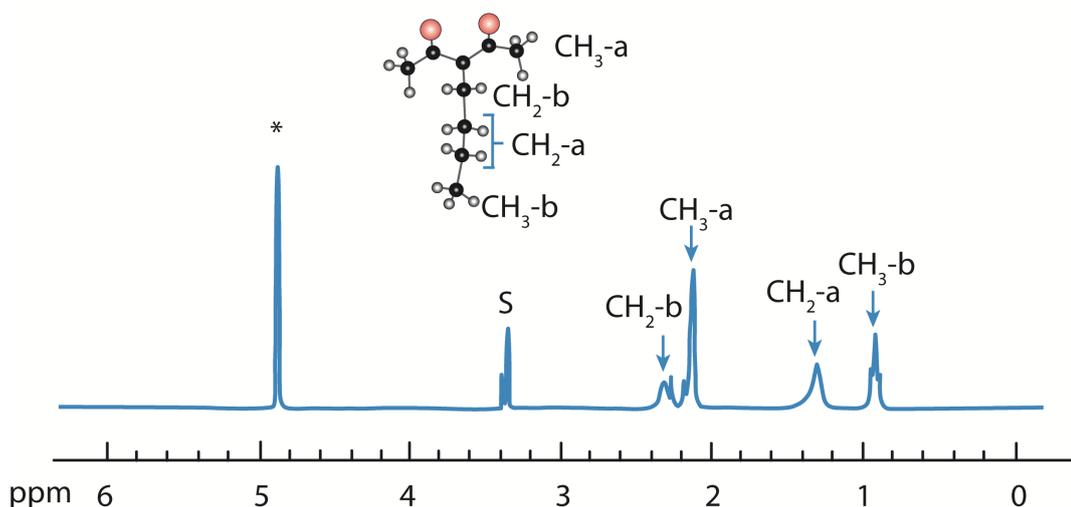


Figure S1: ¹H NMR spectrum of [Mo₃S₄(acacBut)₃(H₂O)₃]Cl·H₂O in MeOD (* = H₂O, S = solvent)

¹H NMR spectrum of the [Mo₃S₄(acacBut)₃(H₂O)₃]⁺ compound in a chloride salt form was recorded in methanol-d₄. It consists of four main resonances located at 0.894 ppm (3 H), 1.291 ppm (4 H), 2.11 ppm (6 H) and 2.29 ppm (2 H). The relative intensities of the signals allowed to assigned the different proton non-equivalent groups. The resonance signal multiplicities is in good agreement with three acacbut ligands equivalents in C_{3v} symmetry arrangement.

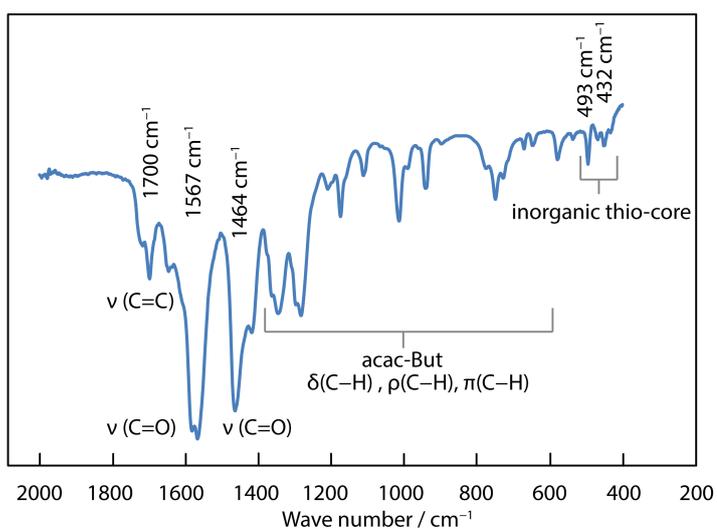


Figure S2: FT-IR spectrum (ATR Diamond) of $[\text{Mo}_3\text{S}_4(\text{acacBut})_3(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{H}_2\text{O}$

FT-IR spectrum displays two absorption bands located at 1567 cm^{-1} and 1464 cm^{-1} assigned to $\nu(\text{C}=\text{O})$ vibration modes whereas $\nu(\text{C}=\text{C})$ vibration mode is observed at 1700 cm^{-1} . Several absorption bands related to the inorganic skeleton of acacbut ligand ($\delta(\text{C}-\text{H})$, $\rho(\text{C}-\text{H})$, $\pi(\text{C}-\text{H})$) are observed between 1400 cm^{-1} and 600 cm^{-1} . Two bands located at 493 cm^{-1} and 432 cm^{-1} are assigned to the inorganic thio core. It has to be noted that the FT-IR spectrum of $[\text{Mo}_3\text{S}_4\text{Pd}(\text{acacBut})_3(\text{H}_2\text{O})_3]\text{Cl}\cdot 2\text{H}_2\text{O}$ is very similar to that of $[\text{Mo}_3\text{S}_4(\text{acacBut})_3(\text{H}_2\text{O})_3]\text{Cl}\cdot 2\text{H}_2\text{O}$. It displays the expected typical band of acacBut ligand coordinated to the metallic cluster $[\text{Mo}_3\text{S}_4\text{Pd}]^{4+}$.

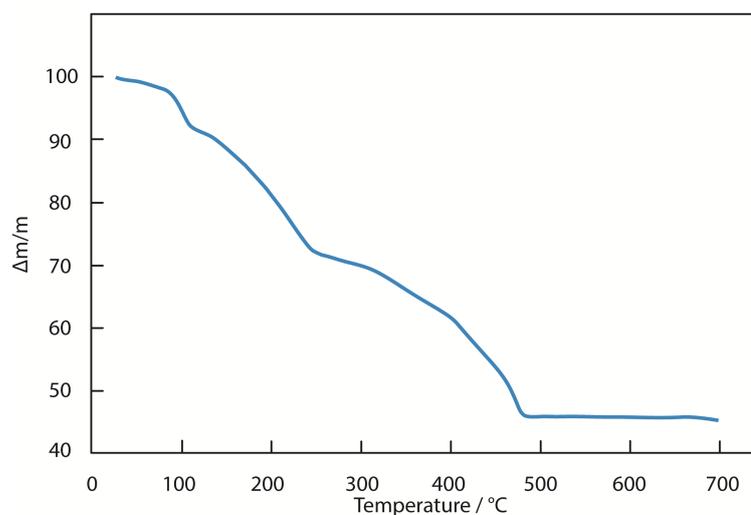


Figure S3: TGA curve obtained for $[\text{Mo}_3\text{S}_4\text{Pd}(\text{acacBut})_3(\text{H}_2\text{O})_3]\text{Cl}\cdot 2\text{H}_2\text{O}$ under O_2 flux, $5^\circ\text{C}/\text{min}$

The hydration rate was determined by **TGA** under oxygen flux at a heating rate of $5^\circ\text{C}/\text{minute}$. A first weight loss is observed between ambient temperature and 120°C , corresponding to *ca* 8% of the initial weight is in good agreement with the presence of 5 water molecules, shared between the three aqua ligands and 2 water crystallization molecules. The weight loss (*ca* 46%) observed between 120 and 500°C is attributed to the combustion of the three acacbut ligands (calculated 41.8%) and the removal of Chloride anion (calculated 3.2%) in good agreement with the formula.

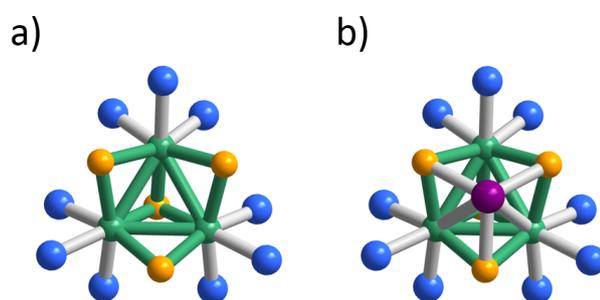


Figure S4: Structural representation of compounds $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (a) and $[\text{Mo}_3\text{S}_4\text{Pd}(\text{H}_2\text{O})_9]^{4+}$ (b)

The electronic spectra recorded in aqueous acidic media (HCl 1 M) in visible area are typical of compounds $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and $[\text{Mo}_3\text{S}_4\text{Pd}(\text{H}_2\text{O})_9]^{4+}$ depicted in **Figure S4** (see for example the review Llusar, R., and Uriel, S. Heterodimetallic chalcogen-bridged cubane-type clusters of molybdenum and tungsten containing first-row transition metals. *Eur. J. Inorg. Chem.*, **2003**,(7), 1271-1290 and references therein).

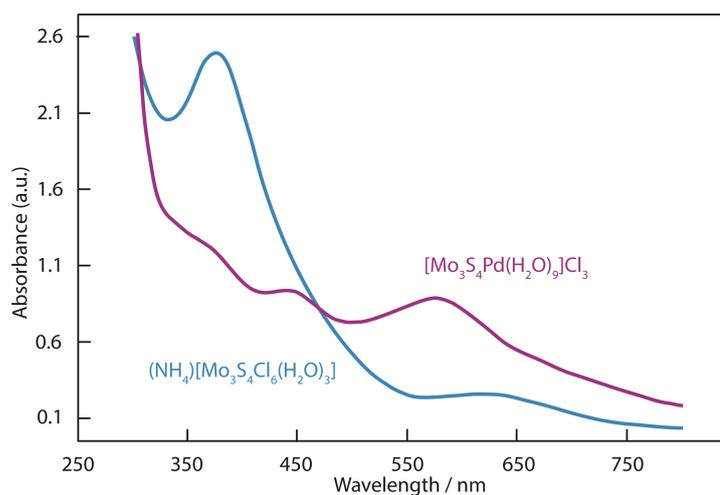


Figure S5: Electronic spectra of clusters $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ et $[\text{Mo}_3\text{S}_4\text{Pd}(\text{H}_2\text{O})_9]^{4+}$ in 1 M HCl aqueous solution.

As depicted in **Figure S5**, the spectrum of cluster $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ displays one d-d absorption band at 620 nm with $\epsilon = 300 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ accordingly to its deep green color. By reacting with Pd^0 , the $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ gives the cluster $[\text{Mo}_3\text{S}_4\text{Pd}(\text{H}_2\text{O})_9]^{4+}$. The electronic properties are modified enough to induce a color change to deep blue. The resulting electronic spectrum displays an absorption band typical of such a cluster with a maximum at 575 nm and ($\epsilon = 1380 \text{ mol} \cdot \text{L}^{-1} \cdot \text{cm}^{-1}$).

By coordination with bidentate ligand such as butyl acetylacetonate, the fingerprint of the clusters is not strongly modified in the visible region accordingly to the integrity of the later. The small shifts observed are attributed to the change of solvent from aqueous 1 M HCl to CH_3CN and the spectra contains also a strong contribution in near UV area, notably due to π - π^* transitions within the coordinated ligands (see Figure S6). Upon addition of increasing quantities of formic acid the spectra are well preserved, indicating a relatively good stability in these conditions. The offset observed in the case of $[\text{Mo}_3\text{S}_4\text{Pd}(\text{H}_2\text{O})_3(\text{acacbutyl})_3]^+$ is due to a very partial precipitation of the chloride salt during the experiment.

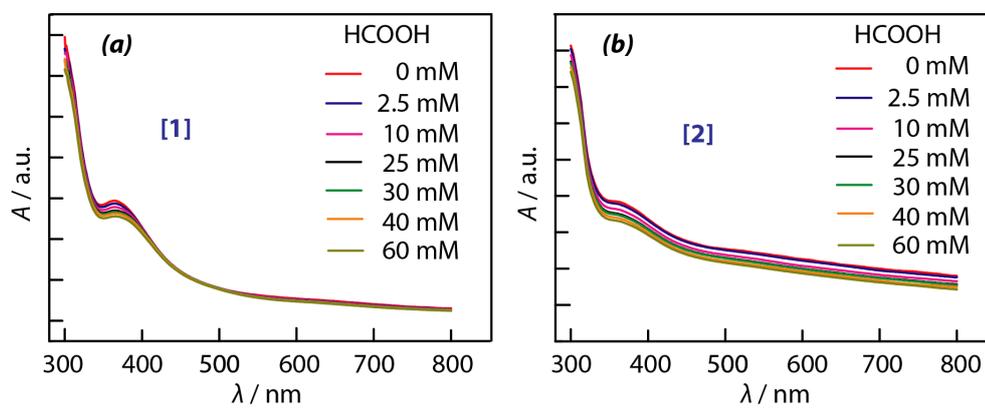


Figure S6: UV-visible spectra of (a) $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_3(\text{acacbutyl})_3]^+ = \mathbf{[1]}$ and (b) $[\text{Mo}_3\text{S}_4\text{Pd}(\text{H}_2\text{O})_3(\text{acacbutyl})_3]^+ = \mathbf{[2]}$ in a 0.2 mM acetonitrile solution in the presence of increasing amounts of HCOOH.