Soluble Gd₆Cu₂₄ clusters: effective molecular electrocatalysts for water oxidation†

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The water oxidation half reaction in water splitting for hydrogen production is extremely rate-limiting. This study reports the synthesis of two heterometallic clusters (Gd₆Cu₂₄-IM and Gd₆Cu₂₄-AC) for application as efficient water oxidation catalysts. Interestingly, the maximum turnover frequency of Gd₆Cu₂₄-IM in an NaAc solution of a weak acid (pH 6) was 319 s⁻¹. The trimetallic catalytic site, H₂O–Gd⁶Cu₂₄–H₂O, underwent two consecutive two-electron two-proton coupled transfer processes to form high-valent Gd¹⁺–O–O–Cu²⁺ intermediates. Furthermore, the O–O bond was formed via intramolecular interactions between the Cu³⁺ and Gd³⁺ centers. The results of this study revealed that synergistic catalytic water oxidation between polymeric sites can be an effective strategy for regulating O–O bond formation.

Introduction

Hydrogen production by water splitting is a promising solution for future energy needs; however, water oxidation is rate-limiting, primarily due to its four-electron transfer process with slow reaction kinetics. Many researchers have been inspired by natural photosynthesis to develop catalytic systems to resolve this rate-limiting issue. Several studies have developed molecular water oxidation catalysts. In particular, significant efforts have focused on mimicking the structure and catalytic properties of the natural oxygen-evolving complex (OEC), a unique heterometallic-oxide Mn₄CaO₅-cluster, in photosystem II (PS II) of plants, algae, and cyanobacteria. Although several multinuclear clusters simulating OEC structures have been reported, their catalytic performance is still far from that of natural OEC, with the mechanism behind the O–O bond formation still not yet conclusively known. Catalysts usually should easily attain four electrons and contain effective synergistic catalytic structural motifs to achieve a similar catalytic activity. Previous studies on structural motifs have mainly focused on the Mn–O–Mn–H₂O bimetallic structure. Recent studies have shown that the redox-inert Ca²⁺ ion in Mn₄CaO₅ may play an important role in maintaining the structural integrity of clusters and supporting ligand sites for water molecules or in assisting proton transfer. However, the poor stability of Ca²⁺-containing Mn₄CaO₅ clusters in polar solvents has hindered their development. Therefore, developing efficient and stable cluster catalysts for water oxidation remains challenging.

Several studies have recently reported that replacing Ca²⁺ ions with lanthanide ions can stabilize the cluster structure in performance simulations. Furthermore, lanthanide ions have high coordination numbers, rich geometries, and...
This study reports the synthesis of two high-nuclearity clusters—\([\text{Gd}_{6}\text{Cu}_{24}\text{IM}]_{12}\{\text{L-Al}_{12}\{\text{H}_{2}\text{O}\}_{24}\}\{\text{ClO}_{4}\}_{16}\}^{3+}\) (\(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\)) and \([\text{Gd}_{6}\text{Cu}_{24}\text{AC}]_{12}\{\text{L-Al}_{12}\{\text{H}_{2}\text{O}\}_{24}\}\{\text{ClO}_{4}\}_{11}\}^{1+}\) (\(\text{Gd}_{6}\text{Cu}_{24}\text{AC}\)) (IM = imidazole, \(\text{L-Al} = \text{L-alanine, AC} = \text{acetate}\))—possessing the same metal core frames (Fig. 1 and S1†). Similar to \(\text{H}_{2}\text{O}^{–}\text{Gd–O–Cu–H}_{2}\text{O}\) in OEC, the trimetallic structural motif of \(\text{H}_{2}\text{O}^{–}\text{Gd–Cu–Gd}\) may be a potentially efficient synergistic catalytic site for water oxidation.

**Results and discussion**

Clusters \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\) and \(\text{Gd}_{6}\text{Cu}_{24}\text{AC}\) were obtained by the reaction of \(\text{Gd(ClO}_{4})_{3}\), \(\text{Cu(ClO}_{4})_{2}\), \(6\text{H}_{2}\text{O}\), and \(\text{L-alanine}\) with imidazole and \(\text{NaAc}\), respectively. The asymmetric structural unit \([\text{GdCu}_{4}]\) of \(\text{Gd}_{6}\text{Cu}_{24}\) can be considered as two corner-deficient \([\text{GdCu}_{2}]\) and \([\text{GdCu}_{2}]\) cubes linked together by sharing a \(\text{Gd}^3+\) ion (Fig. 1c). Six \([\text{GdCu}_{4}]\) units were connected by four \(\mu_3\text{O}^−\), resulting in an octahedral conformational arrangement. The metal core of \(\text{Gd}_{6}\text{Cu}_{24}\) displayed an octahedral inner core of \(\text{Gd}_{6}\text{Cu}_{12}\) connected to six outer \(\text{Cu}_{2}\) units. Each \([\text{GdCu}_{4}]\) unit contained five metal ions, in which \(\text{Gd}\), \(\text{Cu}_{1}\), and \(\text{Cu}_{2}\) were bound to water molecules. Furthermore, the \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\) cluster was protected by 12 amino acids and 12 imidazole ligands, highly resembling the peripheral ligands of the OEC. Furthermore, each cluster core unit of \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\) and \(\text{Gd}_{6}\text{Cu}_{24}\text{AC}\) had 16 and 11 positive charges in addition to \(\mu_3\text{O}^−\) (Fig. S6b†). For \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\), the peak at 1978.73 can be attributed to \([\text{GdCu}_{4}(\text{Ac})_{6}(\text{L-Al})_{10}(\text{H}_{2}\text{O})_{2}\text{Cl}_{10}\text{ClO}_{4})_{2}\] (Fig. S6a†); for \(\text{Gd}_{6}\text{Cu}_{24}\text{AC}\), these peaks are observed and can be attributed to \([\text{GdCu}_{4}(\text{Ac})_{6}(\text{L-Al})_{10}(\text{H}_{2}\text{O})_{2}\text{Cl}_{10}\text{ClO}_{4})_{2}\] (\(X = 0–6\)) (Fig. S6b†). The redox properties of \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\) and \(\text{Gd}_{6}\text{Cu}_{24}\text{AC}\) were analyzed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in a NaAc/HAc buffer solution (0.5 M, \(pH = 6\)) (Fig. 2). The CVs of different scan rates (0.05–0.2 V s\(^{-1}\)) (Fig. 3a) and the CPE data showing charge versus time for a 20 mL solution containing NaAc/HAc buffer solution (0.5 M, \(pH = 6\)) and 0.25 mM \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\) and \(\text{Gd}_{6}\text{Cu}_{24}\text{AC}\) (d) CVs of \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\) (0.25 mM), \(\text{Gd(ClO}_{4})_{3}\) (1.5 mM), and \(\text{Cu(ClO}_{4})_{2}\) (6 mM).

The DPs of \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\) and \(\text{Gd}_{6}\text{Cu}_{24}\text{AC}\) transformed significantly by changing the solvent from superdy acetonitrile anodic shoulder peak, where \(\alpha\) is the transfer coefficient (0.5) and \(n\) was calculated to be 2. These results indicated that the two peripheral \(\text{Cu}^{2+}\) ions in the \([\text{GdCu}]\) unit could be considered equivalent groups for the single-electron reaction, i.e., the quasi-reversible process near 0.15 V can be attributed to the reaction pair of two-electron reduction of \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\) and \(\text{Gd}_{6}\text{Cu}_{24}\text{AC}\) near 1.35 V can be attributed to the two-electron oxidation of \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\) and \(\text{Gd}_{6}\text{Cu}_{24}\text{AC}\) near 1.35 V. The DPV of \(\text{Gd}_{6}\text{Cu}_{24}\text{IM}\) and \(\text{Gd}_{6}\text{Cu}_{24}\text{AC}\) transformed significantly by changing the solvent from superdy acetonitrile.
to an aqueous NaAc/HAc buffer solution (pH = 6; Fig. S11 and S12†). In acetonitrile, the oxidation peak at 1.72 V can be attributed to the two-electron oxidation of the Gd6Cu24/IM/Gd6Cu24+ reaction pair. In the NaAc/HAc buffer, the anodic current was significantly enhanced after 1.35 V, thus indicating the occurrence of aqueous oxidation. A linear relationship was observed in the plot of the catalytic peak current versus Gd6Cu24/IM concentration (Fig. S13†), thus indicating that the rate law for Gd6Cu24/IM catalyzed water oxidation can be expressed in terms of a pseudo-first-order rate reaction (eqn (1)–(3), ESI†). The catalytic peak currents were directly proportional to the square root of the scan rate, thus indicating a diffusion-controlled catalytic redox process. Linear scan voltammograms (LSV) of Gd6Cu24/IM and Gd6Cu24/AC were recorded on an indium tin oxide (ITO) electrode. The significantly enhanced catalytic currents indicated water oxidation (Fig. S14†). The overpotentials for Gd6Cu24/IM and Gd6Cu24/AC required to reach 1 mA cm−2 were 598 and 689 mV, respectively. In comparison to previous reports (Table S2†), the overpotentials represent a relatively lower level. The difference in the overpotentials may be attributed to the different peripheral coordination groups between Gd6Cu24/IM and Gd6Cu24/AC (imidazole and acetate, respectively), and the conjugation effect of imidazole ligands may help to reduce the reaction energy barrier. The apparent rate constants (kapp), called turnover frequency (TOF), for Gd6Cu24/IM and Gd6Cu24/AC at 1.7 V were 319 and 169 s−1, respectively (Fig. 3b and S9†), much higher than those of previously reported mono- and di-nuclear catalysts (0.4–100 s−1).22

A gas-tight double-compartment cell with the cathode and anode separated by a Nafion membrane was utilized to verify the release of oxygen. Gd6Cu24/IM (0.25 mM) was subjected to controlled potential electrolysis (CPE) at 1.70 V in an NaAc/HAc buffer solution (0.5 M, pH = 6) using an ITO electrode (1.00 cm2; Fig. 3c). Electrolysis was performed for 3 h and oxygen production was determined by gas chromatography, where approximately 33 μmol of O2 were formed with a faradic efficiency of 94%. The ratio of H2 to O2 was measured (2 : 1). For Gd6Cu24/IM, neither the blank nor the inorganic salt catalytic tests showed a significant catalytic current. The reproducibility of the 50 times cycle scan, the almost identical UV-Vis spectra, and the CV curves before and after 3 h of controlled potential electrolysis (Fig. 3d and S15–S18†) indicated that water oxidation occurred under homogeneous catalytic conditions in addition to the high activity and stability of Gd6Cu24/IM.23

The DPVs of Gd6Cu24 clusters in a mixture of superdy CH3CN and H2O at different concentrations were recorded to elucidate the water oxidation mechanism. The results (Fig. 4a) revealed that the DPV curves of Gd6Cu24/AC changed significantly with the addition of water, where the oxidation peak current increased dramatically and the oxidation onset potential shifted positively, indicating that the coordination of water can reduce the oxidation onset potential. The DPV curves of Gd6Cu24/IM changed in a pattern similar to that of Gd6Cu24/AC, although its two oxidation peaks did not show significant splitting (Fig. S19†). Changes in the oxidation onset potential were observed by changing the pH of the NaAc/HAc buffer solution, indicating that the oxidation process involved a proton-coupled electron transfer (PCET). The Pourbaix diagram revealed that (Fig. 4b) in an NaAc/HAc buffered aqueous solution (0.5 M, pH 4.98–7), two consecutive oxidation peaks of Gd6Cu24/AC exhibited Nernstian responses at approximately −55 and −50 mV pH−1, consistent with the 2e−/2H+ PCET (−59 mV pH−1, Nernstian ideal),24 while the responses of Gd6Cu24/IM were −54 and −57 mV pH−1 (Fig. S22†). In addition, the catalytic processes of Gd6Cu24/IM and Gd6Cu24/AC showed low solvent kinetic isotope effects of 1.23 and 1.25, respectively, (KIE = kH2O/kD2O, Fig. S23†).25 Significantly different from the hydrophilic nucleophilic attack mechanism of mononuclear catalysts but consistent with the intramolecular O–O bond formation route for Cu3 catalysts.26

Based on the typical mechanisms reported for natural OEC-catalyzed water oxidation,16b–26 it was inferred that the two molecules of water (W1 and W2) that coordinated on the heme-like metal centers CuIII and GdIII can be used as the oxygen source for O–O bond formation (Fig. S24†). W1 and W2 had a distance of 2.81 Å, close to the distance between the two water molecules coordinated on CuII and MnIII in the OEC (3.26 Å).26 Based on the experimental results of previous studies and previously reported catalytic mechanisms for water oxidation by multinuclear molecular catalysts,26 a plausible and reasonable mechanism for water oxidation catalyzed by Gd6Cu24 was proposed (Fig. 5). Under electrolytic catalytic conditions, the trimetallic reaction site is oxidized from the initial GdIII(OH)2 CuIII(OH2) species 1 through a 2e−/2H+ PCET process to give GdIII(OH)CuIII(OH)2 species 2, which can be further oxidized by the 2e−/2H+ PCET process to GdIII(O)2CuIII(O) species 3. The redox potentials of these two steps were 1.35 and 1.55 V, respectively. Species 3 forms species 4, containing O–O bonds through intramolecular interactions, while species 4 releases O2 and completes the cycle by coordinating with two water molecules to form starting cluster 1. The M3–O2 intermediate is stabilized by the trimetallic site of Gd6Cu24, which may facilitate the formation of O–O bonds. This pathway differs from the common mechanism of O–O bond formation by the nucleophilic water attack on the highly oxidized state of MIII=O. The formation of the highly oxidized state of CuIV=O and ligand hydrocarbon oxidation are also avoided.29
Conclusions

In conclusion, this study reported an efficient catalytic water oxidation using water-soluble Gd₆Cu₂₄ clusters in aqueous solutions of weak acids. The trimetallic catalytic site synergistically catalyzed water oxidation by promoting O–O bond formation, while simple amino acid ligands provided both water solubility and stability, which assisted the catalytic process. Interestingly, the TOFs of Gd₆Cu₂₄·IM and Gd₆Cu₂₄·AC at 1.7 V reached 319 and 169 s⁻¹, respectively. This work offers a possibility to understand the synergistic effect of multiple metals in the water oxidation mechanism. Furthermore, Gd₆Cu₂₄ has a tunable molecular structure and metal sites, which is beneficial for designing highly active and stable catalysts in the future.

Data availability

The crystal data and structure of the clusters, experimental details and experimental data for this article are available in the ESI.†

Author contributions

J.-N. C., Z.-H. P. and X.-J. K. conceived and designed the research; J.-N. C. and Z.-H. P. synthesized and characterized the compounds. X.-J. K., J.-N. C., Z.-H. P., Q.-H. Q., C. W., L.-S. L., and L.-S. Z. analyzed the data. J.-N. C., Z.-H. P. and X.-J. K. wrote the manuscript with contributions from all authors. All authors analyzed the data and commented on the manuscript. J.-N. C. and Z.-H. P. contributed equally to this work.

Conflicts of interest

The authors declare no competing financial interest.

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Notes and references
