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Catalytic Water Oxidation by a Bio-inspired Nickel Complex with Redox Active Ligand

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Abstract

The oxidation of water to dioxygen is important in natural photosynthesis. One of nature's strategies for managing such multi-electron transfer reactions is to employ redox active metal-organic cofactor arrays. One prototype example is the copper-tyrosinate active site found in galactose oxidase. In this work, we have implemented such a strategy to develop a bio-inspired nickel-phenolate complex capable of catalyzing the oxidation of water to O₂ electrochemically at neutral pH with a modest overpotential. The employment of the redox-active ligand turned out to be a useful strategy to avoid the formation of high-valent nickel intermediates while a reasonable turnover rate (0.15 s⁻¹) is retained.

The oxidation of H₂O to O₂ is an energetically uphill reaction ($E^{\circ} = +1.23$ V vs. NHE at pH 0) responsible for providing 99% of the driving force for natural photosynthesis.¹ This process occurs at the CaMn₄O₄ oxygen evolving complex (OEC) upon the accumulation of four oxidizing equivalents in a single turnover,² a strategy that minimizes extra energy input (overpotential)³ and avoids the formation of partially oxidized product(s) (e.g. H₂O₂). One of the great challenges in the development of efficient artificial water oxidation electrocatalysts is to manipulate the driving force of the catalytic cycle close to the thermodynamic surface of water oxidation while retaining a reasonable turnover rate.

For single-site, homogeneous transition metal-based electrocatalysts, most efforts have focused on systems where the metal is the only site for the storage of the oxidizing equivalents,⁴ while a few examples are available with both the metal and a redox-active ligand involved in the catalytic cycle.⁵ To date, a system where the redox potentials of the metal and the ligand could be modulated independently has yet to be reported.

We took inspiration from galactose oxidase (GAO), a mononuclear copper enzyme that catalyzes the two-electron oxidation of a range of primary alcohols to their corresponding aldehydes with the concomitant reduction of O₂ to H₂O₂.⁶ The key redox-active component is a Cu(I)-tyrosinate, which is oxidized by two electrons to generate a Cu(II)-tyrosyl radical as the reactive oxidant (Scheme 1A). This example of synergy between a metal and an

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Supporting Information

Experimental methods, Scheme S1, Figures S1–S12. This material is available free of charge on the ACS Publications website.

organic radical provides a useful strategy for mediating multi-electron transfer chemistry. In this work, we implemented this strategy to develop a bio-inspired nickel-phenolate complex capable of catalyzing water oxidation electrochemically at neutral pH and a moderate overpotential, and demonstrated that both redox-active sites were utilized to store and transfer oxidizing equivalents in the catalytic cycle (Scheme 1B). Our findings have thus provided new insights into rational design of molecular water oxidation electrocatalysts.

The complex $\text{Ni}^{\text{II}}\text{-L1}$ (**1**) can be synthesized by the reaction of 1:1 Ni^{2+} salt and ligand L1 (Scheme S1, Figure S1) in wet THF in the presence of one equivalent of tetrabutylammonium hydroxide to deprotonate the phenol *O*-donor. The crystal structure of **1** (Figure 1) shows that the tetradentate ligand L1 supports the formation of a mononuclear octahedral Ni^{II} complex with two water molecules bound in a *cis*- configuration. The Ni-O bond distance of 2.061 Å for the phenolate *O*-donor compares favorably with the ones reported for other phenolate ligands.⁷ Notably, we found that a slight decrease of the steric hindrance from mesityl to 4-fluoro-phenyl (Figure S2) led to the formation of a dinuclear nickel complex $(\text{Ni}^{\text{II}}\text{-L2})_2$ (**2**), in which each phenolate acts as a bridging instead of a terminal ligand (Figure S3), even when the synthesis was carried out under identical conditions. Such a *bis*-phenolate bridged dinuclear structure has been widely observed in Cu-phenolate complexes.^{6c,8}

The optical spectrum of **1** in CH_3CN exhibited two primary absorptions at 309 nm ($\epsilon = 4200 \text{ M}^{-1} \text{ cm}^{-1}$) and 385 nm (sh, $\epsilon = 650 \text{ M}^{-1} \text{ cm}^{-1}$), and two weak peaks at 596 nm ($\epsilon = 14 \text{ M}^{-1} \text{ cm}^{-1}$) and 950 nm ($\epsilon = 22 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure S4). These features resemble the ones reported for other nickel-phenolate complexes.^{7,9} The absorption at 309 nm is assignable to the phenolate-to-nickel charge transfer transition.⁹ When the spectrum was measured in buffered H_2O at pH 7, this band underwent a blue shift and became a shoulder at 296 nm ($\epsilon = 3200 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure S5). This feature began to lose its intensity at pH < 7, suggesting that the phenolate was protonated at low pH. A $\text{p}K_a$ of 6.2 was obtained for the phenolate *O*-donor by a pH titration experiment (Figure S5).

The cyclic voltammogram (CV) of **1** in sodium phosphate (Na-Pi) aqueous buffer at pH 7 using a glassy carbon working electrode (surface area $\sim 0.07 \text{ cm}^2$) showed a strong, irreversible catalytic current with an onset potential of $\sim 1200 \text{ mV}$ vs. Ag/AgCl reference (Figure 2, red). The catalytic current has a linear dependence on the concentration of **1** in the range of 0.05 to 0.5 mM (Figure 2, inset), suggesting that **1** is a single-site catalyst in aqueous solution. The catalytic current became saturated at a catalyst loading higher than 0.5 mM. This observation is similar to that of a Cu-bipyridine water oxidation catalyst recently reported.¹⁰ The CV carried out in D_2O shows a much smaller catalytic current (Figure 2, blue), suggesting that the transfer of proton(s) from H_2O is a significant component of the rate-determining step. A solvent kinetic isotope effect (KIE) of 3.3 was determined according to Eq. 1.^{5d,11} When the CV of the clean buffer was performed using the working electrode removed from the catalyst-containing solution after gentle wash (see SI for details),¹² no catalytic current was observed (Figure 2, purple), indicating that there is no deposit of a heterogeneous layer on the surface of the working electrode. On the other hand, complex **2** showed a lower catalytic activity than **1**.

$$\text{KIE} = k_{\text{cat, H}_2\text{O}} / k_{\text{cat, D}_2\text{O}} = (i_{\text{cat, H}_2\text{O}} / i_{\text{cat, D}_2\text{O}})^2 \quad (1)$$

When normalized on the basis of the square root of the scan rate ($\nu^{-1/2}$), the catalytic current decreased upon the increase of the scan rate from 50 to 500 mV s^{-1} (Figure S6). Together with the notable KIE, these results suggested that the attack of H_2O to form an O-O bond by an active oxidant is the rate-determining step in the catalytic cycle. The turnover frequency (TOF, k_{obs}) was determined to be 0.15 s^{-1} by a widely used method described previously^{5d} based on Eq. 2 (Figure S6, inset),

$$i_{\text{cat}} / i_{\text{diff}} = 2.24n(RT k_{\text{obs}} / F\nu)^{1/2} \quad (2)$$

where $n = 4$, i_{cat} and i_{diff} represent the catalytic current and the diffusional current of the $\text{PhO}^\bullet/\text{PhO}^-$ couple (see below), respectively. This value compares favorably with the ones reported for other nickel-based water oxidation catalysts at neutral pH.^{5b,13}

A solution containing 0.5 mM **1** in Na-Pi buffer at pH 7 was then subject to bulk electrolysis using an indium tin oxide (ITO) working electrode (surface area $\sim 7 \text{ cm}^2$). We applied a potential that is more positive than the onset potential to ensure fast production of O_2 . As shown in Figure S7, the current obtained in the presence of **1** was much larger than that in the solution containing the buffer alone. No lag period was observed, indicating that the catalytic activity was not a result of the decomposed species of **1**. The Faradaic yield of O_2 formation was determined using a Clark electrode to be 80–90% (Figure S8). Importantly, we performed another electrolysis of the clean buffer solution using the working electrode (Figure S9) removed from the catalyst-containing solution after 30 minutes of electrolysis. No significant current was observed relative to a freshly prepared electrode (Figure S7, blue). These observations confirm that there is no formation of a heterogeneous nickel oxide layer at the surface of the ITO electrode.

We also studied the electrochemical properties of $\text{Ni}(\text{NO}_3)_2$, which is known to form heterogeneous nickel oxides active in catalyzing water oxidation at alkaline pHs.¹⁴ As shown in Figure S10, the CV of 0.5 mM $\text{Ni}(\text{NO}_3)_2$ in Na-Pi buffer at pH 7 exhibited distinctly different behavior compared to that of **1**. In the forward scan, a catalytic current was not observed until the potential reached $\sim 1500 \text{ mV}$, which is $\sim 300 \text{ mV}$ higher than the onset potential found for **1**. Moreover, a crossover catalytic wave and a broad cathodic feature at $\sim 950 \text{ mV}$ were observed on the reverse scan. In addition, we carried out bulk electrolysis of 0.5 mM $\text{Ni}(\text{NO}_3)_2$ at pH 7 using an ITO electrode. There is clear formation of a black nickel oxide layer on the electrode surface after electrolysis (Figure S9). Taken together, these results demonstrated that **1** is a homogeneous catalyst but not the precursor of a heterogeneous nickel oxide species.

At low potential, a non-catalytic anodic peak was observed at $E_{\text{p,a}} = 780 \text{ mV}$, which could be assigned to the oxidation of the phenolate to phenoxyl radical (Figure S11).^{6c,7} This process is partially reversible as revealed by the reverse scan even when the forward scan returned at

1000 mV, showing first a cathodic peak at $E_{p,c}(1) = 720$ mV. The peak separation of 60 mV is indicative of a one-electron process; however, the reduced peak current compared to that of the anodic peak suggested that there is another process following the oxidation of the phenolate. Additionally, there is a second cathodic peak at $E_{p,c}(2) = 350$ mV. It is well known that the phenoxyl radical could be stabilized through delocalization over the entire phenol ring.^{6c} We thus attribute $E_{p,c}(2)$ to the one-electron reduction of the delocalized radical species.

In order to probe the mechanism of water oxidation catalysis, we carried out more CV studies in aqueous solutions buffered at a range of pHs from 7 to 11. As shown in Figures S12 and S13, the non-catalytic anodic peak is insensitive to the pH of the solution, consistent with our assignment of this feature to the $\text{PhO}^\bullet/\text{PhO}^-$ couple. In contrast, the onset potential for the catalytic process decreased upon increasing the pH. A plot of the potential measured at a constant current (e.g. $-40 \mu\text{A}$) as a function of pH (Figure S12, inset) is linear with a slope of -60 mV/pH, indicating that the generation of the reactive species for attacking water is a metal-based one-electron process coupled with the transfer of one proton.

We thus propose a mechanism to summarize the key experimental findings (Scheme 2). Overall, the starting Ni(II)-phenolate complex was oxidized by two one-electron steps to generate the reactive oxidant, a Ni(III)-phenoxyl radical species. Both the solvent H/D KIE and the scan rate dependence studies demonstrated that the rate-determining step is the O-O bond formation. The resulting hydroperoxide intermediate likely continues to be oxidized on the electrode surface to produce O_2 . Notably, **1** takes advantage of the phenolate ligand as the second redox-active site besides the metal center. Therefore, the formation of a putative high-valent nickel-oxo species as the reactive intermediate¹⁵ could be avoided while a reasonable turnover rate is retained. On the other hand, **1** has limited stability under catalytic conditions, as revealed in Figure S7. This is likely due to that 1) the phenolate moiety in ligand L1 has unsubstituted *ortho*- and *para*-positions susceptible to the decomposition of the phenoxyl radical, and 2) the oxidation of the phenolate ligand occurs prior to that of the metal, which grants sufficient time for the decomposition of the phenoxyl radical to take place. Further studies are aimed at exploring possible decomposition pathways of **1**¹⁶ and enhancing its stability through the modification of ligand L1.

In conclusion, we have provided proof-of-concept demonstration that a nickel-phenolate complex **1** could act as a single-site, molecular catalyst for the oxidation of H_2O to O_2 at neutral pH and a modest overpotential. Several lines of evidence have confirmed the homogeneous nature of **1** during catalysis. Both the metal and the phenolate ligand were utilized to store and transfer oxidizing equivalents in the catalytic cycle, advantageous strategy to avoid the formation of high-valent nickel intermediates. Furthermore, the flexibility of the ligand scaffold has provided unprecedented opportunities to modulate the redox properties of the metal and the ligand individually to improve the catalytic activity, energy efficiency, and catalyst stability in future studies.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Crystal structure of **1** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances: Ni-O1: 2.061(1) Å; Ni-O2: 2.048(1) Å; Ni-O3: 2.125(2) Å; Ni-N1: 2.086(2) Å; Ni-N2: 2.066(2) Å; Ni-N3: 2.156(2) Å.

Figure 2.

CVs of 0.1 M Na-Pi buffer at pH 7 (black), 0.5 mM **1** in H_2O (red) and D_2O (blue), and clean buffer using the working electrode removed from 0.5 mM **1** containing solution (purple). Scan rate = 100 mV/s. Inset: plot of the catalytic current at 1500 mV vs. [**1**]. The red line represents the best linear fit up to [**1**] = 0.5 mM.

Scheme 1.

Key redox active species involved in the catalytic cycle of (A) galactose oxidase and (B) the nickel-phenolate complex **1** studied in this work.

Scheme 2. Proposed water oxidation mechanism catalyzed by **1**.