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Synthesis of a molecular electrocatalyst based on an iron(III) complex supported by amine-bis(phenolate) ligand for water reduction

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ABSTRACT

Reaction of $FeCl_3$ with 2-pyridylamino-*N*-2-methylene-4-ethyl-6-*tert*-butylphenol, *N*′-2-methylene-4-methyl-6-*tert*-butylphenol (H_2L) affords an iron(III) complex, [LFeCl] **1**, which has been characterized by UV–Vis spectrum and X-ray crystallography. Turnover frequency (TOF) for hydrogen evolution reaches a maximum of 141 moles of hydrogen per mole of catalyst per hour at an overpotential of 878.6 mV (in buffer, pH 7.0). Sustained water reduction catalysis occurs at glassy carbon to give H_2 over a 3 h electrolysis period with 93% faradaic yield and no observable decomposition of the catalyst.

1. Introduction

Hydrogen as a source of clean and renewable fuel has attracted great interest because of its potential to reduce the current dependence on fossil fuels [1]. Effective proton or water reduction to form H_2 has been a subject of intense study and significant effort has been made to design metal complexes for proton or water reduction [2,3]. In Nature, enzymes can perform the hydrogen evolution reaction efficiently through nickel and iron cofactors, which evolve hydrogen catalytically near the thermodynamic potential with high turnover frequencies [4,5]. However, enzymes are difficult to obtain in sufficient amounts to adapt for commercial applications and their stability is often limited outside of their native environment [4–6]. Electrolysis of water is the simplest way to produce hydrogen. To increase the reaction rate, it is necessary to use an efficient hydrogen evolution reaction (HER) electrocatalyst. Many research groups, including ours, have focused on the design and studies of molecular catalysts employing more abundant metals, and several complexes that contain nickel [7,8], cobalt [9–11], iron [12–14], copper [15–19] and molybdenum [20–24] have been developed as electrocatalysts for the reduction of proton or water to form H_2. In general, iron(III) complexes are employed as electrocatalysts for water oxidation [25–31], there is few report on water reduction by the iron(III) complex [32]. It has been shown that the donor type and electronic properties of the ligands play vital roles in determining the structure and reactivity of the corresponding metal complexes [33,34]. Identification of the factors that control the oxidation/reduction site in these complexes, determining of their redox potentials and characterization of their electronic structures, is critical for the design of more effective molecular catalysts for H_2 production. Complexes supported by polypyridyl compounds, the neutral ligands have been used for electrocatalytic hydrogen generation from aqueous solution [9,20]. With this mind, we have been studying ionic ligands such as 2-pyridylamino-*N*-2-methylene-4-ethyl-6-*tert*-butylphenol, *N*′-2-methylene-4-methyl-6-*tert*-butylphenol (H_2L), and its corresponding iron complex. In this paper, we present the synthesis and characterization of an iron(III) complex, [LFeCl] **1**, as well as its electrocatalytic properties thereof.

2. Experimental

2.1. Materials and physical measurements

UV–Vis spectra were measured on a Hitachi U-3010. ^{13}C and ^{1}H NMR spectra were measured on a Bruker AM 500 spectrometer in $CDCl_3$. ESI-MS experiments were performed on a 4000 Q TRAP Spectrometer by introducing samples directly into the ESI source using a syringe pump. Cyclic voltammograms were obtained on a CHI-660E electrochemical analyzer under N_2 using a three-electrode cell in which a glassy carbon electrode was the working electrode, a saturated Ag/$AgNO_3$ electrode was the reference electrode, and platinum wire was the auxiliary electrode. A ferrocene/ferrocenium (1+) couple was used as an internal standard. 0.10 M $[(n\text{-}Bu)_4N]ClO_4$ was used as the supporting electrolyte. Controlled-potential electrolysis (CPE) in aqueous media was

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conducted using an air-tight glass double compartment cell separated by a glass frit. The working compartment was fitted with a glassy carbon plate and an Ag/AgCl reference electrode. The auxiliary compartment was fitted with a Pt gauze electrode. The working compartment was filled with 50 mL of 0.25 M buffer solution, while the auxiliary compartment was filled with 35 mL buffer solution. Adding iron complex, both compartments were sparged for 1 h with nitrogen and cyclic voltammograms were recorded as controls. After electrolysis, a 0.50 mL aliquot of the headspace was removed and replaced with 0.50 mL of CH_4. A sample of the headspace was injected into the gas chromatograph (GC). GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument.

2.2. Synthesis of synthesis of $H_2[O_2NN]BuMeEtPy$ (H_2L)

A mixture containing 2-tert-butyl-4-methylphenol (1.6425 g, 10 mmol), 2-tert-butyl-4-ethylphenol (1.7827 g, 10 mmol), aminomethylpyridine (1.0814 g, 10 mmol), and 37% aqueous formaldehyde (1.6232 g, 20 mmol) in water (25 mL) was refluxed with stirring for 12 h. Cooling to room temperature produced a white precipitate which was collected, and recrystallized from ethanol. Drying under vacuum yielded $H_2[O_2NN]BuMeEtPy$ (87%). *Anal.* Calc. for $C_{31}H_{42}N_2O_2$: C, 78.48; H, 8.86; N, 5.91. Found C, 78.26; H, 8.74; N, 5.87%. ^1H NMR (400 MHz, $CDCl_3$) δ10.50 (s, 2H), 8.71 (d, J = 4.8 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.28 (dd, J = 12.1, 5.3 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.03 (d, J = 7.4 Hz,2H), 6.79 (t, J = 11.3 Hz, 2H), 3.81 (d, J = 25.8 Hz, 6H), 2.56 (q, J = 7.6 Hz, 1.5H), 2.25 (s, 3H), 1.41 (s, 18H), 1.22 (q, J = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ156.13, 154.11, 153.92, 148.16, 137.36, 137.16, 133.65, 129.02, 128.99, 127.57, 127.19, 127.07, 126.05, 123.71, 122.52, 122.11, 122.00, 56.42, 56.19, 55.31, 34.86, 34.80, 29.62, 28.29, 20.77, 15.94. UV–Vis [CH_3CN, λ_{max}/nm (ε/mol^{-1} cm^{-1})]: 282 (3.98×10^3).

2.3. Synthesis of [LFeCl] 1

To a methanolic solution of $H_2[O_2NN]$*BuMeEtPy* (3.10 g, 6.52 mmol) was added a solution of anhydrous $FeCl_3$ (1.06 g, 6.52 mmol) in methanol. To this solution was added triethylamine (1.32 g, 13.0 mmol) and the resulting mixture was stirred for 0.5 h at room temperature. Single crystals were obtained from the filtrate which was allowed to stand at room temperature for several days, collected by filtration, and dried in *vacuo* (2.87 g, 78%). The elemental analysis results (Found C 65.91; H 6.94; N 4.92%. $C_{31}H_{40}ClFeN_2O_2$ requires C 66.02; H 7.09; N 4.97%) were in agreement with the formula of the sample used for X-ray analysis. UV–Vis [CH_3CN, λ_{max}/nm (ε/mol^{-1} cm^{-1})]: 278 (3.55×10^3), 342 (1.74×10^3), 500 (1.12×10^3).

2.4. Crystal structure determination

The X-ray analysis of **1** was carried out with a Bruker SMART CCD area detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. All empirical absorption corrections were applied by using the SADABS program [35]. The structure was solved using direct methods and the corresponding non-hydrogen atoms are refined anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL computer program [36]. Crystallographic data for complex **1** are given in Table S1 and selected bond lengths are listed in Table S2.

3. Results and discussion

3.1. General characterization and crystal structure

In the presence of trimethylamine, the reaction of $FeCl_3$ and H_2L (Figs. S1–S2) provides an iron(III) complex, [LFeCl] **1** (yield = 78%) (Scheme 1), which is in agreement with the result of ESI-MS analysis. The electrospray mass spectrum of **1** exhibits one ion at a mass-to-charge ratio (m/z) of 528.5, with mass and isotope distribution pattern corresponding to $[Fe(III)(L)]^+$ (calculated m/z of 528.4) (Fig. S3). The electronic spectrum of **1** measured in CH_3CN exhibits two intense bands at 500 and 342 nm (Fig. S4). The lower energy band is assigned to a phenolate $p\pi \rightarrow Fe^{III}d\pi^*$ charge transfer (CT) transition [37,38]. And the higher energy band is attributed to phenolate → Fe^{III} CT involving p → $Fe^{III}d\sigma^*$ orbitals [37,38].

As shown in Fig. 1, the iron ion is bonded to two phenolate oxygen atoms and the nitrogen atom of the pyridine group in complex **1**, which defines the trigonal plane of the bipyramid. The central nitrogen atoms of the ligand and the chloride ions occupy the apical sites. The Fe(1)–O(1) distance of 1.8562(18) Å and Fe(1)–O(2) length of 1.8401(19) Å are similar to the iron–phenolate oxygen donor lengths observed in a related trigonal bipyramidal iron(III) complex possessing diamine-bis(phenolate) ligands bearing 2,4-dimethyl-substituted aromatic groups (abbreviated $FeCl[O_2NN']^{MeMeNMe2}$) [39]. These distances are shorter than the average octahedral Fe–O bond length of 1.92 Å, suggesting relatively strong iron–oxygen overlap [39–41]. The Fe(1)–Cl(1) bond distance of 2.2949(8) Å in complex **1** is slightly shorter than Fe–Cl bonds in octahedral iron(III) complexes possessing similar tetradentate ligands [41].

3.2. Cyclic voltammetry studies

Cyclic voltammogram (CV) of a DMF solution of **1** (Fig. 2) shows a reversible redox peak at −0.52 V, and a quasi-reversible wave at −1.70 V (versus $Ag/AgNO_3$), which are assigned to the couples of Fe^{III}/Fe^{II} and Fe^{II}/Fe^{I}, respectively. The current responses of the redox events at −0.52 and −1.70 V show linear dependence on the square root of the scan rate (Fig. S5), which is an indicative of a diffusion-controlled process, with the electrochemically active species freely diffusing in the solution.

3.3. Catalytic hydrogen evolution from acetic acid in DMF

From Fig. 3, it can be seen that the catalytic current near −0.52 V increased with increasing proton concentration (acetic acid concentration increased from 0.67 to 23.44 mM). This indicates that hydrogen evolution electrocatalyzed by **1** requires the reduction of Fe(II) to Fe(I) and protonation. Interestingly, with the acetic acid concentration increased from 0.67 to 23.44 mM (Fig. 3), the onset of the catalytic wave moved to more positive. Based on the above observations, only couple Fe^{II}/Fe^{I} is devoted to proton reduction. This result is similar to previous report that only couple Fe^{II}/Fe^{I} is devoted to proton reduction [32]. Further mechanistic studies are under investigation.

Several control experiments were then carried out to confirm that complex **1** was indeed responsible for the catalytic reaction. The free ligand, $FeCl_3$, and the mixture of the free ligand and $FeCl_3$ were each measured under identical conditions. As can be seen in Figs. S6–S8, the catalytic competency achieved with **1** is not matched by just ligand and $FeCl_3$, nor can it be accomplished with the ligand bound to a redox-inactive metal. Thus, a combination of the redox-active iron ion and the ligand is essential for catalytic activity.

Further evidence for the electro-catalytic activity was obtained by bulk electrolysis of a DMF solution of complex **1** (3.54 μM) with