

Synthesis and characterization of a molecular electrocatalyst based on an iron(III) complex supported by an aminebis(phenolate) ligand for proton or water reduction

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Abstract Reaction of FeCl₃ with *N*,*N*-bis[methyl(2-hydroxy-3-*tert*-butyl-5-methoxyphenyl)]-*N'N'*-dimethylethylenediamine (H₂L) produces an iron(III) complex [LFeCl] **1**, which has been characterized by X-ray crystallography. Electrochemical studies show that **1** can electrocatalyze hydrogen evolution, both from acetic acid with a turnover frequency (TOF) of 11 mol of hydrogen per mole of pre-catalyst per hour at an overpotential of 470 mV (in DMF), and from water with a TOF of 205 mol of hydrogen per mole of pre-catalyst per hour at an overpotential of 987.6 mV (in buffer, pH 7.0).

Introduction

Hydrogen is one of the most ideal energy carriers and a possible alternative to fossil fuels in the future, because of its numerous advantages such as recyclability and pollution-free use [1]. Water splitting is an important method for hydrogen production in high purity and large quantities [2]. Effective proton reduction to form H_2 has been a subject of intense study, and significant effort has been made to design metal complexes for proton reduction [3]. In nature, hydrogenase enzymes are very efficient catalysts for both the reductive generation and oxidative up-

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Shu-Zhong Zhan shzhzhan@scut.edu.cn take of dihydrogen [4]. However, enzymes are difficult to adapt for commercial applications, and their stability is often limited outside of their native environment [5]. Electrolysis of water is the simplest way to produce hydrogen. To increase the reaction rate and lower the overpotential, it is necessary to use an efficient hydrogen evolution reaction (HER) electrocatalyst. Many research groups, including ours, have focused on the development of molecular catalysts employing the more abundant metals, and several complexes of nickel [6], cobalt [7-9], copper [10-12], and molybdenum [13-17] have been developed as electrocatalysts for the reduction of acetic acid or water to form H₂. In general, iron(III) complexes are employed as electrocatalysts for water oxidation [18– 20], and there are few reports on water reduction by the iron(III) complexes [21]. Herein, we present the synthesis and characterization of an iron(III) complex, [LFeCl] 1, as well as its electrocatalytic properties for hydrogen evolution from both acetic acid and water.

Experimental

Materials and measurements

All commercially available reagents were used as received without further purification. The amine-bis(phenolate) ligand, H₂L, was prepared using a literature procedure by involving a Mannich condensation [22]. Elemental analyses for C, H, and N were obtained on a Perkin–Elmer analyzer model 240. Cyclic voltammograms were obtained on a CHI-660E electrochemical analyzer under N₂ using a three-electrode cell in which a glassy carbon electrode GC (1.0 mm in diameter) was the working electrode, a saturated Ag/AgCl or Ag/AgNO₃ electrode was the

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reference electrode, and a platinum wire was the auxiliary electrode. In organic media, the ferrocene/ferrocenium (1+) couple was used as an internal standard and 0.10 M $[(n-Bu)_4N]ClO_4$ was used as the supporting electrolyte. Controlled-potential electrolysis (CPE) in aqueous media was conducted using an airtight 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 charged with 50 mL of 0.25 M phosphate buffer solution, while the auxiliary compartment contained 35 mL of phosphate buffer solution. After addition of the iron complex, the cyclic voltammogram was recorded. After electrolysis, a 0.5-mL aliquot of the headspace was removed and replaced with 0.5 mL of CH₄. The headspace sample was injected into the gas chromatograph. GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument. ESI-MS experiments were performed on a Bruker Daltonics Esquire 3000 spectrometer by introducing samples directly into the ESI source using a syringe pump.

Synthesis of complex 1

To a solution of H₂L (0.235 g, 0.5 mmol) and triethylamine (0.100 g, 1 mmol) in methanol (10 ml), was added a solution of anhydrous FeCl₃ (0.082 g, 0.5 mmol) in methanol and the mixture was stirred for 10 min. The solution was allowed to slowly evaporate, affording darkblue crystals, which were collected and dried in *vacuo* (0.245 g, 88 %). The elemental analysis results (Found C 60.1; H 7.5; N 5.0 %. C₂₈H₄₂N₂O₄FeCl requires C 59.8; H 7.5; N 5.0 %) were in agreement with the formula of the sample used for X-ray analysis.

X-ray crystallography

The X-ray analysis of complex 1 was carried out with a Bruker Smart Apex II DUO area detector using graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature. All empirical absorption corrections were applied by using the SADABS program [23]. The structure was solved using direct methods, and the corresponding non-hydrogen atoms were 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-97 computer program [24]. Crystallographic data for complex 1 are given in Table S1, and selected bond lengths are listed in Table S2.

Results and discussion

General characterization

In the presence of triethylamine, the reaction of FeCl₃ and H₂L affords blue crystals of the complex [LFeCl] **1** in 88 % yield (Scheme 1). This is in agreement with results from MS measurements which exhibited an ion at a mass-to-charge ratio (m/z) of 526.25 (Fig. S1), with the mass and isotope distribution pattern corresponding to that of [Fe(III)(L)]⁺ (calculated m/z of 526.44).

As shown in Fig. 1, in complex 1, the iron ion is bonded to two oxygen atoms, two nitrogen atoms, and one Cl^- ion, which defines the trigonal plane of the bipyramid. The central nitrogen atoms of the ligand and the chloride ions occupy the apical sites. Fe–N distances are 2.273(2) and 2.178(2) Å, respectively. The Fe(1)–O(3) distance [1.846(2) Å] is same as that of Fe(1)–O(4). The Fe(1)–Cl(7) bond distance is 2.3125(9) Å.

Electrochemical studies

When bare platinum or glassy carbon was used as the working electrode, in the absence of complex 1, the proton reduction was not apparent until a potential of -0.88 or -1.62 V versus Ag/AgNO₃, respectively (Fig. S2). Upon addition of complex 1, the onset of catalytic current was observed at about -0.25 V versus Ag/AgNO₃.

As shown in Fig. 2a, the cyclic voltammogram (CV) of a DMF solution of complex 1 shows a reversible redox peak at -0.30 V and an irreversible wave at -1.68 V, which are assigned to the couples of Fe^{III}/Fe^{II} and Fe^{II}/Fe^I, respectively. No significant change was found after 10 scans, indicating that the catalyst is stable under these conditions (Fig. S3). Both current responses of the redox events at -0.30 and -1.68 V show linear dependence on the square root of the scan rate (Fig. S4), indicative of a



Scheme 1 Synthesis of complex 1



Fig. 1 Molecular structure (ORTEP) of **1**. Selected bond lengths (Å): Fe(1)–O(3), 1.846(2); Fe(1)–N(2), 2.273(2); Fe(1)–O(4), 1.846(2); Fe(1)–N(4), 2.178(2); Fe(1)–Cl(7), 2.3125(9)

diffusion-controlled process, with the electrochemically active species freely diffusing in solution.

Catalytic hydrogen evolution in DMF

From Fig. 2b, it can be seen that the catalytic current near -1.68 V increased with increasing proton concentration (acetic acid concentration increased from 0.0 to 66.67 mM). This indicates that hydrogen evolution electrocatalyzed by **1** requires the reduction of Fe(II) to Fe(I) and protonation, with the catalytic onset shifted to more positive potential (from -1.58 V to -1.20 V). Based on these observations, only the Fe^{II}/Fe^I couple is involved in proton reduction, which is similar to a previous report [21]. Further mechanistic studies are in progress.

Several control experiments were then carried out to confirm that complex **1** was indeed responsible for the catalytic reaction. In particular, the free ligand, FeCl₃, and the mixture of the free ligand and FeCl₃ were each investigated under identical experimental conditions. As can be seen in Figs. S5–S7, the catalytic competency achieved with complex **1** is not matched by either the free ligand or FeCl₃, nor can it be accomplished with the ligand bound to a redox-inactive metal. Thus, the combination of the redoxactive Fe center and the ligand is essential for catalytic activity.

Further evidence for the electrocatalytic activity was obtained by bulk electrolysis of a DMF solution of complex $1 (0.714 \ \mu\text{M})$ with acetic acid (40.0 mM) at variable applied potential using a glassy carbon plate electrode in a double-compartment cell. Fig. S8a shows the total charge of bulk electrolysis of complex 1 in the presence of acid; the charge significantly increased when the applied potential was made



Fig. 2 a Cyclic voltammogram of 1.0 mM complex **1** in 0.10 M of $[n-Bu_4N]ClO_4$ DMF solution at a glassy carbon electrode and a scan rate of 100 mV/s. **b** Cyclic voltammograms of a 1.0-mM solution of complex **1**, with varying concentrations of acetic acid in DMF. Conditions: room temperature, 0.10 M [n-Bu_4N]ClO_4 as supporting electrolyte, scan rate: 100 mV/s, GC working electrode (1 mm diameter), Pt counter electrode, Ag/AgNO_3 reference electrode. Fc internal standard (*)

to more negative. When the applied potential was -1.50 V versus Ag/AgNO₃, the maximum charge reached 68 mC during 2 min of electrolysis. A controlled-potential electrolysis (CPE) experiment under the same potential with a catalyst-free solution gave a charge of only 17 mC (Fig. S8b), showing that this complex does indeed serve as an effective hydrogen producer under such conditions. Assuming every pre-catalyst molecule was distributed only on the electrode surface and every electron was used for the reduction of protons, according to Eqs. (1) [6] and [25], we calculated the TOF for the pre-catalyst as reaching a maximum of 11 moles of hydrogen per mole of pre-catalyst per hour at an overpotential of 470 mV (Fig. S9).

$$TOF = \Delta C / (F * n_1 * n_2 * t)$$
(1)

Overpotential = Applied potential
$$-E_{\text{HA}}^{\odot}$$

= Applied potential (2)
 $-(E_{H}^{\odot+} - (2.303\text{RT}/F)pK_{a\text{HA}})$

where ΔC is the charge from the pre-catalyst solution during CPE minus the charge from solution without precatalyst during CPE; F is Faraday's constant, n_1 is the number of moles of electrons required to generate one mole of H₂, n_2 is the number of moles of pre-catalyst in solution, and t is the duration of electrolysis.

Catalytic water reduction experiments

We further explored the electrochemical behavior of complex 1 in buffered aqueous solutions, where pH = 5.6-8.0which is the range associated with catalytic water reduction. The background CV in the absence of 1 exhibits no catalytic current (Fig. 3a), suggesting that water reduction to H₂ is mediated by complex 1 [9]. Figure 3b exhibits a systematic increase in i_{cat} with decreasing pH from 8.0 to 5.6. Further evidence for the electrocatalytic activity of complex 1 was obtained by bulk electrolysis of an aqueous solution of 1 (0.714 µM) with buffer (0.25 M, pH 7.0) at variable potential using a GC electrode in a double-compartment cell. When the applied potential was -1.60 V versus Ag/AgCl, the maximum charge was only 66 mC for 2 min of electrolysis in the absence of complex 1 (Fig. 4a). Under the same conditions, the charge reached 1006 mC during 2 min of electrolysis in the presence of 1 (Fig. 4b), accompanied by evolution of a gas, which was confirmed as H₂ by gas chromatography. According to Fig. S10a, ~ 0.445 mL of H₂ was produced over an electrolysis period of 2 h with a Faradaic efficiency of 93.5 % for H₂ (Fig. S10-b). According to Eqs. (1) and (3) [7, 13], we calculated the TOF for the pre-catalyst as reaching a maximum of 205 mol of hydrogen per mole of pre-catalyst per hour at an overpotential of 987.6 mV (Fig. S11), where



Fig. 3 a CVs of buffers with and without complex **1** (pH 7.0, scan rate: 100 mV/s). **b** Cyclic voltammograms of 0.30 mM complex **1**, showing the variation in catalytic current with pH (scan rate: 100 mV/s)



Fig. 4 a Charge buildup of 0.10 M buffer (pH 7.0) at -1.60 V vs Ag/AgCl. **b** Charge buildup of complex **1** (0.714 μ M) versus a series of applied potentials at pH 7.0. All data have been deducted blank

Overpotential = Applied potential
$$- E(pH)$$

= Applied potential $- (-0.059pH)$ (3)

To prove that complex 1 acts as a homogeneous preelectrocatalyst, we measured the dependence of the catalytic current on the concentration of 1. As shown in Fig. S12, the catalytic current was indeed dependent on the complex concentration. In addition, several other pieces of evidence suggest that this iron complex is a homogeneous pre-catalyst, as follows. (1) There is no evidence for a heterogeneous electrocatalytic deposit. For example, the electrode was rinsed with water and electrolysis at -1.50versus Ag/AgCl was run for an additional 2 min in 0.10 M phosphate buffer at pH 7.0 with no pre-catalyst present in solution. During this period, ca. 67 mC of charge was passed, a similar magnitude as observed for electrolyses conducted with freshly polished electrodes. (2) No discoloration of the electrodes was observed during cyclic voltammetry or bulk electrolysis. In order to determine whether complex 1 retains its activity over longer time periods, a 72-h controlled-potential electrolysis at -1.45 V versus Ag/AgCl was conducted in stirred 0.25 M phosphate buffer solution (pH 7.0), containing 1 (7.14 μ M). On completion of this experiment, the pH has increased by four units (from 7.0 to 11), consistent with accumulation of OH^- by water reduction, $2H_2O + 2e \rightarrow H_2 + 2OH^-$. As depicted in Fig. S13, the pre-catalyst affords an essentially linear charge buildup over time, with no substantial loss in activity over the course of 72 h.

Conclusion

We have described a new iron(III) complex, which is easily obtained from the reaction of simple iron salts with an amine-bis(phenolate) ligand. Our ongoing efforts are focused on modifying the Schiff base ligand to give related water-soluble complexes for further functional studies, with an emphasis on chemistry relevant to sustainable energy cycles.

Supplementary material

CCDC 1044462 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving. html. Acknowledgments This work was supported by the National Science Foundation of China (Nos. 20971045 and 21271073).

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