Effect of ligand modification on hydrogen production catalyzed by iron (III) complexes supported by amine-bis(phenolate) ligands

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ABSTRACT

In the presence of trimethylamine, the reaction of $FeCl_3$ with 2-pyridylamino-N,N-bis(2-methylene-4-methyl-6-tert-butylphenol) (H_2L) and 2-pyridylamino-N,N-bis(2-methylene-4-methoxyl-6-tert-butylphenol) (H_2L') produces two iron(III) complexes, [LFeCl] (**1**) and [L'FeCl] (**2**), respectively. **1** can electrocatalyze hydrogen evolution both from acetic acid, with a turnover frequency (TOF) of 98.5 mol of hydrogen per mole of catalyst per hour at an overpotential (OP) of 941.6 mV (in DMF), and from aqueous buffer solution (pH 7.0), with a TOF of 676.6 mol of hydrogen per mole of catalyst per hour at an OP of 836.6 mV. **2** electrocatalyzes hydrogen generation from acetic acid, with a TOF of 50.6 mol of hydrogen per mole of catalyst per hour at an OP of 941.6 mV, and from aqueous buffer solution (pH 7.0), with a TOF of 554 mol of hydrogen per mole of catalyst per hour at an OP of 836.6 mV. These results indicate that the electronic properties of the ligands play a vital role in determining the catalytic activities of the iron complexes.

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1. Introduction

Increasing energy and environmental concerns have encouraged researchers to explore sustainable and renewable alternatives of conventional fossil fuels, such as hydrogen energy with zero carbon emissions [1]. Water splitting is an ideal method for hydrogen production with high purity and in large quantities [2]. In nature, hydrogenase enzymes are very efficient catalysts for both the reductive generation and oxidative uptake of dihydrogen [3]. However, enzymes are difficult to adapt for commercial applications and their stability is often limited outside of their native environment [4,5]. Therefore, 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 [6]. So far, several complexes that contain nickel [7–10], cobalt [11–14], iron [15–18], copper [19–23] and molybdenum [24–26] have been developed as electrocatalysts for the reduction of water to form H_2. A number of model complexes have been prepared, but an important fundamental question about the enzymes that remains to be answered is the precise role of the ligands in hydrogen production. With this mind, we are trying to explore the possibility of catalysis for hydrogen evolution from water by transition metal complexes with different ligands, because the donor type and electronic properties of the ligands play vital roles in determining the structure and reactivity of the corresponding metal complexes. In general, iron(III) complexes are used as electrocatalysts for water oxidation [27–29], and there are a few reports on water reduction by iron(III) complexes [30]. Herein, we present the synthesis, characterization and electrocatalytic properties for hydrogen evolution from both acetic acid and aqueous buffer of two iron(III) complexes, [LFeCl] (**1**) and [L'FeCl] (**2**), as well as the effect of the modification of the tetradentate ligand on the catalytic properties of two iron(III) complexes.

2. Experimental

2.1. Physical measurements

Elemental analyses for C, H and N were conducted on a Perkin-Elmer analyzer model 240. ESI-MS experiments were performed by introducing samples directly into the ESI source using a syringe pump on a Bruker Daltonics Esquire 3000 spectrometer. Cyclic voltammograms (CVs) 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/AgCl or $Ag/AgNO_3$ electrode was the 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)$_4$N]ClO$_4$ was used as the supporting

electrolyte. Controlled-potential electrolysis (CPE) was 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/AgNO$_3$ (organic medium) or Ag/AgCl (aqueous medium) reference electrode. The auxiliary compartment was fitted with a Pt gauze electrode. The working compartment was charged with 50 mL of 0.10 M [(n-Bu)$_4$N]ClO$_4$ DMF solution (organic medium) or 0.25 M phosphate buffer solution (aqueous medium) containing the iron complex, while the auxiliary compartment contained 35 mL of 0.10 M [(n-Bu)$_4$N]ClO$_4$ DMF solution (organic medium) or 0.25 M phosphate buffer solution (aqueous medium). After electrolysis, a 0.5 mL aliquot of the headspace was removed and replaced with 0.5 mL of CH$_4$. The headspace sample was injected into the gas chromatograph (GC). GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument.

2.2. Synthesis of 2-pyridylamino-N,N-bis(2-methylene-4-methyl-6-tert-butylphenol) (H$_2$L)

A solution of 2-tert-butyl-4-methylphenol (3.28 g, 20 mmol), aminomethylpyridine (1.08 g, 10 mmol) and 37% aqueous formaldehyde (1.62 g, 20 mmol) in water (50 mL) was stirred and refluxed for 8 h. Upon cooling, a large quantity of beige solid formed. The solvents were decanted and the remaining solid residue was washed with cold methanol to give a pure white powder (3.65 g, 79%). A crystalline product was obtained by slow cooling of a hot diethyl ether solution. *Anal.* Calc. for C$_{30}$H$_{40}$N$_2$O$_2$: C, 78.26; H, 8.70; N, 4.38. Found: C, 78.31; H, 8.80; N, 4.38%. ^{1}H NMR (400 MHz, CDCl$_3$) δ, ppm: 10.38 (s, 2H), 8.60 (d, J = 4.8 Hz, 1H), 7.60 (td, J = 7.7, 1.4 Hz, 1H), 7.18 (dd, J = 12.7, 5.5 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.92 (d, J = 1.2 Hz, 2H), 6.66 (s, 2H), 3.73 (s, 2H), 3.67 (s, 4H), 2.16 (s, 6H), 1.31 (s, 18H). ^{13}C NMR (101 MHz, CDCl$_3$) δ, ppm: 155.06 (s), 152.86 (s), 147.09 (s), 136.30 (s), 136.06 (s), 127.91 (s), 126.04 (d, J = 13.6 Hz), 122.60 (s), 121.44 (s), 121.05 (s), 76.29 (s), 75.97 (s), 75.66 (s), 55.18 (s), 54.26 (s), 33.73 (s), 28.55 (s), 19.70 (s).

2.3. Synthesis of 2-pyridylamino-N,N-bis(2-methylene-4-methoxyl-6-tert-butylphenol) (H$_2$L′)

The procedure was performed in the same way as that for the synthesis of H$_2$L except that 2-tert-butyl-4-methylphenol was replaced by 2-tert-butyl-4-methoxylphenol. H$_2$L′ was obtained in a yield of 75% (3.69 g). *Anal.* Calc. for C$_{30}$H$_{40}$N$_2$O$_4$: C, 73.17; H, 8.13; N, 5.69. Found: C, 73.31; H, 8.13; N, 5.70%. ^{1}H NMR (400 MHz, CDCl$_3$) δ, ppm: 10.29 (s, 2H), 8.68 (d, J = 4.6 Hz, 1H), 7.69 (dd, J = 10.9, 4.3 Hz, 1H), 7.26 (dd, J = 14.6, 7.7 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 6.83 (d, J = 2.9 Hz, 2H), 6.51 (d, J = 2.8 Hz, 2H), 3.76 (d, J = 13.6 Hz, 11H), 1.40 (s, 17H). ^{13}C NMR (101 MHz, CDCl$_3$) δ, ppm: 155.84 (s), 151.81 (s), 150.20 (s), 148.18 (s), 138.86 (s), 137.49 (s), 123.95 (s), 122.64 (s), 113.55 (s), 112.40 (s), 77.39 (s), 77.07 (s), 76.75 (s), 56.29 (s), 55.72 (s), 55.00 (s), 35.08 (s), 29.50 (s).

2.4. Synthesis of complex [LFeCl] (1)

To a solution, containing H$_2$L (0.46 g, 1.0 mmol) and triethylamine (0.20 g, 2.0 mmol) in THF (20 ml), FeCl$_3$ (0.162 g, 1.0 mmol) in methanol was added and the mixture was stirred for 15 min. Single crystals were obtained from the filtrate, after standing at room temperature for several days, and these were collected by filtration, and dried in *vacuo* (0.41 g, 75%). The elemental analysis results (Found: C, 65.18; H, 6.92; N, 5.03%; C$_{30}$H$_{38}$N$_2$O$_2$FeCl requires: C, 65.46; H, 6.91; N, 5.09%) are in agreement with the formula of the sample used for X-ray analysis.

2.5. Synthesis of complex [L′FeCl] (2)

The procedure was performed in the same way as that for the synthesis of 1 except that H$_2$L was replaced by H$_2$L′. Complex 2 was obtained in a yield of 71% (0.42 g). The elemental analysis results (Found: C, 61.12; H, 6.52; N, 4.81%; C$_{30}$H$_{38}$N$_2$O$_4$FeCl requires: C, 61.86; H, 6.53; N, 4.81%) are in agreement with the formula of the sample used for X-ray analysis.

2.6. Crystal structure determination

X-ray analyses of complexes 1 and 2 were carried out with a Bruker Smart Apex II DUO 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 [31]. The structures were 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 [32]. Crystallographic data for complexes 1 and 2 are given in Tables S1 and S2 and selected bond lengths are listed in Tables S3 and S4.

3. Results and discussion

3.1. Structures and general characterization

In the presence of triethylamine, the reaction of FeCl$_3$ with H$_2$L and H$_2$L′ (Figs. S1 and S2) affords two iron(III) complexes, [LFeCl] (1) and [L′FeCl] (2), in 75 and 71% yields, respectively (Scheme 1).

The electronic spectra of H$_2$L, H$_2$L′, 1 and 2 were recorded in CH$_3$CN at room temperature. As shown in Figs. S3 and S4, H$_2$L and H$_2$L′ each exhibit one band at 283 and 296 nm, respectively. Compared with that of H$_2$L, two new absorption bands appeared at 335 and 506 nm for 1. The lower energy band can be assigned to a phenolate p$_\pi$ to Fe^{III} d$_\pi^*$ charge transfer (CT) transition, and the higher energy band is attributed to a phenolate p to Fe^{III} dσ^* CT [33,34]. Similar to 1, complex 2 also shows two bands at 348 and 520 nm, which can be attributed to phenolate to Fe^{III} CT transitions.

As shown in Fig. 1, solid complex 1 consists of one iron ion, one L^{2-} ligand and one chloride ion. The iron ion is five-coordinated by two oxygen atoms, two nitrogen atoms and one chloride ion. Fe–N distances are 2.149(2) and 2.2794(18) Å, and the Fe–O distances are 1.8379(16) and 1.8574(15) Å. The Fe–Cl bond distance is
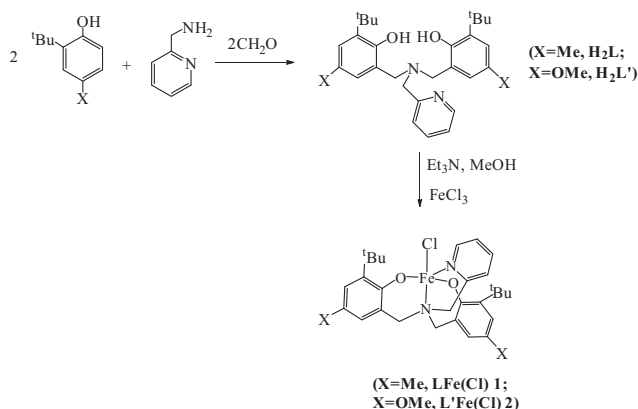
Scheme 1. The synthesis of [LFe(Cl)] 1 and [L′Fe(Cl) 2.