



Short communication

A new molecular electro-catalyst based on a triazenido–cobalt complex for generating hydrogen from both acetic acid and water



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ABSTRACT

The reaction of 1-[(2-carboxymethyl)benzene]-3-[2-pyridine]triazene (HL) with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ affords a six-coordinated cobalt(III) complex, $[\text{CoL}_3]$ **1**, a new molecular electrocatalyst. Electrochemical studies show that complex **1** can catalyze hydrogen evolution from both acetic acid and water. Turnover frequency (TOF) reaches a maximum of 21 and 1973 mol of hydrogen per hour at overpotential (OP) of 992 mV (in DMF) and 838 mV (in phosphate buffer, pH 7.0), respectively. This performance is significantly better than those of other molecular cobalt catalysts reported in the literature for electrochemical hydrogen production. This is attributed to the ionic ligand, L^- that coordinates strongly through four nitrogen atoms to the cobalt center, stabilizing the low oxidation state.

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1. 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 [4] can efficiently catalyze both the production and the oxidation of hydrogen using the earth-abundant metals (such as nickel and iron). Structural studies indicated that the FeFe-hydrogenases function by combining cofactors that couple acid–base and redox reactions mediated by the diiron dithiolate core and its cofactors (Scheme 1) [4–6], and suggested that a basic nitrogen or oxygen atom may be incorporated into the backbone of the dithiolate ligand [5,7]. However, enzymes are difficult to adapt for commercial applications and their stability is often limited outside of their native environment [5].

The amine [8] or oxygen [9] cofactor is proposed to facilitate the cleavage/formation of the hydrogen–hydrogen bond and the transfer of protons to and from the distal metal centre [10]. These considerations have led to the development of molecular catalysts employing the more abundant metals, and several complexes that contain iron [11–14] and cobalt [15–18] have been developed as electrocatalysts for the production of hydrogen. Generally, metal centers of molecular catalysts play an important role for hydrogen evolution in their catalytic cycle. However, the fundamental question concerning the precise roles of both

the ligand and metal center within the enzyme remains to be properly answered. Within this context, we have studied triazenido ligands and their corresponding complexes for catalytic applications, because the central nitrogen of the triazenido ligand imparts greater basicity on the $[\text{N}\cdots\text{N}\cdots\text{N}]^-$ relative to the neutral nitrogen, making the triazenido more electron donating, amenable to binding to H^+ and hydrogen production. Preliminary research suggests that copper, cobalt and palladium complexes supported by triazenido ligands can catalyze proton reduction, but the mechanism is not clear [19–24]. In this paper, we report the synthesis, structure and characterization of a new triazenido–cobalt complex $[\text{CoL}_3]$ **1**, as well as its electrocatalytic function for hydrogen evolution from acetic acid or water thereof.

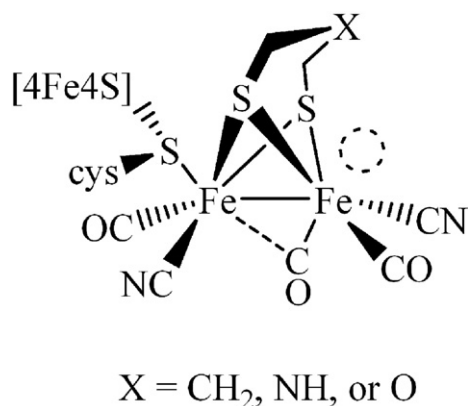
2. Experimental

2.1. Materials and physical measurements

The triazenido ligand, HL was prepared using a literature procedure [25]. 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 N_2 using a three-electrode cell in which a glassy carbon electrode (1.0 mm in diameter) was the working electrode, a saturated Ag/AgCl or Ag/AgNO₃ 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 $[(\text{n-Bu})_4\text{N}]\text{ClO}_4$ was used as the supporting electrolyte. Controlled-potential electrolysis (CPE) in aqueous media 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/AgCl reference electrode. The

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Scheme 1. Structure of active site of the FeFe-hydrogenase and its model.

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 cobalt 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 CH_4 . The headspace sample was injected into the gas chromatograph. GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument.

2.2. Synthesis of complex **1**

To a solution of containing ligand (HL) (0.769 g, 3 mmol) and triethylamine (0.10 g, 1 mmol) in dichloromethane/methanol (40 mL, 1:1), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g, 1 mmol) was added and the mixture was stirred for 30 min. The solution was allowed to slowly evaporate to deep red crystals, which were collected and dried in vacuo (0.462 g, 56%). Anal. Found (calcd) for $\text{C}_{39}\text{H}_{33}\text{N}_{12}\text{O}_6\text{Co}$: C 56.57 (56.80), H 4.03 (4.03), N 20.34 (20.38).

2.3. Crystal structure determination

The X-ray analysis of **1** was carried out with a Bruker SMART CCD area detector using graphite monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. All empirical absorption corrections were applied by using the SADABS program [26]. 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 [27]. The selected bond lengths are listed in Table S1.

3. Results and discussion

3.1. General characterization and electrochemical studies

In the presence of Et_3N , the reaction of ligand HL and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ affords deep red crystals of complex **1** in 65% yield. As shown in Fig. 1, cobalt atom is six-coordinated by nitrogen atoms from three triazenido ligands. The Co–N bond distances of triazenido ligands fall in the range 1.914 (3)–1.917 (3) \AA .

Cyclic voltammogram of complex **1** in DMF exhibits one quasi-reversible couple at -0.80 V versus Ag/AgNO_3 (Fig. 2a), which can be assigned to the couple of $\text{Co}^{\text{III/II}}$. As observed in Fig. S1, the current response of the redox events at -0.84 V versus Ag/AgNO_3 shows a linear dependence on the square root of the scan rate, which is an indicative of

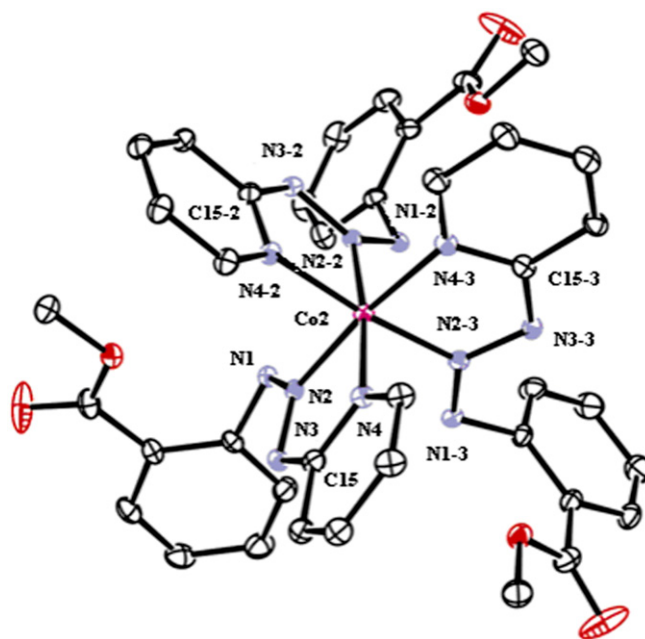


Fig. 1. Molecular structure of complex **1**.

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

3.2. Catalytic hydrogen evolution from acetic acid in DMF

To determine possible electrocatalytic activity of this cobalt complex, cyclic voltammograms of complex **1** were recorded in the presence of acetic acid. Fig. 2b shows a systematic increase in i_{cat} observed near -0.84 V with increasing acid concentration from 0.00 to 1.36 mM. This rise in current can be attributed to the catalytic generation of H_2 from acetic acid [11]. Reduction potentials of complex **1** moved to more anodic values with the sequential increments of acid concentration. This indicates that hydrogen evolution electrocatalyzed by **1** requires the reduction of Co^{III} to Co^{II} and protonation. Interestingly, with the acetic acid concentration increased from 0.0 to 1.36 mM (Fig. 2b), the onset of the catalytic wave also moved to more anodic values with the sequential increments of acid concentration. Based on the above observations, the couple of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ is devoted to proton reduction. This result is different from previous reports that only couple $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ is devoted to proton reduction [28,29]. Further mechanistic studies are in progress.

Several control experiments were carried out to verify that complex **1** is responsible for the catalysis. In particular, acetic acid, the free ligand, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and the mixture of the free ligand and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were each measured under identical conditions. As can be seen in Figs. S2–S5, the catalytic competency achieved with **1** is not matched by just ligand, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, or the mixture of the free ligand and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Thus, a combination of the cobalt center 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 acetic acid (1.36 mM). Fig. 3a shows the charge of bulk electrolysis of solution containing complex **1** in presence of acetic acid, the charge significantly increased when the absolute value of applied potential increased. When the applied potential was -1.45 V versus Ag/AgNO_3 , the maximum charge reached 34 mC during 2 min of electrolysis. CPE experiment under the same potential without complex **1** only gave a charge of 15 mC (Fig. 3b), showing that this complex does serve an effective hydrogen production under such conditions. According to Eq. (1) [15], we calculated TOF for the catalyst reaching a maximum of 21 mol of

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