



# Electrochemical-driven water reduction catalyzed by a water soluble cobalt(III) complex with Schiff base ligand



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## ABSTRACT

A new molecular catalyst based on cobalt complex [LCoCl] (**1**) is formed by the reaction of N, N-dimethylethylenediamino-N,N-bis(2,4-dimethyl) phenol (H<sub>2</sub>L) with CoCl<sub>2</sub>·6H<sub>2</sub>O for electrolytic water reduction. To our knowledge **1** is by far the most active electrocatalyst for hydrogen generation from water with a turnover frequency (TOF) of 2744 mol of hydrogen per mole of catalyst per hour at an overpotential of −638 mV (pH 7.0). This is attributed to the ionic ligand, L<sup>2−</sup>, that coordinates strongly through two nitrogen atoms and two oxygen atoms to the cobalt center, leaving one Cl<sup>−</sup> ion in axial position and making the Cl<sup>−</sup> ion ionize in water.

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## 1. Introduction

Water splitting is one of the most attractive technologies for solar energy harvesting and sustainable energy production [1–6]. Yet, one of the key challenges in water splitting is the development of efficient catalysts for water reduction reactions with low overpotentials, good stability, and high turnover rates [7–9]. Therefore, a great deal of research efforts have been devoted to the development of effective catalysts based on earth-abundant metals, and molecular complexes that contain nickel [10,11], cobalt [12–14], molybdenum [15] and copper [16–18] for the reduction of water to form H<sub>2</sub>. Nevertheless, despite much progress, major improvements in several areas, including lowering overpotentials, increasing catalyst durability, and using earth-abundant elements, are needed before efficient electro- and photocatalytic water splitting can be realized. 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 [12,19,20]. Identification of the factors that control the oxidation/reduction site in these complexes, determination of their redox potentials and characterization of their electronic structures, are among the critical factors in the design of more effective molecular catalysts for H<sub>2</sub> production. Within this context, we have been studying tetradentate ligands such as N, N-dimethylethylenediamino-N,N-bis(2,4-dimethylphenol) (H<sub>2</sub>L),

an potential ionic ligand and its corresponding cobalt complexes for catalytic applications. In this paper, we report a water soluble cobalt(III) complex [LCoCl] (**1**) that exhibited remarkable activity in electro-catalytic reduction of water for hydrogen generation.

## 2. Experimental

### 2.1. Materials and physical measurements

<sup>1</sup>H NMR spectrum was measured on a Bruker AM 500 spectrometer in CDCl<sub>3</sub>. Elemental analyses for C, H, and N were obtained on a Perkin-Elmer analyzer model 240. ESI-MS experiment was performed on a Bruker Daltonics Esquire 3000 spectrometer by introducing sample directly into the ESI source using a syringe pump. SEM of a glassy carbon electrode after 3 h electrolysis was recorded on a PHILIPS XL-30ESEM spectrometer. Cyclic voltammograms were obtained on a CHI-660E electrochemical analyzer under N<sub>2</sub> using a three-electrode cell in which a glassy carbon electrode was the working electrode, a saturated Ag/AgCl electrode was the reference electrode, and platinum wire was the auxiliary electrode. In organic media, a ferrocene/ferrocenium (1+) couple was used as an internal standard, and 0.10 mol L<sup>−1</sup> [(n-Bu)<sub>4</sub>N]ClO<sub>4</sub> 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 auxiliary compartment was fitted with a Pt gauze electrode. The working compartment was filled with 0.050 L of 0.25 mol L<sup>−1</sup> phosphate buffer, while the

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auxiliary compartment was filled with 0.035 L phosphate buffer solution. Cobalt complex was then added and cyclic voltammograms were recorded. After electrolysis, a  $5.0 \times 10^{-4}$  L aliquot of the headspace was removed and replaced with  $5.0 \times 10^{-4}$  L of CH<sub>4</sub>. 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 *N,N*-dimethylethylenediamino-*N,N*-bis(2,4-dimethyl)phenol (H<sub>2</sub>L).

A mixture of 2,4-dimethylphenol ( $2.44 \times 10^{-3}$  kg,  $2.0 \times 10^{-2}$  mol), *N,N*-dimethylethylenediamine ( $8.8 \times 10^{-4}$  g,  $1.0 \times 10^{-2}$  mol), and 37% aqueous formaldehyde ( $1.62 \times 10^{-3}$  kg,  $2.0 \times 10^{-2}$  mol) in water (0.050 L) was stirred and refluxed for 8 h. Upon cooling, a large quantity of solid formed. The solvents were decanted, and the remaining solid residue was washed with cold ethanol to give a pure, white powder ( $2.415 \times 10^{-3}$  kg, 67.8% yield). Crystalline product was obtained by slow cooling of a hot diethyl ether solution. Anal. calcd for C<sub>22</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.16; H, 8.99; N, 7.86%. Found C, 74.33; H, 8.98; N, 7.81%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.84 (s, 2H), 6.66 (s, 2H), 3.57 (s, 4H), 2.55 (s, 4H), 2.30 (s, 6H), 2.19 (s, 12H).

## 2.3. Synthesis of complex 1

To a solution, containing H<sub>2</sub>L ( $1.78 \times 10^{-4}$  kg,  $5 \times 10^{-4}$  mol) and triethylamine ( $1.0 \times 10^{-4}$  kg,  $1.0 \times 10^{-3}$  mol) in methanol (0.010 L), CoCl<sub>2</sub>·6H<sub>2</sub>O ( $1.20 \times 10^{-4}$  kg,  $5 \times 10^{-4}$  mol) was added and the mixture was stirred for 10 min. Brown crystals were obtained from the filtrate which was allowed to stand at room temperature for several days, collected by filtration, and dried *in vacuo* ( $1.7 \times 10^{-4}$  kg, 74%). The elemental analysis results (Found C, 58.67; H, 6.67; N, 6.31. C<sub>22</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>CoCl requires C, 58.81; H, 6.68; N, 6.24) were in agreement with the formula of the sample used for X-ray analysis.

## 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 ( $\lambda = 0.71073$  Å) at room temperature. All empirical absorption corrections were applied by using the SADABS program [21]. 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 [22]. Crystallographic data for complex **1** are given in Table 1 and selected bond lengths are listed in Table 2.

## 3. Results and discussion

### 3.1. General characterization

Experimentally, cobalt (III) complex **1** was prepared by the reaction of CoCl<sub>2</sub> and H<sub>2</sub>L (Fig. S1) in the presence of triethylamine (yield 74 %) (Scheme 1), which was soluble in water and common organic solvents, such as DMF and CH<sub>3</sub>CN.

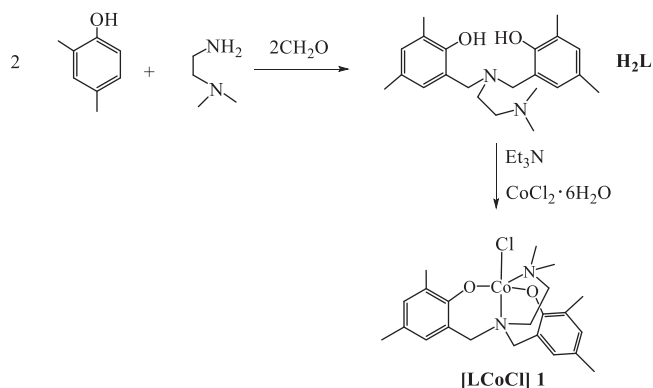
Complex **1** crystallizes in space group P-1, with two formula units present per unit cell. As shown in Fig. 1, in complex **1**, the cobalt ion is bonded to two oxygen atoms (O(3) and O(5)), two nitrogen atoms (N(4) and N(9)) and one Cl-ion, which defines the trigonal plane of the bipyramid. The central nitrogen atom of the ligand and the chloride ion occupy the apical sites. The Co(1)–O(3)

**Table 1**  
Crystallographic data for **1**.

Parameter	Complex <b>1</b>
Empirical formula	C <sub>22</sub> H <sub>30</sub> ClCoN <sub>2</sub> O <sub>2</sub>
Formula weight (g mol <sup>-1</sup> )	448.88
Wavelength (Å)	0.71073
Crystal color	Purple
Crystal system	Triclinic
Space group	P-1
<i>a</i> (Å)	8.8111(11)
<i>b</i> (Å)	11.5138(14)
<i>c</i> (Å)	12.3386(15)
$\alpha$ (°)	60.075(2)
$\beta$ (°)	85.008(2)
$\gamma$ (°)	77.048(3)
Volume (Å <sup>3</sup> )	1115.1(2)
<i>Z</i>	2
Calculated density (Mg/m <sup>3</sup> )	1.3368
F(000)	473.2
<i>q</i> range for data collection (°)	1.81 to 27.47
Reflections collected/ unique	13821/13658
Data/restraints/parameters	5048/0/258
Goodness-of-fit on F <sup>2</sup>	1.026
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0655, wR <sub>2</sub> = 0.1763
R indices (all data)	R <sub>1</sub> = 0.1396, wR <sub>2</sub> = 0.2555

**Table 2**  
The selected bond distances (Å) for complex **1**.

Co(1)–O(3)	2.003(4)	Co(1)–O(5)	1.992(4)
Co(1)–N(4)	2.296(4)	Co(1)–N(9)	2.123(5)
Co(1)–Cl(1)	2.3206(19)		



**Scheme 1.** Schematic representation of the synthesis of [LCoCl] **1**.

and Co(1)–O(5) distances are 2.003(4) and 1.992(4) Å, and those for Co(1)–N(4) and Co(1)–N(9) are 2.296(4) and 2.123(5) Å, respectively. Of interest is the Co–Cl bond at 2.3206(19) Å. This is longer than that (2.23–2.24 Å) of a cobalt(diamine-dioxime) complex, [Co((MO)(MOH) pn)Cl<sub>2</sub>] ((MOH)(MOH) pn = (HON=CH–C(Me)=N–CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), that can not ionize in MeCN [23]. To the extent that the Co–Cl bond has greater ionic character, it may account for better water solubility and more facile hydration, both important features for an effective homogeneous proton reduction catalyst (PRC). This is in agreement with results from ESI-MS measurements which exhibited one ion at a mass-to-charge ratio (*m/z*) of 414.17, with the mass and isotope distribution pattern corresponding to that of [Co(III)(L)H]<sup>+</sup> (calculated *m/z* of 414.37) (Fig. S2).

### 3.2. Electrochemical studies

Fig. 2a depicts the cyclic voltammogram of 2.53 mM complex **1** in DMF where one reversible Co<sup>III</sup>/Co<sup>II</sup> and one quasi-reversible

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