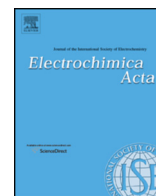


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Electrochemical-driven water reduction catalyzed by a water soluble cobalt(III) complex with Schiff base ligand

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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 (H₂L) with CoCl₂·6H₂O 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^{2−}, that coordinates strongly through two nitrogen atoms and two oxygen atoms to the cobalt center, leaving one Cl[−] ion in axial position and making the Cl[−] 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 H₂. 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 H₂ production. Within this context, we have been studying tetradentate ligands such as N, N-dimethylethylenediamino-N,N-bis(2,4-dimethylphenol) (H₂L),

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

¹H NMR spectrum was measured on a Bruker AM 500 spectrometer in CDCl₃. 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 N₂ 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^{−1} [(n-Bu)₄N]ClO₄ 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^{−1} 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 5.0×10^{-4} L aliquot of the headspace was removed and replaced with 5.0×10^{-4} L of CH₄. 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 (H₂L).

A mixture of 2,4-dimethylphenol (2.44×10^{-3} kg, 2.0×10^{-2} mol), *N,N*-dimethylethylenediamine (8.8×10^{-4} g, 1.0×10^{-2} mol), and 37% aqueous formaldehyde (1.62×10^{-3} kg, 2.0×10^{-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 (2.415×10^{-3} kg, 67.8% yield). Crystalline product was obtained by slow cooling of a hot diethyl ether solution. Anal. calcd for C₂₂H₃₂N₂O₂: C, 74.16; H, 8.99; N, 7.86%. Found C, 74.33; H, 8.98; N, 7.81%. ¹H NMR (400 MHz, CDCl₃) 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 H₂L (1.78×10^{-4} kg, 5×10^{-4} mol) and triethylamine (1.0×10^{-4} kg, 1.0×10^{-3} mol) in methanol (0.010 L), CoCl₂·6H₂O (1.20×10^{-4} kg, 5×10^{-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* (1.7×10^{-4} kg, 74%). The elemental analysis results (Found C, 58.67; H, 6.67; N, 6.31. C₂₂H₃₀N₂O₂CoCl 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 CoCl₂ and H₂L (Fig. S1) in the presence of triethylamine (yield 74 %) (Scheme 1), which was soluble in water and common organic solvents, such as DMF and CH₃CN.

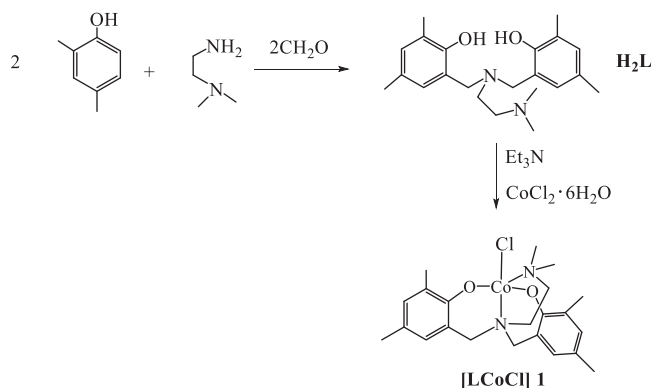
Complex **1** crystallizes in space group P-1, with two formula units present per unit cell. As shown in Fig. 1, in complex **1**, the cobalt ion is bonded to two oxygen atoms (O(3) and O(5)), two nitrogen atoms (N(4) and N(9)) and one Cl-ion, which defines the trigonal plane of the bipyramid. The central 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 1
Empirical formula	C ₂₂ H ₃₀ ClCoN ₂ O ₂
Formula weight (g mol ⁻¹)	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)
α (°)	60.075(2)
β (°)	85.008(2)
γ (°)	77.048(3)
Volume (Å ³)	1115.1(2)
<i>Z</i>	2
Calculated density (Mg/m ³)	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 ²	1.026
Final R indices [I > 2σ(I)]	R ₁ = 0.0655, wR ₂ = 0.1763
R indices (all data)	R ₁ = 0.1396, wR ₂ = 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)Cl₂] ((MOH)(MOH) pn = (HON=CH–C(Me)=N–CH₂)₂CH₂), 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]⁺ (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^{III}/Co^{II} and one quasi-reversible

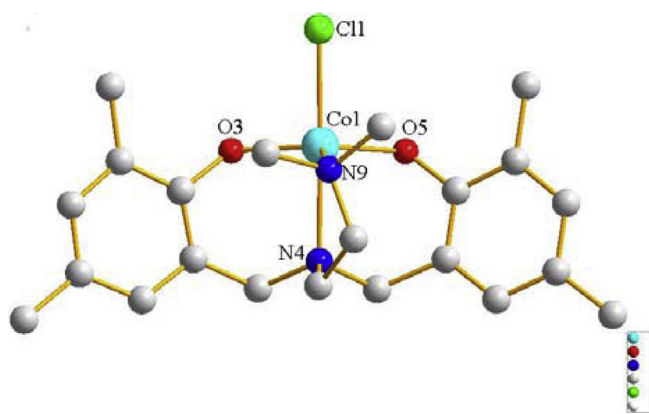


Fig. 1. Molecular structure of **1**. Selected bond distances: Co(1)—O(3), 2.003(4); Co(1)—O(5), 1.992(4); Co(1)—N(4), 2.296(4); Co(1)—N(9), 2.123(5); Co(1)—Cl(1), 2.3206(19).

Co^{II}/Co^I redox couples can be identified at 0.19 and -0.78 V (vs Ag/AgCl), respectively. As depicted in Fig. 2b, with the addition of varied amounts of acetic acid (from 0.0 to 4.05×10^{-2} mol), apparent voltammetric currents emerged at -0.78 V and increased markedly with increasing proton concentration. This indicates that hydrogen evolution electrocatalyzed by **1** requires the reduction of Co(II) to Co(I) and protonation. Interestingly, with the acetic acid concentration increased from 0.0 to 4.05×10^{-2} mol (Fig. 2b), the onset of the catalytic wave remains almost constant at ca. -0.52 V. Based on the above observations, only the Co^{II}/Co^I couple is involved in proton reduction.

Several control experiments were then carried out to confirm that complex **1** was indeed responsible for the catalytic reaction. In particular, acetic acid, free ligands, CoCl₂, and the mixture of free ligands and CoCl₂ were each measured under identical conditions. As can be seen in Figs. S3–S6, none of these showed an apparent catalytic activity. That is, a combination of the cobalt ion and the ligand is essential for the catalytic activity.

On the basis of literature precedents [24–26] and above analyses, we propose a catalytic cycle that is depicted in Scheme 2 for the generation of hydrogen from water mediated by **1**. Two-electron reduction of [LCo^{III}Cl] **1** produces a putative [LCo^I][−] species. Addition of protons yields the Co^{III}-H species, a high reactive intermediate. Further reduction of the Co^{III}-H species affords H₂, and regenerates the starting complex **1**. More detailed mechanistic studies are under investigation.

3.3. Catalytic hydrogen evolution in DMF

Further studies for the electro-catalytic activity were carried out by bulk electrolysis of a DMF solution of complex **1** (4.4×10^{-6} mol L^{−1}) with 2.43×10^{-3} mol L^{−1} acetic acid at various applied potentials using a glassy carbon disk electrode in a double-compartment cell. Fig. 2c shows the total charge of bulk electrolysis of complex **1** in the presence of acetic acid, where the charge increased significantly at increasingly negative potential. Overpotentials were calculated by using the method of Evans et al. [27]. When the applied potential was -1.0 V versus Ag/AgCl, the maximum charge reached 195 mC during 2 min of electrolysis, with accompanying evolution of a gas, which was confirmed as H₂ by gas chromatography. According to Fig. S7, $\sim 4.85 \times 10^{-5}$ L of H₂ was produced over an electrolysis period of 1 h (Eq. S1 [28]). A controlled-potential electrolysis (CPE) experiment under the same potential with a catalyst-free solution only gave a charge of 5 mC (Fig. S8), showing that this complex does indeed serve as an effective hydrogen production catalyst under such conditions.

Assuming every catalyst molecule was distributed on the electrode surface and every electron was used for the reduction of protons, the TOF was estimated to be 134 moles of hydrogen per mole of catalyst per hour by eq. (1) [29], (Eq. S2 and Fig. S9).

$$\text{TOF} = \Delta C / F n_1 n_2 t \quad (1)$$

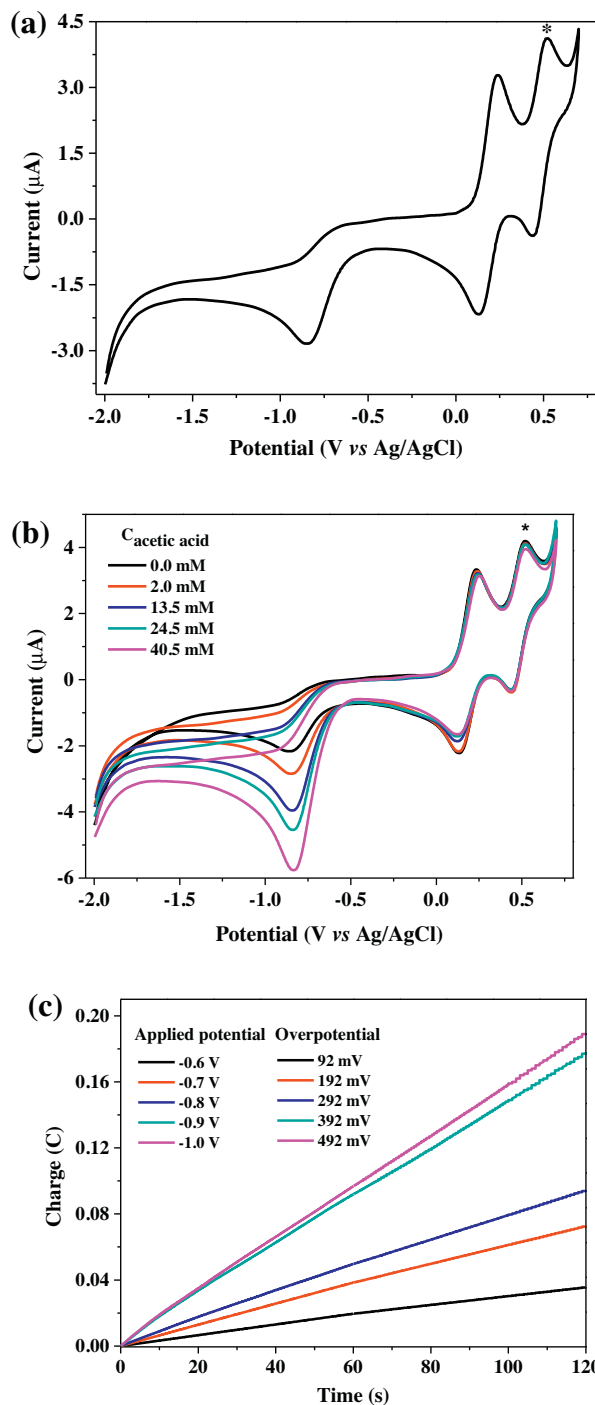
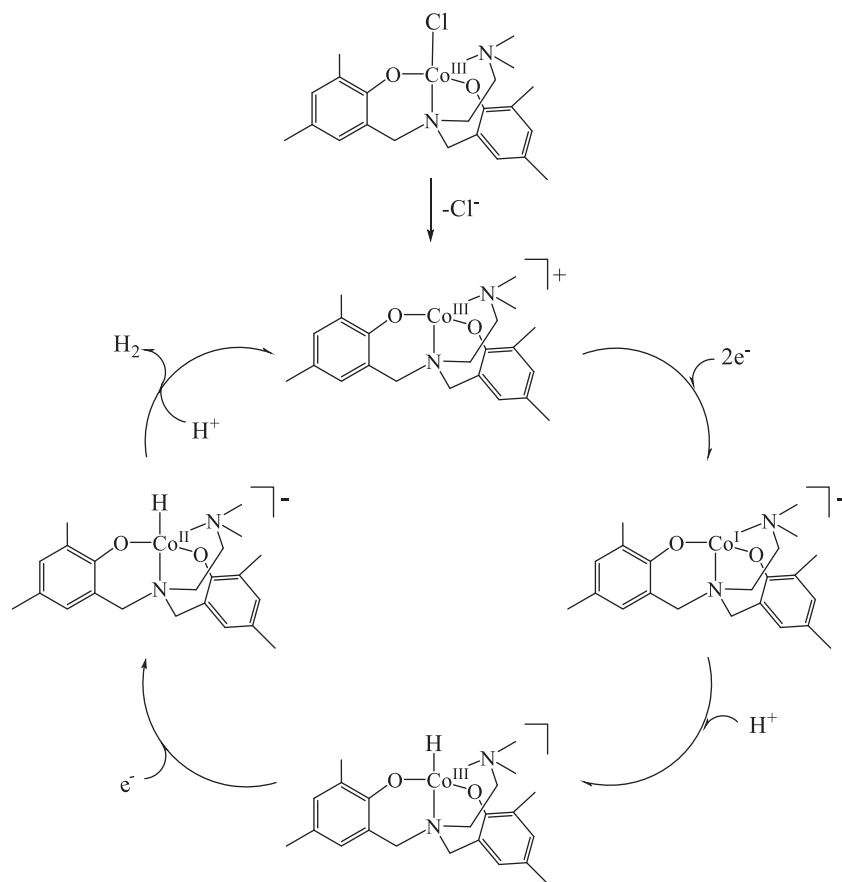


Fig. 2. (a) Cyclic voltammogram of complex **1** (2.53×10^{-3} mol) in a 0.10 mol L^{−1} [n-Bu₄N]ClO₄ solution in DMF. Ferrocene is used as an internal standard (*). (b) Cyclic voltammograms of a 2.53×10^{-3} mol solution of complex **1**, with varying concentrations of acetic acid in DMF. Ferrocene is used as an internal standard (*). (c) Charge buildup versus time from electrolysis of 4.4×10^{-6} mol complex **1** with 2.43×10^{-3} mol acetic acid in DMF under various overpotentials. All data have been baseline-corrected.



Scheme 2. The possible catalytic mechanism for proton reduction by complex **1**.

where ΔC is the charge accumulated from the catalyst solution during CPE minus charge from the same solution but without catalyst, F is Faraday's constant, n_1 is the mol of electrons required to generate a mol of H_2 , n_2 is mol of catalyst in solution, and t is duration of electrolysis.

3.4. Catalytic water reduction

The electrochemical behaviors were then examined in aqueous solutions at pH 4.0–7.0, a range associated with catalytic water reduction. In the cathodic scan an irreversible wave can be seen at -1.40 V, where the peak position varied with solution pH (Fig. S10). This is most likely due to water reduction, and the potential shifts anodically with decreasing pH. Note that cyclic voltammetric measurements in the absence of complex **1** showed no current within the potential range of $+0.5$ to -1.5 V (Fig. S11), indicating that water reduction to H_2 occurred only with complex **1**. The electro-catalytic activity was also evaluated by bulk electrolysis of $1.1 \times 10^{-6} \text{ mol L}^{-1}$ complex **1** in 0.25 mol L^{-1} buffer. At the applied potential of -1.40 V versus Ag/AgCl, the maximum charge was only 44 mC in 2 min of electrolysis in the absence of complex **1** (Fig. 3a). Under the same conditions, the charge reached 0.942C with the addition of complex **1**, and a large number of gas bubbles appeared (Fig. S12), which was confirmed to be H_2 by gas chromatography, as depicted in Fig. S13a, where the activity was estimated to be 14.4 mL of H_2 over an electrolysis period of 1 h with a Faradaic efficiency of 97.4% for H_2 (Fig. S13b). Fig. 3b shows the total charge of bulk electrolysis of complex **1** at pH 7.0. TOF for electrocatalytic hydrogen production by complex **1** is 2744 moles of hydrogen per mole of catalyst per hour at an overpotential of -0.638 V (pH 7.0) (Fig. 3c) [30]. To the best of our knowledge, this value is

significantly higher than that of any other molecular catalysts reported in the literature for electrochemical hydrogen production from neutral water. For instance, a molybdenum-oxo complex shows a maximum of 1600 moles of H_2 per mole of catalyst per hour at an overpotential of -0.642 V [15], and a dinickel complex that exhibits a TOF of 160 moles of H_2 per mole of catalyst per hour at an overpotential of -0.820 V [31], and a cobalt complex that shows a TOF of 300 moles of H_2 per mole of catalyst per hour at an overpotential of -0.98 V [13], and a copper complex that exhibits a TOF of 457 moles of hydrogen per mole of catalyst per hour at an overpotential of -0.817 V [16]. This value is also much higher than that of a molybdenum (VI) complex with the same ligand, $[LMo^{VI}(O)_2]$ (678 moles of hydrogen per mole of catalyst per hour at an overpotential of -0.79 V) [32]. This indicates that complex **1** is a highly active catalysts, most probably because of its unique structure: 1) The ionic ligand, N,N-dimethylethylenediamino-N,N-bis(2,4-dimethylphenol) ion (L^{2-}) can stabilize low oxidation state of cobalt. 2) L^{2-} coordinates strongly through two nitrogen atoms and two oxygen atoms to the cobalt centre, leaving one Cl^- ion in axial position. This observation strongly suggests that the presence of the Cl^- ion in axial position is the key structural feature for eliciting water reduction catalysis [13,14,33].

The observation that the catalytic current varied with the concentration of complex **1** indicated a homogeneous catalytic reaction (Fig. S14), which was also supported by several other pieces of evidence: 1) No heterogeneous deposits were produced and observed. For example, when the electrode was rinsed with water and electrolysis at -1.40 V vs Ag/AgCl was run for an additional 2 min in a 0.25 mol L^{-1} phosphate buffer at pH 7.0, no catalyst was found in solution. During this period, ca. 45 mC of charge was passed, a magnitude similar to that observed when electrolysis was

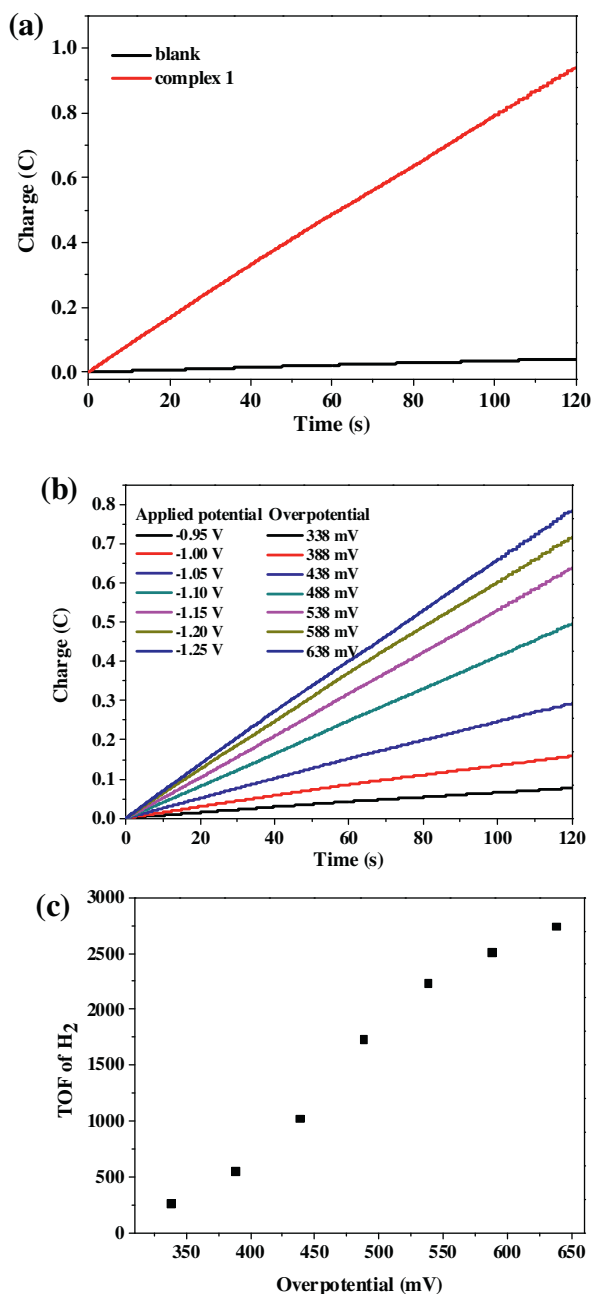


Fig. 3. (a) Charge buildup of 0.25 mol L⁻¹ phosphate buffer (black), and 1.1 × 10⁻⁶ mol L⁻¹ complex **1** (red) at pH 7.0. (b) Charge buildup of complex **1** (1.1 × 10⁻⁶ mol L⁻¹) versus overpotentials (mV) in 0.25 mol L⁻¹ phosphate buffer at pH 7.0. All data have been deducted blank. (c) Turnover frequency (mol H₂/mol catalysts/h) for electrocatalytic hydrogen production by complex **1** (1.1 × 10⁻⁶ mol L⁻¹) under overpotentials (mV) in 0.25 mol L⁻¹ phosphate buffer (pH 7.0). Overpotential = applied -E(pH), where E(pH) = -0.059pH [27].

conducted with freshly polished electrodes. 2) No discoloration of the electrodes was observed during cyclic voltammetry or bulk electrolysis. 3) Under the same conditions, no precipitates were formed on a blank glassy carbon electrode after 3 h of electrolysis, as determined by SEM measurements (Fig. S15).

4. Summary

A water and organic soluble mononuclear cobalt complex **1** was synthesized by a facile procedure and exhibited apparent catalytic activity in electrochemical water reduction. Electrochemical

studies show that **1** is the most rapid water-reduction catalyst, with a TOF of 2744 (pH 7.0) moles of hydrogen per mole of catalyst per hour at an overpotential of -0.638 V in a phosphate buffer solution. The result may offer a new chemical paradigm for the design and engineering of effective cobalt-based molecular catalysts for water reduction that is highly active in both aqueous and organic media.

Supporting information

CCDC 1028848 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>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.plantsci.2004.08.011>.

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