Hydrogen evolution catalyzed by a water-soluble cobalt(II) complex with picolinic acid ions

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ABSTRACT:

A new molecular catalyst based on cobalt(II) complex $[\text{CoA}_2(\text{H}_2\text{O})_2]$ **1** (A: picolinic acid ion) is prepared by the reaction of picolinic acid (HA) with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Electrochemical studies indicate **1** is a homogeneous electrocatalyst for water reduction in a purely aqueous medium. **1** can catalyze hydrogen evolution from water with a turnover frequency (TOF) of 350.6 moles of hydrogen per mole of catalyst per hour at an overpotential of 687.6 mV (in buffer, pH 7.0).

Keywords: Cobalt(II) complex; molecular electrocatalyst; water reduction; hydrogen evolution.

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Introduction

Hydrogen is one of the most ideal energy in the future, because of its numerous advantages such as recyclability and pollution-free use [1-3]. Water is the only waste-free electron-source substrate that could sustain the scale of the process required to supply our energy demands. Thus water splitting is an important method for hydrogen production in high purity and large quantities [4]. And electrolysis of water is the simplest way to produce hydrogen. However, the kinetically slow oxygen evolution reaction (OER) $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$ (in acid) or $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$ (in base) represents a significant efficiency loss in water-splitting systems [5,6]. To increase the reaction rate, it is necessary to use an efficient hydrogen evolution reaction (HER) electrocatalyst. Therefore, many research groups, including ours, have tried to design molecular catalysts by employing the more abundant metals, and several complexes of nickel [7,8], cobalt [9-13], copper [14-16] and molybdenum [17-19] have been developed as electrocatalysts for the reduction of acetic acid or water to form H_2 . Despite much progress in water reduction catalysis, major improvements in several areas, including simplifying structural complexity, increasing catalyst solubility in water, and operating in neutral medium (pH 7.0), are needed before efficient electrocatalytic water reduction can be realized. Within this context, we have been designing molecular catalysts based on the water-soluble complexes with simple ligands. As an expanded work [20], reported here is a water-soluble cobalt(II) electrocatalyst, $[\text{CoA}_2(\text{H}_2\text{O})_2]$ **1** that can electro-catalyze

water reduction with a TOF of 350.7 moles of hydrogen per mole of catalyst per hour at an overpotential of 687.6 mV (in buffer, pH 7.0). We hope this can establish a new method in water reduction catalysis using inexpensive and earth-abundant material in purely aqueous media.

Experimental sections

Physical measurements

Cyclic voltammograms 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 electrode was the reference electrode, and platinum wire was the auxiliary electrode. 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 50 mL of 0.25 M buffer, while the auxiliary compartment was filled with 35 mL phosphate buffer solution. Adding cobalt complex, both compartments were sparged for 1 h with nitrogen and cyclic voltammograms were recorded as controls. After electrolysis, a 0.5 mL aliquot of the headspace was removed and replaced with 0.5 mL of CH_4 . 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. Elemental analyses for C, H, and N were obtained on a Perkin-Elmer analyzer model 240. UV-Vis spectra

were measured on a Hitachi U-3010 spectrometer. ESI-MS experiment was performed on a Bruker Daltonics Esquire 3000 spectrometer by introducing samples directly into the ESI source using a syringe pump. Thermogravimetric (TG) analysis was carried out using a Universal V4 4A Instruments with a heating rate 10°C/min in flowing air. And the Energy Dispersive Spectrometer (EDS) measurement was carried out with a Shimadzu EPMA-1600 Electron Probe X-ray micro analyzer.

Synthesis of complex 1

To a solution of picolinic acid (0.246 g, 2 mmol) in 95% ethanol (20 ml), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g, 1 mmol) in methanol (5 ml) was added and the mixture was stirred for 15 min. Violet crystals were obtained from the filtrate which was allowed to stand at room temperature for several days, collected by filtration, and dried in *vacuo* (0.15 g, 40.0%). The elemental analysis results (Found C, 38.27; H, 4.31; N, 7.49. $\text{C}_{12}\text{H}_{16}\text{CoN}_2\text{O}_8$ requires C, 38.42; H, 4.30; N, 7.47) were in agreement with the formula of the sample used for X-ray analysis.

Crystal structure determination

The X-ray analysis of **1** was carried out with a Bruker Smart Apex II DUO area detector using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) 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-97 computer program [22]. Crystallographic data for complex **1** are given in Table S1 and selected bond lengths and angles are listed in Table S2.

Results and discussion

Structural analysis and general characterization

The reaction of picolinic acid (HA) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ formed the cobalt(II) complex, $[\text{Co}(\text{A})_2(\text{H}_2\text{O})_2]$ **1**, which is soluble both in water and several organic solvents. The UV-Vis spectrum of complex **1** was recorded in an aqueous solution, with a main feature at 264 nm (Fig. S1). The UV-Vis spectra of **1** in buffered aqueous solutions in the pH range of 2.3-11.5 exhibited similar peaks to that in water (Fig. S2), indicating **1** is stable under these conditions.

From Fig. 1, in solid, complex **1** consists of one Co^{2+} ion, two picolinic acid ions, and two H_2O molecules. The cobalt atom is six-coordinated by two nitrogen atoms, two oxygen atoms from picolinic acid ions, and two oxygen atoms from two H_2O molecules. The bond distance of Co and O from picolinic acid (2.0703(17) Å) is shorter than that of Co and O from H_2O (2.144(2) Å). And the Co–N distance is 2.119(2) Å. Interestingly, H_2O did not dissociate from cobalt center in methanol, which is in agreement with the result of ESI-MS analysis. The electrospray mass spectrum of **1** exhibited one ion at a mass-to-charge ratio (m/z) of 340.2823, with

mass and isotope distribution pattern corresponding to $[\text{Co}(\text{A})_2(\text{H}_2\text{O})_2\text{-H}]^+$ (calculated m/z of 340.20) (Fig. S3).

Thermal decomposition process for complex 1

Fig. 2 illustrated the TG curve of complex **1** heat-treated in air using a heating rate of 10 °C/min in the temperature range 40–250 °C. The TG of **1** showed marked mass losses with increasing temperature in two steps. The first TG weight loss of approximately 9.70% in the temperature range 40–120.3 °C with an endothermic peak at 120.3 °C is mainly due to the departure of two lattice (theoretical weight loss 9.60%) water molecules from complex **1**. The subsequent thermal decomposition of complex **1**, with a mass loss of 9.60% in the range 140–170 °C, is contributed to the departure of two (theoretical weight loss 9.60%) coordination water molecules. No significant weight loss was observed for **1** when the temperature above 170 °C.

Electrochemical studies

From Fig. 3, in DMF solution at a glassy carbon electrode, complex **1** displayed two quasi-reversible redox couples at -0.34 and -0.89 V, which can be assigned to the couples of $\text{Co}^{\text{II/I}}$ and $\text{Co}^{\text{I/0}}$, respectively. To obtain kinetic information of this complex, CVs were recorded at different scan rates. As shown in Fig. S4, the current responses of the redox events at -0.99 and -0.48 V show a linear dependence on the square root of the scan rate, which is an indicative of a diffusion-controlled process, with the electrochemically active species freely diffusing in the solution.

In aqueous media, complex **1** also exhibited two reduction processes at -0.45 and -1.43 V, which are assigned to the couples of $\text{Co}^{\text{II/I}}$ and $\text{Co}^{\text{I/0}}$, respectively (Fig. 4). To probe the nature of the first reduction process, we investigated the pH dependence of the cathodic peak potential. The reduction waves were shifted to lower potentials under higher pH, which reflects the shift in the thermodynamic potential for electrocatalysis (Fig. S5a). Fig. S5b showed that $E_{\text{p,a}}$ has nearly linear relationship with the pH values, and a slope of 61 mV per pH unit was obtained. And the slope of 61 mV per pH unit is contributed to a $1\text{e}^- - 1\text{H}^+$ redox process.

Catalytic hydrogen evolution from acetic acid in DMF

Cyclic voltammogram of CH_3COOH in the absence of complex **1** exhibited no catalytic current at the potentials of the couples of $\text{Co}^{\text{II/Co}^{\text{I}}}$ and $\text{Co}^{\text{I/Co}^0}$ (Fig. S6), suggesting that proton reduction from CH_3COOH to H_2 occurs with $\text{Co}^{\text{II/Co}^{\text{I}}}$ and $\text{Co}^{\text{I/Co}^0}$. Addition of the varying amounts of CH_3COOH triggered catalytic currents at potential near the couple of $\text{Co}^{\text{I/Co}^0}$. Fig. 5 showed a systematic increase in i_{cat} observed near -0.97 V with increasing acid concentration from 0.0 to 2.99 mM. This clearly establishes that hydrogen evolution electrocatalyzed by **1** requires the reduction of $\text{Co}(\text{I})$ to $\text{Co}(0)$. This result is different from the reported result that hydrogen evolution electrocatalyzed by catalyst requires the reduction of $\text{Co}(\text{II})$ to $\text{Co}(\text{I})$ and protonation [23,24]. Interestingly, with the acetic acid concentration increased from 0.0 to 2.99 mM (Fig. 5), the onset of the catalytic wave remains almost constant at ca. -0.24 V versus Ag/AgCl . On the basis of literature precedent

[25] and above analyses, we propose the catalytic cycle depicted in Scheme 1 for the generation of hydrogen from acetic acid mediated by **1**. Two one-electron reduction of $[A_2Co^{II}(H_2O)_2]$ **1** gives a putative $[A_2Co^{0}]^{2-}$ species. Addition of hydrogen proton yields the $Co^{II}-H$ species, a high reactive intermediate. Further addition of hydrogen proton of the $Co^{II}-H$ species affords H_2 , and regenerates the starting complex **1**. Further mechanistic studies are under investigation.

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

Further evidence for the electro-catalytic activity was obtained by bulk electrolysis of a solution of complex **1** (2.5 μ M) in DMF with acetic acid (3.0 mM) at variable applied potential using a glassy carbon plate electrode in a double-compartment cell. Fig. 6a showed the total charge of bulk electrolysis of complex **1** in the presence of acid, when the applied potential was -1.45 V versus Ag/AgCl, the maximum charge reached 71 mC during 2 min of electrolysis,

accompanying evolution of a gas, which was confirmed as H₂ by gas chromatography. According to Fig. S7, ~0.065 mL of H₂ was produced over an electrolysis period of 2 h. A CPE experiment under the same potential with a catalyst-free only gave a charge of 25 mC (Fig. 6b), showing that this complex does serve an effective hydrogen production under such conditions. According to *eq.* (1) [18], we calculated TOF for the catalyst reaching a maximum of 42.1 moles of hydrogen per mole of catalyst per hour at an overpotential of 941.6 mV (Eq. S1 and Fig. S8).

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

Where, ΔC is the charge from the pre-catalyst solution during CPE minus the charge from solution without pre-catalyst 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

As shown in Fig. 4, in the absence of complex **1**, a catalytic current was not apparent until a potential of -1.42 V versus Ag/AgCl was attained. With addition of complex **1**, the onset of catalytic current was observed at about -1.0 V versus Ag/AgCl, and the current strength increased significantly with increasing concentrations of complex **1** from 0.5 to 21.1 mM (Fig. S9).

Several control experiments were then carried out to confirm that complex **1** was indeed responsible for the catalytic reaction. In particular, the free ligand, buffer solution, CoCl₂·6H₂O and the mixture of ligand and CoCl₂·6H₂O were each

measured under identical conditions. As can be seen in Fig. S10, when the applied potential was -1.60 V versus Ag/AgCl, the maximum charge was only 58 mC during 2 min of electrolysis from a 0.25 M buffer. Addition of HA or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ led to a slight increase in H_2 evolution at 93 mC and 108 mC, respectively. However, the addition of the mixture of HA and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ led to a significant increase in H_2 evolution at 370 mC. Thus, a combination of the cobalt center and the ligand is essential for catalytic activity. Under the same conditions, the charge reached 1288 mC with addition of complex **1** (Fig. S10), accompanying a large amount of gas bubble appeared, which was confirmed to be H_2 by GC analysis. The evolved H_2 was analyzed by gas chromatography, Fig. S11a, which gave ~ 27.24 mL of H_2 over an electrolysis period of 1 h with a Faradaic efficiency of 95.4% for H_2 (Fig. S11b). Fig. 7 showed the total charge of bulk electrolysis of complex **1** under a series of applied potentials, according to Eq. (1), we calculated TOF for the catalyst reaching a maximum of 350.7 moles of hydrogen per mole of catalyst per hour an overpotential of 687.6 mV (Eq. S2 and Fig. S12). To the best of our knowledge, this value is higher than some reported molecular catalysts for electrochemical hydrogen production from neutral water, including a cobalt(II) complex with 2-tetrahydrofurfurylamino-N,N-bis(2-methylene-4-tert-butyl-6-methyl)phenol that exhibits a turnover frequency of 15 moles of H_2 per mole of catalyst per hour at an overpotential of 689 mV [26] and a cobalt complex with macrocyclic ligand displaying a turnover number of 5 moles of H_2 per mole of catalyst with a turnover number of 0.4 moles of H_2 per mole of catalyst per hour at an overpotential of 390

mV [27], and yet lower than the recently reported cobalt based one [28]. This is attributed to the ionic ligand, A^- , that coordinates through two nitrogen atoms and two oxygen atoms to the cobalt center, leaving two H_2O molecules *trans*-relative positions and stabilizing $Co(0)$. On the basis of above analyses, efficient water reduction catalysts (WRCs) generally prefer softer ligands to generate low-valent active intermediates that can reduce protons at low over-potentials, such as oxime [29-31], and phosphine [32] ligands.

Investigation of the stability and durability of complex 1

In order to determine whether **1** retains activity for water reduction over longer time periods, a 72 h controlled-potential electrolysis at -1.45 V vs Ag/AgCl was conducted in a stirred 0.25 M buffer solution (pH 7.0), containing **1** (6.67 μ M). As shown in Fig. S13, a total of 5605 C was passed during the electrolysis. This catalyst afforded a charge build-up over time, with no substantial loss in activity over the course of 72 h. After a 72 h electrolysis period, pH increases by 5.5 units (from 7.0 to 12.5), consistent with accumulation of OH^- by water reduction, $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$. Interestingly, the original catalytic function was recovered and could be repeated several times when the solution pH was adjusted back to the original 7.0.

In order to prove complex **1** as a homogeneous electrocatalyst, we obtained dependence of the catalytic current on concentration of complex **1**. As shown in Fig. S9, the observation of the catalytic current being dependent of complex **1** concentration could indicate a homogeneous catalyst. And several pieces of

evidence also suggested that this cobalt complex is a homogeneous catalyst: 1) There is no evidence for a heterogeneous electrocatalytic deposit. 2) No discoloration of the electrodes was observed during cyclic voltammetry or bulk electrolysis. 3) At a glassy carbon electrode, there was no evidence for precipitation formation by EDS (Fig. S14) after a 3 h electrolysis period.

Conclusion

In summary, a water soluble cobalt(II) complex **1**, which is very easy to be obtained, can catalyze water reduction with a TOF of 350.7 moles of hydrogen per mole of catalyst per hour at an overpotential of 687.6 mV (pH 7.0). This discovery has established a new chemical paradigm for creating water reduction catalysts that is highly active in purely aqueous media.

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Fig. 1 - X-ray molecular structure of complex **1**

Fig. 2 - The TG curve of complex 1

Fig. 3 - Cyclic voltammogram of 0.25 mM complex **1** in 0.10 M of [n-Bu₄N]ClO₄ DMF solution at a glassy carbon electrode and a scan rate of 100 mV/s.

Fig. 4 - Cyclic voltammogram of complex **1** (1.76 mM) in 0.10 M KCl at a glassy carbon electrode and a scan rate of 100 mV/s. The inset shows a magnified view of the Co^{II}/Co^I couple.

Fig. 5 - Cyclic voltammograms of a 0.25 mM solution of complex **1**, with varying concentrations of acetic acid in DMF. Conditions: 0.10 M [n-Bu₄N]ClO₄ as supporting electrolyte, scan rate: 100 mV/s, glassy carbon working electrode (1 mm diameter), Pt counter electrode, Ag/AgCl reference electrode.

Fig. 6 - (a) Charge buildup versus time from electrolysis of a 2.5 μM complex **1** solution in DMF (0.10 M $[\text{n-Bu}_4\text{N}]\text{ClO}_4$) under various applied potentials. All data have been deducted blank. (b) Charge buildup versus time from electrolysis of a 3.0 mM acetic acid in DMF (0.10 M $[\text{n-Bu}_4\text{N}]\text{ClO}_4$) under 1.45 V versus Ag/AgCl.

Fig. 7 - Charge buildup versus time from the electrolysis of a 6.67 μ M solution in 0.25 M buffer at pH 7.0 under various applied potentials. All data have been deducted blank.