The impact of modifying the ligands on hydrogen production electro-catalyzed by *meso*-tetra-*p*-X-phenylporphin cobalt complexes, CoT(X)PP

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Two molecular electro-catalysts based on cobalt complexes CoT(X)PP **1** (X=Cl) and **2** (X=OMe) are formed by the reaction of *meso*-tetra-*p*-X-phenylporphin, H₂T(X)PP with cobalt compound for electrolytic proton or water reduction. **1** electrocatalyzes hydrogen evolution from acetic acid with a turnover frequency (TOF) of 85.51 moles 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 632.9 moles of hydrogen per mole of catalyst per hour at an OP of 837.6 mV. And **2** electrocatalyzes hydrogen evolution from acetic acid with a TOF of 48.70 moles of hydrogen per mole of catalyst per hour at an OP of 941.6 mV (in DMF), and from aqueous buffer solution (pH 7.0) with a TOF of 120.1 moles of hydrogen per mole of catalyst per hour at an OP of 837.6 mV. These results indicate that the electronic properties of the ligands play vital roles in determining the catalytic activities of the cobalt complexes, and are consistent with an evident increase in the catalytic activity when

electron-withdrawing groups are present at phenylporphin, and *meso*-tetra-*p*-chloro-phenylporphin constitutes the better active catalyst.

Keywords: Porphin-cobalt complexes; molecular electrocatalysts; water reduction; hydrogen evolution.

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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 one of the most attractive technologies for sustainable energy production [2]. 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 [3,4]. Therefore, a great deal of research efforts have been devoted to the development of effective catalysts based on earth-abundant metals, and molecular complexes of nickel [5], cobalt [6-8], molybdenum [9] and copper [10-12] 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-catalytic water splitting can be realized. As we know, the donor type and electronic properties of the ligands play vital roles in determining the structure and reactivity of the corresponding metal complexes [13,14].

Within this context, we have been studying tetradentate ligands, such as *meso*-tetra-*p*-X-phenylporphin H₂T(X)PP (X= Cl, OMe), planar ligands and their corresponding cobalt complexes for catalytic application. In this paper, we report electrocatalytic properties for hydrogen generation of two cobalt(II) complexes CoT(X)PP **1** (X= Cl) and **2** (X= OMe), as well as the effect of tetradentate ligand modifications on the catalytic efficiency of these two cobalt(II) complexes.

2. Experimental

H₂T(X)PP and CoT(X)PP were prepared according to the procedures in the literatures [15,16]. Cyclic voltammograms (CVs) 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, the ferrocene/ferrocenium (1+) couple was used as an internal standard, and 0.10 M [(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 50 mL of 0.25 M buffer, while the auxiliary compartment was filled with 35 mL phosphate buffer solution. After addition of cobalt complexes, CVs were recorded. After electrolysis, a 0.50 mL aliquot of the headspace was removed and replaced with 0.50

mL of CH₄. The headspace sample was injected into the gas chromatograph (GC). GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument.

3. Results and discussion

3.1. Electrochemical studies

To explore the electrochemical properties of **1** and **2**, CVs were conducted in DMF with 0.10 M [(n-Bu)₄N]ClO₄ as the supporting electrolyte. As observed in Fig. 1, complexes **1** and **2** both exhibit two redox waves and followed the order **1** (-0.76 and -1.86 V versus Ag/AgNO₃) → **2** (-0.92 and -1.39 V versus Ag/AgNO₃), respectively. As shown in Fig. 1a, the CV of 3.17 mM complex **1** shows two reversible peaks at -0.76 V and -1.86 V versus Ag/AgNO₃, respectively. For comparison, CV of H₂T(Cl)PP was measured in a similar condition (Fig. 1b). The first reduction wave of **1** at -0.76 V, being close to the first reduction of the free ligand, is assigned to H₂T(Cl)PP. The second redox peak can be assigned to the Co^{II}/Co^I couple. From Fig. 1c, complex **2** also shows two reversible peaks at -0.92 V and -1.39 V versus Ag/AgNO₃, respectively. H₂T(OMe)PP exhibits one reversible peak at -1.12 V versus Ag/AgNO₃ (Fig. 1d). The first reduction wave of **2** at -0.92 V, being close to the first reduction of H₂T(OMe)PP, is assigned to the H₂T(OMe)PP. The second redox peak at -1.39 V versus Ag/AgNO₃ can be assigned to the Co^{II}/Co^I couple. Note, the potential of Co^{II}/Co^I is shifted by 470 mV as a result of substitution of a methoxyl group on the ligand by the more electron withdrawing chloride group.

3.2. Catalytic hydrogen evolution from acetic acid in DMF

As depicted in Fig. 2a, with the addition of varied amounts of acetic acid (from 0.0 to 4.08 mM), apparent voltammetric currents emerge at -1.90 V and increase markedly with increasing proton concentration. The result 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 4.08 mM (Fig. 2a), the onset of the catalytic wave remains almost constant at ca. -1.70 V versus Ag/AgNO₃. Based on the above observations, only the Co^{II}/Co^I couple is involved in proton reduction.

On the basis of literature precedents [17-19] and above analyses, a possible catalytic cycle for the generation of hydrogen from acid mediated by **1** is depicted in Scheme 1. One-electron reduction of [Co^{II}T(Cl)PP] **1** produces a putative [Co^IT(Cl)PP][−] species. Addition of proton yields the Co^{III}-H species, a high reactive intermediate. Further reduction of the Cu^{III}-H species affords H₂, and regenerates the starting complex **1**.

Scheme 1. The possible catalytic mechanism for proton reduction by porphin cobalt complexes

Compared to that of complex **1**, change of catalytic current for complex **2** occurred at the couple of $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ (-1.44 V versus Ag/AgNO_3), and the peak current of $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ also increased markedly with increasing proton concentration (acetic acid concentration increased from 0.0 to 2.33 mM) (Fig. 2b), indicating that complexes **1** and **2** both afford proton reduction from acetic acid. Different from complex **1**, with the acetic acid concentration increased from 0.0 to 2.33 mM (Fig. 2b), the onset of the catalytic wave moves positive for about 290 mV compared to that in the absence of acetic acid.

In order to further assess the catalytic activities of complexes **1** and **2**, bulk

electrolysis were conducted in DMF solutions with acetic acid at variable applied potential using a glassy carbon plate electrode in a double-compartment cell. Figs. 3a-b show the total charges of bulk electrolysis of complexes **1** and **2** in the presence of acid. When the applied potential is -1.45 V versus Ag/AgNO₃, the maximum charges reaches 81 mC and 51 mC, respectively, during 2 min of electrolysis. And a CPE experiment under the same potential without complex **1** or complex **2** gives a charge of only 12 mC (Fig. 3c), showing that these two complexes do indeed serve as effective hydrogen producers under such conditions. Assuming every catalyst molecule is distributed only on the electrode surface and every electron is used for the reduction of protons, according to Equations (1) [20] and (2) [21], complexes **1** and **2** afford 85.51 and 48.7 moles of hydrogen per mole of catalyst per hour at an OP of 941.6 mV, respectively (Eqs. S1-S2). Remarkably, complex **1** is more active than that of complex **2**, which is consistent with an evident increase in the catalytic activity when electron-withdrawing group, such as chloride is present at phenylporphin, and *meso*-tetra-*p*-chloro-phenylporphin constitutes the better active catalyst [22]. And the cobalt complexes with more positive Co^{II/I} redox potentials show lower activity for hydrogen generation.

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

$$\text{Overpotential} = \text{Applied potential} - E_{\text{HA}}^{\ominus}$$

$$= \text{Applied potential} - (E_{\text{H}}^{\ominus} + (2.303RT/F) \text{p}K_{\text{aHA}}) \quad (2)$$

Where, ΔC is the charge from the catalyst solution during CPE minus the charge from solution without catalyst during CPE; F is Faraday's constant, n_1 is the number

of moles of electrons required to generate one mole of H_2 , n_2 is the number of moles of catalyst in solution, and t is the duration of electrolysis.

3.3. Catalytic hydrogen evolution from aqueous buffer

We further explored the electrochemical behavior of complex **1** in buffered aqueous solutions, where $pH = 3.5-7.0$ which is the range associated with catalytic water reduction. And Fig. 4a exhibits a systematic increase in i_{cat} with decreasing pH from 7.0 to 3.5. As shown in Fig. 4b, in the absence of complex **1**, a catalytic current is not apparent until a potential of -1.50 V versus Ag/AgCl is attained. Upon addition of complex **1**, the onset of catalytic current is observed at about -1.30 V versus Ag/AgCl, showing that addition of complex **1** can reduce the potential, and the current strength increases significantly with increasing concentrations of complex **1** from 10.50 to 80.60 μM . From Fig. 4a, the onset of this catalytic current is clearly influenced by the solution pH , the applied potential declines with increasing pH , evidencing the involvement of a proton in the initial stage of electrochemical catalysis.

As shown in Fig. 5a, in the absence of complex **2**, a catalytic current is not apparent until a potential of -1.50 V versus Ag/AgCl is attained. With addition of complex **2**, the onset of catalytic current is observed at about -0.87 V versus Ag/AgCl, and the current strength increased significantly with increasing concentrations of complex **2** from 0.39 to 1.36 μM (Fig. 5a). From Fig. 5b, **2** shows a pH -dependent peak at -1.62 V versus Ag/AgCl, which is responsible for catalytic water reduction,

and the applied potential declines with increasing pH (Fig. 5b).

To further test the electro-catalytic activity of complex **1** in aqueous media, bulk electrolysis was measured in an aqueous solution of **1** (3.09 μ M) with 0.25 M buffer solution (pH 7.0) at variable potential using a glassy carbon electrode in a double-compartment cell. From Fig. 6a, when the applied potential is -1.45 V versus Ag/AgCl, the maximum charge is only 33 mC for 2 min of electrolysis in the absence of complex **1**. Under the same conditions, the charge reaches 541 mC during 2 min of electrolysis in the presence of **1** (Fig. 6b), accompanying a large amount of gas bubble appeared, which is confirmed as H₂ by gas chromatography. According to Fig. S1a, ~2.8 mL of H₂ is produced over an electrolysis period of 1 h with a Faradaic efficiency of 91.12% for H₂ (Fig. S1b). According to Equations (1) and (3) [23], we calculate the TOF for the catalyst as reaching a maximum of 632.9 moles of hydrogen per mole of catalyst per hour at an overpotential of 836.7 mV (Eq. S3), where

$$\text{Overpotential} = \text{Applied potential} - E(\text{pH}) = \text{Applied potential} - (-0.059\text{pH}) \quad (3)$$

To the best of our knowledge, this value is higher than that of some other molecular catalysts reported in the literature for electrochemical hydrogen production from neutral water. For instance, a dinickel complex that exhibits a TOF of 160 moles of H₂ per mole of catalyst per hour at an overpotential of 820 mV [24] and a cobalt complex displaying a turnover number of 5 moles of H₂ per mole of catalyst with a turnover number of 0.4 moles of H₂ per mole of catalyst per hour at an OP of 390 mV [25]. This indicates that complex **1** is a highly active catalyst, probably because of its unique structure: the planar ligand, T(Cl)PP²⁻ can stabilize low oxidation state of

cobalt. This observation suggests that the presence of the ligand is the key structural feature for eliciting proton or water reduction catalysis.

According to Fig. 6c, when the applied potential was -1.45 V versus Ag/AgCl, the maximum charge reaches 131 mC during 2 min of electrolysis in the presence of **2**, accompanied by evolution of a gas, which is confirmed as H₂ by gas chromatography. From Fig. S12a, ~0.80 mL of H₂ is produced over an electrolysis period of 1 h with a Faradaic efficiency of 92.3% for H₂ (Fig. S2b). From Equations (1) and (3), complex **1** affords a TOF of 120.1 moles of hydrogen per mole of catalyst per hour at an OP of 837.6 mV (Eq. S4). Similar to that in organic media, complex **1** also shows higher efficiency for hydrogen production than that of complex **2**. From a 72 h CPE of a 0.25 M buffer solution (pH 7.0) in the presence of complex **1** or **2** under -1.40 V versus Ag/AgCl, we also can found that catalyst **1** is a more active species than **2**. As shown in Fig. S3a, a total of 3445 C is accumulated during the electrolysis catalyzed by complex **1**, and in the presence of complex **2**, only 868 C is passed during a 72 h electrolysis (Fig. S3b).

As we know, it is not easy to compare the catalytic efficiency between different electrocatalytic systems in term of TOF, due to possible differences in the experimental conditions conducted. Under the same conditions, a comparison of the hydrogen evolving activity obtained with electrocatalytic system reported in the literature based on cobalt porphyrin [26], shows that **1** is more active than the tetrakis-(p-sulfonatophenyl)porphyrin cobalt complex, Co(TPPS) reported by Beyene giving 1.83 s⁻¹ at an applied potential of -1.29 V versus SHE in neutral phosphate buffer

solution (Table 1).

Table 1 Catalytic data by porphyrin cobalt complexes from aqueous buffer

Complexes	Co(TPPS)	1	2
TOF (s^{-1})	1.83	5.68	1.17
Applied potential (V <i>vs</i> SHE)	-1.29	-1.29	-1.29

CoTPPS: (p-sulfonatophenyl)porphyrin cobalt complex [26].

4. Summary

In this paper, we have described two electrocatalysts based on *meso*-tetra-*p*-X-phenylporphin cobalt complexes. The cobalt complexes with more positive $Co^{II/I}$ redox potentials show lower activity for hydrogen generation. And the results are consistent with an evident increase in the catalytic activity when electron-withdrawing groups are present at the phenol para-position of the ligand. Our ongoing efforts are focused on modifying phenylporphin ligand to give related water-soluble complexes for further functional studies, with an emphasis on chemistry relevant to sustainable energy cycles.

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Fig. 1. (a) Cyclic voltammogram (CV) of 0.86 mM complex **1** in DMF. (b) CV of H₂T(Cl)PP (31.5 μM) in DMF. (c) CV of 0.86 mM complex **2** in DMF. (d) CV of H₂T(OMe)PP (23 μM) in DMF. Conditions: 0.10 M [n-Bu₄N]ClO₄ as supporting electrolyte, glassy carbon working electrode (1 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode, scan rate 100 mV/s, Ferrocene internal standard (*).

Fig. 2. (a) CVs of a 0.25 mM solution of complex **1**, with varying concentration of acetic acid in DMF. (b) CVs of a 0.43 mM solution of complex **2**, with varying concentration 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/AgNO₃ reference electrode, Fc internal standard (*).

Fig. 3. (a) Charge buildup versus time from electrolysis of 4.0 mM acetic acid with 3.09 μM complex **1** in DMF. All data have been deducted blank. (b) Charge buildup versus time from electrolysis of 4.0 mM acetic acid with 2.28 μM complex **2** in DMF. All data have been deducted blank. (c) Charge buildup versus time from electrolysis of 0.10 M $[\text{n-Bu}_4\text{N}]\text{ClO}_4$ in DMF.

Fig. 4. (a) CVs of 0.081 mM complex **1**, showing the variation in catalytic current with pH (scan rate: 100 mV/s). (b) Cyclic voltammograms of complex **1** in different concentration. Conditions: 0.25 M phosphate buffered solution at pH 7.0, glassy carbon working electrode (1 mm diameter), Pt wire counter electrode, Ag/AgCl reference electrode.

Fig. 5. (a) CVs of 1.36 μM complex **2**, showing the variation in catalytic current with pH (scan rate: 100 mV/s). (b) Cyclic voltammogram of complex **2** in different concentration. Conditions: 0.25 M phosphate buffered solution at pH 7.0, glassy carbon working electrode (1 mm diameter), Pt wire counter electrode, Ag/AgCl reference electrode.

Fig. 6. (a) Charge buildup versus time from electrolysis of a 0.25 M buffer solution (pH 7.0). (b) Charge buildup versus time from electrolysis of 3.09 μM complex **1** in a 0.25 M buffer (pH 7.0) under a series of applied potentials, all data have been deducted blank. (c) Charge buildup versus time from electrolysis of 2.28 μM complex **2** in a 0.25 M buffer (pH 7.0) under a series of applied potentials, all data have been deducted blank.