Synthesis and electro- and photo-catalytic properties of a dinuclear cobalt(III) complex supported by 2-pyridylamino-N,N-bis(2-methylene-4,6-bimethyl)phenol

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ABSTRACT

The reaction of 2-pyridylamino-N,N-bis(2-methylene-4,6-bimethyl)phenol (H_2L) with $CoCl_2 \cdot 6H_2O$ affords the dinuclear cobalt complex $[L_2Co_2Cl_2]$ (**1**), a new molecular catalyst for both electrolytic and photolytic water reduction. **1** can electrocatalyze hydrogen evolution from water with a turnover frequency (TOF) of 921.95 moles of hydrogen per mole of catalyst per hour at an overpotential of 738 mV (pH 7.0). Additionally, under photoirradiation with blue light ($\lambda_{max} = 469$ nm), **1**, together with $[Ru(bpy)_3]Cl_2$ and ascorbic acid in a pH 4.0 aqueous solution also produces hydrogen with a remarkable turnover number (TON) of 14460 mol of H_2 per mol of catalysts. This performance is significantly better than those of other molecular cobalt catalysts reported in the literature for photochemical hydrogen production.

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Keywords: Cobalt complex; molecular structure; molecular electrocatalyst; molecular photocatalyst; hydrogen evolution

1. Introduction

Hydrogen, when generated directly from water or through other carbon-neutral processes, is a promising chemical fuel for sustainable energy applications [1-3]. In particular, electro- and photo-catalytic methods for generating hydrogen from water have been explored as cost-effective ways of producing a carbon-neutral fuel. Currently, one of the key challenges to water splitting is the development of efficient catalysts for water reduction reactions with low overpotentials, good stability and high turnover rates [4,5]. With this aim, a large effort has been devoted to the design and development of molecular catalysts employing more abundant metals for water reduction. As far as the hydrogen evolving reaction (HER) is concerned, during the last few years particular attention has been given to cobalt complexes, as convenient noble-metal free catalysts [6-10]. Among these, cobalt complexes supported by tetra- and pentadentate ligands have been reported for the catalytic production of H₂ in aqueous solution [11-14]. A report from Webster described a cobalt catalyst, Co(DPA-Bpy)Cl₂ (DPA-Bpy = N,N-bis(2-pyridinylmethyl)-2,2'-bipyridine-6-methanamine, a neutral pentadentate ligand) that electro-catalytically reduces water to H₂ at pH 7.0 in aqueous buffer with

a turnover number (TON) of $> 300 \text{ mol H}_2 (\text{mol cat})^{-1}$, and photo-catalytically reduces water to H_2 with a TON of > 1600 per mol of Co catalyst in aqueous media [7]. 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 [15,16]. Identification of the factors that control the oxidation/reduction site in these complexes, determining of their redox potentials and characterization of their electronic structures is critical for the design of more effective molecular catalysts for H_2 production. With this in mind, we have been studying ionic tetradentate ligands, in particular 2-pyridylamino-N,N-bis(2-methylene-4,6-bimethyl)phenol (H_2L) and its corresponding cobalt complex. In this paper, we present the synthesis and characterization of a new dinuclear cobalt(III) complex $[\text{L}_2\text{Co}_2\text{Cl}_2]$ (**1**), as well as its catalytic properties.

2. Experimental

2.1. Materials and physical measurements

UV-Vis spectra were measured on a Hitachi U-3010 spectrometer. ^{13}C and ^1H NMR spectra were measured on a Bruker AM 500 spectrometer in CDCl_3 . An ESI-MS experiment was performed on a Bruker Daltonics Esquire 3000 spectrometer by introducing samples directly into the ESI source using a syringe pump. 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 mm in diameter) was the working electrode, a saturated Ag/AgNO_3 or Ag/AgCl 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 [(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 contained 50 mL of 0.25 M phosphate buffer solution, while the auxiliary compartment was filled with 35 mL phosphate buffer solution. After addition of complex **1**, cyclic voltammograms were recorded. After electrolysis, a 0.5 mL aliquot of the headspace was removed and replaced with 0.5 mL of CH₄. The headspace sample was injected into the gas chromatograph (GC). For the photocatalytic H₂ evolution, each sample was prepared in a 5 mL flask containing 4 mL of buffer in the presence of [Ru(bpy)₃]Cl₂, ascorbic acid, and complex **1**. The flask was sealed with a septum under air or Ar. Each sample was irradiated by LED light (469 nm) at room temperature under constant stirring. The amounts of H₂ produced during photocatalysis were determined by GC. The GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument.

2.2. *Synthesis of 2-pyridylamino-N,N-bis(2-methylene-4,6-bimethylphenol), H₂[O₂NN]BuEtPy (H₂L)*

A solution of 2,4-dimethylphenol (15.02 g, 0.123 mol), aminomethylpyridine (6.61 g, 0.061 mol) and 37% aqueous formaldehyde (9.17 mL, 0.123 mol) in water (50 mL) was refluxed with stirring for 12 h. Cooling to room temperature produced a white precipitate which was collected and recrystallized from methanol. Drying under vacuum yielded $H_2[O_2NN]BuEtPy$ (21.00 g, 91% yield). Anal. calcd for $C_{24}H_{28}N_2O_2$: C, 76.39; H, 7.43; N, 7.43%. Found C, 76.33; H, 7.48; N, 7.41%. 1H NMR (400 MHz, $CDCl_3$) δ , ppm: 10.42 (s, 2H), 8.70 (d, $J = 4.7$ Hz, 1H), 7.69 (t, $J = 7.3$ Hz, 1H), 7.31-7.22 (m, 1H), 7.11 (d, $J = 7.8$ Hz, 1H), 6.86 (s, 2H), 6.70 (s, 2H), 3.83 (s, 2H), 3.75 (s, 4H), 2.21 (s, 12H). ^{13}C NMR (400 MHz, $CDCl_3$) δ , ppm: 156.14, 153.05, 148.26, 137.42, 131.21, 128.46, 127.53, 125.50, 123.69, 122.48, 120.71, 77.32, 77.00, 76.68, 56.39, 55.45, 20.33, 16.18.

2.3. Synthesis of the complex $[L_2Co_2Cl_2]$ (**1**)

To a solution containing H_2L (0.378 g, 1 mmol) and triethylamine (0.10 g, 1 mmol) in THF (20 mL), $CoCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol) in methanol was added and the mixture was stirred for 15 min. Single crystals were obtained from the filtrate, which was allowed to stand at room temperature for several days, and these were collected by filtration, and dried in *vacuo* (66%). The elemental analysis results (Found C, 60.97; H, 5.67; N, 5.91. $C_{24}H_{26}ClCoN_2O_2$ requires C, 61.43; H, 5.55; N, 5.97) were in agreement with the formula of the sample used for X-ray analysis. 1H NMR (400 MHz, $CDCl_3$) δ , ppm: 8.73 (s, 1H), 7.69 (s, 1H), 7.17 (s, 1H), 7.05 (s, 1H), 6.89 (s, 2H), 6.71 (s, 2H), 3.85 (s, 6H), 2.25 (s, 6H), 2.21 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$)

δ , ppm: 152.98, 148.30, 137.48, 131.35, 128.53, 127.65, 125.59, 123.81, 122.60, 120.54, 77.45, 77.14, 76.82, 56.45, 55.55, 20.36, 16.26.

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-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. All empirical absorption corrections were applied by using the SADABS program [17]. The structure was solved using direct methods and the corresponding non-hydrogen atoms were 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 [18]. Crystallographic data for complex **1** are given in Table S1 and selected bond lengths and bond angles are listed in Table S2.

3. Results and discussion

3.1. Synthesis and characterization of the cobalt complex **1**

In the presence of trimethylamine, the reaction of CoCl₂ and H₂L (Fig. S1) provides a dinuclear cobalt(III) complex (**1**) (yield = 66 %) (Scheme 1). The UV/Vis spectrum of **1** in MeCN shows a absorption peak at 263 nm (Fig. S2), which can be assigned to that of the ligand. The UV/Vis spectra of **1** in buffered aqueous solutions

from pH 3.0 to 12.0 exhibit similar peaks to those in water (Fig. S3), indicating that this complex is stable under these conditions.

Scheme 1. Schematic representation of the synthesis of [L₂Co₂Cl₂] **1**

The structure of solid complex **1** was found to be a chloride-bridged dimer (Fig. 1); **1** lies on an inversion center located within the Co₂Cl₂ rhomboid and the Co(III) centers exhibit distorted octahedral geometries. The Co(1)–Cl(1)–Co(1)# angle in **1** was 81.01(16)° and the chlorides are orientated *cis* to the nitrogen atom on the pendant pyridyl group. The Co–Cl bond distances are almost symmetric at 1.927(4) and 1.928(3) Å. From Fig. S4 (NMR spectra of complex **1** in CDCl₃), the title compound also exists as a complex, indicating that the ligand (L²⁻) does not dissociate from the cobalt center. However, this complex exists as a mononuclear unit in methanol solution. This is in agreement with the results from ESI-MS measurements which exhibited one ion at a mass-to-charge ratio (*m/z*) of 434.1415, with the mass

and isotope distribution pattern corresponding to that of $[\text{Co(III)(L)H}]^+$ (calculated m/z of 434.36) (Fig. S5), indicating that complex **1** can ionize in methanol. Therefore, it may account for better water solubility and more facile hydration, both important features for an effective homogeneous proton reduction catalyst (PRC).

3.2. Electrochemical studies

As shown in Fig. 2a, the cyclic voltammogram of 0.40 mM complex **1** in DMF showed one reversible $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ redox couple at $E_{1/2} = -0.84$ V and one quasi-reversible $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ redox couple at -1.58 V versus Ag/AgNO_3 . The current response of the redox event at -1.58 V showed a linear dependence on the square root of the scan rate (Fig. S6), which is indicative of a diffusion-controlled process, with the electrochemically active species freely diffusing in the solution.

We further explored the electrochemical behavior of complex **1** in buffered aqueous solutions where $\text{pH} = 3.9\text{--}7.0$ which is the range associated with catalytic water reduction. In a $\text{pH } 7.0$ phosphate buffer, an irreversible $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ wave at -0.58 V was observed for **1** (Fig. 2-b). Scanning cathodically revealed an irreversible $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ wave at -1.53 V (Fig. 2-b), which is dependent of pH (Fig. 3). As shown in Fig. 3, the onset of this catalytic current was clearly influenced by the solution pH , and the applied potential declined with increasing pH . From Fig. S7, the cyclic voltammogram of the background in the absence of complex **1** exhibited no catalytic current at the potential of the couples of $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$, suggesting that water reduction to H_2 occurs with complex **1**.

Several control experiments were then carried out to confirm that complex **1** was indeed responsible for the catalytic reaction. In particular, the free ligand, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and a 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. S8-S10, the catalytic competency achieved with **1** was not matched by just the 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.

3.3. Catalytic hydrogen evolution from acetic acid in DMF

From Fig. 4-a it can be seen that the catalytic current near -0.84 and -1.58 V versus Ag/AgNO_3 increased markedly with increasing proton concentration (acetic acid concentration increased from 0.00 to 5.42 mM). This indicates that hydrogen evolution electrocatalyzed by **1** requires the reduction of Co(III) to Co(II) , Co(II) to Co(I) and protonation. Interestingly, when the acetic acid concentration increased from 0.0 to 5.42 mM (Fig. 4-a), the onset of the catalytic wave remained almost constant at ca. -0.97 V. Based on the above observations, both the couples $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ and $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ are devoted to proton reduction. These results differ from previous reports that only the couple $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ is devoted to proton reduction [14,19-21]. Further mechanistic studies are under investigation.

Further evidence for the electro-catalytic activity was obtained by bulk electrolysis of a DMF solution of complex **1** (2.5 μM) with acetic acid (50.0 mM) at variable applied potentials using a glassy carbon plate electrode in a

double-compartment cell. Fig. 4-b shows the total charge of bulk electrolysis of complex **1** in the presence of acid; the charge significantly increased when the applied potentials were set as more negative. When the applied potential was -1.40 V versus Ag/AgNO₃, the maximum charge reached 24 mC during 2 min of electrolysis. A controlled-potential electrolysis (CPE) experiment under the same potential with a catalyst-free solution only gave a charge of 8 mC (Fig. S11), showing that this complex does serve effective hydrogen production under such conditions. This study suggests that **1** is capable of catalyzing the reduction of a proton from an acid to H₂. Assuming every catalyst molecule was distributed on the electrode surface and every electron was used for the reduction of protons, according to *eq. (1)* [22], we calculated the TOF for the catalyst, reaching a maximum of 36.4 moles of hydrogen per mole of catalyst per hour at an overpotential of 891.6 mV (Eq. S1 and Fig. S12).

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

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 the electrolysis.

3.4. Catalytic hydrogen evolution in aqueous media

To explore the catalytic hydrogen evolution in aqueous media, CVs were measured in buffers at different pHs. As shown in Fig. 2-b, in the absence of complex **1**, a catalytic current was not apparent until a potential of -1.42 V versus Ag/AgCl was

attained. Upon addition of complex **1**, the onset of catalytic current was observed at about -1.15 V versus Ag/AgCl, and the current strength increased significantly with increasing concentrations of complex **1** from 0.00 to 165.7 μM (Fig. S13). Further evidence for the electro-catalytic activity was obtained by bulk electrolysis of 2.5 μM of complex **1** in 0.25 M buffer at variable applied potentials. When the applied potential was -1.55 V versus Ag/AgCl, the maximum charge was only 26 mC during 2 min of electrolysis in absence of complex **1** (Fig. 5-a). Under the same conditions, the charge reached 593 mC on addition of complex **1** (Fig. 5-b), accompanied by evolution of a gas, which was confirmed to be H_2 by GC analysis. The evolved H_2 was analyzed by gas chromatography, Fig. S14-a, which gave 4.76 mL of H_2 over an electrolysis period of 1 h with a Faradaic efficiency of 92.08% for H_2 (Fig. S14-b). the TOF for electrocatalytic hydrogen production by complex **1** is 921.95 (pH 7.0) moles of hydrogen per mole of catalyst per hour at an overpotential of 738 mV (Eq. S2). To the best of our knowledge, this value is higher than some other reported molecular catalysts for electrochemical hydrogen production from neutral water, including a dinickel complex that exhibits a turnover number of 100 moles of H_2 per mole of catalyst with a turnover frequency of 160 moles of H_2 per mole of catalyst per hour at an overpotential of 820 mV [23], yet lower than a molybdenum-oxo complex which shows a maximum of 1600 moles of H_2 per mole of catalyst per hour at an overpotential of 642 mV [19].

*3.5. Photocatalytic water reduction by complex **1***

We also explored photocatalytic water reduction by complex **1** using ascorbic acid as an electron donor and [Ru(bpy)₃]Cl₂ as a photosensitizer. The capability of **1** to foster hydrogen evolution in light activated experiments was tested upon continuous visible irradiation (LED lamp, $\lambda = 460$ nm) of 0.25 M buffer at pH 4.0 (4 mL) containing different concentrations of **1** in the presence of Ru(bpy)₃Cl₂ as a photosensitizer and ascorbic acid as a sacrificial electron donor, and checking the headspace of the reactor by gas chromatography.

The light-induced H₂ generation catalyzed by **1** also depends on the concentrations of the sacrificial reagent and photosensitizer. For photocatalytic systems containing 0.15 M ascorbic acid, 0.10 mM complex **1** and varying amounts of Ru(bpy)₃Cl₂, the TON used in 2 h increased with increasing concentrations of Ru(bpy)₃Cl₂ until a saturation value of 16844 mol of H₂ (mol of cat)⁻¹ was reached at 0.30 mM. The TON then decreased when the concentration of Ru(bpy)₃Cl₂ was increased further (Fig. S15). For photocatalytic systems containing 0.30 mM Ru(bpy)₃Cl₂, 0.10 mM complex **1** and varying amounts of ascorbic acid, the TON used in 2 h increased with increasing concentrations of ascorbic acid until a saturation value of 1744 mol of H₂ (mol of cat)⁻¹ was reached at 0.15 M (Fig. S16).

To investigate the concentration effect on H₂ production, we carried out photolysis at different concentrations of **1**, ranging from 0.02 to 0.10 mM at pH 4.0. As shown in Fig. 6, **1** catalyzed H₂ production with a TON of 5866 mol of H₂ (mol of cat)⁻¹ at 0.10 mM **1**. When the concentration of **1** was lowered to 0.02 mM, the TON increased significantly to 14460 mol of H₂ (mol of cat)⁻¹, suggesting that the

concentration of **1** has a significant effect on the photocatalytic activity for H₂ production (Fig. S17). This value is significantly larger than the values for any other reported molecular cobalt catalysts for photochemical hydrogen production, including a pentadentate cobalt complex reported by Webster and Zhao [24], yielding a TON of 450 at 50 μ M concentration, and some of the cobalt complexes studied by Castellano, Long, and Chang [25,26], for which TONs of up to ca. 2000 were measured at 20 μ M concentration. Furthermore, we carried out the photolysis under air and Ar. The amount of H₂ (1.53 mM) produced in the presence of air during the first three hours of irradiation was 69% of that produced when the H₂ evolution was conducted under Ar (2.21 mM), suggesting that O₂ can inhibit the evolution of H₂ (Fig. S18).

In order to identify the factors responsible for the photocatalytic H₂ evolution in the above system, we added one of the three components (ascorbic acid, [Ru(bpy)₃]Cl₂ or complex **1**) or CoCl₂·6H₂O to a reaction flask after cessation of the H₂ evolution to see if the H₂ production could be resumed. However, addition of any of the four components, in the same amount as used in the photocatalytic reaction, resulted in no significant amount of H₂ generation. Both complex **1** and [Ru(bpy)₃]Cl₂ need to be added to resume the production of 0.021 mmol H₂ (Fig. S19). The addition of both ascorbic acid and [Ru(bpy)₃]Cl₂ led to a slight increase in H₂ evolution (0.03 mmol), suggesting the decomposition of both **1** and [Ru(bpy)₃]²⁺ during photolysis. However, no significant amount of H₂ was produced when both ascorbic acid and [Ru(bpy)₃]Cl₂ were added.

4. Conclusion

The dinuclear cobalt complex **1**, which is very easy to be obtained, can electrocatalyze and photocatalyze water reduction to generate H₂. Electrochemical studies show that **1** can electrocatalyze water reduction to hydrogen with a TOF of 921.95 moles of hydrogen per mole of catalyst per hour at an overpotential of 738 mV (pH 7.0). Complex **1** in pH 4.0 aqueous solution under air, together with [Ru(bpy)₃]Cl₂ and ascorbic acid as a sacrificial electron donor, in the presence of blue light ($\lambda_{\text{max}} = 469 \text{ nm}$) produces hydrogen with a TON = 14460 mol of H₂ (mol of cat)⁻¹. This discovery has established a new chemical paradigm for creating a water reduction catalyst that is highly active in aqueous media.

Appendix A. Supplementary data

CCDC 1037133 contains the supplementary crystallographic data for this paper. These 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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A new molecular catalyst based on the cobalt complex $[L_2Co_2Cl_2]$ (**1**) was formed by the reaction of 2-pyridylamino-N,N-bis(2-methylene-4,6-bimethyl)phenol (H_2L) with $CoCl_2 \cdot 6H_2O$ and has been tested for both electrolytic and photolytic water reduction.

Fig. 1. Molecular structure of complex 1.

Fig. 2. (a) Cyclic voltammogram of 0.40 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. Ferrocene internal standard (*). (b) Cyclic voltammograms of buffers with and without complex **1** (pH 7.0, scan rate: 100 mV/s).

Fig. 3. (a) CVs of 0.20 mM complex **1**, showing the variation in catalytic current with pH (scan rate: 100 mV/s). (b) Catalytic current maximum (i_c) as a function of pH.

Fig. 4. (a) Cyclic voltammograms of a 0.40 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, GC working electrode (1 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode, Fc internal standard (*). (b) Charge buildup versus time from electrolysis of a 2.5 μM complex **1** in DMF (0.10 M [n-Bu₄N]ClO₄) under various applied potentials. All data have been deducted blank.

Fig. 5. (a) Charge buildup versus time from electrolysis of 0.25 M buffer (pH 7.0). (b) Charge buildup versus time from electrolysis of 2.5 μM complex **1** in a 0.25 M buffer (pH 7.0) under a series of applied potentials.

Fig. 6. Hydrogen evolution kinetics obtained upon continuous visible irradiation ($\lambda = 469 \text{ nm}$) of pH 4.0 solutions (4 mL) containing 0.30 mM $\text{Ru}(\text{bpy})_3\text{Cl}_2$, 0.15 M ascorbic acid, and **1** at 0.02 mM (black trace), 0.05 mM (red trace), and 0.10 mM (blue trace) concentration.