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Water oxidation catalytic ability of polypyridine complex containing a μ -OH, μ -O₂ dicobalt(III) core

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ABSTRACT

Two polypyridine complexes containing μ -OH, μ -O₂ dicobalt(III) cores, [(TPA)Co^{III}(μ -OH)(μ -O₂)Co^{III}(TPA)](ClO₄)₃ and [(BPMEN)Co^{III}(μ -OH)(μ -O₂)Co^{III}(BPMEN)](ClO₄)₃ (TPA = tris(2-pyridylmethyl)amine, BPMEN = *N,N'*-dimethyl-*N,N'*-bis(pyridin-2-ylmethyl)ethane-1,2-diamine), have previously been reported as inactive in the light-driven water oxidation reaction (*ACS Catal.*, **2016**, *6*, 5062–5068). Herein, another dicobalt(III) compound, μ -OH, μ -O₂-[enN4₂Co₂](ClO₄)₃ (enN4 = 1,6-bis(2-pyridyl-2,5-diazaocta-2,6-diene), with a similar core structure was synthesized, characterized, and applied to the light-driven water oxidation reaction. Collective experiments showed that the complex itself was also inactive in the light-driven water oxidation, and that the activity observed originated from Co(II) impurities. This research establishes that complexes possessing a μ -OH, μ -O₂ dicobalt(III) core structure are not appropriate choices for true molecular catalysts of water oxidation.

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1. Introduction

The large-scale use of fossil fuels has resulted in various environmental problems. Accordingly, the development and utilization of renewable and environmentally friendly energy are needed [1–3]. Hydrogen is a promising alternative to traditional fossil fuels because it is a clean energy source with a high heat value [4,5]. Water splitting inspired by photosynthesis is considered an ideal pathway for the conversion of solar energy and water into hydrogen energy [6–8]. The overall water splitting process comprises two half reactions, namely water oxidation ($2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$) and proton reduction ($4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$). The water oxidation step has a high activation energy

and is regarded as the limiting step of water splitting [9–11]. To improve the efficiency of water oxidation, much research has been focused on exploring water oxidation catalysts (WOCs) [3, 12,13]. However, the development of efficient WOCs remains challenging. Owing to their low cost and abundance, much recent research effort has focused on WOCs based on first row transitional metals [14–25]. Compared with heterogeneous WOCs, homogeneous WOCs, especially molecular organic complexes, have advantages in structure modification and mechanism research [26]. There are two main categories of homogeneous WOCs, namely inorganic polyoxometallates and organic ligand-based complexes.

Among the homogeneous WOCs, organic complexes con-

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taining Co have been widely investigated because they usually show good catalytic activity in light-driven water oxidation. Polycore complexes, such as cubane-like complexes with M_4O_4 (M = transition metal) frames, are attractive because of their biomimetic structures [27–31], which are similar to that of the oxygen-evolving Mn_4CaO_5 cluster in natural photosynthesis system II (PSII). For example, a $Co_4O_4(Ac)_4(py)_4$ cluster and related derivatives were initially regarded as homogeneous WOCs [27,32]. However, a follow-up study by Nocera *et al.* [33] suggested that pure $Co_4O_4(Ac)_4(py)_4$ cluster was inactive. Photochemical and electrochemical experiments confirmed that Co(II) impurities were responsible for the apparent catalytic ability [33]. A recent study by Lu *et al.* [34] showed that two dinuclear cobalt polypyridine complexes containing μ -OH and μ -O₂ core were unable to catalyze water oxidation. Chelating experiments and controlled potential electrolysis measurements attributed the observed catalytic activity of these synthesized samples to Co(II) impurities introduced during synthesis.

Sufficient experiments should be carried out to identify true WOCs, especially for Co-based molecular catalysts. Co(II) impurities can transform into CoO_x species, which are true WOCs. Therefore, the possibility that the catalytic activity originates from impurities should be ruled out before identifying substrates as true homogeneous WOCs.

Herein, binuclear complex μ -OH, μ -O₂-[$\{(enN4)_2Co_2\}(ClO_4)_3$ ($1(ClO_4)_3$, enN4 = 1,6-bis(2-pyridyl)-2,5-diazahehex-1,5-diene) (Fig. 1) was synthesized and used to catalyze water oxidation. Its catalytic ability was investigated using a series of methods, which showed that **1** was inactive as a catalyst for light-driven water oxidation. The apparent activity of the as-synthesized catalyst originated from Co impurities introduced during synthesis. This finding supplements previous reported results and establishes that complexes containing a μ -OH, μ -O₂ dicobalt(III) core might be unsuitable as WOCs for light-driven water oxidation. This rule provides guidelines for the future exploration of efficient WOCs.

2. Experimental

2.1. Synthesis of $1(ClO_4)_3$

Purified water (18.2 M Ω ·cm) for the preparation of buffer solutions was obtained from a Molecular Lab Water Purifier. All chemical agents were commercially available and used without further purification.

The enN4 ligand was synthesized according to a literature

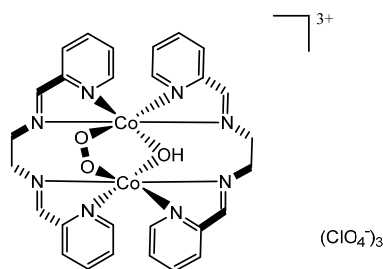


Fig. 1. Chemical structure of complex **1**.

procedure [35]. 2-Pyridinecarboxaldehyde (3.2 g, 30 mmol) and ethylenediamine (0.9 g, 15 mmol) were dissolved in methanol (25 mL). The solution was refluxed for about 7 h, cooled to room temperature, and concentrated by rotary evaporation to obtain a yellow solid. A pure ligand sample was obtained by recrystallization from *n*-hexane followed by drying in a vacuum oven.

Compound **1** was synthesized according to a literature procedure [36] in the form of $1(ClO_4)_3 \cdot 2MeCN \cdot H_2O$ accompanied by one molecule of py-HClO₄. This microcrystalline solid was obtained by adding $Co(ClO_4)_2 \cdot 6H_2O$ to an acetonitrile solution of 1,6-bis(2-pyridyl)-2,5-diazahehex-1,5-diene and a small quantity of pyridine. The solution became red-brown within minutes, and then changed to dark brown. After stirring for 16 h under air to complete the metal oxidation, black microcrystals were formed. These crystals were collected by filtration and washed with Et₂O several times. Crystals suitable for X-ray diffraction analysis were obtained by slowly evaporating a saturated solution of the black microcrystals in acetonitrile/toluene (3:1, v/v). The addition of a few drops of pyridine aided crystal formation. Elemental analysis of $C_{37}H_{43}Cl_4Co_2N_{11}O_{20}$ gave the following results: calcd, C 36.38%, H 3.55%, N 12.61%; found, C 35.82%, H 3.45%, N 12.70%.

2.2. Electrochemical measurements

Cyclic voltammetry (CV) was recorded on a CHI660D electrochemical analyzer. Glassy carbon (GC; 0.071 cm²), Ag/AgCl (3.5 mol/L KCl), and Pt wire were used as the working, reference, and auxiliary electrodes, respectively. CV tests were carried out in buffer solutions at pH = 9.0 and room temperature using a scan rate of 100 mV/s. For controlled potential electrolysis experiments, indium-tin oxide (ITO) glass slides (2.0 cm × 1.0 cm, 1.0 cm² immersed in electrolyte), Ag/AgCl, and Pt wire were used as the working, reference, and auxiliary electrodes, respectively. ITO glass slides were cleaned by sonication in acetone, ethanol, and ultrapure water for 30 min, successively.

2.3. Photocatalytic water oxidation

Photocatalytic water oxidation was performed as follows. Catalyst was added to the reaction solution (80 mmol/L borate buffer solution) containing $[Ru(bpy)_3]Cl_2$ (bpy = 2,2'-bipyridine) (1 mmol/L) and $Na_2S_2O_8$ (10 mmol/L). The above solution was deaerated by purging with Ar gas for 10 min in a flask (total volume = 28 mL) and then sealed with a rubber septum (reaction solution volume = 15 mL). The reaction was initiated by irradiating the solution using light-emitting diodes (LEDs) as the light source (light intensity = 15.8 mW, beam diameter = 2 cm) through a transmitting glass filter ($\lambda \geq 420$ nm) at ambient temperature. After each irradiation period, Ar gas (150 μ L) was injected into the flask and the same volume of gas was withdrawn from the flask headspace using an SGE gas-tight syringe and analyzed by gas chromatography. The oxygen in the sampled gas was separated by passing through a packed molecular sieve 5A column (2 m ×

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