Polyhedron 126 (2017) 239–244

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, characterization and electro-catalytic properties of a water-soluble nickel(II) complex supported by picolinic acid ions

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ARTICLE INFO

Article history:
Received 19 December 2016
Accepted 25 January 2017
Available online 4 February 2017

Keywords:
Nickel(II) complex
Molecular structure
Molecular electrocatalyst
Electrochemical investigation
Proton or water reduction
Hydrogen generation

ABSTRACT

The reaction of picolinic acid (HA) with $NiCl_2 \cdot 6H_2A$ affords a nickel(II) complex, $[NiA_2(H_2O)_2]$ **1** (A: picolinic acid ion), which has been characterized by using physics-chemical and spectroscopic methods. Electrochemical investigations shows that **1** can act as a homogeneous electrocatalyst for water reduction in a purely aqueous medium. **1** catalyzes hydrogen evolution from a neutral water (pH 7.0) with a turnover frequency (TOF) of 568 mol of hydrogen per mole of catalyst per hour at an overpotential (OP) of 687.6 mV. To prove that the combination of nickel center and picolinic ion is the key structural feature for eliciting proton or water reduction catalysis, we also investigate the electro-catalytic activities of $[NiA_2(H_2O)_2]$ **1** and $Ni(Ac)_2 \cdot 2H_2O$ and provide a possible catalytic mechanism for hydrogen generation by this nickel complex. The result also exhibits that nickel center constitutes the better active catalyst than the cobalt sample with same ligands.

1. Introduction

To avoid energy crisis and reduce environmental pollution, people are developing new systems for new energy sources. And hydrogen is one of the most ideal energy in the future, because of its numerous advantages such as recyclability and pollution-free use [1]. Water is the only waste-free electron-source substrate that could sustain the scale of the process required to supply our energy demands. Thus splitting water is an important and simple method for hydrogen production in high purity and large quantities [2]. Among current technologies for hydrogen production, electrocatalytic water reduction via hydrogen evolution reaction (HER) is considered as one of the most attractive and simple methods [3]. So far, many research groups, including ours, have developed several molecular catalysts for hydrogen generation from organic acid and water based on transition metal complexes, such as nickel [4–13], cobalt [14–17], copper [18,19], iron [20] and manganese [21]. Despite much progress in water reduction catalysis, major improvements in several areas, including decreasing structural complexity and increasing solubility in aqueous media, are needed before efficient electrocatalytic water reduction can be realized [22]. Our works focus on the design of molecular electrocatalysts that are water soluble and can efficiently catalyze water reduction. In this paper, we present the synthesis, characterization and catalytic properties of the complex, $[NiA_2(H_2O)_2]$ **1**, as well as the effect of the metal centers on the electrocatalytic activity. We hope this can afford a method for the improvement in electrocatalytic hydrogen production by the structural modification of complexes.

2. Experimental

2.1. Physical measurements

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. 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 organic and aqueous media were conducted by using the literature procedure [23]. Gas chromatograph (GC) experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument.

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http://dx.doi.org/10.1016/j.poly.2017.01.044

*2.2. Synthesis of complex $[NiA_2(H_2O)_2]\cdot 2H_2O$, **1** 2 H_2O*

To a solution of $NiCl_2\cdot 6H_2O$ (0.238 g, 1 mmol) in methanol (10 ml), picolinic acid (0.246 g, 2 mmol) in methanol (10 ml) was added and the mixture was stirred for 30 min. Standing at room temperature for several days gave green crystals, which were collected by filtration, and dried in *vacuo* (0.17 g, 45%). The elemental analysis results (Found C, 38.24; H, 4.27; N, 7.48. $C_{12}H_{16}NiN_2O_8$ requires C, 38.44; H, 4.3; N, 7.47) were in agreement with the formula of the sample used for X-ray analysis.

2.3. Crystal structure determination

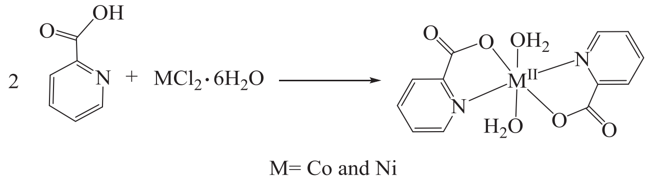
The X-ray analysis of **1** was carried out with a Bruker Smart Apex II DUO area detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. All empirical absorption corrections were applied by using the SADABS program [24]. The structure was solved using direct methods 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 [25]. Crystallographic data for complex **1** are given in Table S1 and selected bond lengths and angles are listed in Table S2.

3. Results and discussion

3.1. Structural analysis and general characterization

The reaction of picolinic acid (HA) and $NiCl_2\cdot 6H_2O$ forms one nickel(II) complex, $[Ni(A)_2(H_2O)_2]$ **1** (Scheme 1), which is soluble both in water and several organic solvents. As shown in Fig. S1, complex **1** exhibits an absorption band at about 264 nm, which corresponds to a pi–pi* transition of the A^- moiety. From Figs. S2-3, in the pH range 2.0–12.0, the intensity of the absorption band at 264 nm decreases, suggesting new components are being formed. These observations point to the formation of dinuclear or polynuclear species [14].

According to Fig. 1, in solid, complex **1** is formed by one Ni^{2+} ion, two picolinic acid ions, and two H_2O molecules. The nickel 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 Ni–N distance is 2.0661(16) Å. And the bond distance of Ni and O from picolinic acid (2.0492(13) Å) is shorter than that of Ni and O from H_2O (2.0980(13) Å). To prove that the different length of Ni–O bonds can affect the forms in solution, ESI-MS measurement for complex **1** was conducted in methanol. As shown in Fig. S4, the electrospray mass spectrum of **1** exhibits one ion at a mass-to-charge ratio (*m*/*z*) of 342.9835, with mass and isotope distribution pattern corresponding to $[Ni(A)_2(H_2O)Na]^+$, indicating that one coordinated H_2O dissociates from nickel center in methanol.



Scheme 1. Synthesis of complexes, $[M(A)_2(H_2O)_2]$ (M = Co and Ni).

*3.2. Thermal decomposition process for complex **1***

In order to check the stability of complex **1** in solid, TG curve of complex **1** was measured in the temperature range 50–250 °C. According to Fig. 2, with increasing temperature, complex **1** exhibits marked mass losses in two steps. The first TG weight loss of approximately 9.70% in the temperature range 50–129.3 °C with an endothermic peak at 129.3 °C is mainly due to the departure of two lattice water molecules from complex **1** (theoretical weight loss 9.60%). The subsequent thermal decomposition of complex **1**, with a mass loss of 9.60% in the range 140–203 °C, is contributed to the departure of two coordination water molecules (theoretical weight loss 9.60%), indicating the combination of nickel atom with water molecules is weak. This result is agreement with the above ESI-MS analysis. When the temperature increases further, no significant weight loss was observed for **1**.

3.3. Linear scan voltammetry

Based on that nickel complexes can electrocatalyze hydrogen generation both from acetic acid or aqueous buffer via an unstable hydride intermediate [6,26], we tried to test if this nickel complex also can act as an electrocatalyst for hydrogen evolution. To study the electrochemical behavior of the complex, first we used linear scan voltammetry (LSV) to investigate the reduction of water at the glassy carbon electrode surface with or without complex **1**. As shown in Fig. 3, the onset of water reduction moves to more anodic values with the sequential increments of complex **1** concentration. Moreover, the catalytic current increases significantly with decrease of pH values from 7.0 to 3.5 (Fig. S5), suggesting that there is a protonation step in the catalytic reaction.

3.4. Cyclic voltammetry

Flowingly, we tested its electrochemical properties by using cyclic voltammetry. With 0.10 M $[(n\text{-}Bu)_4N]ClO_4$ as the supporting electrolyte in CH_3CN at a glassy carbon electrode, complex **1** displayed one reversible redox couple at −1.41 V versus $Ag/AgNO_3$, which can be assigned to the $Ni^{II/I}$ couple (Fig. 4). To further get the information of this nickel complex, cyclic voltammograms (CVs) were recorded at varying scan rates. According to Fig. S6, the current responses of the redox event at −1.58 V shows a linear dependence on the square root of the scan rate, which is an indicative of a diffusion-controlled process in the solution.

3.5. Electrocatalytic hydrogen generation from acetic acid in CH_3CN

To check catalytic activity of complex **1**, we chosen acetic acid as proton resource. From Fig. 5, with the sequential increments of acetic acid concentration (from 0.00 to 5.00 mM), the current strength near −1.58 V versus $Ag/AgNO_3$ increased markedly, which can be assigned to the catalytic generation of H_2 from acetic acid [27]. The result shows that H_2 production electrocatalyzed by complex **1** requires the reduction potential of Ni(II) to Ni(I). On the basis of literature precedent [26], ESI-MS and above analyses, a possible mechanism for electro-catalyst of complex **1** can be presented in Scheme 2. According to Scheme 2, one-electron reduction of $[A_2Ni^{II}(H_2O)_2]$ **1** gives a putative $[A_2Ni^{I}(H_2O)]^-$ species via losing one water molecule. Addition of hydrogen proton yields the Ni^{III}-H species, a high reactive intermediate. Further addition of hydrogen proton of the Ni^{III}-H species affords H_2, and regenerates the starting complex **1**.

The above catalytic system was further characterized by bulk electrolysis from 5.34 μM complex **1** with acetic acid in CH_3CN under variable applied potential. As shown in Fig. S7a, when the applied potential was −1.45 V versus $Ag/AgNO_3$, the maximum