

Effect of metal centers on electrocatalytic hydrogen generation catalyzed by coordinatively saturated metal-1,10-phenanthroline complexes



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ABSTRACT

It is apparent that coordinatively unsaturated transition complexes can catalyze hydrogen production from acid or water via metal-hydride intermediates. To test if coordinatively saturated complexes can also act as electrocatalysts for hydrogen evolution, two electrocatalytic systems based on coordinatively saturated metal-1,10-phenanthroline (phen) complexes, $[M^{II}(\text{phen})_3](\text{PCPP})_2$ (PCPP = pentacyanopropenide; M = Fe, **1**; Ni, **2**), have been designed. The electrochemical investigations show that both **1** and **2** can act as electrocatalysts for hydrogen generation from aqueous buffer with a turnover frequency (TOF) of 630.1 and 673.5 mol of hydrogen per mole of catalyst per hour (mol H₂/mol catalyst/h) at an overpotential (OP) of 838 mV. These results also show that the nickel center constitutes the better active catalyst.

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1. Introduction

In order to avoid an energy crisis, people are developing new systems to generate energy and hydrogen is of particular interest as a secondary energy carrier, with its generation from water being a current topic of intensive research [1,2]. Electrochemical driven hydrogen generation from water has been explored as a cost-effective way of producing a carbon-neutral fuel. To increase the reaction rate and to decrease the energy consumption, it is necessary to employ an efficient catalyst for the hydrogen evolution reaction (HER). Previous studies revealed that transition metal complexes can indeed catalyze hydrogen production from organic acids or water, and the properties of the ligands of the complexes play an important role for hydrogen evolution in the catalytic cycle [3–6]. It is widely regarded that transition metals capable of forming metal-hydride intermediates are essential to the HER mechanism [7–9]. Based on the above considerations, much effort has been made to design coordinatively unsaturated complexes supported by tetra- or pentadentate ligands for proton or water reduction [6]. So far, several cobalt [10–14], copper [15,16], iron [17–20], manganese [21] and nickel [22–25] complexes have been developed as electrocatalysts for the production of hydrogen from organic acids or aqueous buffer. Despite these advances, few electrocatalytic systems for hydrogen production based on coordinatively saturated complexes are known [26]. In light of these

considerations, we focused our work on the design and studies of electrocatalytic systems based on coordinatively saturated complexes. As a part of the research results, herein we report the synthesis, structures and characterization of two coordinatively saturated complexes, $[M(\text{phen})_3](\text{PCPP})_2$ (PCPP = pentacyanopropenide; M = Fe, **1**; Ni, **2**). Both the coordinatively saturated complexes exhibit remarkable activity for the electrocatalytic reduction of water to hydrogen in purely aqueous media.

2. Experimental section

2.1. Physical measurements

Elemental analysis for C, H and N were obtained on a Perkin-Elmer analyzer model 240 instrument. A Bruker AV 500 spectrometer was used to measure the NMR spectrum. The ESI-MS experiments were performed on a Bruker Daltonics Esquire 3000 spectrometer, introducing the samples directly into the ESI source using a syringe pump. Electrochemical measurements were conducted 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/AgNO₃ or Ag/AgCl electrode was the reference electrode and a 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.

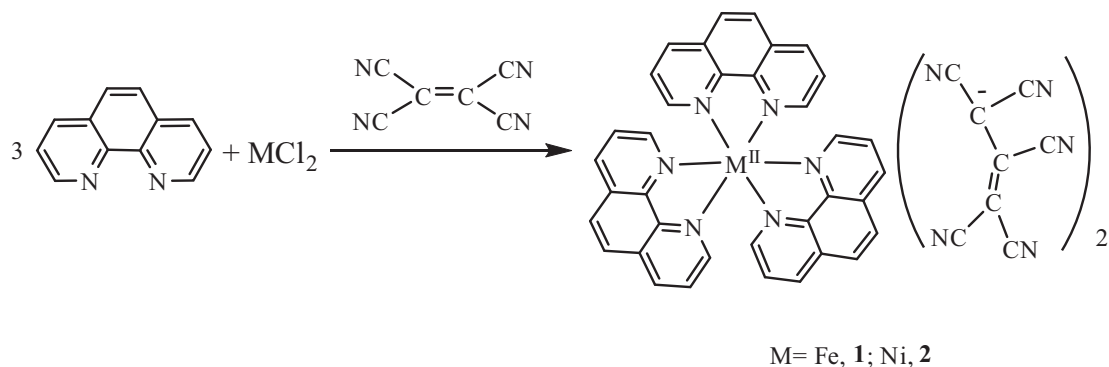
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The working compartment was filled with 50 mL of 0.25 M buffer with varying pH values, while the auxiliary compartment was filled with 35 mL phosphate buffer solution. Adding the complex to the working compartment, both compartments were bubbled for 1 h with nitrogen and then the cyclic voltammograms (CVs) were recorded as controls. After electrolysis, a 0.50 mL aliquot of the headspace was removed and replaced with 0.50 mL of CH_4 . A gas chromatograph (GC) instrument was turned on for about 1 h, then the headspace sample was injected for testing. GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument.

2.2. Synthesis of complex 1

To a solution containing $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.20 g, 1 mmol) and 1,10-phenanthroline monohydrate (0.594 g, 3 mmol), tetracyanoethylene (TCNE) (0.258 g, 2 mmol) in CH_3CN (20 mL) was added and the mixture was stirred for 30 min. Brown crystals were obtained from the filtrate after allowing it to stand at room temperature for several days, which were collected by filtration, and dried *in vacuo* (0.66 g, 71%). *Anal. Calc.* for $\text{C}_{52}\text{H}_{24}\text{N}_{16}\text{Fe}$: C, 67.25; H, 2.61; N, 24.13. *Found:* C, 67.64; H, 2.60; N, 24.24%. $^1\text{H NMR}$ (DMSO, ppm) δ : 8.81 (d, $J = 8.0$ Hz, 2H, phen), 8.40 (s, 2H, phen),



Scheme 1. Synthesis of the complexes $[\text{Fe}(\text{phen})_3](\text{PCPP})_2$ **1** and $[\text{Ni}(\text{phen})_3](\text{PCPP})_2$ **2**.

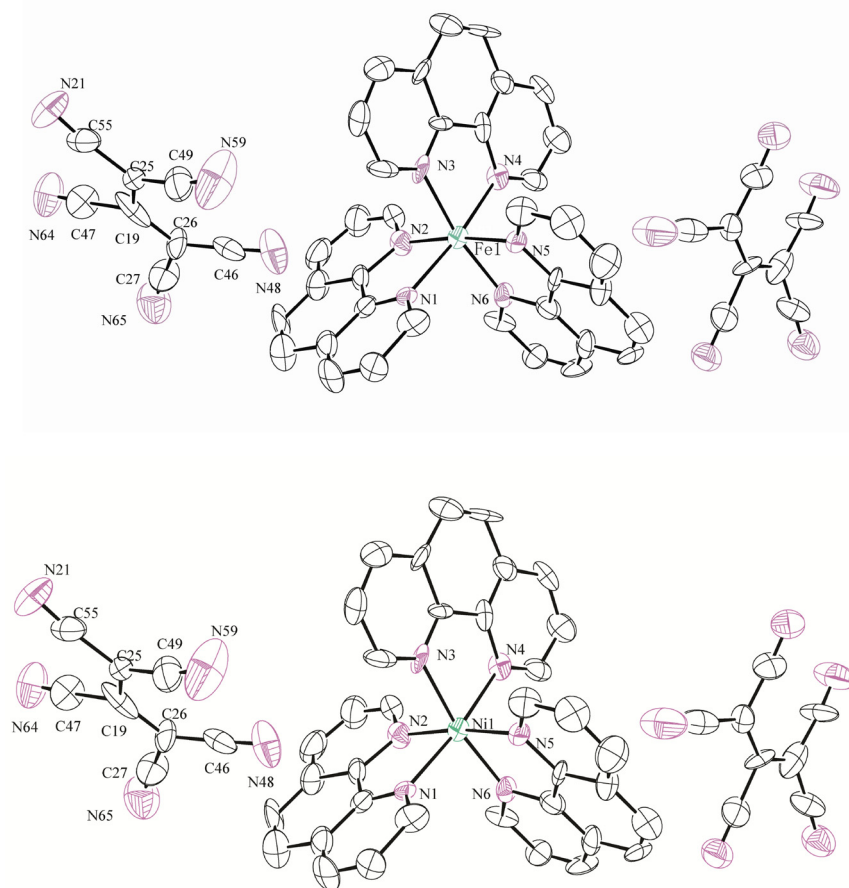


Fig. 1. ORTEP drawing of complexes **1** (top) and **2** (bottom) with thermal ellipsoids at the 50% probability level (hydrogen atoms are not shown).

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