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Function of 7,7,8,8-tetracyanoquinodimethane (TCNQ) on electrocatalytic hydrogen generation catalyzed by N,N′-benzene bis (salicylideniminato)nickel(II)

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ABSTRACT

In the presence of trimethylamine, the reaction of N,N′-benzene bis(salicylidenimine) (H_2L) with $NiCl_2{\cdot}6H_2O$ affords a nickel(II) complex, [NiL] (**1**), and the reaction of H_2L with $NiCl_2{\cdot}6H_2O$ and TCNQ provides a TCNQ compound, [LNi(TCNQ)] (**2**). Electrochemical studies show that **1** electrocatalyzes hydrogen evolution, both from acetic acid with a turnover frequency (TOF) of 53.25 moles of hydrogen per mole of catalyst per hour at an overpotential (OP) of 941.6 mV (in DMF), and from an aqueous buffer solution (pH 7.0) with a TOF of 462.33 moles of hydrogen per mole of catalyst per hour at an OP of 836.7 mV. **2** can electrocatalyze hydrogen evolution, both from acetic acid with a TOF of 62.56 moles of hydrogen per mole of catalyst per hour at an OP of 941.6 mV (in DMF), and from an aqueous buffer solution (pH 7.0) with a TOF of 909.58 moles of hydrogen per mole of catalyst per hour at an OP of 836.7 mV. To testify that TCNQ plays a vital role in determining the catalytic activities of the nickel complex, we have systematically studied the electrocatalytic activities of **1** and **2**, to provide a possible catalytic mechanism for hydrogen generation by the nickel complexes. This observation suggests that the presence of TCNQ is a key structural feature for eliciting proton or water reduction catalysis. This can be attributed to negatively charged TCNQ, formed from **2**, that can stabilize the low oxidation state of the nickel ion.

1. Introduction

Hydrogen is one of the most ideal sources for energy in the future, because of its numerous advantages such as recyclability and pollution-free use [1–3]. Water is the only waste-free electron-source substrate that could sustain the scale of the process required to supply our energy demands. Thus water splitting is an important and simple method for hydrogen production with high purity and in large quantities [4]. The generation of hydrogen by electrochemical reduction of a proton source, such as water, represents an attractive approach for storing the electrical energy transiently produced by renewable energy sources [5,6]. To increase the reaction rate, it is necessary to use an efficient hydrogen evolution reaction electrocatalyst. Therefore, many research groups, including ours, have designed molecular catalysts by employing abundant metals, and several complexes of nickel [7,8], cobalt [9–13], copper [14–17] and molybdenum [18,19] have been developed as electrocatalysts for the reduction of protons or water to form H_2. Despite much progress in water reduction catalysis, major improvements in several areas, including lowering overpotentials, increasing catalyst durability and using earth-abundant elements, are needed before efficient electrocatalytic water reduction can be realized. Especially, structural complexity, insolubility in aqueous media and low pH conditions severely limit their practical utility [20].

Our interest focuses on the design of molecular electrocatalysts that are water soluble and can efficiently catalyze water reduction. To the best of our knowledge, there is as yet no report on electrochemical water reduction by TCNQ compounds. As we know, TCNQ is electron poor and forms numerous donor–acceptor compounds [21], where radical anions are stabilized by charge and spin delocalization, forming numerous stable electron transfer salts. Generally, compounds containing TCNQ exhibit metal-like electrical conductivity [22] and ferromagnetic ordering [23]. Reported here is an electrocatalyst based on one nickel-TCNQ complex, [LNi (TCNQ)] (**2**), for hydrogen evolution from both acetic acid and aqueous buffer solution, as well as the effect of TCNQ on the catalytic properties of the nickel(II) complex. We hope this can

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establish a new method for the improvement in electrocatalytic hydrogen production by structural modification of the catalyst.

2. Experimental section

2.1. Materials and physical measurements

The nickel complex [LNi] (**1**) was prepared by using the literature procedure [24]. Elemental analyses for C, H and N were obtained on a Perkin-Elmer analyzer model 240. 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. IR spectra were obtained as KBr pellets on a Bruker 1600 FT-IR spectrometer from 4000 to 400 cm^{-1}. Electronic spectra were recorded on a Lambda-900 spectrophotometer. 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, an $Ag/AgNO_3$ or saturated 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 a solution of 0.10 M $[(n\text{-}Bu)_4N]ClO_4$ was used as the supporting electrolyte. Controlled-potential electrolysis (CPE) in DMF 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 $Ag/AgNO_3$ reference electrode. The auxiliary compartment was fitted with a Pt gauze electrode. The working compartment was filled with 50 mL of 0.10 M $[(n\text{-}Bu_4N)]ClO_4$ DMF solution with acetic acid, while the auxiliary compartment was filled with 35 mL of 0.10 M $[(n\text{-}Bu_4N)]ClO_4$ DMF solution, resulting in equal solution levels in both compartments. Both compartments were purged for 1 h with N_2 and cyclic voltammograms (CVs) were recorded as controls. 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. Adding nickel complexes, both compartments were purged for 1.5 h with nitrogen and CVs were recorded as controls. After electrolysis, a 0.5 mL aliquot of the headspace was removed and replaced with 0.5 mL of CH_4. The headspace sample was injected into the gas chromatograph (GC). GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument.

2.2. Synthesis of [LNi] (**1**)

To a solution of o-phenylenediamine (1.08 g, 10 mmol) in methanol (20 ml), salicylaldehyde (2.45 g, 20 mmol) was added, and the mixture was refluxed for 8 h. To the above yellow mixture was added triethylamine (2.00 g, 20 mmol) and $NiCl_2{\cdot}6H_2O$ (2.34 g, 10 mmol) with stirring for 20 min, the color of the solution changed from yellow to brown. On slow evaporation at room temperature for several days, brown crystals appeared. The crystals were collected and dried in *vacuo* (3.15 g, 85%). *Anal.* Calc. for $C_{20}H_{14}N_2NiO_2$: C, 64.75; H, 3.26; N, 7.55;. Found: 64.86; H, 3.76; N, 7.54%.

2.3. Synthesis of [LNi(TCNQ)] (**2**)

A solution of o-phenylenediamine (0.54 g, 5.0 mmol) and salicylaldehyde (1.23 g, 10.0 mmol) in 50 ml methanol was refluxed with stirring for 8 h, whereupon a yellow powder was obtained. To the above yellow mixture was added triethylamine (1.00 g, 10.0 mmol), $NiCl_2{\cdot}6H_2O$ (1.17 g, 5.0 mmol) and TCNQ (1.02 g, 5.0 mmol) in 50 ml CH_2Cl_2 with stirring. The color of the solution changed from yellow to deep-green, and it was allowed to react for 3 h at room temperature, and then it was filtered. On slow evaporation at room temperature for several days, deep green crystals appeared. The crystals were collected and dried in *vacuo* (1.26 g, 43.8% based on TCNQ). *Anal.* Calc. for $C_{32}H_{18}N_6NiO_2$: C, 66.82; H, 2.80; N, 14.61. Found: 66.86; H, 2.79; N, 14.64%. IR band (KBr pellets, cm^{-1}) ν: 2217.

2.4. Crystal structure determination

X-ray analysis of the complex [LNi(TCNQ)] (**2**) 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 using the SADABS program [25]. 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 the full-matrix least-squares refinement. All calculations were performed using the SHELXTL computer program [26]. Crystallographic data for complex **2** are given in Table 1 and selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of the nickel complexes [LNi] (**1**) and [LNi(TCNQ)]·MeOH (**2**·MeOH)

Typically, the reaction of the TCNQ molecule with transition metal centers leads to di-, tri- or tetranuclear nitrile-bonded σ compounds, to π compounds with side-on coordination, or to the corresponding ion pair compounds without direct coordination [27–31]. However, when the Ni^{II} complex NiL was used as a metal source to react with TCNQ, an unprecedented TCNQ-compound **2** (Scheme 1) resulted, which is soluble in both aqueous media (1.5×10^{-3} mol L^{-1}) and general organic solvents, such as CH_3OH and CH_3CN, *etc.* The infrared spectrum of **2** shows one peak at 2217 cm^{-1}, which is assigned to the $\nu_{(CN)}$ band of the TCNQ molecule of **2** (Fig. S1), indicating that the four cyano groups are in the same state.

Table 1
Crystallographic data for [LNi(TCNQ)]·MeOH (**2**·MeOH).

Empirical formula	$C_{33}H_{22}N_6O_3Ni$
Formula weight	609.27
λ (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Volume ($Å^3$)	1382.61(13)
a (Å)	11.2467(7)
b (Å)	11.6531(5)
c (Å)	11.7725(6)
α (°)	73.1900(10)
β (°)	69.628(2)
γ (°)	81.457(2)
Z	2
Dc(Mg m^{-3})	1.464
F(000)	628
θ range for data collection	6.252–50.052
Data/restraints/parameters	4873/0/390
Goodness-of-fit (GOF) on F^2	1.091
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0342$, $wR2 = 0.0718$
R indices (all data)	$R1 = 0.0728$, $wR2 = 0.0875$