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Short communication

Reactivity of tetracyanoethylene (TCNE): Synthesis and catalytic properties of a nickel complex supported by pentacyanopropenide derived from TCNE

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ABSTRACT

The reaction of 2,2-bipyridine (bpy), $NiCl_2 \cdot 6H_2O$ and tetracyanoethylene (TCNE) affords a nickel complex, $[Ni(bpy)_3] \cdot (PCPP)_2$ **1** (PCPP: pentacyanopropenide, a compound derived from TCNE). Its structure has been characterized by physics-chemical and spectroscopic methods. This complex can electrocatalyze hydrogen generation both from acetic acid, with a turnover frequency (TOF) of 152.88 mol of H_2 per mole of catalyst per hour an overpotential (OP) of 941.6 mV (in CH_3CN), and from aqueous buffer (pH 7.0) with a TOF of 1464 mol of H_2 per mole of catalyst per hour at an OP of 837.6 mV.

We focus our works on tetracyanoethylene (TCNE) chemistry, because of its versatile reactions in different directions [1–5]. Additionally, TCNE also has the ability to accept one or two electrons to form anions and to bond with metal ions or complexes. So far, several molecular magnetic materials have been provided by reactions of TCNE with paramagnetic metal ions [5–9]. Despite these advances, few materials based on nickel complexes supported by TCNE are known. To meet this need, we tried the reaction of $NiCl_2 \cdot 6H_2O$, 2,2-bipyridine (bpy) and tetracyanoethylene (TCNE) with a molar ratio set of 1:2:2. Surprisingly, an unexpected product, $[Ni(bpy)_3] \cdot (PCPP)_2$ was obtained. In this paper, we describe the synthesis, structure and properties of this complex, as well as its electrocatalytic hydrogen generation from both acetic acid and aqueous buffer.

Experimentally, $[Ni(bpy)_3] \cdot (PCPP)_2$ **1** was formed by the reaction of $NiCl_2 \cdot 6H_2O$, bpy and TCNE with a molar ratio set of 1:2:2 or 1:3:2 (Scheme 1) [10]. Based on the literature precedent [2,11,12], a possible mechanism for the formation of $PCPP^-$ was illustrated by Scheme **2**. The addition of nickel salt or bpy leads to the formation of $[TCNE]^{\cdot -}$, then provides an intermediate $[C_2(CN)_3]^{\cdot}$ by losing one CN^-. Further reaction with water gives bicyanomethanide $[C(CN)_2]^{\cdot -}$ by losing one $NC\text{-}CO^-$. Finally, $[C(CN)_2]^{\cdot -}$ reacts with $[C_2(CN)_3]^{\cdot}$ provides $PCPP^-$ anion. The result is consistent with that TCNE undergoes numerous reactions [13]. As shown in Fig. S1, the infrared spectrum of **1** showed one $\nu(C{\equiv}N)$ stretch at 2160 cm^{-1} at lower energy than that of the free tetracyanoethylene (2215 and 2258 cm^{-1}) (Fig. S2), assigning to the cyanide mode of **1**. To test the stability of complex **1**, electronic spectra were measured in both organic and aqueous media. The UV-Vis spectrum of **1** in acetonitrile shows an absorption peak at 295 nm (Fig. S3), which corresponds to a pi-pi* transition of the bpy moiety. From Fig. S4, in buffered aqueous solutions at the pH range 2.0–12.0, the intensity of the absorption band at 295 nm increases, suggesting new components are being formed. These observations point to the formation of dinuclear or polynuclear species [14].

As shown in Fig. 1, X-ray structure of complex **1** revealed a six-coordinated nickel atom in an octahedral surrounding. The Ni—N bond lengths fall in the range 2.0633(15) to 2.0925(15) Å. In order to check the purity of complex **1**, powder X-ray diffraction of the as-synthesized sample was measured at room temperature. According to Fig. S5, the peak positions of experimental patterns are in good agreement with the simulated ones, which clearly indicates good purity of the complex **1**. Interestingly, the introduction of methanol into mononuclear complex **1** led to the formation of a dimer. This was in agreement with result from ESI-MS measurement which exhibited one ion at a mass-to-charge ratio (*m*/*z*) of 277.1281, with the mass and isotope distribution pattern corresponding to that of $[(bipy)_6Ni_2(H_2O)_3]^{4+}$ (Fig. S6).

It has been shown that coordinatively unsaturated complexes can electro-catalyze hydrogen production via an unstable hydride intermediate [15,16]. To explore if this coordinatively saturated complex also can act as an electrocatalyst, the electrochemical

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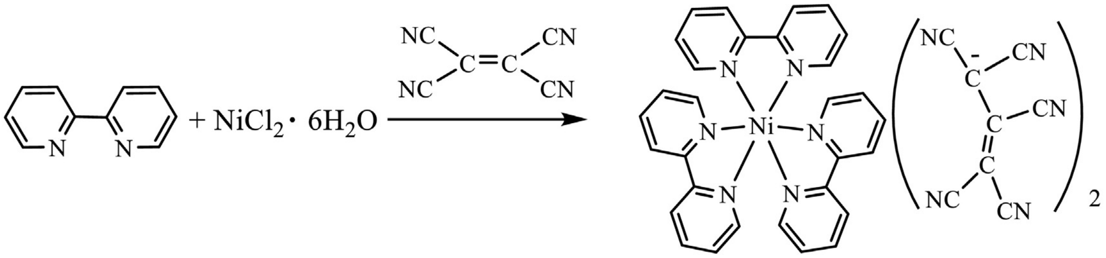


Scheme 1. Synthesis of complex **1**.

measurements for complex **1** were conducted in CH_3CN with 0.10 M $[(n\text{-}Bu)_4N]ClO_4$ as the supporting electrolyte. Fig. 2 represented the CV of 0.48 mM complex **1**, and two reversible redox couples were found in the potentials of −1.47 and 2.04 V versus Fc^+/Fc, which can be assigned to the couples of Ni^{II}/Ni^{I} and Ni^{I}/Ni^{0}, respectively. According to Fig. S7, the current responses of the redox events at −2.06 and −1.54 V versus Fc^+/Fc showed linear dependence on the square root of the scan rate, indicating this is a diffusion-controlled process.

To determine catalytic activity of this nickel complex, cyclic voltammograms of complex **1** were measured in the presence of acetic acid. From Fig. 3 it can be seen that the catalytic current near −2.06 and −1.54 V versus Fc^+/Fc increased markedly with the sequential increments of acetic acid concentration (from 0.00 to 1.36 mM). This rise in current can be attributed to the catalytic generation of H_2 from acetic acid [17]. The result indicates that H_2 production electrocatalyzed by complex **1** requires the reduction potentials of Ni(II) to Ni(I) and Ni(I) to Ni(0). Interestingly, with the acetic acid concentration increased from 0.0 to 1.36 mM (Fig. 3), the reduction potential near −1.54 V versus Fc^+/Fc remained almost constant and the wave near −2.06 V versus Fc^+/Fc moved to more anodic value from −2.06 V to −2.00 V versus Fc^+/Fc. On the basis of above analyses and literature precedents [5,15,16,18,19], we also tried to propose the catalytic cycle depicted in Scheme 3 for the generation of H_2 from acetic acid mediated by **1**. One-electron reduction of $[(bpy)_3Ni^{II}]^{2+}$ provides a putative $[(bpy)_2Ni^{I}]^{+}$ species by losing 1 bpy. Addition of hydrogen proton to $[(bpy)_2Ni^{I}]^{+}$ gives the Ni^{III}-H species. Then one-electron reduction of the Ni^{III}-H species affords H_2, and further regenerates the starting complex **1**. Although the relative contributions are indistinguishable in this analysis, we suspect that these processes are complementary H_2 evolution pathways.

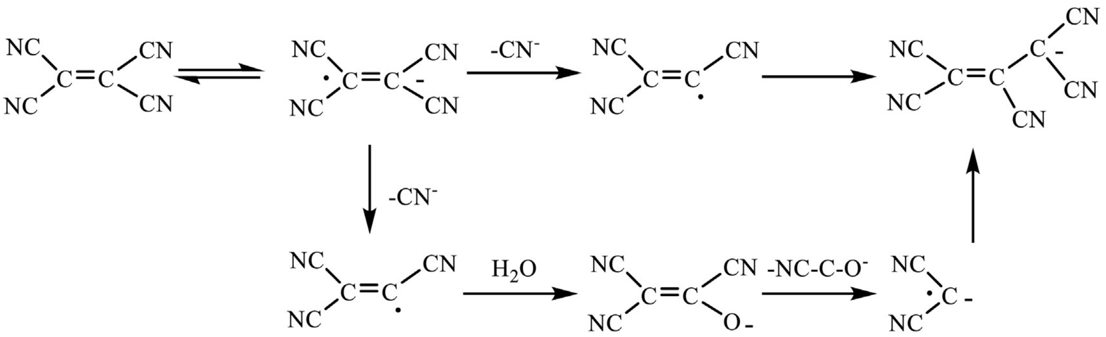
Several control experiments were carried out to verify that complex **1** is responsible for the catalysis. For example, acetic acid and $NiCl_2 \cdot 6H_2O$ were each measured under identical conditions. As can be seen in Figs. S8–S9, the catalytic competency achieved with **1** is not matched by either acetic acid or $NiCl_2 \cdot 6H_2O$ alone. Thus, a combination of the nickel center and bpy is essential for catalytic activity.

To further testify the catalytic activities of this complex, bulk electrolysis was conducted in CH_3CN with acetic acid at variable applied potential. Fig. 4a showed the total charges of bulk electrolysis from complex **1** in the presence of acetic acid, and the charge significantly increased when the applied potential was set to more negative. When an applied potential was −1.45 V versus $Ag/AgNO_3$, the maximum charge reached 123 mC used 2 min, with accompanying evolution of a gas, which was confirmed as H_2 by gas chromatography. According to Fig. S10, ~0.05 mL of H_2 was produced over an electrolysis period of 2 h under −1.45 V versus $Ag/AgNO_3$. And a controlled-potential electrolysis (CPE) experiment under the same potential without **1** gave a charge of only 5 mC (Fig. 4b), indicating that this coordinatively saturated complex does indeed serve as effective hydrogen producer under such conditions. From Eqs. (1) [20] and (2) [21], the TOF was estimated to be 152.88 mol of hydrogen per mole of catalyst per hour at an overpotential of 941.6 mV (Eq. S1 and Fig. S11), which is higher than a coordinatively unsaturated nickel complex supported by 2,3-bis(2-hydroxybenzylideneimino)-2,3-butenedinitrile ligand that shows a TOF of 126 mol of H_2 per mole of catalyst per hour at an overpotential of 941.6 mV [16].

$$\mathrm{TOF} = \Delta C/(F^{*} n_1 * n_2 * t) \tag{1}$$

$$\begin{aligned}\text{Overpotential} &= \text{Applied potential} - E^{e}_{HA}\\ &= \text{Applied potential} - \left(E^{e}_{H^+} - (2.303RT/F)pK_{aHA}\right)\end{aligned} \tag{2}$$

where, ΔC is the charge from the catalyst solution during CPE minus the charge from solution without catalyst during CPE; F is



Scheme 2. The procedure for the formation of $PCPP^-$ anion.