



Short communication

Synthesis and electrocatalytic properties of a nickel(II) complex supported by bis(diphenylphosphino)methane

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ABSTRACT

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ reacts with bis(diphenylphosphino)methane (dppm) and tetracyanoethylene (TCNE) to afford one unexpected dinuclear nickel complex $[\text{Ni}_2(\text{dppm})_2(\text{CN})_4]$ **1**, which have been characterized by electrochemical and spectroscopic methods. Two nickel atoms are doubly bridged by two dppm groups to form an eight membered $\text{Ni}_2\text{P}_4\text{C}_2$ ring. And **1** exists in the same form in solid as that in liquid. Magnetic studies exhibit that nickel ion is at one low spin state (no free electron), and no magnetic exchange interaction between two nickel ions mediated by dppm groups. In liquid, **1** can electrocatalyze hydrogen generation from acetic acid with a turnover frequency (TOF) of 24 mol of hydrogen per mole of catalyst per hour at an overpotential (OP) of 941.6 mV (in DMF).

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Hydrogen is one 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 water splitting is an important and simple method for hydrogen production, which can be used as a cheap, green fuel [2]. The generation of hydrogen from electrochemical reduction of a proton source, such as weak acid and water, represents an attractive approach for storing the electrical energy transiently produced by renewable energy sources [3]. In Nature, hydrogenase enzymes are very efficient catalysts for reductive generation of dihydrogen [4]. However, enzymes are difficult to adapt for commercial applications and their stability is often limited outside of their native environment [5]. A challenging method for overcoming this problem would be to develop efficient, and stable catalysts that employ abundant, and as a consequence cheap, metals such as iron, cobalt, nickel, and copper. Therefore, many research groups, including ours, have designed molecular catalysts by employing the abundant metals, and several complexes of nickel [6,7], cobalt [8–12] and copper [13–16] have been developed as electrocatalysts for the reduction of proton or water to form H_2 . As a continue work on the design of molecular catalysts, reported here is an electrocatalyst based on a dinuclear nickel complex, $[\text{Ni}_2(\text{dppm})_2(\text{CN})_4]$ **1** for hydrogen evolution from acetic acid.

Typically, the reaction of TCNE with transition metal centers led to di-, tri- or tetranuclear nitrile-bonded σ compounds, to π compounds with side-on coordination. However, the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, dppm and TCNE provides one unprecedented complex $[\text{Ni}_2(\text{dppm})_2(\text{CN})_4]$ **1**

[17], which cannot be obtained by the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, dppm, and KCN. The infrared spectrum of **1** shows two $\nu(\text{CN})$ stretching at 2124 and 2095 cm^{-1} at higher energies than that of the free CN^- ion (2080 cm^{-1}), assigning to the cyanide mode in complex **1** (Fig. S1). Magnetic measurement shows that nickel ion is at one low spin state ($S = 0$), and no magnetic exchange interaction between two nickel ions mediated by dppm groups.

Complex **1**. 2MeOH crystallizes in a monoclinic system, space group $P2(1)/n$ with two formula units present per unit cell. As shown in Fig. 1, each nickel atom exhibits square-planar geometry with two *trans*-cyano groups and two *trans*-P atoms from bridging dppm molecules. And the two $\text{NiP}_2(\text{CN})_2$ units in the dimer are in normal face-to-face orientation, with the $\text{Ni} \cdots \text{Ni}$ separation of 3.258 Å. However, it is longer than the $\text{Ni} \cdots \text{Ni}$ distances of 2.957 (1) Å in $[\text{Ni}_2(\text{dcpm})_2(\text{CN})_4]$ (dcpm: bis(dicyclohexylphosphino)methane) [18], 3.209 (8) Å in $[\text{Ni}_2(\text{dmpm})_2(\text{CN})_4]$ (dmpm: bis(dimethylphosphino)methane) [18], and 2.542 (2) Å in $[\text{HgNi}_4(\text{dppm})_2]$ [19]. The P–Ni–P angle is 175.93 (6)° and the C–Ni–C angle is 161.5 (2)°. The Ni–C distances are 1.954 (5) and 1.854 (6) Å, respectively. And the Ni–P distances are 2.2087 (13) and 2.2174 (13) Å, respectively.

The stability of the title complex in liquid has been examined using multiple physicochemical methods. First, in methanol or *N,N*-dimethylformamide (DMF), $[\text{Ni}_2(\text{dppm})_2(\text{CN})_4]$ **1** exhibits the same state as that in solid, which are in agreement with results from ESI-MS measurements which exhibit one ion at a mass-to-charge ratio (m/z) of 1011.1116 in both methanol and DMF (Figs. S2–S3), with the mass and isotope distribution pattern corresponding to that of $[\text{Ni}_2(\text{dppm})_2(\text{CN})_4\text{Na}]^+$. Second, the UV/Vis spectrum of **1** in DMF shows an absorption peak at 506 nm (Fig. S4), which corresponds to a ligand-metal-charge-transition (LMCT) between the ligands and nickel ion. From Fig. S4, the

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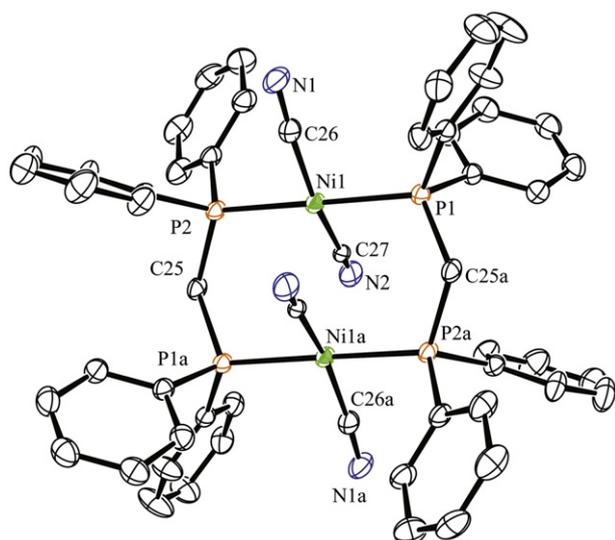


Fig. 1. Molecular structure of complex **1**.

intensity of the absorption band at 506 nm slightly increases with increasing the temperature from 298 to 353 K, but the peak position does not move, indicating this complex is stable under these conditions. Third, the following electrochemical studies.

To study the electrochemical behavior complex **1**, cyclic voltammogram (CV) was measured in DMF with 0.10 M $[(n\text{-Bu})_4\text{N}]\text{ClO}_4$ as the supporting electrolyte. From Fig. 2, **1** shows a quasi-reversible redox couple at -0.95 V versus Ag/AgNO₃, which can be assigned to that of Ni^{II}/Ni^I. To investigate the effect of the temperatures of media on the electrochemical behaviors of complex **1**, CVs were measured in the range 303 to 348 K. According to Fig. S5, the current strength slightly increase near -0.96 V with varying temperature from 303 to 348 K, suggesting that complex **1** is stable in above system. From Fig. S6, the current response of the redox event at -0.96 V shows linear dependence on the square root of the scan rate, indicating a diffusion-controlled process, with the electrochemically active species freely diffusing in solution [20]. According to Fig. S7, the impedance is small due to homogeneous catalytic system. This is consistent with the above electrochemical behavior.

From Fig. 3 it can be seen that the catalytic currents near -0.96 V increase with increasing acetic acid concentration from 0.0 to 19.61 mM, showing that hydrogen generation electrocatalyzed by **1** requires the

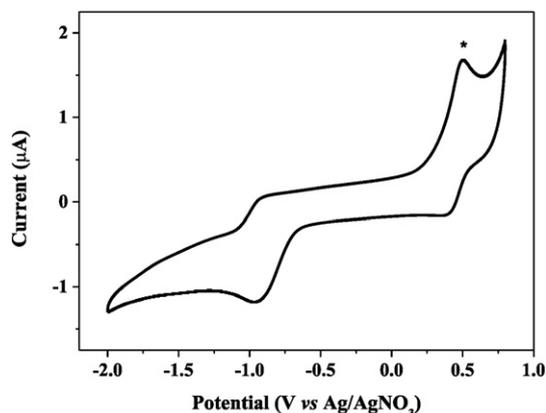


Fig. 2. CV of 1.00 mM complex **1** in DMF. Conditions: room temperature, 0.10 M $[(n\text{-Bu})_4\text{N}]\text{ClO}_4$ as supporting electrolyte, scan rate: 100 mV/s, glassy carbon working electrode (1 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode, Ferrocene internal standard (*).

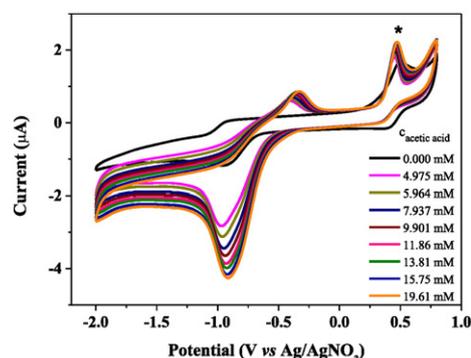


Fig. 3. CVs of a 1.00 mM solution of complex **1**, with varying concentration of acetic acid in DMF. Conditions: 0.10 M $[(n\text{-Bu})_4\text{N}]\text{ClO}_4$ as supporting electrolyte, scan rate: 100 mV/s, glassy carbon working electrode (1 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode, Fc internal standard (*).

reduction of Ni(II) to Ni(I) and protonation [21]. Interestingly, with the acetic acid concentration increase from 0.0 to 19.61 mM, the potential of Ni^{II}/Ni^I moves positive about 40 mV from -0.96 V to -0.92 V, and the onset of the catalytic wave also moves positive about 330 mV from -0.65 to -0.32 V compared to that in the absence of **1**. Based on the above observations and literature precedent [22,23], we postulate the catalytic cycle depicted in Scheme 1 for the generation of hydrogen from acid mediated by **1**. Two-electron reduction of $[\text{Ni}^{\text{II}}(\text{dppm})_2(\text{CN})_4]$ provides one species, $[\text{Ni}^{\text{I}}_2(\text{dppm})_2(\text{CN})_4]^{2-}$. Addition of proton (acetic acid) affords the intermediate species, $[(\text{Ni}^{\text{III}}\text{-H})_2(\text{dppm})_2(\text{CN})_4]$. Further two-electron reduction gives one reactive $[(\text{Ni}^{\text{II}}\text{-H})_2(\text{dppm})_2(\text{CN})_4]^{2-}$, then generates H₂ and gives rise to a cycle. More detailed mechanistic studies are under investigation.

To testify the catalytic activities of this nickel complex, bulk electrolysis by complex **1** was conducted in DMF solution with acetic acid at variable applied potential using a glassy carbon plate electrode in a double-compartment cell. According to Fig. 4a, when the applied potential was -1.45 V versus Ag/AgNO₃, the maximum charge reaches 24 mC during 2 min of electrolysis, with accompanying evolution of a gas, which was confirmed as H₂ by gas chromatography. According to Fig. S8, ~ 0.03 mL of H₂ was produced over an electrolysis period of 2 h under -1.45 V versus Ag/AgNO₃. And a controlled-potential electrolysis (CPE) experiment under the same potential without **1** gives a charge of only 8 mC (Fig. 4b), showing that this nickel complex does indeed serve as effective hydrogen producer under such conditions. Assuming every catalyst molecule was distributed only on the electrode surface and every electron was used for the reduction of protons, from Eqs. (1) [12] and (2) [24], we calculated the TOF for the catalysts as reaching a maximum of 24 mol of hydrogen per mole of catalyst per hour at an overpotential of 941.6 mV (Fig. S9).

$$\text{TOF} = \Delta C / (F * n_1 * n_2 * t) \quad (1)$$

$$\begin{aligned} \text{Overpotential} &= \text{Applied potential} - E_{\text{HA}}^{\ominus} \\ &= \text{Applied potential} - \left(E_{\text{H}^+}^{\ominus} - (2.303RT/F) \text{p}K_{\text{aHA}} \right) \end{aligned} \quad (2)$$

where, ΔC is the charge from the catalyst solution during CPE minus the charge from solution without catalyst during CPE; F is Faraday's constant, n_1 is the number of moles of electrons required to generate one mole of H₂, n_2 is the number of moles of catalyst in solution, and t is the duration of electrolysis.

In this paper, we have described one nickel(II) complex, that is obtained from the reaction of the simple nickel salt, dppm and TCNE, which has been characterized by electrochemical and spectroscopic methods. This sample of complex **1** can electrocatalyze hydrogen generation from acetic acid. Our ongoing efforts are focused on modifying the

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