



Short communication

Synthesis and electrocatalytic function for hydrogen generation of cobalt and nickel complexes supported by phenylenediamine ligand



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ABSTRACT

To study the effect of different metal centers on catalytic function, two complexes [L-M] (M = Co, **1**; Ni, **2**) were prepared by the reactions of *N,N'*-bis(2-amino-3,5-di-*tert*-butylphenyl)-*o*-phenylenediamine, H₂L, with Co(ClO₄)₂·6H₂O or Ni(ClO₄)₂·6H₂O, respectively. Electrochemical investigations show **1** and **2** can electrocatalyze hydrogen generation both from acetic acid and aqueous buffer. Complexes **1** and **2** afford a turnover frequency (TOF) of 738.23 and 1331.23 mol of hydrogen per mole of catalyst per hour (mol h⁻¹) at an overpotential (OP) of 0.838 V from a neutral buffer, respectively, indicating that the nickel center constitutes the better active catalyst.

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In order to avoid energy crisis, people are developing new systems to get new energy. And hydrogen is of particular interest as a secondary energy carrier, its generation from water is a current topic of intensive research [1,2]. In particular, electro-catalytic method for hydrogen generation from organic acid or water have been explored as cost-effective ways of producing a carbon-neutral fuel. However, one of the key challenges for hydrogen generation by proton or water reduction is the development of efficient catalysts with low overpotential, good stability, and high turnover rate [3,4]. Therefore, a great deal of research efforts have been devoted to the development of effective catalysts based on transition metal complexes, such as manganese [5], nickel [6–9], cobalt [10–12] and copper [13–15] for the reduction of proton or water to form H₂. There are several reports about that the donor type and electronic properties of the ligands play vital roles in determining the structure and reactivity of the corresponding metal complexes [16–18], and few studies on catalytic properties by different metal complexes with the same ligand show us. To meet this goal, we have been studying tetradentate ligands, such as N₂O₂ Schiff-base ligand, H₂L, and its corresponding metal complexes for catalytic application. In this paper, we report two complexes [L-M] (M = Co, **1**; Ni, **2**) that exhibit remarkable activity in hydrogen generation by electro-catalytic reduction of proton or water.

As shown in Scheme 1, in the presence of trimethylamine, the reactions of H₂L (Fig. S1) with Co(ClO₄)₂·6H₂O or Ni(ClO₄)₂·6H₂O afford complexes **1** and **2**, respectively (see Supplementary materials).

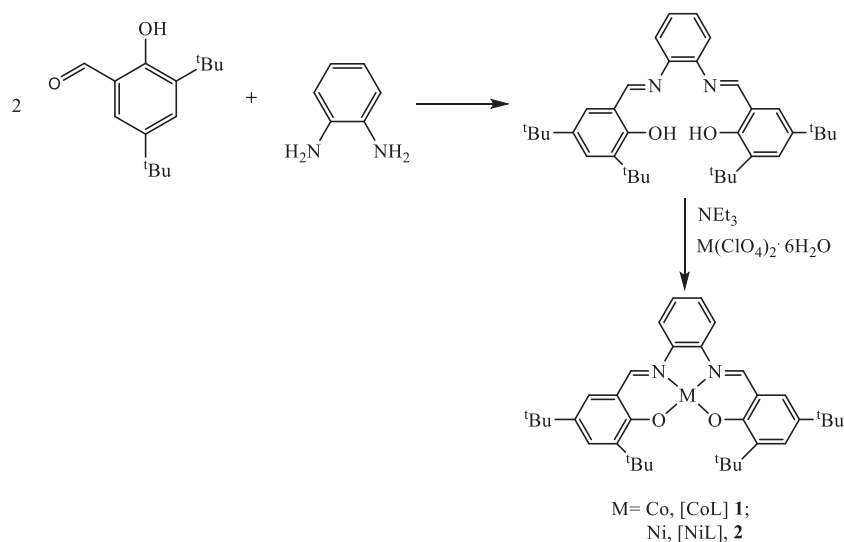
Both complexes **1** and **2** crystallize in space group P-1. As shown in Fig. 1, both cobalt and nickel atoms are four coordinated by two nitrogen

atoms and two oxygen atoms from the ligand ion, L²⁻. Coordination geometries of cobalt and nickel atoms are almost planar with an angle sum of 360.58° and 360.7°, respectively. The M—O bond lengths vary over a small range of 1.841(6)–1.848(2) Å, and the M—N distances are in the range of 1.841(7) to 1.851(2) Å (M = Co and Ni). Note, in methanol, complex **1** exits the same state as that in solid. This is in agreement with results from ESI-MS measurement which exhibits one ion at a mass-to-charge ratio (*m/z*) of 597.2893, with the mass and isotope distribution pattern corresponding to that of [Co(L)] (calculated *m/z* of 597.68) (Fig. S2). Similarly, complex **2** also exits the same state in methanol as that in solid. Fig. S3 exhibits one ion at a mass-to-charge ratio (*m/z*) of 619.2805, with the mass and isotope distribution pattern corresponding to that of [Ni(L)-Na] (calculated *m/z* of 620.443).

Fig. 2a exhibits CV of 4.0 × 10⁻⁴ mol L⁻¹ complex **1** in CH₃CN where two reversible Co^{III}/Co^{II} and Co^{II}/Co^I redox couples can be identified at E_{1/2} = +0.06 and -1.27 V (vs Ag/AgNO₃), respectively. Under same conditions, complex **2** shows one reversible redox couple at -1.55 V, which can be assigned to the couple of Ni^{II}/Ni^I (Fig. 2b). The peak currents at -1.31 V (Co^{II}/Co^I) and -1.59 V (Ni^{II}/Ni^I) show linear dependence on the square root of scan rate (Figs. S4–S5), which are indicative of a diffusion-controlled process. As shown in Fig. 3a, with the addition of varied amounts of acetic acid (from 0.0 to 1.19 × 10⁻³ mol L⁻¹), apparent voltammetric currents emerge at -1.31 V and increase with increasing proton concentrations. This indicates that hydrogen evolution electrocatalyzed by **1** requires the reduction of Co(II) to Co(I) and protonation. Interestingly, with the acetic acid concentration increased from 0.0 to 1.19 × 10⁻³ mol L⁻¹, the onset of the catalytic wave remains almost constant at ca. -1.10 V versus Ag/AgNO₃. Similar to complex **1**, with the addition of varied amounts of acetic acid (from 0.0 to 1.19 × 10⁻³ mol L⁻¹), apparent voltammetric

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Scheme 1. Schematic representation of the synthesis of [CoL] **1** and [NiL] **2**.

currents emerge at -1.59 V and also increase with increasing proton concentration (Fig. 3b). This indicates that hydrogen generation electrocatalyzed by **2** requires the reduction of Ni(II) to Ni(I) and protonation.

On the basis of the above observations, analyses and literature precedents [19–21], a possible catalytic cycle for the generation of hydrogen from acetic acid mediated by **1** or **2** is depicted in Scheme 2. One-

electron reduction of $[LM^{II}]$ **1** or **2** produces a putative $[LM^I]^-$ species. Then addition of the proton yields the $M^{III}-H$ species. Another one-electron reduction of the $M^{III}-H$ species affords H_2 , and regenerates the starting **1** or **2**. Similar catalytic mechanism were designed in the reported samples [22,23]. More detailed mechanistic studies are under investigation.

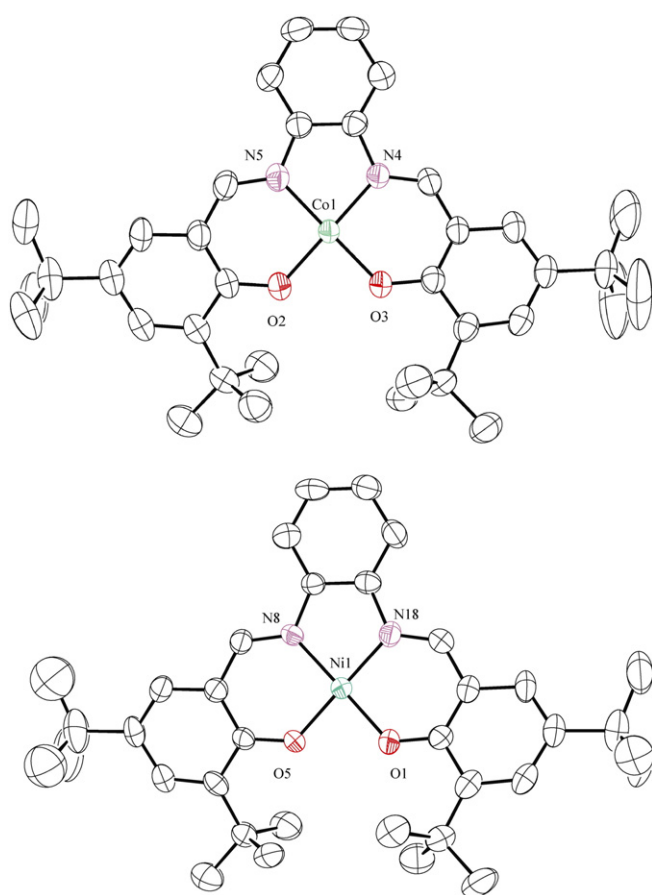


Fig. 1. ORTEP drawing of complexes **1** (top) and **2** (down) with thermal ellipsoids on the 50% probability level (hydrogen atoms are not shown).

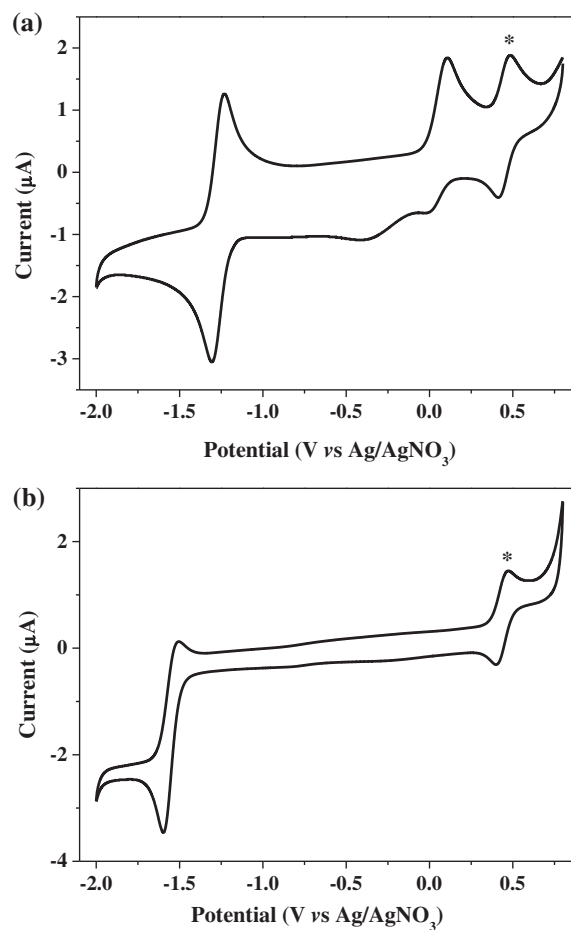


Fig. 2. CVs of 4.0×10^{-4} mol L^{-1} complex **1** (a) and complex **2** (b) in 0.10 mol L^{-1} in CH_3CN with $[n-Bu_4N]ClO_4$ at a glassy carbon electrode and a scan rate of 0.10 V s^{-1} . Fc internal standard (*).

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