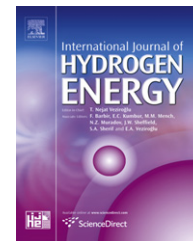


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# Synthesis, characterization and electrocatalysis of mono- and di-nickel tetraaminodiphenolate macrocyclic complexes as active site models of [NiFe]-hydrogenases

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## ABSTRACT

A series of mononuclear Ni<sup>II</sup> and binuclear Ni<sup>II</sup>Ni<sup>II</sup> macrocyclic complexes were investigated as functional models of the active site of [Ni–Fe]-hydrogenase. The electrocatalytic properties of the compounds were assessed and their efficiency was correlated with the availability of donor atoms in the structure of the macrocycle to accept the proton. The catalysts exhibited a regular activity for proton reduction. Redox levels and plausible electrochemical mechanisms for H<sub>2</sub> production are presented as well.

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## 1. Introduction

Nickel hydrogenases have been intensively investigated due to the hydrogen economy, in which the molecular hydrogen is a green alternative to the fossils and nuclear fuels. The chemical production of hydrogen through the direct reduction of water is still a challenge, as it is a complicated and slow multielectronic process. The structural characterization of [NiFe] hydrogenase was an important step toward the understanding of the mechanism of the active site and promoted the using of less expensive and accessible synthetic metal ion complexes in replacement of platinum electrodes [1–6].

Tetraazamacrocyclic nickel complexes are among the first compounds to exhibit catalytic activity to hydrogen evolution from the reduction of water [7–9]. These catalysts are of particular interest due to their lower market price compared

to platinum. Complexes containing N,S-donor ligands can catalyze H<sup>+</sup>/D<sup>+</sup> exchanges just like the nickel-hydrogenases [10]. The third type of ligand that has been recently studied is phosphine. Using a P<sub>2</sub>S<sub>2</sub>N-ligand, Holm and co-workers reported the stoichiometric reduction of hydrogen chloride to H<sub>2</sub>(g) in the presence of a pentacoordinated nickel(I) complex [11] and DuBois explored nickel(II) complexes containing cyclic phosphine ligands with pendant nitrogen base as functional models for hydrogenases [12,13].

Regardless of the nature of the metal or the operative mechanism, the formation of a metal–hydride bond is a key step to hydrogen generation. These metal–hydride complexes are important intermediates and act as hydride donors, a property known as hydricity [13–17]. It should be emphasized that both hydricity and acidity can be controlled separately. Indeed, theoretical studies have indicated that the best performances toward hydrogen evolution can be achieved by

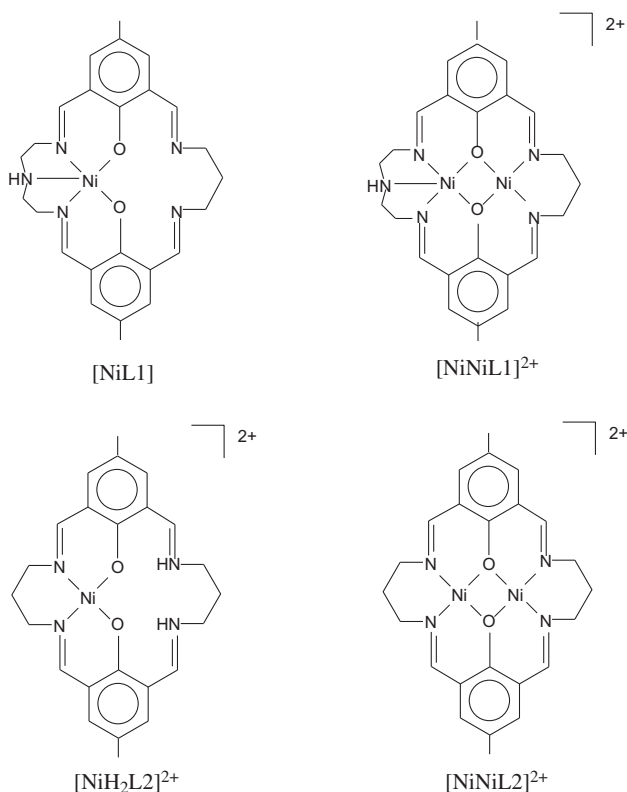
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combining the moderate interactions between hydride ( $\text{H}^-$ ) and metal ion (acting as hydride acceptor) as well as between the proton ( $\text{H}^+$ ) and the bases (donor atoms with high electronic density) [18]. A typical mechanism of proton reduction involves the following steps: a) reduction of the metal center concomitant with proton transfer from the acid to the pendant base; b) protonation of the metal ion in low oxidation state generating of a metal–hydride complex; c) release of molecular hydrogen parallel with a second electron transfer and recovery of the catalyst. In the absence of the pendant base, the second protonation is simultaneous with the dihydrogen evolution [3,19].

In search for mimetic systems of enzymes, exploring the chelate effect of macrocyclic ligands has proven to be a successful approach. Macrocyclic complexes designed from tetraiminediphenolate ligands have been investigated in our group [20–22] due to the several advantages such as: a) relatively simple preparation from straightforward or template Schiff-base reactions; b) can accommodate one or two metal ions in close proximity, leading to metallic (homo- and hetero-) complexes; c) careful choice of reagents allow preparation of symmetric or non-symmetric environments around the metal ions; d) chelate effect guide to thermodynamic and kinetic stability, thus reducing ligand dissociation reactions.

Continuing our interest in the properties of macrocyclic complexes, herein we report on the preparation and electrocatalytic proton reduction to molecular hydrogen by tetraiminediphenolate mononuclear and binuclear nickel(II) complexes represented in Scheme 1.



**Scheme 1** – Representations of  $[\text{NiL1}]$ ,  $[\text{NiNiL1}]^{2+}$ ,  $[\text{NiH}_2\text{L2}]^{2+}$  and  $[\text{NiNiL2}]^{2+}$ .

## 2. Experimental

### 2.1. Materials

The chemicals used in this work were purchased from Sigma–Aldrich. The stated purity of the chemicals was between 98 and 99%.

#### 2.1.1. $[\text{NiL}^1(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$

Diethylenetriamine (0.31 mL, 3.0 mmol) and 0.74 (3.0 mmol) of  $[\text{Ni}(\text{CH}_3\text{CO}_2) \cdot 4\text{H}_2\text{O}]$  were added under stirring to a suspension of 4-methyl-2,6-diformylphenol (0.985 g, 6.0 mmol) in 20 mL of DMF at 40 °C. The system was kept under heating and stirring for 1 h. After concentration and addition of isopropyl alcohol an orange powder was produced. It was recovered by filtration, washed with methanol and dried under vacuum. Yield was 47%. Elemental analysis for  $\text{C}_{22}\text{H}_{29}\text{N}_3\text{O}_7\text{Ni}$ , 505.89 g mol<sup>-1</sup>. Calcd.: C, 52.18; H, 5.78; N, 8.30%. Found: C, 52.36; H, 5.45; N, 8.36%. FTIR in KBr (cm<sup>-1</sup>): 1670  $\nu(\text{C}=\text{O})$ ; 1626  $\nu(\text{C}=\text{N})$ ; 1542  $\nu(\text{C}-\text{C aromatic ring})$ .

#### 2.1.2. $[\text{NiL1}(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$

This complex was prepared by the slow addition of a 10 mL methanolic solution of 1,3-diaminopropane (0.05 mL, 0.63 mol) to 0.306 g (0.63 mol) of  $[\text{NiL}^1]$  under stirring at 40 °C. After stirring overnight, an orange solid was recovered, washed with cold diethyl ether and dried under vacuum. The yield was 46%. Elemental analysis for  $\text{C}_{25}\text{H}_{37}\text{N}_5\text{O}_6\text{Ni}$ , 561.97 g mol<sup>-1</sup> Calcd.: C, 53.38; H, 6.64; N, 12.46%. Found: C, 52.99; H, 6.39; N, 12.06%. FTIR in KBr (cm<sup>-1</sup>): 3280m  $\nu(\text{N}-\text{H})$ ; 1652s  $\nu(\text{C}=\text{N})$ ; 1540s  $\nu(\text{C}-\text{C aromatic ring})$ .

#### 2.1.3. $[\text{NiHL1}(\text{H}_2\text{O})]\text{PF}_6 \cdot \text{H}_2\text{O}$

This complex was prepared as described in Section 2.1.2. The orange product isolated upon addition of  $\text{NH}_4\text{PF}_6$  (0.10 g 0.63 mmol), was washed with ether and vacuum dried. Yield was 72%. Elemental analysis for  $\text{C}_{25}\text{H}_{34}\text{N}_5\text{O}_4\text{NiPF}_6$  671.92 g mol<sup>-1</sup> Calcd.: C, 44.65; H, 5.10; N, 10.42%. Found: C, 44.69; H, 5.08; N, 10.53%. FTIR in KBr (cm<sup>-1</sup>): 3280m  $\nu(\text{N}-\text{H})$ ; 1652s  $\nu(\text{C}=\text{N})$ ; 1540m  $\nu(\text{C}-\text{C aromatic ring})$ ; 850vs and 559vs  $\nu(\text{PF}_6)$ .

#### 2.1.4. $[\text{NiNiL1}(\text{NEt}_3)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$

Triethylamine (0.03 mL, 0.20 mol) and 0.073 g (0.20 mol of nickel perchlorate were mixed with 0.13 g (0.20 mol) of  $[\text{NiHL1}]$   $\text{PF}_6$  in 12 mL of methanol. The solution was stirred overnight at room temperature, after which an orange powder was isolated by filtration, washed with cold ether and dried under vacuum. The yield was 65%. Elemental analysis for  $\text{C}_{31}\text{H}_{48}\text{N}_6\text{O}_{12}\text{Ni}_2\text{Cl}_2$  884.62 g mol<sup>-1</sup>. Calcd.: C, 42.05; H, 5.47; N, 9.50%. Found: C, 41.35; H, 5.26; N, 9.63%. FTIR in KBr (cm<sup>-1</sup>): 3240 m  $\nu(\text{N}-\text{H})$ ; 1652s  $\nu(\text{C}=\text{N})$ ; 1540s  $\nu(\text{C}-\text{C aromatic ring})$ ; 1100vs  $\nu(\text{ClO}_4)$ .

#### 2.1.5. $[\text{NiMgL1}(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2$

Magnesium perchlorate (0.35 g, 1.50 mol) and 1,3-diaminopropane (0.13 mL, 1.50 mol) were slowly added to 0.76 g (1.5 mol) of  $[\text{NiL}^1]$  dissolved in 30 mL of MeOH. The system was kept under stirring at 40 °C for 2 h. After stirring overnight, at room temperature, an orange solid was isolated,

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