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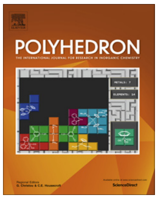

Iron complexes of BIANs: Redox trends and electrocatalysis of hydrogen evolution

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ABSTRACT

We report new iron(II, III) complexes in the framework of redox non-innocent BIAN ligands acting as highly active electrocatalysts for proton reduction. The iron complexes have been investigated by cyclic voltammetry, electron paramagnetic resonance and UV–Vis spectroscopy. The formation of Fe(III) complexes owing to electron transfer from metal to ligand has been discovered in acetonitrile and dichloromethane solutions. The hydrogen evolution catalysis is fast and efficient with a turnover frequency up to 460 s^{-1} and a very low overpotential of only 0.17–0.19 mV in MeCN. The catalysis is first order with respect to [catalyst] and second order with respect to [acid]. Steric hindrance of dpp-BIAN decreases the catalytic activity of the complexes. The best catalyst is the *p*-MeO-substituted BIAN iron complex.

1. Introduction

The progress in the study of hydrogenases has injected new vitality into the investigation of homogeneous catalyst systems for H_2 production. The development of iron-based catalysts is of particular interest because of the abundance of this metal and its lack of toxicity to the environment [1,2]. Catalysts based on earth-abundant metals are of particular interest because most low-temperature fuel cells for oxidation of hydrogen are based on platinum. The study of model complexes has resulted in remarkable advances in our understanding of how the [FeFe]-hydrogenase functions [3–7] and iron catalysts are now known for both hydrogen production [4,8–13] and oxidation [4,14–16].

Although about one hundred [FeFe]–H_2ase mimics have been reported for electrochemical H_2 generation, large overpotentials, low efficiency, poor stability of the iron-based catalyst system and the necessity of organic solvents are still serious limits for the application of [FeFe]–H_2ase mimics in large-scale H_2 production [17–20].

There are iron complexes with a good catalytic activity for evolution/oxidation of hydrogen. Thus, catalysis occurs at 1.18 V versus Fc^+/Fc, resulting in overpotential of 300 mV and with a turnover frequency TOF of 550 s^{-1} for the iron complex containing a nitro-functionalized polypyridyl ligand [21]. The iron complex containing a tetradentate polypyridyl monophenolate ligand has been found effective for hydrogen evolution at −1.17 V vs SCE in MeCN with TOFs up to 1000 s^{-1} and an overpotential of 660 mV (800 mV in the presence of water) [22]. There are a lot of iron complexes with η^5-C_5H_5, bridging or terminal CO groups, redox active ligands as promising catalysts for hydrogen evolution [23–25]. The role of redox active ligands in enhancing the stability of various redox states, decreasing the working potential for catalysis, and facilitating different catalytic pathways is evident when the redox-active ligand participates in the electronic structure of the whole complex. Bis(imino)acenaphthenes (BIANs) are high-demand redox active ligands [26-31] and the synthesized acenaphthene-1,2-diimine complexes of iron exhibit high catalytic activity in the olefin polymerization and ethylene oligomerization; their synthesis, structure, and magnetic properties were described earlier [32,33]. The naphthalene backbone of this ligand facilitates rich redox chemistry [34–38]. Moreover, BIAN is capable of undergoing four successive one-electron reductions [34].

We assumed that the ability of BIAN metal complexes to form protonated forms with different acids (HCl, HBF_4, H_2O, benzoic acid) can be used for creating new catalytic systems for generation of hydrogen [39–41].

Some examples of BIAN complexes as catalysts for hydrogen evolution are known. Recently, analogous BIAN-cobaloxime has been prepared and used as electrocatalyst for hydrogen evolution. But high overpotentials (1.1–1.5 V) are their main disadvantages [42]. We assumed that the replacement of the cobalt center with

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iron could significantly affect the overpotential. Surprisingly, so far there are no full electrochemical and EPR investigations of BIANs and their metal complexes.

This article deals with a class of iron-BIAN-derived complexes as new hydrogen evolution catalysts; the detailed experimental analysis of the redox and catalytic properties using cyclic voltammetry and EPR spectroscopy suggests the involvement of the active Fe(III) species in the catalytic cycle.

2. Results and discussion

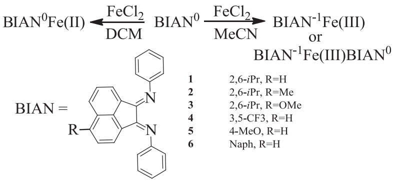
2.1. Cyclic voltammetry and ESR spectroscopy of BIANs

The electrochemical properties of bisiminoacenaphtenes were not studied earlier in detail. There are a few papers on electrochemical investigations [42,43]. However, the ability of BIANs to stepwise four electron chemical reduction by alkali metals from neutral BIAN to tetraanion radical is well-known [34].

Earlier several attempts' to study of redox properties of BIAN-derivatives was made [42,43]. But differences in reference electrode nature were not allowing correctly compares potential values. In our work the redox properties of BIANs (**1**–**6**, Scheme 1) were studied by cyclic voltammetry in acetonitrile solution and potentials was referenced vs. Fc^+/Fc couple. Thus, the neutral BIAN stepwise reduces to trianion in MeCN. Three one-electron reversible peaks at −1.35 to −1.94; −1.90 to −2.43 and −2.40 to −3.10 V (vs. Fc^+/Fc) correspond to BIANs 0/•-/2-/3•- (See SI) in acetonitrile solutions. The linear dependence of current vs. square root scan rate demonstrates diffusion-controlled electron transfer. Unfortunately, the reduction of trianion-radical form of BIAN to tetraanion state was not observable on CVs at room temperature in acetonitrile.

The electrochemical data for BIANs **1**–**6** was demonstrated in Table 1. The analysis of reduction potential leads to conclude some regularities. Thus, the introduction of donor or acceptor groups in phenyl substituents influences the redox properties. The introduction strong acceptor trifluoromethyl group in 3 and 5 position of phenyl (**4**) shifts reduction potential on 0.48 V. But the methoxy group in 4 position (**5**) has a small impact on potentials in comparison with *i*-Pr groups in 2 and 6 positions (**1**–**3**). The changing phenyl groups at nitrogen into naphthyl (**6**) leads to anodic potential shifting (0.16 V). The introduction of Me (**2**) or OMe (**3**) groups in naphthalene backbone did not significantly affect on redox potentials. The CVs for BIANs **1**–**6** are close in acetonitrile and dichloromethane.

Paramagnetic anion radical forming after electrochemical reduction has been detected and studied by EPR-spectroelectrochemistry (Fig. 1). Controlled-potential electrolysis of BIAN solution in spectroelectrochemical cell [44] at the first reduction potential leads to signal of paramagnetic anion radical with five lines (splitting from nitrogens) and *g*-factor = 2.0013 close to those obtained earlier after reduction by alkali metals [34]. The signal of electrochemically generated paramagnetic anion radical detected for the first time.



Scheme 1. Proposed scheme for the formation Fe(II) and Fe(III) complexes.

Table 1
Electrochemical data for investigated BIANs in MeCN. $\Delta E = E_{pa} - E_{pc}$, mV. (Potentials vs. Fc^+/Fc, scan rate – 0.1 V/s, supporting electrolyte – Bu_4NBF_4).

BIANs	E_p^1red, V (ΔE, mV)	E_p^2red, V (ΔE, mV)	E_p^3red, V (ΔE, mV)
1*	−2.03 (100)	−2.58 (100)	−3.02 (160)
2	−1.93 (90)	−2.46 (80)	−2.92 (150)
3	−1.93 (100)	−2.52 (90)	−3.00 (150)
4	−1.35 (105)	−1.90 (81)	−2.40 (110)
5	−1.82 (90)	−2.40 (100)	−2.77 (170)
6	−1.66 (100)	−2.48 (90)	−3.10 (140)

* CVs was recorded in THF.

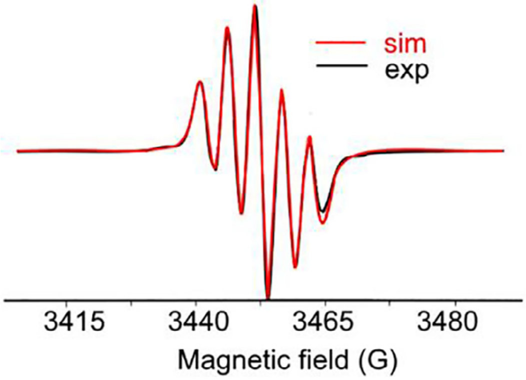


Fig. 1. Typical EPR spectra for anion radical of **1** in THF solution at room temperature.

2.2. CV and EPR investigation of iron complexes of BIANs

1–**6**-$FeCl_2$ iron complexes have been obtained by the previously reported method in DCM (Scheme 1) [45–47]. The molecular peak $[BIAN\text{-}FeCl]^+$ corresponding for complexes with ligand:metal ratio 1:1 was observed on MALDI-TOF mass spectra in case of ligands 1–4. Single crystal of **1**-$FeCl_2$ suitable for X-ray diffraction analysis was obtained from dichloromethane (Fig. 2) and MeCN solutions (similar crystal data to previously described [45]) at −32 °C. The complexes with composition 2:1 were formed in case of other ligands.

The redox properties of **1**–**6**-$FeCl_2$ complexes have been studied using cyclic voltammetry method in MeCN and DCM. Typical CVs for **1**–**6**-$FeCl_2$ are shown in Fig. 3. Two quasi-reversible reduction peaks at the potentials of −0.35 ÷ −0.40 V and −0.82 ÷ −1.00 V

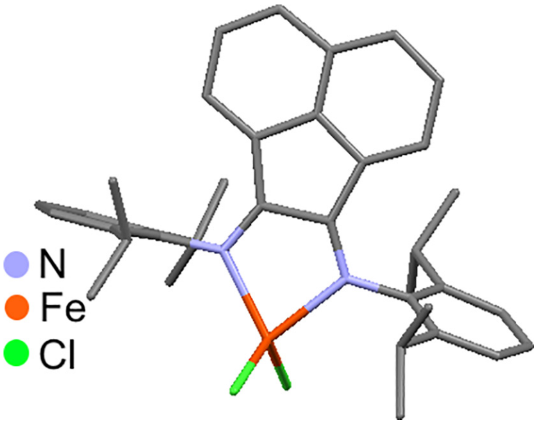


Fig. 2. ORTEP projection of complex **1**-$FeCl_2$ showing anisotropic displacement ellipsoids at the 50% probability level. Hydrogen atoms, minor disordered fragments, and solvent molecules are omitted for clarity.