FACULTY RESEARCH GRANT 2010

FINAL REPORT

PROJECT TITLE

Iron Carbonyl Cluster linked to Naphthalenedithiolates

PRINCIPAL INVESTIGATOR

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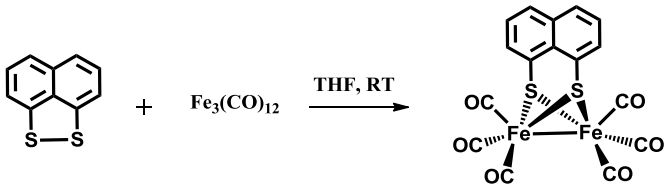
STATEMENT OF PROBLEM: This project is a combined computational and experimental study on the structure, electronic, and catalytic properties of iron-clusters containing naphthalenedithiolate ligands. These clusters are of interest as catalysts for the production of hydrogen, an environmentally benign alternative to fossil fuels. The development of efficient catalysts for hydrogen generation is an important step toward achieving the hydrogen economy.

BRIEF REVIEW OF THE RESEARCH PROCEDURE UTILIZED: One of the proposed complexes (**1**) was prepared by the reaction of $Fe_3(CO)_{12}$ and naphthalene-1,8-disulfide in THF at room temperature (see scheme below). Separation and purification of the product was accomplished by column chromatography on silica gel with dichloromethane as eluent. Electrocatalytic production of hydrogen by **1** in the presence of acetic acid was examined using cyclic voltammetry. Computational study (Density Functional Theory) on the structure and electronic properties of compound **1** was performed using the supercomputing facilities of Shodor Eductaional Foundation Inc, North Carolina.



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SUMMARY OF FINDINGS: Compound **1** effectively catalyzes the reduction of acetic acid to produce hydrogen at -2.00 V (vs Fc/Fc^+). Density Functional Theory study reveals the frontier orbitals to be centered on the Fe-Fe bond.

CONCLUSIONS AND RECOMMENDATIONS: Compound **1** has been prepared and examined as a catalyst for the reduction of acetic acid to produce hydrogen. The structure, electronic, and frontier orbitals of the compound have been probed using Density Functional Theory. The results have been accepted for publication in Journal of Undergraduate Research in Chemistry (see attached article) and were presented at the 3rd Georgian Bay International Conference on Bioinorganic Chemistry in Parry Sound, Ontario, Canada (May 30 – June 4, 2011).

Journal of Undergraduate Chemistry Research, **2011**, 10(2), 166

(NAPHTHALENE-1,8-DITHIOLATO)DIIRONHEXACARBONYL COMPLEX: CATALYTIC REDUCTION OF ACETIC ACID, UV-VISIBLE SPECTROSCOPY, AND DENSITY FUNCTIONAL THEORY STUDY

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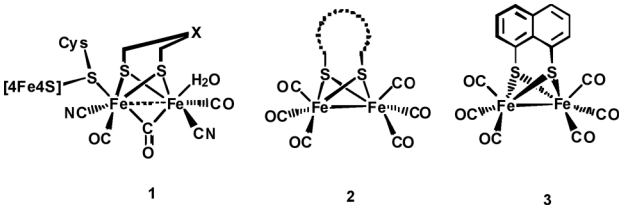
Abstract

The electrocatalytic reduction of acetic acid to produce hydrogen by previously reported (naphthalene-1,8-dithiolato)diironhexacarbonyl complex has been studied. A catalytic proton reduction peak and overpotential of -2.00 V and -0.54 V (vs Fc/Fc$^+$) respectively were obtained. The electronic structure and frontier orbitals of the complex have been probed using UV-visible spectrospcopy, cyclic voltammetry, and Density Functional Theory (DFT). DFT/B3LYP calculated vibrational frequencies and structural parameters for the complex are remarkably close to the experimental values.

Keywords: Computational chemistry, Hydrogen production, Hydrogenase enzyme, Iron carbonyl, Organometallic model, Electrocatalysis, Spectroscopy, Overpotential

Introduction

Hydrogen has emerged as an environmentally benign means of storing energy. To achieve a sustainable hydrogen economy, we need to produce hydrogen efficiently and cheaply using abundant and renewable natural resources. One approach is to develop efficient catalysts that can generate hydrogen from water (1,2). In this light, many studies have focused on the design, preparation, and characterization of organometallic compounds that are models for the active site of the efficient hydrogen producing [Fe-Fe] hydrogenase enzyme (3,4). The structure, **[1]** (X = CH_2, NH, or O), is a description of the active site of [Fe-Fe] hydrogenase. It is composed of a diiron center ligated by carbonyls, cyanides, bridging dithiolate, and a cysteinyl-linked [4Fe4S] unit (5). Structure **[2]** is a typical generic model of **[1]** with different dithiolate ligands used to tune the stereoelectronic, stability, and electrocatalytic properties of the compounds (4,6).



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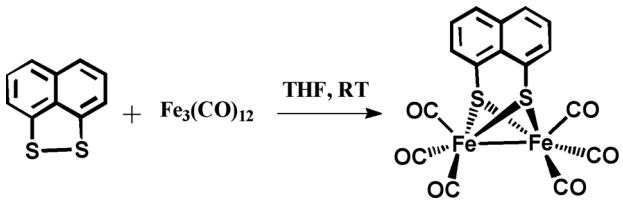
Structures [1-3].

In a study published by T. D. Tilley *et al.* (7), the model compound **[3]** containing naphthalene-1,8-ditholate was synthesized and evaluated as an electrocatalyst for the reduction of proton to hydrogen using a strong acid (*p*-toluenesulfonic acid; pKa = 8.7 in acetonitrile). Most models have been studied in acetonitrile in the presence of a much weaker acid such as acetic acid (6). Hence, for the purpose of comparison with other models, it is desirable to examine the electrocatalysis of **[3]** with acetic acid (pKa = 22.3) in acetonitrile (8). Also, the mechanism of the catalysis depends on the strength of the acid. The electrocatalytic generation of hydrogen by hydrogenase model complexes involves electron transfer and proton transfer reactions. Generally, the model complex is reduced followed by protonation. The proton transfer step and therefore the mechanism are influenced by the acid strength (6).

In this report, we present results on the electrocatalytic production of hydrogen from a weak acid (acetic acid) by compound **[3]**. A comparison of the catalytic properties of **[3]** with two well studied models is presented. We discuss herein, the electronic properties and frontier orbital energies of **[3]** probed using cyclic voltammetry, UV-visible spectroscopy, and Density Functional Theory (DFT) computations. The DFT calculations are performed at the B3LYP level using three basic sets and the results compared to X-ray crystallographic data (7).



Scheme 1. Synthesis of compound [3].

Experimental

Electrocatalytic studies were conducted using an Epsilon Bas potentiostat. Cyclic voltammograms were obtained using a three-electrode cell under nitrogen at room temperature. The electrodes used were glassy carbon working electrode, platinum auxiliary electrode, and Ag/AgCl reference electrode. The platinum and glassy carbon electrodes were polished with aluminum paste and rinsed with water and acetone. A 0.1 M CH_3CN solution of Bu_4NPF_4 was used as supporting electrolyte. The concentration of compound **[3]** was 1 mM and the scan rate was 100 mV/s.

All reagents were obtained from commercial sources. Naphtho[l,8-cd]-l,2-dithiole was synthesized as described in the literature (9). Compound **[3]** was prepared following the procedure similar to that reported in the literature (7). Naphtho[l,8-cd]-l,2-dithiole was treated with $Fe_3(CO)_{12}$ in THF and stirred at room temperature overnight (Scheme 1). Removal of solvent followed by chromatographic separation on silica gel using dichloromethane afforded **[3]**. Spectroscopic data for **[3]** obtained via this method are identical to those reported for the literature preparation of **[3]** (7). The UV/Visible spectrum of **[3]** was measured using a Shimadzu UV-2501 PC spectrophotometer and the infrared spectrum was recorded on a Nicolet FT/IR Magna spectrophotometer.

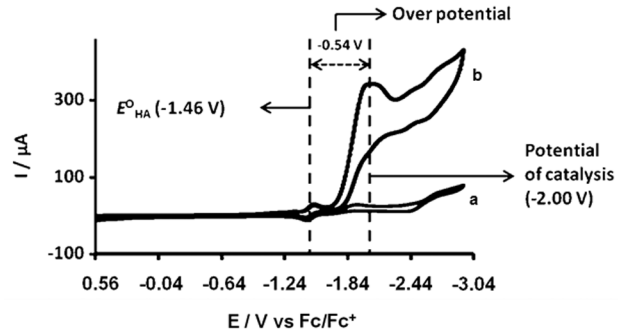


Figure 1. Cyclic voltammograms of [3] in the absence of acetic acid (a) and after addition of 14 µL of acid (b). Solution: Volume 10 mL; [3], 1 mM; 0.1 M nBu_4NPF_6; scan rate 100 mV/s; solvent, CH_3CN. Overpotential is the catalytic peak potential minus the standard potential of acetic acid (E^o_{HA}) (6).

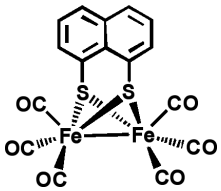
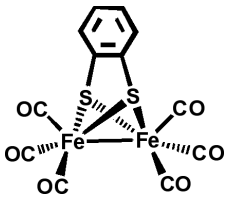
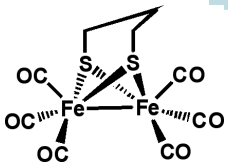
The computations were performed using Gaussian 09 with WebMO interface (10). The geometry of **[3]** was optimized at the DFT/B3LYP level of theory with 3-21G, 6-31G(d), and 6-311+G(d,p) basis sets using the crystal structure data of **[3]** (7). The structures are minima on potential energy surface with positive harmonic vibrational frequencies. The computational results were compared with available experimental values.

Results and Discussion

Electrochemistry

The electrocatalytic generation of hydrogen by **[3]** from *p*-toluenesulfonic acid (a strong acid) has been reported in dichloromethane and THF. The mechanism proposed involved the formation of the monoanion followed by protonation and the overpotential was determined to be -0.85 V (vs Fc/Fc^+) (7). Figure 1 contains cyclic voltammograms of **3** in the absence of acid and after adding 14 µL of acetic acid. The catalytic wave corresponding to the reduction of proton to molecular hydrogen is observed at -2.00 V (vs Fc/Fc^+). The overpotential was determined to be -0.54 V as

Table 1. A comparison of overpotential and catalytic potential of [3] with similar models.[a]

Model			
Overpotential / V	**-0.54**	**-0.65**	**-0.89**
E_{cat} / V	**-2.00**	**-2.11**	**-2.35**

[a] Values for similar models were obtained from reference (6).

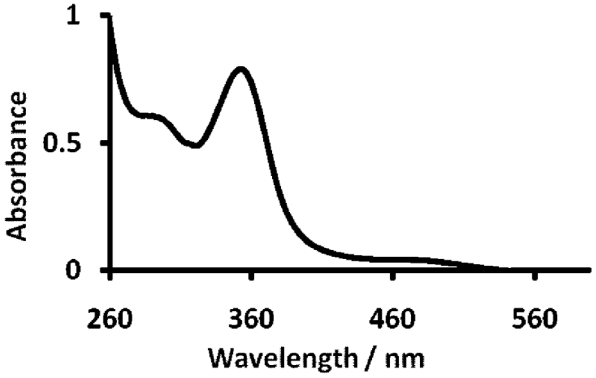


Figure 2. UV-Visible spectrum of [3] in dichloromethane.

shown in Figure 1 using the standard reduction (E^{o}_{HA}) of -1.46 V (vs Fc/Fc^{+}) for acetic acid (6).

The overpotential and potential for the reduction of acetic acid to hydrogen (E_{cat}) by compound **[3]** are contained in Table 1 alongside those of two well studied models; [$Fe_2(CO)_6(SCH_2CH_2CH_2S)$] and [$Fe_2(CO)_6(1,2\text{-}S_2C_6H_4)$] (6). The overpotential and E_{cat} for **[3]** are lower than those of [$Fe_2(CO)_6(SCH_2CH_2CH_2S)$] and [$Fe_2(CO)_6(1,2\text{-}S_2C_6H_4)$]. These results indicate the importance of the nature of thiolate ligand (particularly the use of aromatic groups) in modulating the catalytic properties of hydrogenase diiron model compounds.

The cyclic voltammetric data for **[3]** are employed to estimate its frontier orbital energies (Table 2). Highest Occupied Molecular Orbital energy (E_{HOMO}), Lowest Unoccupied Molecular Orbital energy (E_{LUMO}), and electrochemical HOMO-LUMO gap ($E_{gap\text{-}Echem}$) were determined from the onset of the first oxidation and the first reduction waves. The calculations are referenced to ferrocene (4.8 eV) (11). As shown in Table 2, the electrochemical HOMO-LUMO gap is 2.39 eV, similar to the optical HOMO-LUMO gap ($E_{gap\text{-}opt}$ = 2.29 eV, *vide infra*) but lower than the value obtained from DFT computation ($E_{gap\text{-}DFT}$ = 3.84 eV, *vide infra*).

UV-Visible Spectroscopy

The UV-visible spectrum of **[3]** was recorded in dichloromethane and is presented in Figure 2. Three peaks are observed at 482, 352, and 292 nm. The peak at 482 nm (ε = 9.6 x 10^2 M^{-1} cm^{-1}) is similar to those reported for other hydrogenase models (12,13). The UV-visible spectrum of [$Fe_2(CO)_6(SCH_2CH_2CH_2S)$] recorded in acetonitrile has a shoulder at 452 nm ascribed to d-d electronic transition (12). The peaks at 352 nm and 292 nm may be tentatively assigned to $\pi \rightarrow \pi^*$ and/or charge transfer transitions. Direct evidence of frontier orbital energy levels in compound **[3]** can be obtained from its electronic spectrum. The optical HOMO-LUMO energy gap ($E_{gap\text{-}opt}$) can be calculated using the onset of the lowest-energy visible absorption band (λ_{onset}) as described in the equation, $E_{gap\text{-}opt}$ (eV) = 1240/(λ_{onset}) (11). For compound **[3]** (λ_{onset} = 542 nm), the optical HOMO-LUMO energy gap is determined to be 2.29 eV.

Density Functional Theory Calculations

To further probe the electronic properties of compound **[3]**, Density Functional Theory calculations were performed. Crystal structure data of **[3]** were used as input for the geometric optimizations. Calculations were done at B3LYP level using three basis sets; 3-21G, 6-31G(d), and 6-311+G(d,p). Some structural parameters obtained by the DFT calculations are presented in Table 3 alongside experimental values. In general, computed bond lengths and bond angles are very close to the X-ray crystallographic data. There are no significant differences among results obtained with the different basis sets. Also contained in Table 3 are DFT determined vibrational frequencies for the terminal metal carbonyls of **[3]** ($\nu_{(CO)}$). The results show three peaks similar to those experimentally obtained (7). The $\nu_{(CO)}$ values using 6-31G(d) and 6-311+G(d,p) basis sets are remarkably close to experimental values. However, with 3-21G basis set, the $\nu_{(CO)}$ values are about 54-103 cm^{-1} lower than experimental values.

We computed the frontier orbital energies and HOMO-LUMO gap ($E_{gap\text{-}DFT}$) for **[3]** and the results are contained in Tables 1 and 4. Also reported in Table 4 are the total energies (E), and dipoles of the optimized structures. The $E_{gap\text{-}DFT}$ values are similar among the

Table 2. Frontier orbital energies for [3].

E_{pc} (V)[a]	E_{pa} (V)[a]	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{gap\text{-}Echem}$	$E_{gap\text{-}opt}$	$E_{gap\text{-}DFT}$[b]
-1.52	**0.87**	**-5.67**	**-3.28**	**2.39**	**2.29**	**3.84**

[a]Values from reference (7) and identical to those obtained by us. [b] Average of the values using three basis sets (*vide infra*)

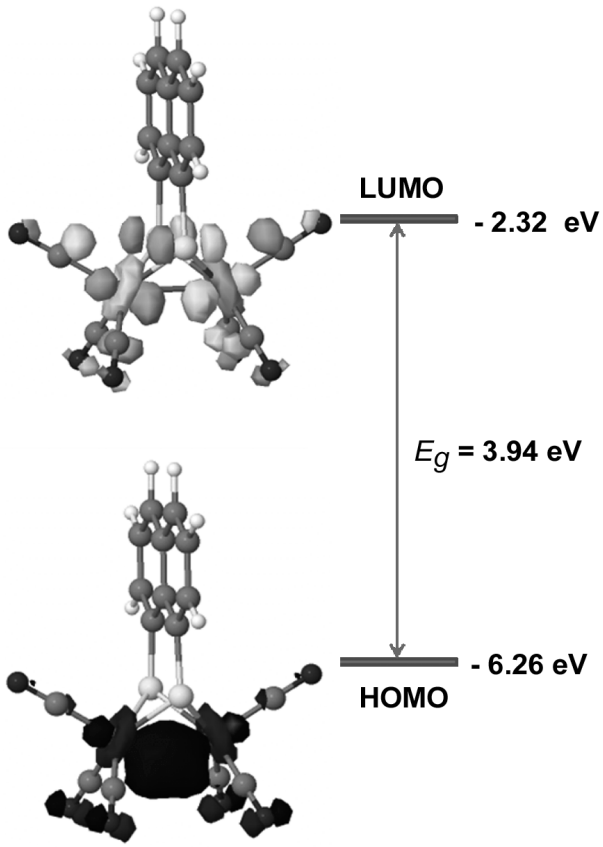


Figure 3. HOMO and LUMO diagrams of [3] (using the DFT/B3LYP/6-31G(d)).

basis sets but are 1.55 eV higher than the electrochemical and optical HOMO-LUMO gaps (see Table 1).

Figure 3 is a pictorial representation of the frontier orbitals of **[3]**. As has been observed from computational results of similar model complexes (14,15), the HOMO of **[3]** is basically the bonding orbital between the two Fe atoms, and the LUMO has significant Fe-Fe anti-bonding character.

Conclusions

The production of hydrogen from a weak acid (acetic acid) by **[3]** is reported with overpotential of -0.54 V compared to -0.83 V (vs Fc/Fc^+) for *p*-toluenesulfonic acid (strong acid). Frontier orbital energies and electronic properties of **[3]** have been probed using UV-visible spectroscopy, cyclic voltammetry, and DFT computations at the B3LYP level.

Acknowledgment

The authors gratefully acknowledge support for this work from Arkansas Tech University Faculty Research Grant (2010). Computational study was performed using the facilities at SHODOR (www.shodor.org).

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Table 3. Calculated Bond lengths (Å), Bond angles (°), and IR data (cm^{-1}) for [3].

	X-ray[a]	6-311+G(d,p)[b]	6-31G(d)[b]	3-21G[b]
Fe-Fe	2.506	2.539	2.491	2.541
Fe-S	2.255[c]	2.296	2.290	2.363
S-S	3.016	3.072	3.077	3.168
S-Fe-S	84.105[c]	83.982	84.412	84.188
$\nu_{(CO)}$	2074, 2039, 2001[d]	2070, 2031, 2013[e]	2071, 2036, 2016[e]	2002, 1963, 1947[e]

[a] Experimental values from reference (7). [b] DFT computed values. [c] Average values. [d] Recorded in hexane. [e] The computed frequences are scaled using scaling factors reported in reference (16).

Table 4. DFT data on the frontier orbitals of [3] using three basis sets.

	6-311+G(d,p)	6-31G(d)	3-21G
E (Hatree)	-4389.010	-4388.424	-4366.831
Dipole (Debye)	4.2509	4.6602	5.1990
HOMO (eV)	-6.403	-6.262	-6.517
LUMO (eV)	-2.568	-2.319	-2.770
$E_{gap\text{-}DFT}$ (eV)	3.835	3.943	3.747

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