Synthesis and electrochemical characterization of a tridentate Schiff-base ligated Fe(II) complex

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Abstract

The structural and electronic properties of an Fe(II) Schiff-base complex, [Fe(N₂S)₂][ClO₄]₂ (N₂S = 2-pyridyl-N-(2'-methylthiophenyl)methylenimine), are described and compared to an analogous Ni(II) species known to degrade to a H₂-evolving electrocatalytic film. Although structurally similar, the two complexes exhibit stark differences in their electrochemical and optical properties, and decompose via different pathways under reducing potentials. At potentials negative of the Fe(II/I) reduction wave, the complex degrades to a species that weakly adsorbs to the electrode surface. Prolonged electrolysis leads to the deposition of an Fe-containing film on the electrode.

Keywords

Electrochemistry, redox, iron, coordination chemistry, electrochemical-initiated degradation

Introduction

The pursuit of hydrogen-evolving electrocatalysts has received much attention in the past decade as a response to global energy challenges.[1–3] Motivation to find catalysts designed around inexpensive, earth abundant transition metals such as Co, Ni, or Fe has resulted in numerous examples of complexes both active and inactive for hydrogen evolution.[2,4,5]

Catalysts for hydrogen evolution are usually intentionally designed either as homogenous or heterogeneous systems. This distinction can be blurred by the covalent attachment of molecular catalysts to solid electrodes.[6–9] Additionally, molecular catalysts can transform under reducing and protic conditions (such as those utilized for hydrogen evolution) to electrode-bound heterogeneous species potentially active for hydrogen evolution.[10] In recent years, researchers have begun to investigate these transformations, however, only a few examples have been reported. [10–21] These studies have included both molecular Ni and Co complexes that undergo degradation and have highlighted the susceptibility of complexes that contain C=N bonds, N-O bonds, and/or Ni-S bonds. While a number of examples of Fe-based H₂-evolving catalysts have been reported,[22–24] including many Fe-hydrogenase mimics,[4,25–28] there are no examples to our knowledge that detail the degradation of Fe complexes under electrocatalytic conditions.

Inspired by our recent investigation of the decomposition of [Ni(N₂S)₂][BF₄]₂ under electrocatalytic conditions, (N₂S = 2-pyridyl-N-(2'-methylthiophenyl)methylenimine), which occurs through hydrogenation of the Schiff-base ligands,[18] we targeted the Fe analogue. The Fe complex, while structurally similar to the Ni species, has dissimilar electrochemical and spectroscopic characteristics.[29] The Fe species was also found to decompose exclusively under applied electrochemical potentials. The decomposition of this iron species in the absence of acid underscores that protic conditions are not always necessary for degradation.

Experimental

General Procedures

Syntheses were performed using standard glovebox or Schlenk line techniques. Acetonitrile (Fischer Scientific, HPLC grade, >99.9%) was dried and degassed with argon using a Pure Process Technology solvent system. 2-pyridinecarboxaldehyde (Alfa Aesar, 99%), iron perchlorate hydrate (Aldrich, 98%), 2-(methylthioaniline) (Acros Organics, >97%), water for polishing (Milli-Q system), magnesium sulfate (Sigma Aldrich, >99.5%), sodium chloride (Aldrich, >99%), diethyl ether (Fisher, >99.0%), methanol (Fisher, >99.9%), deuterated acetone (Cambridge Isotope Labs, Inc., >99.8%), deuterated acetonitrile (Cambridge Isotope Labs, Inc.,

99.8%) were all used as received. Tetrabutylammonium hexafluorophosphate (TCI, >98%) was recrystallized from hot ethanol (Decon Labs, Inc., 200 proof), filtered, washed with cold ethanol, and dried at ca. 80 °C under vacuum for eight hours. 2-pyridyl-N-(2'-methylthiophenyl)methylenimine was prepared by literature methods.[30]

NMR spectra were recorded on a Bruker 400 MHz spectrometer and were referenced to proteo solvent impurities.[31] Elemental analysis was performed by Atlantic Microlabs, Inc. UV-vis spectra were recorded using an Agilent Cary 60 UV-vis spectrophotometer. The Fourier transform infrared spectra of the ligand and complex were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with a germanium single crystal horizontal attenuated total reflectance detector in the range 4000 – 400 cm⁻¹.

The complex was analyzed with a hybrid LTQ FT (ICR 7T) (ThermoFisher, Bremen, Germany) mass spectrometer. Samples were introduced via a micro-electrospray source and a flow rate of 3 µL/min. Xcalibur (ThermoFisher, Bremen, Germany) was used to analyze the data. Molecular formula assignments were determined with Molecular Formula Calculator (v 1.2.3). Low-resolution mass spectrometry (linear ion trap) provided independent verification of molecular weight distributions. All observed species were singly or doubly charged, as verified by unit *m/z* separation between each mass spectral peak and its corresponding ¹³C isotope peak.

Electrochemical methods

Electrochemistry was performed in a nitrogen-filled glovebox with a Pine Instruments WaveDriver potentiostat using glassy carbon working electrodes (CH Instruments, 3 mm diameter), a glassy carbon counter electrode (CH Instruments, 3 mm diameter), and a silver wire pseudoreference. Electrode leads were connected to the WaveDriver potentiostat located outside the glovebox via a custom cable fitted through a glovebox port. All scans were performed in 250 mM [Bu₄N][PF₆] CH₃CN solution and referenced absolutely to ferrocene. Glassy carbon electrodes were polished with 0.3 micron alumina powder and 0.05 micron alumina powder (CH Instruments, contained no agglomerating agents) Milli-Q water slurries, rinsed and ultrasonicated in Milli-Q water to remove residual polishing powder. The pseudoreference electrode was

submerged in a glass tube fitted with a porous glass Vycor tip containing 250 mM [Bu₄N][PF₆] CH₃CN solution.

Each working electrode was pretreated with two cyclical scans from approximately 0.7 V to −2.8 V (the exact potential varied) at 300 mV/s in 250 mM [Bu₄N][PF₆] CH₃CN solution.[32] For all experiments, background voltammograms at the respective scan rate were taken. For each scan, a fresh, pretreated working electrode was used, and the solution was agitated between scans.

Synthesis of Fe(N-N-SCH₃)₂(ClO₄)₂

[Fe(N₂S)₂][ClO₄]₂ ([Fe(N₂S)₂]²⁺, Scheme 1) was prepared similarly to [Ni(N₂S)₂][ClO₄]₂. [18] N₂S (N₂S = 2-pyridyl-N-(2'-methylthiophenyl)methylenimine; 0.050 g, 0.22 mmol) was dissolved in 7 mL acetonitrile before being added dropwise to 3 mL of a vigorously stirring CH₃CN solution of Fe(ClO₄)₂ (0.047 g, 0.18 mmol) in a nitrogen-containing glovebox. The solution color immediately turned dark purple and was stirred for 3 h. The solution was partitioned into 5 mL volumes before each was layered with 15 mL Et₂O. The vials stood at room temperature for 24 h and then at 0 °C for an additional 72 h. The supernatant was decanted and the crystals were rinsed with Et₂O. After drying for eight hours under vacuum, 56 mg of small, dark-blue/purple crystals were collected (Yield: 72%). Selected IR frequencies and assignments (Ge, *neat*): ca. 1600, 1478, 1447, 1422, 1307, 1163, 1080 (ClO₄¹⁻), [30] 972, 919, 776, 746, 621 (C-S) [33] cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ (ppm): 10.19 (s, 1H, N=CH), 8.57 (d, 1H, phenyl ring proton), 8.33 (d, 1H, pyridine proton), 8.03 (t, 1H, pyridine proton), 7.9-7.7 (m, 4H, phenyl ring protons (3) and ortho pyridine proton), 7.39 (t, 1H, pyridine proton), 2.16 (broad s, 3H, -SCH₃). Electrospray MS (CH₃CN), *m/z* calculated for [C₂₆H₂₄FeN₄S₂][ClO₄]: 611.0277, Found: 611.0258; *m/z* calculated for [C₂₆H₂₄FeN₄S₂]: 256.0396, Found: 256.0389 Absorption spectrum [λ_{max} , nm (ϵ , M⁻¹cm⁻¹) in MeCN]: 224 (31150), 262 sh (12340), 324 (23210), 366 sh (9710), 527 sh (2350), 599 (3410).

Results and Discussion

Synthesis and Characterization

Solutions of $\text{Fe}(\text{ClO}_4)_2$ and 2-pyridyl-N-(2'-methylthiophenyl)methylenimine in CH_3CN were combined slowly under nitrogen to produce a dark purple solution, which was then layered with Et_2O to afford crystals of $[\text{Fe}(\text{N}_2\text{S})_2][\text{ClO}_4]_2$ of similar color. An alternative synthesis was recently reported in which the tetrafluoroborate salt was produced from an FeBr_2 precursor.[34] In the ^1H NMR spectrum of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$, all of the aromatic protons can be clearly identified and several resonances are shifted downfield relative to the free ligand (see SI, Figures S1-S3). By contrast, although the $-\text{SCH}_3$ protons appear as a sharp singlet for the isolated ligand (2.48 ppm, Ref. [18]), the same protons in the metallated species appear upfield as a broad singlet (2.16 ppm, Figure S1). The broadness of the $-\text{SCH}_3$ protons is likely the result of rapid τ_1 relaxation by the quadrupolar sulfur nuclei (^{33}S spin = 3/2), and the 0.32 ppm shift of its peak position suggests that the Fe(II) core and trans pyridine increase the electron density on the coordinated sulfur. The diamagnetic spectrum is consistent with a low spin Fe(II) species.

Infrared spectroscopy revealed a shift in the thioether stretching frequency of the N_2S ligand upon coordination to iron ($\nu_{\text{C-S}} = 693 \text{ cm}^{-1}$ for N_2S , $\nu_{\text{C-S}} = 621 \text{ cm}^{-1}$ for $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$, Figure S4-S7). The imine stretch ($\nu_{\text{C=N}}$) is observed at 1622 cm^{-1} for the uncoordinated ligand; an assignment of this stretch in the $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ spectra cannot be definitively made, although there are some weak bands observed ca. 1600 cm^{-1} . An intense, broad band, indicative of the perchlorate counterion, is also observed at 1080 cm^{-1} .[30]

Electronic Structure

The electronic absorption spectrum (Figure 1) of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ in CH_3CN exhibits three absorption bands centered at $\lambda = 224, 324$ and 599 nm ($\epsilon = 31150, 23210$ and $3410 \text{ M}^{-1} \text{ cm}^{-1}$), Table 1. By comparison to the Ni(II) analogue and the isolated ligand, the higher energy bands are assigned to intra-ligand transitions.[35,36] We cannot definitively assign the lower energy transition ($\lambda = 599 \text{ nm}$); absorption features in related complexes have been assigned as both metal-to-ligand ($d_\pi(\text{M}) \rightarrow \pi^*(\text{L})$)[34] and ligand-to-metal ($\sigma(\text{S}) \rightarrow d_{\sigma^*}(\text{M})$)[35,36] charge transfer transitions. An analogous transition is not observed for $[\text{Ni}(\text{N}_2\text{S})_2]^{2+}$. No d-d transitions were

resolved for $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$, in contrast to $[\text{Ni}(\text{N}_2\text{S})_2]^{2+}$ for which a broad, low energy transition dominates the near-IR region of the spectrum ($\lambda_{\text{max}} = 803 \text{ nm}$, $\epsilon = 46 \text{ M}^{-1} \text{ cm}^{-1}$).[30]

Figure 1. The electronic absorption spectrum of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ in CH_3CN .

Table 1. Electronic spectral properties of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ and $[\text{Ni}(\text{N}_2\text{S})_2]^{2+}$.

Complex	λ_{max} , nm (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$)
$[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$	224 (31150), 262 sh (12340), 324 (23210), 366 sh (9710), 527 (2350), 599 (3410)
$[\text{Ni}(\text{N}_2\text{S})_2]^{2+ \text{ a}}$	234 sh (30290), 246 sh (26160), 318 sh (22170), 333 (23790), 347 sh (21910), 366 sh (13650), 520 sh (166), 803 (46), 940 sh (22)

^aRef. [30]

Structural Analysis

The tetrafluoroborate salt of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ was recently reported by Rose and coworkers.[34] The reported ^1H NMR and select IR bands are identical to the perchlorate salt prepared, indicating that the cations, $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$, are identical. This is further supported by preliminary single-crystal X-ray diffraction (XRD) analysis of $[\text{Fe}(\text{N}_2\text{S})_2][(\text{ClO}_4)]_2$, which is

found to be isomorphous and isostructural to $[\text{Fe}(\text{N}_2\text{S})_2][(\text{BF}_4)]_2$. Unfortunately the preliminary XRD analysis was plagued by problems of twinning, so a full crystal structure was not obtained.

Scheme 1

Based on the structure obtained by Rose and coworkers, $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ consists of an Fe(II) core ligated by two tridentate Schiff bases, the rigid backbones of which restrict the complex to a meridional conformer with near C_2 symmetry (Scheme 1).[34] Pendant pyridines decorate the molecule, as do two C=N double bonds, which have been shown to predispose a catalyst to electrode-initiated decomposition.[13,14,16,17] The crystal structure of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$, although fundamentally similar to the Ni(II) analogue,[30] contains some important distinctions. Despite the smaller atomic radius for Ni(II) compared to Fe(II), the M–L bond lengths for the Fe species are uniformly smaller (Table 1). The bond lengths are consistent with the low-spin Fe(II) assignment made based on the spectroscopic data.

Table 1. Structural comparison of bond distances for $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ and the Ni(II) analogue.^a

	M-Py	M-imine	M-S
Ni(II)	2.08(1)	2.04(1)	2.44(2)
Fe(II)	1.98(2)	1.93(1)	2.27(1)

^aThe numbers in parentheses are the standard deviations among chemically equivalent bonds. There are two such bonds in the nickel complex (one molecule per asu, 2 ligands per molecule), and 8 such bonds in the iron complex (four molecules per asu). Data for Ni(II) taken from ref. [30] and data for Fe(II) from ref. [34].

Also noteworthy is the slightly longer C=N bonds in $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$, (Fe(II), 1.31 Å; Ni(II), 1.27 Å). This is consistent with better back-bonding into the imine functionality from Fe(II) than from Ni(II). In both complexes the imine nitrogens are nearly perfectly trans (N-M-N > 177°), while the S-M-Pyr angles are constrained by ligand geometry and so have slightly smaller angles (Fe^{II}, ca. 168°; Ni^{II}, ca. 162°).

Electrochemical Analysis

A reversible one electron wave is observed via cyclic voltammetry (CV) ($E_{1/2} = -1.10$ V vs Fc^+/Fc , Figure S8). A similar redox feature is observed for $[\text{Ni}(\text{N}_2\text{S})_2]^{2+}$ ($E_{1/2} = -1.03$ V vs Fc^+/Fc).^[18] For the nickel complex, this feature corresponds to a metal-based Ni(II/I) reduction, as supported by EPR spectral analysis of the electrogenerated species.^[30] Direct reduction of the ligand occurs at much more negative potentials.^[18] As such, we tentatively assign this redox feature to the Fe(II/I) couple.

While a reversible Ni(I/0) wave is observed ($E_{1/2} = -1.25$ V vs Fc^+/Fc), the second reduction wave of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ is irreversible ($E_{p,c} = -1.37$ V vs Fc^+/Fc , Figure 2). After traversing this second redox process for $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$, a new oxidation feature is observed on the anodic scan ($E_{p,a} = -1.10$ V vs Fc^+/Fc , Figure 2). The symmetry of this anodic wave suggests a heterogeneous or surface-adsorbed species.^[37] The shape and intensity of this oxidation wave are dependent on the cathodic trace – as the switching potential becomes more negative, the intensity of this peak decreases to reveal the original Fe(II/I) oxidation, which is otherwise obscured (Figure S9). This behavior suggests that the surface-adsorbed species can be displaced or reacts further under stronger reducing potentials.

At higher scan rates (>10 V/s), the anodic feature at -1.10 V partitions into two distinguishable peaks, one of which corresponds to the oxidation of the Fe(I) species. At the fastest scan rates probed (20 V/s), the Fe(II/I) couple appears fully reversible, the second reduction becomes quasi-reversible, and the symmetrical oxidation is still observed at -0.85 V (Figure 3). The quasi-reversibility of the second reduction at fast scan rates indicates that the formation of the surface-adsorbed species can be outcompeted by rapid re-oxidation of the reduction product.

To determine if the oxidation feature at -0.85 V arises from a surface-adsorbed species, a rinse test was conducted.[10,38] A freshly polished electrode in a solution of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ was scanned cathodically from -0.77 V to -1.62 V vs. Fc^+/Fc , passing through both reduction waves. The treated electrode was removed from solution, rinsed with CH_3CN , and scanned anodically from -1.62 V to -0.77 V in an electrolyte-only solution. No current beyond the background was passed, indicating no strongly electrode-adsorbed redox-active species (Figure S10). The rinse test, however, does not preclude a weakly-adsorbed species; a simple rinse or wash can inadvertently remove a weakly-bound species.

Next, a solution of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ was electrolyzed at -1.68 V for 45 minutes with a clean glassy carbon electrode. The treated electrode was rinsed and a cyclic voltammogram was recorded in an electrolyte-only solution. The voltammogram revealed the oxidation of a surface adsorbed species with an onset at ca. -0.8 V vs Fc^+/Fc , 300 mV positive of the feature observed in voltammograms of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$. Using the same electrode, a second anodic scan passed no current beyond the background, suggesting that the oxidized material is removed from the electrode surface during the first scan (Figure S11). A control experiment was performed in which another electrode was treated under similar conditions in a solution of 0.5 mM $\text{Fe}(\text{ClO}_4)_2$ to produce a heterogeneous deposit of Fe. For this treated electrode, a large stripping wave is observed with a similar onset potential ($E_{\text{onset}} \sim -0.8$ V vs Fc^+/Fc) to that observed for the electrode subjected to controlled potential electrolysis in a solution of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$; this wave also is diminished on repeated scans (Figure S12).

These longer electrolysis times appear to transform a transient, surface adsorbed species observed in CVs of $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ ($E_{p,a} = -1.10$ V) into a second species ($E_{\text{onset}} \sim -0.8$ V), as highlighted by the significant difference in oxidation potentials. Prolonged electrolysis results in an Fe-based film, an observation consistent with the linear sweep voltammograms of $\text{Fe}(\text{ClO}_4)_2$ -treated electrodes. Additionally, these experiments demonstrate that a rinse test may not detect weakly adsorbed surface-bound species.

By contrast, $[\text{Ni}(\text{N}_2\text{S})_2]^{2+}$ remains homogeneous throughout voltammetry experiments and was found to degrade with applied potential only under protic conditions.[18] Mechanistic studies revealed the hydrogenation of the Schiff-base to form a species that is unstable upon

reduction. Its degradation leads to a heterogeneous Ni- and S-containing film embedded with Ni(0) nanoparticles. While we cannot definitively identify the initial surface-adsorbed Fe species formed upon the second reduction, our data does not suggest initial ligand hydrogenation, especially given the lack of protic species. Instead, weak adsorption and observations that the production of this transient species is highly dependent on scan rate and switching-potentials, suggest this Fe-containing species is molecular in nature. Only under prolonged electrolysis does the species decompose to a heterogeneous Fe-containing material.

Figure 2. Voltammograms of 0.4 mM $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$, recorded at 100 mV/s in a 250 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$ CH_3CN solution. The solid black voltammogram was recorded with a switching potential of past the second reduction; the dashed blue voltammogram was recorded with a switching potential prior to the second reduction.

Figure 3. Voltammograms of 0.4 mM $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ recorded at various scan rates (0.1–20 V/s). As the scan rate is increased, the anodic peak splits into two waves. At very high scan rates (i.e., 20 V/s) partial reversibility is observed in the second redox couple and the large oxidation partitions into distinct peaks. Voltammograms recorded in a 250 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$ CH_3CN solution.

Conclusion

Characterization of $[\text{Fe}(\text{N}_2\text{S})_2][(\text{ClO}_4)]_2$ has revealed that its structure is nearly identical to the Ni(II) analogue, with $[\text{Fe}(\text{N}_2\text{S})_2]^{2+}$ exhibiting uniformly reduced M-L bond distances as a manifestation of the d orbital population. However, despite nearly identical ligand frameworks, the optical and electrochemical properties of the Fe(II) species differ substantially from those of the analogous Ni(II) complex.[18] While both the Ni(I) and Fe(I) species are stable on the electrochemical timescale, further reduction of the Fe(I) species leads to the formation of a weakly adsorbed surface species. Extended electrolysis leads to the formation of a Fe-containing film which is readily stripped from the electrode surface.

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Table of Contents Synopsis

Characterization of an Fe(II) complex reveals that it is structurally similar to an analogous Ni(II) species known to degrade to a H₂-evolving electrocatalytic film under reducing protic conditions. However, the Fe species degrades under purely reducing conditions and does not require a proton source.