First–Row Transition Metal Coordination Compounds for the Electrocatalytic Generation of Hydrogen from Organic and Aqueous Solutions

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First-Row Transition Metal Coordination Compounds for the Electrocatalytic Generation of Hydrogen from Organic and Aqueous Solutions

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelor of the Sciences in Department of Chemistry from The College of William and Mary

by Patrick M Crossland

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Williamsburg, VA
April 17, 2015
# Table of Contents

**Acknowledgements** 4

**List of Figures, etc.** 6

**Chapter 1: Introduction and Background** 9

The Global Energy Crisis 9

Harnessing Solar Energy 11

Mimicking Nature 12

Hydrogen as a Renewable Fuel 13

Developing Functional Mimics of Hydrogenase 14

Photocatalytic Systems for Hydrogen Generation 15

**Chapter 2: Cobalt Salen Complexes for Proton Reduction** 17

Abstract 17

Introduction 18

Redox Active Ligands 19

Experimental 20

Materials 20

Instrumentation 20

X-Ray Diffractometry 21

Syntheses 21

Crystal Structure 26

High Resolution Mass Spectrometry 27

Catalyst Concentration Experiments 27

Acid Concentration Experiments 27
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Nickel Catalysts for Proton Reduction</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Abstract</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Materials</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Instrumentation</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>X-Ray Diffractometry</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Catalyst Concentration Experiments</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>Acid Concentration Experiments</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>Determination of Overpotential</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>Results and Discussion</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Conclusions</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Appendix</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>72</td>
</tr>
</tbody>
</table>
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List of Figures, Schemes, Equations and Tables

Figures:

1. The Global Energy Crisis 9
2. NiFe hydrogenase active site 14
3. Representative CV 15
4. Cobalt (difluoroboryl)dimethylglyoxime 18
5. CV of 4 31
6. Comparison of 2 and 4 32
7. CV of 2 33
8. Peak Current Density vs. Acid Concentration for 2 34
9. Catalyst Concentration Experiment for 2 35
10. Peak Current Density vs. Catalyst Concentration for 2 36
11a. $i_c/i_p$ vs. acid concentration 0.5 V/s 39
11b. $i_c/i_p$ vs. acid concentration 1 V/s 39
11c. $i_c/i_p$ vs. acid concentration 5 V/s 40
12. Slope for determining $k$ 41
13. Water addition test 42
14. $^1$H NMR of 1 46
15. High res Mass Spectrum of 2 47
16. $^1$H NMR of 3 48
17. $^1$H NMR of 5 49
18. Determination of Overpotential 50
19. Determination of $i_c/i_p$  
20. Rinse Test  
21. CV of Co(BF$_4$)$_2$*6 H$_2$O  
22. Nickel pyridinethiolate catalysts  
23. ORTEP Diagram of 8  
24. CV of 8  
25. Peak Current Density vs. Acid Concentration 8  
26. Catalyst Concentration 8  
27. Peak current density vs. catalyst concentration 8  
28. Rinse test for 8  
29. CV of NiCl$_2$  
30. $^1$H NMR of H$_3$ttfasbz  
31. $^{13}$C NMR of H$_3$ttfasbz

Schemes:
1. Synthesis of 1  
2. Synthesis of 2  
3. Synthesis of 3  
4. Synthesis of 4  
5. Synthesis of 5  
6. Synthesis of 6  
7. Synthesis of 7  
8. Possible catalytic mechanisms
Equations:

1. Definition of Slope 37
2. Definition of $i_c/i_p$ 38
3. Slope in terms of $k$ 38
4. $k$ in terms of slope 38

Tables:

1. Selected bond lengths and angles for 8 70
2. Selected crystallographic data for 8 71
Chapter 1: Introduction and Background

The Global Energy Crisis:

As the 21st century progresses the need for a renewable alternative fuel source is increasing. In 2013, 16 Terrawatts (TW) of energy were consumed globally.¹ This number is projected to increase to 27.6 TW per year in 2050 and 43 TW per year in 2100, an increase of almost 300%.² Troublingly, much of this energy is derived from fossil fuels, such as coal, natural gas and liquid fuels such as oil. In 2013, the United States Energy Information Association (USEIA) predicted that over 80% of the world’s energy consumption would come from fossil fuels through 2040. Figure 1 shows the dependence on fossil fuels over carbon-free sources of energy like hydroelectric power or nuclear energy for the past 6 years as well as projections through 2040.

![Energy consumption chart](image)

**Figure 1.** Energy consumption by type through 2040

¹ This number is projected to increase to 27.6 TW per year in 2050 and 43 TW per year in 2100, an increase of almost 300%.

² Troublingly, much of this energy is derived from fossil fuels, such as coal, natural gas and liquid fuels such as oil.
The combustion of hydrocarbons poses serious environmental concerns. The combustion of fossil fuels releases carbon emissions into the atmosphere, a major source of pollution. Carbon emissions also contribute greatly to global warming.\(^3\) Carbon dioxide acts as a greenhouse gas by absorbing infrared radiation from the sun and trapping heat in the atmosphere. The USEIA predicts a 1.3% increase annually in CO\(_2\) emissions between 2010 and 2040, which could have devastating environmental effects. This problem is compounded by the fact that carbon dioxide can exist in the atmosphere for 400 to several thousand years.\(^2\)

The mass consumption of non-renewable fossil fuels also poses a question of sustainability. Models based on consumption rates in 1998 show that there are 50-150 years of oil reserves, 270-590 years of gas reserves, and 1000-2000 years of coal reserves that are readily extractable.\(^2\) While this indicates that humanity can continue to use fossil fuels for hundreds of years as an energy source, fossil fuels still pose two major problems; they will eventually be exhausted and the use and the extraction of fossil fuels poses dangers to human health and the environment. Oil production is largely price dependent; because of this, oil production will peak when demand peaks, then decrease over time. The United States Department of Energy predicts that profitable oil production will peak around 2025.\(^4\) Fossil fuel extraction is also harmful to human and environmental health. Two recent examples of this are the 2010 Deepwater Horizon oil spill in the Gulf of Mexico, and the 2010 Upper Big Branch Mine disaster in West Virginia. In the mining accident a coal dust explosion killed 29 miners. Coal mining is so dangerous, that although only 1% of the world’s workforce is engaged in mining activities mining accounts for
~8% of all work-related deaths. Along with work-related injuries fossil fuel extraction is responsible for significant lead, cadmium, sulfur, mercury and nitrogen emissions and air pollution is the cause of millions of premature deaths every year.\textsuperscript{3} Clearly a sustainable, alternative fuel source must be found in order to circumvent these shortcomings.

**Harnessing Solar Energy**

The sun provides a potential solution to the fossil fuel problem. In just one hour, 120,000 TW of sunlight hit the Earth.\textsuperscript{2} Sunlight provides a nearly limitless source of energy that is less constrained by geographical location than other alternative energies. Harnessing solar energy involves three processes: capture, conversion, and storage. Current technologies exist for the capture and conversion of solar energy. Photovoltaics accomplish this by coupling an n-doped semiconductor with a p-doped semiconductor. These semiconductors are usually silicon doped with an element with one more valence electron (n-type) or one fewer valence electron (p-type). This doping method allows the photovoltaics to separate electrons and positive holes to create a current. However, photovoltaics present a series of challenges. First, they are inefficient and expensive when compared to fossil fuels. Solar energy is too diffuse for current technology to be an economically viable alternative. Solar-derived electricity costs \$0.35/kw-h, fossil fuel-derived electricity costs \$0.02-0.05/kw-h.\textsuperscript{2} Furthermore, storing energy derived from photovoltaics is a challenge. Due the diurnal nature of sunlight, in order for grid regulation to be achieved, solar-derived electricity must be stored for use during the evening. However, until recently there was no battery that could accomplish this,
and these batteries are still a burgeoning technology. Another method of solar energy storage is mechanical, where solar-derived electricity could be used to pump water uphill, when released downhill the water would spin turbines to generate electricity. However, the scale needed for this to succeed is too large to be practical. If an easily-produced, readily-storable solar fuel was developed it could address both of these issues.

**Mimicking Nature**

Energy in its simplest form is stored in chemical bonds. By breaking a chemical bond, energy is released to do mechanical work. The potential energy of a bond is not released until it is broken, meaning it can be stored and transported as long as the molecule remains intact. A model system of this kind of process is photosynthesis. In photosynthesis plants use sunlight to drive redox chemistry that synthesizes energy-rich sugar molecules. Other organisms consume these for energy, or they can be burned as a non-carbon neutral, renewable biofuel.

Photosynthesis is just one example of a process that uses physical energy to produce chemical energy. One of the most basic molecules, diatomic hydrogen, stores 13.6 kJ of energy per mole. Not only that, there are numerous enzymes found in nature that catalytically reduce protons to dihydrogen. Perhaps most excitingly, hydrogen is a carbon-free combustible fuel.

**Hydrogen as a Renewable Solar Fuel**
In Nature, a family of enzymes known as hydrogenases catalyze the reduction of protons to hydrogen gas. Hydrogenases show that hydrogen can be produced through a variety of pathways, because of this hydrogen has large implications of being a clean, renewable fuel. The chemical energy stored in hydrogen is well documented, and photosynthesis illustrates that the energy from solar radiation, a truly inexhaustible resource, can be used to drive chemical reactions. Hydrogen is also clean burning. This means that when it is combusted no greenhouse gases are formed, the only products are water and energy. This combination of factors makes hydrogen an ideal candidate for a solar fuel. Hydrogen as a solar fuel also solves the problems inherent with other solar energy devices. Hydrogen can be utilized as a fuel to generate electricity at any time of day by using fuel cell technology or by combusting it to power a steam-driven turbine (like current coal-fired electricity), solving the problem with diurnal electricity generation.

While hydrogen does show great promise as a chemical fuel, it is difficult to use solar energy to form chemical bonds, even for a simple molecule. A molecule, or system of molecules must be developed that can complete the redox chemistry required to convert two protons and two electrons to hydrogen gas. This reaction is achieved in nature by finely-tuned hydrogenase enzymes that utilize abundant transition metals to catalyze this reaction. Fortunately, organometallic and coordination complexes have been synthesized that also catalyze the reduction of protons to hydrogen gas.

Developing Functional Mimics of Hydrogenase
The structures of Fe-Fe hydrogenase and Ni-Fe are both known. While these proteins are very complex, their active sites are fairly simple (figure 2). These can serve as inspirations for organometallic and coordination compounds that are functional mimics of hydrogenases. Current synthetic catalysts can be split into two categories: those that use rare-earth metals like platinum, palladium and iridium and those that use earth-abundant metals like nickel, iron or cobalt. Catalysts that use rare earth metals are very effective at hydrogen conversion because of their low operating potential, which is very close to 0 V vs. SHE. However, catalysts that use these metals are not viable in the long term due to the high cost of rare-earth metals. Earth abundant metals are less expensive and therefore represent a more realistic solution to the energy problem.

Developing a transition metal catalyst requires three things, it must be commercially viable, robust, and operate at a low overpotential. A catalyst’s robustness is a measure of its stability. A robust catalyst is stable in air and water, and has a high turnover number (turnover number is the number of catalytic cycles a catalyst can complete before decomposition). A catalyst should be able to be reduced reversibly, if reducing protons causes an irreversible oxidation of the complex, it is useless as a catalyst, because the original catalytic species won’t be regenerated. Cyclic voltammetry (CV) is a useful tool for probing the redox activity of a metal complex. If a proton source (acid) is introduced, CV can also be used to probe catalytic activity. If hydrogen is being formed, current enhancement is
observed with increasing proton concentration (figure 3). Cyclic voltammetry can also be used to determine overpotential. Overpotential is a measure of how much energy is required for a catalyst to reduce protons. A high overpotential suggests that the energy of activation barrier is too large for a catalyst to be useful.

**Figure 3.** Representative cyclic voltammogram showing increasing current with increasing proton concentration.

**Photocatalytic Systems for Hydrogen Generation**

While electrochemistry provides good insight into catalytic activity, ultimately the goal with any catalyst is to incorporate it into a photochemical system. This type of system draws even further inspiration from nature. In photosynthesis, photo-excited electrons are used to reduce NADP⁺ to NADPH. In an artificial photosynthetic system, a photosensitizer, which functions as a light absorber and a photoreductant, injects high-energy electrons into a semiconductor that mediates electron transfer to the catalyst to reduce protons. In an ideal system, water would act as both the proton and the electron source. In order for this to occur, the water must be split by a water oxidation catalyst, which would help promote forward electron flow as well as replenish the oxidized photosensitizer.
While this is an elegant theoretical solution, in practice this process is difficult to achieve. Splitting water into protons and oxygen requires a four electron oxidation, which is very difficult. Consequently, the best catalysts for water oxidation use noble metal centers. Also, back transfer of electrons from the semiconductor to the photosensitizer results in a loss of efficiency. In addition, electrons can be trapped in excited states below the conduction band of the semiconductor, which further decreases efficiency.\textsuperscript{10} For these reasons the water oxidation portion of this system can be replaced with a sacrificial electron donor like triethylamine, ascorbic acid or triethanolamine.

While hydrogen can be generated using artificial photosynthesis in a system that uses an organic solvent, a commercially feasible device must be able to work in an aqueous environment. For this reason, it is critical to research catalysts made from earth abundant metals that can reduce protons to hydrogen gas in aqueous environments before decomposing so as to maximize the efficiency of the system.
Chapter 2: Cobalt Catalysts for Proton Reduction

Abstract:

The development of stable proton reduction catalysts is imperative due to their importance as a source of a carbon-neutral fuel. A cobalt-salen complex with electron withdrawing groups was synthesized. This complex generated protons from organic solutions at a 190 mV overpotential with a $k_{obs}$ of $42000 \text{ M}^{-2}\text{s}^{-1}$, and a corresponding turnover frequency of $420 \text{ s}^{-1}$. This is one of the lowest overpotentials reported for a cobalt proton reduction catalyst. While insoluble in water, an experiment where water was added to an electrochemical cell showed a 20% increase in catalytic activity. This indicates that cobalt-salen complexes could be highly active in aqueous solutions.
**Introduction**

Currently, there are a number of molecular cobalt catalysts. Cobalt is frequently used because it is d⁹ like rhodium and iridium, which are both known to be catalytically active for hydrogen transfer reactions due to their ability to form hydride bonds. Currently some of the most efficient cobalt catalysts are the modified cobaloximes synthesized by Peters et al (figure 4). These derivatives were designed to be more stable and have lower overpotentials than cobalt dimethylglyoxime (Co dmg). Cobaloximes are easily prepared and evolve hydrogen from organic and aqueous solution at low overpotentials. Cobaloximes are also known to photocatalytically evolve hydrogen. A photosensitizer like Ru(bpy)₃²⁺ can be attached to a cobaloxime through the axial ligands. Unfortunately, these ligands are labile once the cobalt center is reduced and dissociate, leading to poor activity. Cobalt dithiolene (CoBDT) has also shown electro-and photocatalytic activity with high turnovers. Unfortunately benzene di-thiol is difficult to synthesize and expensive to purchase. While both of these catalysts are highly active, neither is suitable for a realistic artificial photosynthesis system. For this reason a cobalt catalyst must be developed that is both stable and affordable.
Redox Active Ligands:

In order for a first-row transition metal catalyst to catalyze multi-electron processes effectively, these metals must be complexed with non-innocent, or redox active ligands. Frequently redox changes occur one electron at a time for first row transition metals; multiple, consecutive one-electron transfers at a metal can lead to side reactions that are not conducive for catalysis. This can be avoided by using redox active ligands. Redox active ligands have multiple electronic structures which can complicate assigning a formal oxidation state to the metal. This allows for multi-electron processes to occur more efficiently because redox reactions can occur on both the ligand and the metal. Because of this, noble-metal free systems can show activity previously only achieved using noble metals, which easily perform multi-electron processes.

Salen ligands are known to be redox active, and their complexes with first row transition metals are useful as oxidation catalysts that mimic galactose oxidase. Furthermore, salens are easily synthesized, and synthesis of a salen proton reduction compound could potentially be scaled up to an industrial level. This combination of factors made studying a cobalt-salen complex for proton reduction of great interest.
Experimental

Materials:

All reactions were performed in air unless otherwise noted. All reagents were purchased from Fisher Scientific and used without further purification unless otherwise noted.

Instrumentation:

$^1$H and $^{13}$C NMR spectra were taken using a Varian Mercury VX 400 MHz spectrometer operating in pulse Fourier transform mode. All chemical shifts were referenced to residual solvent. All electrochemical experiments were carried out under argon atmosphere using a CH Instruments 620D potentiostat. Cyclic voltammograms were obtained using a three-electrode cell with a glassy carbon working electrode, a platinum auxiliary electrode, and a standard calomel electrode for the reference. Before each acquisition the working and auxiliary electrode were polished on a cloth-covered polishing pad in a paste made using 0.05 μm alumina powder and water. The electrodes were then washed with water and acetonitrile to remove alumina from the electrode surface before acquisition. Ferrocene was used as an internal standard to account for the drifting of the reference. Controlled-potential coulommetry was carried out in a four-neck flask using vitreous carbon working and auxiliary electrodes and a silver wire reference electrode. A CH Instruments 620D potentiostat was used for this as well. Gas analysis for $\text{H}_2$ was performed on a Bruker Scion 436 gas chromatograph using Ar carrier gas and calibrated with multiple known mixtures of $\text{H}_2/\text{CH}_4$ gas.
X-Ray Diffractometry:

Single crystals were mounted on glass fibers. All data for 3 were collected using graphite-monochromated Cu Kα radiation (λ= 1.54187 nm) on a Bruker-AXS three-circle diffractometer, equipped with a SMART Apex II CCD detector. The data were corrected for Lorentz effects and absorption using SADABS.

Syntheses:

\[
\begin{align*}
2 & \quad (\text{OH})_2 \quad (\text{O}_2\text{N})_2 \\
\text{H}_2\text{N} & \quad \text{NH}_2 \\
\text{EtOH} & \quad -2 \text{H}_2\text{O}
\end{align*}
\]

Scheme 1. Synthesis of the nitro substituted salen ligand.

2,2'-(\((1E,1'E)\)-(cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene) bis(4nitrophenol) \((1)\). Trans-1,2-diaminocyclohexane (0.180 mL, 1.50 mmol) and potassium hydroxide (0.169 g, 3.01 mmol) were dissolved in 1.5 mL ethanol and heated to reflux. The amine solution was then added dropwise to a hot, ethanolic solution of 5-nitrosalicylaldehyde (0.499 g, 2.99 mmol) and then refluxed for 30 minutes. A clear, deep red solution was formed. The product was evaporated under vacuum to give a red solid. 84% yield. \(^1\)H NMR (DMSO): δ 8.55 (d, 2H), 8.40 (d, 2H), 7.74 (s, 2H), 6.1 (d, 2H), 3.46 (s, 2H), 1.78 (m, 8H).
**Scheme 2.** Synthesis of cobalt dinitro-cyclohexyl salen (2)

**Cobalt dinitro-cyclohexyl salen:** .1 g of 1 was dissolved in 30 mL of methanol and .082 g of Co(BF)$_4$*6H$_2$O was dissolved in 11 mL of methanol. Both solutions were heated to reflux and then the cobalt solution was added dropwise to the ligand solution. After complete addition of the cobalt solution, the combined solution was refluxed for 30 minutes. A brown precipitate was formed. After reflux the solution was filtered through a celite plug and the filtrate was mixed with activated carbon to remove organic impurities. The filtrate was then filtered through celite until the solution was free of particulate matter. This solution was concentrated and slow diffusion of methanol through toluene yielded dark red needle crystals. 42% yield. The desired product was confirmed by high-resolution mass spectrometry. The radical cation was observed with a difference of less than 1 ppm.

**Scheme 3.** Synthesis of the unsubstituted salen ligand 3
2,2′-((1E,1′E)-(cyclohexane1,2diylbis(azanylylidene))bis(methanylylidene))

diphenol (3): Trans-1,2-diaminocyclohexane (0.120 mL, 1.00 mmol) was dissolved in 25 mL ethanol and was added dropwise to an ethanolic solution of salicylaldehyde (0.215 mL, 2.02 mmol). The resulting solution was then refluxed for thirty minutes. A clear, yellow solution was produced. Solvent was removed by evaporation under vaccuum leaving a bright yellow solid behind. NMRs matched literature values.\(^1\) H NMR (CDCl\(_3\)): \(\delta 13.33\) (s, 2H), 8.25 (s, 2H), 7.23 (m, 2H), 7.15 (m, 2H), 3.32 (m, 2H), 1.65 (m, 10H).

Cobalt cyclohexyl salen (4): Cobalt(II) tetrafluoroborate hexahydrate (0.106 g, 0.31 mmol) and 3 (0.101 g, 0.31 mmol) were both dissolved in 30 mL of methanol. Both solutions were heated to near reflux, then the cobalt solution was added dropwise to the ligand solution. The resulting solution was refluxed for thirty minutes. A clear, red-orange solution was formed and stored in the refrigerator overnight. Solvent was removed by evaporation under vacuum leaving a brown solid behind. Crystals of 4 were grown by the slow diffusion of hexanes through dichloromethane.
3-formyl, 4-hydroxy benzoic acid (5). The synthesis of 5 was adapted from literature procedure.\textsuperscript{34} 3 g (21.7 millimoles) of 4-hydroxy benzoic acid was degassed with argon in a 3-neck round bottom flask. 3.06 g of hexamethylenetetramine (21.8 millimoles) was dissolved in 9 mL of trifluoroacetic acid and degassed with argon. 8 mL of TFA was degassed with argon and then added via canula to the degassed 4-hydroxy benzoic acid. The amine solution was then added to the acid solution via canula. This solution was then refluxed under argon for 3 hours, the solution turned from a milky white color to a clear orange color. After refluxing, the solution was allowed to cool to room temperature, then stirred in 60 mL of 4 M HCl for 2 hours. A pink precipitate formed. This precipitate was filtered by vacuum and washed abundantly with water to remove excess acid. This filtrate was dried overnight. 36% yield. \textsuperscript{1}H NMR (DMSO): $\delta$ 10.72 (s, 1H), 8.21 (s, 1H), 8.03 (d, 1H), 7.07 (d, 1H).
Potassium 3,3’-((1E,1’E)-cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(4-oxidobenzoate) (6):

230 mg of 3-formyl, 4-hydroxy benzoic acid (1.4 mmoles) was dissolved in 10 ml of 1:1 ethanol:water. 1 molar equivalent of trans-1,2-diamino cyclohexane tartrate was dissolved in 10 mL of 1:1 ethanol:water along with a molar equivalent of potassium carbonate. The acid was added dropwise to the amine solution. Upon complete addition the solution was refluxed for 1 hour. The solution turned yellow and a solid was obtained by evaporation of the solvent. This solid was recrystallized in ethanol to yield the desired product as a pale yellow powder. 57% yield. $^1$H NMR (DMSO): δ 8.55 (d, 2H), 8.40 (d, 2H), 7.74 (s, 2H), 6.1 (d, 2H), 3.46 (s, 2H), 1.78 (m, 8H).

Scheme 6. Synthesis of potassium 3, 3’-((1E,1’E)-cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(4-oxidobenzoate)
Scheme 7. Synthesis of cobalt di carboxylic acid salen (7)

Cobalt di-carboxylic acid-cyclohexyl salen (7). 25 mg of (3) (.004 mmoles) was dissolved in 5 mL of methanol. An equimolar amount of cobalt acetate tetrahydrate was dissolved in 5 mL of water. The two were mixed for 2 hours. A brown precipitate was formed and isolated by filtration. The solid was then washed with methanol to remove impurities and further dried by high vacuum.

Crystal Structure:

The crystal structure of 4 has been previously reported. Crystals were successfully grown using the published procedure (see scheme 4)

While crystals of 2 were obtained by slow diffusion of methanol through toluene, every crystal that was large enough to diffract was twinned. This lead to poor diffraction and as a result the structure was unsolvable. However, the Bravais lattice was obtained for 2 (monoclinic P).
**High Resolution Mass Spectrometry:**

High-resolution mass spectrum of 2 was recorded in THF/MeOH. Analysis was completed through positive electrospray ionization on a Burker 12 Tesla APEX-Qe FTICR-MS with an Apollo II ion source. The radical cation of 2 was observed with a difference of less than 1 ppm. (Spectrum located in appendix).

**Catalyst Concentration Experiments:**

A stock solution of 4.5 mM 2 was prepared by dissolving 2.1 mg of crystals in acetonitrile in a 10 mL volumetric flask. A 5 mL solution of .1 M tetrabutylammonium hexaphosphate (TBAPF₆) was prepared in an electrochemical cell with 44 mM TFA. The cell was then degassed with Ar. CVs were taken from 0 to -0.80 V without any catalyst and then catalyst stock solution was added to form a solution of 0.2, 0.3, 0.4, and 0.5 mM 2. CVs were obtained using a glassy-carbon working electrode, a platinum auxiliary electrode, and a SCE reference. The working and auxiliary electrodes were polished on cloth polish pad with a 0.05 μm alumina powder paste and rinsed with water and acetonitrile between acquisitions.

**Acid Concentration Experiments:**

0.5 mg of 2 was dissolved in an electrochemical cell containing 5 mL of acetonitrile and 0.1 M TBAPF₆. The cell was purged with argon. A CV was then taken from 0 to -0.85 V to show the reduction wave of the catalyst without acid. Subsequently 1.1 M TFA was added in 20 μL aliquots. As acid was added current enhancement was observed. CVs were obtained using a glassy-carbon working electrode, a platinum
auxiliary electrode, and a SCE reference. The working and auxiliary electrodes were polished on cloth polish pad with a 0.05 μm alumina powder paste and rinsed with water and acetonitrile between acquisitions.

**Determination of Overpotential:**
Overpotential was determined according to literature procedure. The potential at half the height of the catalytic wave was compared to the thermodynamic potential for proton reduction of TFA.

**Electrochemical tests for homogeneity**
Metal complexes are known to occasionally form heterogeneous compounds with electrode surfaces. To make sure that 2 does not form such compounds a rinse test was performed. A cell with .5 mg of 2 was prepared with .1 M TBAPF₆ in 5 mL of CH₃CN, along with .33 mM TFA. A CV was then taken from 0 to -1.4 V. A catalytic wave was observed. The electrodes were then rinsed with ~ 200 mL of CH₃CN without polishing. They were then placed in a clean cell containing no catalyst and 30 uL of acid. Another CV was taken using the same parameters. No catalysis was observed. This indicates that no heterogeneous substance is formed on the electrode surface.

Another control experiment was performed to assure that the metal precursor is not responsible for hydrogen catalysis. To test this, an electrochemical cell with 0.5 mg of Co(BF₄)₂ and .1M TBAPF₆ in 5 mL of CH₃CN was prepared. An acid addition experiment was then performed following the same procedure as
previously listed. No reversible redox couple, or catalytic wave was observed in this experiment, indicating that Co(BF$_4$)$_2$ is not the catalytic species.
Results and Discussion

Once complex 4 was successfully synthesized it was important to characterize it as an electrocatalyst. Cyclic voltammetry (CV) was used to test its catalytic activity. However, the catalytic potential of the un-substituted ligand was far too cathodic for it to be a useful catalyst (figure 5). However, we theorized that adding electron-withdrawing groups to the ligand would anodically shift the reduction potential. This occurs because drawing electron density away from the metal makes it easier to reduce.

After synthesizing 2, it was important to confirm that the desired product was obtained. However, this proved to be challenging. Co^{II} is a paramagnetic species, which prevented 2 from being characterized by \(^1\)H NMR. In many cases X-ray crystallography can also be used to confirm the structure of a compound. While crystals of 2 large enough to diffract were obtained by slow diffusion of methanol through toluene, these large crystals were twinned, which lead to poor diffraction. The desired product was confirmed with high-resolution mass spectrometry, which showed the radical cation with less than 1 ppm difference (figure 15).

After confirming that the desired product was obtained, it was important to compare the dinitro- substituted complex to the original un-substituted complex. CV showed that the reduction potential of 2 was -0.65 V, 0.80 V more positive than 4 (figure 6). This anodic shift was the desired result of adding the nitro substituents and yielded a complex with a useful redox potential. Acid addition experiments determined that 2 was able to reduce protons at a much lower potential than 4.
Figure 5. CV of 4 with 2.2 mM (red), 4.4 mM (green), 6.6 mM blue, and 8.8 mM (orange) TFA added. No catalytic wave is observed, even at very negative potentials. This indicates that 4 is not useful as a catalyst.
After determining that the redox potential of 2 was not too cathodic for proton reduction, it was important to characterize it as an electrocatalyst. CVs of 2 in acetonitrile show a reversible redox couple at -0.65 V. Upon the addition of a proton source, trifluoroacetic acid (TFA), an irreversible reduction was observed at
nearly the same potential as the original redox couple. As additional acid was added greater current enhancement was observed at this potential (figure 7), and an $i_c/i_p$ of 6.22 was observed. $i_c/i_p$ is the ratio between the peak current density of the catalytic wave and the current density of the redox wave before acid is added. An $i_c/i_p$ of greater than 4 indicates that a catalytic process was occurring (for determination of $i_c/i_p$ see appendix).

![Figure 7](image.png)

**Figure 7.** CV of 0.5 mg 2 in 5 mL acetonitrile with .1 M TBAPF$_6$ from 0 to -0.85 V, without acid (black) and with 2.2 mM (red) 4.4 mM (green), 6.6 mM (blue) and 8.8 mM (orange) TFA. A catalytic wave is observed at the reduction potential with an $i_c/i_p$ of 6.22
Kinetic data can also be obtained from CV. By plotting current density versus acid concentration, the rate law dependence on proton concentration can be deduced. A linear relationship between current density and acid concentration indicates a second order dependence on hydrogen, if hydrogen elimination is the rate-determining step. A linear relationship is observed because, in the electrochemical cell, proton concentration is much greater than catalyst concentration. This causes the electrocatalytic process that is observed in CV to be the reaction of the metal hydride with the acid to form hydrogen (figure 8).13

![Graph](image)

**Figure 8.** The peak current density from figure 7 plotted against [TFA]. The linear relationship indicates a second order dependence on [$\text{H}^+$].
After determining the rate dependence on proton concentration, it was of interest to determine the rate dependence on catalyst concentration. This was determined by performing a catalyst concentration experiment (figure 9). The linear relationship between peak current density and catalyst concentration shows a first order dependence on catalyst concentration (figure 10). This give an overall rate law of Rate=$k[2][H^+]^2$.

Figure 9. CVs of 2 in acetonitrile and 44mM acid. The first trace is with only acid and no catalyst. As catalyst is increased from 0.2 to 0.5 mM current is enhanced, as expected for a first-order process.
After determining the kinetics of the catalytic process it was important to probe the efficiency of 2 as a catalyst. A catalyst’s efficiency is measured by determining the overpotential.

As previously discussed, the overpotential of a catalyst is a measurement of how far beyond the thermodynamic minimum a catalyst reduces protons. It is

Figure 10. A plot of peak current density with respect to catalyst concentration. The linear relationship indicates a first order dependence on catalyst concentration.
desirable for a catalyst to have a low overpotential so that the energy requirement to reduce protons is small.

To determine the overpotential of 2, the half potential of the catalytic wave (-0.65 V vs. SCE) was compared to the thermodynamic reduction potential of trifluoroacetic acid (-0.46 V vs. SCE) (a graphical representation of the determination of overpotential can be found in the appendix). It is necessary to compare the half potential to the thermodynamic potential, because hydrogen saturation at the electrode surface can lead to error when using the peak current density. The difference between these two potentials gives the overpotential of 190 mV. This value compares favorably with literature values. This value can also be lowered by modification of the ligand backbone. Preliminary studies have shown that the addition of two more nitro substituents lowers the overpotential close to the thermodynamic potential.

An estimation of catalytic rate is important for determining how active a catalyst is. While many authors have used a method that assumes that the catalytic process isn’t diffusion-limited at high scan rates, this method proved to be insufficient for Co-2, which even at high scan rates was not diffusion-limited. Due to these difficulties a different method needed to be used. Chang et al, showed that a $k_{obs}$ could be determined from a plot of $i_c/i_p$ vs. $[H^+]$ with respect to the inverse square root of scan rate. The slope of this line can be defined as:

$$m = \frac{(i_c/i_p)^*\sqrt{v}}{[H^+]^2} \quad (1)$$
For a second order process with respect to protons the equation that defines $i_c/i_p$ is:

$$\frac{i_c}{i_p} = \frac{n}{.4463} \cdot \sqrt{\left(\frac{RTk[H^+]}{Fv}\right)}$$  \hspace{1cm} (2)

where $n$ is the number of electrons in the process, $R$ is the gas law constant, $T$ is temperature, $F$ is the Faraday constant, and $v$ is the scan rate in $V/s$. From this equation we can solve for the previously defined slope giving the equation:

$$\frac{\left(\frac{i_c}{i_p}\right)\sqrt{v}}{[H^+]^2} = \frac{n}{.4463} \cdot \sqrt{\frac{RTk}{F}}$$  \hspace{1cm} (3)

From this equation we can solve for $k$ in terms of $m$ and constants giving the equation:

$$k_{obs} = \frac{F}{RT} \cdot \left(\frac{.4463m}{n}\right)^2$$  \hspace{1cm} (4)

This gives a $K_{obs}$ value in M$^{-2}$s$^{-1}$, which can be multiplied by the acid concentration for a given experiment to give the turnover frequency in inverse seconds.
Figure 11a. Graph of $i_c/i_p$ vs. $[H^+]$ at .5 V/s

Figure 11b. Graph of $i_c/i_p$ vs. $[H^+]$ at 1 V/s
Figures 11 and 12 show the plots used to determine $k_{obs}$. Substituting the slope in figure 12 into equation 4 gives a $k_{obs}$ of 42000 M$^{-2}$s$^{-1}$. This corresponds to a modest turnover frequency in 100 mM acid of 420 s$^{-1}$.

**Figure 11c.** Graph of $i_c/i_p$ vs. [H$^+$] at 5 V/s
An ideal catalyst is also robust. This means that it is has a high turnover number and is stable in aqueous environments. Although 2 is insoluble in water, by adding water to an electrochemical cell we can see how the presence of water affects catalytic activity. When 50 μL of H₂O was added to a cell containing 1.5 mM catalyst and 11 mM TFA. This increased the catalytic current by 20% (figure 13). These results indicate that a similar, water-soluble complex would be highly active in aqueous media.

**Figure 12.** The slopes of each graph from figure 11 plotted against $v^{-1/2}$. When the slope of this line is substituted into equation 4 it gives a $k_{obs}$ of 42,000 M$^{-2}$s$^{-1}$. 
Because these results suggest that a water-soluble salen would be highly active for proton reduction, it is of great interest to develop a water-soluble analog of 2. It is well known that adding a carboxylic acid or sulfonate substituent to a complex can increase its solubility in water.\textsuperscript{28} Schemes 5-7 show the synthesis of a carboxylic acid derivative salen that preliminary studies show is soluble in water. Further electrochemical tests will have to be done to determine its suitability for proton reduction.

**Figure 13.** CVs of 2 in acetonitrile without any acid added (black), with 11 mM TFA (pink) and with 11 mM TFA plus 50 μL of water (orange). The increase in current suggests that a similar, water soluble complex could be highly active.
These CVs also provide some measure of mechanistic insight. The original redox potential remains the same upon the addition of acid. This indicates that the first step in the catalytic process is an electrochemical step. This means that the mechanism is either ECEC or ECCE, electron transfer-chemical reaction-electron transfer-chemical reaction, or electron transfer-chemical reaction-chemical reaction-electron transfer. Studies have shown for other cobalt macrocycles that catalysis is a combination of ECEC and ECCE processes.9 Because our electrochemical data closely resembles those of similar compounds we can tentatively assign a similar mechanism to 2. Scheme 8 shows possible pathways by which hydrogen generation can occur. In these pathways the original Co(II) species is reduced to the corresponding Co(I) species which then reacts with a proton source to form a Co(III) hydride. This hydride can then either evolve a hydrogen radical, react with the acid to form hydrogen, or undergo another reduction to form a Co(II) hydride. This hydride can then undergo the same reactions as the first Co(III) species.

**Scheme 8.** Catalytic cycles proposed for similar cobalt complexes. Because our data resembles that of other complexes, 2 might catalyze hydrogen through similar pathways.
Conclusions:

A Co(II) Salen complex was synthesized and characterized to determine its feasibility as a catalyst for proton reduction. Cyclic voltammetry revealed 2 to be an active catalyst for proton reduction in acetonitrile. Protons were reduced at -.65 V vs. SCE, which gives an overpotential in trifluoroacetic acid of 190 mV. The catalytic rate of this reaction was measured to be 42000 M\(^{-2}\)s\(^{-1}\). Both of these values are comparable to values for other catalysts. For example, Co(dmg) has a turnover frequency of of 42s\(^{-1}\), and the overpotential of a modified bi-metallic cobaloxime is 954 mV.\(^{13,30}\) Furthermore, the overpotential can be improved by adding more electron withdrawing substituents to the ligand framework. Despite solubility issues in aqueous environments, catalytic activity was enhanced in the presence of water. For this reason it is of great interest to develop a water-soluble cobalt-salen complex.

To increase solubility in aqueous solutions a salen with carboxylic acid substituents was synthesized. These substituents increased solubility in water and further experiments will have to be done to determine its catalytic activity.

Future work with these complexes would include increasing turnover frequency, as other cobalt catalysts are capable of higher turnover frequencies. This could be accomplished by modifying the ligand to have a proton relay in the second coordination sphere.\(^{29}\) The photocatalytic activity of these complexes would also be of interest. If highly photocatalytic, the complex could be easily incorporated into a molecular system for hydrogen generation due to the easily modifiable ligand
backbone. Furthermore because these catalysts are more active in water, an artificial photosynthesis system that incorporates a water-soluble salen could be feasible.
Appendix

Figure 14. $^1$H NMR of 1
Figure 15. High res mass spectra of 2
Figure 16. $^1$H NMR of 3
Figure 17. $^1$H NMR of 5
Determination of Overpotential:

![Graph showing the determination of overpotential](image.png)

**Figure 18.** A graphical representation of the determination of overpotential. $E_{TFA}$ is the thermodynamic potential for the reduction of protons to hydrogen for TFA in acetonitrile. $E_{1/2}$ is one half of the peak current density. The difference between these two values is the overpotential.
Determination of $i_c/i_p$

Figure 19. A representative cyclic voltammogram showing where the values for $i_c$ and $i_p$ are obtained.
Electrochemical Tests for Homogeneity

**Figure 20.** A CV of 2 in a 5mL cell with .33mM acid (red), and after rinsing, in a cell that contains only .33mM acid (blue).
Figure 21. CV of Co\((\text{BF}_4)_2\) with no acid (green), .22 mM TFA (red) and .44 mM TFA (blue).
Chapter 3: Nickel Catalysts for Proton Reduction

Abstract:

Developing first row transition metal complexes for electro- and photocatalytic hydrogen evolution is of great interest. A photocatalyst for proton reduction could be incorporated into an artificial photosynthesis device to generate hydrogen gas as a solar fuel. Nickel was complexed with the H$_3$ttfasbz ligand, which is known to be redox active.$^{35}$ In order to assess its catalytic ability electrochemical tests, including proton concentration experiments, and catalyst concentration experiments were performed. These tests showed the nickel complex to be highly active for hydrogen reduction at a cathodic potential (-1.37 V vs. SCE). Due to the high overpotential of this complex, it was integrated into a photocatalytic system with fluorescein as a chromophore.
**Introduction**

Nickel is an ideal metal center for a proton reduction catalyst for a variety of reasons. In nature, nickel-iron hydrogenases are prolific. For this reason synthetic catalysts frequently use nickel to provide a robust metal-center for the catalytic generation of hydrogen gas. Furthermore, nickel is d-like platinum, which is one of the most effective metals for proton reduction. The similar electronic structure could potentially lead to similar catalytic activity.

Nickel catalysts for proton reduction are well documented. Some of the most active proton reduction catalysts reported use nickel as the metal center. For example, DuBois et. al. report a P₂N₂ nickel complex that reduces protons at ~ -0.48 V vs. standard calomel electrode (SCE) at turnover frequencies of over 100,000 s⁻¹.

Nickel compounds have also been shown to exhibit photocatalytic activity. Han et. al. reported a noble-metal free system for the photocatalytic generation of hydrogen. This system was able to generate hydrogen for over 30 hours and had over 7000 turnovers.

Our goal was to construct a similar system that efficiently evolved hydrogen.

**Figure 22:** Nickel pyridinethiolate complexes that have been shown to be electro- and photocatalytically active.
photocatalytically. However, electrochemical experiments needed to be performed first to determine our catalyst’s suitability for this application.
Experimental

Materials:

All materials were purchased from Fisher Scientific and used without further purification unless otherwise noted.

Instrumentation:

All electrochemical experiments were carried out under argon atmosphere using a CH Instruments 620D potentiostat. Cyclic voltammograms were obtained using three electrode cell with a glassy carbon working electrode, a platinum auxiliary electrode, and a standard calomel electrode for the reference. Before each acquisition the working and auxiliary electrode were polished on a cloth-covered polishing pad in a paste made using 0.05 μm alumina powder and water. The electrodes were then washed with water and acetonitrile before being put into the cell. Ferrocene was used as an internal standard to account for the drifting of the reference.

X-Ray Diffractometry:

Single crystals were mounted on glass fibers. All data for were collected using graphite-monochromated Cu Kα radiation (λ= 1.54187 nm) on a Bruker-AXS three-circle diffractometer, equipped with a SMART Apex II CCD detector. The data were corrected for Lorentz effects and absorption using SADABS. The structure was solved using direct methods. Least squares refinement was carried out for F² for all reflections. The structure was refined using the SHELXTL software package.
Catalyst Concentration Experiments

A stock solution of 1.0 mM 6 was prepared by dissolving 3.2 mg of crystals in acetonitrile in a 5 mL volumetric flask. A 5 mL solution of .1 M TBAPF₆ was prepared in an electrochemical cell with 0.66 mM TFA. The cell was then degassed with Ar. CVs were taken from 0 to -1.4 V without any catalyst and then catalyst stock solution was added to form a solution of 0.02, 0.03, 0.04, and 0.05 mM 6. CVs were obtained using a glassy-carbon working electrode, a platinum auxiliary electrode, and a SCE reference. The working and auxiliary electrodes were polished on a paste of 0.05 um alumina powder and water on a cloth polish pad and rinsed with water and acetonitrile in between acquisitions.

Acid Concentration Experiments

0.5 mg of 8 were dissolved in an electrochemical cell containing 5 mL of acetonitrile and 0.1 M TBAPF₆. The cell was degassed with Ar. A CV was then taken from 0 to -1.4 V to show the reduction wave of the catalyst without acid. Subsequently TFA was added in 20 uL aliquots. As acid was added current enhancement was observed. CVs were obtained using a glassy-carbon working electrode, a platinum auxiliary electrode, and a SCE reference. The working and auxiliary electrodes were polished on a paste of 0.05 um alumina powder and water on a cloth polish pad and rinsed with water and acetonitrile in between acquisitions.
Determination of Overpotential

Overpotential was determined according to literature procedure. The potential at half the height of the catalytic wave was compared to the thermodynamic potential for proton reduction of TFA.
Results and Discussion:

After determining that the desired nickel catalyst had been obtained it was of interest to deduce its structure. X-ray crystallography was used to determine the structure. An interesting, asymmetrical binding pattern was observed (figure 22). H₃ttfasbz can exist as a tri-anionic or di-anionic ligand. In order to keep the preferred Ni^{II} oxidation state, and square planar geometry, it adopts a di-anionic form, which leads to the observed asymmetrical binding pattern.

![ORTEP diagram](image)

Figure 23. ORTEP diagram of Ni(Httfasbz) (8). Orbs are at 50% probability. Hydrogens have been omitted for clarity. Ni (teal), S (yellow), N (blue), Fl (green). Selected bond lengths and angles have been included in the appendix.

Once the structure of Ni(Httfasbz) was determined it was important to test its catalytic properties. CVs of 8 in acetonitrile reveal a semi-reversible redox couple at -0.85 V vs. SCE. Upon the addition of a proton source (TFA), an irreversible reduction was seen at -1.35 V vs. SCE. The addition of more TFA caused
an increase in current, with an $i_c/i_p$ of 6.4 observed in the presence of .66 mM TFA (figure 24).

![Figure 24](image)

**Figure 24.** CV of 6 in .1 M TBAPF$_6$ with no acid (black), 0.22 mM acid (red), 0.33 mM acid (orange), 0.44 mM acid (green), 0.55 mM acid (blue), and 0.66 mM acid (purple).

This acid addition experiment also reveals kinetic information about 8. By plotting peak current density vs. proton concentration the rate law dependence on acid concentration can be determined. A linear relationship suggests a second-order dependence on proton concentration (figure 25).
In order to determine the full rate equation the catalytic dependence on catalyst concentration must be determined. This dependence was determined by doing a catalyst concentration study (figure 25). The linear relationship between peak current density and catalyst concentration shows a first order dependence on catalyst concentration (figure 26). This gives an overall rate law of \( k = [B][H^+]^2 \)

**Figure 25.** The peak current density from plotted against [TFA]. The linear relationship indicates a second order dependence on \([H^+]\).
Figure 26. CVs of 6 in 0.66mM TFA with 0.02 mM 6 (black), 0.03 mM 6 (red), 0.04 mM 6 (green), and 0.05 mM 6 (blue)
After determining that 8 was catalytic, it was important to verify that a heterogeneous substance wasn’t being formed and generating hydrogen. Nickel catalysts have been shown to form heterogeneous compounds with glassy carbon during electrocatalysis.\textsuperscript{31} To make sure that Ni(Httfasbz) was not being absorbed onto the electrode to make a heterogeneous species a rinse test was done. A cell with .5 mg of 8 was prepared with .1 M TBAPF\textsubscript{6} in 5 mL of CH\textsubscript{3}CN, along with .33 mM TFA. A CV was then taken from 0 to -1.4 V vs. SCE. A catalytic wave was observed. The electrodes were then rinsed with~ 200 mL of CH\textsubscript{3}CN without polishing. The electrodes were then placed in a clean cell containing no catalyst and .33 mM acid.

\textbf{Figure 27.} Peak current density vs. [8]. The linear relationship suggests a first order dependence on catalyst concentration.
Another CV was taken using the same parameters. No catalysis was observed. This indicates that no heterogeneous substance is formed on the electrode surface (figure 27).

![Figure 28](image)

**Figure 28.** An overlay of the CVs in the rinse test. No catalysis was observed after rinsing the electrodes (purple).

For any metal catalyst, it is important to make sure that the metal precursor is not the species catalyzing the reduction of protons. To see if NiCl₂ was responsible for proton reduction, a cell was prepared with .5 mg of NiCl₂, .1 M TBAPF₆ in 5 mL of CH₃CN. CVs were taken from 0 to -1.4 V vs. SCE (figure 28). No reversible redox couple was and upon addition of acid a current enhancement was observed, however, it was not catalytic. These results indicate that NiCl₂ is not the catalytic species.
Figure 29. CVs of NiCl₂ in CH₃CN. No reversible redox couple is observed, and while there is current enhancement when acid is added it is not catalytic.
Conclusions

Ni(Httfasbz) has been characterized as an electrocatalyst. A rate law has been determined to be \( R=k[8][H^+]^2 \). The overpotential was determined to be 890 mV. CV shows that it is an active catalyst for the electrocatalytic reduction of protons to hydrogen. Despite the high overpotential of 8 it could be incorporated into a photochemical system for proton reduction if a highly reducing chromophore was employed.
Appendix

Figure 30. $^1$H NMR spectra of H$_3$ttfasbz
Figure 31. $^{13}$C NMR of H$_{3}$ttfasbz
Table 1. Selected bond lengths [Å] and angles [°] for 8.

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References:


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(35) Ali, M.; Berhardt, P. V.; Brax, M. A. H.; England, J.; Farlow, A. J.; Hanson, G. R.