

5-2014

Cobalt Salen Complexes for Catalytic Hydrogen Production

Matthew J. Van Dongen
College of William and Mary

Follow this and additional works at: <https://scholarworks.wm.edu/honorsthesis>

 Part of the [Inorganic Chemistry Commons](#)

Recommended Citation

Van Dongen, Matthew J., "Cobalt Salen Complexes for Catalytic Hydrogen Production" (2014).
Undergraduate Honors Theses. Paper 68.
<https://scholarworks.wm.edu/honorsthesis/68>

This Honors Thesis is brought to you for free and open access by the Theses, Dissertations, & Master Projects at W&M ScholarWorks. It has been accepted for inclusion in Undergraduate Honors Theses by an authorized administrator of W&M ScholarWorks. For more information, please contact scholarworks@wm.edu.

Cobalt Salen Complexes for Catalytic Hydrogen Production

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

by

Matthew Joseph Van Dongen

Accepted for _____
(Honors)

William R. McNamara, Director

Robert D. Pike

Kristin L. Wustholz

Scott B. Ickes

Williamsburg, VA
May 1, 2014

TABLE OF CONTENTS

Acknowledgments	4
List of Figures	6
Abstract	8
Introduction	9
Global Energy Concerns and Climate Change	9
Renewable Energy and Solar	10
Artificial Photosynthesis	11
Earth Abundant Catalysts for Proton Reduction	13
Cobalt-salen Complexes	14
Experimental	17
Materials	17
Instrumentation	17
Synthesis of Ligands	18
Synthesis of Complexes	29
Crystal Growth	37
Electrochemistry of Cobalt Cyclohexylsalen Complexes	37

Results and Discussion	38
Catalyst Design	38
Electrochemical Studies	40
Conclusions	48
References	49

Acknowledgements

First and foremost, I would like to thank Dr. William McNamara for his guidance throughout this project. Completing research in this group has been one of the most rewarding experiences of my college career, and I regard this honors thesis as my most significant academic accomplishment to date. Thank you for welcoming me into your lab while you were still a post-doc at Rochester and knew almost nothing about me except that I was enthusiastic about inorganic chemistry research. I greatly appreciate your mentorship and advice and thank you for giving me a solid foundation in chemical research.

I would also like to thank the rest of the chemistry department here at the College. I have had nothing but positive experiences throughout my studies here, and I am truly thankful for the research opportunities I have been afforded thanks to this department's focus on undergraduate research. Particular thanks go to Dr. Gary DeFotis for giving me my first opportunity as a research student in his lab. Special thanks go to Dr. Robert Pike as well for helping me decide to pursue a chemistry major as my academic adviser and general chemistry professor freshman year.

Thank you Dr. Pike, Dr. Wustholz, and Dr. Ickes for serving on my honors committee. Each of you has put up with me for at least two semesters of classes, and I regard each of your classes as some of the most interesting and important of my college career. Dr. Pike and Dr. Wustholz, it was because of your teaching that I realized my interest in inorganic and physical chemistry. And Dr. Ickes, your public health and epidemiology courses further developed my passion to pursue a career in healthcare and opened my eyes to the importance of understanding health outside the realm of the doctor's office.

Additionally, I would like to honor and thank my late high school chemistry teacher Mr. Paul “Kaz” Kazmierczak. It was through his tutelage and friendship that I first developed an interest in chemistry. Kaz was the catalyst that eventually led me to choose chemistry over my original intent to major in biology. I am sad that I will not be able to share my accomplishment with him, but know that he would have been proud and excited to discuss my research.

Finally, I would like to thank the rest of the members of the McNamara lab. You all have made research a thoroughly enjoyable experience and I appreciate the bonds we have made as friends and chemists. Particular thanks go out to Patrick Crossland and Michael Allen for their work on the salen project. And extra special thanks go to Gannon Connor for keeping me sane throughout my honors work.

To everyone who has ever been there for me, in one capacity or another, thank you. Without all of your collective influences I would not be where I am today.

List of Figures

Fig. 1: Molecular Photosystem Setup	13
Fig. 2: [Fe-Fe] Hydrogenase Structure and Recent Salen Structure	15
Fig. 3: General Salen Synthesis Reaction	18
Fig. 4: Structures of Ligands with Unsubstituted Diamine Backbone	20
Fig. 5: Structures of Ligands with Phenyl Substituents on Diamine Backbone	22
Fig. 6: ^1H NMR Spectrum of 8	23
Fig. 7: ^{13}C NMR Spectrum of 8	24
Fig. 8: ^1H NMR Spectrum of 10	26
Fig. 9: ^1H NMR Spectrum of 11	27
Fig. 10: Structures of Ligands with Cyclohexyl Substituent on Diamine Backbone	28
Fig. 11: General Complex Synthesis Reaction	29
Fig. 12: Cobalt Complexes with Unsubstituted Backbone Ligands	31
Fig. 13: Cobalt Complexes with Phenyl Substituted Backbone Ligands	33
Fig. 14: Cobalt Complexes with Cyclohexyl Substituted Backbone Ligands	36
Fig. 15: CV of 21 in Acetonitrile Without Acid	31
Fig. 16: CV of 20 in Acetonitrile Without Acid	42
Fig. 17: CV of 18 in Acetonitrile Without Acid	43
Fig. 18: CV of 21 With TFA Additions	45
Fig. 19: CV of 20 With TFA Additions	46
Fig. 20: CV of 18 With TFA Additions	47

List of Tables

Table 1: Summary of Redox Couple Potentials	44
Table 2: Summary of Redox Couple and Catalytic Onset Potentials	47

Abstract

Several cobalt salen complexes were synthesized. Early solubility issues were solved by adding cyclohexyl and phenyl substituents to the diamine backbone of the ligand. Crystals were obtained for complexes **18**, **20**, and **21**. These complexes represent a series of compounds differing only in number of electron withdrawing substituents. Cyclic voltammetry was performed on **18**, **20**, and **21** to probe the catalytic activity of each compound. Initial CVs were taken in acetonitrile solutions. Subsequent CVs were taken with additions of TFA to prove the catalytic activity of each complex. It was found that **21**, containing the most electron withdrawing substituents, was the most active and had the most positive redox couple followed by **20**. **18** exhibited a very negative redox couple at -1.37 V and showed no catalytic activity.

INTRODUCTION

Global Energy Concerns and Climate Change

There are currently global crises concerning pollution, climate change, and long term energy security.¹ Approximately 17.5 TW of energy were consumed globally in 2010. Energy consumption is projected to rise to around 27.4 TW by the year 2050.² The vast majority of this energy is obtained from non-renewable resources; particularly fossil fuels like oil, natural gas, and coal.³ A couple of very important problems are associated with fossil fuel consumption. For one, fossil fuels are regenerated very slowly over millennia. Since these fuels are being consumed many orders of magnitude faster than they are being produced they will eventually be depleted. It is projected that there is enough oil, natural gas, and coal to last for several centuries with current projections of consumption rates, but it is important to develop solutions to the eventual issue of depletion before lack of energy resources becomes a critical problem.⁴ One of the most important current issues with fossil fuels is that obtaining and burning fossil fuels is environmentally unfriendly directly through destruction of natural spaces and indirectly by production of greenhouse gasses. Anthropogenic emission of greenhouse gasses, in particular CO₂, is considered to be the main factor in the current global warming trend. CO₂ emissions have steadily increased at an alarming rate since the Industrial Revolution. Current projections predict that CO₂ emission rates will continue to rise which could result in a global temperature increase of as much as 4°C by 2100. A temperature increase of such magnitude could prove to be disastrous ecologically with major changes in climates resulting in mass extinctions, land lost to rising ocean levels, and changing seasonal patterns disrupting flora and fauna.⁵

Renewable Energy and Solar

Efforts are being made to develop renewable, green technologies for energy production to help slow or even reverse anthropogenic climate change as well as to ensure ample energy sources will be available long into the future. Current renewable energy sources include wind, hydro, geothermal, and solar. Of these, solar offers perhaps the greatest potential as a major renewable resource worldwide. Solar energy has the advantage of being available in every region of the world unlike the other renewable sources mentioned. Solar is also advantageous because an enormous excess of energy strikes the Earth each year; approximately 1.2×10^5 TW annually, or about 7000 times the world's annual consumption.^{2,4} However, solar power does have issues with regard to storage for times when the Sun is not shining. It is also currently a rather inefficient and expensive process with a theoretical maximum efficiency of 68% energy conversion when using unconcentrated sunlight.⁶ The current cost of solar energy makes it quite prohibitive. Solar electricity cost about \$0.35 per kW-hr in 2006 compared to only \$0.02-0.05 per kW-hr for fossil fuel derived electricity.⁴ This cost is largely because solar energy is much more diffuse than other forms making collection more difficult and costly.

Most solar energy is produced by photovoltaics which utilize charge separation across a light absorbing material, usually a semiconductor, to generate an electrical current.⁷ Photovoltaics work well while the sun is shining, but long term storage for later use presents a major problem. Some possible storage techniques include kinetic methods (use solar energy to move water up a hill then capture energy as it is allowed to flow back down), electrochemically in the form of a battery, or chemically in atomic bonds. Of these methods, storing solar energy in chemical bonds is perhaps the most important in current research.

Artificial Photosynthesis

One method of using solar energy to synthesize a chemical fuel is through artificial photosynthesis. The goal of photosynthesis in organisms is to utilize solar radiation to store energy in the chemical bonds of glucose and other sugars. Plants and some single-celled organisms, collectively known as photoautotrophs, convert carbon dioxide and water into sugars using the energy of the sun to fuel several reactions occurring in specialized organelles. The goal is the same in artificial photosynthesis. However, unlike organisms which produce glucose and other carbon based chemical fuels, artificial photosynthesis is usually utilized for production of hydrogen gas. Hydrogen gas is formed via the catalytic reduction of water. Pure hydrogen can in turn be used to create fuel cells; clean energy sources whose only byproducts are H₂O when burned.

Hydrogen is an excellent choice as a clean fuel source for many reasons. For one, it is easily produced from electricity and can easily be converted back into electrical energy.⁷ The main raw material for hydrogen production via artificial photosynthesis is water, which is ideal because of its abundance and because it poses little risk to the environment. Hydrogen's energy can be obtained through multiple different routes including standard flame combustion and electro-chemical conversion. Hydrogen also produces very few pollutants when burned with air; H₂O being the main byproduct of combustion. Hydrogen has the ability to potentially replace much of our current hydrocarbon consumption in a new "hydrogen economy".⁸ The hydrogen economy is a vision where hydrogen is utilized as the main source of energy. In order to realize this vision while being truly environmentally friendly, however, clean methods of producing hydrogen are necessary.

Currently the largest proportion of hydrogen is produced from hydrocarbon sources like methane.⁹ The process is known as steam-reforming and involves reacting methane with steam and a small amount of catalyst under high temperature and pressure conditions. This process produces hydrogen and carbon monoxide, with carbon dioxide produced from a subsequent reaction between carbon monoxide and water.¹⁰ Though it is clean burning, hydrogen is still a not a carbon neutral fuel source because of these production methods. Artificial photosynthesis offers an answer to this problem.

Though the overall process of biological photosynthesis is congruous with what is achieved in artificial photosynthesis, it is the reactions which occur in photosystem I and photosystem II which are most relevant to research in catalytic hydrogen production. In photosystem II two water molecules are oxidized to yield diatomic oxygen and four protons. In photosystem I the electrons taken from the oxidation of water in photosystem II fill an electron deficit in an electron acceptor thereby reducing the acceptor. Photosystem I is what is replicated in the catalytic reduction of water, with electrons provided by an electric current and protons being reduced to hydrogen.

The ultimate goal of artificial photosynthesis research is to develop molecular photosystems which can be placed in aqueous solution and generate hydrogen upon illumination with sunlight. The basic structure of these photosystems is a dye-sensitized chromophore attached to a semiconductor which is attached to a catalyst (**Fig. 1**). When sunlight excites the chromophore an electron can be transferred into the conduction band of the semiconductor. The electron then transfers to the catalyst where the catalytic reduction of protons occurs at the metal center.

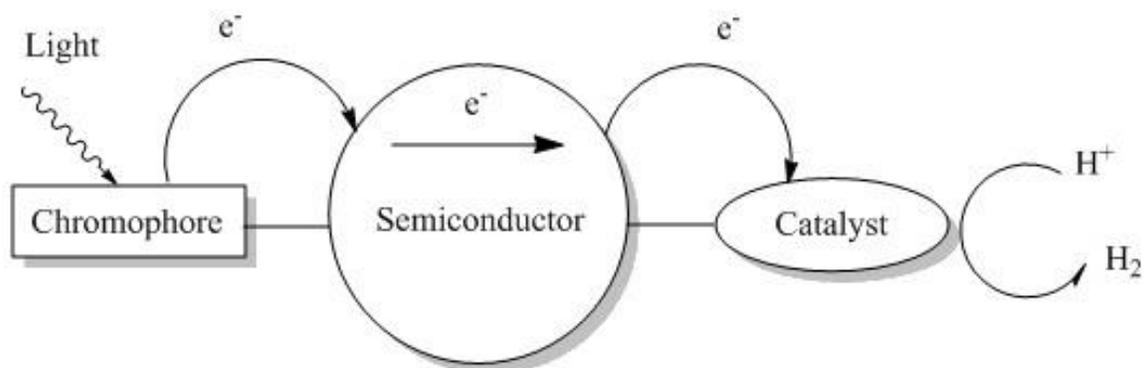


Figure 1. Basic design of a molecular photosystem for photocatalytic production of hydrogen in aqueous solution.

Precious metals such as platinum and their associated complexes are very efficient catalysts for proton reduction, but their undesirably high cost and scarcity make them impractical for any sort of real world application. Because of the prohibitive costs associated with precious metals, current research in artificial photosynthesis focuses largely on developing new catalysts containing abundant earth metals. Catalysts for this process must be inexpensive, must not decompose quickly, and must not require too negative of a potential to work effectively. That the catalysts work at a relatively positive potential is important in order to reduce the amount of energy necessary to start the catalytic process. Much research has been devoted to the development of nickel, cobalt, iron, and molybdenum coordination complexes in particular.¹¹

Earth Abundant Catalysts for Proton Reduction

An ideal catalyst for hydrogen production must be robust, have a low overpotential, and be stable in aqueous solutions. The catalyst must also be made of earth abundant for commercial purposes where cost-effectiveness is of utmost important. The turnover number (TON) of a catalyst is defined by the number of catalytic cycles it can withstand before decomposing, and

the higher the turnover number the more active the catalyst. TON is an indicator of robustness. A catalyst must be able to be both oxidized and reduced in a full catalytic cycle. If the complex cannot be regenerated at the end of a catalytic cycle it is effectively useless for any practical applications. Another related term is the turnover frequency (TOF); which is defined as the number of moles of hydrogen produced per unit time per mole of catalyst. TOF gives a good idea of the catalytic activity of a complex. The catalyst must have a low overpotential; which is a thermodynamic measure defined as the difference between the applied potential and the standard potential for hydrogen formation. The overpotential can be thought of as a parameter quantifying the driving force of a reaction. A good catalyst for hydrogen production via artificial photosynthesis must also be stable in water. Hydrogen production in aqueous solutions would be impossible if the catalyst decomposed in water.

Cobalt-salen Complexes

Catalysts for artificial photosynthesis have often been modeled after the hydrogenase enzyme found in biological systems.¹² In the natural context hydrogenase is a very effective catalyst of hydrogen production from water. Hydrogenase has a low overpotential and high turnover frequency which makes it similar to platinum catalysts in efficiency at catalyzing reductive splitting of water.¹³ Hydrogenase contains iron and nickel metal centers, demonstrating that earth abundant metals can be used effectively in hydrogen production. It is proposed that the nitrogen of an azadithiolate ligand mediates proton transfer at the active site in [FeFe] hydrogenase (**Fig. 2**).¹⁴ Because of the effectiveness of hydrogenase, coordination complexes containing metal-nitrogen bonds are expected to be potentially effective catalysts that have been inspired by hydrogenase.

One class of ligands that includes these metal-nitrogen bonds are salen. The most basic salen ligand is tetradentate and is synthesized by reacting ethylenediamine with two molar equivalents of salicylaldehyde in a condensation reaction. Salens are great ligands for study because they are highly tunable, easily synthesized, tetradentate, and very stable. One of the most famous uses of a salen-type ligand is in Jacobsen's catalyst, a manganese-salen complex originally described for catalytic epoxidation of unfunctionalized olefins.¹⁵ A cobalt complex with ligands closely related to salen was recently studied and has been found to catalyze hydrogen production. Mechanistic studies point to the metal bound nitrogens facilitating hydrogen production, an important discovery for the design of proton reduction catalysts (**Fig. 2**).¹⁶ It is worth noting that the oxygen containing derivative in **2b** is not active for proton reduction due to the presence of electron donating groups.

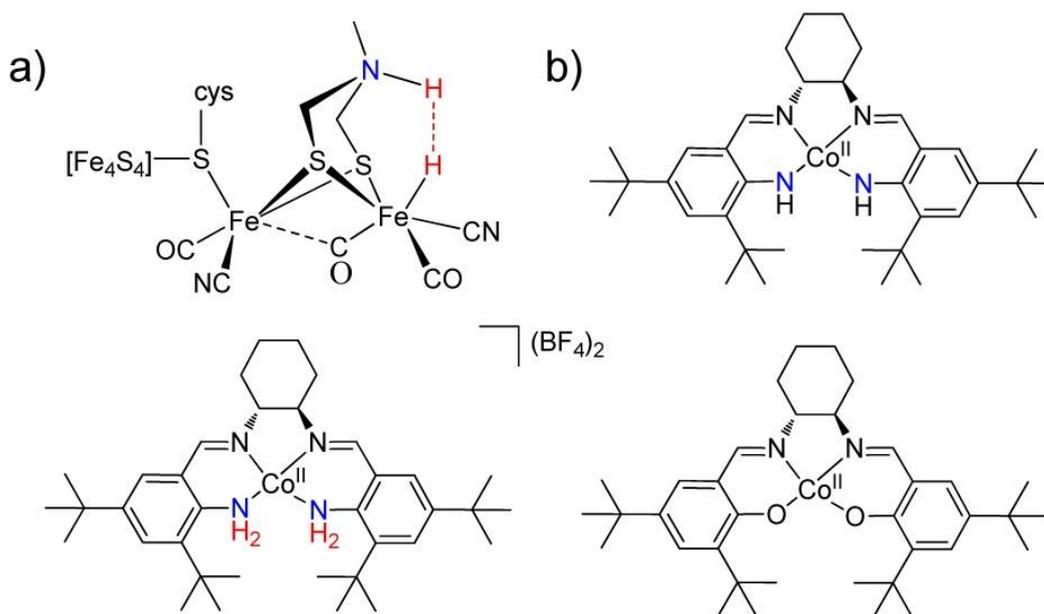


Figure 2. (a) The active site of [FeFe] hydrogenase highlighting the azadithiolate ligand and (b) the structures of some recently studied cobalt salen complexes.¹⁶

Though only nickel and iron are found in the metal centers of the active region of hydrogenase enzymes, complexes with cobalt as the metal center are also of great interest. Cobalt is a good choice for use in electrocatalytic complexes because it is earth abundant, highly active, and the +1, +2, and +3 oxidation states are accessible in redox chemistry.¹⁷ Drawing inspiration from hydrogenase, it is a major goal to create effective proton reduction catalysts from first row transition metals. Because cobalt salen complexes form tetradentate chelates they are very stable in general and potentially stable in water which is important because water is the main solvent of interest for proton reduction.

EXPERIMENTAL

Materials

All reactions were completed in the presence of air unless otherwise noted. All reagents were purchased from Thermo Fisher Scientific and used without purification unless indicated otherwise.

Instrumentation

^1H 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 containing a glassy carbon working electrode, a platinum auxiliary electrode, and a SCE reference electrode. The glassy carbon and platinum electrodes were polished before each run on a cloth polishing pad using 0.05 μm alumina powder mixed with water to form a paste. They were then washed with water and acetonitrile prior to being placed in solution. The SCE was rinsed with water and acetonitrile before the first run, and then left in place throughout the rest of the experiments.

Synthesis of Ligands

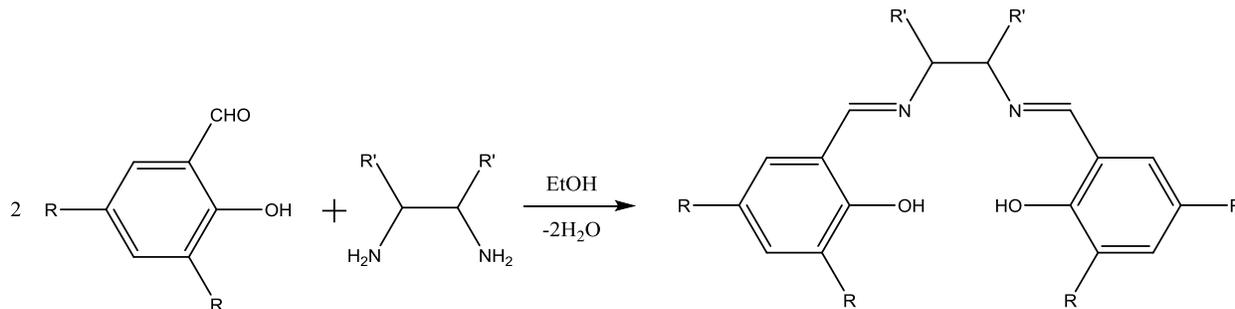


Figure 3. General scheme for salen ligand syntheses. 2 molar equivalents of aldehyde added to 1 molar equivalent of diamine in alcohol to yield salen ligands.

2,2'-((1E,1'E)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))diphenol (1).

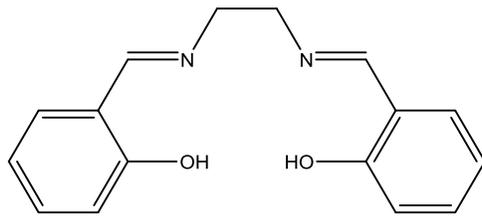
Ethylenediamine (0.14 mL, 2.05 mmol) was added to salicylaldehyde (0.44 mL, 4.09 mmol) dissolved in 5.2 mL absolute ethanol and left to stir for 45 minutes. The resultant solution was bright yellow and contained a yellow precipitate. 0.245 g of bright yellow solid was obtained upon filtration (yield = 45%). ¹H NMR (CDCl₃): δ 13.20 (s, 1H), 7.27 (m, 5H), 6.90 (m, 5H), 3.95 (s, 4H).

3,3''-((1E,1'E)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis([1,1'-biphenyl]-4-ol) (2). Ethylenediamine (33.5 μL, 0.50 mmol) was dissolved in 2.5 mL absolute ethanol and was added to an ethanolic solution of 4-hydroxy-biphenyl-3-carbaldehyde (0.200 g, 1.00 mmol). The aldehyde solution was heated to near reflux then the amine solution was added and refluxed for an additional hour. An orange solution with brown precipitate formed. About 0.080 g of light brown solid was obtained upon filtration (yield = 38%). ¹H NMR (CDCl₃): δ 13.25 (s, 1H), 8.45 (d, 2H), 7.45 (m, 16H), 4.20 (s, 4H).

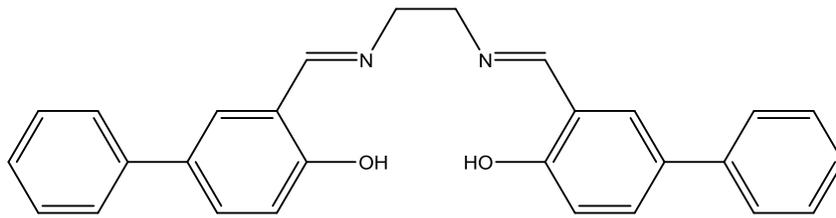
6,6'-((1E,1'E)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2,4-dibromophenol) (3). Ethylenediamine (59.5 μL, 0.89 mmol) and potassium hydroxide (0.102 g,

1.79 mmol) were dissolved in 1 mL absolute ethanol and added to an ethanolic solution of 3,5-dibromosalicylaldehyde (0.502 g, 1.79 mmol). The solution was refluxed for one hour producing a bright yellow solution with yellow precipitate. 0.096 g of yellow solid was obtained upon filtration (yield = 19%). ¹H NMR (CDCl₃): δ 8.25 (s, 2H), 7.70 (d, 2H), 7.35 (d, 2H), 4.00 (s, 4H).

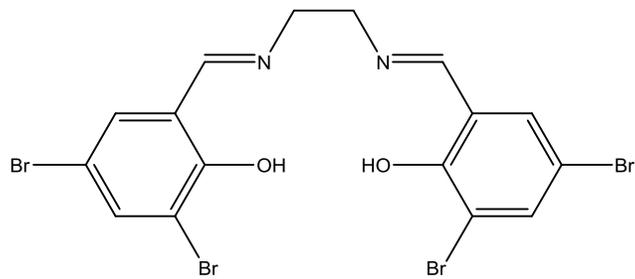
2,2'-((1E,1'E)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(4-nitrophenol) (4). Ethylenediamine dihydrochloride (.199 g, 1.50 mmol) and potassium hydroxide (0.168 g, 2.99 mmol) were dissolved in 1.6 mL absolute ethanol. 2-hydroxy-5-nitrosalicylaldehyde (0.500 g, 2.99 mmol) was weighed separately and dissolved in 10 mL dichloromethane and 3.6 mL ethanol. The amine solution was added to the aldehyde solution and refluxed. After half an hour an orange solution with orange precipitate was formed. 0.425 g of orange solid was obtained by filtration (yield = 79%).



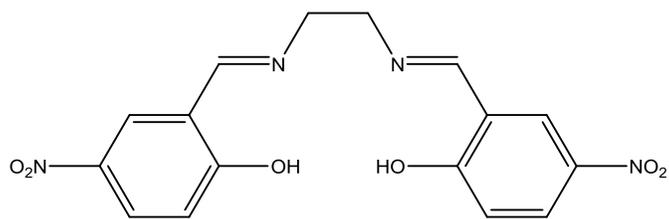
(1)



(2)



(3)



(4)

Figure 4. Structures of the four ligands synthesized without substitutions to the diamine backbone.

3,3'-((1E,1'E)-((1,2-diphenylethane-1,2-diyl)bis(azanylylidene))bis(methanylylidene))bis([1,1'-biphenyl]-4-ol) (5).

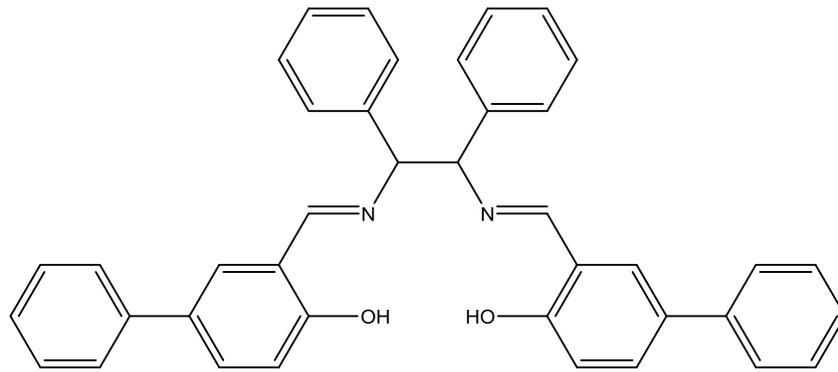
Diphenylethylenediamine (0.102 g, 0.48 mmol) dissolved in 2.5 mL ethanol was added to an ethanolic solution of 4-hydroxy-biphenyl-3-carbaldehyde (0.201 g, 1.01 mmol). This solution was refluxed for one hour. A dark brown solution with brown precipitate was formed. 0.184 g of light brown was obtained by filtration (yield = 67%). The filtrate was evaporated under vacuum giving another dark brown solid.

6,6'-((1E,1'E)-((1,2-diphenylethane-1,2-diyl)bis(azanylylidene))bis(methanylylidene))bis(2,4-dibromophenol) (6).

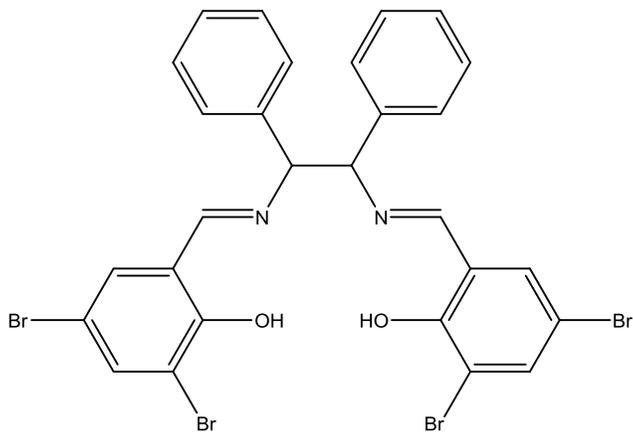
Diphenylethylenediamine (0.501 g, 2.36 mmol) and potassium hydroxide (0.132 g, 2.36 mmol) dissolved in 2.4 mL absolute ethanol was added to an ethanolic solution of 3,5-dibromosalicylaldehyde (1.322 g, 4.72 mmol) and heated to reflux. After an hour and fifteen minutes a clear, dark red-orange solution was produced. This solution was evaporated under vacuum giving a red-orange powder.

6,6'-((1E,1'E)-((1,2-diphenylethane-1,2-diyl)bis(azanylylidene))bis(methanylylidene))bis(2,4-dinitrophenol) (7).

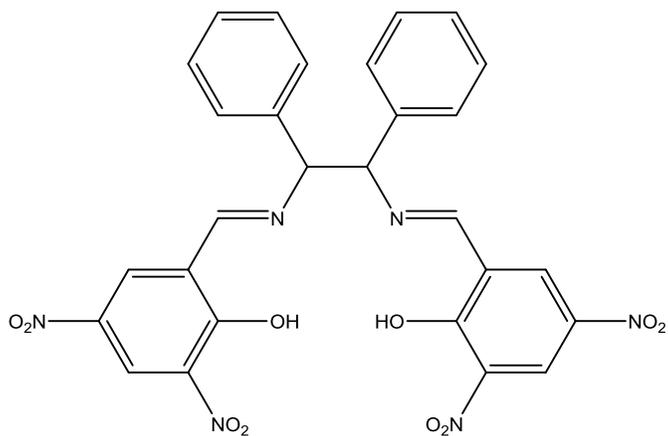
Diphenylethylenediamine (1.25 g, 5.89 mmol) and potassium hydroxide (0.332 g, 5.92 mmol) were dissolved in 5.9 mL absolute ethanol and added to an heated, ethanolic solution of 3,5-dinitrosalicylaldehyde (2.50 g, 11.8 mmol). The solution was refluxed for two hours and ten minutes. A bright red-orange solution with orange precipitate was produced. A dark orange-red solid was obtained upon filtration (yield = 55%). ¹H NMR (CDCl₃): δ 10.03 (s, 2H), 8.25 (s, 2H), 7.90 (d, 4H), 7.6 (m, 10H), 4.72 (s, 2H).



(5)



(6)



(7)

Figure 5. Structures of ligands synthesized with two phenyl groups substituted on diamine backbone.

2,2'-((1E,1'E)-(cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))diphenol (8). Trans-1,2-diaminocyclohexane (0.120 mL, 1.00 mmol) was dissolved in 25 mL ethanol was slowly added dropwise to and ethanolic solution of salicylaldehyde (0.215 mL, 2.02 mmol). The solution was refluxed for thirty minutes. A clear, yellow solution was produced. Solvent was drawn off under vacuum giving a bright yellow solid. ^1H NMR (CDCl_3 , **Fig. 6**): δ 13.33 (s, 2H), 8.25 (s, 2H), 7.23 (m, 2H), 7.15 (m, 2H), 3.32 (m, 2H), 1.65 (m, 10H). ^{13}C NMR (CDCl_3 , **Fig. 7**): δ 164.89, 161.14, 132.36, 131.68, 118.80, 116.96, 72.85, 33.32, 31.18, 24.39.

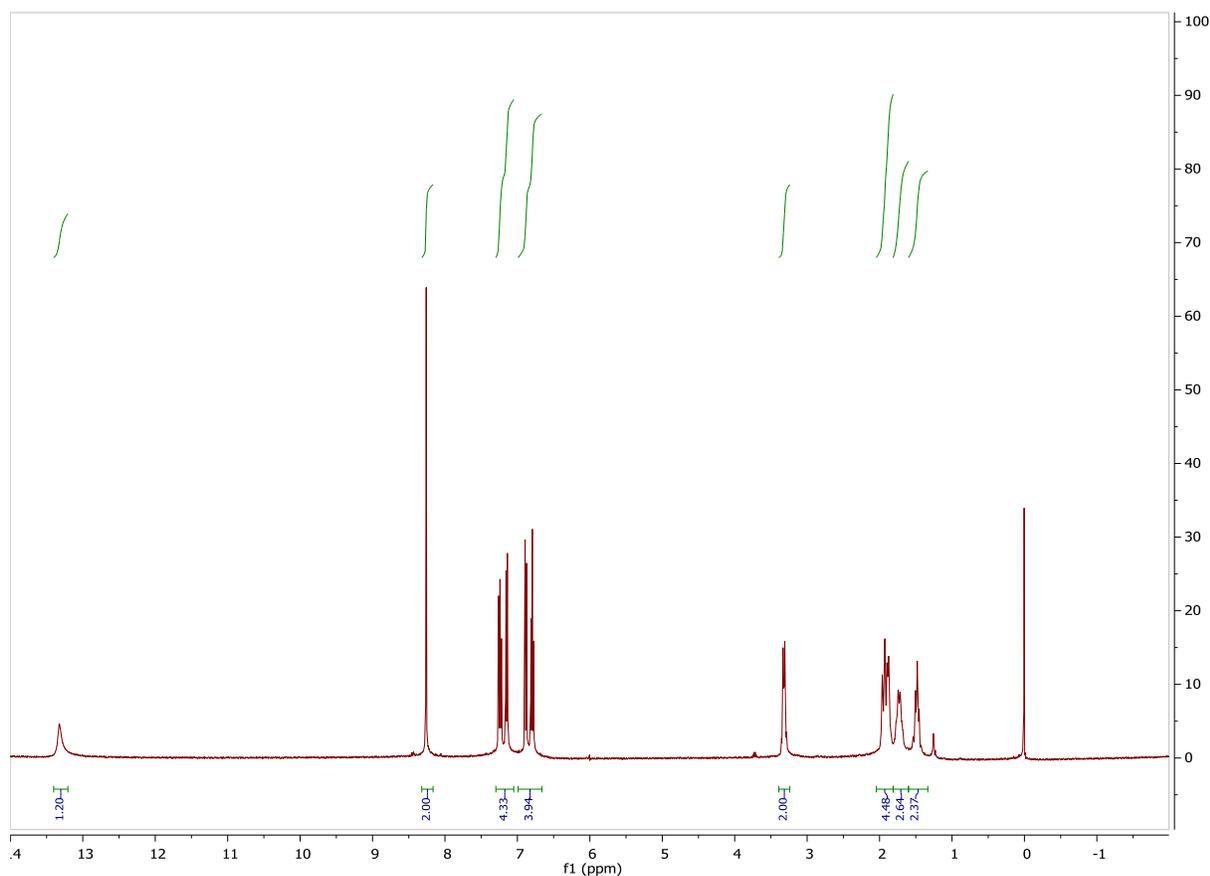


Figure 6. ^1H NMR spectrum of **8**.

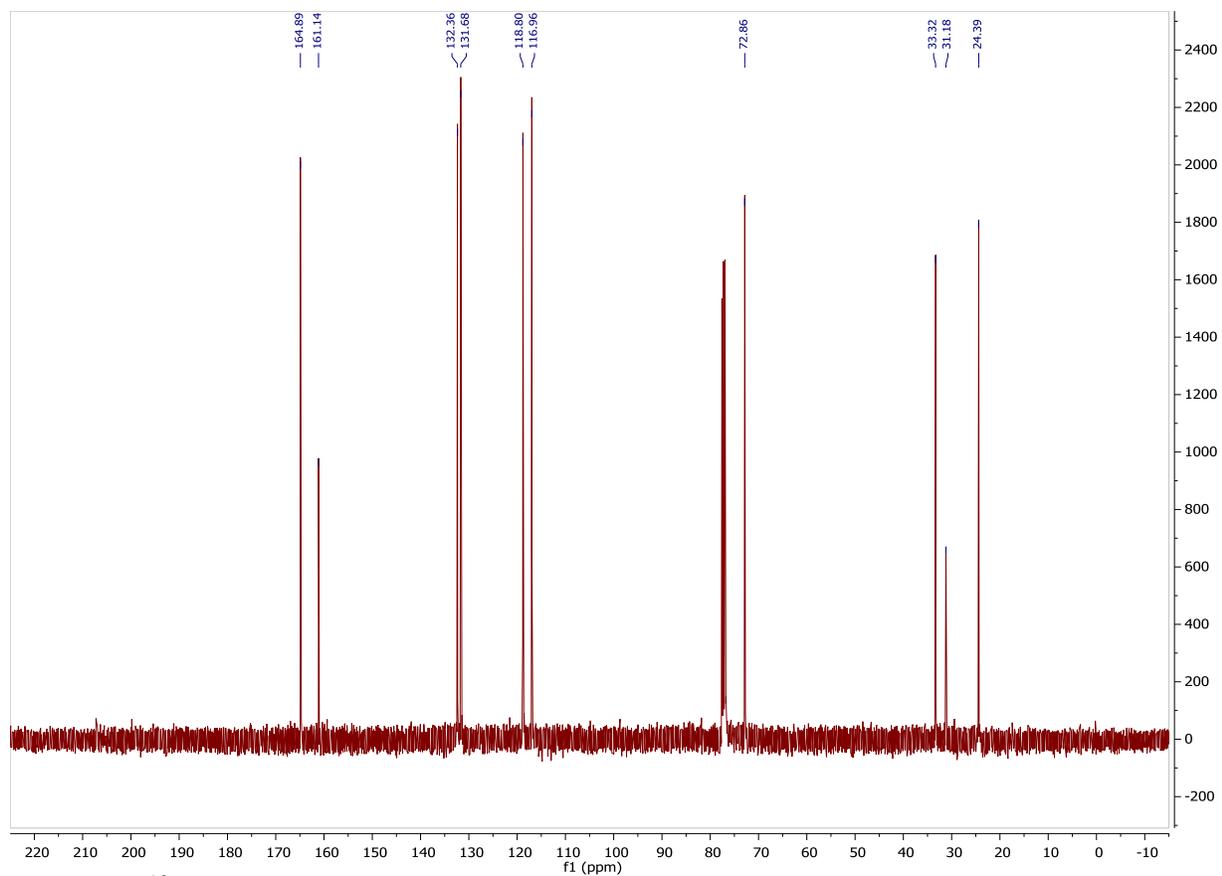


Figure 7. ^{13}C NMR spectrum of **8**.

6,6'-((1E,1'E)-(cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2,4-dibromophenol) (9). trans-1,2-diaminocyclohexane (0.100 mL, 0.83 mmol) and potassium hydroxide (0.100 g, 1.78 mmol) were dissolved in 0.9 mL ethanol and added to a heated, ethanolic solution of 3,5-dibromosalicylaldehyde (0.500 g, 1.78 mmol). The solution was refluxed for forty-five minutes. A clear yellow solution was obtained. This solution was evaporated under vacuum giving a yellow-orange powder.

2,2'-((1E,1'E)-(cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(4-nitrophenol) (10). 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 then added to a heated, ethanolic solution of 2-hydroxy-5-nitrosalicylaldehyde (0.499 g, 2.99 mmol). The solution was refluxed for 30 minutes. A clear, deep red solution was formed. The product was evaporated under vacuum obtaining a red-orange solid. ¹H NMR (CDCl₃, **Fig. 8**): δ 8.42 (s, 2H), 8.25 (d, 2H), 8.21 (d, 1H), 8.18 (d, 1H), 6.95 (d, 2H), 3.72 (m, 10H).

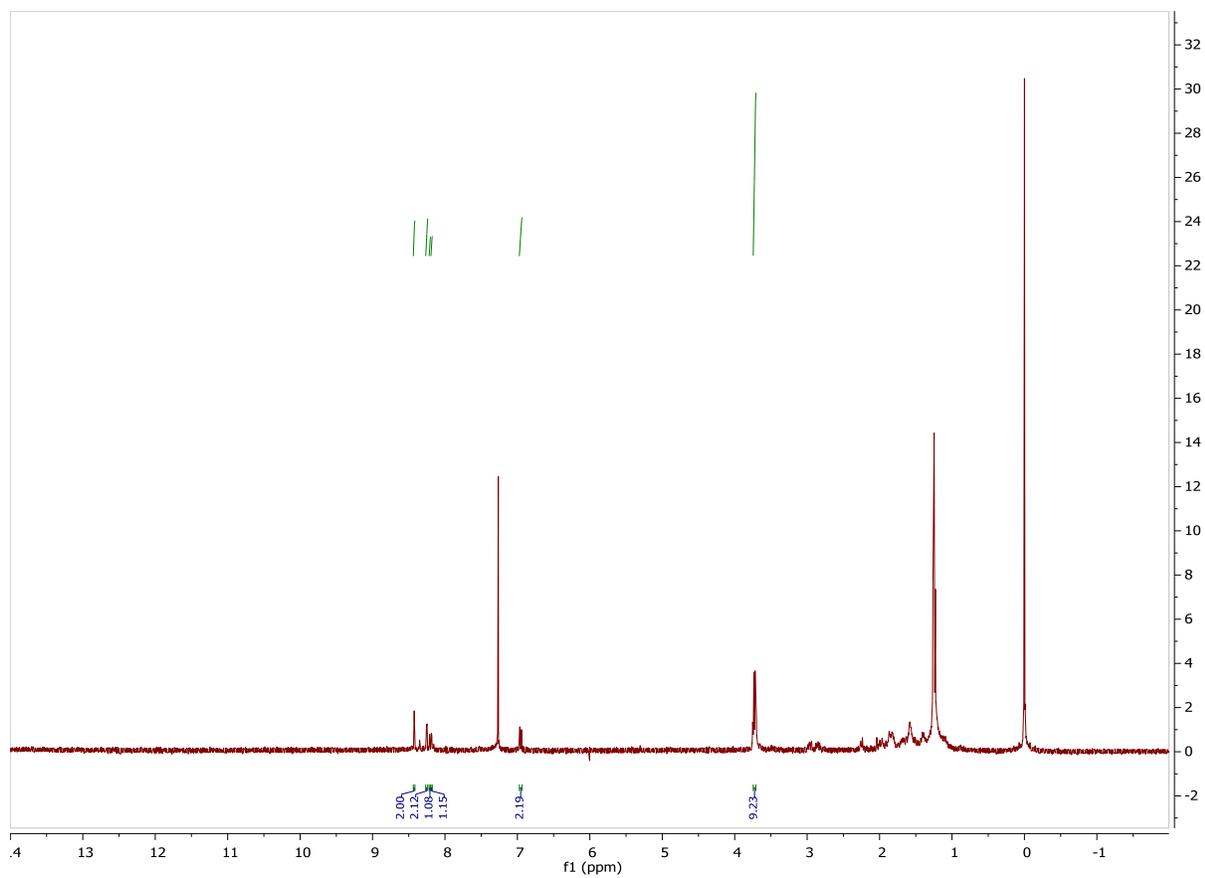


Figure 8. ^1H NMR spectrum of **10**.

6,6'-((1E,1'E)-(cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2,4-dinitrophenol) (11). Triethylamine (0.328 mL, 2.35 mmol) was dissolved in 6 mL ethanol and added to a solution of 3,5-dinitrosalicylaldehyde (0.502 g, 2.37 mmol) dissolved in 23.5 mL warm ethanol. An ethanolic solution of trans-1,2-diaminocyclohexane (0.140 mL, 1.17 mmol) was slowly added to the aldehyde solution dropwise. The solution was refluxed for thirty minutes. A clear, yellow-orange solution was formed. The solvent was pulled off using vacuum leaving a bright yellow solid. ^1H NMR (CDCl_3 , **Fig. 9**): δ 9.01 (d, 1H), 8.95 (d, 1H), 8.49 (d, 1H), 8.44 (d, 1H), 8.32 (s, 1H), 5.75 (s, 1H), 3.72 (m, 2H), 3.60 (m, 6H), 3.18 (m, 2H).

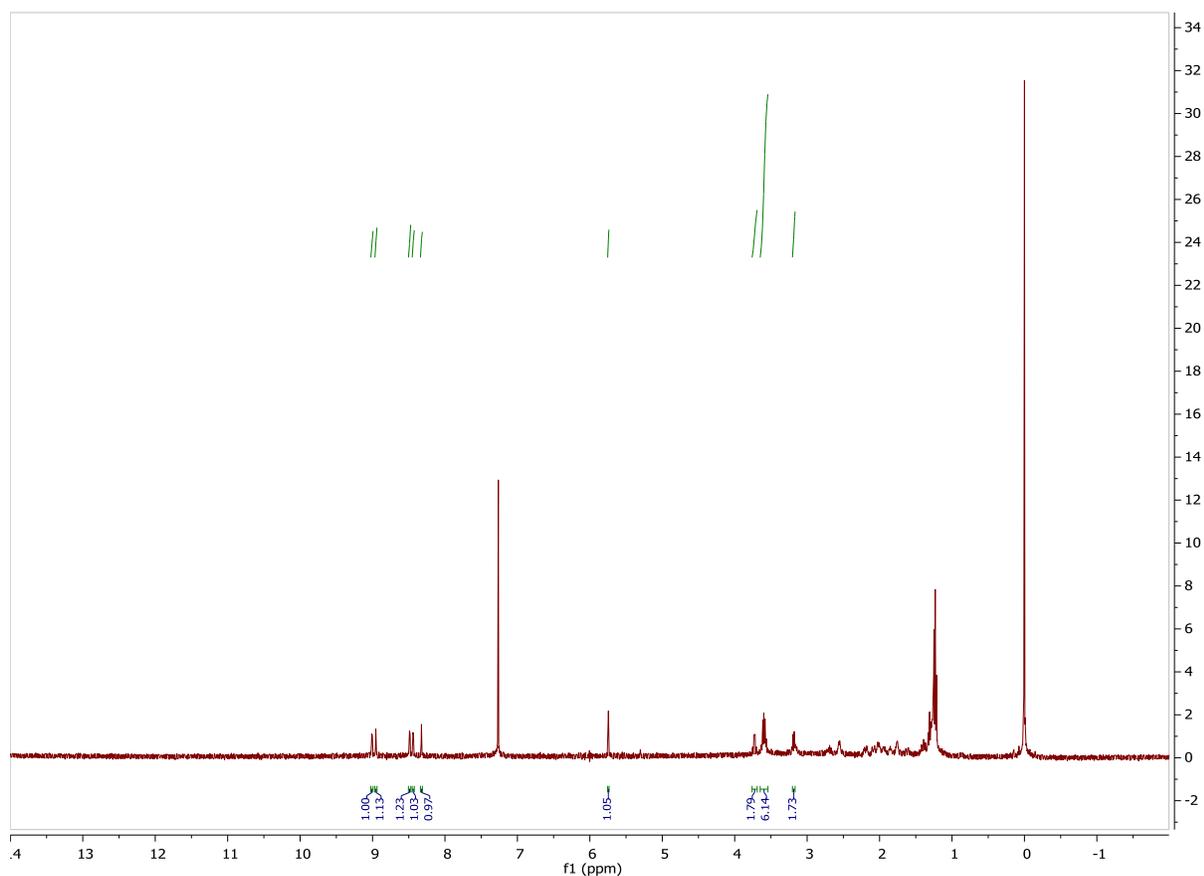
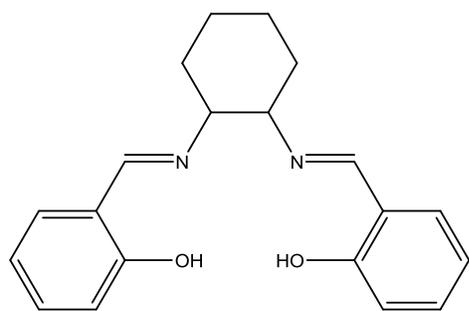
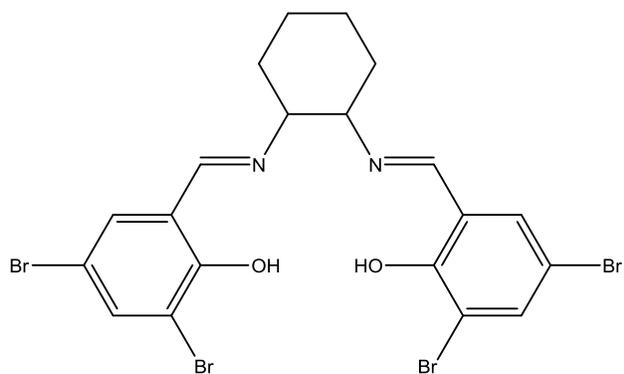


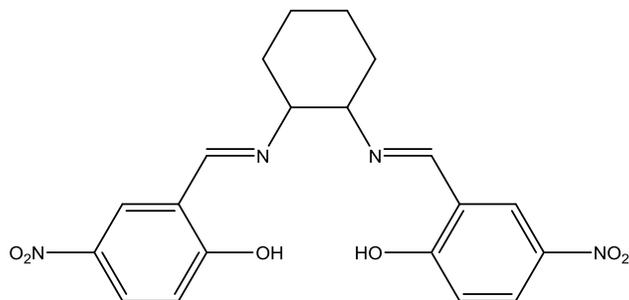
Figure 9. ^1H NMR spectrum of **11**.



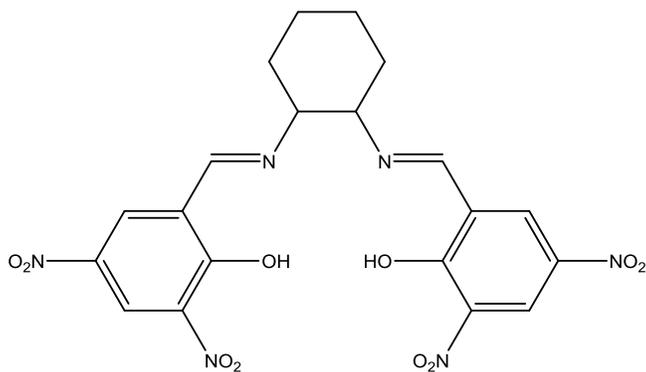
(8)



(9)



(10)



(11)

Figure 10. Ligands synthesized with a cyclohexyl group substituted on the diamine backbone.

Synthesis of Complexes

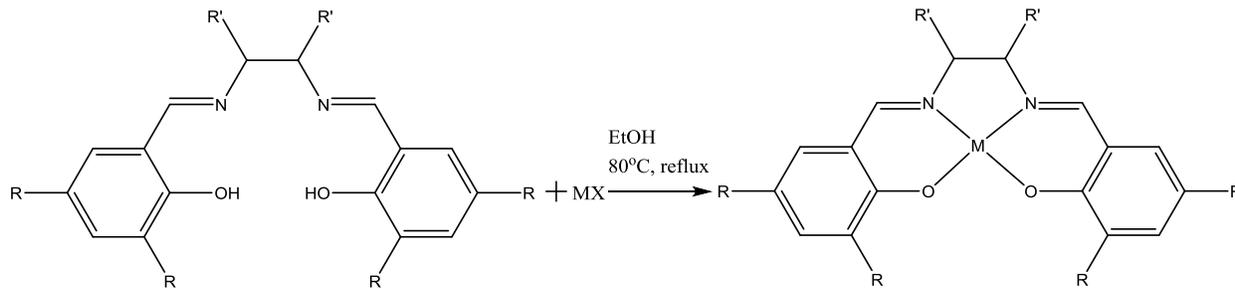


Figure 11. General scheme for complex syntheses. 1 to 1 salen ligand to metal salt were added to alcohol solvent then refluxed to produce the complex.

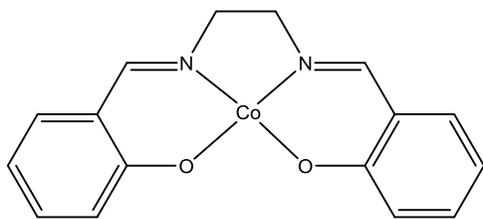
[Co-1] (12). **1** (0.052 g, 0.19 mmol) was dissolved in 2.3 mL dichloromethane and added to a methanolic solution of cobalt(II) acetate tetrahydrate (0.094 g, 0.38 mmol). Solution was allowed to stir overnight producing a dark brown solution with fine precipitate. The solvent was removed under vacuum giving a dark brown solid. This solid was dissolved in 6.9 mL dichloromethane, and 6 mL of 0.5 M triflic acid was added to give a biphasic gray-brown solution which stirred overnight. 2.3 mL of methanol was added to the solution and it was transferred to a separatory funnel where the organic layer was washed three times with 9 mL 0.5 M triflic acid each time. The aqueous layers were thrown out and the dichloromethane layer was removed leaving behind some solid. This solid was dissolved in ethyl acetate and collected; the solution was dried under vacuum giving a black powder. The solid was insoluble in dichloromethane and formed an oil that was soluble in water. This complex and all other cobalt salen complexes are paramagnetic at room temperature and thus no ^1H NMR is observed.¹⁸

[Co-2] (13). Cobalt(II) chloride hexahydrate (0.029 g, 0.12 mmol) was dissolved in 7.5 mL ethanol and added to a heated, ethanolic solution of **2** (0.051, 0.12 mmol). The resulting solution was refluxed for one hour. A dark green-brown solution with a dark precipitate was formed. A dark green solid and a clear, dark green filtrate were obtained by filtration. The

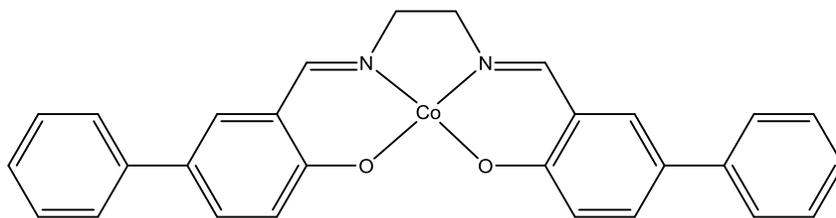
filtrate was dried to give more dark green powder. Both the original solid and solid from the filtrate were insoluble in dichloromethane.

[Co-3] (14). Cobalt(II) tetrafluoroborate hexahydrate (0.030 g, 0.09 mmol) dissolved in 1.25 mL ethanol was added dropwise to an ethanolic solution of **3** (0.050 g, 0.09 mmol) dissolved in 1.0 mL ethanol. 1 mL of 0.5 M NaOH was added to the reaction solution followed by reflux for 30 minutes. A dark brown solution with dark precipitate was formed. A brown solid was obtained by filtration with cold ethanol. A brown filtrate was also obtained which yielded more brown powder upon evaporation. Neither solid was soluble in acetonitrile.

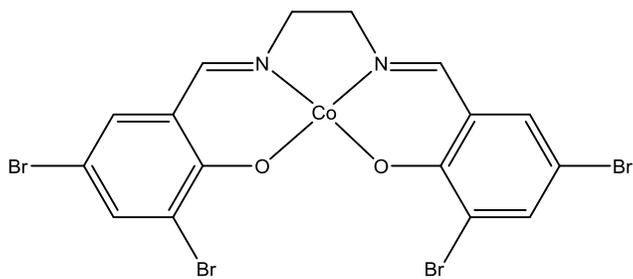
[Co-4] (15). Cobalt(II) acetate tetrahydrate (0.153 g, 0.61 mmol) was dissolved in 4.5 mL methanol and added to a solution of **4** (0.200 g, 0.61 mmol) dissolved in 2.5 mL toluene. Both solutions were degassed with argon and then the cobalt solution was added to the ligand solution and left to stir overnight in argon atmosphere. A dark red solution with red precipitate was formed. 0.211 g of red-brown solid was obtained upon filtration (yield = 83%).



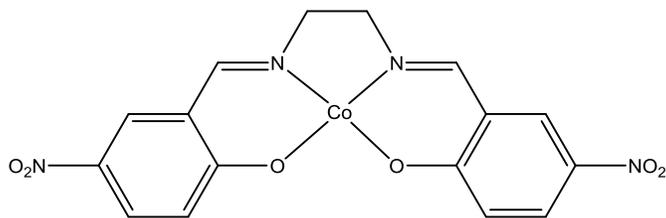
(12)



(13)



(14)

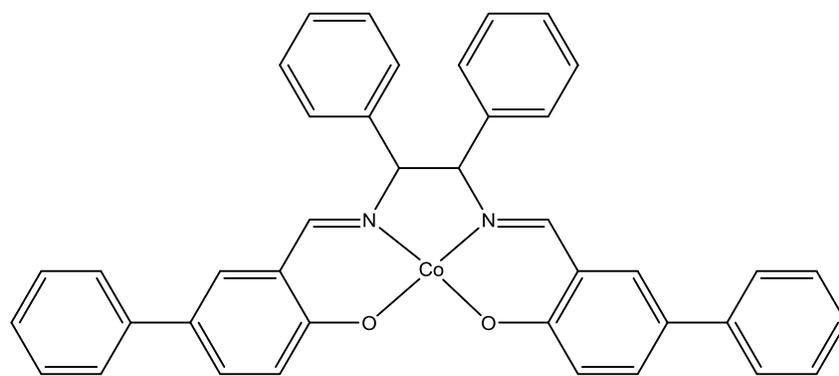


(15)

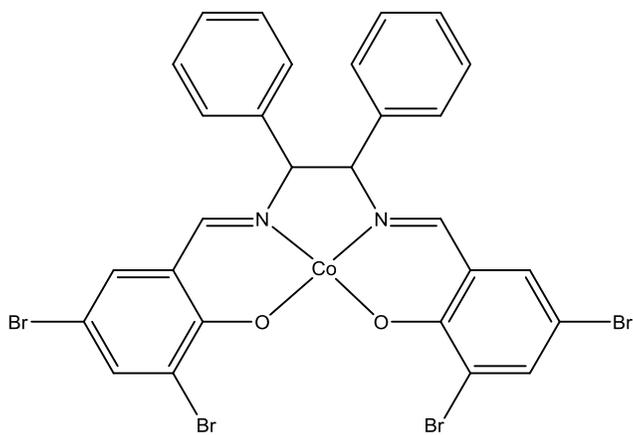
Figure 12. Cobalt(II) complexes synthesized using non-substituted diamine backbone ligands.

[Co-5] (16). Cobalt(II) chloride hexahydrate (0.021 g, 0.09 mmol) was dissolved in 7.5 mL ethanol was added to a heated, ethanolic solution of **5** (0.051 g, 0.09 mmol). The solution was refluxed for one hour forming a clear, dark green-brown solution. This solution was evaporated to give a dark green solid that was soluble in dichloromethane.

[Co-6] (17). Cobalt(II) chloride hexahydrate (0.033 g, 0.14 mmol) was dissolved in 7.5 mL ethanol was added to a heated, ethanolic solution of **6** (0.101 g, 0.14 mmol). The solution was refluxed for one hour forming a dark, red-brown solution with a dark precipitate. 0.066 g of a dark green powder were obtained upon filtration (yield = 59%). This solid was partially soluble in dichloromethane. The filtrate was saved and evaporated to give a dark green-brown solid which was also soluble in dichloromethane.



(16)



(17)

Figure 13. Cobalt complexes synthesized using ligands with phenyl substituents on the diamine backbone.

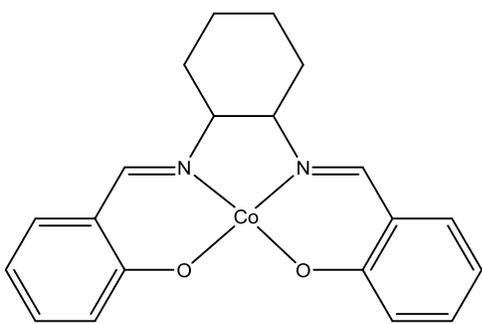
[Co-8] (18). Cobalt(II) tetrafluoroborate hexahydrate (0.106 g, 0.31 mmol) and **8** (0.101 g, 0.31 mmol) were added to separate flasks and flushed with argon while about 70 mL of methanol was degassed with argon in another flask. 30 mL of degassed methanol was added to the ligand flask and 11 mL degassed methanol was added to the cobalt flask. Both solutions were heated to near reflux before transferring the cobalt solution to the ligand solution. The resulting solution was refluxed under argon for thirty minutes. A clear, red-orange solution was formed and stored in the refrigerator overnight. The cooled solution was filtered through celite and put back in the refrigerator in an attempt to grow crystals. This reaction was also run in air with the same apparent results, except the solution was evaporated to obtain a dark brown solid which was soluble in methanol, acetone, and acetonitrile.

[Co-9] (19). Cobalt(II) chloride hexahydrate (0.020 g, 0.09 mmol) dissolved in 15 mL ethanol was added to **9** (0.049 g, 0.09 mmol). The solution was refluxed for one hour. A brown solution with brown precipitate was formed. 0.043 g of red-brown solid was obtained upon filtration (yield = 69%). The solid was fairly soluble in chloroform and dichloromethane.

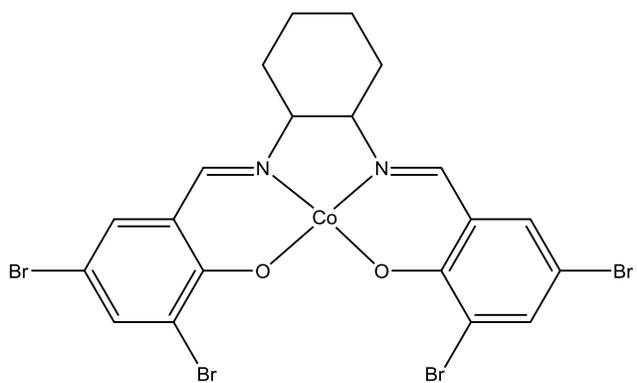
[Co-10] (20). Cobalt(II) tetrafluoroborate hexahydrate (0.0824 g, 0.24 mmol) and **10** (0.100 g, 0.24 mmol) were flushed with argon separately while about 80 mL methanol was degassed with argon in another flask. 30 mL of methanol was added to the ligand flask and 11 mL was added to the cobalt flask. Both solutions were heated to near boiling before the cobalt solution was added to the ligand solution. The resulting solution was refluxed under argon for half an hour. A red-brown solution with red precipitate was formed and stored in the refrigerator overnight. The solution was filtered through celite and the clear red-orange filtrate was evaporated to give a yellow-brown solid. This solid was soluble in acetonitrile. This reaction

was also carried out in normal air conditions, but gave a green-brown precipitate that was only slightly soluble in acetonitrile.

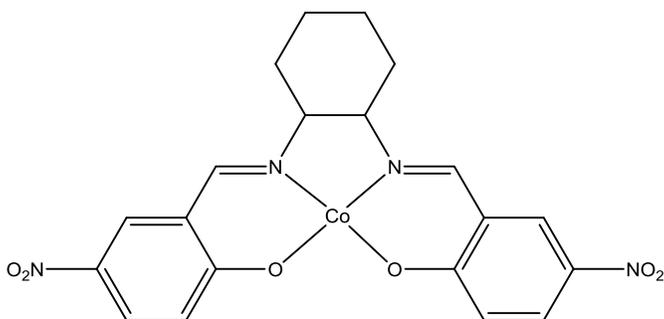
[Co-11] (21). Cobalt(II) tetrafluoroborate hexahydrate (0.123 g, 0.36 mmol) and **11** (0.150 g, 0.30 mmol) were placed in separate flasks and flushed with argon while about 70 mL methanol was degassed with argon in another flask. 30 mL degassed methanol was added to the ligand flask and 12 mL was added to the cobalt flask. Both solutions were heated to near boiling before the cobalt solution was transferred to the ligand solution. The resulting solution was refluxed for 30 minutes. A clear, dark red-brown solution was formed. This solution was put in the refrigerator for the night. The cooled solution was filtered through celite then put in the refrigerator again to form crystals.



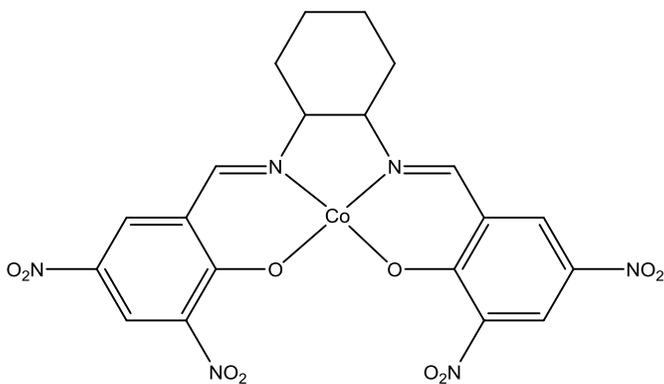
(18)



(19)



(20)



(21)

Figure 14. Cobalt complexes synthesized using ligands with cyclohexyl group substituent on diamine backbone.

Crystal Growth

Crystallizations were attempted for all complexes which were found to be soluble in at least one solvent. Two methods were used. The first was basic recrystallization in which the compound was dissolved in a solvent, heated to evaporate off some of the solvent, and then cooled in a refrigerator to develop crystals. All of the ligands were recrystallized in an effort to purify them. The second approach was slow diffusion, wherein the complex was dissolved in a solvent and then layered with another solvent which was miscible with the first, but in which the complex was insoluble. The two solvents would diffuse into one another causing crystals to slowly form.

Electrochemistry of Cobalt Cyclohexylsalen Complexes

Cyclic voltammetry experiments were performed on crystals of **18**, **20**, and **21**. All experiments were done airfree in argon flushed acetonitrile solutions 0.5 mM in catalyst with a glassy carbon working electrode, platinum counter electrode, and saturated calomel (SCE) reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was used as a supporting electrolyte. All experiments were performed at a scan rate of 200 mV/s. From these studies we were able to probe of the catalytic activity of each compound.

Results and Discussion

Catalyst Design

The main goal in studying cobalt salen complexes was to characterize metal complexes made with highly tunable, easily synthesized ligands. In particular the effects of adding electron withdrawing groups to the salen ligand were of great interest. It has been proposed and demonstrated that adding electron withdrawing groups reduces the d-orbital electron density at the metal center, thus allowing for easier reduction and subsequent protonation of the metal center at more positive potentials.²⁰ With this in mind the first ligands studied included nitro or bromide groups on the phenyl rings of the ligand. However, cobalt complexes of these compounds were noted to be insoluble or only slightly soluble in both polar and nonpolar solvents when using the synthesis described by Böttcher et al.²¹ Insolubility presented major issues with regards to crystallizing the complexes. Different synthetic methods were tested in the complexation reaction to form **14** and **15**.^{22,23} Unfortunately, these syntheses produced complexes with similar solubility issues. Testing these different syntheses demonstrated that the solubility problem could not be solved by modifying synthetic routes.

Our next step in attempting to improve solubility was to modify the diamine backbone of the complexes. We proposed that the solubility issues could be stemming from pi-stacking between the phenyl rings of the salen ligands due to the planar geometry of the molecules. To remedy this two different structural additions were tested. One was the introduction of two additional phenyl groups on the diamine backbone. We hoped that the phenyl groups would be able to orient out of plane with the other phenyl rings and thus could interrupt the pi-stacking present. The other method was to introduce a cyclohexyl group on the diamine backbone.^{22,24}

The cyclohexyl group would also interrupt pi-stacking through its orientation out of the plane of the rest of the molecule.

We first tested the two proposed modifications by adding the two phenyl groups on the diamine backbone with the synthesis of **6**. **6** was complexed with cobalt to give **17**, which was fairly soluble in dichloromethane and somewhat soluble in acetonitrile. Though the solubility issue seemed to have been fixed, crystals were not obtained for this complex despite several attempts with the complex dissolved in dichloromethane diffusing into ether or hexanes.

As proof of concept another salen ligand was synthesized with two phenyl groups replacing the electron withdrawing groups on the phenyl rings of the aldehydes. The resulting diphenyl-salen ligand (**2**) was complexed with cobalt to give **13**, but was not found to be very soluble in any solvents; likely because the added phenyl groups remained in plane with the rest of the molecule allowing pi-stacking to remain.

The diamine backbone was then modified with a cyclohexyl group through synthesis of **9** and **10**. These were both complexed with cobalt to give **19** and **20**. **19** was soluble in dichloromethane and chloroform, and it was somewhat soluble in methanol, hexanes, toluene, water, and acetonitrile. **20** was soluble in acetonitrile and somewhat soluble in methanol, dichloromethane, toluene, chloroform, and water. Most importantly, crystals of **20** were obtained by slow diffusion of the complex dissolved in acetonitrile diffusing with ether. Obtaining crystals was a significant breakthrough and allowed us to move forward with X-ray diffraction attempts as well as electrochemical studies.

A synthesis of the cyclohexyl and diphenyl substituted diamine bridges along with crystal formation methods for these compounds was found in a paper by the Gray group.¹⁹ Following this synthetic route we were able to obtain crystals of **18**, **20**, and **21**. Single crystals of both **18**

and **20** were subject to attempted X-ray diffraction experiments for structure elucidation, but twinning of the crystals led to poor-quality X-ray data. **21** has yet to be studied by X-ray diffractometry. Being able to crystallize and purify **18**, **20**, and **21** allowed us to see if adding electron withdrawing groups would activate cobalt salen complexes toward hydrogen generation catalysis.

Electrochemical Studies

Once the solubility issues had been solved and crystals had been grown for a series of complexes differing only in the electron-withdrawing substituents we were able to move ahead with electrochemical experiments to characterize their catalytic activity. Crystals were important to obtain for electrochemical experiments in order to ensure high quality results free from erroneous data resulting from impurities. All of our electrochemical experiments on cobalt salen complexes were performed in acetonitrile using a solution that is 0.5 mM complex and 0.1 M in (TBAPF₆). The potentials for the Co(II)/Co(I) redox couples varied from -0.48 to -1.37 between **18**, **20**, and **21**. The structures of **18**, **20**, and **21** provided a series of complexes with different electron densities around the metal. Therefore, this series was of particular interest to study for proton reduction.

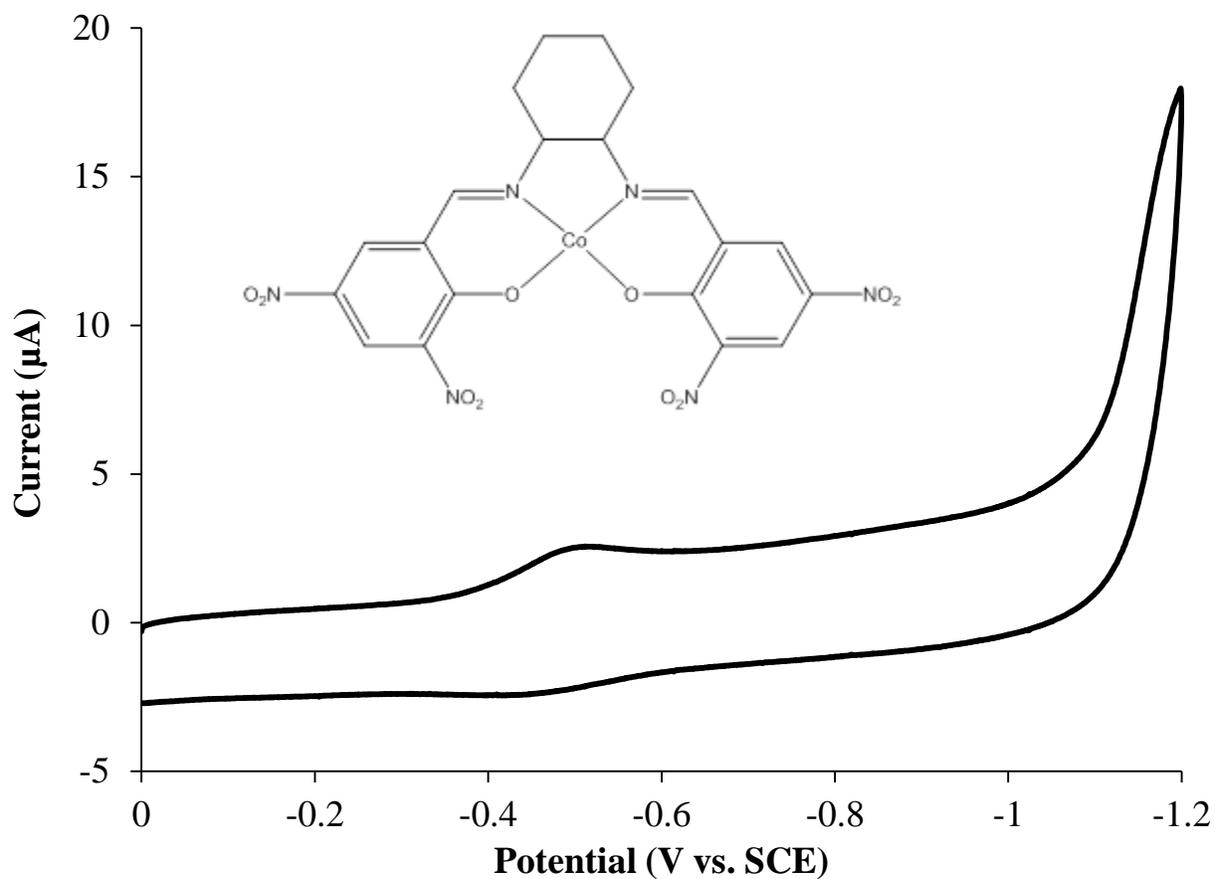


Figure 15. CV of 0.5 mM **21** and 0.1 M TBAPF₆ taken in acetonitrile without any acid added.

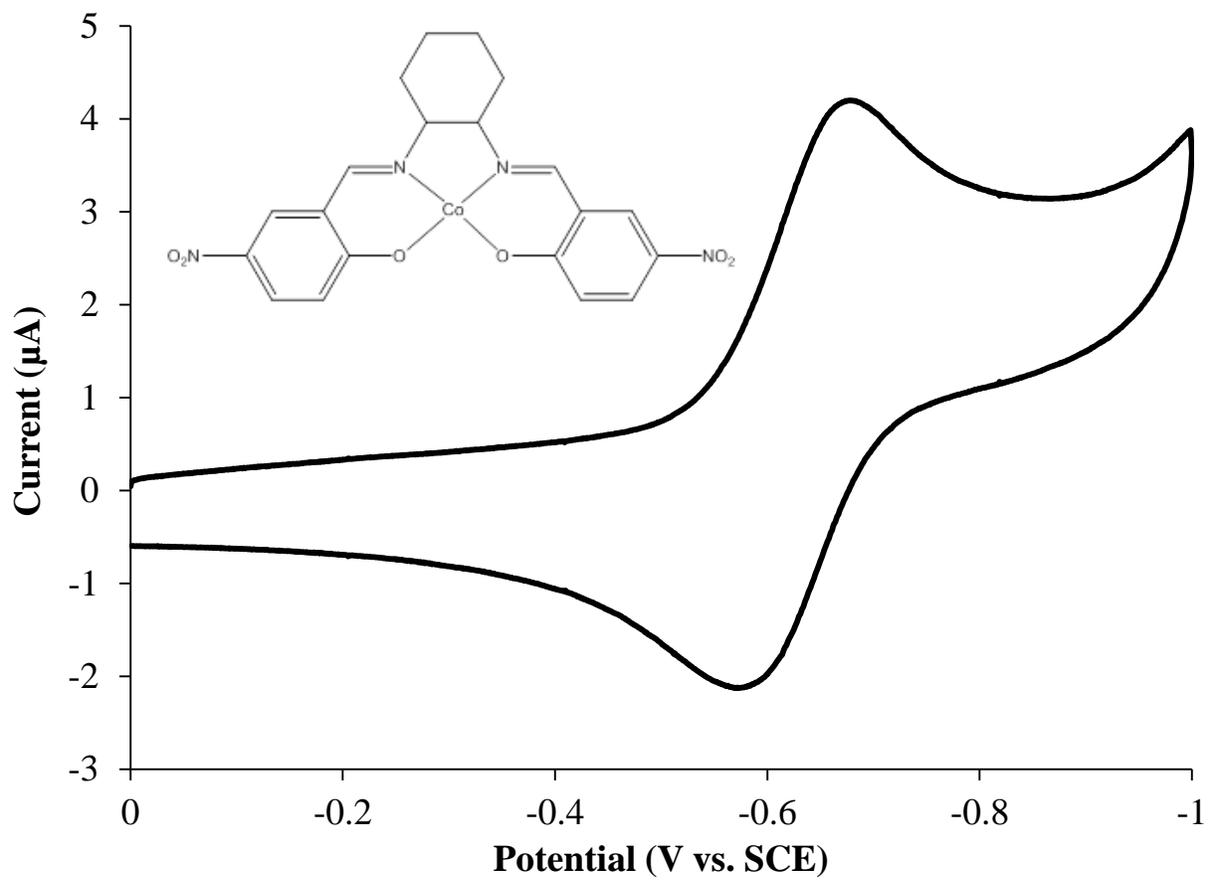


Figure 16. CV of 0.5 mM **20** and 0.1 mM TBAPF₆ in acetonitrile without acid added.

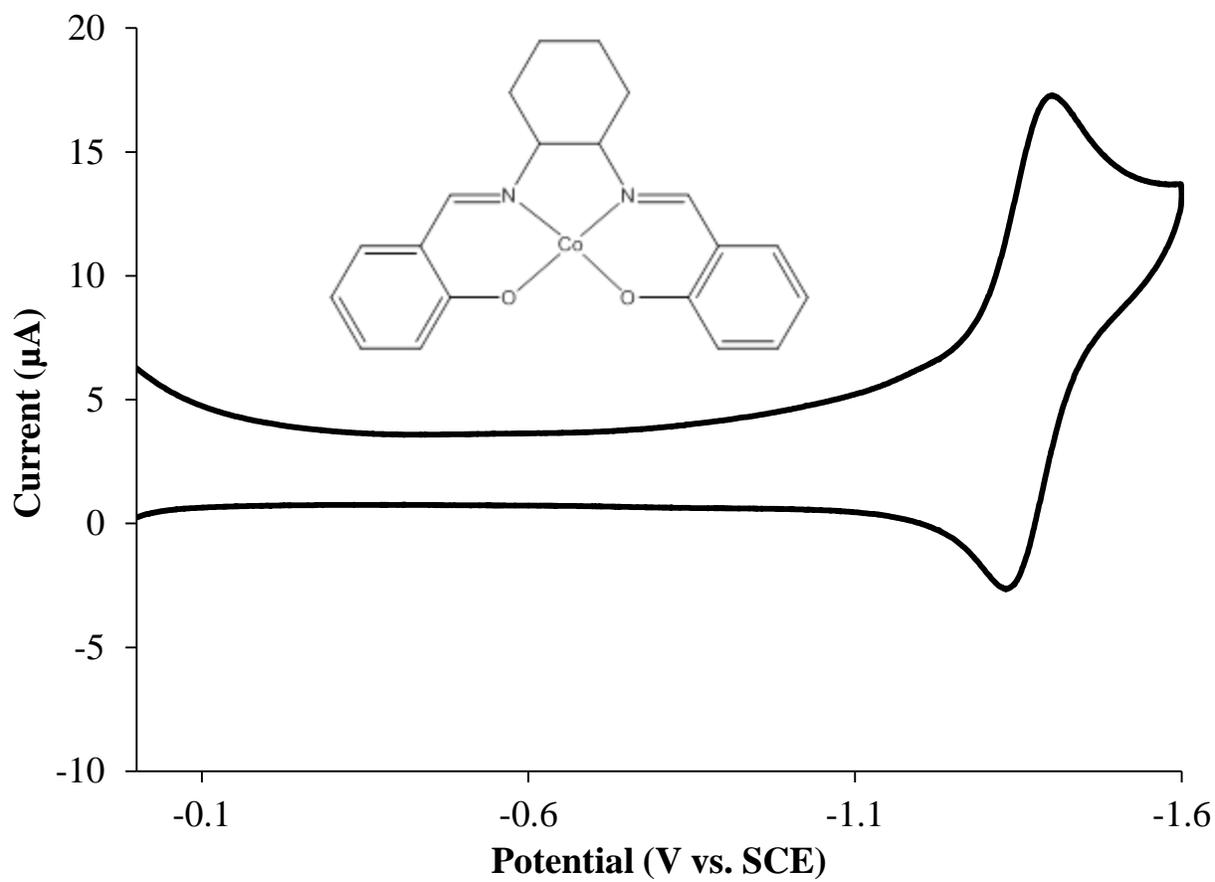


Figure 17. CV of 0.5 mM **18** and 0.1 mM TBAPF₆ taken in acetonitrile without any acid added.

It was necessary to take a baseline, acid-free run in order to determine at what potential a redox couple appears. The redox couple gave an idea of the potential at which catalytic activity occurs. The acid free runs gave a good point of comparison between the three complexes of interest. It was hypothesized that **21** would have the most positive redox couple because it had the most electron withdrawing groups followed by **20** and finally **18**. The series of cyclic voltammograms (CVs) highlighted in **Fig. 11**, **Fig. 12**, and **Fig. 13** and summarized in **Table 1** shows that this is the case. In **Fig. 11** we see **21** has a redox couple at about -0.48 V followed by a more negative redox couple at -0.62 V for **20** in **Fig. 12** and a redox couple at about -1.37 for **18** in **Fig. 13**.

Complex	$E_{1/2}$
18	-1.37 V
20	-0.62 V
21	-0.48 V

Table 1. Summary of the potentials at which Co(II)/Co(I) redox couples are observed ($E_{1/2}$).

Cyclic voltammetry can be used to probe the catalytic activity of these complexes. In a typical experiment, an organic acid, which acted as a proton source, was introduced and a CV was obtained to determine if a catalytic wave was present. We used 1.1 M trifluoroacetic acid (TFA) for our acid additions. The first acid addition experiment was performed on **21**. Upon acid addition a catalytic reduction wave was noted to grow on top of a redox couple at the relatively positive potential -0.6 V.

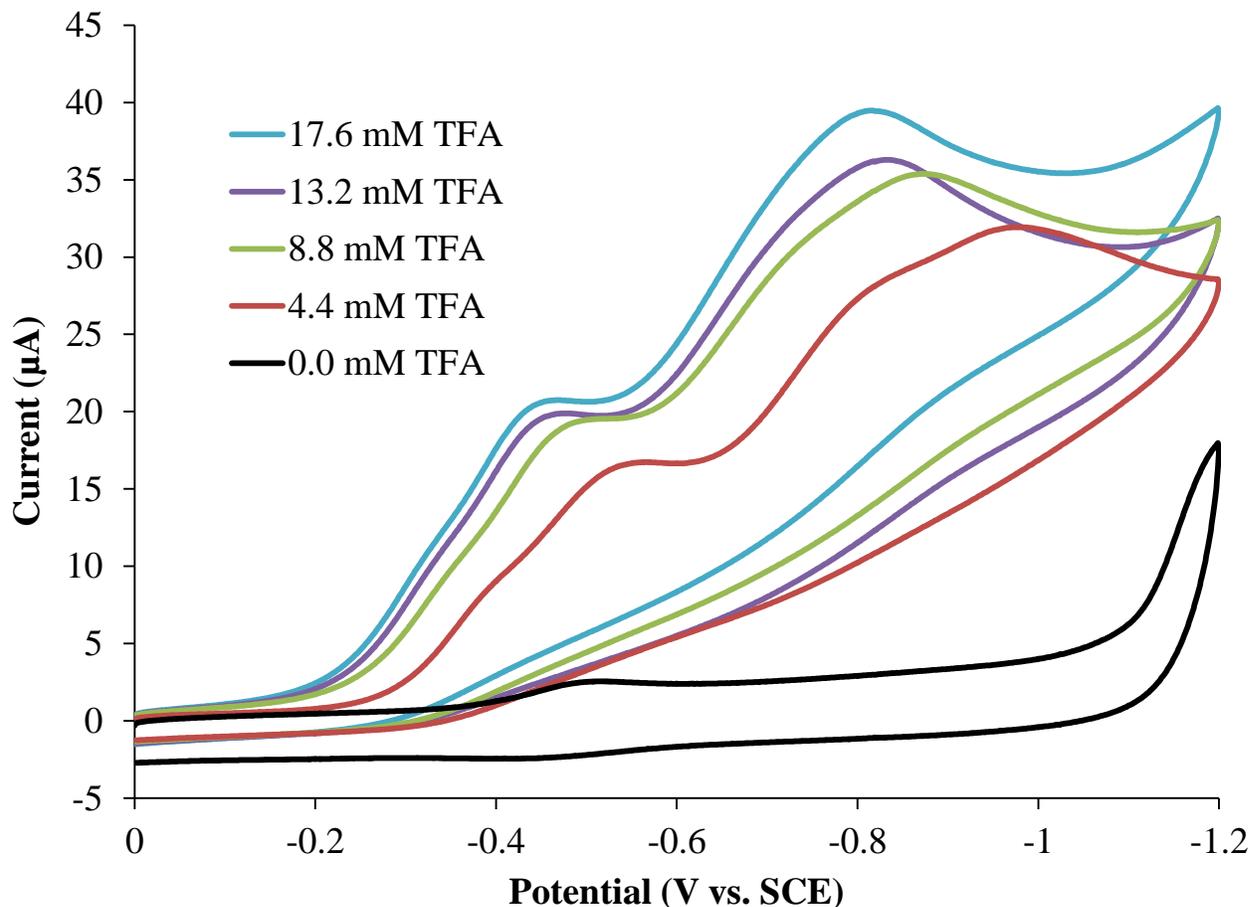


Figure 18. Study of solution of 0.5 mM **21** and 0.1 M TBAPF₆ taken in acetonitrile with no acid (black), 2.2 mM TFA (red), 4.4 mM TFA (green), 6.6 mM TFA (purple), 8.8 mM TFA (blue).

The next complex studied was **20**, containing two fewer nitro groups in its structure. The electrochemical runs were performed using small crystals of the complex recrystallized using the Gray paper synthesis.¹⁹ Compared to **21** this complex did exhibit a redox couple at a more negative potential of -0.62 V with a catalytic wave growing on top at about -0.8 V with acid additions (**Fig. 15**).

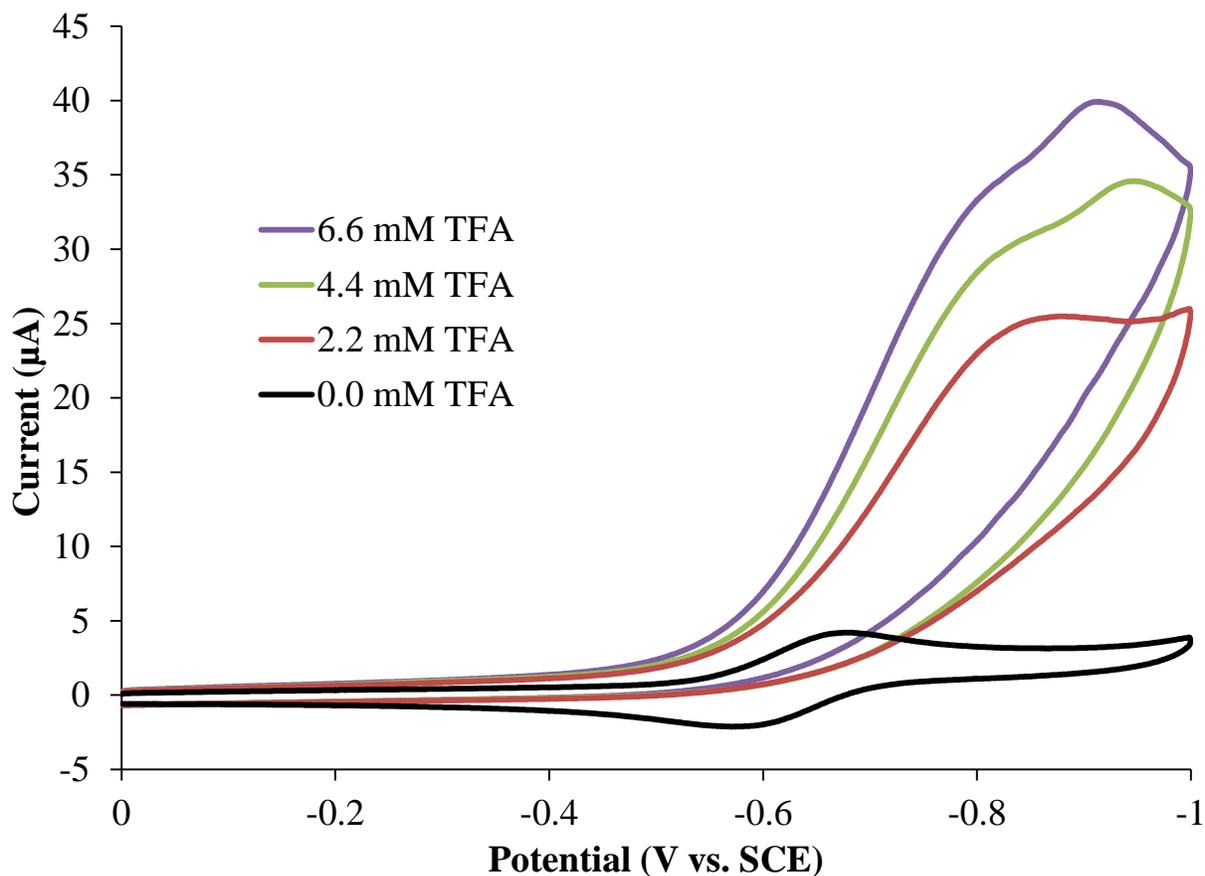


Figure 19. Study of solution of 0.5 mM **20** and 0.1 M TBAPF₆ in acetonitrile with with no acid (black), 2.2 mM TFA (red), 4.4 mM TFA (green), 6.6 mM TFA (purple).

18 was studied lastly in this series of complexes. Since this complex contained no electron-withdrawing substitutions to the phenolate rings it was expected to have the least catalytic activity at relatively positive potentials. Acid addition studies did indeed show that **18** was not a catalyst for proton reduction, with a redox couple in no acid at a very negative value of -1.37 V and no noticeable catalytic wave (**Fig 16**).

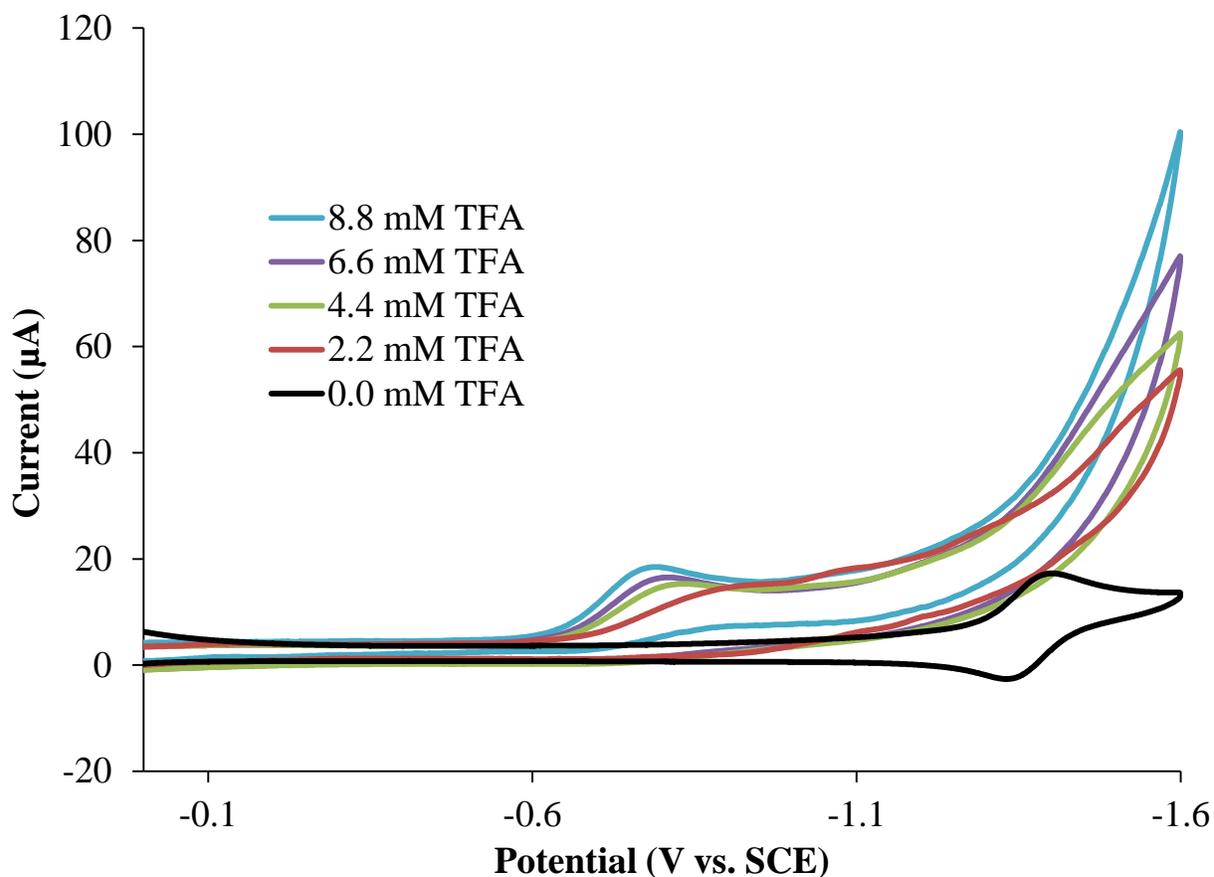


Figure 20. Study of solution of 0.5 mM **18** and 0.1 M TBAPF₆ in acetonitrile with no acid (black), 4.4 mM TFA (red), 8.8 mM TFA (green), 13.2 mM TFA (purple), 17.6 mM TFA (blue).

All of the electrochemical data obtained from CVs with and without acid are summarized neatly in **Table 2**. As expected, **21**, with the greatest number of electron withdrawing groups, was the most active catalyst at positive potentials.

Complex	$E_{1/2}$	Onset of Catalytic Wave
18	-1.37 V	N/A
20	-0.62 V	-0.8 V
21	-0.48 V	-0.6 V

Table 2. Summary of the potentials at which Co(II)/Co(I) redox couples are observed ($E_{1/2}$) and potentials at which the onset of a catalytic wave is noted for each of the three complexes studied.

Conclusion

Many different salen ligands and cobalt salen complexes were synthesized. Early solubility issues were solved by synthesizing salen ligands with phenyl and cyclohexyl substituents on the diamine backbone to disrupt pi-stacking and improve solubility. Having more soluble complexes allowed crystals of **18**, **20**, and **21** to be obtained and electrochemistry to be performed. These three complexes were studied to demonstrate the relationship between the number of electron withdrawing substituents and catalytic activity.

Further research into cobalt salen complexes is necessary. Ongoing efforts involve obtaining better single crystals to study crystallographic data for **18**, **20**, and **21**. Other directions include studying the properties of other cobalt salen complexes, and eventually studying iron salen complexes.

We report that addition of electron withdrawing groups to cobalt salen complexes produces proton reduction catalysts. Electrochemical data supported the hypothesis that more electron withdrawing groups in cobalt salen complexes operate at more efficient potentials with high activity.

REFERENCES

1. Delucchi, M. A.; Jacobson, M. Z. Providing all global energy with wind, water, and solar power, Part I: Technologies, energy resources, quantities, and areas of infrastructure, and materials. *Energy Policy*. **2011**, *39*, 1154-1169.
2. U.S. Energy Information Association. International Energy Outlook 2013.
<http://www.eia.gov/forecasts/ieo/index.cfm> (accessed April 16, 2014).
3. Lewis, N. S. Powering the Planet. *MRS Bulletin*. **2007**, *32*, 808-820.
4. Lewis, N. S.; Nocera, D. G. Powering the Planet: Chemical Challenges in Solar Energy Utilization. *Proc. Natl. Acad. Sci.* **2006**, *103*(43), 15729-15735.
5. Intergovernmental Panel on Climate Change. Climate Change 2014: Mitigation of Climate Change. <http://www.ipcc.ch/report/ar5/wg3/> (accessed April 18, 2014)
6. De Vos, A. Detailed balance limit of the efficiency of tandem solar cells. *J. Phys. D: Appl. Phys.* **1980**, *13*, 839-846.
7. Bhubaneswari, P.; Iniyar, S.; Goic, R. A review of solar photovoltaic technologies. *Renewable and Sustainable Energy Reviews*. **2011**, *15*(3), 1625-1636.
8. Sherif, S. A.; Barbir, F.; Veziroglu, T. N. Wind energy and the hydrogen economy—review of the technology. *Solar Energy*. **2005**, *78*(5), 647-660.
9. National Renewable Energy Laboratory.
http://www.nrel.gov/hydrogen/proj_production_delivery.html (accessed April 23, 2014).
10. U.S. Department of Energy. Hydrogen Production – Natural Gas Reforming.
http://www1.eere.energy.gov/hydrogenandfuelcells/production/natural_gas.html (accessed April 18, 2014).

11. Helm, M. L.; Stewart, M. P.; Bullock R. M.; Rakowski, R. M.; DuBois, D. L. A Synthetic Nickel Electrocatalyst with a Turnover Frequency Above 100,000 s⁻¹ for H₂ Production. *Science*. **2011**, *333*(6044), 863-866.
12. Efros, L. L.; Thorp, H. H.; Brudvig, G. W.; Crabtree, R. H. Towards a functional model of hydrogenase: electrocatalytic reduction of protons to dihydrogen by a nickel macrocyclic complex. *Inorg. Chem.* **1992**, *31*, 1722-1724.
13. Canaguier, S.; Artero, V.; Fontecave, M.; Modelling NiFe hydrogenases: nickel-based electrocatalysts for hydrogen production. *Dalton Transactions*. **2008**, 315-325.
14. Nicolet, Y.; de Lacey, A. L.; Vernede, X.; Fernandez, V. M.; Hatchikian, E. C.; Fontecilla-Camps, J. C. Crystallographic and FTIR Spectroscopic Evidence of Changes in Fe Coordination Upon Reduction of the Active Site of the Fe-Only Hydrogenase from *Desulfo Vibrio desulfuricans*. *J. Am. Chem. Soc.* **2001**, *123*, 1596-1601.
15. Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. Enantioselective Epoxidation of Unfunctionalized Olefins Catalyzed by (Salen)manganese Complexes. **1990**, *112*(7), 2801-2803.
16. Kochem, A.; Thomas, F.; Jarjayes, O.; Gellon, G.; Philouze, C.; Weyhermüller, T.; Neese, F.; van Gestel, M. Structural and Spectroscopic Investigation of an Anilinosalen Cobalt Complex with Relevance to Hydrogen Production. *Inorg. Chem.* **2013**, *52*, 14428-14438.
17. King, A. E.; Surendranath, Y.; Piro, N. A.; Bigi, J. P.; Long, J. R.; Chang, C. J. A mechanistic study of proton reduction catalyzed by a pentapyridine cobalt complex: evidence for involvement of an anation-based pathway. *Chem. Sci.* **2013**, *4*, 1578-1587.
18. Floriani, C.; Calderazzo, F. Oxygen Adducts of Schiff's Base Complexes of Cobalt Prepared in Solution. *J. Chem. Soc. (A)*. **1969**. 946-953.

19. Böttcher, A.; Grinstaff, M. W.; Labinger, J. A.; Gray, H. B. Aerobic oxidation of hydrocarbons catalyzed by electronegative iron salen complexes. *J. Mol. Catal. A: Chem.* **1996**, *113*, 191-200.
20. Ridley, F.; Ghosh, S.; Hogarth, G.; Hollingsworth, N.; Holt, K. B.; Unwin, D. G. Fluorinated models of the iron-only hydrogenase: An electrochemical study of the influence of an electron-withdrawing bridge on the proton reduction overpotential and catalyst stability. *J. Electroanal. Chem.* **2013**, *703*, 14-22.
21. Böttcher, A.; Elias, H.; Jäger, E.; Langfelderova, H.; Mazur, M.; Müller, L.; Paulus, H.; Pelikan, P.; Rudolph, M.; Valko, M. Comparative Study on the Coordination Chemistry of Cobalt(II), Nickel(II), and Copper(II) with Derivatives of Salen and Tetrahydrosalen: Metal-Catalyzed Oxidative Dehydrogenation of the C-N Bond in Coordinated Tetrahydrosalen. *Inorg. Chem.* **1993**, *32*, 4131-4138.
22. Kurahashi, T.; Fujii, H. Unique Ligand-Radical Character of an Activated Cobalt Salen Catalyst That Is Generated by Aerobic Oxidation of a Cobalt(II) Salen Complex. *Inorg. Chem.* **2013**, *52*, 3908-3919.
23. Huang, Y.; Iwama, T.; Rawal, V. Design and Development of Highly Effective Lewis Acid Catalysts for Enantioselective Diels-Alder Reactions. *J. Am. Chem. Soc.* **2002**, *124*, 5950-5951.
24. Cozzi, P. G. Metal-Salen Schiff base complexes in catalysis: practical aspects. *Chem. Soc. Rev.* **2004**, *33*, 410-421.