ELECTROCHEMICAL REDUCTION OF 1-BROMOOCTANE

CATALYZED BY A DICOBALT COMPLEX

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ELECTROCHEMICAL REDUCTION OF 1-BROMOOCTANE

CATALYZED BY A DICOBALT COMPLEX

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ACKNOWLEDGEMENTS

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ABSTRACT

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A dicobalt complex [Co^{II}_2L] has been synthesized according to previous methods.[1,2] The [Co^{II}_2L] complex-catalyzed electrochemical reduction of 1-bromooctane was investigated in dimethylformamide (DMF) using cyclic voltammetry (CV) in comparison to the corresponding non-catalyzed reduction. Due to the presence of atmospheric oxygen in the electrochemical cell, degradation of the dicobalt [Co^{II}_2L] catalyst occurred and catalytic reduction of 1-bromooctane could not be accurately characterized. Further research would include repeating the synthesis of the dicobalt complex [Co^{II}_2L] with greater purity standards and the use of an electrochemical cell fitted with a rubber septum(s) to prevent oxygen contamination.

1. INTRODUCTION

1.1. Organobromides

Organobromides are organic compounds containing carbon bonded to bromine. They are generally synthesized industrially by brominating hydrocarbons or by the action of hydrobromic acid on alcohols or alkenes. Organobromine compounds are used extensively as fire-retardants, biocides, dyes, pharmaceuticals, and other chemicals. Several organobromides are naturally produced, but of the few organobromides synthesized by human cells, the first to be found, a bromoester in cerebrospinal fluid induces rapid-eye-movement (REM) sleep.[3,4]

Certain brominated flame-retardants, especially polybrominated diphenyl ethers (PBDEs), are considered persistent organic pollutants (POPs) because of their resistance to environmental degradation through chemical, biological, and photolytic processes. Because of this, PBDEs have been observed to persist in the environment and bioaccumulate in human and animal blood, breast milk, and fat tissues. PBDEs can cause a variety of health problems such as reduced fertility in humans at levels found in households,[5] developmental impairment of the nervous system (affecting behavior and intelligence quotient, IQ), and endocrine system disruption (especially estrogen and thyroid hormones).[6,7]

Aside from the toxicity of PBDEs, organobromides play an important role as intermediates in the synthesis of other chemicals. Bromine is more electronegative than carbon, which causes the carbon to be electrophilic and the organobromine compound to be a good alkylating agent. Grignard reactions, Wurtz reductive coupling, and nucleophilic substitution are only a few of the possible organobromine reactions.

1.2. Electrochemical Reduction

Organobromides are in an oxidized state and need to be reduced in order to eliminate the carbon-bromine bond. Electrochemical reduction offers an alternative method to traditional reducing agents such as magnesium, sodium, lithium, zinc, hydrogen with catalyst, and metal hydrides. In an electrochemical cell, oxidation occurs at the anode and reduction occurs at the cathode. Electricity can be passed through an organobromide solution to cause reduction and oxidation reactions at the cathode and anode respectively.

The reduction of organobromides (RBr) cleaves the bromine atom from the molecule, forming an alkyl carbanion, R^-, by an intermediate radical step and a bromide ion, Br^-.

$$RBr + e^- \rightarrow R\cdot + Br^-$$

$$R\cdot + e^- \rightarrow R^-$$
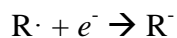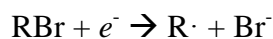
The alkyl carbanion accepts protons, H^+, from the solvent or from the supporting electrolyte cation to yield an alkane, RH:

$$R^- + H^+ \rightarrow RH$$
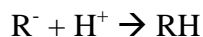
The radical produced can also undergo reductive coupling to produce a dimer, RR:

$$2\,R\cdot \rightarrow RR$$
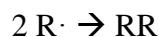
Other side reactions are also possible. The products from this reduction are an alkane hydrocarbon solvent and ionic bromine. Thus, the electrochemical debromination of toxic PBDEs could have beneficial environmental applications. Also, the coupling side reaction that occurs in this process has potential application in the synthesis of larger organic molecules. In theory, halogenated chemical waste could be electrochemically treated and the hydrocarbon products could be isolated for their commercial value and/or recycled / reused for further use as solvents.

One example of this type of reaction is the electrochemical reduction of benzyl bromide to toluene (simple dehalogenation / removal of bromine, Br) and bibenzyl (cleaving followed by coupling reaction). This example reaction is shown in Figure 1.
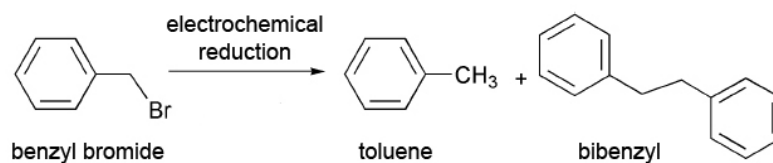
Figure 1. The electrochemical reduction of benzyl bromide to toluene and bibenzyl.

1.3. Cyclic Voltammetry

Cyclic voltammetry (CV) is a type of electrochemical measurement, which utilizes a cyclic scan of different voltages, typically for analyzing the electrochemical properties of a compound in solution. The potential of the working electrode (the electrode on which the reaction of interest is taking place) is ramped linearly with time. In the reduction of organobromides, the working electrode is cathodic. When the working electrode reaches a set potential, the potential ramp is inverted. This inversion can occur multiple times during a measurement if desired. The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram plot. When the current polarity is anodic positive, minimum (I_{pc}) and maximum (I_{pa}) currents observed correspond to the voltages at which reduction (E_{pc}) and oxidation (E_{pa}) reactions respectively take place.

CV utilizes three electrodes: a working electrode, a counter or auxiliary electrode, and a reference electrode. The potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. An electrolyte such as tetrabutylammonium tetrafluoroborate ($TBABF_4$) or tetramethylammonium tetrafluoroborate ($TMABF_4$) is usually added to the solution to increase conductivity.

These concepts are best explained with the example of the electrochemical analysis of ferrocene, which contains an iron cation sandwiched between two aromatic cyclopentadienyl rings.

Ferrocene oxidizes at a low potential around 0.4 V versus a saturated calomel electrode (SCE), a common reference electrode. The oxidation of ferrocene produces a stable cation called ferrocenium, which can be reduced back to ferrocene as shown in Figure 2 or isolated and analyzed.
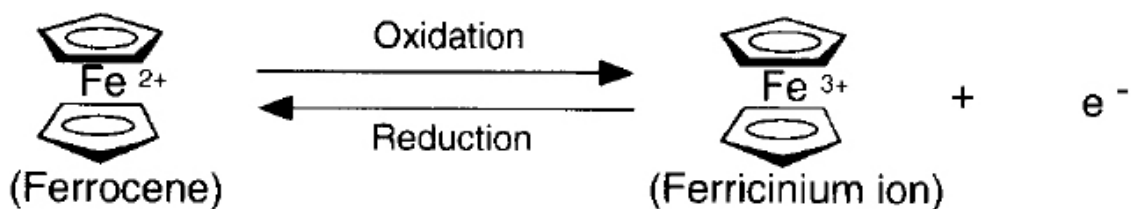
Figure 2. Scheme for the electrochemical oxidation of ferrocene to the ferrocenium ion and its corresponding reverse reduction reaction.

Ferrocene is initially present in the reduced state where iron has an oxidation number of +2. The voltage scan starts at a potential (0 V) less than the estimated oxidation potential, increases past this potential to 1 V, and reverses direction returning to 0 V.   In the forward (positive) scan direction, an oxidation peak is observed where the current flow reaches a maximum (E_{pa}, I_{pa}). Likewise, in the reverse scan direction, a reduction peak is observed where current flow reaches a minimum (E_{pc}, I_{pc}). Figure 3 presents the cyclic voltammogram for the reduction of ferrocene recorded at a scan rate of 100 mV s^{-1} with a glassy carbon electrode in DMF containing 0.05 M TMABF$_4$.
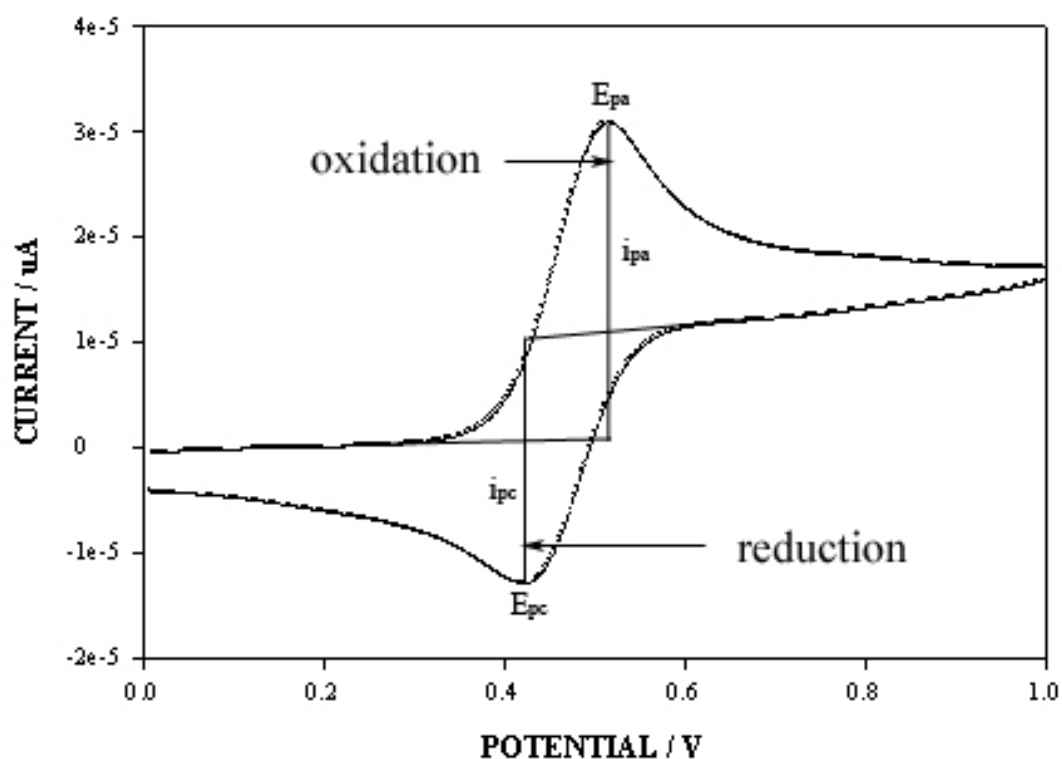
Figure 3. Cyclic voltammogram recorded at a scan rate of 100 mV/s for the oxidation of 1.12 mM ferrocene in DMF containing 0.05 M TMABF$_4$ at a glassy carbon electrode (3 mm diameter). Anodic positive current polarity.

1.4. Catalysis

A catalyst provides an alternative mechanistic pathway with a different transition state and lower activation energy, without being consumed in the process or more specifically, is regenerated continuously. The different transition states can promote some products to form and demote others. They can also cause certain products to form which would not have been produced otherwise, or at any significant or observable concentration or rate of reaction. For example, a particular catalyst might cause radicals produced to be more likely to couple and dimerize with each other than to abstract a proton from the surrounding solvent or electrolyte.

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If enough voltage is applied to a solution, the solvent will reduce. If an analyte in solution has a similar reduction potential to the solvent, an appropriate catalyst could lower the reduction potential of the analyte because lower activation energy equates to less voltage required for the reaction. On a larger scale, a catalyst could help reduce industrial energy costs.

1.5. Previous Research

Salen, shown in Figure 4, is a popular chelating ligand that has been used in homogeneous catalysis. SalenH$_2$ forms metal-ligand complexes with most transition metals with the loss of the two hydrogen atoms bonded to oxygen.
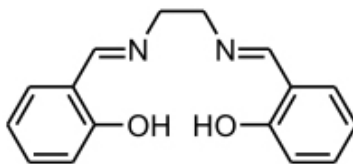
Figure 4. Structure of salenH$_2$.

Cobalt-salen complexes have been used previously as catalysts. The cobalt in these complexes bonds to the alkyl group in organohalides to form an alkylated complex. This cobalt-carbon bond in these alkylated complexes can be cleaved to reproduce the cobalt-salen complex and a corresponding alkyl radical.[2] Radicals are highly reactive and very useful in organic synthesis.

Numerous investigations have been conducted for the reduction of organohalides at glassy carbon cathodes in either DMF or acetonitrile with and without cobalt or nickel salen complex catalysts.[2,8-24] The electrolysis of benzyl bromide in DMF at a glassy

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carbon cathode at -1.4 V versus Ag-AgCl in the presence of the dicobalt complex [Co^{II}$_2$L] catalyst and irradiation by visible light has been shown in previous research to yield bibenzyl as the major product. When the corresponding mononuclear complex [Co^{II}(salen)] was used as a catalyst, toluene was obtained as the major product. No reaction occurred in the absence of the catalyst under the same conditions.[2] For at least some organobromides, research has shown that reduction will occur without a catalyst but at a greater negative potential and current.[8,17] However, organobromides other than benzyl bromide have not been electrochemically studied in the presence of the dicobalt complex [Co^{II}$_2$L] catalyst.

2. EXPERIMENTAL

2.1. Reagents and solvents

    All solvents and chemicals used in the procedures were of reagent grade, used without further purification. Table 1 lists their purity and the manufacturer from which each was purchased.

Table 1. List of Chemicals Used with their Purity and Manufacturer

Chemical	Purity	Manufacturer
1-bromooctane	98%	Alfa Aesar
acetic acid, glacial	99+%	Alfa Aesar
acetone	99.5%	Fischer Scientific
benzene	99.0%	EMD Chemicals
chloroform	99.9%	Fischer Scientific
cobalt (II) acetate tetrahydrate	99%	Alfa Aesar
dimethylformamide	99.94%	EM Science
ethanol	94.0+%	Mallinckrodt
ethylenediamine	99%	Alfa Aesar
methanol	99.8%	EMD Chemicals
petroleum ether	99%	Fischer Scientific
salicylaldehyde	99%	Alfa Aesar
sulfuric acid	96%	Fischer Scientific
trioxane	98%	Alfa Aesar

    Procedures calling for an inert atmosphere were carried out with industrial grade compressed argon and nitrogen gas purchased from Praxair. In-house deionized water was used without further purification. Tetrabutylammonium tetrafluoroborate, TBABF$_4$

(Sigma Aldrich, 99%), was stored in a vacuum oven at 60 °C for dehydration prior to mixture as the supporting electrolyte in the electrochemical reactions. Organobromine compounds are considered light-sensitive and were kept in amber bottles stored in closed cabinets. Smaller clear vials containing the bromo compounds were covered in aluminum foil to protect from light. The single-cobalt [Co^{II}L] catalyst, N,N'-bis(salicylidene)ethylenediamino cobalt(II) (99%) was purchased from Sigma Aldrich and used as reference in electrochemical analysis.

2.2. Synthesis of 5,5'-Methylene-bis-salicylaldehyde

7.0 g (0.206 mole) of trioxane were dissolved into a solution of 80 g of salicylaldehyde (69 ml, 0.655 mole) and 50 ml of glacial acetic acid. A mixture of 0.5 ml of concentrated sulfuric acid and 2.5 ml of glacial acetic acid was placed into an addition funnel above a round bottom flask containing the previous mixture. Nitrogen or argon gas was passed through the apparatus to ensure that air was flushed out for 30 min before the reaction and continuously after its start. The sulfuric acid – acetic acid mixture was slowly added with magnetic stirring under this inert atmosphere at a temperature of 90-95 °C. Magnetic stirring and the temperature of 90-95 °C was continued for 22 hr. This reaction scheme is displayed in Figure 5.
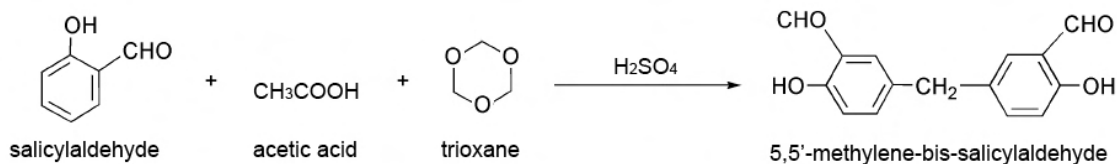
Figure 5. Salicylaldehyde, acetic acid, and trioxane react with sulfuric acid to synthesize 5,5'-methylene-bis-salicylaldehyde.

The reaction mixture was then poured into a 3:1 ice-water solution and allowed to stand overnight. The precipitated solid was vacuum-filtered and washed with two 100 ml portions of petroleum ether. The solid was then vacuum-filtered and washed with 80 ml of petroleum ether three times, thoroughly grinding before each time. The remaining solid was heated below boiling (56 °C) into 300 ml of acetone until dissolved with magnetic stirring. The solution was allowed to cool overnight to recrystallize the pure dialdehyde product. This recrystallized solid was then vacuum-filtered. The filtrate solution was collected and saved for further recrystallization, while the filtrand crystal was washed twice with 80 ml of petroleum ether. The crystallized product was then analyzed using a gas chromatograph (GC, Agilent Technologies 6890N) fitted with a mass spectrometer (MS, Agilent Technologies 5973Network) and flame ionization detector (FID) to determine purity as well as confirm the identity. If the crystal was pure, the sample was saved as a reagent. If the crystal contained impurities, then the sample was re-dissolved in acetone and allowed to recrystallize according to the steps above.[1]

2.3. Synthesis of the Ligand (L)

To a solution of 7.3 g (28.4 mmol) of 5,5'-methylene-bis-salicylaldehyde and 7.0 g (6.1 ml, 57.2 mmol) of salicylaldehyde in 150 ml of benzene, a solution of 3.4 g (56.8 mmol) of ethylenediamine in 40 ml of benzene was slowly added drop-wise, and the reaction mixture refluxed for 30 min at 75-80 °C. This reaction scheme is displayed in Figure 6.
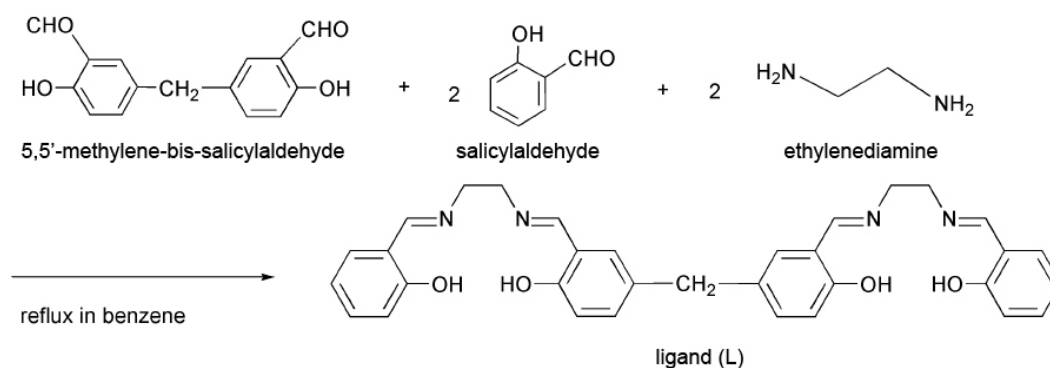
Figure 6. 5,5'-methylene-bis-salicylaldehyde, salicylaldehyde, and ethylenediamine condense under reflux in benzene to synthesize the ligand (L).

It was cooled to room temperature and the precipitated polymeric product was removed by vacuum-filtration. The filtrate was concentrated to dryness using a Buchi Rotavapor R-3000 at 50 °C under reduced pressure to remove benzene. The solid was dissolved with 50 ml of chloroform, and the insoluble solid was vacuum-filtered off and the filtrate dried using a rotary evaporator and collected again. This procedure was repeated three times or until no insoluble polymeric solid remained. The resulting product was washed with hot ethanol to remove the monomeric by-product (H_2(salen)), affording the pure compound L (1.02 g). This product was analyzed by nuclear magnetic resonance (NMR) to verify identity and determine purity.[2]

2.4. Synthesis of the Dicobalt [Co^{II}_2L] Catalyst

This procedure was carried out using ChemGlass Air-Free glassware apparatus under an argon atmosphere to avoid oxidation by atmospheric oxygen. Air in the apparatus was flushed out with argon for 45 minutes. To a degassed solution of 0.25 g (0.46 mmol) of L in 12 ml of chloroform was drop-wise added via an addition funnel a

degassed solution of 0.24 g (0.96 mmol) of Co(OAc)$_2$·4H$_2$O in 20 ml of methanol. This reaction scheme is displayed in Figure 7.

ligand (L)

Co^{II}(OAc)$_2$•4H$_2$O

under N$_2$, at rt,
in MeOH–CHCl$_3$

dicobalt complex [Co^{II}$_2$L] catalyst
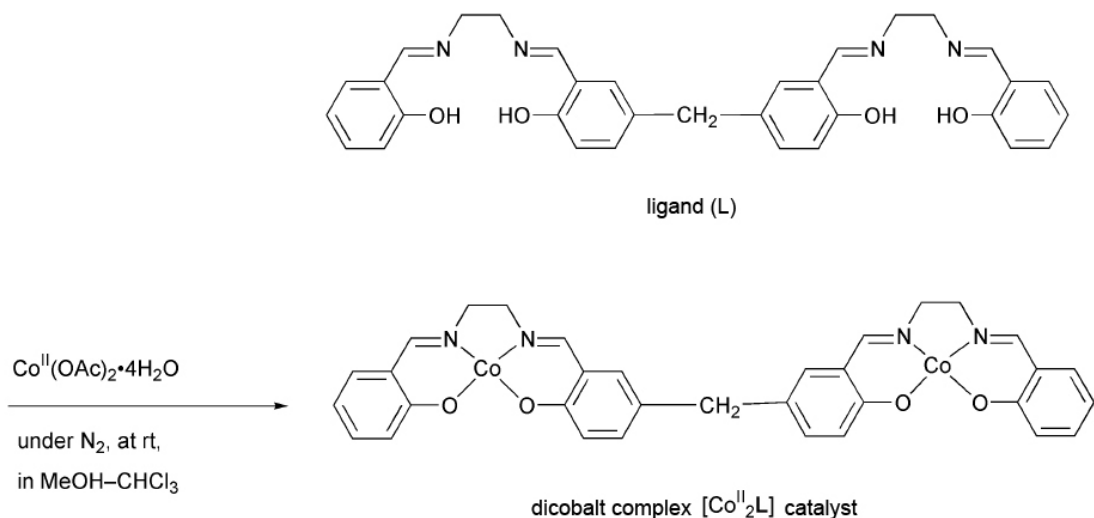
Figure 7. The ligand reacts with cobalt (II) acetate under an inert atmosphere to synthesize the dicobalt catalyst [Co^{II}$_2$L].

A reddish brown solid was immediately precipitated and the mixture magnetically stirred at room temperature for 1 hour. The resulting solid was collected by pressurized filtration using an in-line glass frit chamber while still under argon. This solid was allowed to dry overnight on the glass frit under a continuous flow of positive argon pressure to afford the reddish-brown powder [Co^{II}$_2$L] (0.21 g). The dicobalt catalyst was analyzed by cyclic voltammetry (CV) with a benzyl bromide standard to determine its quality.[2]

2.5. Cyclic Voltammetry of the Organobromides with [Co^{II}$_2$L]

The electrochemical cell for CV, shown in Figures 8 and 9, was used as previously described: A 2 cm (diameter) x 6 cm (height) cylindrical cell (Part No. MF-1083, Bioanalytical Systems, Inc.), a 3 mm diameter glassy carbon working electrode

(Part No. CHI104, CH Instruments, Inc.), and a Ag/AgCl pseudo reference electrode

were used. A platinum wire was employed as the auxiliary electrode. All CV

experiments were carried out with a CH Instruments model 620B electrochemical

analyzer.[4,5]
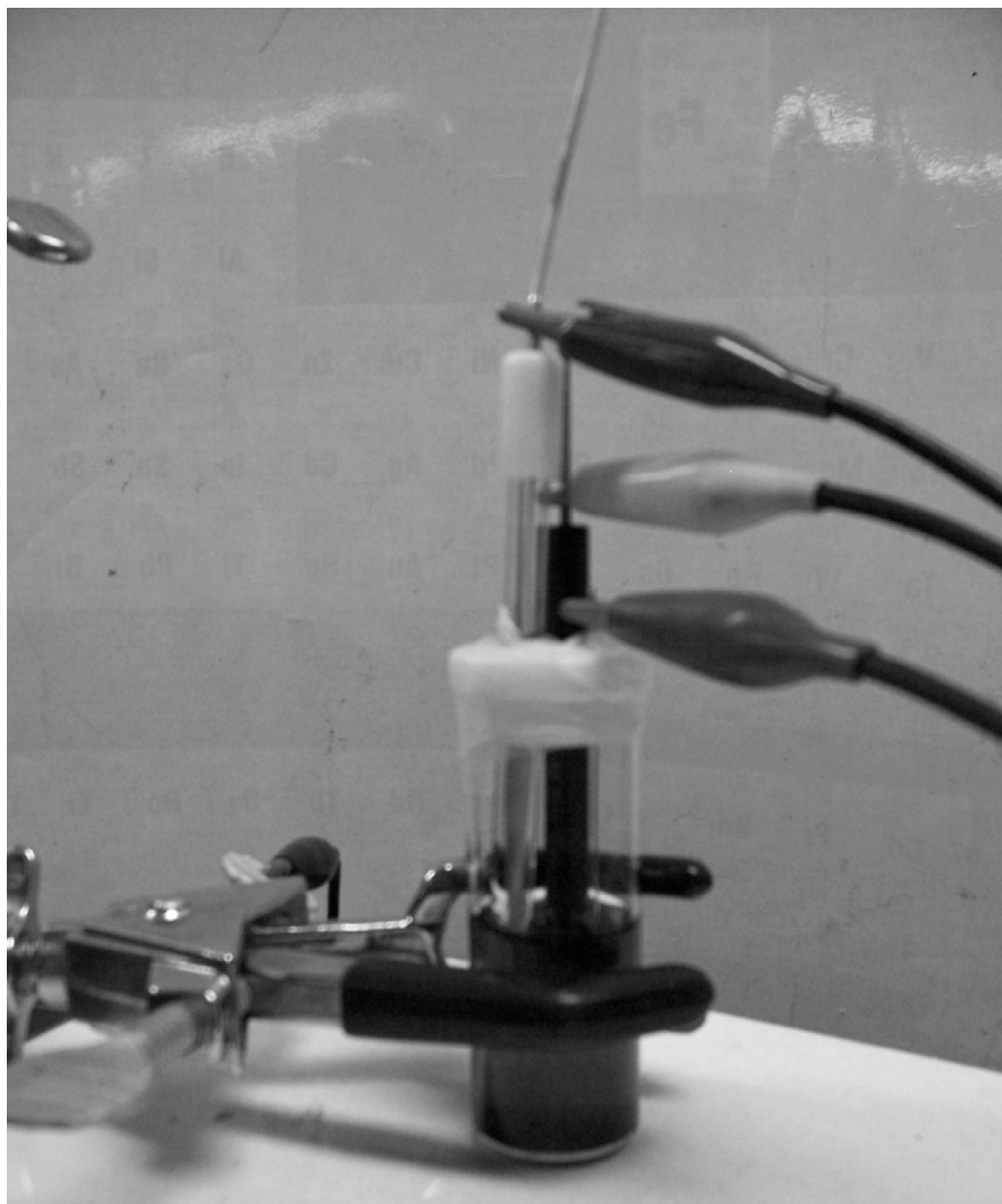
Figure 8. The Parafilm-wrapped electrochemical cell containing the DMF/TBABF$_4$ solution with the [Co$^{II}_2$L] catalyst and 1-bromooctane. Three electrodes (glassy carbon working, platinum counter, Ag/AgCl pseudo reference) and a cannula are inserted into the cell.

An electrolyte solution containing approximately 0.05 M TBABF$_4$ in 10 mL of DMF was prepared and degassed with argon for 10-15 minutes to displace dissolved oxygen. The degassed DMF solution is cannulated by positive argon pressure to the test tube containing the [Co$^{II}_2$L] catalyst. The dicobalt complex is air-sensitive when in solution, but it is air-stable when it is a dry solid.
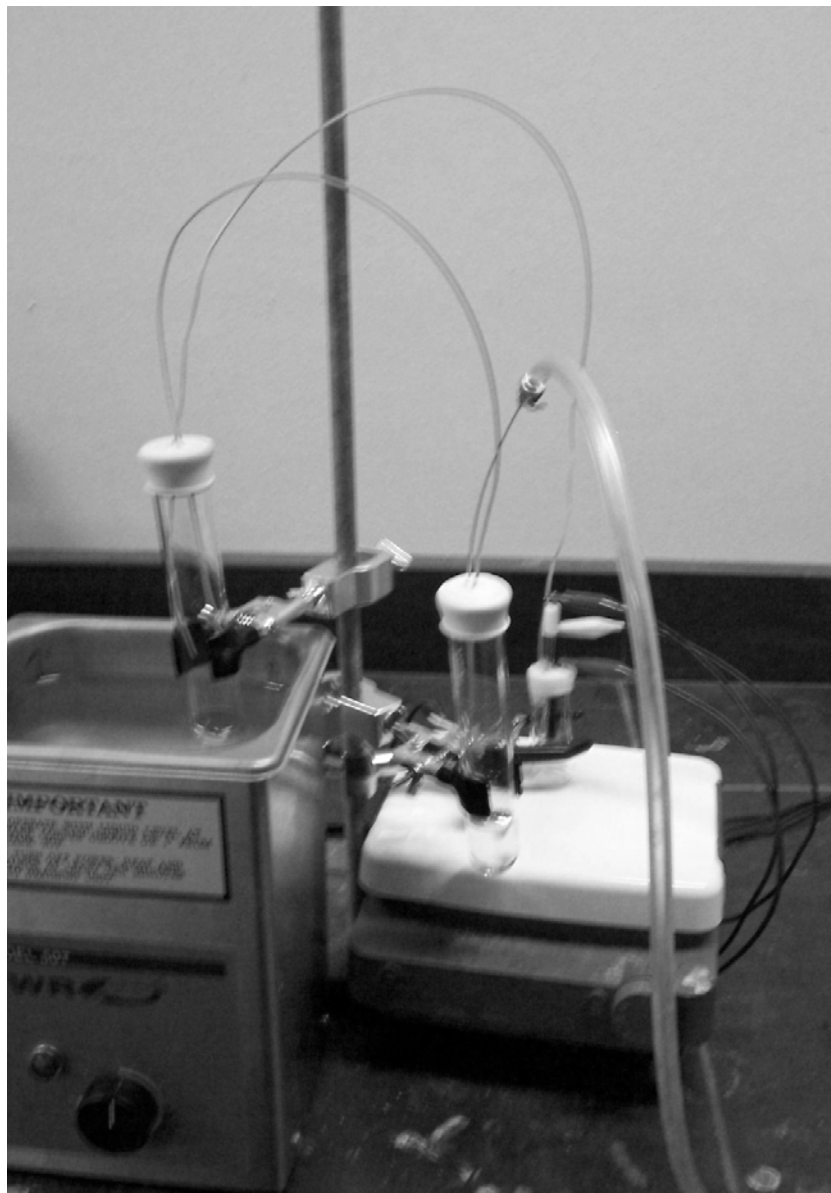
Figure 9. The electrochemical cell setup with cannulas from test tubes fit with septums. An argon gas line is inserted into the first test tube containing the DMF/TBABF$_4$ solution which was cannulated to the second test tube containing the [Co$^{II}_2$L] catalyst. After sonicating, the dissolved catalyst solution was cannulated to the electrochemical cell.

A VWR model 50T sonicator bath was used to easily dissolve the $[Co^{II}_2L]$ into the DMF solution. The dissolved catalyst-DMF solution was then cannulated by positive argon pressure to the electrochemical cell. Varying amounts of the organobromide were injected into the cell by temporarily removing the cannula. Cyclic voltammograms were collected at the scan rates (v) of 100 and 200 mV/s.

Experiments which did not use a cobalt catalyst did not require cannulating. In these cases, the compounds were added directly into the electrochemical cell before degassing of the DMF solution.

2.6. Procedural Hazards

Synthesis of the di-salen ligand (L) utilized ethylenediamine which is highly corrosive, irritating to breathe and hazardous to one's health; it must be carried out in a fume hood. Even opening the bottle of ethylenediamine produces dangerous vapors. Utmost care must be taken with this chemical.

Organobromides were disposed of separately. They are also considered irritating to the skin and to breathe. DMF is considered carcinogenic and can be harmful or fatal if inhaled or absorbed through the skin. Nitrile gloves were worn when handling organobromides and DMF.

Standard laboratory safety was practiced at all times. Safety glasses, nitrile gloves, and a fume hood are a must in many parts of this procedure.

3. RESULTS AND DISCUSSION

The dicobalt complex [Co$^{II}_2$L] was synthesized and characterized after each stage of synthesis by various methods to determine purity and identity of compound(s) present.

3.1. Analysis of 5,5'-Methylene-bis-salicylaldehyde

GC and FID results vary widely for all compounds depending on the parameters set for collecting the data and the concentration of the solution injected into the instrument; thus, GC and FID results are used as general qualitative purity indicators. Figure 10 displays the GC analysis of 5,5'-methylene-bis-salicylaldehyde produced.
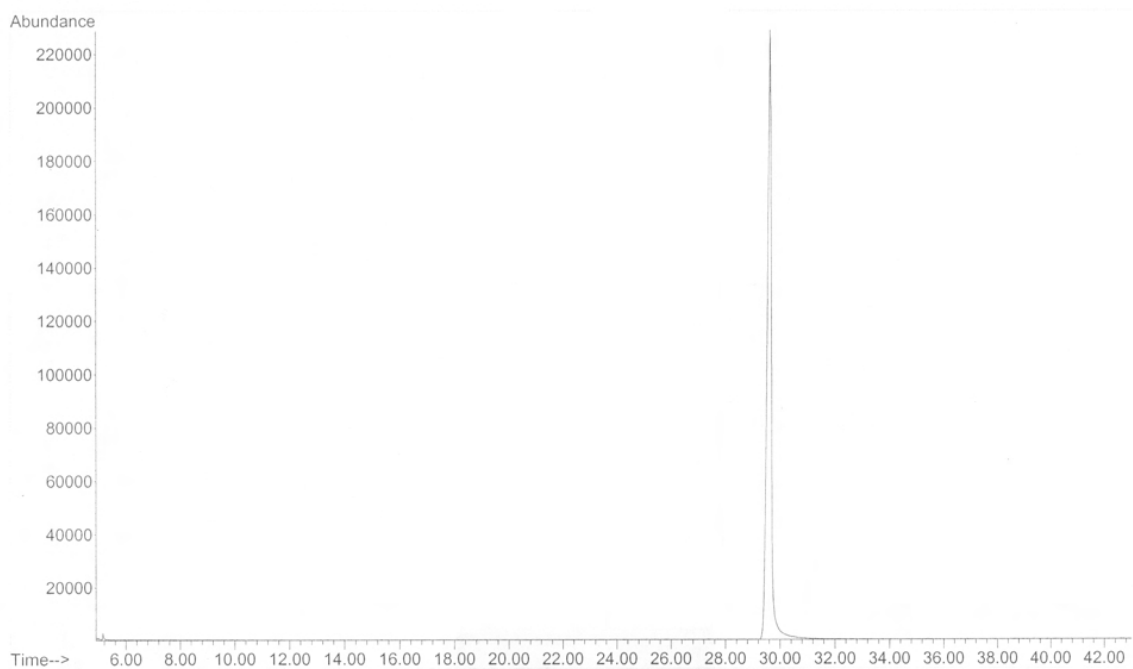
Figure 10. Gas chromatograph of a solution of 5,5'-methylene-bis-salicylaldehyde dissolved in acetone. Time is listed in units of minutes.

The minor first peak at 5.2 minutes was acetone and the major second peak at

29.6 minutes was 5,5'-methylene-bis-salicylaldehyde. Relative purity of the 5,5'-

methylene-bis-salicylaldehyde was established by this GC analysis.

The mass to charge ratios (*m/z*) in mass spectra are unique and inherent to each

compound, invariable to the parameters set; thus, MS data is used to accurately identify

an organic compound. Figure 11 displays the MS of the major second peak in the GC in

Figure 10.
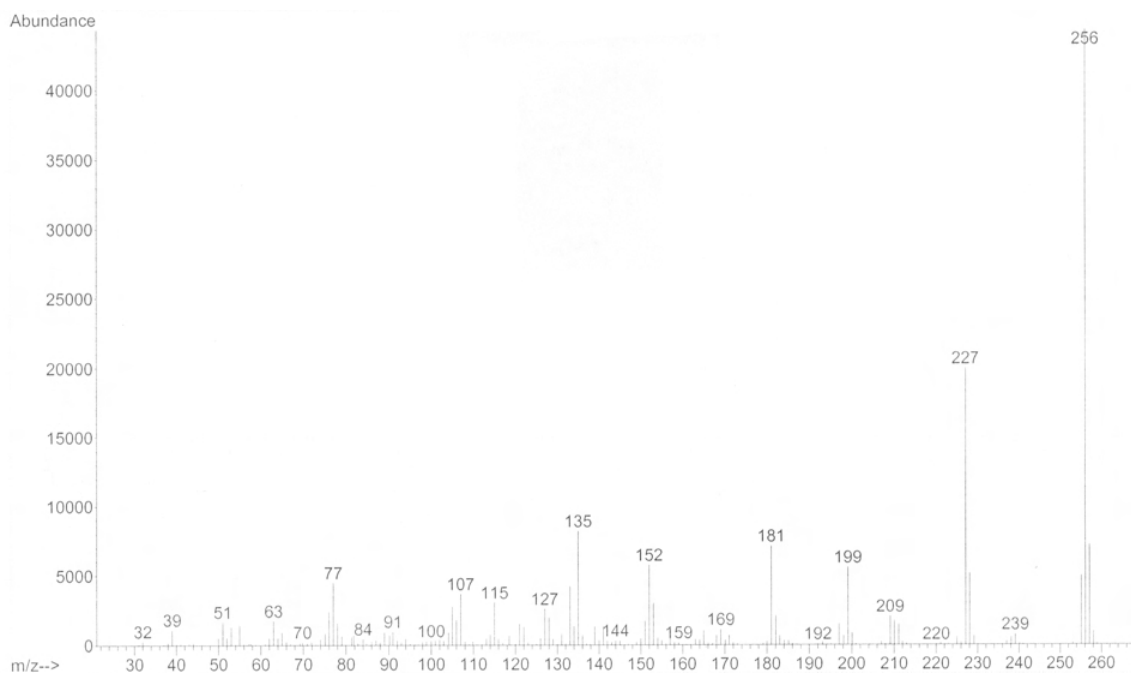
Figure 11. The mass spectrum of 5,5'-methylene-bis-salicylaldehyde found in the gas chromatograph
shown in Figure 10.

5,5'-methylene-bis-salicylaldehyde results found: GC-MS *m/z* (% relative

intensity, ion): 258 (2, M + 2), 257 (16, M + 1), 256 (100, M$^+$), 227 (45, M – CHO). The

observed GC-MS values for 5,5'-methylene-bis-salicylaldehyde matched the predicted

values for this compound.

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Figures 12-15 display GC-FID plots of the 5,5'-methylene-bis-salicylaldehyde compound dissolved in acetone. The complete GC-FID is displayed in Figure 12; however, details cannot be seen because of the overwhelming intensity of the solvent response.

Figure 12. Flame ionization detection (FID) gas chromatograph of a solution of 5,5'-methylene-bis-salicylaldehyde dissolved in acetone. Retention time is listed in units of minutes.

Figure 13 offers a magnification of the GC-FID in Figure 12. Two main peaks are shown. The first peak at 0.4 minutes is the solvent peak, while the second peak at 21.2 minutes is the 5,5'-methylene-bis-salicylaldehyde analyte peak.
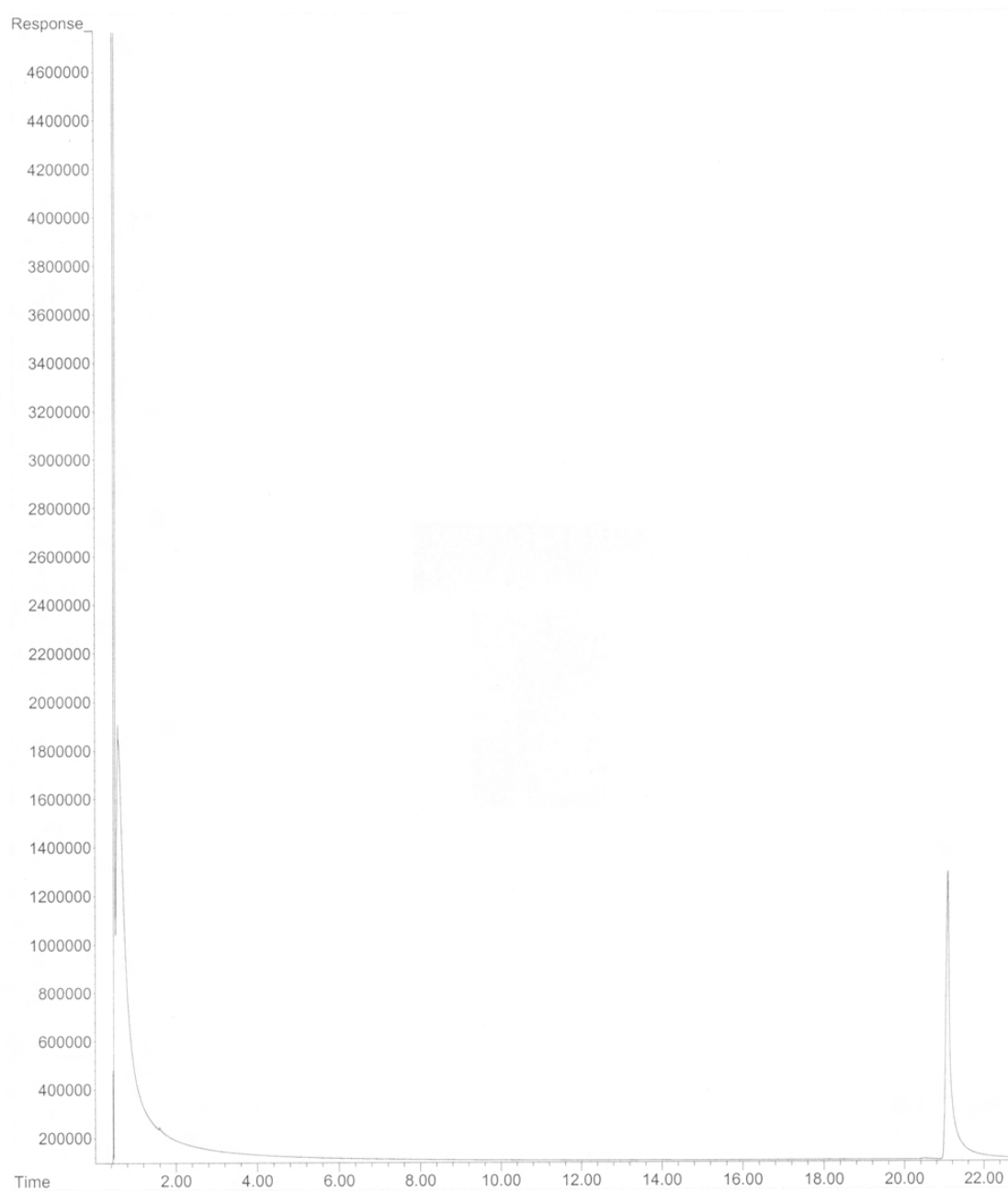
Figure 13. Magnification of the flame ionization detection (FID) gas chromatograph of a solution of 5,5'-methylene-bis-salicylaldehyde dissolved in acetone. Retention time is listed in units of minutes.

A greater magnification of the GC-FID of the solvent peak from Figure 13 is
shown in Figure 14.
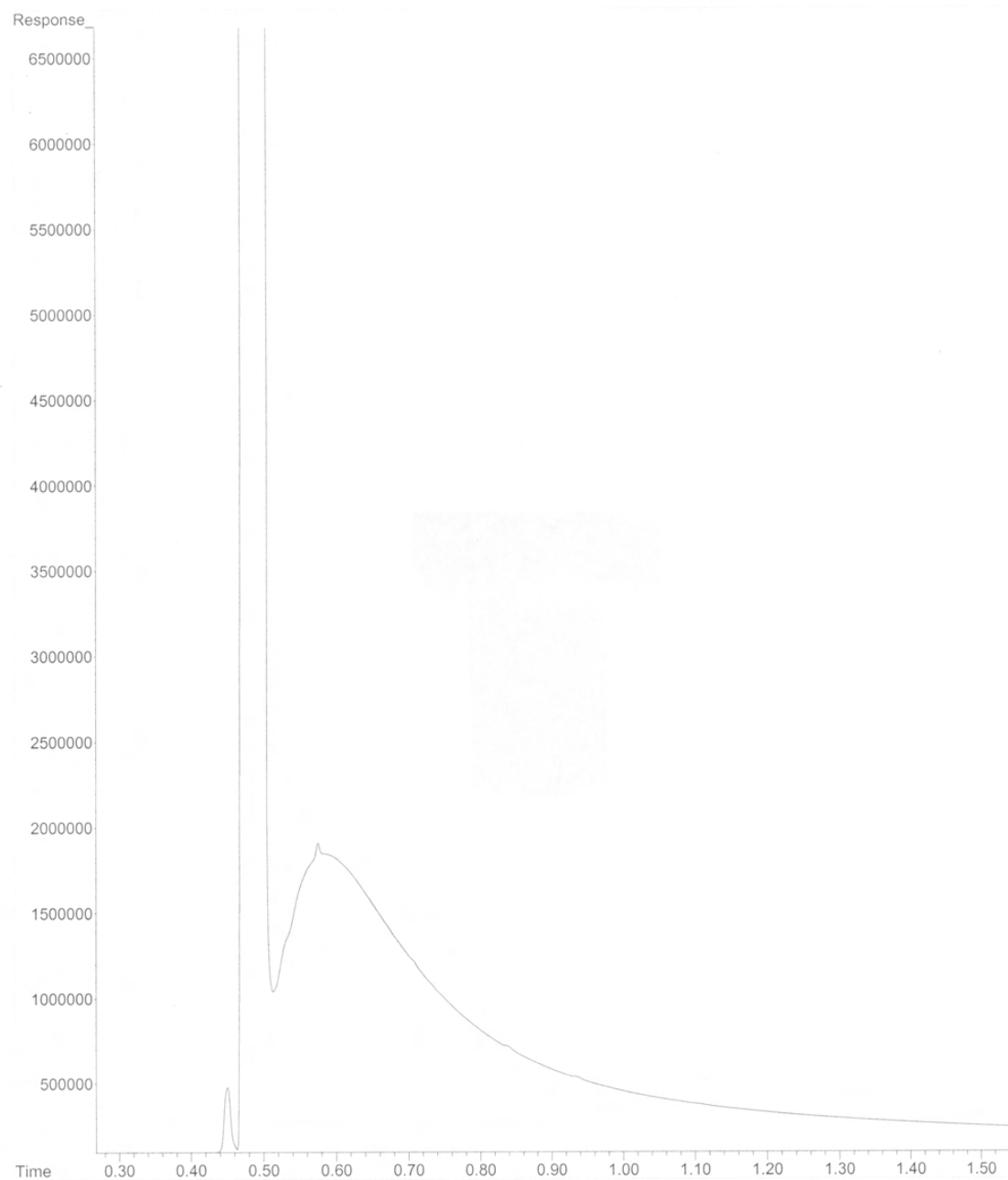
Figure 14. Magnification of the solvent region of the flame ionization detection (FID) gas chromatograph of a solution of 5,5'-methylene-bis-salicylaldehyde dissolved in acetone. Retention time is listed in units of minutes.

While three separate peaks are shown in this region, this is typical for a FID of acetone. Small irregularities in these peaks might be accounted for other solvent present in the acetone as impurities. A greater magnification of the GC-FID of the analyte second peak from Figure 13 is shown in Figure 15.
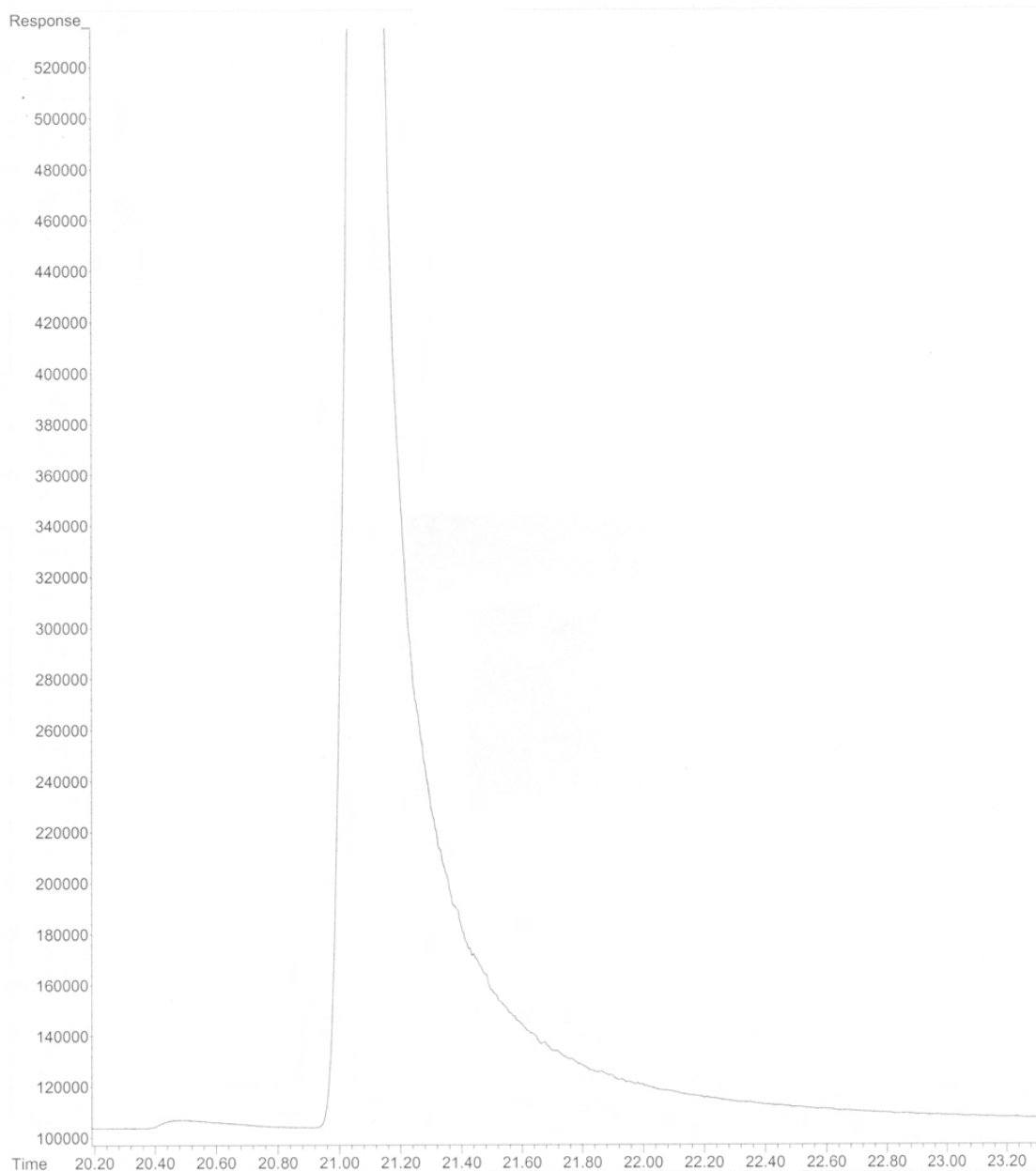
**Figure 15**. Magnification of the solute region of the flame ionization detection (FID) gas chromatograph of a solution of 5,5'-methylene-bis-salicylaldehyde dissolved in acetone. Retention time is listed in units of minutes.

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5,5'-methylene-bis-salicylaldehyde is shown in the GC-FID in Figure 15 to be relatively pure. Small amounts of impurities might exist based on the tailing of the major peak and the small peak of low intensity which precedes the major peak of the analyte.

3.2. Analysis of the Ligand (L)

The ligand synthesized was too large of a molecule to be analyzed by the available GC-MS; therefore, NMR was a more suitable method of analysis. A colleague analyzed the ligand produced via NMR, but results were not of high enough quality to be reported.

3.3. Electrochemical Analysis of the Dicobalt [Co^{II}_2L] Catalyst

To fully analyze the dicobalt [Co^{II}_2L] catalyst, cyclic voltammograms of a blank solution of DMF / TBABF$_4$ (Figure 16), direct reduction of 1-bromooctane (Figure 17), and the single-cobalt [$Co^{II}L$] catalyst (Figures 18 and 19) were collected as reference points. The CV of the dicobalt [Co^{II}_2L] catalyst synthesized is shown in Figure 20. Cyclic voltammograms of [Co^{II}_2L] in the presence of 1-bromooctane in DMF / TBABF$_4$ are shown in Figures 21 and 22.

Figure 16. Negative potential CV of a DMF / 0.05 M TBABF$_4$ blank solution without catalyst nor bromide compound. Potential range of -1.5 V to -2.8 V. 0.1 V/s scan rate. Anodic positive current polarity. Solvent reduction at -2.8 V observed.

The CV of the blank DMF / TBABF$_4$ solution shows solvent reduction occurring at approximately -2.8 V. There is a moderate and uneven current gap between the forward and reverse ramp segments, which is more than likely caused by small amounts of dissolved oxygen in the solution.
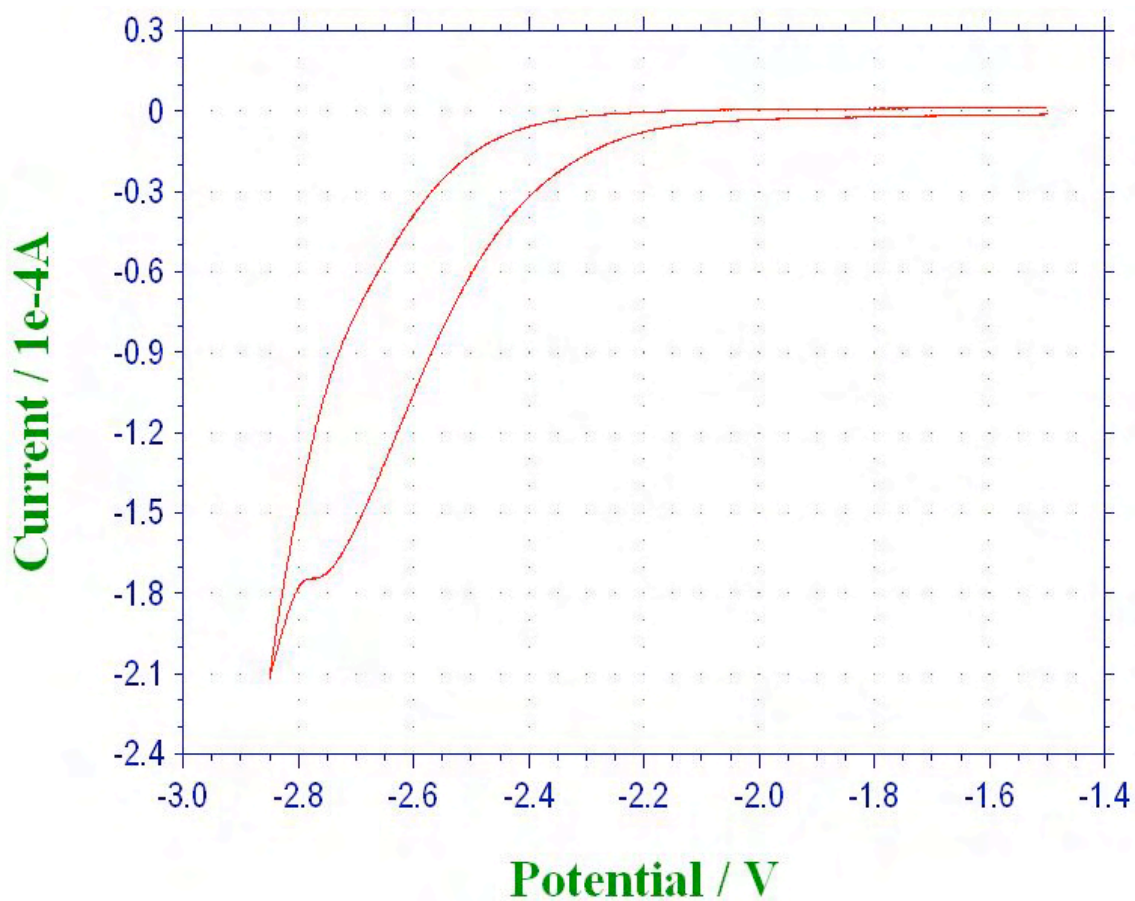
Figure 17. Negative potential CV of a 4 mM 1-bromooctane solution in DMF / 0.05 M TBABF$_4$ without catalyst. Potential range of -1.5 V to -2.85 V. 0.2 V/s scan rate. Anodic positive current polarity. 1-bromooctane reduction at -2.70 V to -2.75 V observed and solvent reduction at -2.85 V observed.

The CV of the 1-bromooctane solution shows solvent reduction occurring at -2.85 V and 1-bromooctane reduction occurring at -2.70 V to -2.75 V. The current gap between the two segments has lowered to correct levels.
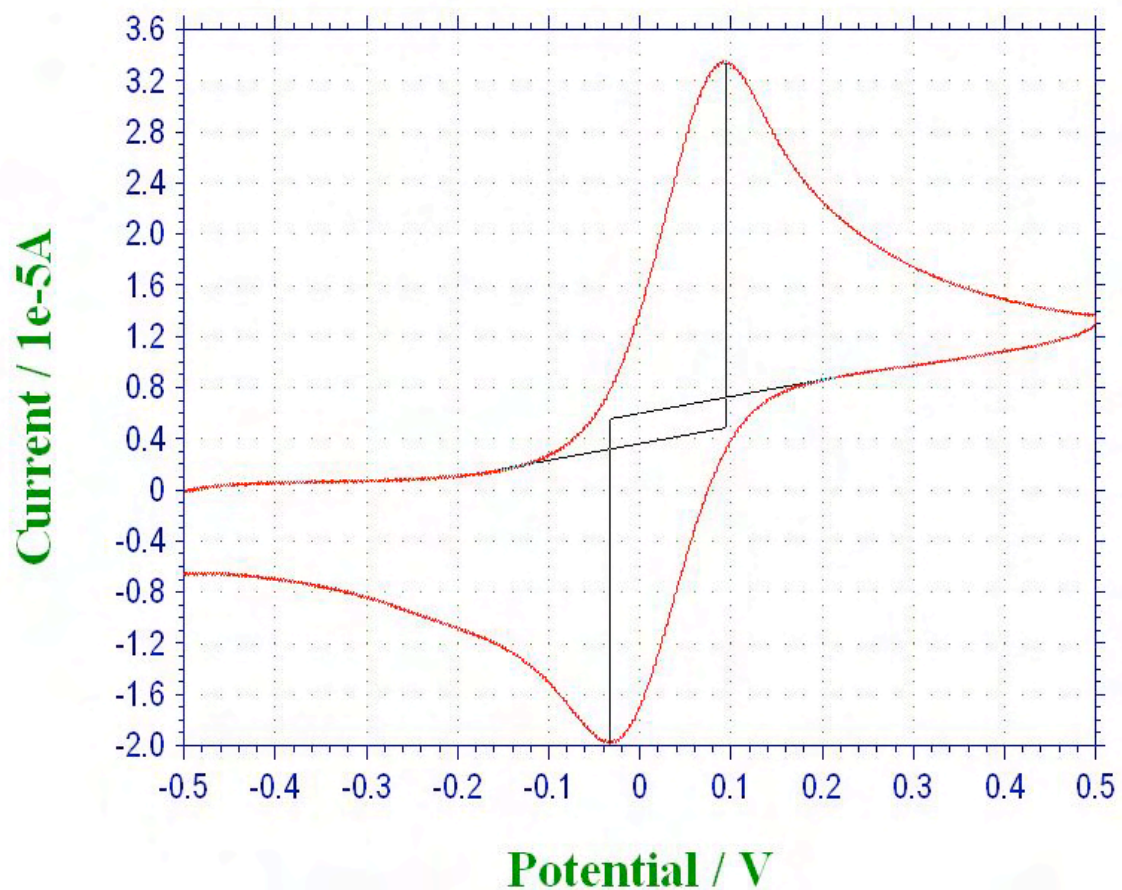
Figure 18. Positive potential CV of 2.3 mM single-cobalt [Co^{II}L] catalyst in DMF / 0.05 M TBABF$_4$ solution without bromide compound. Potential range of -0.5 V to 0.5 V. 0.2 V/s scan rate. E$_{pa}$ = 0.095 V, E$_{pc}$ = -0.033 V. Anodic positive current polarity.

The CV of the single-cobalt [Co^{II}L] catalyst in the positive voltage region shows a distinct oxidation peak at 0.095 V and a distinct reduction peak at -0.033 V. This particular CV shows little if any interference.
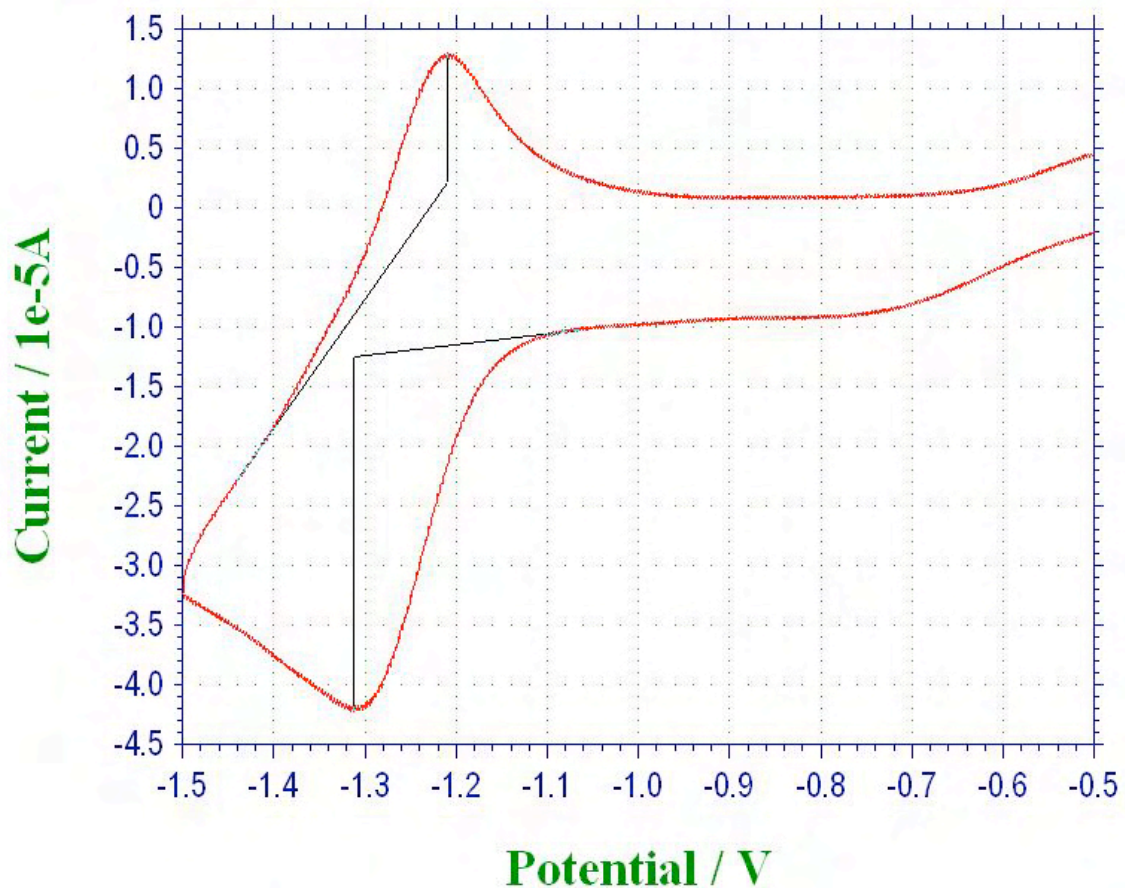
Figure 19. Negative potential CV of 2.3 mM single-cobalt [Co^{II}L] catalyst in DMF / 0.05 M TBABF$_4$ solution without bromide compound. Potential range of -0.5 V to -1.5 V. 0.2 V/s scan rate. E$_{pa}$ = -1.210 V, E$_{pc}$ = -1.312 V. Anodic positive current polarity.

The CV of the single-cobalt [Co^{II}L] catalyst in the negative voltage region shows a distinct reduction peak at -1.312 V and a distinct oxidation peak at -1.210 V. Oxygen leaked into the cell based on the large current gap between the two segments and the small but significant signature oxygen reduction peak around -0.7 to -0.8 V. The reduction peak of the catalyst is not exactly symmetrical; however, the oxidation peak is approximately symmetrical.
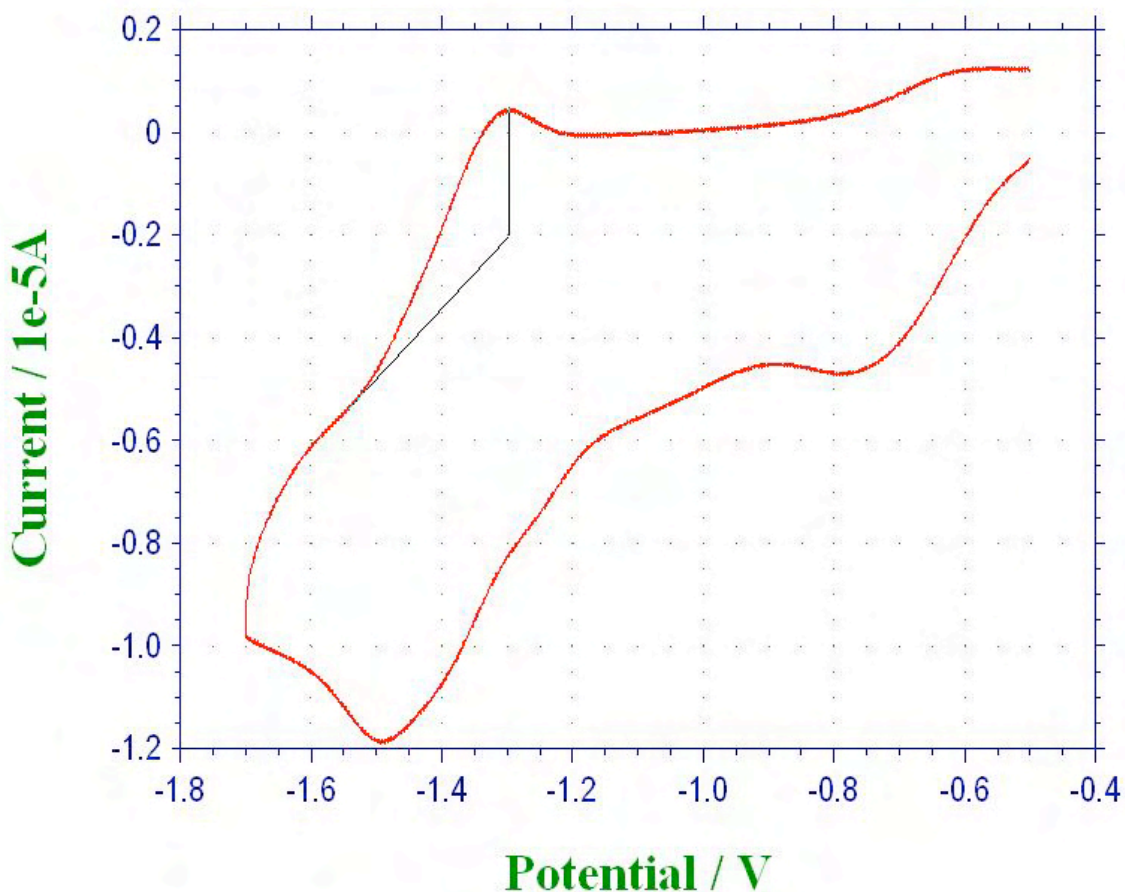
Figure 20. Negative potential CV of 0.64 mM dicobalt [Co$^{II}_2$L] catalyst in DMF / 0.05 M TBABF$_4$ solution without bromide compound. Potential range of -0.5 V to -1.7 V. 0.1 V/s scan rate. E$_{pa}$ = -1.298 V. Anodic positive current polarity.

The CV of the dicobalt [Co$^{II}_2$L] catalyst in the negative voltage region shows a distinct oxidation peak at -1.298 V but no distinct reduction peak. This oxidation peak is close to but differs significantly from the single-cobalt oxidation peak at -1.210 V in Figure 19. A significant presence of oxygen in the cell is apparent from the large current gap, the signature oxygen reduction peak at -0.8 V, and the extensive peak broadening observed. The catalyst reduction peak appears indistinct at approximately -1.3 to -1.5 V because of the peak broadening due to oxygen. This particular reduction voltage corresponds with the single-cobalt reduction peak at -1.312 V in Figure 19.

Cyclic voltammograms of [Co$^{II}_2$L] in the presence of 1-bromooctane in DMF / TBABF$_4$ are shown in Figures 21 and 22.
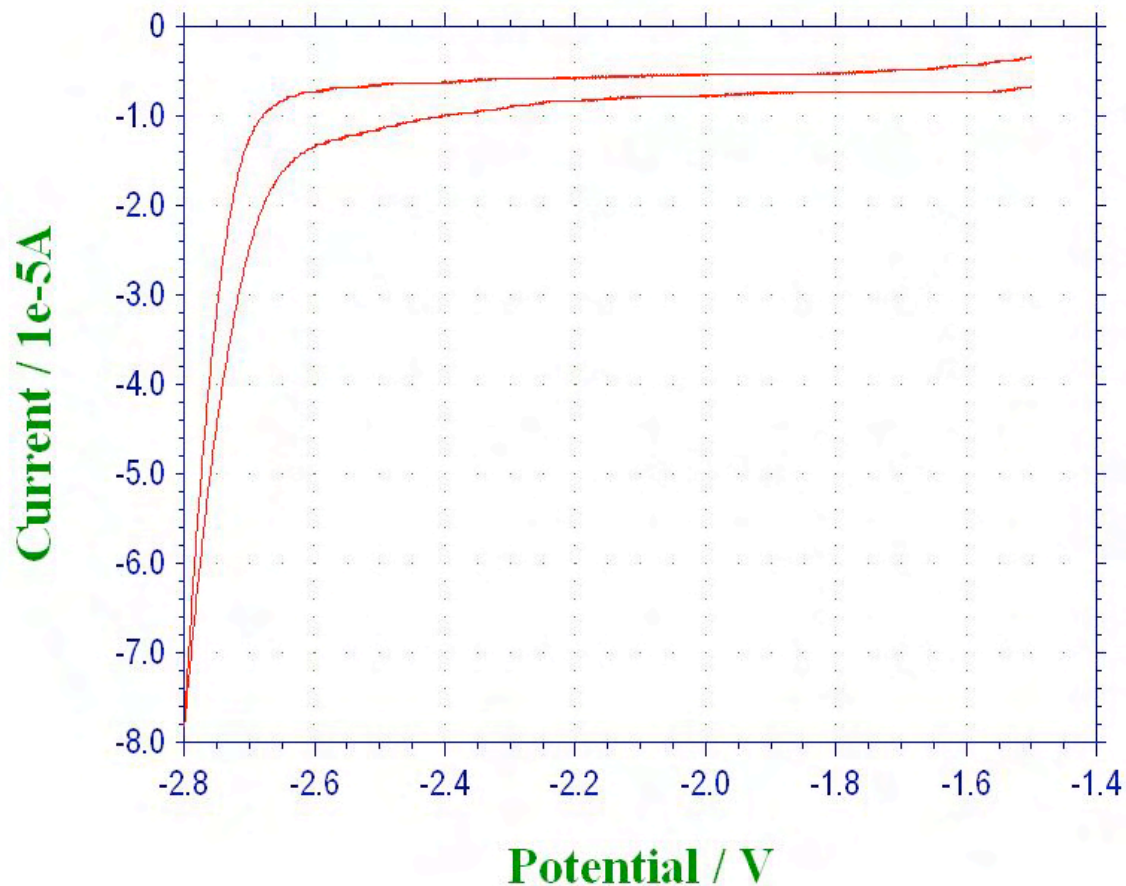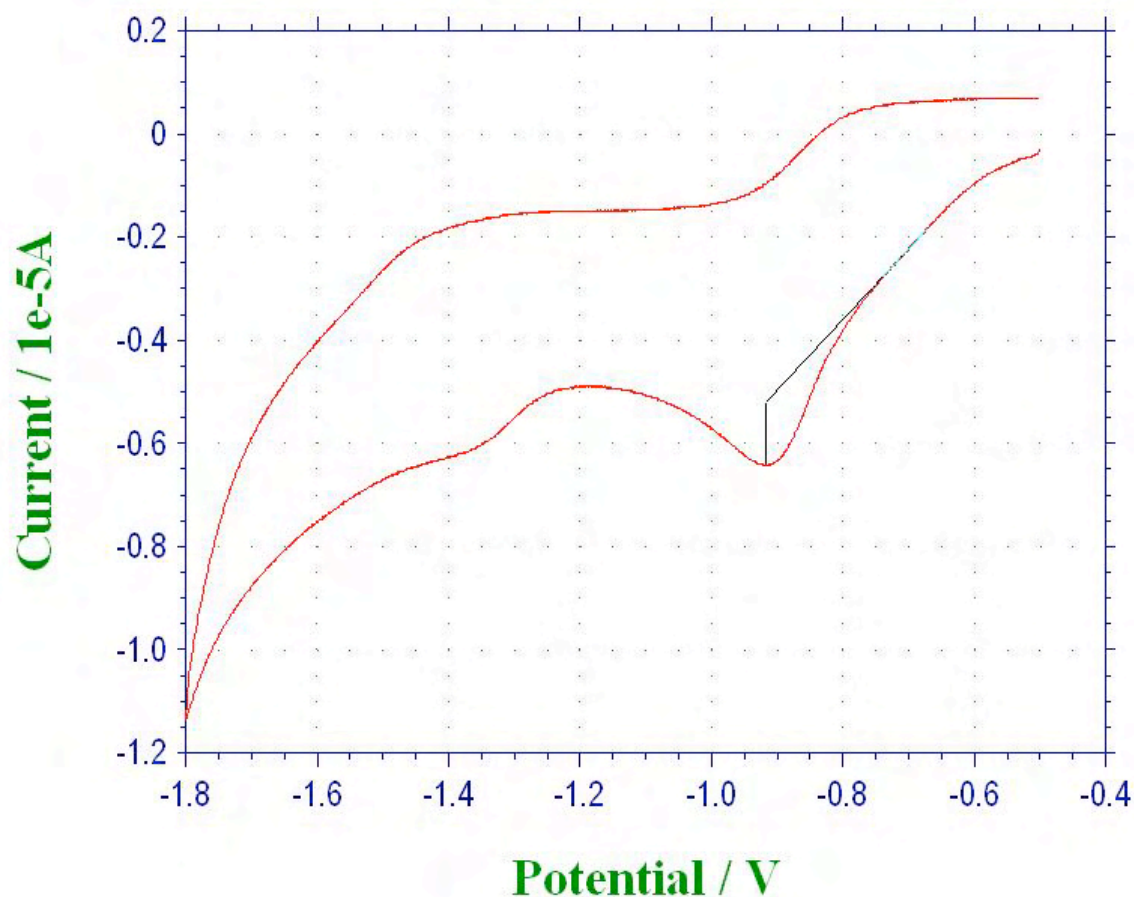

Figure 21. Negative potential CV of a 8 mM 1-bromooctane and 0.65 mM dicobalt [Co$^{II}_2$L] catalyst solution in DMF / 0.05 M TBABF$_4$. Potential range of -0.5 V to -1.8 V. 0.1 V/s scan rate. Anodic positive current polarity. Oxygen reduction observed at -0.918 V.

The CV of 1-bromooctane in the presence of the dicobalt [Co$^{II}_2$L] catalyst in the negative voltage region shows a distinct oxygen reduction peak at -0.918 V. A large current gap also signifies the presence of oxygen in the cell. A small reduction peak around -1.35 to -1.5 V might account for the reduction of the catalyst subdued by peak broadening from oxygen.
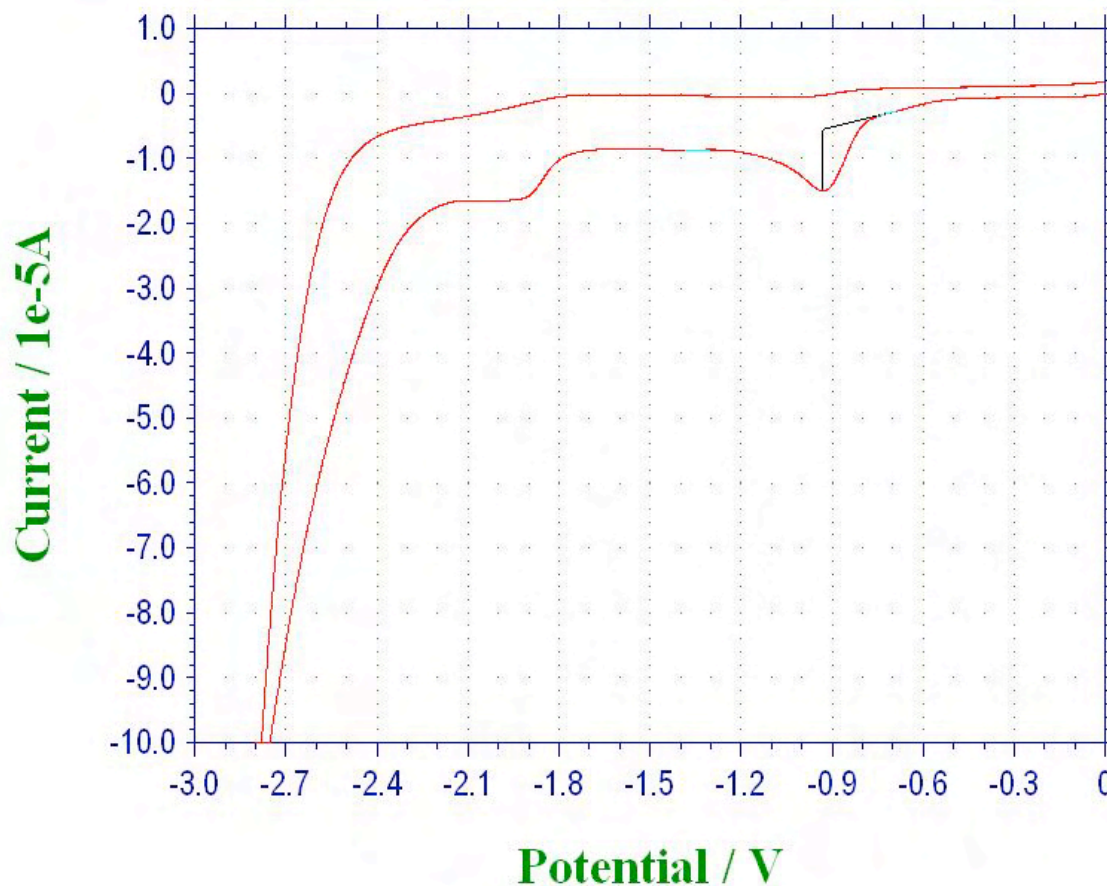
Figure 22. Negative potential CV of a 8 mM 1-bromooctane and 0.50 mM dicobalt [Co$^{II}_2$L] catalyst solution in DMF / 0.05 M TBABF$_4$. Potential range of 0 V to -2.8 V. 0.1 V/s scan rate. Anodic positive current polarity. Oxygen reduction observed at -0.931 V and solvent reduction observed at -2.8 V. Reduction peak observed at
-1.383 V.

The CV of 1-bromooctane in the presence of the dicobalt [Co$^{II}_2$L] catalyst in the negative voltage region shows solvent reduction at -2.8 V and a distinct oxygen reduction peak at -0.931 V. A very small yet distinct reduction peak at -1.383 V might account for the reduction of the dicobalt [Co$^{II}_2$L] catalyst. Another reduction peak occurs around -1.9 to -2.2 V, which was unidentified because the direct reduction of 1-bromooctane occurs at -2.7 to -2.75 V based on the CV of 1-bromooctane in Figure 17.

4. CONCLUSIONS

The CVs of the dicobalt [Co$^{II}_2$L] catalyst in Figures 20-22 indicate the impurity of the catalyst and/or the severe interference of oxygen in the cell. Since the catalyst is sensitive to oxygen when in solution, degradation of the catalyst certainly occurred. It is difficult to determine the purity of the catalyst before being put into solution other than visual appearance because CV was the only method of analysis of the final product.

Since the NMR analysis of the synthesized di-salen ligand showed possible impurities, the dicobalt [Co$^{II}_2$L] catalyst produced from the ligand might have also contained impurities. Also, the small peak preceding the major FID peak of 5,5'-methylene-bis-salicylaldehyde in Figure 15 indicates small amounts of impurities. Whether or not these impurities would have affected electrochemical analysis of the final dicobalt [Co$^{II}_2$L] catalyst produced is unknown.

Additional issues which affected the collection of CVs were: the Ag-AgCl reference electrode needing to be remade and the standardization of subsequent CVs collected, accidental use of acetone for cleaning caused interference, and the light sensitivity of organobromine compounds.

With additional time, I would re-synthesize the dicobalt $[Co^{II}_2L]$ catalyst, better

ensuring its purity by being aware of where to look for the impurities. Also, I would use

a different model of electrochemical cell which included a rubber septum for the cannula

and for the injection of the organobromide. This particular cylindrical cell (Part No. MF-

1083, Bioanalytical Systems, Inc.) was too difficult to keep oxygen from leaking into and

contaminating the catalyst and the CV data. The catalyst would be electrochemically

analyzed with benzyl bromide and the results would be compared with those from

Shimakoshi, Ninomiya, and Hisaeda.[2]

Ideas for additional research include the synthesis of 1,4-butanediol by the

electrochemical reduction of ethylene halohydrins[25] and the catalytic reduction of

environmentally harmful organobromides, such as PBDEs. Also, the electrochemical

reduction of countless organohalides catalyzed by the dicobalt $[Co^{II}_2L]$ catalyst could be

researched.

5. APPENDIX: CHEMICAL HAZARDS

1-bromooctane: Harmful if inhaled. Causes eye, skin, and respiratory tract irritation. Combustible liquid and vapor.

Acetic acid, glacial: Poison. Corrosive. Liquid and mist cause severe burns to all body tissue. May be fatal if swallowed. Harmful if inhaled. Inhalation may cause lung and tooth damage. Flammable liquid and vapor.

Acetone: Extremely flammable liquid and vapor. Vapor may cause flash fire. Harmful if swallowed or inhaled. Causes irritation to skin, eyes, and respiratory tract. Affects central nervous system.

Argon: Simple asphyxiant. Non-toxic, but may cause suffocation by displacing oxygen in air.

Benzene: Flammable. Blood toxin and carcinogen. Absorbed through skin. Affects central nervous system. Harmful or fatal if swallowed or inhaled.

Chloroform: May be fatal if swallowed, inhaled, or absorbed through the skin. Causes irritation to the skin, eyes, and respiratory tract. May affect central nervous system, cardiovascular system, liver, and kidneys. Suspect cancer hazard. May cause cancer. Risk of cancer depends on level and duration of exposure.

Cobalt (II) acetate tetrahydrate: Possible mutagen. Harmful if swallowed, absorbed through the skin, or inhaled. May cause allergic skin reaction. Causes eye, skin mucous membrane, and respiratory tract irritation.

Dimethylformamide: Harmful if swallowed, inhaled or skin contact. May be fatal if swallowed or absorbed through the skin. Possible carcinogen. Exposure may result in fetal death. Long-term exposure may result in kidney or liver damage. Irritant.

Ethanol: Flammable liquid and vapor. May cause central nervous system depression. Causes moderate irritation to skin and respiratory tract and severe irritation to eyes. Causes adverse reproduce and fetal effects. May cause liver, kidney, and heart damage

Ethylenediamine: Corrosive. Flammable liquid and vapor. May cause liver and kidney damage. May cause cardiac disturbances. May cause central nervous system effects. Causes skin, eye, digestive tract, and respiratory tract burns. Hygroscopic. Lachrymator (substance which increases the flow of tears). May cause allergic skin and respiratory reaction. Harmful if swallowed or absorbed through the skin. May cause lung damage.

Methanol: Poison. Causes eye and skin irritation. May be absorbed through intact skin. Causes adverse reproductive and fetal effects. Flammable liquid and vapor. Harmful if inhaled. May be fatal or cause blindness if swallowed. May cause central nervous system depression. May cause digestive tract irritation with nausea, vomiting, and diarrhea. Causes respiratory tract irritation. May cause liver, kidney and heart damage.

Nitrogen: Simple asphyxiant. Non-toxic, but may cause suffocation by displacing oxygen in air.

Petroleum ether: Extremely flammable liquid and vapor. Vapor may cause flash fire. Harmful or fatal if swallowed. Harmful if inhaled. May affect central nervous system. May cause irritation to skin, eyes, and respiratory tract.

Salicylaldehyde: May be harmful if swallowed, inhaled or absorbed through the skin. Causes irritation to skin, eyes, and respiratory tract. Combustible liquid and vapor.

Sulfuric acid: Poison. Corrosive. Liquid and mist cause severe burns to all body tissue. May be fatal if swallowed or contacted with skin. Harmful if inhaled. Affects teeth. Water reactive. Cancer hazard. Strong inorganic acid mists containing sulfuric acid can cause cancer. Risk of cancer depends on duration and level of exposure.

Tetrabutylammonium tetrafluoroborate: Causes eye, skin, and respiratory tract irritation.

Trioxane: Flammable solid. Causes eye, skin, and respiratory tract irritation. Harmful if swallowed or vapors inhaled.

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VITA

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