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KINETICS OF THE LIGAND EXCHANGE REACTIONS BETWEEN BIDENTATE LIGANDS AND TRIETHYLENETETRAMINE NICKELATE (II)

and

SYNTHESIS OF BORON (III) SUBPHTHALOCYANINES WITH VARIOUS BORON SUBSTITUTIONS

by

Michael Christopher Cate

Thesis

Submitted to the Department of Chemistry
Eastern Michigan University
in partial fulfillment of the requirements
for the degree of

MASTERS OF SCIENCE
in
CHEMISTRY

Thesis Committee:
Vance Kennedy, PhD, Chair
Timothy Brewer, PhD
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April, 2007
Ypsilanti, Michigan

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Michael Cate

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I owe my deepest gratitude to the entire faculty of the Department of Chemistry at Eastern Michigan University for their continual advice that has made the completion of this research study possible.

Finally, I would like to thank my wife, Kristi, whose love, support, and understanding have enabled me to attain this. I would also like to thank my friends and family who have given me support and encouragement.

PREFACE

This work was completed in two parts. The first part (Chapters 1-4) was done under the direction of Professor Larry Kolopajlo. The second part (Chapter 5-8) was completed under the direction of Professor Vance Kennedy.

ABSTRACT

Part 1. The kinetics of the ligand exchange reaction between 5-methyl-1,10-phenanthroline and triethylenetetramine nickel (II) were studied spectrophotometrically over the pH range of 5.2 to 8.0 at 25°C. A ternary complex Ni(Trien)(5MP) forms within a few seconds and subsequently reacts with 5MP to form $Ni(5MP)_3$. The reaction is first-order with respect to: [5MP], [Ni(Trien)(5MP)] and [H+]. The rate law is given by:

$$\frac{-d[Ni(trien)]}{dt} = (k_{MP}^{Ni(trien)(5MP)} + k_{H,\,5MP}^{Ni(trien)(5MP)}\,[H^+])\,[Ni(trien)][5mp]$$

where: 5MP is 5-methyl-1,10-phenanthroline and k is the first order rate constant that has units of 1/time.

$$k_{H,\,5mp}^{Ni(trien)(5mp)} = 9.78 \text{ X } 10^{4}\ M^{-2}\ s^{-1}$$

$$\text{and } k_{5mp}^{Ni(trien)(5mp)} = 9.42 \text{ X } 10^{-3}\ M^{-2}\ s^{-1}$$

Part 2. Axial substitution on boron (III) subphthalocyanines (SubPcs) were investigated. The Boron subphthalocyanines BsubPcCl and BsubPcOH were synthesized. These derivatives were then used to prepare $BsubPcSiHx_3$, BsubPcBu, and $BsubPcOSi(CH_2CH_2CH_2CH_3)_3$. This study represents the first synthesis of axial substitution on boron subphthalocyanine with a tributylsiloxy group. The products were characterized by infrared spectroscopy, ^{1}H nuclear magnetic resonance analysis, and high resolution mass spectroscopy.

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CHAPTER 1: Introduction and Background

1.1 Nickel Reaction: Introduction and History.

In order to understand the environmental fate and toxicity of strongly complexed nickel in industrial waste streams, it is important to understand the kinetics and mechanisms of nickel reactions. Part per million concentrations of dissolved nickel can be found in municipal wastewater effluents, surface runoff, and natural waters. This typically comes from computer hard drive manufacturers, printed circuit board manufacturers, and metal finishers.[1] Industrial companies frequently perform waste water treatment of nickel waste streams themselves or send the wastes to hazardous waste disposal facilities for treatment. Typically, the pH of the waste is adjusted higher and a solid nickel hydroxide precipitate forms. When the solid is filtered, the precipitated nickel remains in the solid phase and the liquid is discharged to the local water treatment municipality.

Nickel is generally a six-coordinate Ni^{+2} cation that can complex with organic ligands. This usually lowers its affinity for surfaces and can lead to its passage through waste water treatment systems untreated. Left untreated, metal toxicity can occur to organisms. By taking kinetic measurements of ternary complex formation between nickel complexes and bidentate ligands, a bonding mechanism can be proposed. This mechanism could then be applied to complexes containing other metal ions and other unbranched multidentate ligands. This study of nickel kinetics will be helpful in solving precipitation problems associated with the waste water treatment of chelated nickel compounds.

1.2 Ternary Complex Formation Kinetics.

The kinetics of ligand substitution of *n*-phenanthrolines has been previously studied over very narrow pH ranges.[2-3] By examining phenanthrolines with different R groups over a wider pH range, different reaction rates can be determined that alter the mechanism. A proposed mechanism can then be compared to similar systems, such as other nickel polyamine formation and dissociation studies.

Previously published papers have examined mechanisms of formation / dissociation reactions involving multidentate ligands and nickel. One of the first examinations observed the reaction of triethyleneteramine and tetraethylenepentamine with nickel.[4] The author suggested that these 4- and 5-dentate ligands react with nickel by the stepwise formation of coordinate bonds where the rate determining step is the formation of the first nickel-nitrogen bond. Formation of subsequent bonds is then held to be very rapid. In the same way, the dissociation mechanism proposed involves the pre-equilibration of intermediately bonded species leading to the rate-determining step of breaking the last nickel-nitrogen bond. From this data, the author was able to estimate the equilibrium constants for each of the reaction intermediates. This comprehensive analysis of the nickel polyamine mechanism showed an initial point from which the common kinetic behavior of multidentate ligands could be examined.

The same authors also examined the exchange of ethylenediamine-tetraacetate ions in the presence of triethylenetetraminenickel(II) and tetraethylenepentaminenickel(II).[5] Here the exchange reactions involve one multidentate ligand replacing another in a metal complex. The effects of steric hindrance, protonation, rate of water loss, and rotational barriers influence the rate of the reaction. The reactions investigated were:

$$HY^{3-} + NiT^{2+} \text{ ----> } NiY^{2-} + HT^{+}$$

$$HY^{3-} + NiHTe^{3+} \text{ ----> } NiY^{2-} + H_2Te^{2+}$$

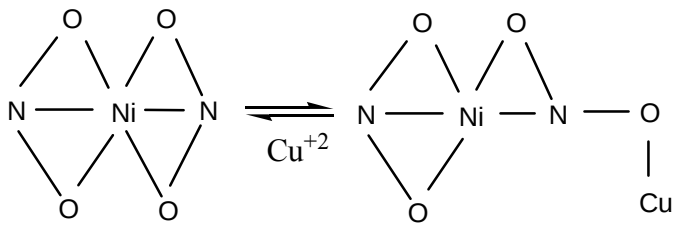
where T represents the quadridentate polyamine, triethylenetetramine (trien), Te represents the quinquedentate polyamine, tetraethylenepentamine (tetren), and Y^{3-} represents ethylenediaminetetraacetate ion (EDTA). A mechanism that involved numerous mixed ligand intermediate complexes was proposed. Each successive intermediate had increasing coordination to EDTA and decreasing coordination to the polyamine. The rate determining step in each case involved the loss of one of the water molecules from nickel followed by the rapid bonding of one of the nitrogen centers of the EDTA ligand.

Based on the previous two articles, another ligand exchange reaction was examined between 1,10-phenanthroline and triethylenetetraminenickel(II). Steinhaus et al. examined the dissociation involving two repeated steps, first the nickel-nitrogen bond breakage followed by nickel-solvent bond formation.[3] The nickel-nitrogen bond breakage continued until the polyamine completely dissociated from the nickel ion. The rate-determining step for the formation reaction was the nickel-water loss, while the rate-determining step for the dissociation was the nickel-nitrogen bond dissociation. The kinetics of the following reaction were examined to investigate the mechanism and effects to be studied:

$$Ni(trien)^{2+} + 3phen \text{ ----> } Ni(phen)_3^{2+} + trien$$

A comparison was made at varying pH ranges. Comparing the rate constants for both the dissociation of the trien from $Ni(trien)(phen)^{2+}$ and the dissociation of trien from $Ni(trien)^{2+}$ showed that both the rate of formation and dissociation rate constants were virtually identical. Previous studies showed that when similar rate constants for several related systems were obtained, the same mechanism holds true for those systems.[5]

While the substitution of multidentate ligands from one metal to another had been considered, the effect that an already coordinated ligand had upon an exchange reaction had not been examined. A general mechanism was proposed between copper(II) and bis(iminoacetato)nickelate(II).[6] Comparisons to other nickel-ligand exchange reactions with copper were introduced. This led to the conclusion that systems where the binuclear intermediate is formed early in the unwrapping process will not show a reaction order shift as the concentration of the attacking metal is increased.



binuclear intermediate

Figure 1. Example of Binuclear Intermediate

This is also true if the attacking metal does not fully bond to the unwrapping ligand. If a significant amount of the ligand unwraps and bonds to the attacking metal before the rate-determining step, a shift in reaction order can be predicted.

Two years later Steinhaus et al. investigated the effect of coordinated (triethylenetetramine)nickel(II) upon formation reactions of bidentate ligands using both 1,10-phenanthroline and glycine.[7] The reaction between Ni(trien) and 1,10-phenanthroline did not show a kinetic rate order dependence upon ligand concentration as Ni(trien) and glycine did. This was due to the difference in dissociation rates and provided evidence that the carbonyl group of glycine bonded first in complex formation.

Later that year, Steinhaus analyzed the kinetics of the ligand exchange reaction between 1,10-phenanthroline and ethylenediaminediacetato-nickelate(II).[2] When the ligand exchange

reaction of 1,10-phenanthroline and $Ni(trien)^{2+}$ was studied previously, the outcome showed an initial fast formation of $Ni(trien)(phen)^{+2}$,followed by slow replacement of trien by phen. Steinhaus then investigated the same exchange reaction using another tetradentate ligand, ethylenediaminediacetic acid (EDDA).

$$Ni(EDDA) + 3phen \text{ ----> } Ni(phen)_3^{2+} + EDDA^{2-}$$

This gave a complex with two terminal sites that were less sterically hindered due to the smaller amount of room required by the acetate groups compared to the amino groups.

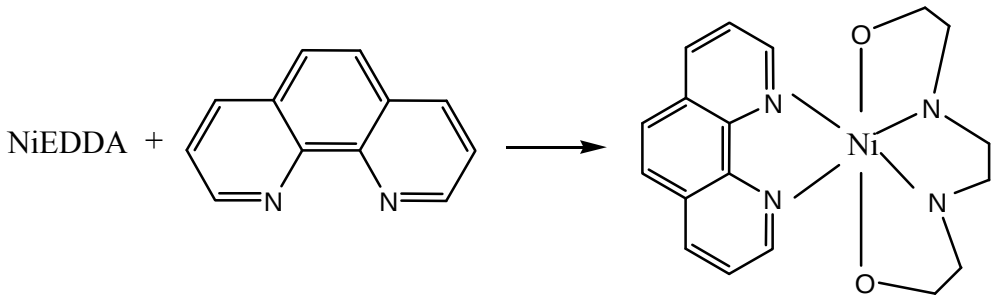


Figure 2. Ni(EDDA) Reaction with Phenanthroline

Years later, in 1985, the reactions between (ethylenediamine-N,N'-diacetato)nickel(II) and various other ligands were examined. The effects of steric hindrance were observed in the reaction of both 1,10-phenanthroline and bipyridine with $Ni(trien)^{+2}$ when the product was found to have three of the trien nitrogen atoms coordinated to the nickel center.[8] In this instance, there was not enough room for complete coordination of all sites on the metal. In some cases, the coordinated ligand appears to be able to decrease ring closure of the attacking ligand through distortion of the metal coordination sphere.[8]

Most recently, an electronic ligand effect was examined in which protonation of the amine

groups inhibited recoordination of the ligand to the nickel.[9] Acid catalyzes the dissociation of the ligand from the metal center by preventing recoordination of the free ligand. The ligand exchange reactions of bipyridine with Ni(EDDA) and Ni(trien) were evaluated and mechanisms were proposed. The ligand exchange kinetics demonstrated how steric hindrance from the trien did not allow ligand replacement of bipyridine until all four amine sites of the trien were dissociated from the nickel.

It is obvious that the rate of the reaction can be affected by the size of the ligand and the hydrogen ion concentration of the solution. By examining new ligand/nickel complex reactions, previous mechanisms can be reinforced or new mechanisms can be established. Based on this observation, we decided to explore three different reactions. To examine the effect of sterics on the reaction rate, we used two substituted phenanthroline ligands: one with an additional methyl group at the 5 position and one with a methyl group at the 5 and 6 positions. Also, to examine the effect of an electron withdrawing group on the ligand, we used a chlorine group at the 5 position.

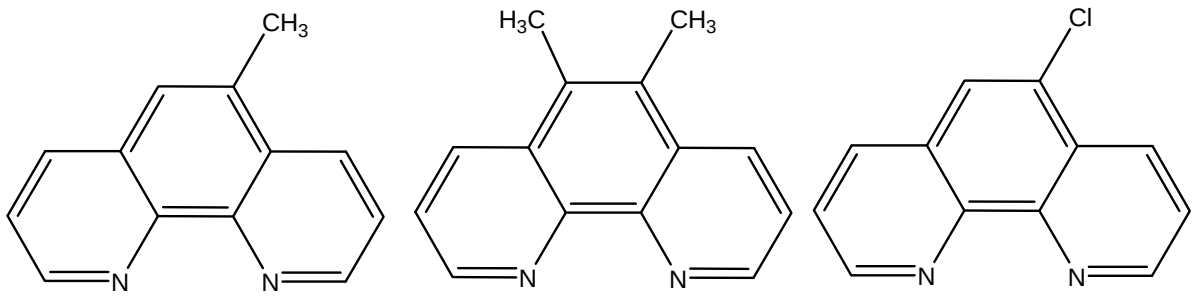


Figure 3. Ligands used in this Study.

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CHAPTER 2: Experimental

2.1 Reaction of triethylenetetramine nickel [Ni(trien)] with 5-methyl phenanthroline (5MP).

The spectra of all reactants and products were obtained from 900 nm to 200 nm. Comparison of these spectra showed that the greatest change in molar absorptivity between reactants and products at the concentrations used in this study occurred at 356 nm, as shown in Figure 11. All reactions were monitored at this wavelength to follow the product formation of $Ni(5MP)_3$:

$$Ni(trien)^{2+} + 3(5MP) \rightarrow Ni(5MP)_3^{2+} + Trien$$

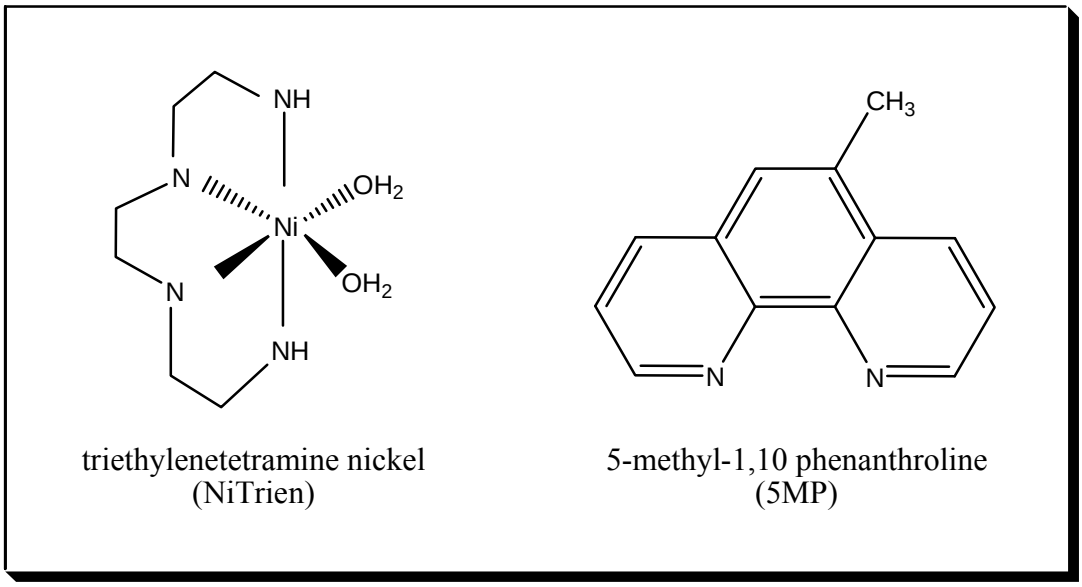


Figure 4. Representation of Reactants Ni(Trien) and 5MP

Sodium chloride was used to maintain an ionic strength of 0.1 M. A pH meter was used to adjust the pH of each solution by adding hydrochloric acid or sodium hydroxide to the appropriate buffer. The molar absorptivities of $Ni(trien)^{+2}$, 5MP, $H5MP^{+}$, and $Ni(5MP)_3^{2+}$ were determined by measuring the absorbance of each stock solution under the above

conditions. The slope of a plot of concentration vs. absorbance was used to determine the molar absorptivity (Table I and II). The Ni(trien) molar absorptivity was not determined since the addition of 5MP coordinates very quickly with nickel at one coordination site.[1] The molar absorptivity of a proposed mixed ligand complex, $Ni(trien)(5MP)^{+2}$, was measured by adding an excess of trien to a solution of $Ni(5MP)^{+2}$. The absorbance of this solution was measured and the molar absorptivity calculated. Once the molar absorptivity was determined, reactions were measured adjusting the pH at constant concentration of ligand to nickel complex in duplicate. Next, reactions were measured at constant pH and increasing ligand concentration.

2.2 Reaction of triethylenetetramine nickel [Ni(trien)] with 5-chloro phenanthroline (5CLP).

The spectra of all reactants and products were obtained from 900 nm to 200 nm. Comparison of these spectra showed that the greatest change in molar absorptivity between reactants and products at the concentrations used in this study occurred at 350 nm, as shown in Figure 16. All reactions were monitored at this wavelength to follow the product formation of $Ni(5CLP)_3$:

$$Ni(trien)^{2+} + 3(5CLP) \rightarrow Ni(5CLP)_3^{2+} + Trien$$

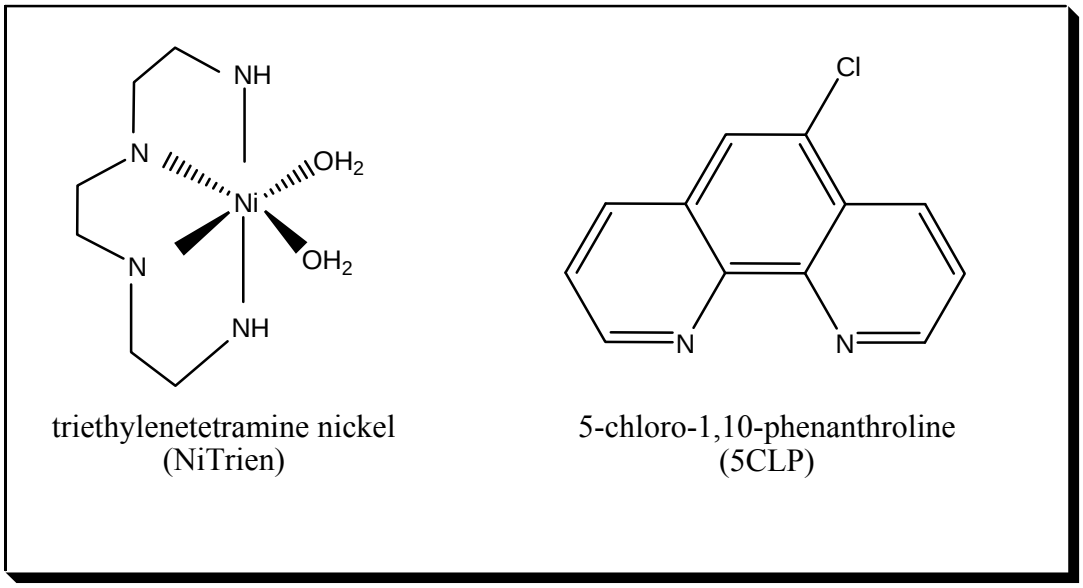


Figure 5. Representation of Reactants Ni(Trien) and 5CLP

Sodium chloride was used to maintain an ionic strength of 0.1 M. A pH meter was used to adjust the pH of each solution, using with a hydrochloric acid or a sodium hydroxide buffer. The molar absorptivities of $Ni(trien)^{+2}$, 5CLP, $H5CLP^{+}$, and $Ni(5CLP)_3$ were determined by measuring the absorbance of each stock solution under the above conditions. The slope of a plot of concentration vs. absorbance was used to determine the molar absorptivity. The Ni(trien) molar absorptivity was not determined since the addition of 5CLP coordinates very quickly with nickel at one coordination site.[1] The molar absorptivity of a proposed mixed ligand complex, $Ni(trien)(5CLP)^{+2}$, was measured by adding an excess of trien to a solution of $Ni(5CLP)^{+2}$. The absorbance of this solution was measured and the molar absorptivity calculated. Once the molar absorptivity was determined, reactions were measured adjusting the pH at constant concentration of ligand to nickel complex in duplicate. Next, reactions were measured at constant pH and increasing ligand concentration.

2.3 Reaction of triethylenetetramine nickel [Ni(trien)] with 5,6-dimethyl phenanthroline (5,6-DMP).

The spectra of all reactants and products were obtained from 900 nm to 200 nm. Comparison of these spectra showed that the greatest change in molar absorptivity between reactants and products at the concentrations used in this study occurred at 343 nm. All reactions were monitored at this wavelength to follow the product formation of Ni(5,6-DMP)$_3$:

$$Ni(trien)^{2+} + 3(5,6\ DMP) \rightarrow Ni(5,6\text{-}DMP)_3^{2+} + Trien$$

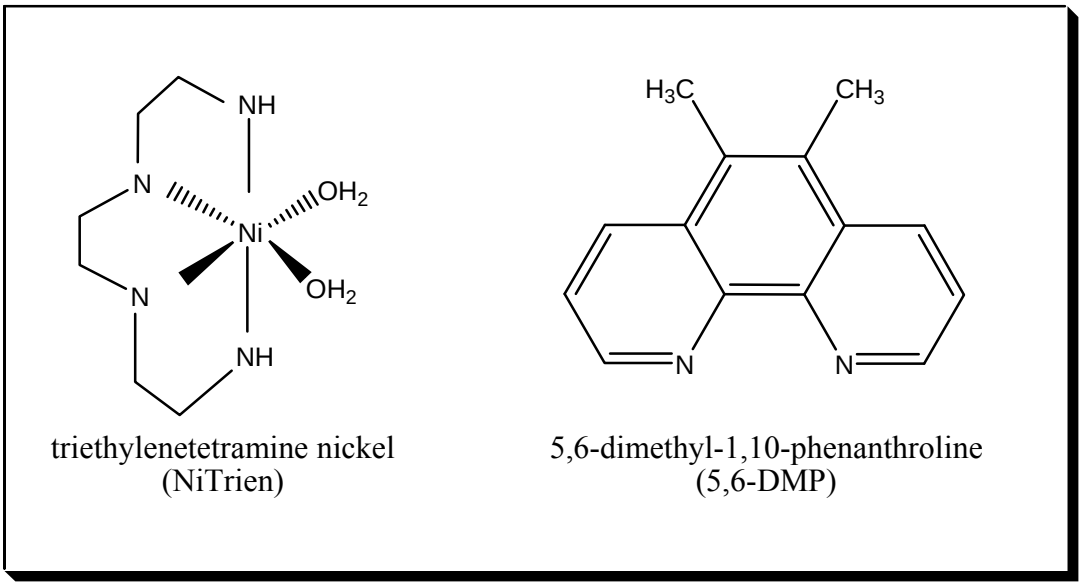


Figure 6. Representation of Reactants Ni(Trien) and 5,6-DMP

Sodium chloride was used to maintain an ionic strength of 0.1M. A pH meter was used to adjust the pH of each solution, using with a hydrochloric acid or a sodium hydroxide buffer. The molar absorptivity of Ni(5,6-DMP)$_3$, DMP, H(5,6-DMP)$^{2+}$, and Ni(trien)(5,6-DMP)$_2$ was determined by measuring the absorbance of each stock solution under the above conditions. The slope of a plot of concentration vs. absorbance was used to determine the molar absorptivity. The molar absorptivity of a proposed mixed ligand complex,

$Ni(trien)(5,6\text{-}DMP)^{2+}$, was measured by adding an excess of trien to a solution of $Ni(5,6DMP)^{2+}$. The absorbance of this solution was measured and the molar absorptivity calculated. Once the molar absorptivity was determined, reactions were measured adjusting the pH at constant concentration of ligand to nickel complex in duplicate.

2.4 Apparatus and Reagents.

Apparatus

Spectra and kinetic reactions 5MP and 5CLP reactions were studied on a Perkin Elmer UV/VIS Lambda 20 spectrophotometer equipped with thermostated cells capable of maintaining a constant temperature ± 0.05^{o}C at 25°C. Spectra and kinetic reactions for 5,6-DMP were studied on an Agilent 8593 Diode Array spectrophotometer. The instrument was operated at maximum slit height and a slit width of 0.3 mm.

A Fisher Isotemp Refrigeration Circulator Model 900 was used to control a constant temperature bath for the stability constant study. This controlled the temperature with ± 0.01^{o}C.

All pH measurements were made on an Accumet AB15 pH Meter using a silver chloride reference electrode, which was filled with a saturated solution of NaCl. The pH meter was standardize daily and recorded using 3 reference standards at pH = 4 and 10. An acceptable calibration curve of greater than 95% confidence was used as an indication for a proper calibration.

Reagents

All high purity grade chemicals were used unless otherwise specified, and all solutions were prepared with deionized water prepared by passing distilled water through a mixed bed ion exchange column (Amberlite MB-3). All reagents were obtained from Aldrich Chemical Company, except HEPES, which was obtained from EM Science.

Triethylenetetraminetetrahydrochloride (97%).

Triethylenetetraminetetrahydrochloride was diluted to 100 mL with agitation for 30 minutes. The solution was then filtered with a Milicron, 5 micron, 47 mm filter (water suction) to remove the solids and the pH of the solution was adjusted with hydrochloric acid to a pH = 7.00.

Triethylenetetramine Nickel (II).

Triethylenetetraminetetrahydrochloride (high purity, 98%) and nickel nitrate were used to prepare the nickel polyamine solutions. An excess 0.10 M nickel nitrate was added to the trien solution, and then the pH was raised to pH = 11.00 by the addition of sodium hydroxide to precipitate the excess nickel. The blue solution was filtered through a 5 micron, 47 mm Millipore filter and the pH lowered to between 7.5 and 8.0. The concentration was determined by analyzing the complex for the amount of nickel it contained. This was accomplished by adjusting the pH to 10.00, adding a 1000-fold excess of cyanide, and comparing the absorbance at 272 nm with a standard $Ni(CN)_4^{-2}$ solution.

5-Methyl-1,10-phenanthroline 99+%.

Phenanthroline solutions were prepared from the monohydrate and were agitated for 30 minutes at 50°C with the addition of sodium hydroxide.

5-Chloro-1,10-phenanthroline 99+%.

Phenanthroline solutions were prepared from the monohydrate and were agitated for 30 minutes at 50°C with the addition of sodium hydroxide.

5,6-dimethyl-1,10-phenanthroline 99+%.

Phenanthroline solutions were prepared from the monohydrate and were agitated for 30 minutes at 50°C with the addition of sodium hydroxide. This was prepared by Lawrence Kolopajlo.

0.1M (2-[N-morpholino]ethanesulfonic acid) (MES)

Solutions were prepared using 2-[N-morpholino]ethanesulfonic acid to prepare 0.5 liter solutions. Buffer solutions were agitated for 30 minutes at 50°C with the addition of hydrochloric acid to pH 4.00.

0.5M (N-2-hydroxyethylpiperazine-N'-2-ethane-sulfonic acid) 99.0% (HEPES)

Solutions were prepared using N-2-hydroxyethylpiperazine-N'-2-ethane-sulfonic acid to prepare 0.5 liter solutions. Buffer solutions were agitated for 30 minutes at 50°C with the addition of sodium hydroxide to pH 6.50.

2.5 Instrumental Analysis.

Reaction of triethylenetetramine nickel [Ni(trien)] with 5-methyl phenanthroline (5MP)

Molar absorptivities of all relevant species were determined by measuring the absorbance of each stock solution at different concentrations (see Table I). The slope of a plot of concentration vs. absorbance was used to determine the molar absorptivity of 5MP, $H5MP^{+}$, $Ni(5MP)_3$ and $Ni(trien)(5MP)^{+2}$ (See Table II).

Table I. Absorbance at 356 nm and Concentration Data Used to Calculate Molar Absorptivities.

$H5MP^{1+}$

Concentration, M	Cell Length, cm	Absorbance
1.00E-04	10	0.0923
2.00E-04	10	0.1952
5.00E-04	10	0.4972
1.00E-03	10	1.0081
2.00E-03	10	1.9664

$Ni(5MP)_3^{2+}$

Concentration, M	Cell Length, cm	Absorbance
1.50E-05	10	0.0187
2.50E-05	10	0.0516
5.00E-05	10	0.1072
7.50E-05	10	0.1643
1.00E-04	10	0.2228
2.00E-04	10	0.4322
4.00E-04	10	0.8477
5.00E-04	10	1.0961

5MP

Concentration, M	Cell Length, cm	Absorbance
1.00E-04	10	0.0460
7.50E-04	10	0.0791
1.00E-03	10	0.1002
2.00E-03	10	0.1951

$Ni(trien)(5MP)^{2+}$

Concentration, M	Cell Length, cm	Absorbance
1.00E-04	10	0.0553
5.00E-04	10	0.3049
6.00E-04	10	0.3222
8.00E-04	10	0.4489

From the absorbance and concentration data in Table I, the molar absorptivities were determined and compiled in Table II. The molar absorptivities were then used to determine the kinetic data in Tables XV and XVI.

Table II. Principal Absorption Maxima and Molar Absorptivities of all Reactants and Products.

Compound	Wavelength, nm	Molar Absorptivities $M^{-1}cm^{-1}$	pH
$H5MP^{+}$	356	987.1	4.00
$Ni(5MP)_3^{2+}$	356	2168	7.50
5MP	356	97.2	7.50
$Ni(trien)(5MP)^{2+}$	356	556.8	6.00

The pH used for each compound was the proper reaction condition in order to keep the compound in solution. The difference in pH between each compound was negligible since the pH was varied during kinetic runs. Two different instruments were used for the 5MP data that gave 2 different wavelengths at 339.5 nm and 356.0 nm.

Figure 7. H5MP at pH = 4.00.

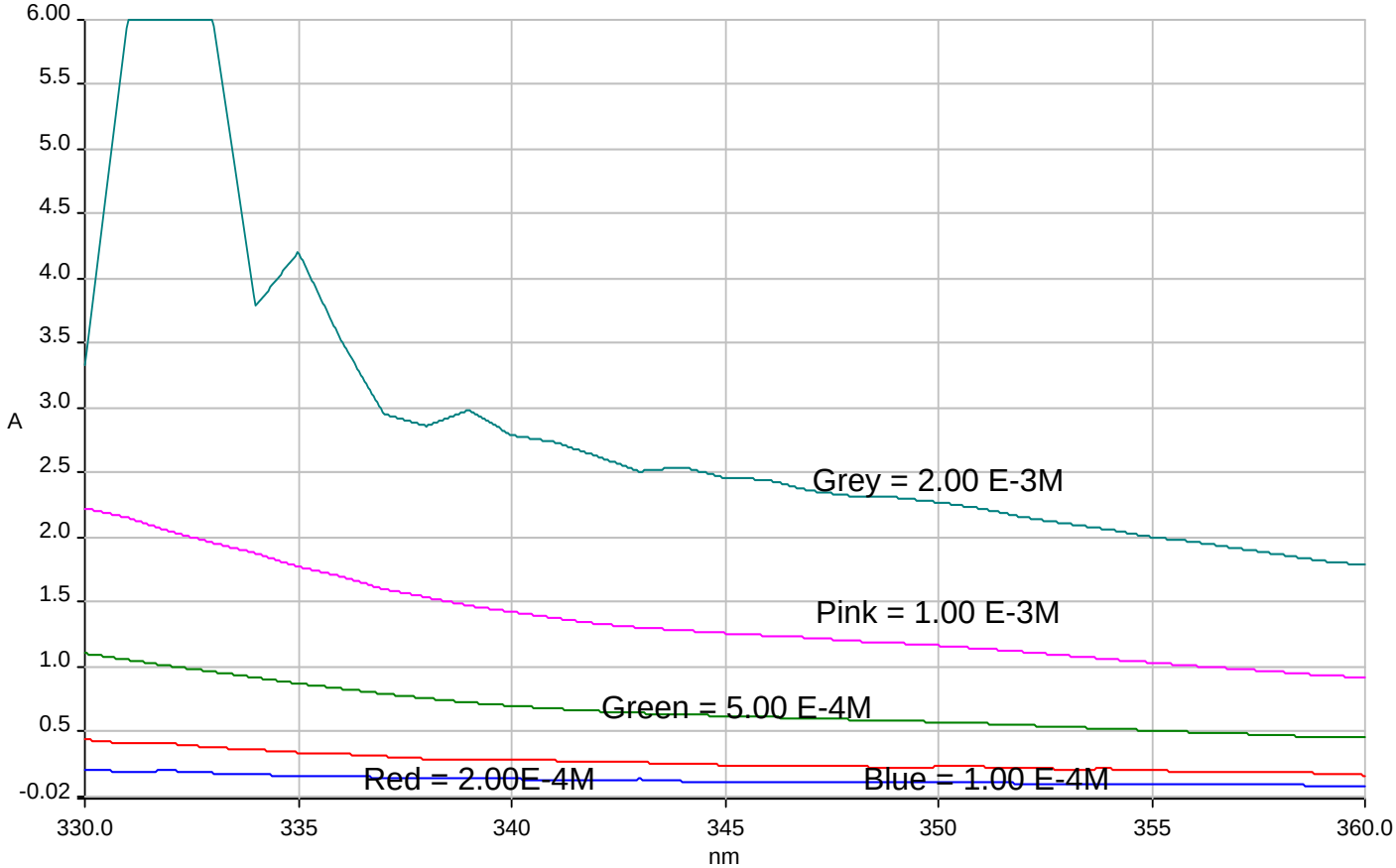


Table III. Absorbance Obtained for H5MP in Duplicate.

	Absorbance at 339.5nm	Absorbance at 356.0nm
Blue 1.00E-4M	0.1401	0.0923
Red 2.00E-4M	0.2848	0.1952
Green 5.00E-4M	0.7144	0.4972
Pink 1.00E-3M	1.4502	1.0081
Grey 2.00E-3M	2.8869	1.9664

Correlation Coefficient = 0.9999 for 356.0 nm
Slope = Molar Absorptivity = 987.1
Y-Intercept = 0.0014

Figure 8. 5MP at pH = 7.50.

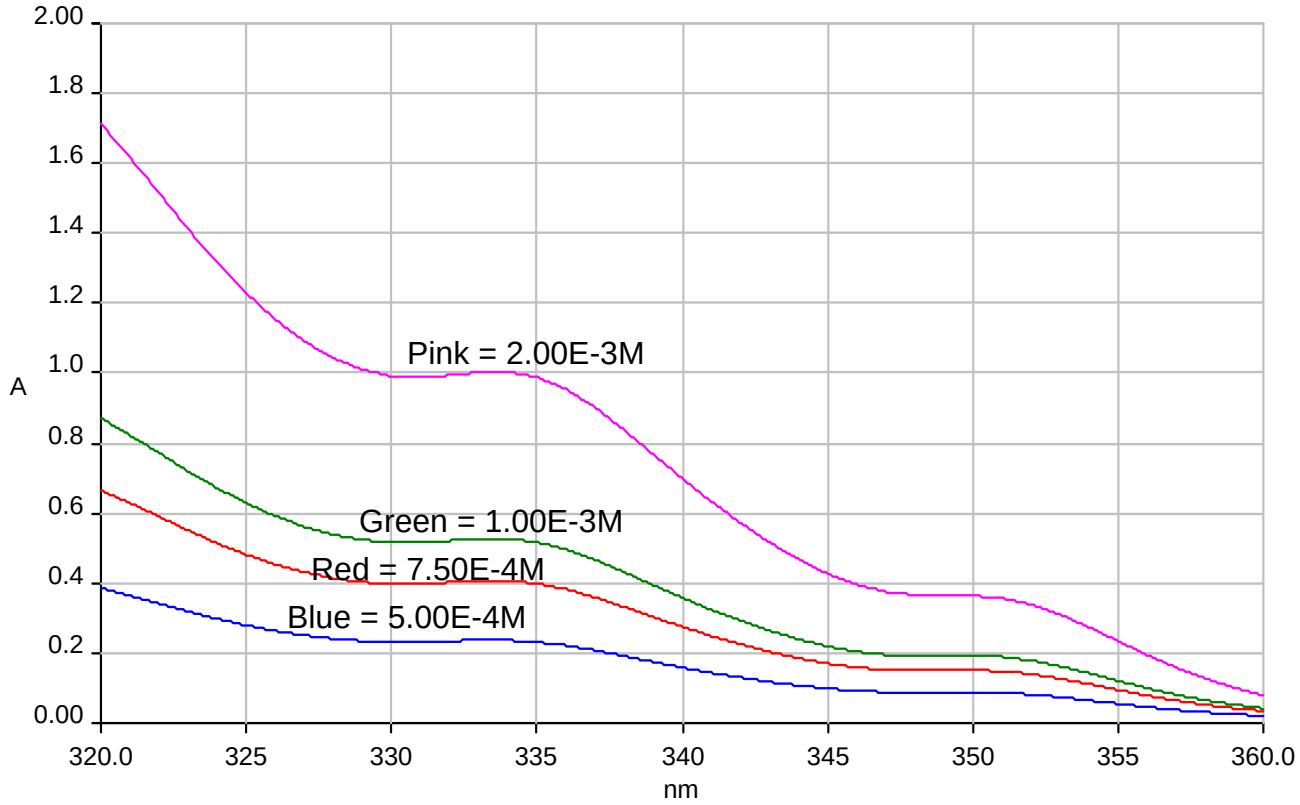


Table IV. Absorbance Obtained for 5MP in Duplicate.

	Absorbance at 339.5nm	Absorbance at 356.0nm
Blue 5.00E-4M	0.1665	0.046
Red 7.50E-4M	0.2885	0.0791
Green 1.00E-4M	0.3755	0.1002
Pink 2.00E-3M	0.7326	0.1951

Correlation Coefficient = 0.9983 for 356.0 nm
Slope = Molar Absorptivity = 97.20
Y-Intercept = 0.0018

Figure 9. Ni(trien)(5MP) at pH = 6.00.

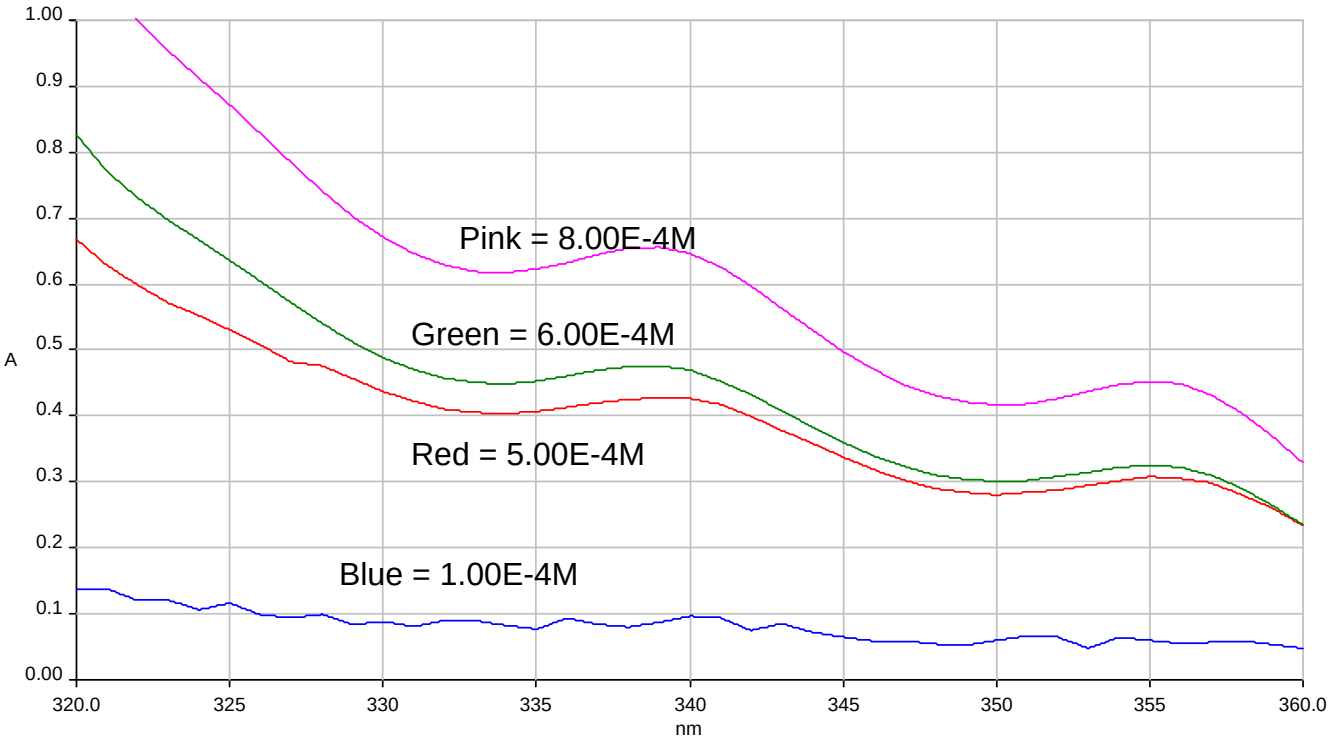


Table V. Absorbance Obtained for Ni(trien)(5MP) in Duplicate.

	Absorbance at 339.5nm	Absorbance at 356.0nm
Blue 1.00E-4M	0.0926	0.0553
Red 5.00E-4M	0.4279	0.3049
Green 6.00E-4M	0.4739	0.3222
Pink 8.00E-4M	0.6523	0.4489

Correlation Coefficient = 0.9952 for 356.0 nm
Slope = Molar Absorptivity = 556.8
Y-Intercept = 0.0044

Figure 10. $Ni(5MP)_3$ at pH = 6.00.

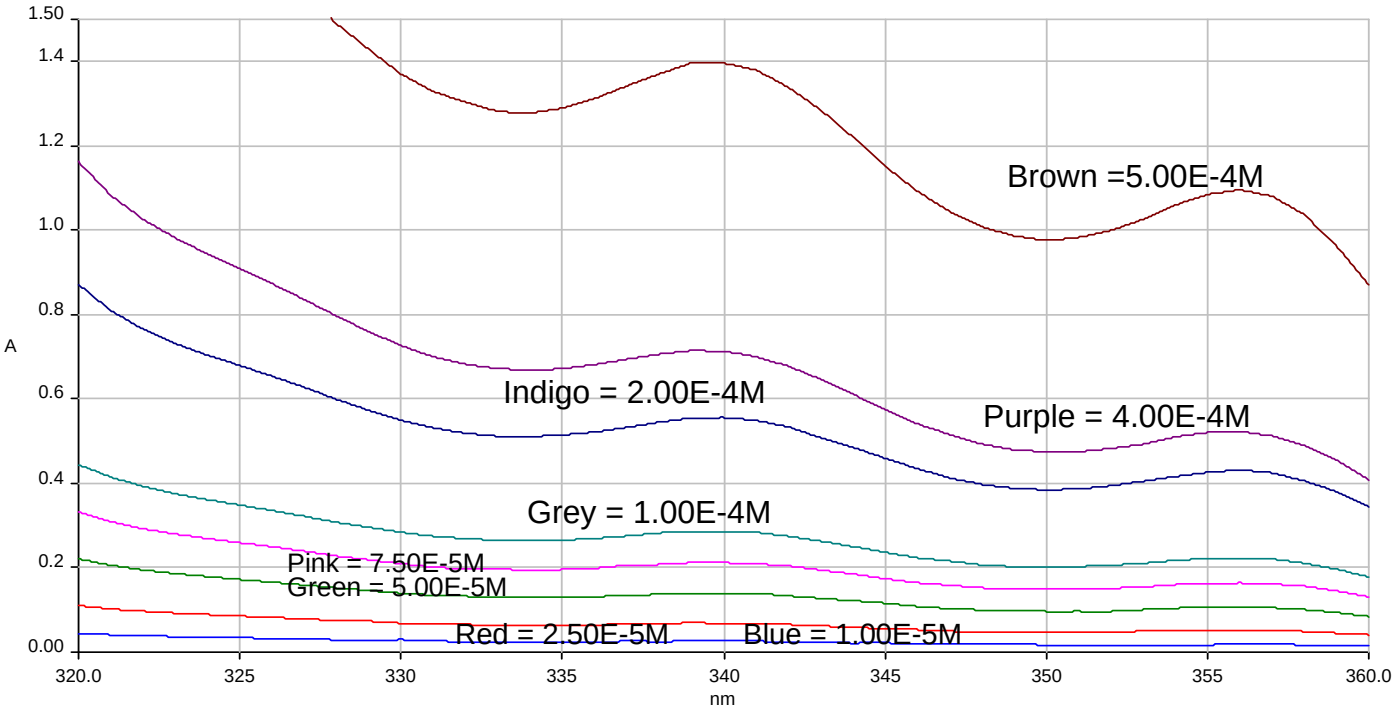


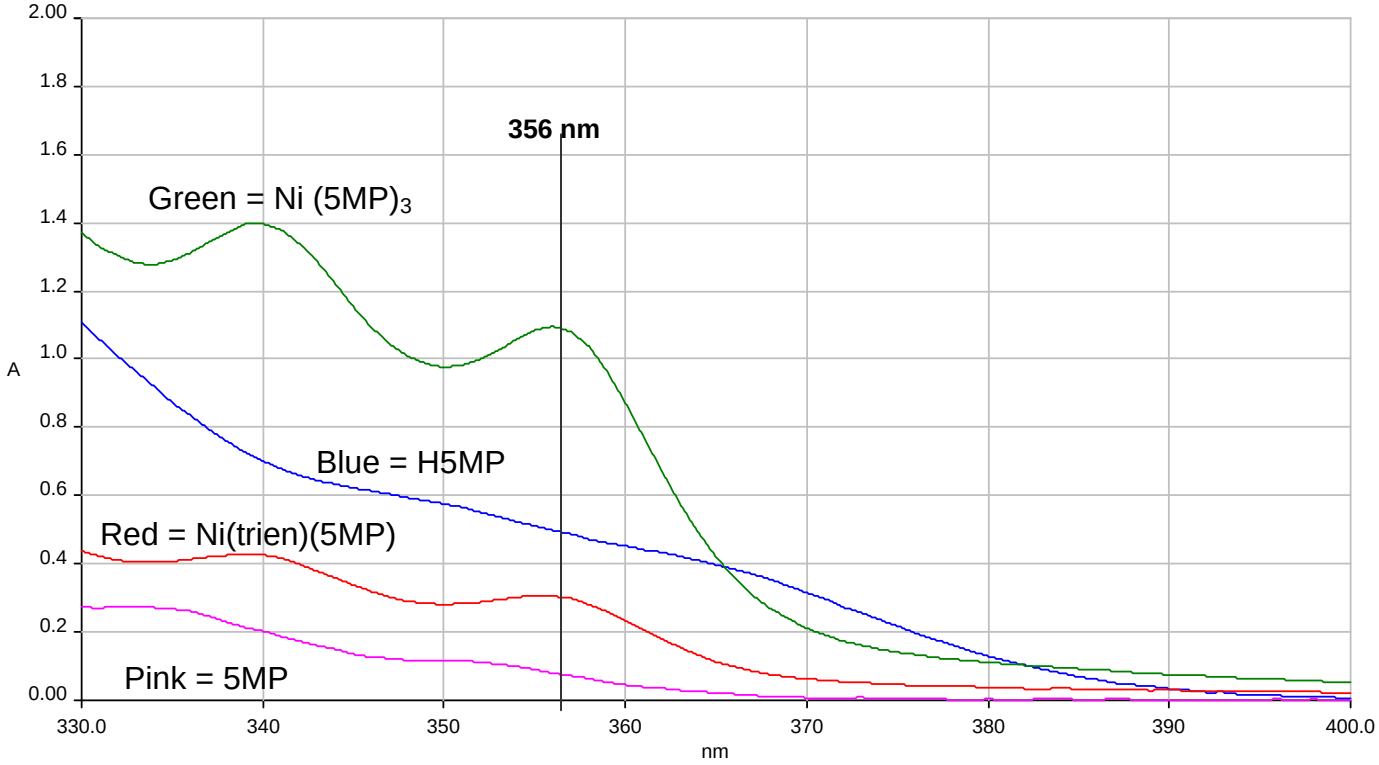
Table VI. Absorbance Obtained for $Ni(5MP)_3$ in Duplicate.

	Absorbance at 339.5nm	Absorbance at 356.0nm
Blue 1.00E-5M	0.026	0.0187
Red 2.50E-5M	0.0692	0.0516
Green 5.00E-5M	0.1396	0.1072
Pink 7.50E-5M	0.2126	0.1643
Grey 1.00E-4M	0.2869	0.2228
Indigo 2.00E-4M	0.5566	0.4322
Purple 4.00E-4M	1.0964	0.8477
Brown 5.00E-4M	1.3992	1.0961

Correlation Coefficient = 0.997 for 356.0 nm
Slope = Molar Absorptivity = 2168
Y-Intercept = -0.0009

Figure 11. Reaction Mixture Spectra Reaction of

5.00E-4M of 5MP, $Ni(5MP)_3$, Ni(trien)(5MP), 5HMP.



Reaction of triethylenetetramine nickel [Ni(trien)] with 5-chloro phenanthroline (5CLP)

Molar absorptivities of all relevant species were determined by measuring the absorbance of each stock solution at different concentrations (see Table VII). The slope of a plot of concentration vs. absorbance was used to determine the molar absorptivity of 5CLP, $H5CLP^{+}$, $Ni(5CLP)_3^{+2}$ and $Ni(trien)(5CLP)^{+2}$ (See Table VII).

Table VII. Absorbance at 350 nm and Concentration Data Used

to Calculate Molar Absorptivities.

$H5CLP^{+1}$

Concentration, M	Cell Length, cm	Absorbance
7.50E-05	10	0.0849
1.50E-04	10	0.1712
3.00E-04	10	0.3474
4.50E-04	10	0.5226

$Ni(5CLP)_3^{+2}$

Concentration, M	Cell Length, cm	Absorbance
5.00E-05	10	0.0751
7.50E-05	10	0.1155
1.00E-04	10	0.1559
1.25E-04	10	0.2038
1.50E-04	10	0.2481

5CLP

Concentration, M	Cell Length, cm	Absorbance
3.00E-04	10	0.0442
4.50E-04	10	0.0585
3.00E-03	10	0.0795
1.67E-03	10	0.1054

$Ni(trien)(5CLP)^{2+}$

Concentration, M	Cell Length, cm	Absorbance
1.50E-04	10	0.0632
2.25E-04	10	0.0783
3.00E-04	10	0.1061
5.00E-04	10	0.1828

From the absorbance and concentration data, the molar absorptivities were determined and compiled in Table VIII.

Table VIII. Principal Absorption Maxima and Molar Absorptivities of all Reactants and Products.

Compound	Wavelength, nm	Molar Absorptivities $M^{-1}cm^{-1}$	pH
$H5CLP^{+}$	350	1169	3.00
$Ni(5CLP)_3^{2+}$	350	1737	7.50
5CLP	350	42.52	6.00
$Ni(trien)(5CLP)^{2+}$	350	351.6	6.00

The pH for each compound was the proper reaction condition in order to keep the compound in solution. The difference in pH between each compound was negligible since the pH was varied during kinetic runs. The same instrument was used for the 5CLP data, and time constraints did not allow duplicate data to be produced.

Figure 12. H5CLP at pH = 3.00.

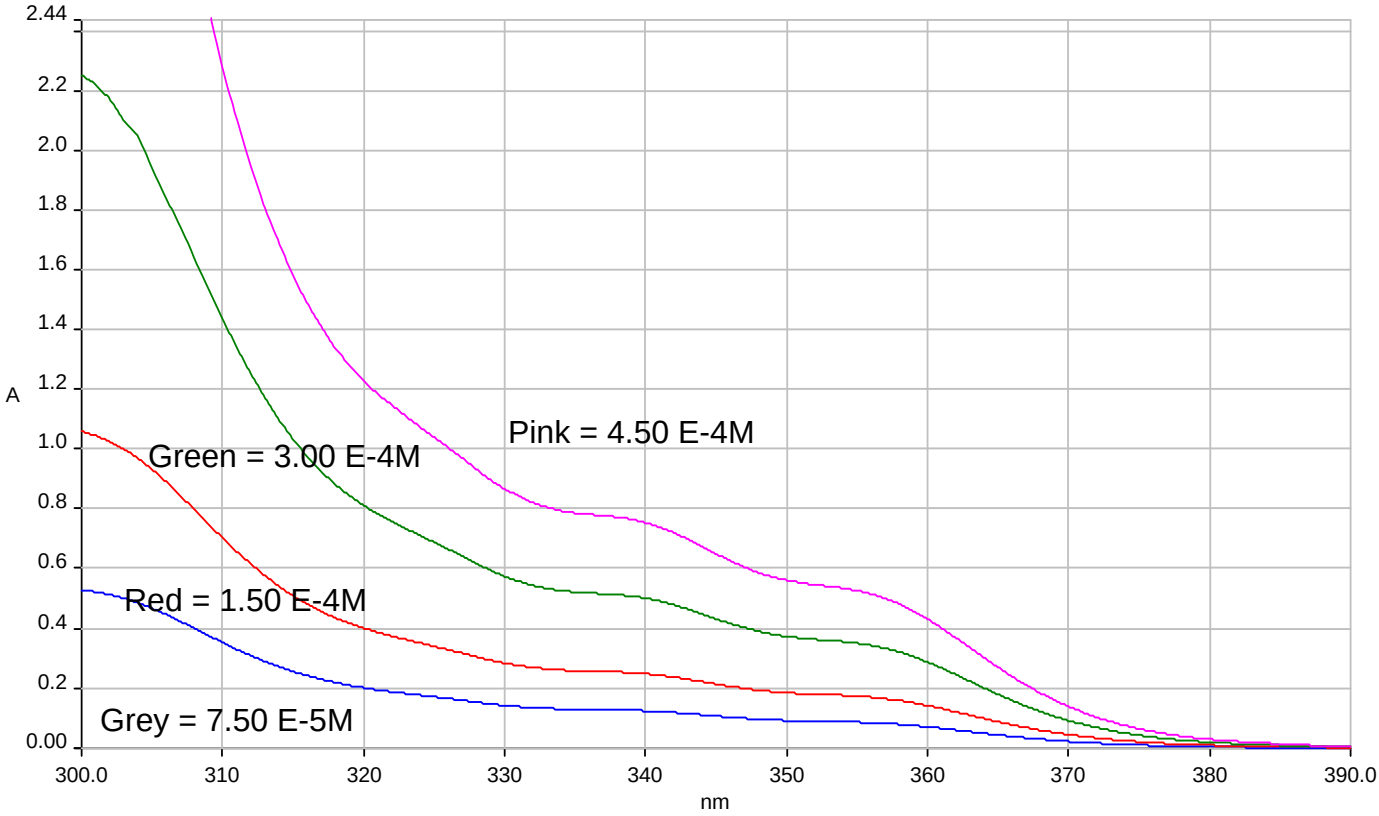


Table IX. Absorbance Obtained at H5CLP.

	Absorbance at 350 nm
Blue 7.5E-5 M	0.0849
Red 1.50E-4 M	0.1712
Green 3.00E-4 M	0.3474
Pink 4.5E-4 M	0.5226

Correlation Coefficient = 0.9999 for 350.0 nm
Slope = Molar Absorptivity = 1168
Y-Intercept = 0.0033

Figure 13. 5CLP at pH = 7.50.

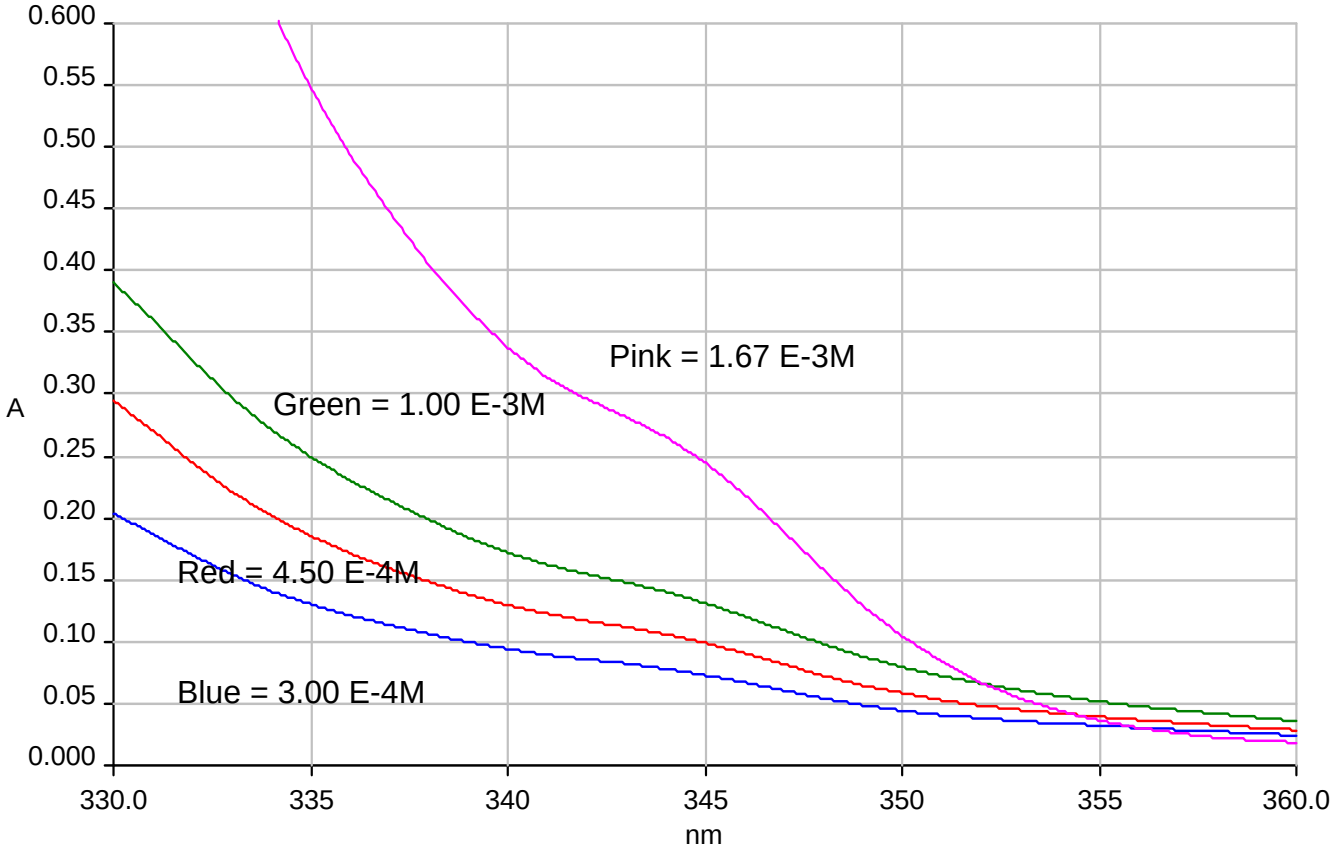


Table X. Absorbance Obtained for 5CLP.

	Absorbance at 350 nm
Blue 3.00E-4 M	0.0442
Red 4.50E-4 M	0.0585
Green 1.00E-3 M	0.0795
Pink 1.67E-3 M	0.1054

Correlation Coefficient = 0.9918 for 350.0 nm
Slope = Molar Absorptivity = 42.52
Y-Intercept = 0.0355

Figure 14. Ni(trien)(5CLP) at pH = 6.00.

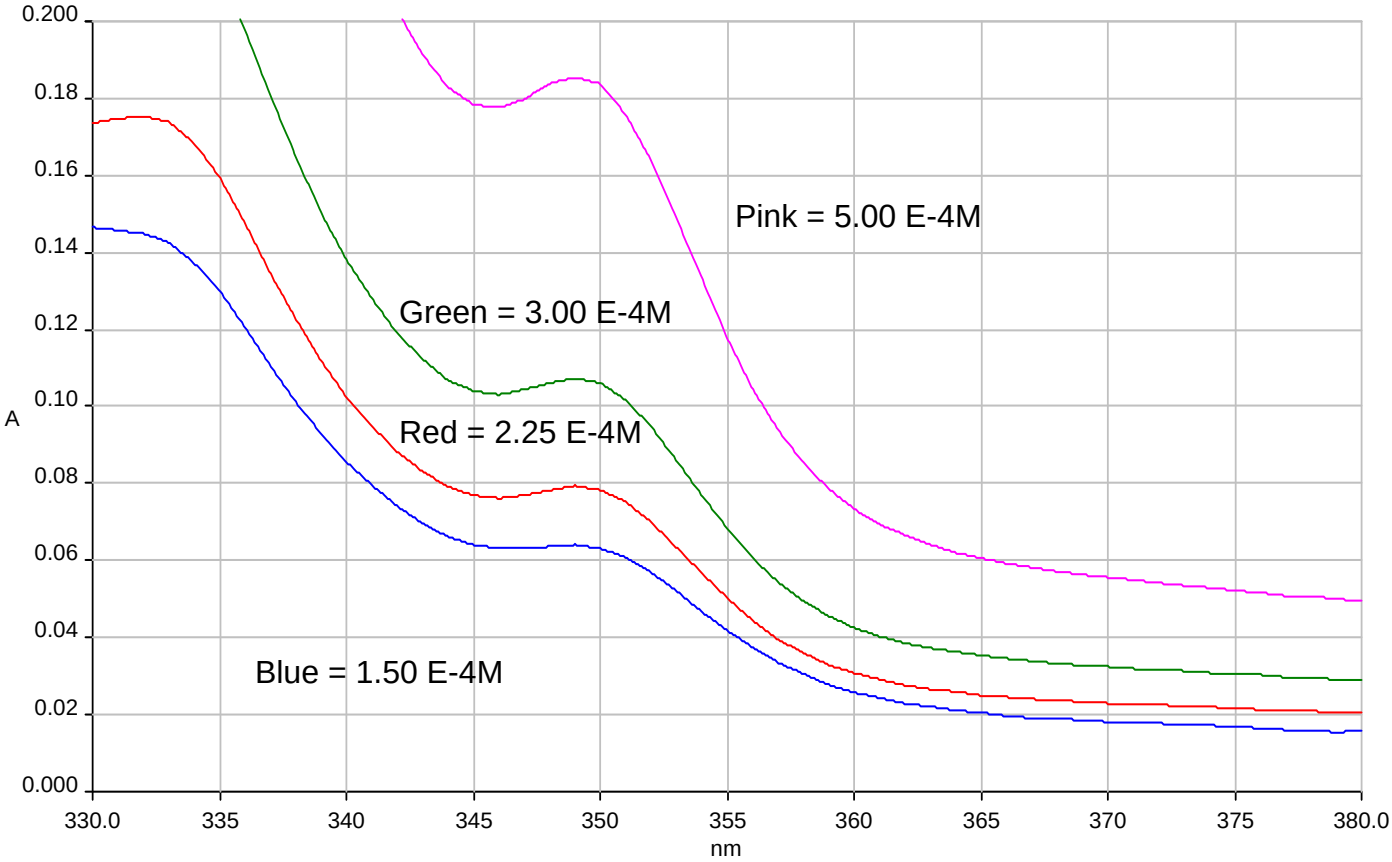


Table XI. Absorbance Obtained for Ni(trien)(5CLP).

	Absorbance at 350 nm
Blue 1.50E-4 M	0.0632
Red 2.25E-4 M	0.0783
Green 3.00E-4 M	0.1061
Pink 5.00E-4 M	0.1828

Correlation Coefficient = 0.9950 for 350.0 nm
Slope = Molar Absorptivity = 351.6
Y-Intercept = 0.0043

Figure 15. $Ni(5CLP)_3$ at pH = 6.00.

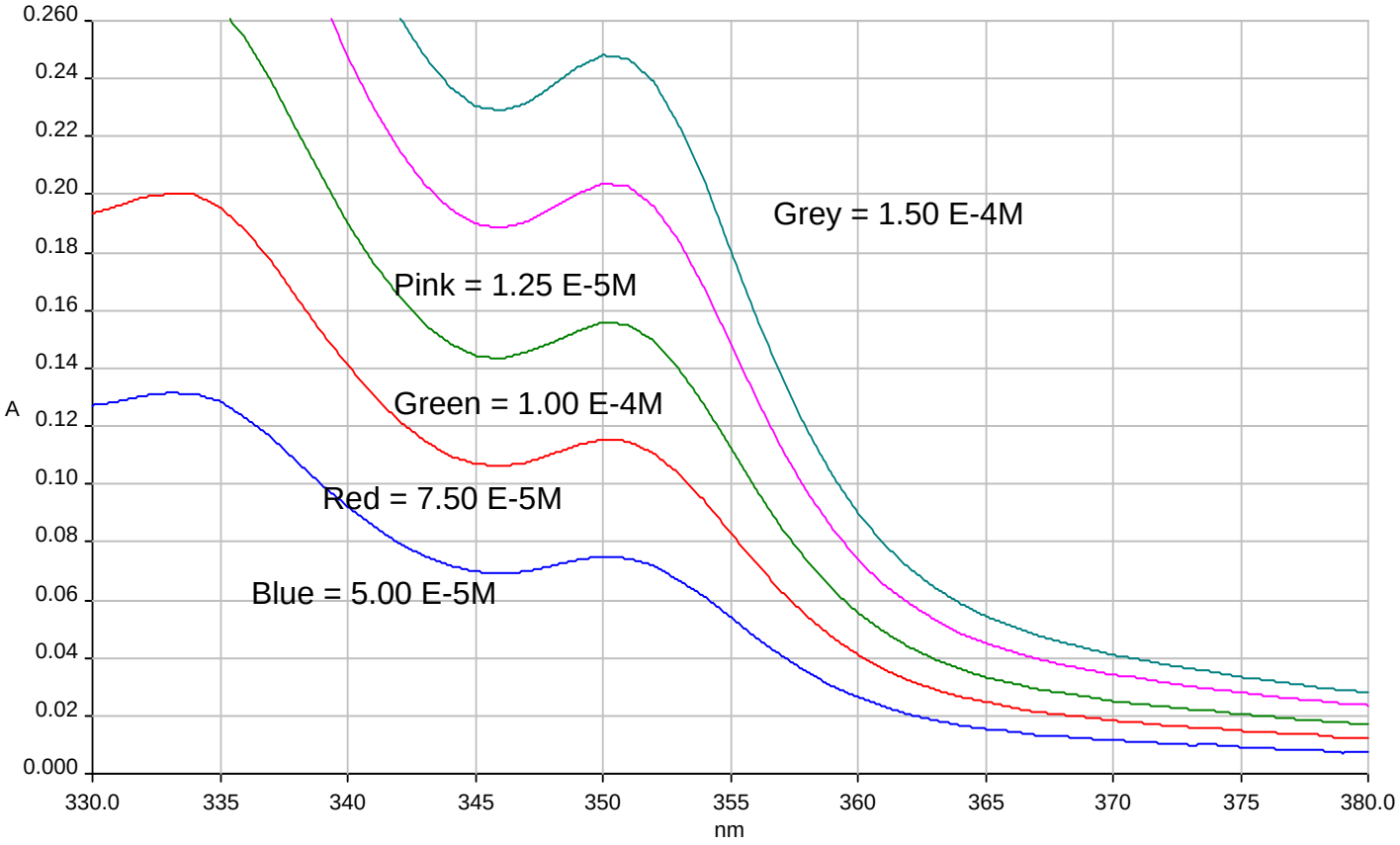
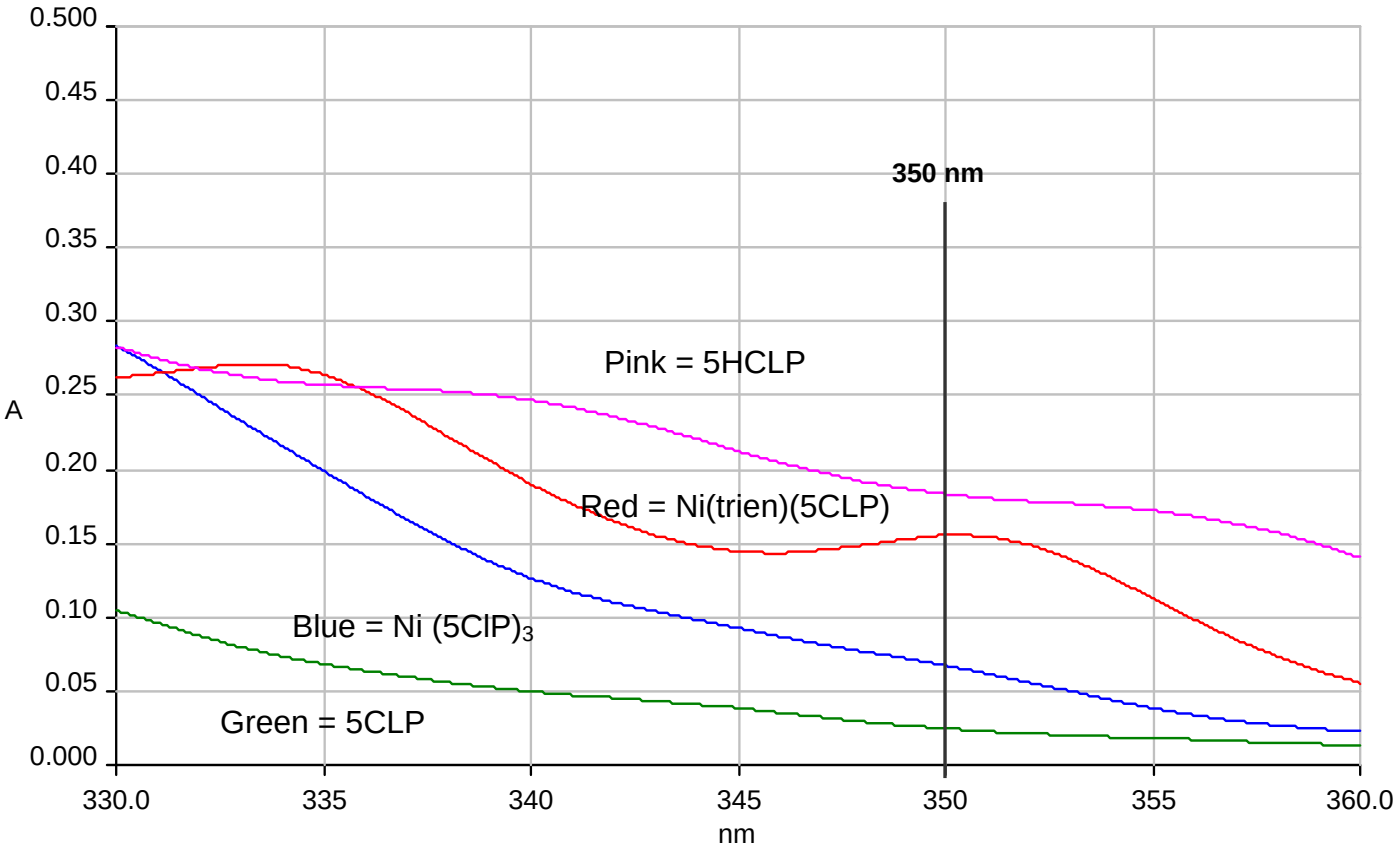


Table XII. Absorbance Obtained for $Ni(5CLP)_3$.

	Absorbance at 350 nm
Grey 1.50E-4 M	0.2481
Pink 1.25E-4 M	0.2038
Green 1.00E-4 M	0.1559
Red 7.50E-5 M	0.1155
Blue 5.00E-5 M	0.0751

Correlation Coefficient = 0.9994 for 350.0 nm
Slope = Molar Absorptivity = 1737
Y-Intercept = -0.0140

Figure 16. Reaction Mixture Spectra of 1.50E-4M of 5CLP, $Ni(5CLP)_3$, Ni(trien)(5CLP), 5HCLP.



<u>Reaction of triethylenetetramine nickel [Ni(trien)] with 5,6-dimethyl phenanthroline (5,-DMP)</u>

Molar absorptivities of all relevant species were determined by measuring the absorbance of each stock solution at different concentrations (see Table XIII). The slope of a plot of concentration vs. absorbance was used to determine the molar absorptivity of 5,6-DMP, H5,6-DMP, $Ni(5,6\text{-}DMP)_3$ and Ni(trien)(5,6-DMP) (See Table XIV).

Table XIII. Absorbance at 343 nm and Concentration Data Used to Calculate Molar Absorptivities.

H5,6-DMP

Concentration, M	Cell Length, nm	Absorbance
1.00E-04	10	0.1241
1.50E-04	10	0.1579
2.00E-04	10	0.2041
2.50E-04	10	0.2560
3.00E-04	10	0.3206

Ni(5,6-DMP)

Concentration, M	Cell Length, nm	Absorbance
2.50E-05	10	0.0273
5.00E-05	10	0.0827
6.00E-05	10	0.1294
7.50E-05	10	0.1590

5,6-DMP

Concentration, M	Cell Length, nm	Absorbance
1.50E-04	10	0.0506
2.00E-04	10	0.0747
2.50E-04	10	0.1073
3.00E-03	10	0.1346

Ni(Trien)(5,6-DMP)

Concentration, M	Cell Length, nm	Absorbance
2.00E-04	10	0.1859
2.50E-04	10	0.2266
3.00E-04	10	0.2513

From the absorbance and concentration data in Table XIII, the molar absorptivities were determined and compiled in Table XIV.

Table XIV. Principal Absorption Maxima and Molar Absorptivities of all Reactants and Products.

Compound	Wavelength, nm	Molar Absorptivities $M^{-1}cm^{-1}$	pH
H5,6-DMP	343	982.08	4.00
Ni(5,6-DMP)	343	2703.8	7.50
5,6-DMP	343	569.32	7.50
Ni(Trien)(5,6-DMP)	343	653.70	6.00

2.6 Kinetics Computational Methods.

Reaction of triethylenetetramine nickel [Ni(trien)] with 5-methyl phenanthroline (5MP)

The concentration of the mixed ligand complex Ni(trien)(5MP) was calculated from the absorbance data at 356nm considering the contribution of all of the relevant absorbing species. The equation below was derived to correct for overlapping absorbances, assuming there are no stable intermediates and that

Beer's law is obeyed:

$$[\text{Ni(Trien)(5MP)}]: \frac{\{\text{Absorbance}_{\text{infinity}}\} - \{\text{Absorbance}_{\text{time t}}\}}{b\{\varepsilon(\text{Ni}(5\text{MP}_3)) - 2\varepsilon(5\text{MP}) - \{2\varepsilon(\text{H5MP})\}\{[\text{H}+]/K_a\} - \varepsilon(\text{Ni(trien)(5MP)})\}}$$

where 5-methyl-1,10-phenanthroline[2]: pKa = 5.27, Ka = 5.73E-6

b = 1cm

$\varepsilon(\text{Ni}(5\text{MP}_3))$ = extinction coefficient = 2168 M^{-1} cm^{-1}

$\varepsilon(5\text{MP})$ = extinction coefficient = 97.2 M^{-1} cm^{-1}

$\varepsilon(\text{H5MP})$ = extinction coefficient = 987.1 M^{-1} cm^{-1}

$\varepsilon(\text{Ni(trien)(5MP)})$ = extinction coefficient = 556.8 M^{-1} cm^{-1}

The summary of data for all kinetic runs is shown in Tables XV and XVI. Each reaction was run in duplicate. The values of k_o was calculated by taking the slope of the plot of [Ni(Trien)(5MP)] vs time at 30% of completion.

Table XV. Calculated Kinetic Data for Ni(trien) and 5MP at Constant [5MP].

Run	Ni(trien) **M**	5MP **M**	Ratio	Initial pH	Final pH	k_o/Sec * 10^{-4}	k_o /Sec * 10^{-4}	[H+]
1	7.75E-05	2.25E-03	30	5.28	5.31	8.92 (MC25)	10.48 (MC26)	3.8019E-06
2	7.75E-05	2.25E-03	30	5.60	5.63	5.83 (MC30)	5.85 (MC29)	2.5119E-06
3	7.75E-05	2.25E-03	30	5.90	5.94	2.20 (MC40)	2.24 (MC35)	1.2589E-06
4	7.75E-05	2.25E-03	30	6.21	6.22	0.93 (MC55)	1.17 (MC52)	6.3096E-07
5	7.75E-05	2.25E-03	30	7.01	7.03	0.26 (MC60)	0.26 (MC58)	1.0000E-07
6	7.75E-05	2.25E-03	30	8.00	8.01	0.016 (MC50)	0.02 (MC45)	1.0000E-08

Table XVI. Calculated Kinetic Data for Ni(trien) and 5MP at Constant pH.

Run	Ni(trien) **M**	5MP **M**	Ratio	Initial pH	Final pH	k_o /Sec * 10^{-4}	k_o /Sec * 10^{-4}	[H+]
7	7.75E-05	1.00E-03	15	5.93	5.94	2.09 (MC80)	1.54 (MC78)	1.1749E-06
8	7.75E-05	1.50E-03	20	5.91	5.93	1.75 (MC68)	2.18 (MC135)	1.2303E-06
3	7.75E-05	2.25E-03	30	5.90	5.94	2.20 (MC40)	2.24 (MC35)	1.2589E-06
9	7.75E-05	3.00E-03	40	5.90	5.91	2.44 (MC72)	2.44 (MC70)	1.2589E-06

Reaction of triethylenetetramine nickel [Ni(trien)] with 5-chloro phenanthroline (5CLP)

The concentration of the mixed ligand complex Ni(trien)(5CLP) was calculated from the absorbance data at 350nm considering the contribution of all of the relevant absorbing species. The equation below was derived to correct for overlapping absorbances[3], assuming there are no stable intermediates and that Beer's law is obeyed.

$$[\text{Ni(Trien)(5CLP)}]: \frac{\{\text{Absorbance}_{\text{infinity}}\} - \{\text{Absorbance}_{\text{time t}}\}}{b\{\varepsilon(\text{Ni(5CLP)}_3 - 2\varepsilon(\text{5CLP}) - \{2\varepsilon(\text{H5CLP})\}\{[\text{H+}]/\text{Ka}\} - \varepsilon(\text{Ni(trien)(5CLP)})\}}$$

where 5-chloro-1,10-phenanthroline[2]: pKa = 4.07, Ka = 8.51E-5

b = 1cm

$\varepsilon(\text{Ni(5CLP)}_3)$= extinction coefficient = 1737 $M^{-1}cm^{-1}$

ε(5 CLP) = extinction coefficient = 42.52 $M^{-1}cm^{-1}$

ε(H5CLP) = extinction coefficient = 1169 $M^{-1}cm^{-1}$

ε(Ni(trien)(5CLP) = extinction coefficient = 351.6 $M^{-1}cm^{-1}$

Table XVII. Calculated Kinetic Data for Ni(trien) and 5CLP at Constant [5CLP].

Run	Ni(trien) M	5CLP M	Ratio	Initial pH	k_o /Sec * 10^{-3}	k_o/Sec * 10^{-3}	[H+]
1	4.00E-05	1.00E-03	25	5.70	5.23	8.77	1.9953E-06
2	4.00E-05	1.00E-03	25	6.03	7.48	7.95	9.3325E-07
3	4.00E-05	1.00E-03	25	6.40	0.69	1.48	3.9811E-07
4	4.00E-05	1.00E-03	25	6.70	0.45	0.35	1.9953E-07
5	4.00E-05	1.00E-03	25	6.99	1.33	1.59	1.0233E-07
6	4.00E-05	1.00E-03	25	7.70	0.77	0.16	1.9953E-08
7	4.00E-05	1.00E-03	25	8.00	0.02	0.04	1.0000E-08

Table XVIII. Calculated Kinetic Data for Ni(trien) and 5CLP at Constant pH.

Run	Ni(trien) M	5CLP M	Ratio	Initial pH	k_o/Sec * 10^{-3}	k_o/Sec * 10^{-3}	[H+]
8	4.00E-05	5.00E-04	12.5	5.70	0.09	0.08	1.9953E-06
9	4.00E-05	7.52E-04	18.8	5.70	0.08	0.10	1.9953E-06
10	4.00E-05	1.00E-03	25	5.70	0.13	0.15	1.9953E-06

REFERENCES: Chapter 2

1) Steinhaus, R. K.; Boersma, J. A. *Inorg. Chem.* **1972,** 11 **(7)**, 1505.

2) Martwell, A.; Smith, R. M.; *Critical Stability Constants*, Plenum Press: New York City, NY, 1982.

3) Brewer, T. R.; Mattieson, M.; Kolopajlo, L. H. *J.Coord. Chem*. **2003**, 56 (10), 851.

CHAPTER 3: Results and Discussions

3.1 5-methyl-1,10-phenanthroline

For the kinetic runs 1-6 in Table XV, the ratio [5MP] / [Ni(trien)] ≥ 30. Therefore it can be assumed that

$$\frac{d[Ni(5MP)_3]}{dt} = -\frac{d[NiTrien]}{dt}$$

$$= k\,[5MP]^a\,[NiTrien]^b$$

$$= k_o[NiTrien]^b$$

If first-order,

$$-\frac{d[Ni(Trien)]}{dt} = k_o[NiTrien]$$

$$\ln\{[Ni(Trien)]\} = \ln\{[Ni(Trien)]t_o\} - k_o t$$

Figures 17 and 18 show an example of data and analysis for one of the kinetic runs (MC40). Clearly the plot of log[Ni(Trien)] vs t is linear, indicating that the reaction is first order with respect to [Ni(Trien)].

Figure 17. Example of a Kinetic Run for Ni(trien) and 5MP Mixture.

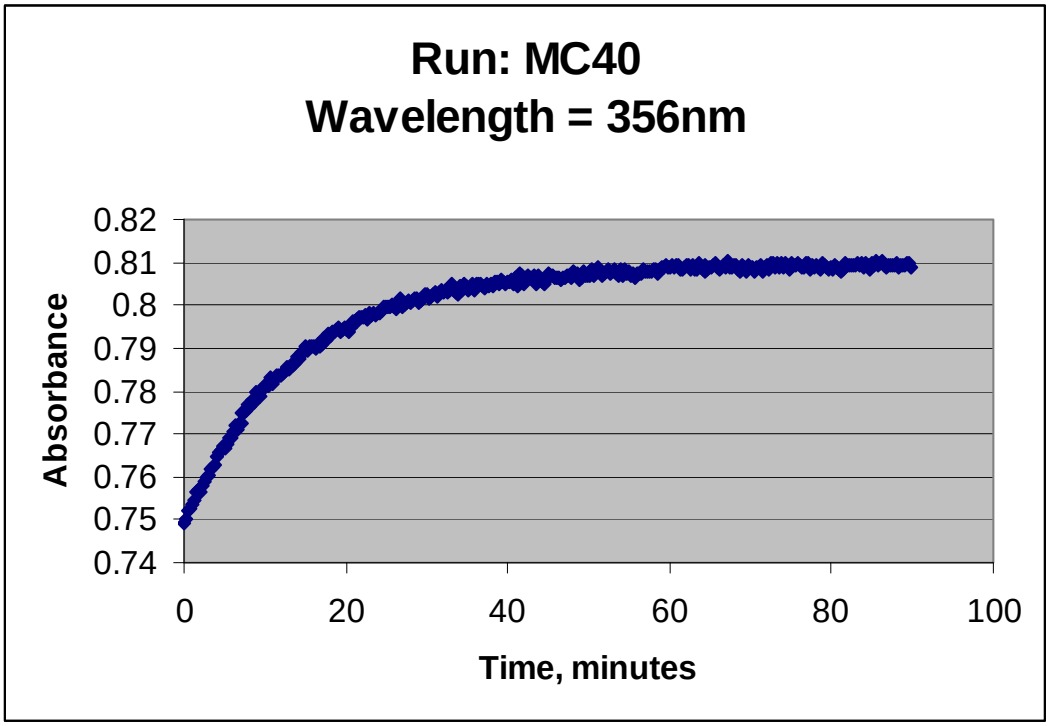
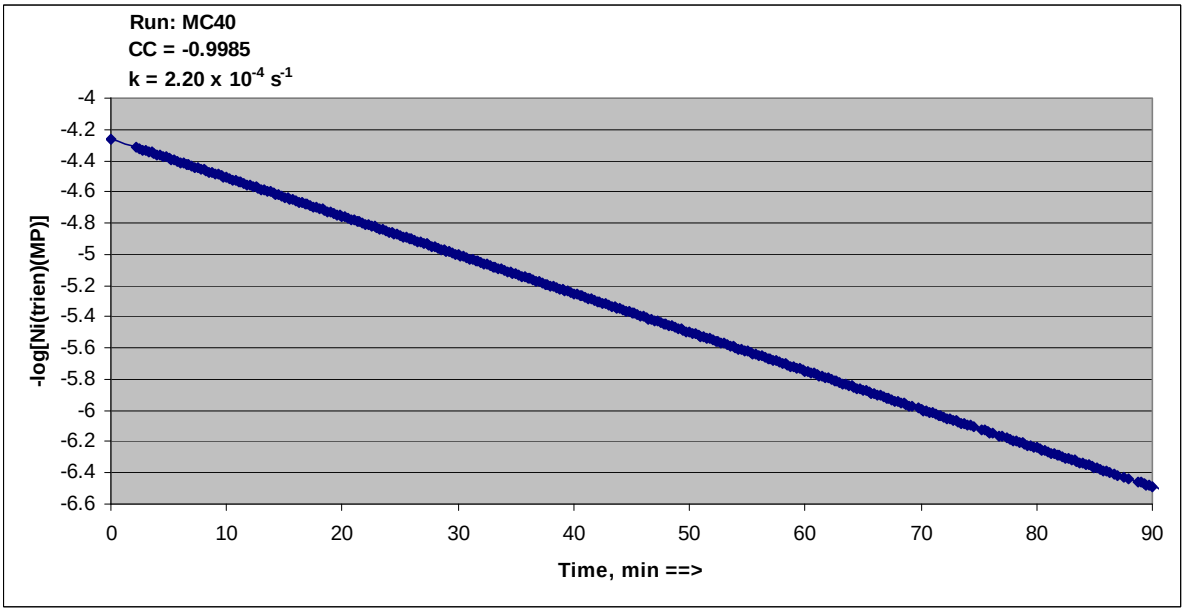


Figure 18. First Order Plot for one of the kinetic runs.



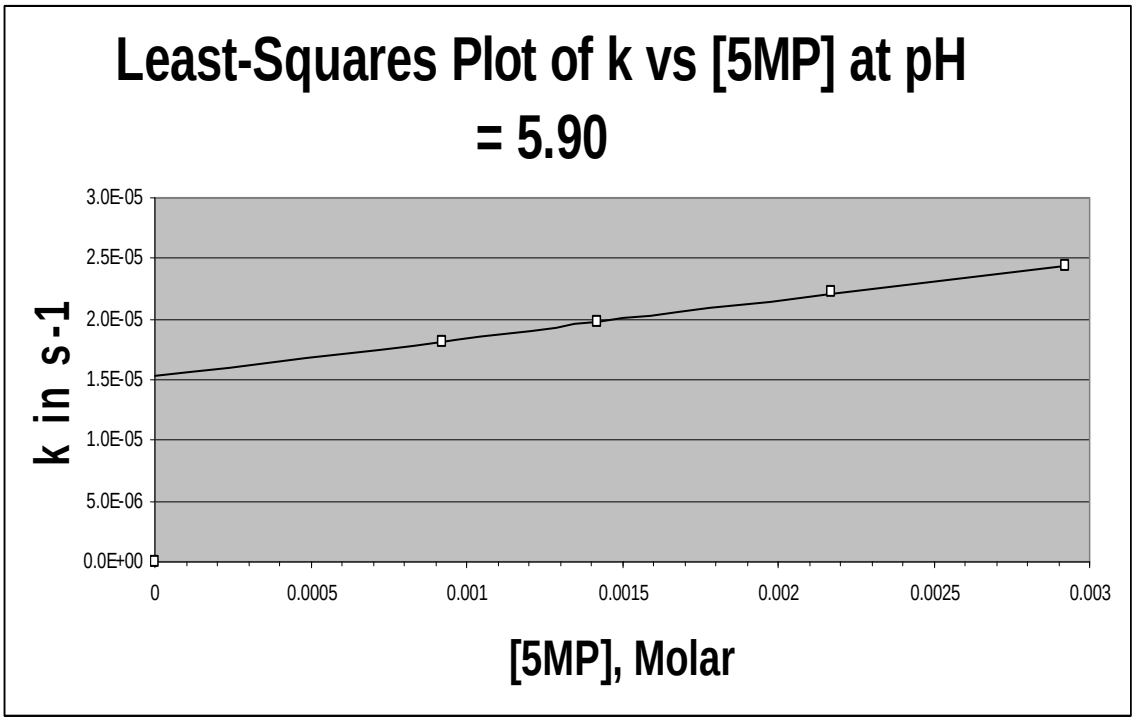
The dependence of the rate on 5MP concentration can be determined by analyzing the data summarized in Table XIX. Since in these kinetic runs [NiTrien] and $[H^+]$ are constant, $k_o = k\,[5MP]^a$. Therefore a plot of k_o vs. [5MP] can be used to determine the order with respect to [5MP]. Such a plot is shown in Figure 19. The graph is obviously linear, and the following information can be obtained:

$$\mathbf{k = 3.12E\text{-}03[5MP] + 1.53E\text{-}05}$$

Table XIX. Rate Determined Using Corrected 5MP Concentration.

Run	pH	Uncorrected [5MP], Molar	Corrected [5MP], Molar	k_o/s		
7	5.94	1.00E-03	9.23E-04	1.82E-04	CC =	0.99969
8	5.93	1.50E-03	1.42E-03	1.97E-04	Slope =	3.12E-03
3	5.94	2.25E-03	2.17E-03	2.22E-04	Y-int =	1.53E-05
9	5.91	3.00E-03	2.89E-03	2.44E-04		

Figure 19. Least-Squares Plot of k vs. [5MP] at pH = 5.90.



Lastly, the pH-dependance of k can be determined by analyzing the data in Table XX. In these runs, the only variable is $[H^+]$.

Table XX. Data Used to Determine Slope and Y-Intercept.

Run	pH	Corrected [5MP]	k_o/Sec	Corrected k_o/[5MP]		
1	5.31	2.42E-03	8.92E-04	3.69E-01		
2	5.63	2.42E-03	5.83E-04	2.41E-01	CC =	0.994890101
3	5.94	2.42E-03	2.20E-04	9.09E-02	slope =	97755.3262
4	6.22	2.42E-03	9.30E-05	3.84E-02	y-int =	-0.0094177
5	7.03	2.42E-03	2.60E-05	1.07E-02		
6	8.01	2.42E-03	1.60E-05	6.61E-03		

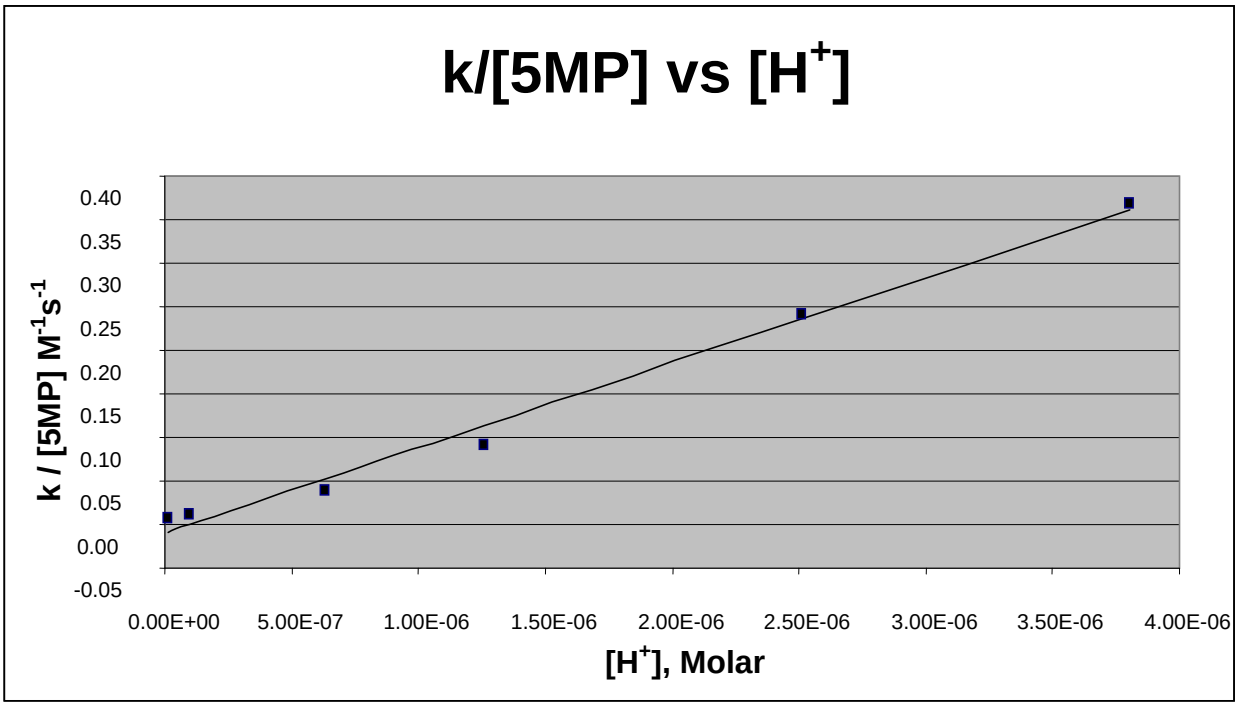


Figure 20. Plot to Determine Rate

Again, the plot is linear, indicating that k is linearly dependent on $[H^+]$.

3.2 5-chloro-1,10-phenanthroline

While data were collected on this ligand exchange reaction, insufficient time was given to determine acceptable duplicate rate data. The rates were calculated in Tables XVII (changing pH) and XVIII (changing ligand concentration). This data may assist in the future study of this particular reaction.

3.3 5,6-dimethyl-1,10-phenanthroline

This reaction was too slow to follow. In order for this type of reaction to proceed, the nitrogens in the ligand must orient themselves in the coordination sites on the nickel complex. The additional methyl group must distort the phenanthrolene ligand so that it cannot react with nickel to form the nickel complex.

CHAPTER 4: Conclusions

For the reaction

$$Ni(trien)^{2+} + 3(5MP) \text{ --> } Ni(5MP)_3^{2+} + trien$$

it was determined that the reaction is first order with respect to each of the two reagents. In addition, the rate constant is found to be pH dependent. The values for the rate constant are as follows:

$k_{5mp}^{NiTrien5MP} = 9.42 \times 10^{-3}\ M^{-1}\ s^{-1}$ $[H^+]$ independent

$k_{H,5mp}^{NiTrien5MP} = 9.78 \times 10^{4}\ M^{-2}\ s^{-1}$ $[H^+]$ dependent

In summary, the rate law for the reaction is as follows:

$$-d[Ni(trien)^{2+}]/dt = (k_{5mp}^{NiTrien5MP} + k_{H,5mp}^{NiTrien5MP}[H^+])[Ni(trien)^{2+}][5MP]$$

Based on the data obtained, a few observations can be made. Data from Table XV show that as the pH increases, a decrease in the rate of the reaction is observed. Acid catalyzes the unwrapping of the trien from nickel by protonating the ligand's basic sites, which prevents reattachment to the metal center. Data from Table XVI show that as the 5MP ligand concentration is increased, the rate of the reaction also increases. Therefore, the rate is dependent on the 5MP concentration for trien ligand exchange and produces a linear plot, which indicates a first order reaction. Previous literature has not analyzed the reaction of NiTrien with a 5MP ligand.

Understanding the kinetics and mechanisms of nickel reactions will assist in finding new ways to dispose of complexed nickel in industrial wastestreams. The complicated nature of those reactions has evoked the study of other metals that pose environmental and toxicity issues.

CHAPTER 5: Introduction and Background

5.1 Boron (III) subphthalocyanine: Introduction and Background.

Subphthalocyanines (SubPcs) have been examined recently because of their distinct properties including nonlinear optics[1], medicinal purposes[2,] and dyes[3]. SubPcs are commonly used as a component of a recordable DVD and ink dyes. Due to the aromatic nature of subphthalocyanines, they often exhibit unique optical and electrical properties that have led to their use in non-linear optics.[4] Thin film preparations using SubPcs have been developed that give second-order linear optics or frequency doubling.

Recently, SubPcs have been used in cancer treatment for their photosensitizing properties.[5] When SubPcs containing compounds are injected into tumors and irradiated with light, energy is absorbed. This energy creates free radicals that terminate surrounding tumerous tissue. This therapy is beneficial because the injection is made directly into the tumor without destroying surrounding tissue.

While phthalocyanines (Pcs) are 2-dimensional macrocyclic 18- л- electron conjugated systems[6] with four diiminoisoline units, SubPcs are composed of three diiminoisoindole rings fused around a boron core (Figure 21).

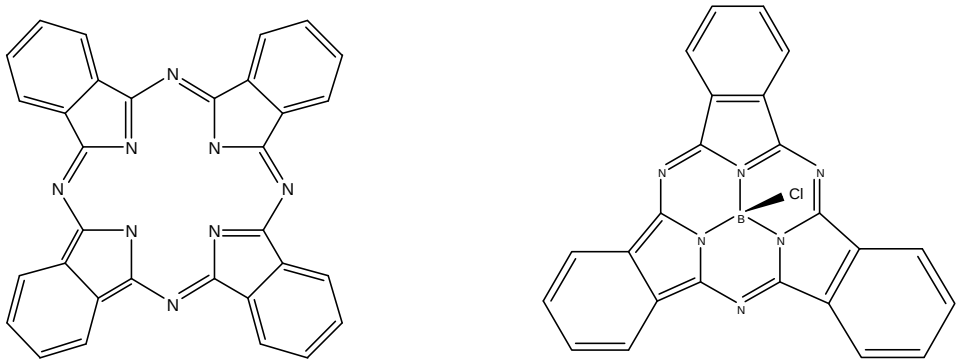


Figure 21. Representation of Phthalocyanine and Subthalocyanine

Compared to Pcs, SubPcs have been much less studied due to difficulties encountered with their purification.[7] It has been shown that repeated chromatography could separate out the desired product.[8]

While they have a cone-shaped structure, SubPcs exhibit an aromatic nature.[9] SubPcs were first synthesized in 1972 by Meller and Ossko.[10] SubPcs are synthesized by dissolving 1,2-dicyanobenzene in 1-chlorobenzene and reacting with BCl_3. This procedure gives fairly high yields (about 60%). 1-Chlorobenzene is typically used as a solvent since it has a high vapor pressure and is easily distillable.

Some SubPcs are obtained as a mixture of C1 and C3 constitutional isomers when the 1,2 dicyanobenzene is substituted in the 4 position (Figure 22). Each isomer is a racemic mixture when the peripheral substituents are different.[11] Currently, these compounds have not been synthesized enantioselectively.

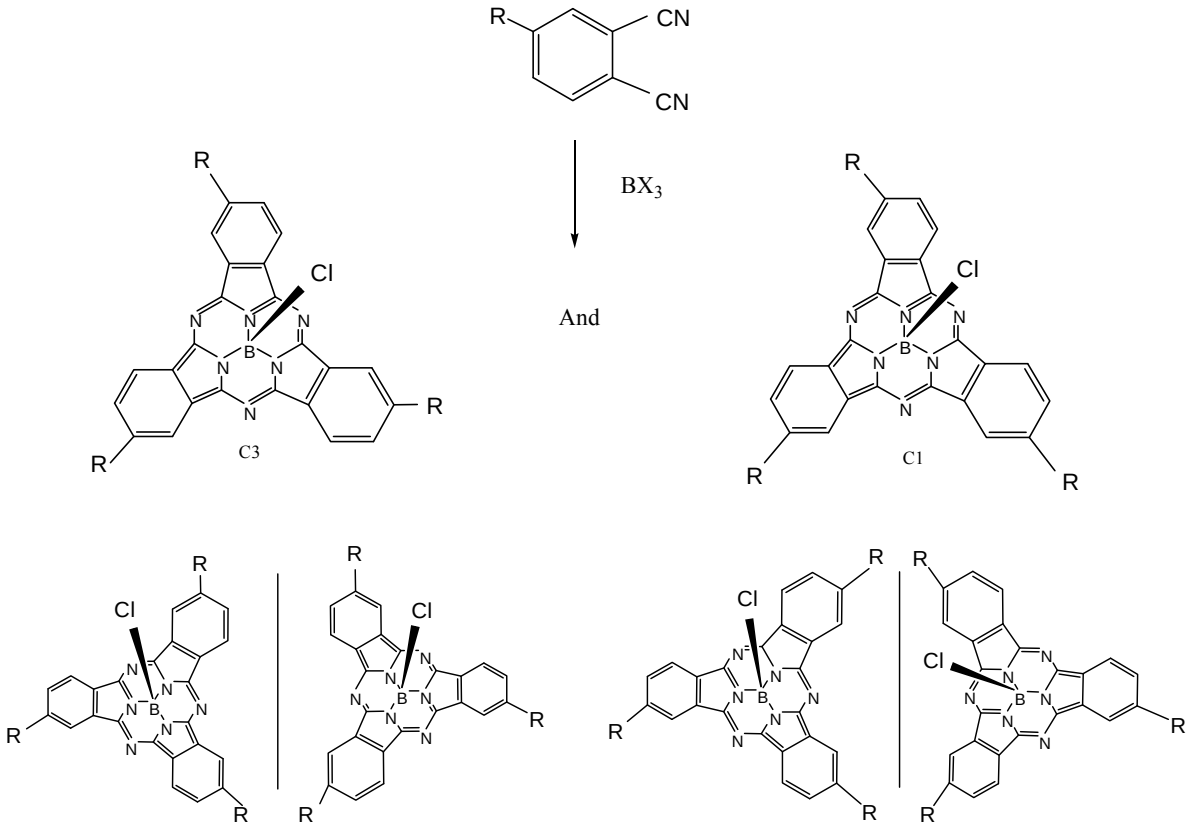


Figure 22. Representation of Subphthalocyanine Enantiomers.

While many substituted SubPcs have been examined and chromatographically separated since the late 1990s, there has been limited research on the use of metals other than boron. Among the different boron reagents investigated, BCl_3 is used the most compared to BBr_3, BPh_3, and $BPhCl_2$.[11] Although BCl_3 is moisture sensitive and a hazardous gaseous reagent, it offers the best compromise between high yields and stabilities of the chloroSubPc compounds. Studies have confirmed that chloroSubPcs tend to decompose over a few weeks in solution in the presence of light.[11] This instability is due to the weak boron-chlorine bond. It is important to run reactions in the absence of light in order to avoid this decomposition.

5.2 Hydroxyl Substitution.

Thus, boron chlorosubphthalocyanine was used as the core compound, and tends to be a

reactive compound in that the axial chloride can be displaced by nucleophiles. Boron chloroSubPcs were reacted with a range of oxygen nucleophiles to produce axially substituted SubPcs.[11] Currently, there are four methods that have been used that allow the substitution of the axial halide (Cl) by a hydroxyl group (Figure 23). The highest yield procedure consists of refluxing a solution of SubPc in water and acetonitrile (92%).[11]

In 1996, Geyer et al. synthesized SubPcs(OH) using sodium hydroxide in p-xylene with low yield (2.2%).[12] This axial substitution reaction did not produce peripheral substituted products. The second reaction that successfully produced SubPcs(OH) had a peripheral group bonded to each ring (I) and used water and heat. Good percent yields were obtained using this method (55%).[13] The third axial substitution reaction used water and acetonitrile where the peripheral group bonded to each ring was SC_8H_{17}. Excellent percent yields were obtained using this method (92%).[13] Water and pyridine were used in the last synthesis where the peripheral group bonded to each ring was a chlorosulfonyl group. This reaction was also produced in good yield (60%).[14] SubPcsB(OH) is typically used as an intermediate to produce other SubPcs compounds.

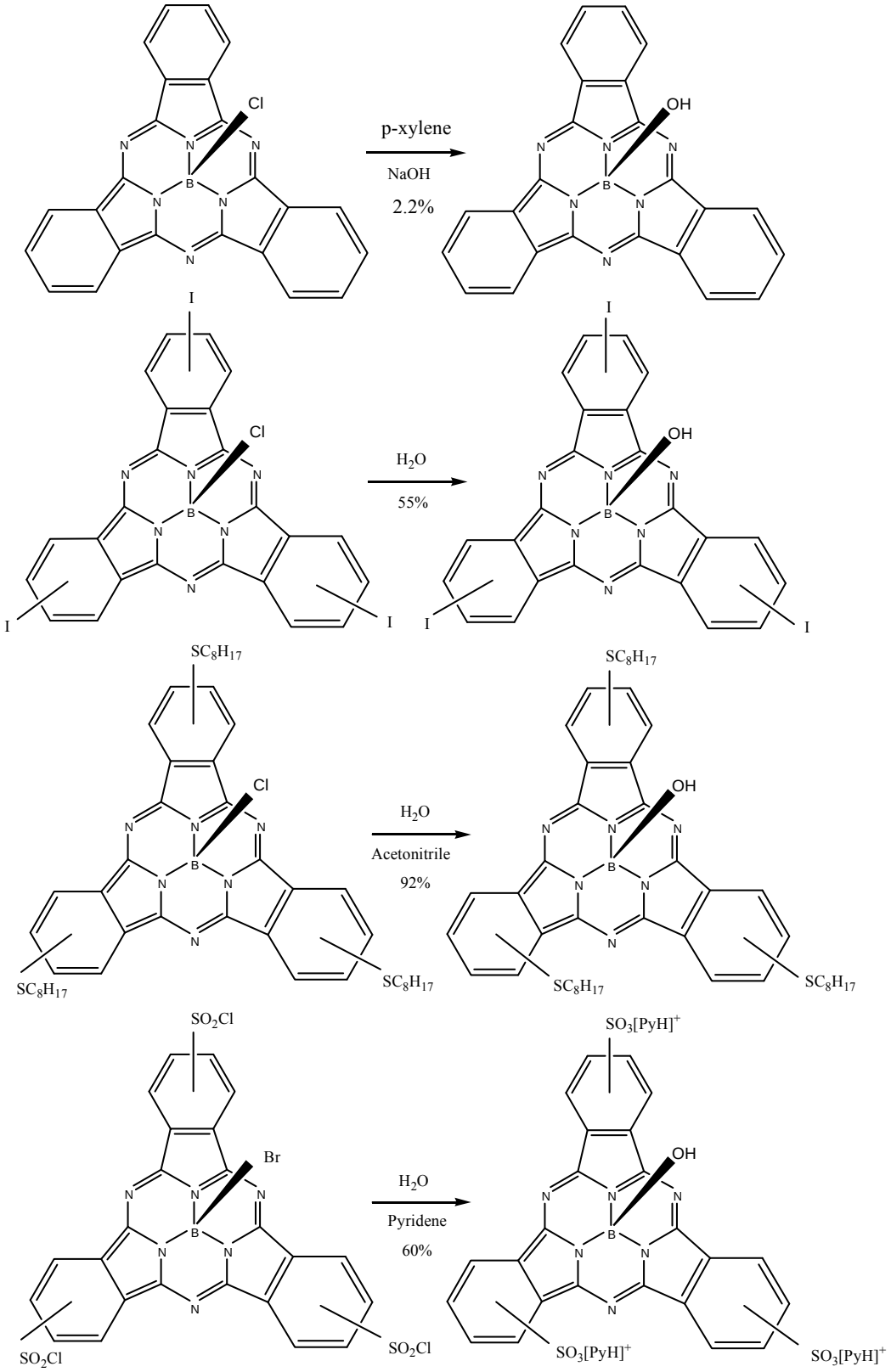


Figure 23. Synthesis of SubPcs with a Hydroxyl Substituent.

5.3 Alkoxy Substitution.

There have been many reactions completed recently where the axial chloride is replaced by alkoxy groups. In 2002, Classens and Torres synthesized an alkoxy substituted SubPcs in good yield (80%) using 3,5-di-tert-butylphenol.[15]

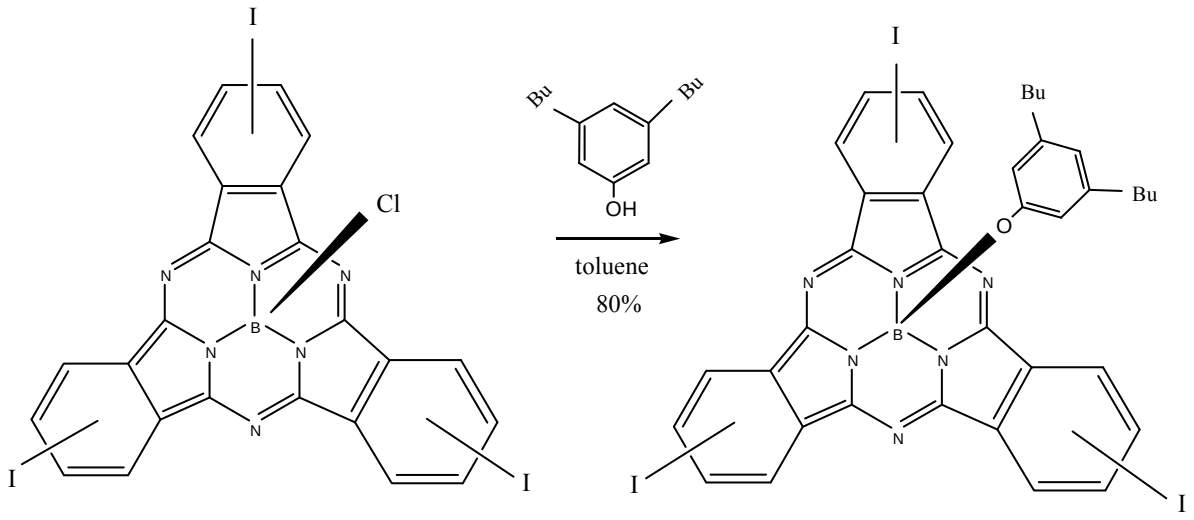


Figure 24. Synthesis of SubPcs with the Alkoxo Substituent.

Claessens et al. reviewed different reactions of several oxygen nucleophiles to produce

several axially substituted SubPcs. It was noted that peripheral donor groups increased the rates and yields of substitution by stabilization of an eventual positive charge on the boron atom.[14]

Fukuda, et al. prepared a BINOL ([SubPc]B)$_2$ where the SubPcCl was reacted with either racemic Binol or [(R)-(+)-1,1'-bi-2-naphthol] to produce a chiral Subpc dimer (12% yield).[16]

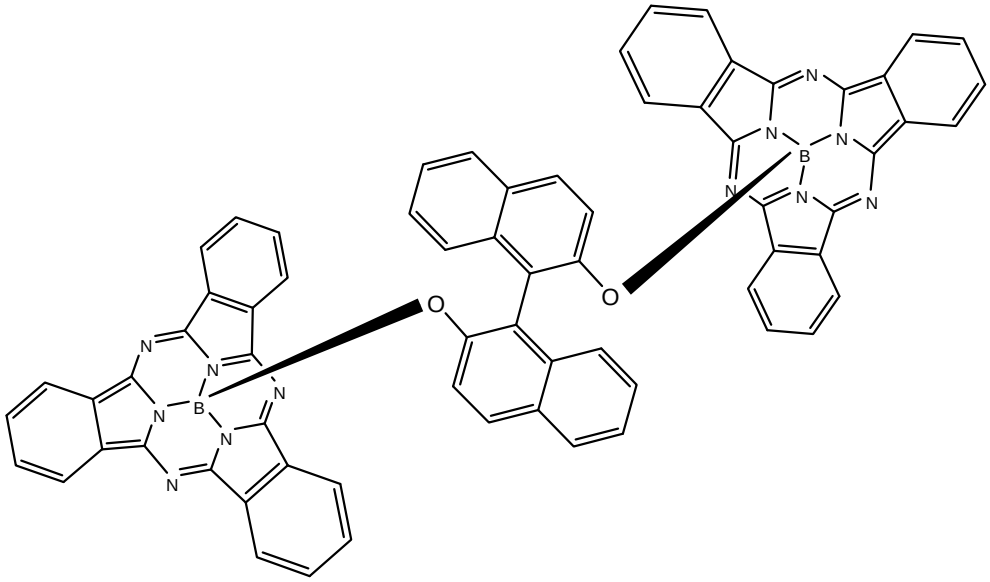


Figure 25. Example of a SubPcs Dimer with the Alkoxo Substituent.

A similar type of reaction was examined when three different SubPcs-C60 dyads were

synthesized with phenyl groups as axial substituents to boron by Rodriguez et al. The fullerene ensemble was examined for electrochemical and photophysic properties.[17]

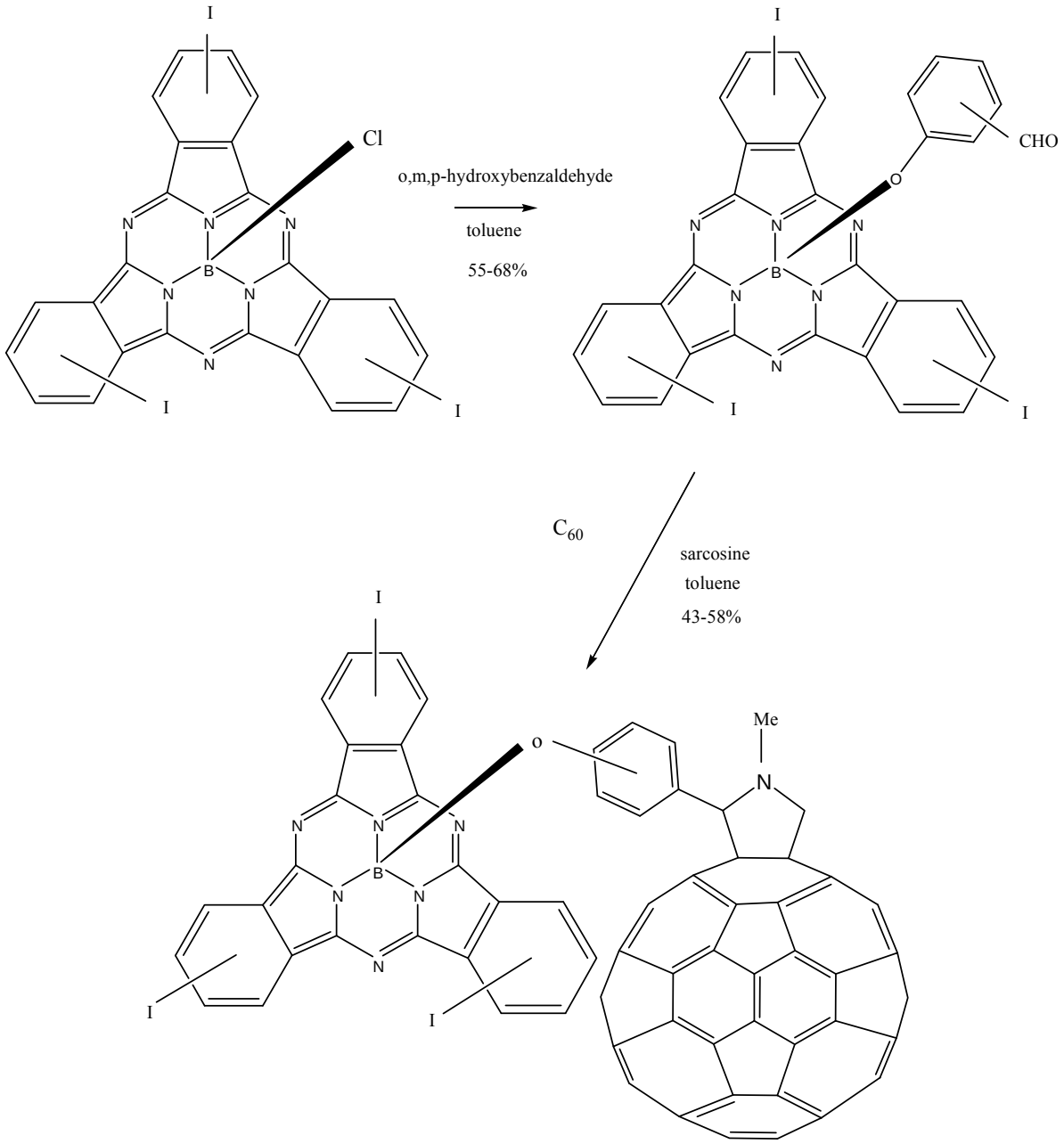
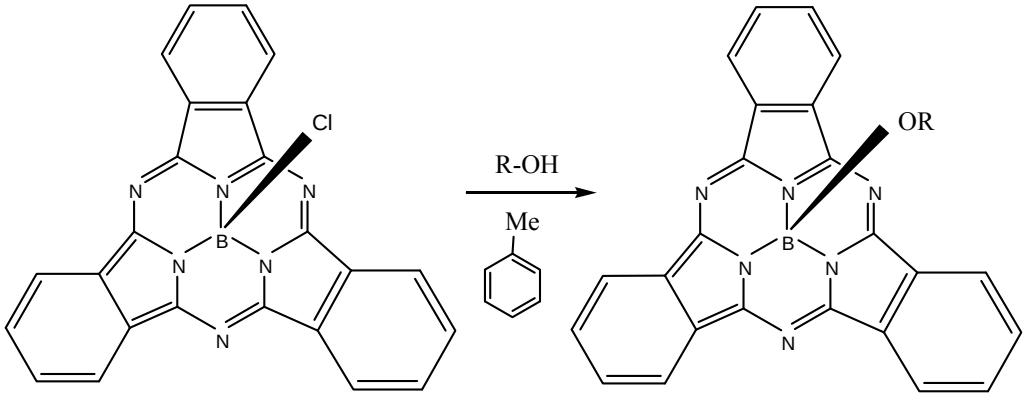


Figure 26. Representation of SubPcs-C60 dyad.

In 2006, Adachi and Watarai prepared several axially alkoxy-substituted SubPcs by the

condensation Cl-Subpc and the appropriate alcohol.[18]



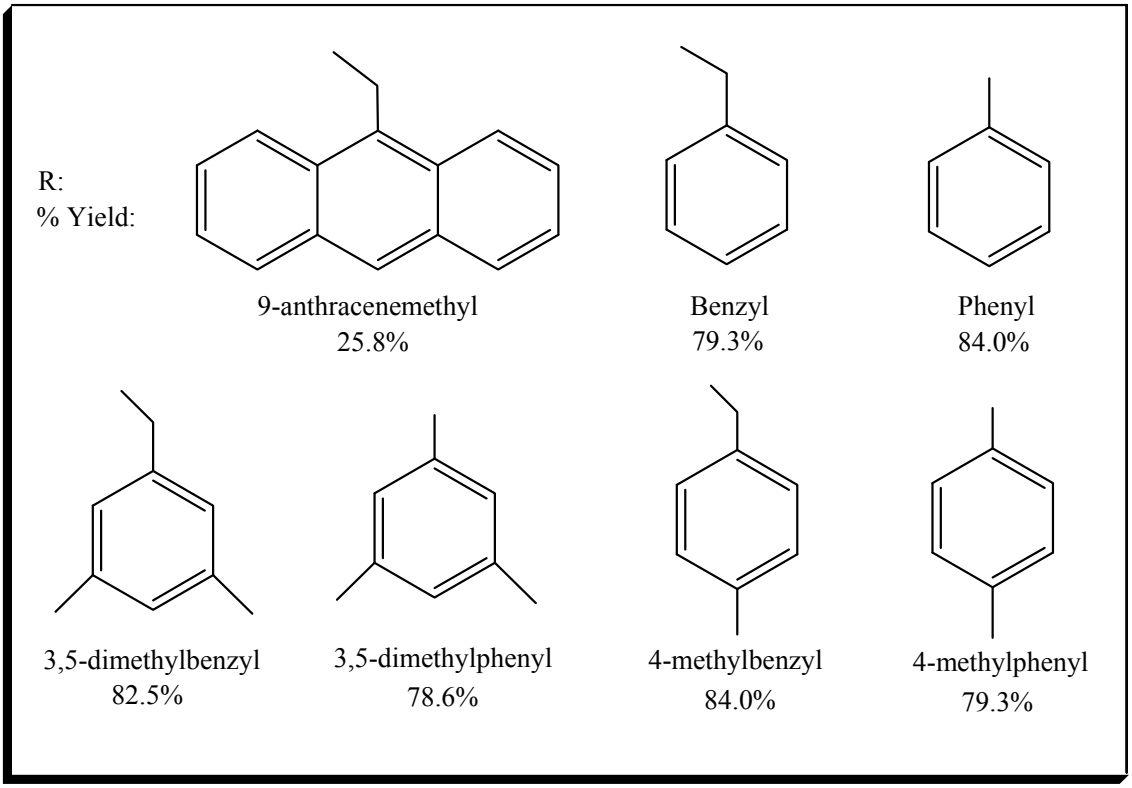


Figure 27. Representation of SubPcs with Several Alkoxo Substitutents.

All of the products except 9-anthracenemethyl had good yields using the same starting Cl-SubPc.

5.4 **Carbon Substitution.**

In 1995, Geyer et al. sucessfully synthesized a SubPcB bearing a butyl group as the axial ligand using Bu_2BBr_2 with 1,2-dicyanobenzene in naphthalene with very low yields (0.5%) and was not an axial substituted reaction.[12] In 1987, the same group used the superbase phopsphazene[1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[trisdiemthylamino]phosphoranylidenamino]-2λ^5, 4λ^5 –catenadi(phosphazene)] (P4-t-Bu) as a catalyst with low yield (3%).[12] The use of the superbase was needed to obtain the product due second methyl group added to each ring. Geyer et al. produced a SubPcBPh in good yield (17%) using phenyllithium. [12] Another synthesis involved preparing SubPcBPh without a halogen-containing reagent by reacting dicyanobenzene with triphenylboron in good yield.[12]

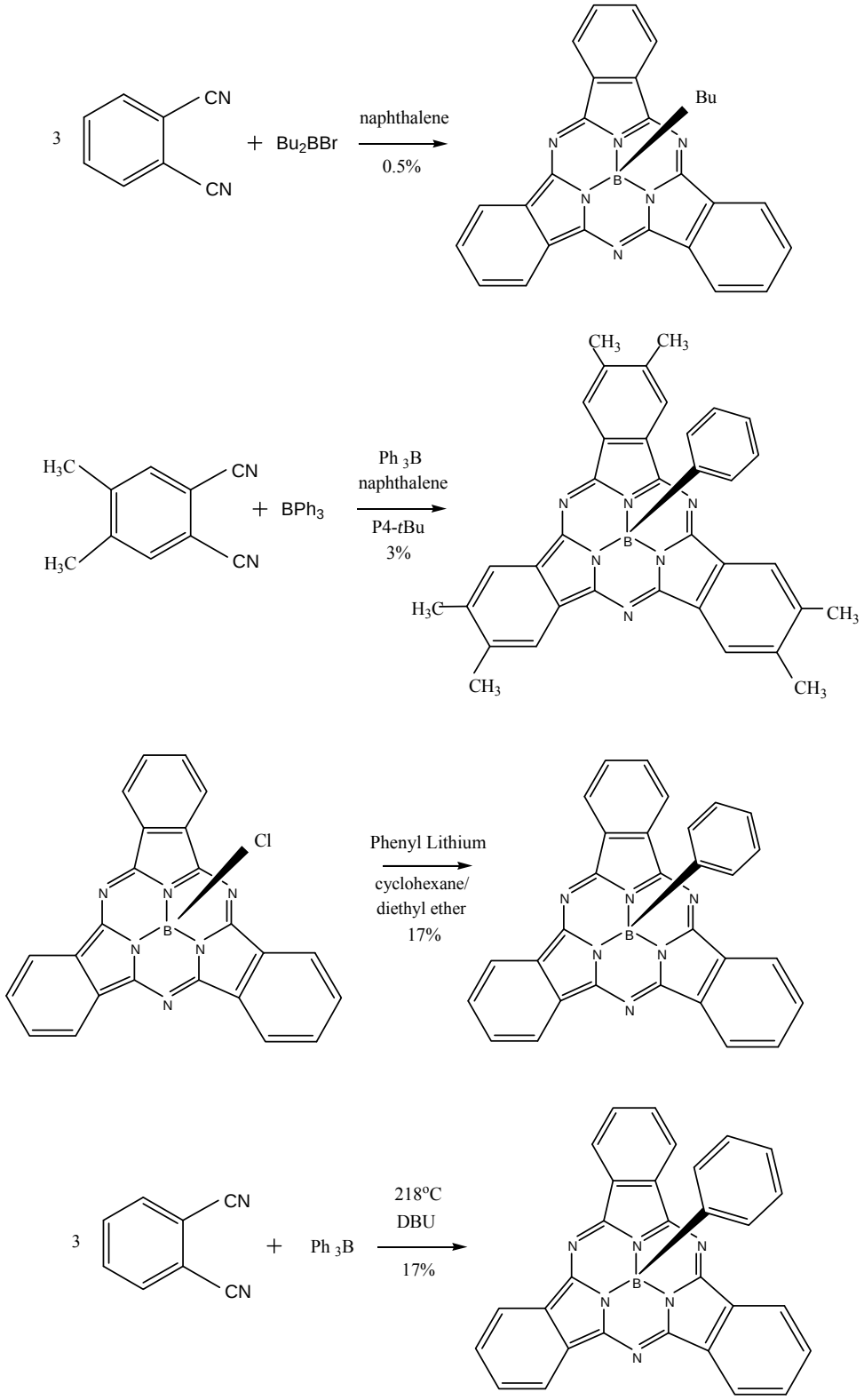


Figure 28. Synthesis of SubPcs with a Carbon Substituent.

5.5 Siloxy Substitution.

Axial siloxy boron SubPcs have been produced by two methods. In a 2-step process, triiodosubphthalocyanine was used as a reactant and refluxed with water to give the hydroxyl derivative in good yield (55%). This hydroxyl derivative was then reacted with triethylsilanol in chlorobenzene to produce the siloxy boron SubPcs in good yield (50%).[12]

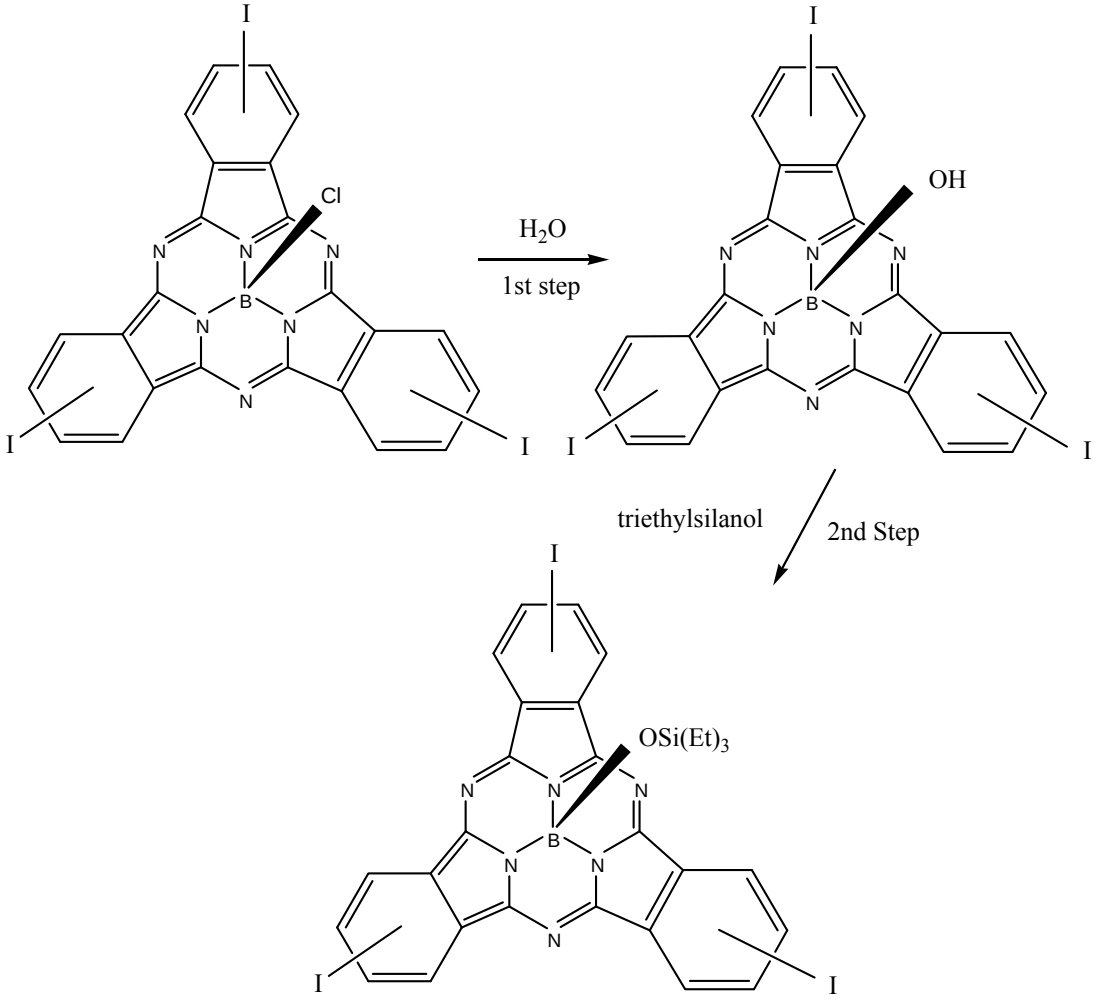


Figure 29. Synthesis of SubPcs with a Siloxy Substituent.

In a 1-step process, Zyskowski and Kennedy reacted SubPc with trihexyl silanol to produce the axial siloxy-SubPc at 84% yield (Figure 30).[8]

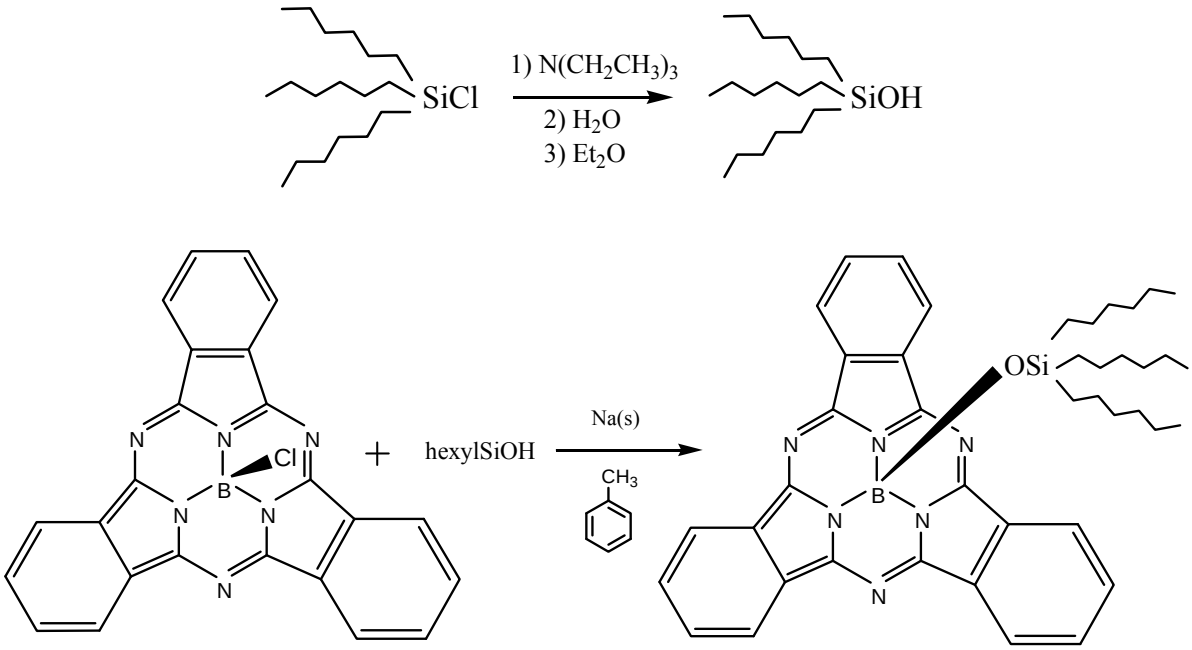


Figure 30. Synthesis of Trihexylsilanol and Siloxy Substituent.

All of the reactions I performed did not involve the use of peripheral donor groups on the SubPcs ring in order to simplify starting compound synthesis and compare percent yields.

While it is obvious that SubPcs have many applications, each of these require SubPcs that are structured to fit specific uses. As the need for different SubPcs derivatives increases, the need for more customized compounds will increase as well. This will require the creation of new synthetic methods for SubPcs derivatives.

The purpose of this investigation is to expand the scope of a new method for preparing siloxy substituted compounds, synthesize axial alkyl-substituted BSubPcs, and to develop skills by replicating hydroxyl substitution reactions. I have synthesized previously prepared

compounds to sharpen my synthetic techniques and confirm percent yields. In the course of this investigation I have synthesized a new compound and confirmed its structure using FTIR, ^{1}H NMR, and HRMS.

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CHAPTER 6: Experimental

6.1 Apparatus and reagents.

1,2-Dicyanobenzene, trialkyl silyl chlorides and boron trichloride were obtained from Aldrich Chemical Company and were used without further purification. 1-Chlorobenzene was obtained from Sargent Welch.

6.2 Instrumental Characterization Methods.

Proton Nuclear Magnetic Resonance (^{1}H NMR)

All solution spectra were run in $CDCl_3$ and recorded on a JEOL / AS400. ^{1}H NMR spectra were obtained at 400 MHz and using a 5000-Hz spectral width, a relaxation delay of 1 s, a pulse width of 83°, and 16K data points.

The residual hydrogen signal in $CDCl_3$ was used as an internal reference at 7.25 ppm.

Infrared Spectroscopy (IR)

Spectroscopic characterization of the products was performed on Nicolet, Impact 410, Class IIA Laser, HeNe Laser 633 nm (EZ OMNIC E.S.P. Software). The IR spectra of the products were obtained as Nujol mulls on NaCl plates.

High Resolution Mass Spectrometry

Exact mass measurements were determined at the University of Michigan Laboratory using a Micromass Ultima high resolution magnetic sector mass spectrometer using DEI (desorption electron ionization) for the mass determination of BSubPcCl and BSubPcOH and Electrospray with formic acid added for BSubPcOSi(Bu)$_3$.

6.3 Synthesis and Characterization of substituted Boron Ligands.

Preparation of Chloro[subphthalocyaninato]boron(III)

Under N_2 gas, 0.5006 g of 1,2- dicyanobenzene (Aldrich, 98 wt %) were added to 20 mL of 1-chlorobenzene (Sargent Welch) to a 100 mL three-necked, round-bottom flask and stirred for 30 minutes at approximately 80°C. The flask was covered with aluminum foil during the reaction to remove light. After cooling to room temperature, 3 mL of a 1.0 M solution of boron trichloride in heptane was added dropwise and heated to 100° C for 1 hour until a prominent red color persisted. After cooling to room temperature, the solvent was evaporated under rotary vacuum, and the solid was placed in a cellulose soxhlet extraction thimble. The resultant solution was washed with hexane (10 mL), extracted with methanol (Soxhlet, 150 mL), and dried (60 torr, 75°C) for 1 hour to yield a reddish brown solid (1.288 g, 57.4 %). ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 7.95(m, 2,3-sPc H), 8.90(m, 1,4-sPc H). IR (nujol): v(cm^{-1}) = 1460 (m), 1377 (vs), 1260 (s), 1091 (w), 1020 (w), 799 (m), 723 (m). MS-HREI exact mass m/z: calcd for $C_{24}H_{12}N_6BCl$, 430.0905; found, 430.0889.

Preparation of Hydroxy[subphthalocyaninato]boron(III)

Under N_2 gas, 0.0139 g of chloro[subphthalocyaninato]boron(III) were added to a 50:50 solution of pyridine in water (6.0 mL of pyridine and 6.0 mL of deionized water) to a 100 mL three-necked, round-bottom flask. This solution was heated to 100°C for 1 hour until a prominent red/purple color persisted. The flask was covered with aluminum foil during the reaction to remove light. The solution was evaporated under rotary vacuum, and the remaining solid was removed from the round-bottom flask. The solid was

dried (60 torr, 75°C) for 1 hour (0.0086g, 64.7%). ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 7.89(m, 2,3-sPc H), 8.84(m, 1,4-sPc H). IR (nujol): v(cm^{-1}) = 3587 (br, OH), 1460 (m), 1377 (vs), 1261 (vs), 1091 (m), 1019 (m), 799 (s). MS-HREI exact mass m/z: calcd for $C_{24}H_{12}N_6BOH$, 412.1244; found, 412.1249.

Preparation of Butyl[subphthalocyaninato]boron(III)

Under N_2 gas, 0.0136 g of chloro[subphthalocyaninato]boron(III) were added to 5.0 mL of anhydrous ethyl ether and 5.0 mL of toluene (dried over alumina for 24 hours) to a 25 mL two-necked, round-bottom flask. To this solution, 0.10 mL of n-butyllithium (2.0 M in hexane) was added by syringe. This solution was heated to 100°C for 1 hour until a prominent red color persisted. The flask was covered with aluminum foil during the reaction to remove light. The solution was evaporated under rotary vacuum, and the remaining solid was removed from the round-bottom flask. The solid was dried (60 torr, 75°C) for 1 hour (0.00457g, 32.16%). Characterization by ^{1}H NMR was attempted, but did not yield peaks for the subphthalocyanine rings at 8 and 9 ppm as anticipated. This reaction was repeated on numerous times the same results were obtained.

Preparation of Trihexylsilanol

0.5 mL of deionized water, 20 mL of diethyl ether, and 2.0 mL of triethylamine (1M in hexane) were added to a 100-mL, three-necked flask. To a separatory funnel were added 20 mL of diethyl ether and 5.0 g chlorotrihexylsilane. The separatory funnel was attached to the middle neck of the round-bottom flask and the flask was placed on ice. The solution in the separatory funnel was added to the round-bottom flask dropwise under agitation. After the

solutions were mixed, the resultant white slurry was vacuum-filtered, and the filtrate was evaporated under rotary vacuum. The oily product was transferred to a separatory funnel, dissolved in 40 mL of hexane, and washed with 40 mL of water. The hexane layer containing the trihexylsilanol was dried overnight with anhydrous magnesium sulfate. The material was vacuum-filtered and evaporated under rotary vacuum to give 1.6703 g of viscous oil (36.2%).

Preparation of Trihexylsiloxy[subphthalocyaninato]boron(III)

Under N_2 gas, 5.0 mL of dried toluene (dried in alumina for 24 hours), 0.058 g of freshly cut sodium, and 0.50 mL of trihexylsilanol were added to a 100-mL, three-necked, round-bottom flask. This solution was heated to 100°C for 1 hour to generate the sodium salt of the silanol. The solution was cooled to room temperature, and 0.2671g of chloro[subphthalocyaninato]boron(III) was added. The flask was then heated to reflux for 1.5 hours and was covered with aluminum foil during the reaction to remove light. The solution was transferred to a 100-mL round-bottom flask and evaporated under rotary vacuum. The solids were removed from the flask and chromatographic separation on Al_2O_3 (I) was performed. The solids were dissolved in a minimal amount of hexane and chromatographed. A 50:50 toluene/hexane mixture was the eluent to separate the unwanted products. The solution from the desired fraction was evaporated under rotary vacuum. A bronze solid was obtained and had a mass of 0.1771 g (41.10%). ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 7.85(m, 2,3-sPc H), 8.86(m, 1,4-sPc H), 0.85(t,CH_2), 0.62(q,CH_3), 0.45(m,$\mathit{CH_2}CH_2Si$), 0.45(m,$\mathit{CH_2}CH_2CH_2Si$), 0.45(m,$\mathit{CH_2}CH_2CH_2CH_2Si$), -0.44(t,$\mathit{CH_2}Si$).

Preparation of Tributylsilanol

0.5 mL of deionized water, 20 mL of diethyl ether, and 2.0 mL of triethylamine (1M in hexane) were added to a 100-mL, three-necked flask. To a separatory funnel were added 20 mL of diethyl ether and 5.0 g chlorotributylsilane. The separatory funnel was attached to the middle neck of the round-bottom flask and the flask was placed on ice. The solution in the separatory funnel was added to the round-bottom flask dropwise under agitation. After the solutions were completely mixed, the resultant white slurry was vacuum-filtered, and the filtrate was evaporated under rotary vacuum. The oily product was transferred to a separatory funnel, dissolved in 40 mL of hexane, and washed with 40 mL of water. The hexane layer containing the tributylsilanol was dried overnight with anhydrous magnesium sulfate. The material was vacuum-filtered and evaporated under rotary vacuum to give 1.8803 g of viscous oil (40.8%).

Preparation of Tributylsiloxy[subphthalocyaninato]boron(III)

Under N_2 gas, 5.0 mL of alumina dried toluene, 0.049 g of freshly cut sodium, and 0.50 mL of tributylsilanol were added to a 100-mL, three-necked, round-bottom flask. This solution was heated to 100°C for 2 hours to generate the sodium salt of the silanol. The solution was cooled to room temperature, and 0.0806 g of chloro[subphthalocyaninato]boron(III) was added. The flask was covered with aluminum foil during the reaction to remove light. The solution was transferred to a 100 mL round-bottom flask and evaporated under rotary vacuum. The solids were removed from the flask, dissolved in a minimal amount of hexane, and chromatographed on Al_2O_3 (II). A 50:50 toluene/hexane mixture was the eluent. The solution from the desired collected fraction was

evaporated under rotary vacuum. A second chromatographic separation was performed using a toluene/hexane mixture as the eluent. The solution from the desired collected fraction was evaporated under rotary vacuum. A bronze solid was obtained generating 0.0523 g (45.76%). ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 7.87(m, 2,3-sPc H)), 8.84(m, 1,4-sPc H), 0.87(t,CH_2), 0.58(q,CH_3), 0.44(t,$CH_2$$CH_2$Si), -0.42(t,$CH_2$Si). MS-HREI exact mass m/z: calcd for $C_{36}H_{40}N_6BOSi$, 611.3120; found, 611.3126.

CHAPTER 7: Results and Discussion

Chloro[SubPc]boron(III) needed to be prepared in order to obtain the axial substituted products. The procedure was performed on several occasions to yield enough of the starting compound to perform the axial substitution reactions. To determine the % yield with 1,2-dichlorobenzene as the limiting reagent,

% yield = actual mass of product / predicted mass of product (100)

and the molecular weights are as follows:

Compound	Molecular Weight
1,2-Dicyanobenzene	128.133 g/mol
Boron Trichloride	117.169 g/mol
Chloro[SubPc]boron (III)	430.663 g/mol

Each reaction had changing concentrations of chemical constituents:

Label	1,2-Dicyanobenzene	1.0M Boron Trichloride	Chlorobenzene
MC-4	0.5006g or 3.907E-3 mol	3.0ml or 3.661E-2mol	20.0mL
MC-5	0.5001g or 3.903E-3 mol	3.0ml or 3.661E-2mol	20.0mL
MC-6	1.0009g or 7.811E-3 mol	6.0ml or 7.322E-2mol	20.0mL
MC-7	0.7498g or 5.852E-3mol	4.5ml or 5.492E-2mol	20.0mL
MC-8	2.0008g or 1.562E-2mol	12.0ml or 1.465E-1mol	25.0mL
MC-9	2.0031g or 1.563E-2mol	12.0ml or 1.465E-1mol	25.0mL

To determine the percent yield, the moles of the limiting reagent can be determined by the following equation:

grams of L.R. (1 mole of L.R./M.W. of L.R.) = moles of L.R.

For MC-4, (0.5006 g) (1 mole / 128.133g) = 3.907 X 10-3 moles

The ratio between 1,2-dicyanobenzene (limiting reagent) and BSubPc-Cl (product) is 3 moles of 1,2-dicyanobenzene to 1 mole of BSubPc-Cl. Determine the moles of product,

3.907E-3 moles of L.R. (1 mole BSubPc-Cl / 3 moles of L.R.) = 1.302E-3 mole

Converting back to grams,

1.302E-3 moles (430.663 g/mole) = 0.5607 grams of BSubPc-Cl

The percent yield was then determined:

Label	Actual yield	Predicted Yield	% Yield
MC-4	0.2891g	0.5607g	51.56%
MC-5	0.2423g	0.5603g	43.25%
MC-6	0.5466g	1.1213g	48.75%
MC-7	N.R.	0.8401g	N.R.
MC-8	0.8122g	2.2423g	36.22%
MC-9	1.2879g	2.2438g	57.40%

Since the actual yield from MC-4 = 0.2891g, the percent yield =

0.2891g actual /0.5607g predicted (100%) = 51.56 % yield

Although the highest yield product would seem to be MC-9, all of the reactions were prepared at the same ratio of 1,2-dicyanobenzene to boron trichloride. Therefore, the highest yield reaction was either coincidental or likely due to the higher amount of reactants. The reaction times and temperatures were the same in all cases. Since boron trichloride is an air-sensitive reagent, each reaction contained an excess. The reaction that did not produce any of the BSubPcCl, MC-7, used the last of the boron trichloride from the source bottle.

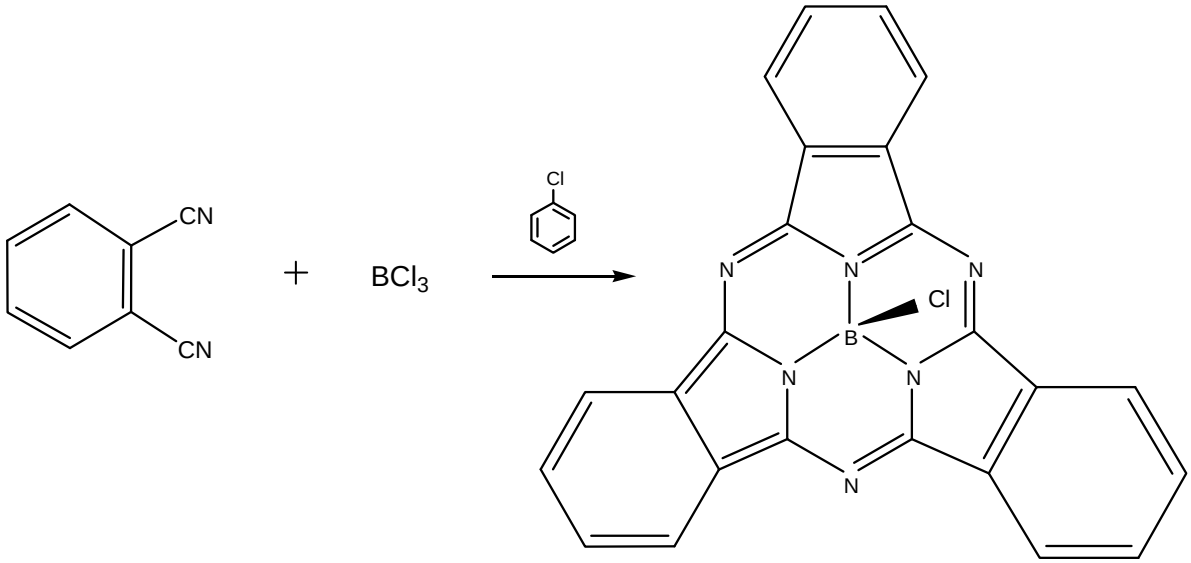
In comparison, the results for the other 4 reactions were as follows:

Compound	Molecular Weight
Hydroxy[SubPc]boron (III)	412.220 g/mol
Butyl[SubPc]boron(III)	453.332 g/mol
Trihexylsiloxy[SubPc]boron(III)	694.800 g/mol
Tributylsiloxy[SubPc]boron(III)	610.639 g/mol

Percent yield for the remaining products:

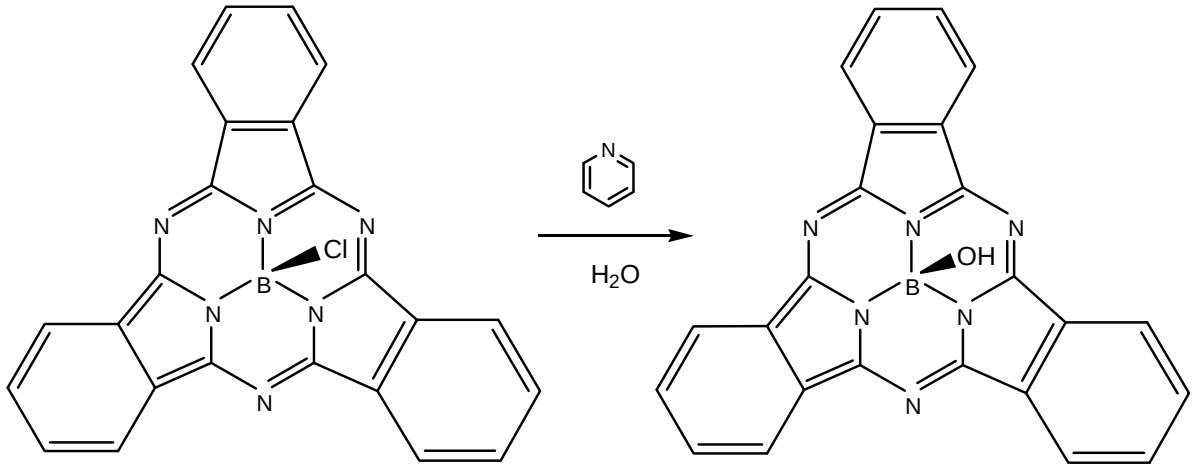
Compound	Actual yield	Predicted Yield	% Yield
Hydroxy[SubPc]boron (III)	0.0086g	0.0133g	64.70%
Butyl[SubPc]boron(III)	0.0143g	0.0046g	32.16%
Trihexylsiloxy[SubPc]boron(III)	0.1771g	0.4310g	41.10%
Tributylsiloxy[SubPc]boron(III)	0.0523g	0.1143g	45.76%

The BSubPcCl were prepared by the following reaction:



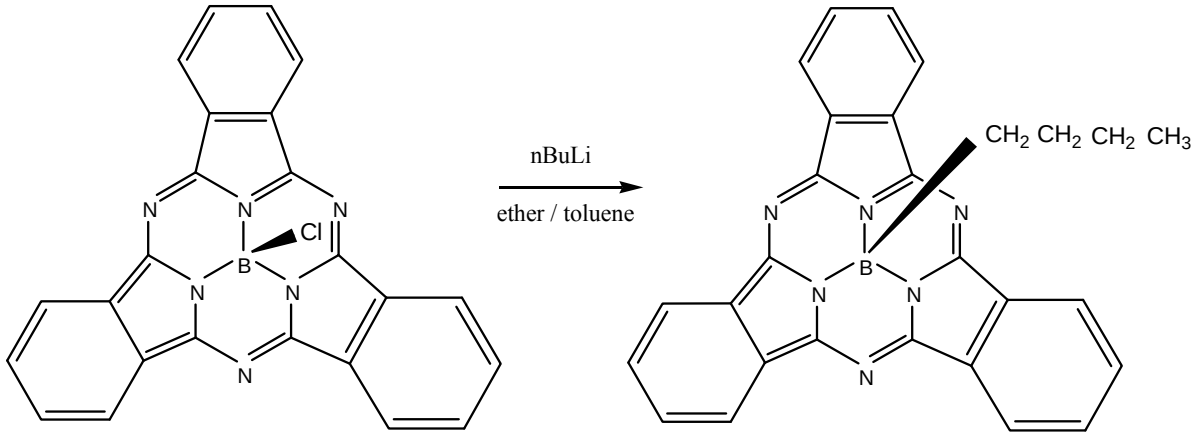
Scheme 1. Synthesis of chloro[subphthalocyaninato]boron (III).

After obtaining sufficient quantities of BSubPcCl, the axial substitution reaction to replace the chlorine with a hydroxyl group was performed to prepare hydroxy[subphthalocyaninato]boron(III).



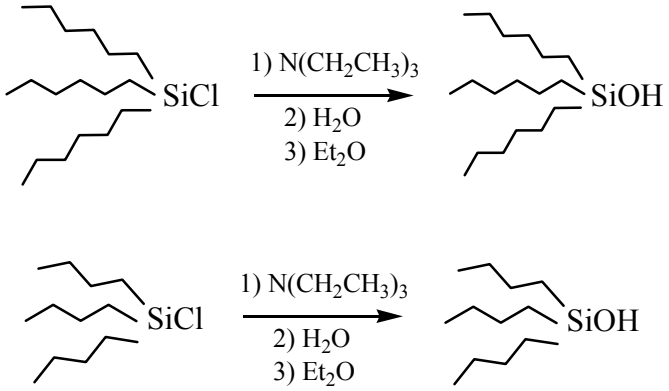
Scheme 2. Synthesis of hydroxy[subphthalocyaninato]boron(III).

Another axial substitution reaction involves nucleophilic substitution reaction of chlorine on the BSubPcCl with a butyl group using n-butyl lithium.



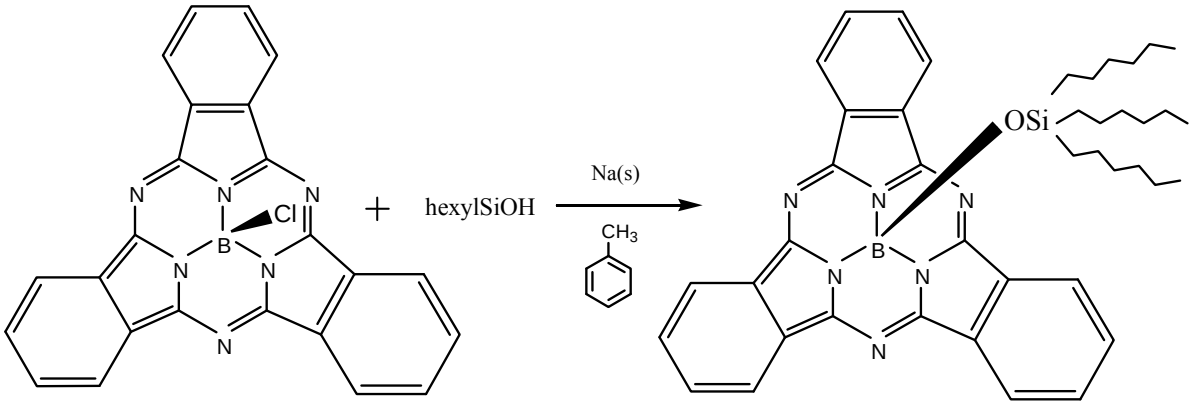
Scheme 3. Synthesis of butyl[subphthalocyaninato]boron(III).

To accomplish the synthesis of trihexylsiloxy [subphthalocyaninato] boron(III) and tributylsiloxy [subphthalocyaninato] boron(III), the sodium salt of trihexylsilanol and tributylsilanol had to be prepared:



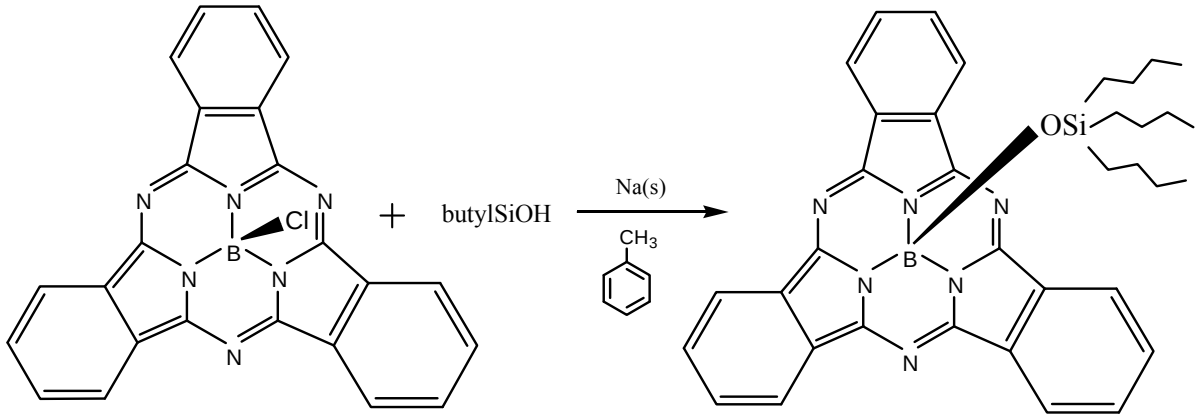
Scheme 4. Synthesis of trihexylsilanol and tributylsilanol.

After the trihexylsilanol compound is prepared, the reaction can proceed according to scheme 5:



Scheme 5. Synthesis of trihexylsiloxy[subphthalocyaninato]boron(III).

Likewise, after tributylsilanol is prepared, the reaction can proceed according to scheme 6:



Scheme 6. Synthesis of tributylsiloxy[subphthalocyaninato]boron(III).

Characterization of each of these compounds was performed by FTIR, ^{1}H NMR, and/or high-resolution electron impact spectrometry. Characterization of tributylsilanol and trihexylsilanol was not determined since both tributylsiloxy[subphthalocyaninato]boron(III) and trihexylsiloxy[subphthalocyaninato]boron(III) were later characterized. All of the compounds previously prepared before this work were consistent with previous reports.[11, 13, 17]

The FTIR spectrum shows a complex band pattern for the ring bands in subphthalocyanines:

Ring peaks at 1459 (s), 1376 (s), 1261 (s), 748 (s) cm^{-1}

Ring C-H in-plane bend at 798 (vs) and 748 (s) cm^{-1}

Carbon-nitrogen stretch peaks are seen at 1091 (m) cm^{-1}

Sample MC-7 did not produce predictable FTIR spectrum and was therefore not used in subsequent reactions. The addition of the hydroxyl group for the BSubPcOH shows a FTIR spectrum similar to the BSubPcCl with the addition at 3587 (b) cm^{-1} indicative of the OH band.

High-resolution mass spectrometry was analyzed at the University of Michigan Laboratory. An exact mass measurement was determined by DEI (desorption electron impact) for the BSubPcCl and BSubPcOH spectrums where a parent peak was found. The spectrum of BSubPcOSi$(Bu)_3$ was obtained using an electrospray technique with formic acid. Since the added acid supplied an additional hydrogen to the compound $[M + H]^+$, the predicted mass per charge ratio of BSubPcOSi$(Bu)_3$ is 611.3126 (611.3154 found). Additional daughter ions are present at 612.3150 $[M + 2H]^{++}$, 613.3215 $[M + 3H]^{+++}$, and 614.3290 $[M + 4H]^{++++}$.

^{1}H NMR show multiplet peaks indicative of subphthalocyanines at 7.87 to 7.95 that represent the hydrogens labeled H 2 and H 3 in Figure 21. There is another set of multiplet peaks at 8.84 to 8.90 that represent the hydrogens labeled H 1 and H 4 in Figure 31. This arrangement of hydrogen atoms gives a peak pattern in the ^{1}H NMR, which is called an AA'BB' pattern. This pattern resembles a doublet of doublet.

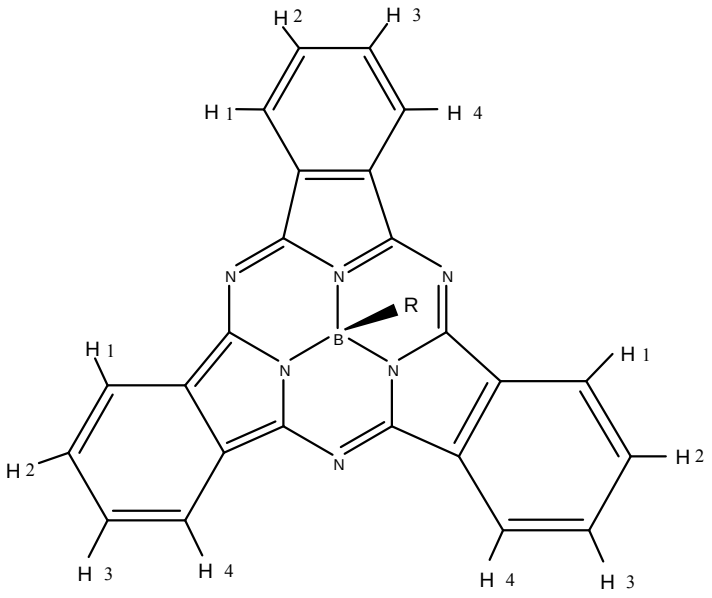
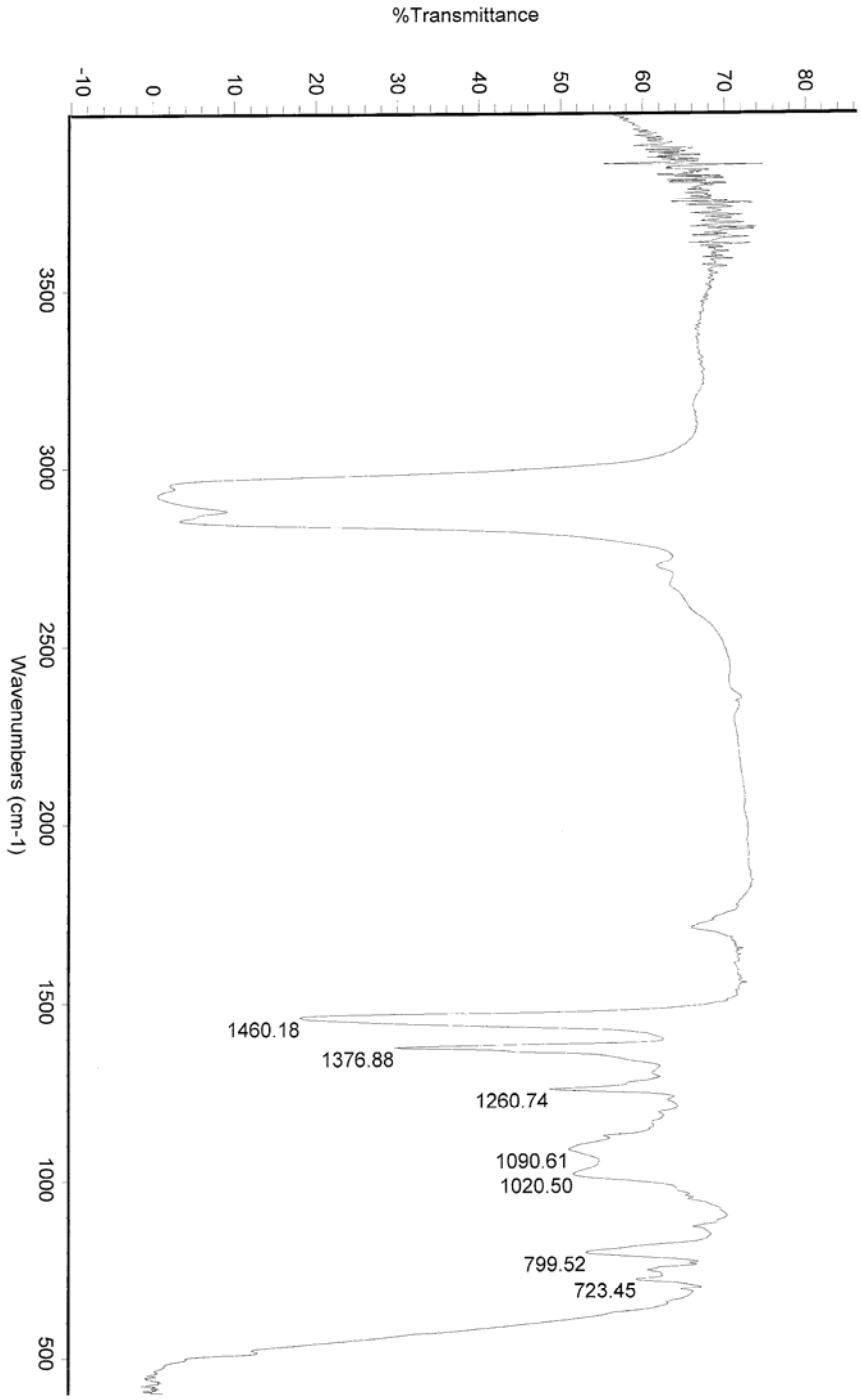


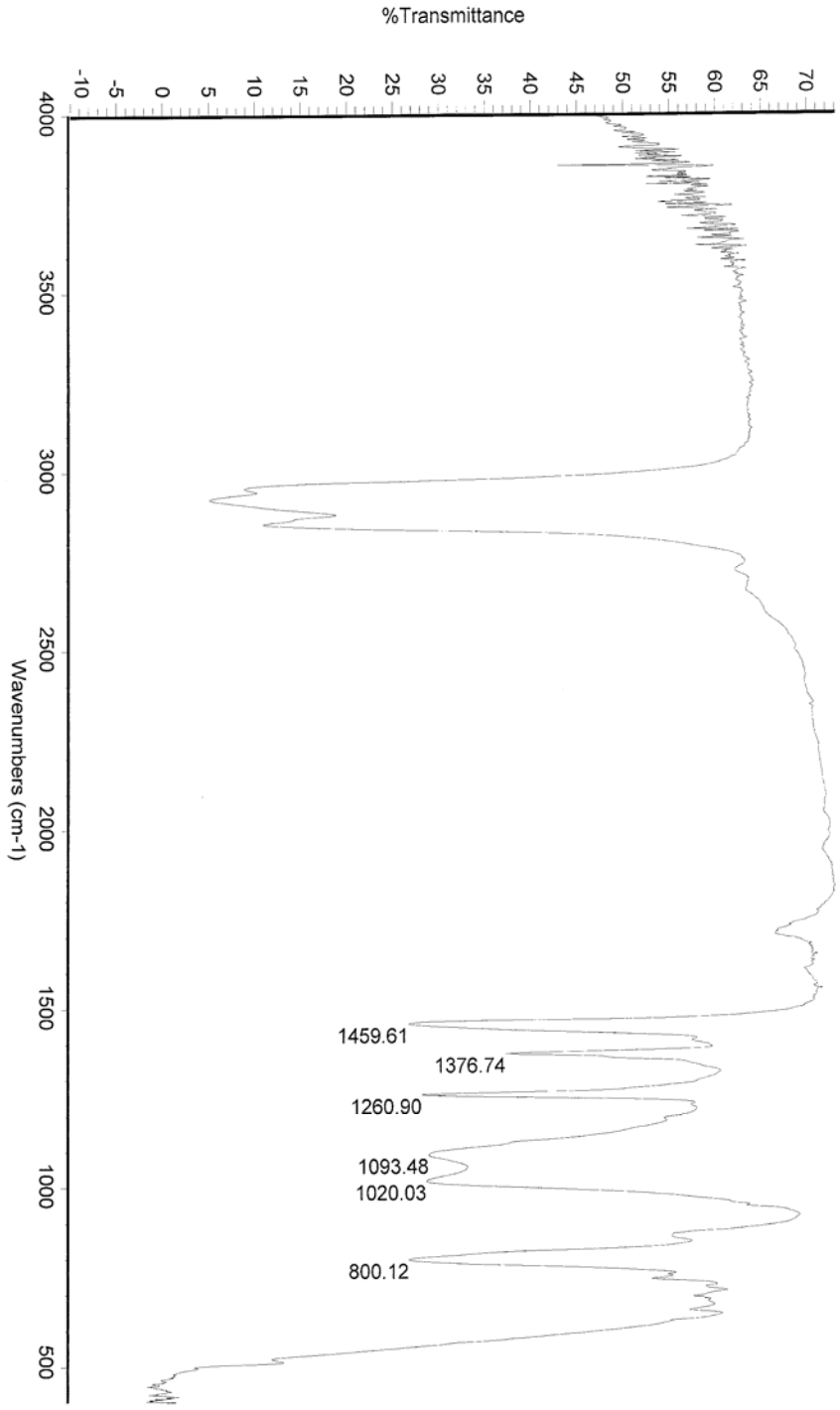
Figure 31. Representation of Hydrogens Associated with ^{1}H NMR peaks.

7.1 FTIR Scans.

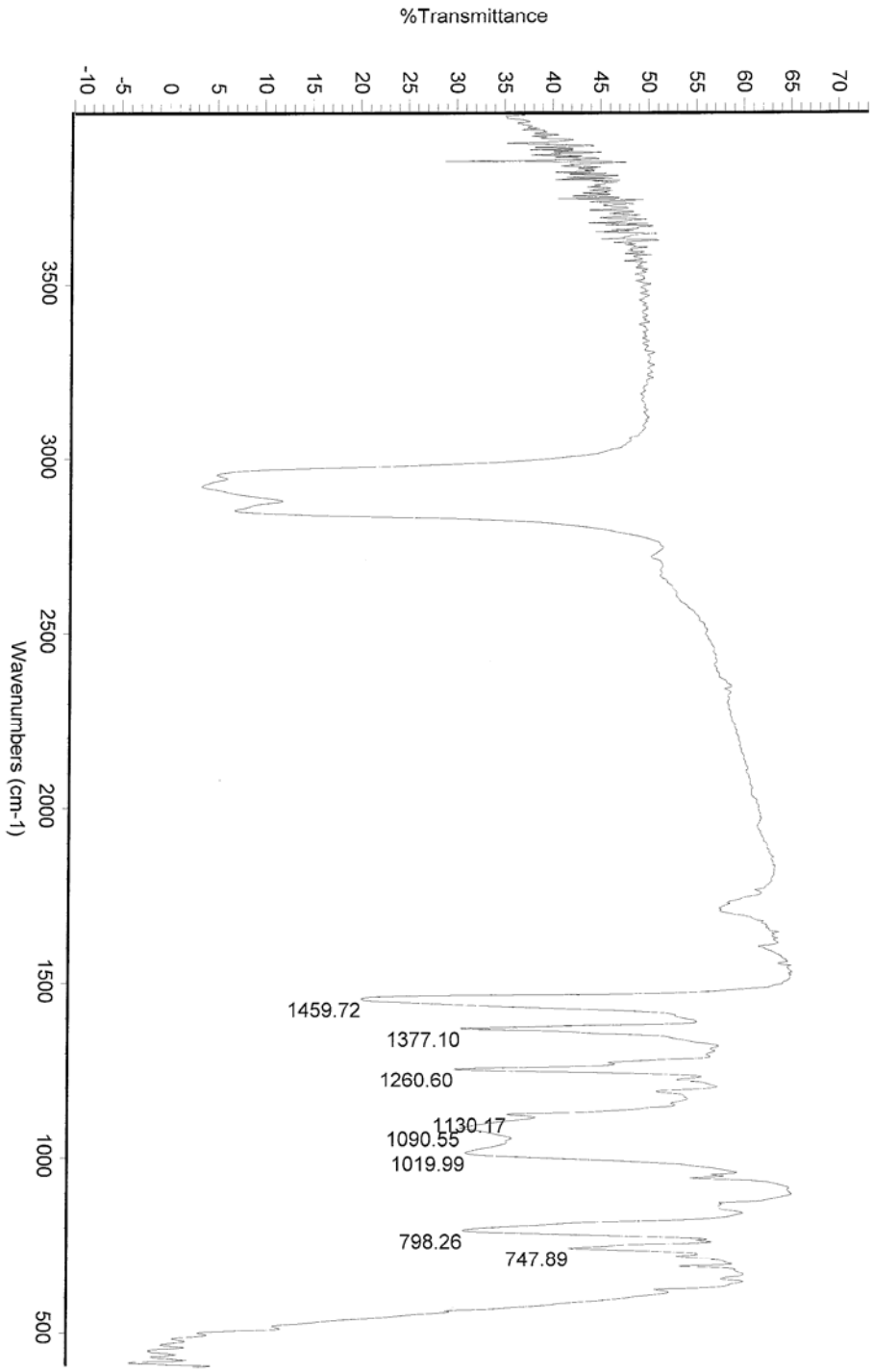
Sample MC-4 BSubPcCl



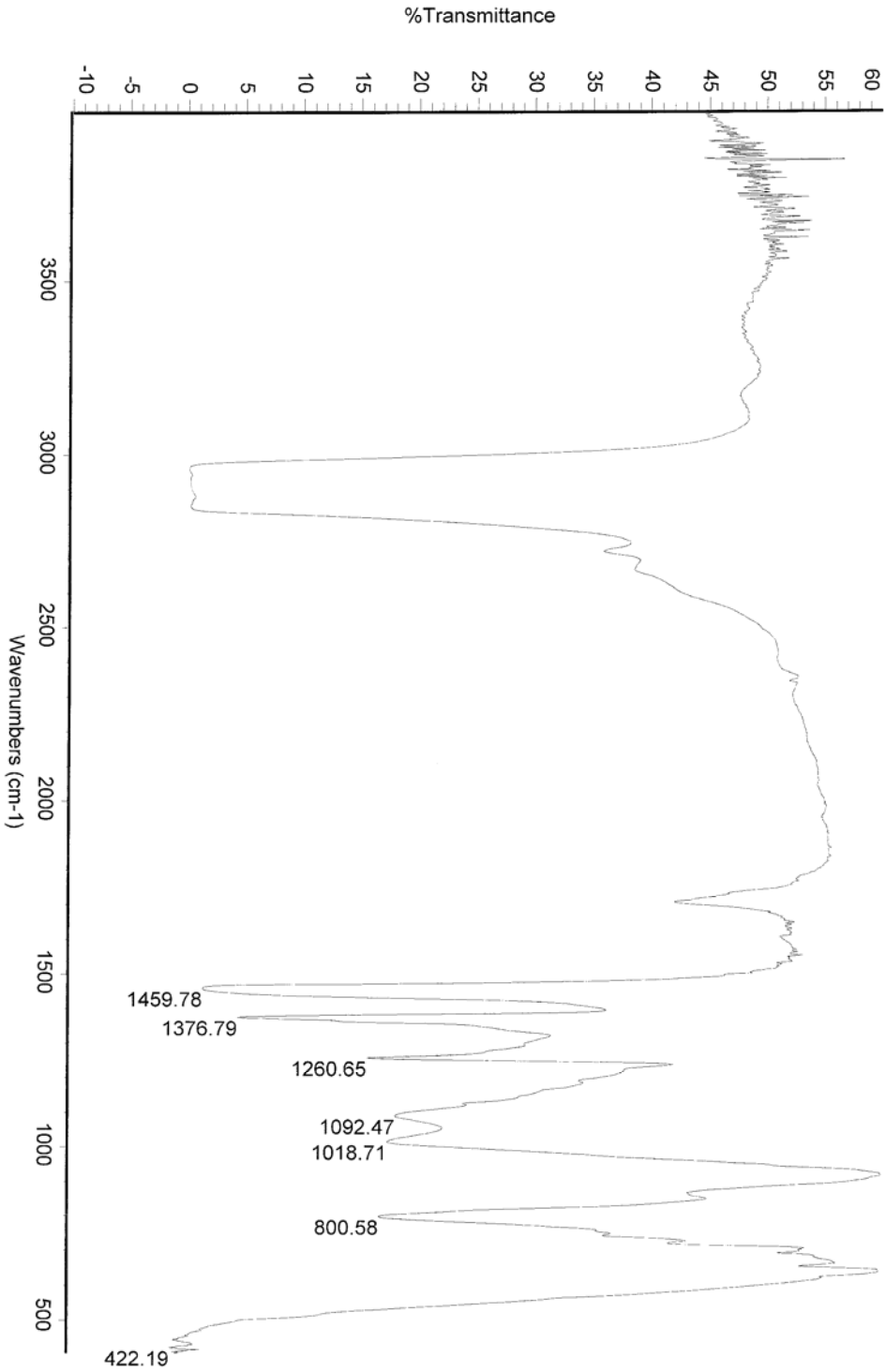
Sample MC-5 BSubPcCl



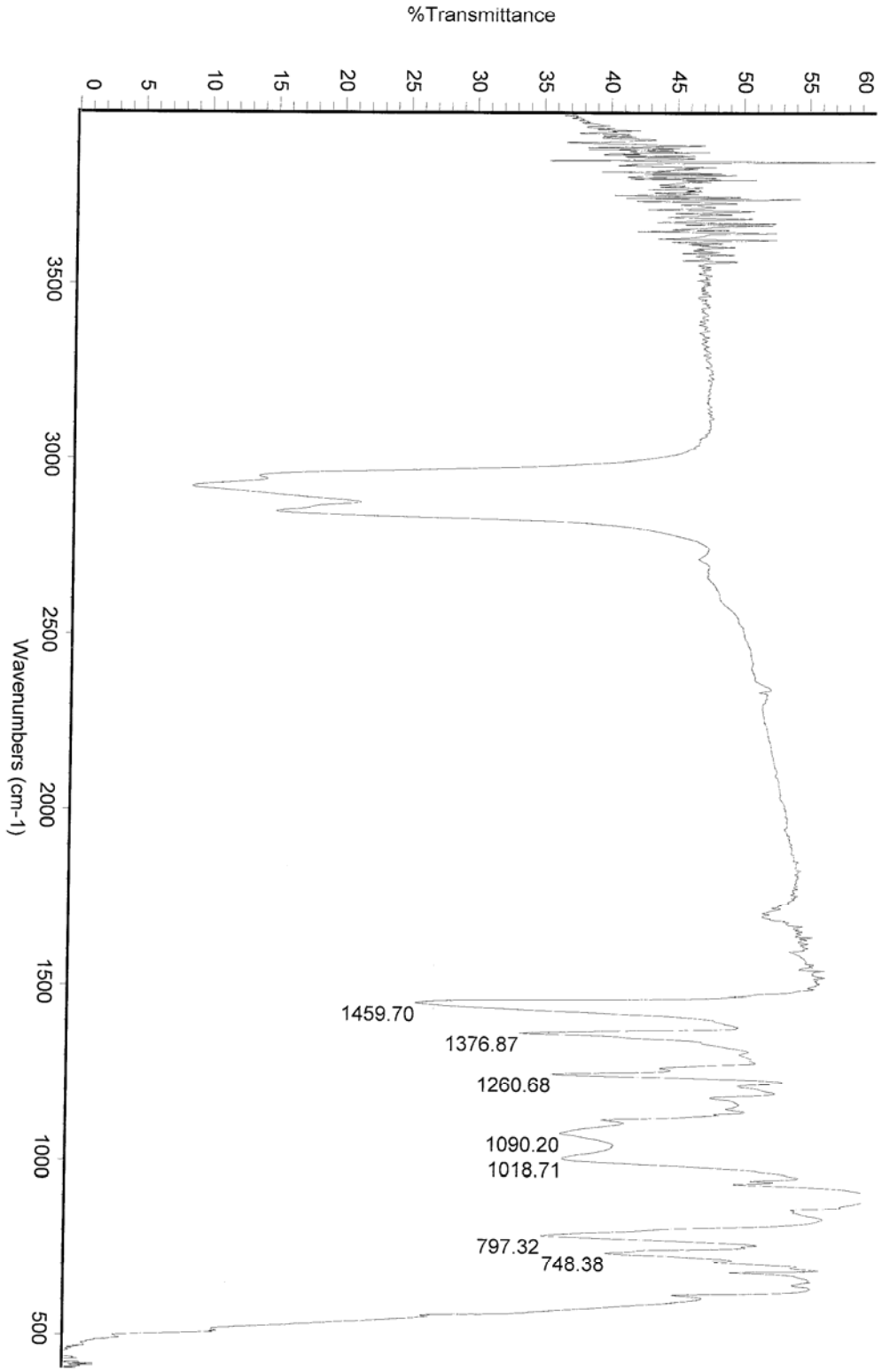
Sample MC-6 BSubPcCl



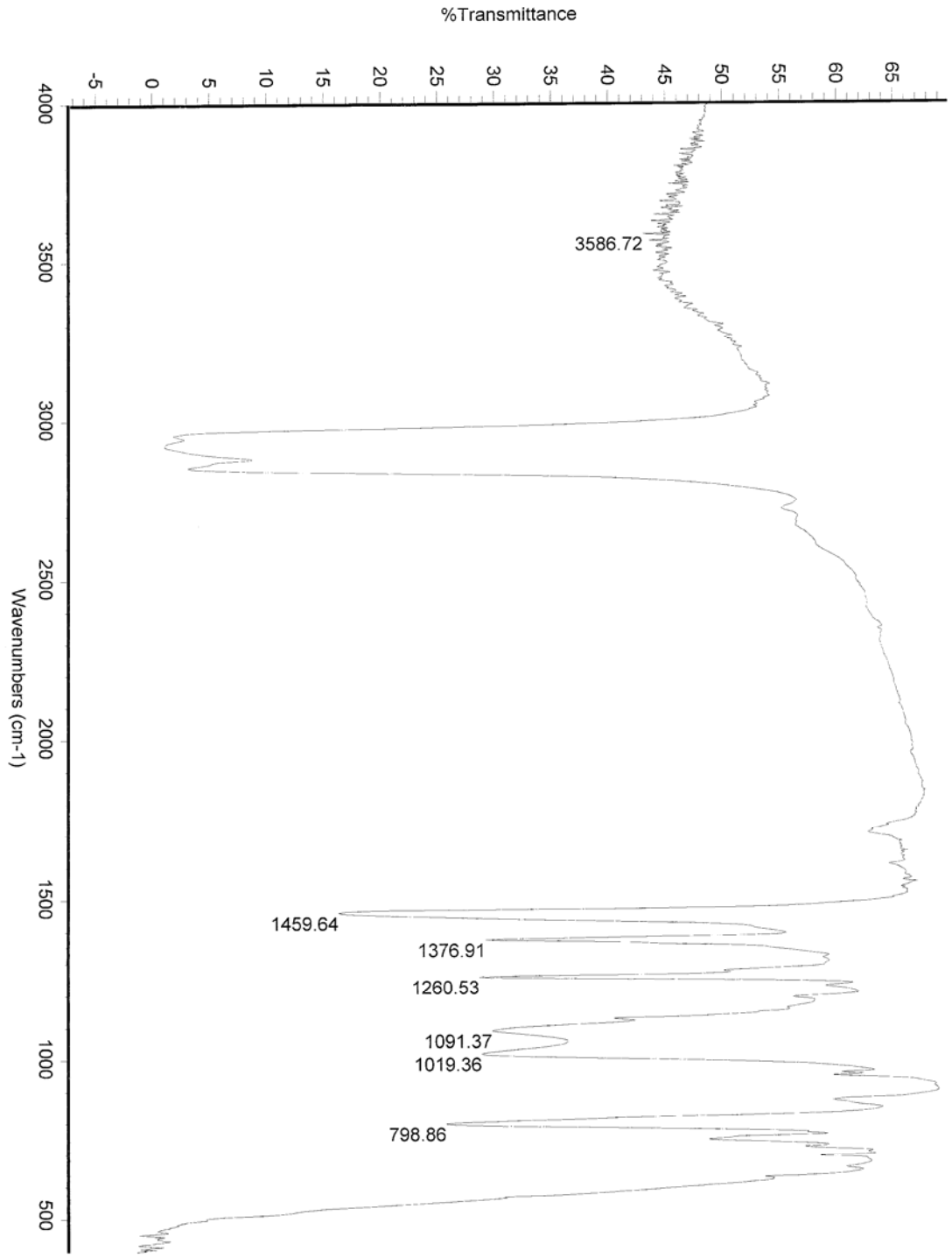
Sample MC-8 BSubPcCl



Sample MC-9 BSubPcCl

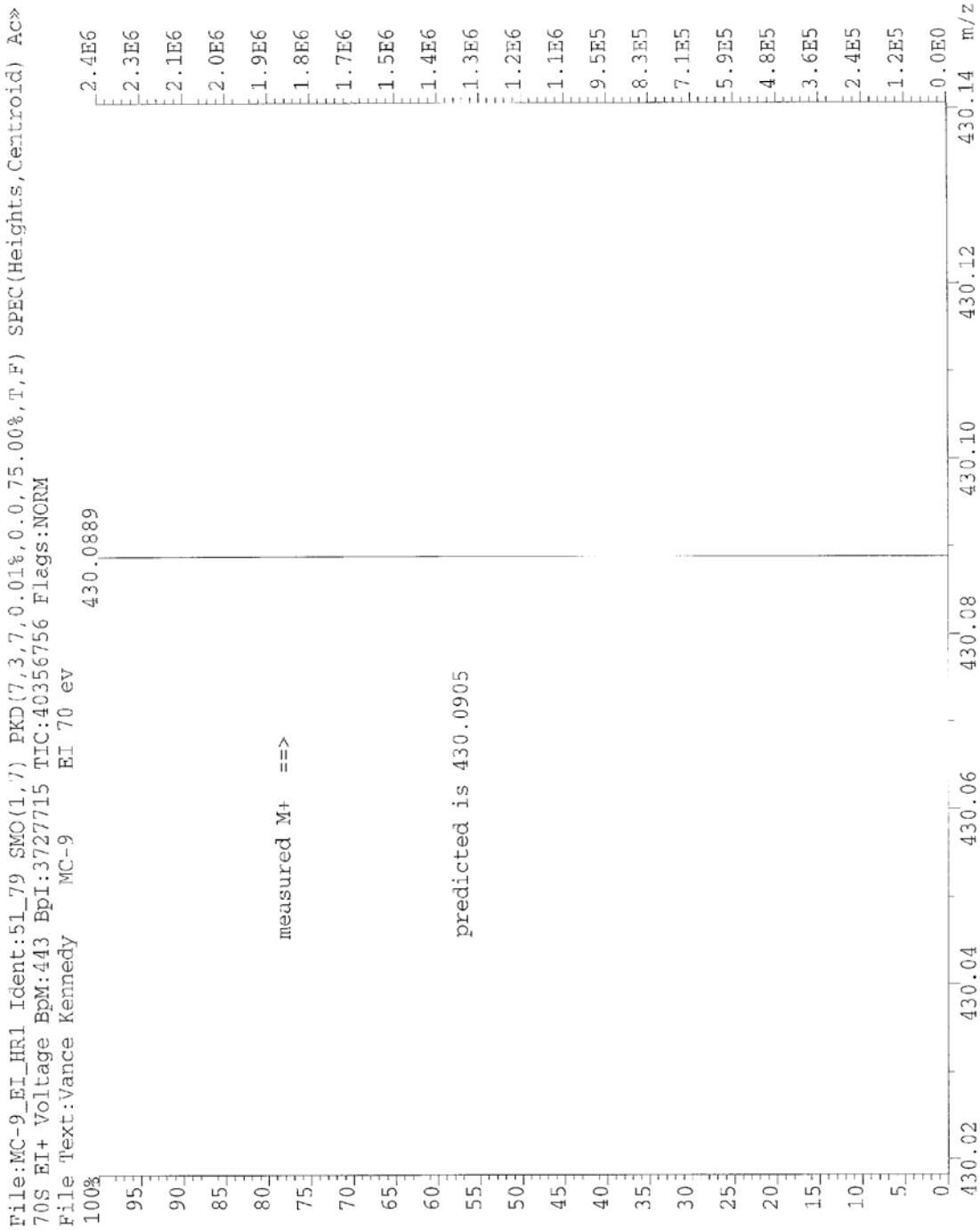


Infrared Spectrum of BSubPCOH.

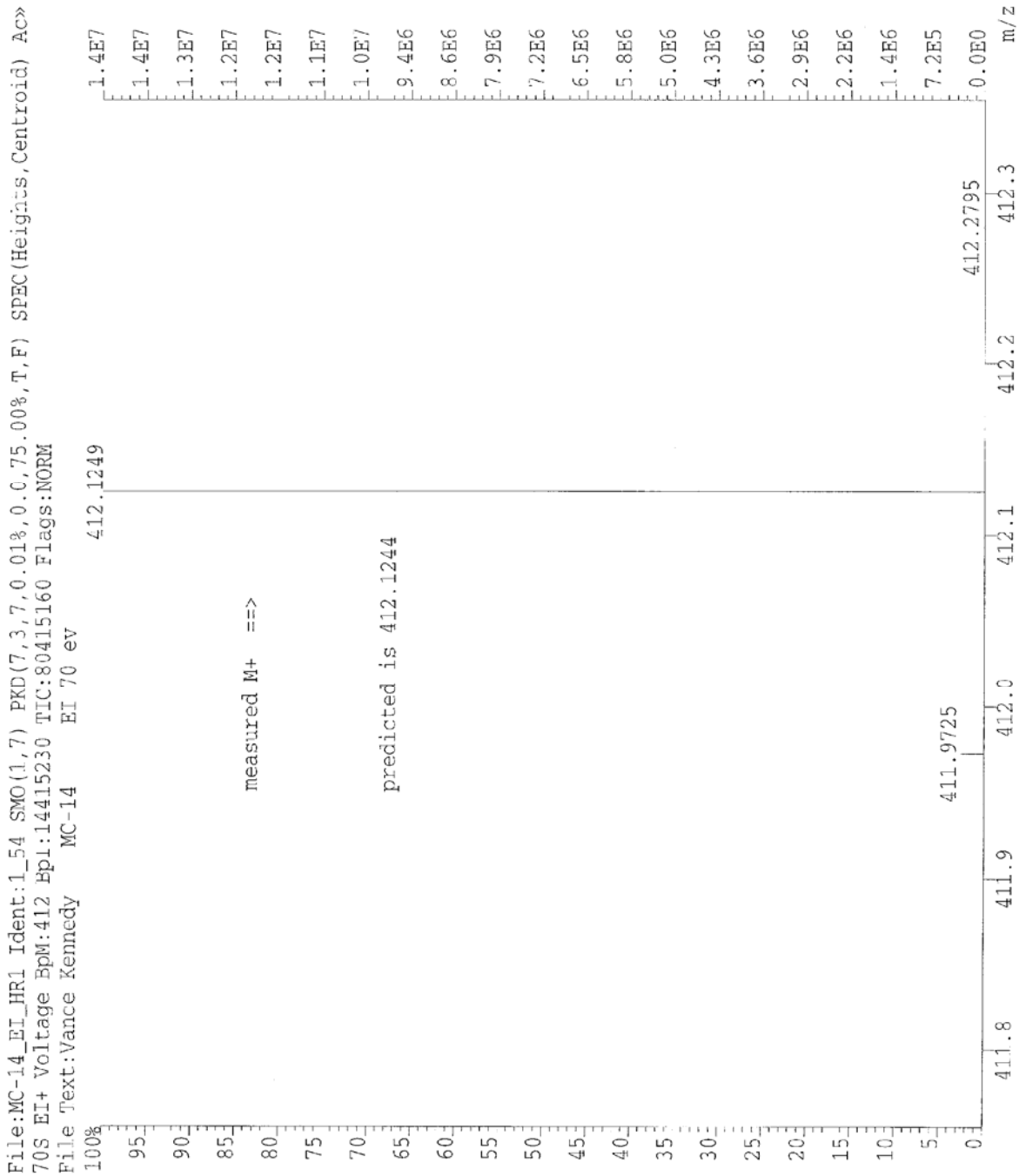


7.2 **Mass Spec Scans.**

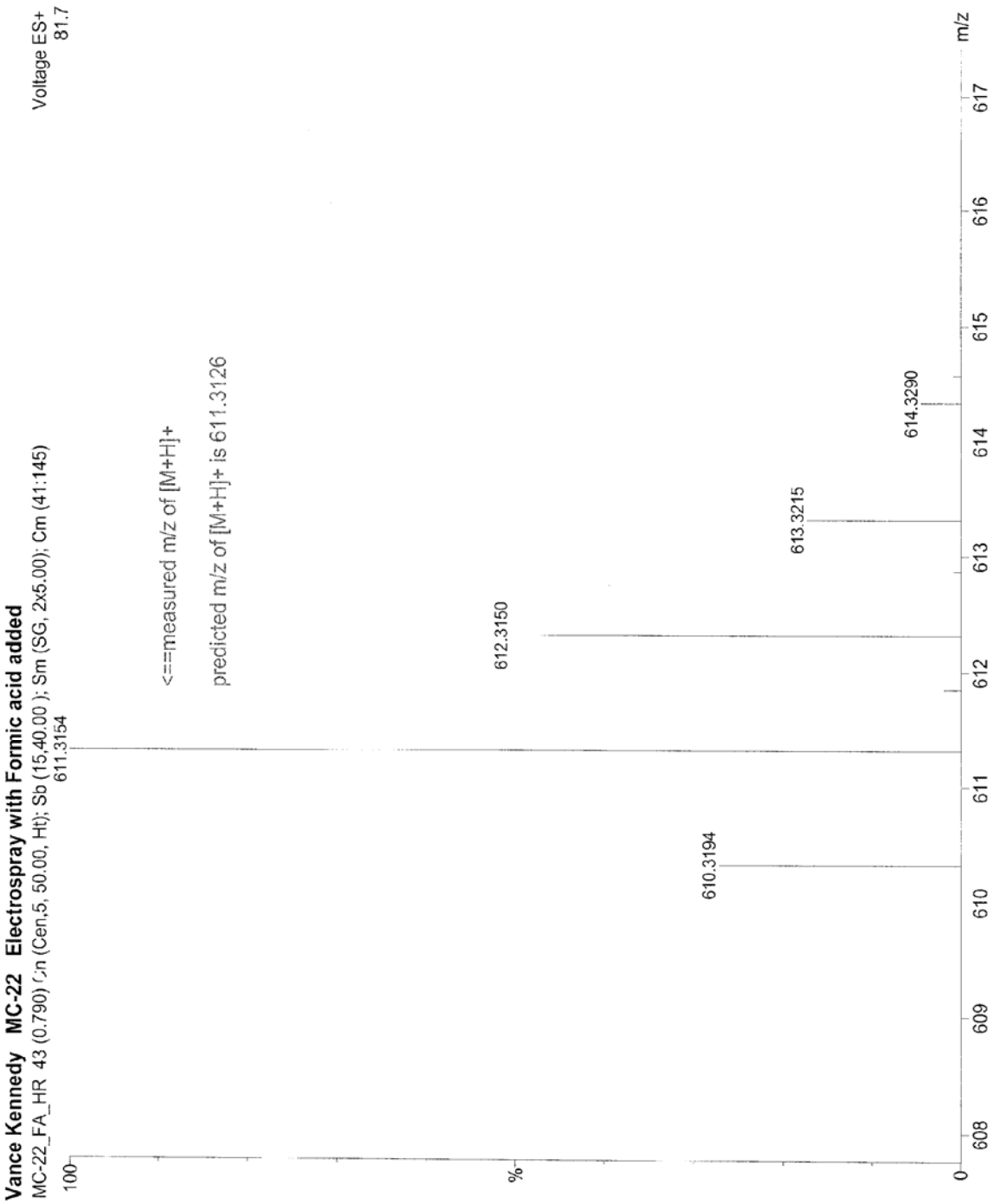
Sample MC-9 BSubPcCl



Mass Spec of BSubPcOH.

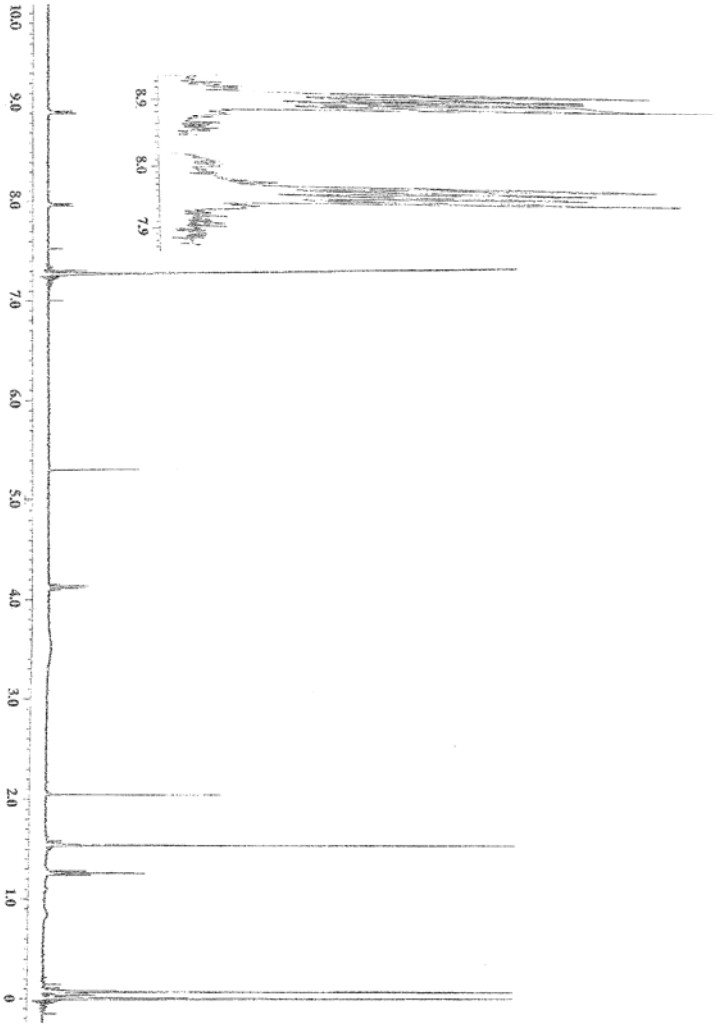


Mass Spec of BSubPcOSi(Bu)$_3$.

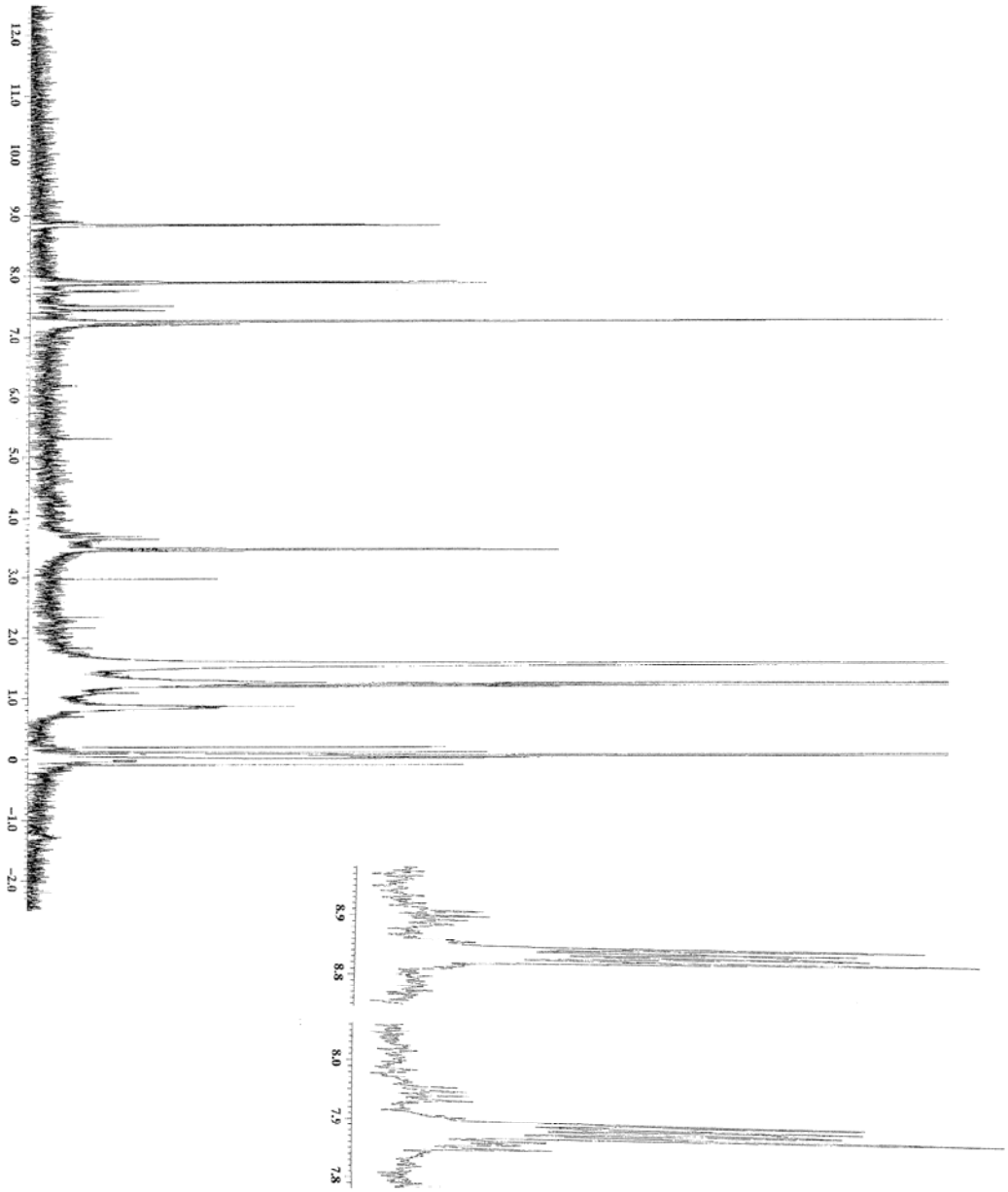


7.3 ^{1}H NMR Scans.

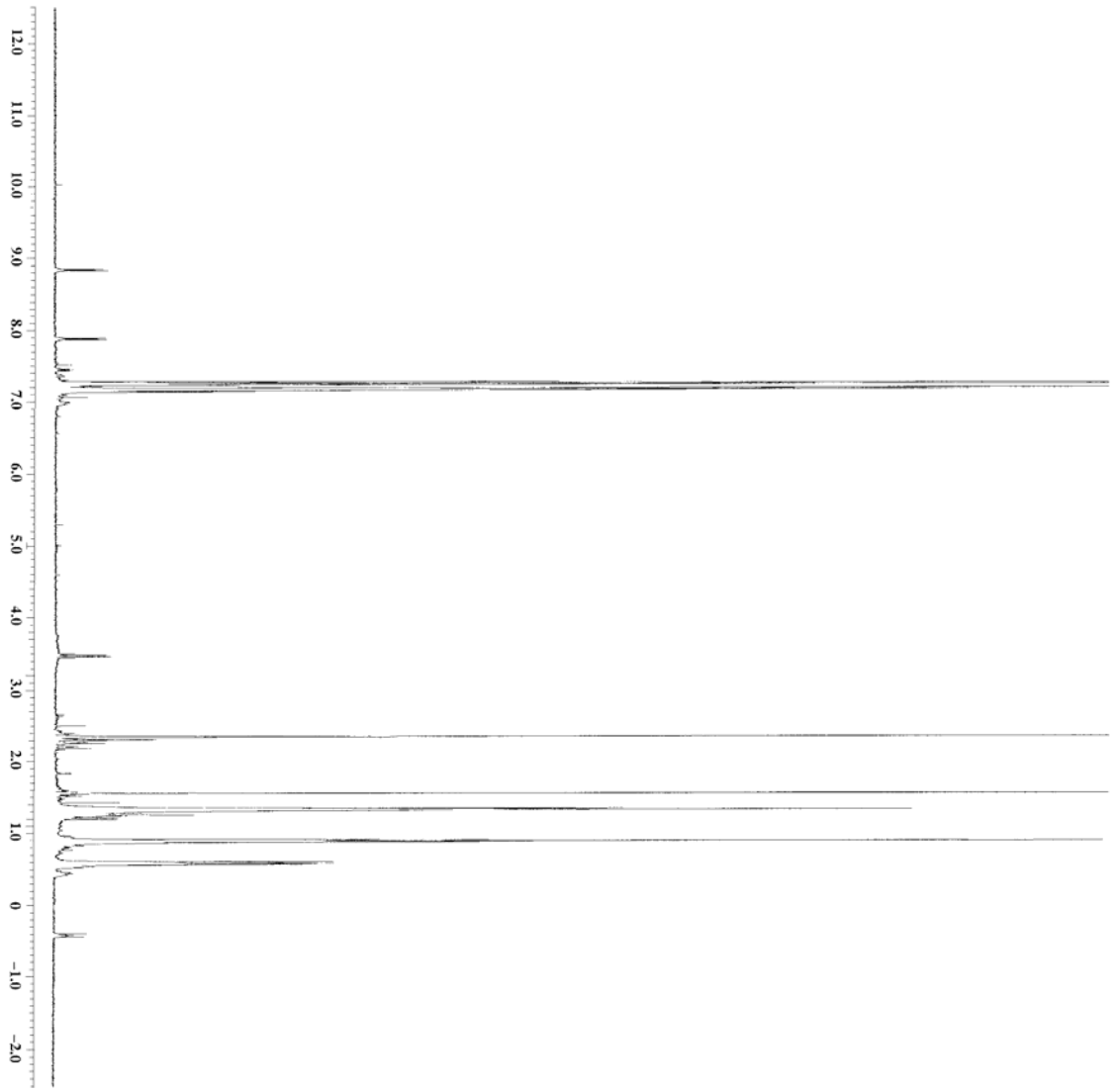
^{1}H NMR BSubPcCl



^{1}H NMR BSubPcOH



^{1}H NMR of BSubPcOSi(Bu)$_3$.



^{1}H NMR of BSubPcOSi(Hexyl)$_3$

CHAPTER 8: Conclusions

This study shows that several axial substituted subphthalocyanines can be successfully prepared and purified. Of particular importance is the preparation and structural confirmation of $BSubPcOSi(Bu)_3$, which has never been prepared. The synthesis of new SubPc compounds with different axial siloxy substituents are significant because reaction conditions used to synthesize them can yield good quantities in fewer steps.[12] Specifically, the method used to synthesize these compounds is novel. It involves a 1-step process where the axial substituted $R_3SiO(SubPc)B$ compounds were synthesized by axial substitution of a chloride with of trialkylsilanol (46% yield) instead of using the 2-step process where the hydroxyl SubPcB intermediate is prepared by substitution and is then silylated using trialkyl silanol (27.5% yield for 2-step).

The starting material in each of the reactions was the symmetrical BsubPc-Cl compound, and all of the reactions yielded successful symmetrical axial substitutions. These methods are valuable because many new compounds can be formed from the same starting material.

My results showed that SubPcOH could be made without peripheral addition to the ring in a 1-step process using heat, water, and pyridine. While I prepared a SubPcOH without peripheral groups, the percent yield (64%) was consistent with a prior synthesis where the peripheral groups were iodide (55%). The axial carbon substitution reaction was not successful using n-butyl lithium since the temperature formation of SubPc(Bu) is small (between $100^{o}C$ – $120^{o}C$) where decomposition begins at $120^{o}C$ resulting in low yields.[12] While an attempt to keep the temperature at $100^{o}C$ was made, the exact temperature was not carefully monitored. Thus product decomposition could have occurred.

More applications will continue on the use of subphthalocyanines in non-linear optics,

photodynamic tumor therapy for cancer, and semi-conductors. New compounds may yield different results with respect to increasing interest in tumor therapy and cancer treatments. The synthesis of new subphthalocyanines, like the one prepared in this study, will aid in that research. Finding alternate synthetic pathways and the preparation of SubPcs with central atoms different from boron remain a challenging task in the future.