The Attempted synthesis of novel BIS(quadridentate) niobium(IV) complexes and the analyses of the products resulting from the attempted synthesis of tetrakis (8-hydroxyquinolinato) niobium (IV)

John R. Pinkes

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THE ATTEMPTED SYNTHESIS OF NOVEL BIS(QUADRIDENTATE)NIOBium(IV) COMPLEXES AND THE ANALYSES OF THE PRODUCTS RESULTING FROM THE ATTEMPTED SYNTHESIS OF TETRAKIS(8-HYDROXYQUINOLINATO)NIOBium(IV)

BY

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THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

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THE ATTEMPTED SYNTHESIS OF NOVEL BIS(QUADRIDENTATE)NIOBium(IV) COMPLEXES AND THE ANALYSES OF THE PRODUCTS RESULTING FROM THE ATTEMPTED SYNTHESIS OF TETRAKIS(8-HYDROXYQUINOLINATO)NIOBium(IV)

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Date: 8/2/87
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Abstract

Four previously reported quadridentate ligands were synthesized, and the attempts made to synthesize the corresponding bis(quadridentate)niobium(IV) complexes are documented. Attempts made to synthesize the previously reported tetrakis(bidentate)niobium(IV) complexes of benzoyl trifluoroacetyleacetone (Nb(BTA)4)\textsuperscript{1} and of 8-hydroxyquinoline (Nb(8-Q)4)\textsuperscript{1} are also discussed. Though neither of the desired complexes was synthesized, the resulting complexes from the attempted synthesis of the Nb(8-Q)4 complex, and their subsequent analyses, are examined in detail. Along with the ligand syntheses and the attempted complexations, modifications in the experimental techniques and the apparatus are also discussed.

Table of Contents

Acknowledgements......................................................... i

Abstract........................................................................... ii

I. Introduction..................................................................... 1

II. Experimental................................................................. 3

A. Starting Materials for the Complexation Reactions........................................... 8

Niobium tetrachloride, NbCl₄............................................. 8

Tris(acetonitrile)tetrachloroniobium(IV), NbCl₄(NCMe)₃......................... 9

B. Syntheses of the Ligands.................................................. 11

1,2-Bis(2-aminophenoxy)ethane, H₂BAPE......................... 11

Bistrifluoroacetylacetone-ethylenediamine, H₂BTAE................ 12

N,N’-Bis(o-hydroxybenzyl)ethylenediamine, H₂BHBE............. 13

N,N’-Disalicylidene-1,2-phenylenediamine, H₂DSP................ 13

C. Attempted Syntheses of Bis(quadridentate)niobium(IV) Complexes............. 15

The Attempted Synthesis of Bis(1,2-Bis(2-aminophenoxy)ethanato)niobium(IV), Nb(BAPE)₂.

trial 1................................................................. 15

trial 2................................................................. 33

trial 3................................................................. 33
The Attempted Synthesis of Bis(N,N'‐Disalicylidene‐1,2‐phenylenediamino)niobium(IV), Nb(DSP)₂.

The Attempted Synthesis of Bis(Bistrifluoroacetylacetonato ethylenediamino)niobium(IV), Nb(BTAE)₂.

D. Attempted Syntheses of Tetrakis(bidentate)niobium(IV) Complexes..... 37

The Attempted Synthesis of Tetrakis(benzoyltrifluoroacetonato)nibium(IV), Nb(BTA)₄.

The Attempted Synthesis of Tetrakis(8‐hydroxyquinolinato)niobium(IV), Nb(8‐Q)₄.

iv
E. Analytical Methods Used to Characterize the yellow/green and purple compounds from the Attempted Synthesis of Nb(8-Q)₄

1. Pyrolysis
2. Thin Layer Chromatography (T.L.C.)
3. Sodium Fusion
4. Electron Spin Resonance (E.S.R.)
5. Infrared
6. ¹H N.M.R.
7. ¹³C N.M.R.
8. UV/visible
9. Elemental Analysis
10. Vapor Phase Osmometry (V.P.O.)
11. Crystal Growth
12. Analysis of the purple compound for HCl(g) Formation as the Sample Decomposes

III. Results and Discussion

A. Starting Materials
B. Ligand Syntheses
C. Attempted Syntheses of Bis(quadridentate)niobium(IV) Complexes
D. Attempted Syntheses of Tetrakis(bidentate)niobium(IV) Complexes
E. Analytical Methods Used to Characterize the yellow/green and purple compounds from the Attempted Synthesis of Nb(8-Q)₄

1. Pyrolysis
2. Thin Layer Chromatography (T.L.C.)........... 76
3. Sodium Fusion................................. 77
4. Electron Spin Resonance (E.S.R.)............... 77
5. Infrared........................................... 78
6. $^1$H N.M.R........................................ 80
7. $^{13}$C N.M.R...................................... 82
8. UV/visible........................................ 85
9. Elemental Analysis.............................. 89
10. Vapor Phase Osmometry (V.P.O.)............... 89
11. Crystal Growth.................................. 89
12. Analysis of the purple compound for HCl(g) Formation as the Sample Decomposes........ 91

F. Structural Hypotheses for the yellow/green and the purple compounds............... 91

IV. Conclusion...................................... 98

V. Appendix of Spectra................................ 100

VI. References...................................... 131
List of Abbreviations

BNPE 1,2-Bis(2-nitrophenoxy)ethane
DMF N,N-dimethylformamide
DMSO dimethyl sulfoxide
8-HQ 8-hydroxyquinoline
E.S.R. electron spin resonance
Et ethyl
H₂BAPE 1,2-Bis(2-aminophenoxy)ethane
H₂BHBE N,N′-Disalicylidene-1,2-phenylenediamine
HBTA 4,4,4-trifluoro-1-phenyl-1-butanedione or benzoyl trifluoroacetylacetone
H₂BTAE Bistrifluoroacetylacetone-ethylenediamine
H₂DSP N,N′-Disalicylidene-1,2-phenylenediamine
Me methyl
N.M.R. nuclear magnetic resonance
THF tetrahydrofuran
T.L.C thin layer chromatography
V.P.O. vapor phase osmometry
List of Figures

Figure 1. First glovebag system .............................................. 4
Figure 2. Improved glovebag system utilizing a hot copper trap......................... 5
Figure 3. Pyrex reaction tube apparatus used for synthesizing NbCl₄ ......................... 6
Figure 4. Apparatus used for filtration in the glovebag .................................. 10
Figure 5. Complexation apparatus used for the combination of reactants in the glovebag............................................... 17
Figure 6. System for complexation reactions, solvent removal, and product isolation .... 18
Figure 7. Complexation apparatus for the combination of reactants in the glovebag.. 19
Figure 8. An improved system for complexation reactions, solvent removal, and product isolation ........................................... 20
Figure 9. Apparatus used for the distillation of dry solvents into the complexation reaction flask .............................................. 21
Figure 10. Sealed addition funnel, into which dry hexane is distilled .................... 22
Figure 11. Apparatus for filtration and concentration of product solution .............. 23
Figure 12. Complexation reaction flask ......................................... 24
Figure 13. System for the removal of solvent while allowing the reaction mixture to reflux ... 25
Figure 14. Complete apparatus for filtration under nitrogen ............................. 26
Figure 15. Apparatus for the distillation of dry solvents into the reaction flask under nitrogen ................................................. 27
Figure 16. Reaction flask........................................... 28

Figure 17. Complete apparatus for the filtration and isolation of filtrate under nitrogen...... 29

Figure 18. Apparatus for the distillation of dry solvents into the reaction flask under nitrogen...................................................... 30

Figure 19. Complexation apparatus used for the combination of reactants and for the isolation of the product under nitrogen... 31

Figure 20. Micro soxhlet extractor used for dissolving NbCl4 in acetonitrile under nitrogen...... 32
List of Tables

Table 1. Summary of Apparatus Used for the Complexation Reactions.......................... 16

Table 2. A. Relevant Formulae for Magnetic Susceptibility Calculations...................... 58

B. Sample Calculation of the Number of Unpaired Electrons for NbCl₄(NCMe)₃ from a Magnetic Susceptibility Measurement... 58

Table 3. Infrared Stretching Frequencies (cm⁻¹) for the Ligands, KBr Pellets.................. 63

Table 4. Table of ¹H N.M.R. shifts (200 MHz) relative to TMS in CDCl₃...................... 64

Table 5. Comparison of the Infrared Stretching Frequencies (cm⁻¹) for 8-HQ, yellow/green, and purple compounds, KBr pellets.............. 79

Table 6. Table of ¹H N.M.R. shifts (200 MHz) for 8-HQ, the yellow/green compound and the purple compound in DMSO-d₆....................... 81

Table 7. ¹³C Spectra (25 MHz, 512 scans) of 8-HQ, the yellow/green compound, and the purple compound in CDCl₃............................... 83

Table 8. ¹³C Spectra (50 MHz, 9600 scans) of 8-HQ and the yellow/green compound in DMSO-d₆.... 84

Table 9. UV/visible Data for 8-HQ, yellow/green, and purple compounds in methylene chloride...... 87

Table 10. UV/vis spectra showing the decomposition of the purple compound (conc. = 0.4680 g/L) to the yellow/green compound in methylene chloride................................. 88

Table 11. Elemental Analyses of the yellow/green and the purple compounds..................... 90

Table 12. Calculated Percentages of the Elements in the Proposed Structure of the yellow/green
compound, with the Experimentally Determined Percentages in Parentheses...... 93
I. Introduction

The goal of this project was to synthesize, and later analyze, at least one of a new series of eight coordinate niobium(IV) complexes which utilizes a set of two quadridentate ligands. This synthesis was based upon data and theory of previously reported similar eight coordinate species. A series of eight coordinate tetrakis(bidentate)niobium(IV) complexes were reported in the early 1970's by Kepert and Deutscher. This coupled with the fact that similar bis(quadridentate)zirconium(IV) complexes have been previously been synthesized, points to the possibility of synthesizing similar niobium complexes. The major difference between the two species is the fact that the niobium complexes possess a single d electron, whereas the zirconium complexes have an empty d shell. The stereochemical preferences already displayed in the eight coordinate bidentate systems, along with predictions by Orgel's orbital overlap model, both suggest that a dodecahedral geometry would be prevalent in the bis(quadridentate)niobium(IV) complexes, with different donor atom site preferences as compared to zirconium. Also, with reference to the stabilities associated with some of the complexes in the bidentate systems, bulkiness of the ligands, as well as the electron withdrawing nature of fluorinated substituents has been taken into account in
the selection of appropriate quadridentate ligands.

With all of this in mind, the efforts of this project have been focused on the synthesis of these novel complexes by employing and modifying the procedures reported in the Kepert and Deutscher paper in which the eight coordinate tetrakis(bidentate)niobium(IV) complexes (analogous to the tetrakis(bidenatate)zirconium(IV) complexes\(^4\)) were first synthesized. A number of quadridentate ligands with nitrogen and oxygen donor atoms have been synthesized and used in attempts to synthesize the desired niobium complexes. The purpose of this paper is to report on the results of these ligand syntheses and attempted complexation reactions.
II. Experimental

The procedures for the syntheses of the ligands and the starting materials for the complexations were previously published. The reagents used to synthesize the ligands, as well as the 4,4,4-trifluoro-1-phenylbutanedione (HBTA) and 8-hydroxyquinoline (8-HQ) ligands, and the reagents used to synthesize the niobium starting materials (NbCl4 and NbCl4(NCMe)3) for the complexation reactions were obtained from Aldrich Chemical Company. All melting points were determined with a Mel-Temp apparatus, and are uncorrected. The actual complexation reactions were carried out, and modified, according to the procedures prescribed by Kepert and Deutscher. The combination of reagents for both the synthesis of the niobium starting materials and the complexation reactions was done in an Aldrich Atmosbag (glovebag, Figures 1 and 2). The synthesis of NbCl4(NCMe)3 and the actual complexation reactions were done under a nitrogen stream in a closed glassware system. Nitrogen flow through the various systems was monitored with a silicone oil bubbler. The vacuum tube reaction to prepare NbCl4 was done in pyrex reaction tubes (Fig.3) obtained from Blaessig glass and carried out in a Lindberg tube furnace (approximately 50 of these reactions were done). Infrared and UV/visible spectra were carried out on Perkin-Elmer 681 infrared and
Figure 1. First glovebag system.
Figure 2. Improved glovebag system utilizing a hot copper trap.
Figure 3. Pyrex reaction tube apparatus used for synthesizing NbCl₄.
552A UV/visible instruments, respectively. For the UV/visible spectra, a matched set of 1 cm quartz cuvettes was used. $^1$H N.M.R. spectra were carried out on Perkin-Elmer R-600 and Nicolet NT-200 instruments by Brian Cleary, and on a Bruker WP-200 instrument by Dr. L. Paul Rosenberg at Fisons. $^{13}$C N.M.R. spectra were obtained on Bruker WP-100 (25 MHz) and WP-200 (50 MHz) instruments by Dr. James Boiani (at S.U.C. Geneseo) and Dr. L. Paul Rosenberg (at Fisons), respectively. The E.S.R. spectrum of NbCl₄ in acetonitrile was carried out on a 200 MHz low field instrument, built by Dr. Joseph Hornak. Thin layer chromatography (T.L.C.) was carried out on silica and alumina plates (from Kodak), cellulose plates (from EM Science), and on reversed phase plates (from VWR), with the eluting and spotting solvents (chloroform, methylene chloride, THF, DMF, DMSO, ethyl ether, and hexane) being obtained from JT Baker. Elemental analyses of compounds were carried out at 1000°C by Microlytics. Vapor phase osmometry was attempted on a Wescan model 233 molecular weight apparatus. A Johnson Matthey magnetic susceptibility balance was used to check the complexes for the desired paramagnetism, with a positive value indicating the presence of unpaired electrons in the sample. The sensitivity of the balance was confirmed experimentally by making and testing a series of percent by weight mixtures of paramagnetic CrCl₃ in sand, which is diamagnetic. It
was determined that the lower limit for detecting the presence of a paramagnetic substance is approximately 5% by weight (paramagnetic to diamagnetic).

A. Starting Materials for the Complexation Reactions

**Niobium tetrachloride, NbCl₄.** Niobium tetrachloride was synthesized by a vacuum tube reaction of niobium metal and NbCl₅. A pyrex reaction tube was flamed out (heated by an oxygen/natural gas flame), under vacuum, to remove any oxygen and moisture from the tube, and kept evacuated. Next, approximately 0.5 g of niobium metal and 5.0 g of niobium pentachloride were carefully weighed out and combined in the pyrex reaction tube under nitrogen in the glovebag. The system sealed with a rubber hose connected to a two way stopcock (Fig.3) was then removed from the glovebag, attached to a vacuum pump, and the pyrex reaction tube was sealed with a torch under vacuum. The sealed tube was then placed in the tube furnace for a period of seven days at a temperature of 300°C. On the final day of the reaction, the tapered end of the tube was moved to the open (cool) end of the furnace to ensure that any unreacted (volatile) materials would be attracted to that end, leaving the pure product. The resulting niobium tetrachloride appeared as fine, needle-like dark brown crystals (as reported).
Tris(acetonitrile)tetrachloroniobium(IV), \( \text{NbCl}_4(\text{NCMe})_3 \). For this preparation, acetonitrile was dried at reflux over (activated) molecular sieves (5 angstrom) overnight, followed by distillation. A hot copper trap (150°C) was used in conjunction to a CaCl₂ trap in the purification of nitrogen for use in the glovebag and the general reaction itself (Fig. 2). In the glovebag, niobium pentachloride (2.4 g, 8.8 mmol) was added to a suspension of aluminum powder (0.08 g, 2.98 mmol) in 20 ml of acetonitrile. The flask with the reactants was removed from the glovebag and stirred for four hours under nitrogen to ensure a complete reaction. The reaction yielded a dark brown/orange solution (\( \text{NbCl}_4(\text{NCMe})_3 \)), with a gray/brown solid (AlCl₃). The desired brown solution product was then obtained by filtering off the solid with a coarse frit filter in the glovebag (Fig. 4). In order to make sure that the reaction yielded the proper product (\( \text{NbCl}_4(\text{NCMe})_3 \)), the product solution was taken off under vacuum, yielding a dark brown solid. A magnetic susceptibility determination was made on a sample of the product, by adding the brown solid into a preweighed sample tube (under nitrogen, up to the line on the tube, and sealing the tube with parafilm), weighing the tube (to obtain the sample weight), inserting the tube into the balance, and recording the sample reading. A positive value was obtained from the measurement, indicating that the sample was paramagnetic.
Figure 4. Apparatus used for filtration in the glovebag.
B. Syntheses of the Ligands

1,2-Bis(2-aminophenoxy)ethane, H₂BAPE.

Dimethylformamide (DMF) was dried over activated molecular sieves at reflux overnight and distilled by vacuum distillation. The starting material 2-nitrophenol was dried overnight in a desiccator over phosphorus pentoxide and CaCl₂. The reaction proceeds in two major steps, the first being the synthesis of 1,2-Bis(2-nitrophenoxy)ethane, BNPE, which is then reduced with Zn to give H₂BAPE. A solution of 2-nitrophenol (27.8 g, 0.20 mol) in 100 ml of dry DMF was added over a period of 45 minutes to a vigorously stirred suspension of NaH (4.8 g, 0.20 mol) in 100 ml of dry DMF under nitrogen. The resulting deep orange/red mixture was stirred for 4 hours to ensure complete reaction, after which 1,2-dichloroethane (7.9 ml, 0.10 mol) was added, and the mixture was heated at reflux for 6 hours. The reaction mixture was cooled to room temperature and poured into 1 liter of ice-cold water. The resulting off-white product was suction filtered and washed successively with 2M NaOH (3x50 ml), water (5x100 ml), 95% ethanol (5x100 ml) and diethylether (3x100 ml). The yield of the off-white BNPE product was 14 g (45%); mp 164-166°C (lit.mp 169-170°C). The H₂BAPE ligand was prepared by the addition of Zn dust (164 g, 2.5 mol) to the mechanically stirred suspension of BNPE (13 g, 42.7 mmol)
in 78% ethanol/water (600 ml). A solution of CaCl₂ (6.0 g) in 10 ml of water was then added to the blue/gray suspension, and the mixture was allowed to reflux for three hours. The suspension was filtered through a glass fritted filter funnel, packed with a 3-cm layer of celite topped with a layer of glass wool, to give a yellow filtrate. The resulting gray sludge was washed with 100 ml of boiling 78% ethanol. The filtrate was cooled to room temperature and poured into 2 liters of cold water. The pearly white product was filtered off, washed twice with 50 ml of water, and dried over suction overnight. The yield was 6.88 g (66%); mp 126-128°C (lit.mp 130-132°C).  

**Bis(trifluoroacetylacetone)ethylenediimine, H₂BTAE**. Ethylenediamine was dried over molecular sieves at reflux overnight and distilled. First, ethylenediamine (2.14 ml, 0.033 mol) and 1,1,1-trifluoro-2,4-pentanedione (7.8 ml, 0.65 mol) were each cooled to 0°C on an ice bath. The ethylenediamine was then added dropwise to the 1,1,1-trifluoro-2,4-pentanedione, resulting in the immediate formation of the white product (with an orange supernatent liquid), H₂BTAE, via an exothermic reaction. The resulting product was then recrystallized five times with benzene to yield fluffy white crystals 5.0 g (50%); mp 151-154°C (lit.mp 157°C).
**N,N'-Bis(o-hydroxybenzyl)ethylenediamine, H₂BHBE**

The first step in this reaction is to synthesize bis(salicylaldehyde)ethylenediamine, H₂DSEN, by a standard Schiff base procedure. To a stirred suspension of ethylenediamine (3.47 ml, 0.053 mol), salicylaldehyde (12.5 ml, 0.108 mol) was added. The reaction immediately yielded the desired product as bright yellow crystals. The mixture was then allowed to reflux for 3 hours, cooled, and the yellow crystals were separated by suction filtration. The resulting product, H₂DSEN, was washed with absolute ethanol yielding a yellow needle-like product 12.94 g (93%); mp 121-125°C (lit.mp 125-126°C). Next, the H₂DSEN (5.4 g, 0.02 mol) was dissolved in 100 ml of absolute ethanol. To this solution, 0.5 g of 10% Pd-C catalyst was added, and the mixture was hydrogenated for five hours at 14 psi. The resulting solution was then filtered, to remove the catalyst, to give a light green solution, which was then concentrated using a rotary evaporator, to remove the ethanol. After recrystallization with an ethanol/petroleum ether solvent pair, the white H₂BHBE product was obtained in a yield of 3.0 g (56%); mp 122-124°C, (lit.mp 124°C).

**N,N'-Disalicylidene-1,2-phenylenediamine, H₂DSP**

To a stirred suspension of 1,2-phenylenediamine (8.0 g, 0.104 mol) in 250 ml of absolute ethanol, salicylaldehyde (12.5
ml, 0.108 mol) was added. The light orange mixture was allowed to reflux overnight (16 hours) and was isolated to yield bright orange crystals of H₂DSP, 16.4 g (66%); mp 164-165°C (lit. mp 167°C).²
C. Attempted Syntheses of Bis(quadridenate)niobium(IV) Complexes

This section and the following section (D. Attempted Syntheses of Tetrakis(bidentate)niobium(IV) complexes) serve as a summary of how the complexation reactions were carried out. The niobium complex which was proposed to be synthesized is given first, followed by the trials of the same or a similar reaction. Accompanying all of the attempted reactions and trials is an Apparatus Sequence of Figures (see Table 1 and Figures 1-20) employed, which give a pictorial representation of the apparatus used in each attempted synthesis.

The Attempted Synthesis of Bis(1,2-Bis(2-aminophenoxy)ethanato)niobium(IV), Nb(BAPE)$_2$. Trial 1. using the Apparatus Sequence of Figures 1, 5, 6. The solvents (acetonitrile, benzene, and triethylamine) were dried by allowing to reflux over molecular sieves (5 angstrom) overnight and followed by distillation. A suspension of NbCl$_4$ (1.12 g, 4.8 mmol) and 3 ml of triethylamine in 100 ml of acetonitrile and a solution of H$_2$BAPE (2.40 g, 9.8 mmol) in 100 ml of acetonitrile were placed in the glovebag (Fig.1). The two portions were combined in the system (Fig.5) to give a slightly green solution. The system was removed from the glovebag and heated at reflux for 20 minutes under a nitrogen stream.
<table>
<thead>
<tr>
<th>Attempted Complexation With Ligand Used and Trial #.</th>
<th>Apparatus Sequence of Figures</th>
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<tbody>
<tr>
<td>H₂BAPE-1; H₂DSP</td>
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</tr>
<tr>
<td>H₂BAPE-2</td>
<td>1,4,5,6</td>
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<td>H₂BAPE-3,4; H₂BTAE-1; HBTA-1,2</td>
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<td>H₂BTAE-2ᵃ; HBTA-3,4</td>
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<tr>
<td>8-HQ-4</td>
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</tr>
</tbody>
</table>

ᵃFor these trials NbCl₄(NCMe)₃ was used in place of NbCl₄ as a starting material.
Figure 5. Complexation apparatus used for the combination of reactants in the glovebag.
Figure 6. System for complexation reactions, solvent removal, and product isolation.
Figure 7. Complexation apparatus for the combination of reactants in the glovebag.
Figure 8. An improved system for complexation reactions, solvent removal, and product isolation.
Figure 9. Apparatus used for the distillation of dry solvents into the complexation reaction flask.
Figure 10. Sealed addition funnel, into which dry hexane is distilled.
Figure 11. Apparatus for filtration and concentration of product solution.
Figure 12. Complexation reaction flask.
Figure 13. System for the removal of solvent while allowing the reaction mixture to reflux.
Figure 14. Complete apparatus for filtration under nitrogen.
Figure 15. Apparatus for the distillation of dry solvents into the reaction flask under nitrogen.
Figure 16. Reaction flask.
Figure 17. Complete apparatus for the filtration and isolation of filtrate under nitrogen.
Figure 18. Apparatus for the distillation of dry solvents into the reaction flask under nitrogen.
Figure 19. Complexation apparatus used for the combination of reactants and for the isolation of the product under nitrogen.
Figure 20. Micro soxhlet extractor used for dissolving NbCl4 in acetonitrile under nitrogen.
(Fig. 6) to give a light green suspension which eventually turned completely white. The solvent was removed under vacuum to give a dark tan product, which upon washing with benzene yielded a light brown solid that tested diamagnetic (negative value obtained from the magnetic susceptibility).

**Trial 2. using the Apparatus Sequence of Figures 1.4.5.6.** The solvents were dried in the previous manner, but were then purged with nitrogen for 15 minutes. The H2BAPE, was recrystallized twice with a chloroform/petroleum ether solvent pair before use in the complexation reaction. The total volume of acetonitrile was reduced to approximately 60 ml, and all of the reactants were combined at once in the system. The rest of the procedure was followed as before. Upon thorough mixing of the reactants, the white/brown suspension was allowed to reflux for 5 minutes (with stirring) to give a green/brown suspension. The suspension was cooled to room temperature and the solvent was removed under vacuum to give a gold solid. In the glovebag, the solid was washed with benzene and suction filtered (Fig. 4) to yield a dark brown product. The vacuum dried product tested diamagnetic.

**Trial 3. using the Apparatus Sequence of Figures 1.4.7.8.** The procedure used was identical to the previous procedure, but with a 2 minute, instead of a 5 minute
reflux time, the omission of the benzene washing, and the use of a slightly different apparatus (Fig. 7). The reactants were combined to give a green/brown suspension which was then refluxed, cooled, and the solvent was removed under vacuum to give a light green solid. The solid was vacuum dried overnight to yield a light brown product gave a negative value from the magnetic susceptibility balance, indicating that it was diamagnetic.

**Trial 4, using the Apparatus Sequence of Figures 1.4.7.8.** The procedure used was identical to the previous procedure, but with the omission of any heating and the immediate isolation of the product. The reactants were combined and mixed as previously to give a light brown suspension, which was then stirred for 15 minutes to give a white solid. The white solid was isolated by filtration (as described before) in the glovebag, and tested to be diamagnetic (a negative value was obtained from the magnetic susceptibility balance).

**The Attempted Synthesis of Bis(N,N'-Disalicylidene-1,2-phenylenediamino)niobium(IV), Nb(DSP)2.** **Trial 1, using the Apparatus Sequence of Figures 1.5.6.** The procedure used was very similar to the third trial of the H2BAPE complexation (Figs. 5 and 6), with some modifications. In the glovebag, a mixture of NbCl₄ (0.68 g, 2.9 mmol), H₂DSP
(1.80 g, 5.8 mmol), and 3 ml of triethylamine was made in approximately 80 ml acetonitrile (see Figs. 5 and 6 for system used). The dark brown suspension was heated at reflux for 5 minutes, and cooled to room temperature to give a coffee colored suspension, with a green tinge on the surface of the liquid. The dark brown solution was then vacuum filtered off, using a small glass frit attachment (Fig. 5), leaving behind a dark brown solid, which after being vacuum dried tested to be diamagnetic (as indicated by the negative value obtained from the magnetic susceptibility balance).

The Attempted Synthesis of Bis(Bistrifluoroacetylacetone-ethylenediimino)niobium(IV), Nb(BTAE)2. Trial 1, using the Apparatus Sequence of Figures 1, 4, 7, 8. The solvents (hexane, toluene, and triethylamine) were dried at reflux over activated molecular sieves (5 angstrom), followed by distillation. In the glovebag (Fig. 1), a slurry of NbCl4 (0.4 g, 1.7 mmol) and 4 ml of triethylamine in 60 ml of toluene, along with a solution of H2BTAE (1.13 g, 3.4 mmol) in 40 ml of toluene, were made, and then combined. The system (Fig. 7) was then removed from the glovebag and then allowed to reflux (under nitrogen, with stirring, Fig. 8) for 5 minutes giving a light green solution, with solid on the bottom. The solid was filtered off in the glovebag as previously
(Fig. 4), the filtrate was then concentrated under vacuum, and hexane was added by a separatory funnel (Fig. 8) to precipitate a white, diamagnetic solid.

**Trial 2, using the Apparatus Sequence of Figures 2, 4, 7, 8.** The solvents were prepared in the previous manner (see trial 1), but following their distillation were deaerated with nitrogen for 15 minutes. A hot (150°C) copper trap (for oxygen removal) was also connected in series (after the nitrogen tank) with the CaCl₂ trap for both the glovebag and the outside nitrogen line (Fig. 2). Lastly, NbCl₄(NCMe)₃ was substituted for NbCl₄, as a starting material. The procedure was otherwise unchanged from the previous procedure. The system (Fig. 7) containing the resulting dark brown solution was removed from the glovebag and heated at reflux as previously (Fig. 8). The reaction mixture was then allowed to cool down to room temperature, followed by the removal of the solvent under vacuum, and yielding a dark brown solid which was determined to be paramagnetic (positive test).

Trial 2 was repeated twice, under the same conditions as before, but with neither of the attempted syntheses yielding a paramagnetic product. The dark brown diamagnetic product which was isolated, decomposed overnight to a white compound.
D. Attempted Syntheses of Tetrakis(bidentate)niobium(IV) Complexes

The Attempted Synthesis of Tetrakis(benzoyltrifluoroacetonato)niobium(IV), Nb(BTA)$_4$.

Trial 1, using the Apparatus Sequence of Figures 1,4,7,8.

This is a previously reported complex, whose attempted complexation was done according to the procedure by Kepert and Deutscher$^1$. The ligand used for the attempted complexation, benzoyltrifluoroacetylacetone:

\[
\text{HBTA}
\]

is commercially available. The solvents (toluene, triethylamine, and hexane) were dried at reflux over activated molecular sieves (5 angstrom) overnight, followed by distillation. In the glovebag (Fig.1), a slurry of NbCl$_4$ (0.72 g, 3.1 mmol) and triethylamine (4 ml) in 100 ml of toluene was made, along with a solution of HBTA (2.80 g, 13.8 mmol) in 100 ml of toluene. The two components were then combined and the system (Fig.7) was removed from the glovebag and attached to a nitrogen line. The mixture was then heated at reflux (Fig.8) for 5 minutes (with stirring) to give an olive green solution, which was then allowed to cool to room temperature. The system was then placed in
the glovebag, and filtered with a glass frit (as done previously, Fig.4) to remove any unreacted starting materials and/or biproducts. The filtrate was concentrated under vacuum, and hexane was added (via a separatory funnel, Fig.8) resulting in the precipitation of a brown solid. The solid which was isolated by filtration in the glovebag was found to be diamagnetic (negative value) by a magnetic susceptibility measurement.

**Trial 2. using the Apparatus Sequence of Figures 1,4,7,8.** The solvents were dried overnight at reflux over sodium (toluene), calcium hydride (triethylamine), and lithium aluminum hydride (hexane) overnight, followed by distillation. The reaction was conducted under the identical circumstances as trial 1. The reactants were combined to give a mixture with a green tinge. Upon heating at reflux for 5 minutes, the solution turned olive green with some solid on the bottom of the flask. The solution was filtered off and concentrated as before to give an olive green solution. Addition of hexane resulted in a green oil formation and no solid product. The green oil was refrigerated in hexane overnight, and decomposed to brown by the following morning.

Trial 2 was repeated, showing that the results were reproducible.
**Trial 3, using the Apparatus Sequence of Figures 2.4.7.8.** A hot copper trap was added to purify the nitrogen system (this was described previously in the second trial of the attempted complexation of BTAE, see Fig.2). The procedure was repeated exactly as before. The reactants were mixed in the glovebag (mixture with a green tinge), the system was removed, heated at reflux for 5 minutes (olive green solution with solid), and allowed to cool to room temperature. The mixture was then filtered and concentrated as before (green concentrate). This was followed by the addition of hexane, which resulted in the precipitation of a brown solid. The solid was isolated by filtration and it tested to be diamagnetic.

Trial 3 was repeated, and the observations were the same as the previous sequence of reactions, but the solid that was eventually isolated was a light yellow precipitate which tested to be diamagnetic.

Trial 3 was repeated a second time, and the observations were consistent with those for the two previous trials, with the only difference being that the solid that was isolated was brown (as in first run of trial 3), but it was also diamagnetic.
Trial 4, using the Apparatus Sequence of Figures 2.4.7.8. The glassware was rinsed with the dry solvents prior to its use and the addition of hexane (to precipitate the product) was accomplished in the glovebag, after the filtration. Aside from the modifications, the reaction was conducted exactly like the third trial. The reactants were combined in the glovebag (Fig.2) to give a transparent green mixture, followed by heating at reflux for 5 minutes (intense olive green colored solution with solid), and allowing to cool to room temperature. The mixture was filtered as before to give a dark green filtrate, which was concentrated under vacuum to give a dark green concentrate. Upon addition of hexane to the concentrate, a light brown precipitate was formed and isolated by filtration in the glovebag. The light brown solid was tested to be diamagnetic.

Trial 5, using the Apparatus Sequence of Figures 2.9.10.11.12. A new set-up for the apparatus was incorporated (Figs.9-12) for this reaction. The solvents were dried as before but, the solvents (primarily toluene and triethylamine) were distilled (under a nitrogen stream) into the flamed out reaction flask (Fig.9). Hexane was also distilled in a flamed out separatory funnel under a nitrogen stream at the necessary time (Fig.10). The amount of toluene used was decreased to a total volume of 100 ml.
and the need for filtration in the glovebag was eliminated with the inception of the new apparatus (Fig.11). The same procedure as used in the previous reactions (trials 1-4) was again employed. In the glovebag (Fig.2), the NbCl₄, HBTA, triethylamine, and toluene were combined in the reaction flask (Fig.12) to immediately give an olive green solution upon mixing. The system was removed from the glovebag, the mixture was heated at reflux for 5 minutes (under nitrogen) giving an even darker green solution, which was allowed to cool to room temperature. The green mixture was then transferred to the second system (Fig.11) where it was filtered through the double filter (to remove any solids) in the system under a nitrogen stream and into the second vessel in the apparatus. The green filtrate was then concentrated by bubbling nitrogen through the small coarse frit filter adaptor (Fig.11) for a period of about 2 days. At this point, the hexane was added with an addition funnel to the system (Fig.10A to Fig.11A), which resulted in a brown precipitate. The brown solid was then filtered through the double filter and dried under nitrogen. The brown solid tested to be diamagnetic.

**Trial 6. using the Apparatus Sequence of Figures 2,9,10,11,12,13.** Benzene was substituted for toluene and during the reflux, additional benzene was attempted to be removed (Fig.13). The procedure was otherwise unchanged from the previous one. In the glovebag (Fig.2), the
reactants were combined in the first system (Fig. 12) to give a dark green mixture. The reaction flask was then attached to a second system (Fig. 13, to facilitate benzene removal during the reflux), heated at reflux for 5 minutes (more intense green mixture), and then allowed to cool to room temperature. The dark green mixture was then transferred to the second system as before (Fig. 11), and filtered through the double filter to give a dark green filtrate. The filtrate was concentrated as before by bubbling nitrogen through the small coarse frit filter adaptor. The freshly distilled dry hexane was then added to the green concentrate to precipitate a light green solid. The solid was isolated as before and tested to be diamagnetic.

**Trial 7. using the Apparatus Sequence of Figures 2, 9, 12, 14.** The procedure used was similar to that used in trial 6, however, the apparatus was modified, and also, benzene was removed under vacuum in the glovebag. The solvents were dried and distilled (Fig. 9) as before. In the glovebag (Fig. 2), the reactants were combined in the reaction flask (Fig. 12), to give a dark green mixture. The mixture was heated at reflux for 5 minutes (a more intense green mixture) and allowed to cool to room temperature. The dark green mixture was then filtered (Fig. 14), to give a dark green solution. The filtrate was concentrated under
vacuum in the glovebag (about 4 hours) to give about 25 ml of a dark green oil. Upon addition of dry hexane to the oil, a slight green color was imparted to the solvent, with no solid precipitate forming from the oil.

**Trial 8, using the Apparatus Sequence of Figures 2, 9, 12, 14.** This trial was identical to trial 7, with the only difference being that the solvent system was switched (back) from benzene to toluene. The observations and results obtained were the same as those in trial 7, with a green oil being formed, from which no solid was precipitated.

**Trial 9, using the Apparatus Sequence of Figures 2, 15, 16, 17.** This procedure was very similar to the previous one (trial 8), with some modifications, and also a new system of apparatus being used. The solvents (toluene, triethylamine, and hexane) were dried as previously, however, the distillation apparatus was slightly modified (Fig.15) so that a positive pressure of nitrogen (monitored by a silicone oil bubbler) was always present on the system during the distillation. In the glovebag (Fig.2), the reactants were combined in the same fashion as before in the reaction flask (Fig.16) to give a dark green mixture. The mixture was allowed to reflux for 5 minutes, giving a darker green mixture. After allowing it to cool to room
temperature, the mixture was filtered (Fig.17) to give a dark green solution. The filtrate was concentrated, as previously, under vacuum in the glovebag, yielding a dark green oil. Dry hexane was then distilled into the oil resulting in no solid product being precipitated from the oil.

Trial 9 was repeated twice, with the only modification to the procedure being that a U-shaped tube connected to a steam line (outside the glovebag) was used to heat the green filtrate (which was inside the glovebag), in order to facilitate faster solvent removal under vacuum. The observations and results of the two trials were the same as those in Trial 9, with a green oil being formed, and no solid formation upon the addition of hexane.

The Attempted Synthesis of Tetrakis(8-
hydroxyquinolinate)niobium(IV), Nb(8-Q)4.

Trial 1, using the Apparatus Sequence of Figures 2, 18, 19. This is also a previously reported complex, whose attempted complexation was carried out according to the procedure by Kepert and Deutscher. The ligand used for the attempted complexation, 8-hydroxyquinoline:
8-HQ

is commercially available. The solvents (200 ml of acetonitrile and 6 ml of triethylamine) were dried over CaH₂ and distilled under nitrogen (Fig.18) into a flamed out flask. The reactants, 0.6 g (2.55 mmol) of NbCl₄ and 1.50 g (10.34 mmol) of the ligand, 8-HQ, were weighed out. In the glovebag (Fig.2), the solution of acetonitrile and triethylamine was divided into 2 equal parts; with the ligand being dissolved in one part to give a pale yellow solution, and with the NbCl₄ being added to the second portion giving a brown suspension. The NbCl₄ mixture was then filtered into the ligand solution (Fig.19), to give a dark brown solution, which was heated at reflux for 5 minutes. After allowing the solution to cool to room temperature, a lighter brown solution with a yellow/green solid was observed. The solid was isolated via filtration back through the double filter frit (Fig.19), and dried under a nitrogen stream for 2 hours. The yellow/green powder was tested to be diamagnetic.
Trial 1 was repeated, but due to difficulties in dissolving the NbCl₄ in acetonitrile, no subsequent reaction took place (as denoted by little change in the color of the ligand solution upon addition of the NbCl₄ solution).

Trial 1 was repeated an additional time, with the same difficulty in dissolving the NbCl₄. However, a reaction did take place to a small extent. Upon filtration of the NbCl₄ suspension into the ligand solution, a dark brown solution was formed. After allowing the solution to reflux for 5 minutes, the solution remained dark brown in color, and was cooled to room temperature. Although no solid appeared to crystallize upon cooling of the solution, when the solution was filtered, a tiny amount of microcrystalline purple material was present on the filter frit and on the sides of the reaction flask. However, the purple product was not present in a sufficient amount to be isolated.

**Trial 2. using the Apparatus Sequence of Figures 2.18.19.** Trial 1 was repeated, but in order to attempt to combat the solubility problems of dissolving NbCl₄ in acetonitrile, NbCl₄(NCMe)₃ was synthesized (see Starting Materials, p.9) and was substituted for NbCl₄. The solvents, 100 ml of acetonitrile and 6 ml of triethylamine,
were dried and distilled into a flamed out flask (Fig.18). In the glovebag (Fig.2), a solution of 1.50 g of the ligand was made in the acetonitrile/triethylamine solvent system. Into the ligand solution, a 25 ml solution of NbCl$_4$(NCMe)$_3$ (2.47 mmol) was filtered (Fig.19), giving a burnt brown solution with some white gas evolving. The solution was heated at reflux for 5 minutes, and allowed to cool to room temperature, resulting in a lighter brown solution with some precipitated solid. The mixture was filtered (Fig.19), to isolate a yellow/green solid, which was tested to be diamagnetic.

**Trial 3, using the Apparatus Sequence of Figures 2, 18, 19.** The procedure for this trial is also very similar to that of trial 1, with the major modification being that the NbCl$_4$ was stirred for 1.5 hours in 100 ml of dry, distilled acetonitrile in an attempt to dissolve it. Into a second flamed out flask, 100 ml of acetonitrile and 6 ml of triethylamine were distilled (Fig.18) under nitrogen. In the glovebag (Fig.2), the ligand was dissolved in the solution of acetonitrile and triethylamine. Next, the brown suspension of NbCl$_4$ in acetonitrile was filtered into the ligand solution (Fig.19). As in the first repeat of trial 1, the NbCl$_4$ did not dissolve sufficiently to form a solution, resulting in no reaction occurring when it was filtered into the ligand solution.
Trial 3 was repeated, with the only modification being that the stirring time for the NbCl₄ was increased to about 2 days. The brown suspension of NbCl₄ was filtered into the yellow ligand solution (Fig. 19) as before, resulting in the formation of a dark black solution, with white smoke evolution. The solution was then heated at reflux for 5 minutes, and allowed to cool to room temperature. The resulting purple microcrystalline product was then isolated by filtration (Fig. 19) and dried for 2 hours under a nitrogen stream. Next, a small sample of the product was tested to be diamagnetic, by magnetic susceptibility, and the majority of the sample was transferred into a flamed out glass tube, which was sealed under vacuum. The percent yield of the purple compound could not accurately be determined due to its air sensitivity. Any remaining product which was not isolated, decomposed to a yellow/green compound within 24 hours.

**Trial 4, using the Apparatus Sequence of Figures 2, 18, 19, 20.** The procedure for this trial is similar to the previous trial, with the only modification being that the NbCl₄ was dissolved in 20 ml of dry acetonitrile, under nitrogen, via a soxhlet extraction (Fig. 20) for 1 day. In the glovebag (Fig. 2), the brown NbCl₄ solution was filtered into the ligand solution (Fig. 19), resulting in a dark black solution, with white smoke evolution. The solution
was allowed to reflux for 5 minutes, and cooled to room
temperature, resulting in the formation of a dark
precipitate. The microcrystalline purple product was
isolated by filtration (Fig. 19) and dried for 2 hours under
a nitrogen stream. In the glovebag, the purple crystals
were transferred into a flamed out glass tube, which was
then sealed under vacuum. A sample of the product was
analyzed to be diamagnetic by magnetic susceptibility.
This sample turned yellow/green upon exposure to the
atmosphere within 24 hours.

Trial 4 was repeated with the same observations and
results as before; a diamagnetic purple product was
isolated, which when exposed to the atmosphere, decomposed
to a yellow/green powder.

A small sample of the purple compound was also placed in
a desiccator, but no color change was observed.

E. Analytical Methods Used to Characterize the yellow/green
and purple compounds from the Attempted Synthesis of
Nb(8-Q)4

1. Pyrolysis. The yellow/green and the purple products
were pyrolyzed by carefully heating each sample in a
ceramic crucible with a bunsen burner (for approximately 10
minutes, until only a white residue remained in each case.
2. Thin Layer Chromatography (T.L.C.). Initially, T.L.C. of 8-HQ, the yellow/green and the purple compounds was carried out on oven dried silica gel plates in the glovebag (Fig. 2), using anhydrous ether and dried THF. The 3 samples were then dissolved in THF, spotted (side by side) on a silica gel plate, and eluted with a 90:10 mixture of ether/THF. The result was the presence of 3 streaks (side by side) corresponding to the ligand, the yellow/green, and the purple, in descending order (approximate Rf values of 0.5, 0.4, and 0.2). Other attempts at analyzing 8-HQ and the yellow/green compound via T.L.C. were made on alumina, cellulose, and reversed phase plates, employing a variety of solvents in varying combinations (chloroform, methylene chloride, THF, DMF, DMSO, ethyl ether, and hexane). In every case, only the ligand spot was moveable, with the yellow/green spot remaining at the origin.

3. Sodium Fusion. Sodium fusion was carried out according to the procedure prescribed by Shriner, Fuson, Curtin, and Morrill on both the yellow/green and the purple compounds, with only a slightly cloudy solution being observed in each instance (inconclusive test). An additional test which was carried out on NbCl4, as a control, yielded a white precipitate (a positive test).
4. Electron Spin Resonance (E.S.R.). An approximately 0.1 M solution of NbCl₄ was prepared in dry acetonitrile via a micro soxhlet extraction (Fig.20). In the glovebag, the resulting solution was transferred into a screw capped pyrex sample tube, and sealed by wrapping the cap with teflon tape. The attempt to obtain a spectrum of the sample was then conducted using Dr. Joseph Hornak's homebuilt, low field E.S.R. instrument.

5. Infrared. The infrared spectra of 8-HQ, the yellow green and the purple compounds were obtained in KBr pellets, which were prepared from oven dried, spectroscopic grade KBr, with the KBr pellet of the purple compound being prepared in the glovebag.

6.¹H N.M.R. Two sets of ¹H N.M.R. spectra were obtained for 8-HQ, the yellow/green and the purple compounds. For each set of spectra, the sample tube for the purple compound was prepared in the glovebag, and both the yellow/green and the purple sample solutions were saturated. The first set of spectra was obtained at ambient temperature in CDCl₃ (relative to TMS) at R.I.T., by Brian Cleary, on a 200 MHz instrument. The second set of spectra were obtained at ambient temperature in DMSO-d₆ on a 200 MHz instrument, by Dr. L. Paul Rosenberg, at Fisons.
7. \textsuperscript{13}C N.M.R. Two sets of \textsuperscript{13}C N.M.R. spectra were obtained. The first set of spectra, included the samples 8-HQ, the yellow/green and the purple compounds, was obtained at ambient temperature in CDCl\textsubscript{3} (as prepared previously) on a 25 MHz instrument (with 512 scans), by Dr. James Boiani, at S.U.C. Geneseo. The second set of spectra, of 8-HQ and the yellow/green compound, was obtained at ambient temperature in DMSO-\textsubscript{d8} (with the samples prepared as previously) on a 50 MHz instrument (with 9600 scans), by Dr. L. Paul Rosenberg, at Fisons.

8. UV/Visible. The UV/visible spectra of 8-HQ, the yellow/green and the purple compounds were obtained in methylene chloride at wavelengths from 250 to 800 nm, using quartz cuvettes. The samples were accurately weighed out and the corresponding solutions were prepared by dissolving each sample in a volumetric flask, by adding the appropriate amount of solvent. The sample solution for the spectrum of the purple compound was prepared under nitrogen (Fig.2), with dry methylene chloride, and by sealing the cuvette containing the sample solution with a glass disk coated with a layer of high vacuum grease. The concentrations for the sample solutions were as follows: 0.029 g/L for 8-HQ, 0.052 g/L for the yellow/green compound, and 0.468 g/L for the purple compound. A spectrum for the decomposed purple compound solution (now
yellow/green in color) was prepared by diluting it 1:10 with methylene chloride.

9. **Elemental Analysis.** Elemental analysis for the percentages of C, H, and N, as well as the percent ash, was carried out on the yellow/green and the purple compounds at 1000°C by Microlytics.

10. **Vapor Phase Osmometry (V.P.O.).** V.P.O. was attempted on samples of the yellow/green compound dissolved in methylene chloride at concentrations of 0.02, 0.04, 0.06, and 0.08 g/L, at an oven temperature of approximately 33°C. Only the first two samples were able to be attempted due to problems involving the calibration of the instrument and the clogging of the injector unit.

11. **Crystal Growth.** Attempts at growing single crystals of the yellow/green compound were attempted using freshly cleaned and oven dried apparatus. Saturated solutions of the yellow/green compound were prepared (in methylene chloride, THF, DMF, and DMSO) in vials by adding an excess of the solid to the solvent, followed by filtration into a flask through a medium glass frit, and transferred into another vial. For the saturated solutions in the volatile solvents (methylene chloride and THF), crystal formation was induced by allowing the solution to slowly evaporate in
a loosely capped vial. For the less volatile solutions (DMF and DMSO), a small vial containing the saturated sample solution was placed in a larger vial containing a small amount of pentane (more volatile nonsolvent), and the large vial was tightly capped.

12. Analysis of the purple compound for HCl(g) Formation as the Sample Decomposes. Six samples of the purple compound were prepared by adding enough solid to cover the bottom of a small vial, and by suspending a water moistened piece of universal indicator paper over each sample. 3 of the sample vials were left uncapped, and the remaining 3 samples were in capped vials. As a control, the same procedure, as used for the 3 uncapped vials, was done using 3 empty vials.
III. Results and Discussion

A. Starting Materials

The synthesis of the NbCl₄ proceeded in most cases with very little difficulty.⁴

\[(1) \text{Nb} + 4\text{NbCl}_5 \rightarrow 5\text{NbCl}_4\]

It was easy to observe that the reaction was proceeding on the right track by the presence of the brown needle-like crystals of the product. The results of the reaction became more consistent over time with practice at both combining the reactants in the reaction tube and the actual sealing of the tube under vacuum. An important step that was used in the synthesis, which facilitated the isolation of a purer product, was the moving of the neck of the tube into the cooler part of the tube furnace shortly before turning the reaction off. This allowed the unreacted NbCl₅ and other undesirable volatile oxide components (such as NbOCl₃) to be separated from the desired NbCl₄, since they were more rapidly condensed in the cool end of the tube.

The second starting material used was the NbCl₄(NCMe)₃ adduct of NbCl₄.⁵

\[(2) 3\text{NbCl}_5 + \text{Al} \rightarrow 3\text{NbCl}_4(\text{NCMe})_3 + \text{AlCl}_3 (s)\]

The reason why this was incorporated as a starting material for some of the reactions was the difficulty in dissolving the NbCl₄ in acetonitrile. Since, one of the complexation
reactions called for a solution of NbCl₄ to be made, one way to do this expediently was to make the solubilized adduct NbCl₄(NCMe)₃, by reducing dissolved NbCl₅ with aluminum powder in acetonitrile. At first, the reaction did not appear to be working, so the next logical steps were to test every aspect of the reaction and the system. By trial and error of all the possibilities, the culprit was identified as the nitrogen, under which the reaction was conducted (refer to the Experimental section, p.36). In the earlier reactions, the nitrogen going into the glovebag was only passed through a CaCl₂ trap, but the line which was used for passing nitrogen over the complexation reactions (etc.) came directly from the tank. Hence, the nitrogen contained oxygen which was destroying the air and moisture sensitive NbCl₅. This was tested by passing the nitrogen over both solid NbCl₅ and a solution of NbCl₅ in dry acetonitrile. In both cases, each system turned from the yellow NbCl₅ color to white in a matter of minutes. In order to resolve this problem, the nitrogen system was rearranged from Fig.1 to Fig.2, which involved the addition of a 150°C copper trap to the already existing CaCl₂ trap which would function to purify the nitrogen for both the glovebag and the auxiliary nitrogen line. When the system was tested as before, the NbCl₅ reagents showed no decomposition over a period of hours. After modifying the system the NbCl₄(NCMe)₃ was able to be synthesized quite
readily. This was proved by both a comparison with the observations in the published procedure to the procedure which was conducted, and by a paramagnetic magnetic susceptibility. The magnetic susceptibility calculation (see Table 2) indicated that the desired one d electron species was present to a smaller extent (with n = 0.36, rather than n = 1) than expected, due to possible decomposition.

B. Ligand Syntheses

All of the ligands were synthesized by previously published procedures.2,6-8 according to the following reactions.

\[
\begin{align*}
2 & \text{OH} & \text{NaH} & \text{DMF} & \text{stir 4 hrs.} \\
\text{NO}_2 & \rightarrow & 2 & \text{O-Na}^+ \\
\text{OH} & \rightarrow & \text{NO}_2 \\
\end{align*}
\]

\[
\text{ClCH}_2\text{CH}_2\text{Cl} \\
\text{reflux 6 hrs.}
\]

BNPE
Table 2.

A. Relevant Formulae for Magnetic Susceptibility Calculations

\[ x_g = \frac{[C1(R-R_o)]}{(10^9 \times m)} \]

* \( x_g \) = gram magn. susc. (cgs)
* \( C \) = Curie constant (1.088)
* \( l \) = sample tube length (cm)
* \( R \) = sample reading
* \( R_o \) = empty tube reading
* \( m \) = sample mass (g)

\[ x_m = x_g \times \text{sample molecular weight} \]

* \( x_m \) = molar magn. susc. (cgs)

\[ u_{eff} = 2.828(x_m \times T)^{1/2} \]

* \( u_{eff} \) = effective magn. moment (BM)
* \( T \) = Temperature in Kelvin

\[ u_{eff} = [n(n+2)]^{1/2} \]

* \( n \) = number of unpaired electrons

B. Sample Calculation of the Number of Unpaired Electrons for \( \text{NbCl}_4(\text{NCMe})_3 \) from a Magnetic Susceptibility Measurement.

\[ x_g = \frac{[(1.088)(3.7 \text{ cm})(29 - (-35))]}{(10^9 \times 0.26 \text{ g})} \]

\[ x_g = 0.99 \times 10^{-6} \text{ cgs} \]

\[ x_m = (0.99 \times 10^{-6} \text{ cgs})(357.6 \text{ g/mole}) \]

\[ x_m = 0.35 \times 10^{-3} \text{ cg}^2\text{s/mole} \]

\[ u_{eff} = 2.828[(0.35 \times 10^{-3})(300 \text{ K})]^{1/2} = 0.92 \text{ BM} \]

0.92 = \[n(n+2)]^{1/2} \; ; \; \text{n} \sim 0.36 \text{ electrons}
\[
\text{BNPE} \xrightarrow{78\% \text{EtOH, CaCl}_2, \text{reflux 3 hrs.}} \text{H}_2\text{BAPE}
\]

\[
\text{H}_2\text{N} - \text{NH}_2 + \text{CH}_3\text{CH}_2\text{CCF}_3 \xrightarrow{0^\circ \text{C}, -2 \text{H}_2\text{O}} \text{H}_2\text{BTAE}
\]

\[
\text{H}_2\text{N} - \text{NH}_2 + 2 \text{CH}_3\text{OH} \xrightarrow{\text{EtOH, 3 hrs.}} \text{H}_2\text{DSEN}
\]
\[ \text{H}_2\text{DSEN} \xrightarrow{\text{H}_2, \ 10\% \ \text{Pd-C}} \ \text{H}_2\text{BHBE} \]

5 hrs. @ 14 psi.
\[
\text{NH}_2 \quad + \quad 2 \quad \text{OH}
\]

\[
\begin{align*}
\text{reflux 16 hrs.} \\
\text{EtOH}
\end{align*}
\]

\[\text{H}_2\text{DSP}\]
their identities and purity were confirmed primarily by melting point, chromatography, infrared data, and proton N.M.R. (for H₂BAPE and 8-HQ). The infrared stretching frequencies for the synthesized ligands are listed in Table 3. Proton N.M.R. data for the H₂BAPE and 8-HQ ligands are listed in Table 4. The H₂BAPE ligand was first prepared in relatively low yield, which was disturbing because the reaction required a large amount of time to conduct, and only enough ligand was produced for one complexation. The major problem was that the second part of the procedure called for about 13 g. of BNPE to be reduced to give 7-9 g. of the desired ligand, and only about 8 g. of BNPE was being synthesized in the first part of the procedure. It was discovered that the problem with the commercially available material was that the 2-nitrophenol had a large water content, which destroyed the NaH needed to strip away the phenolic hydrogens, thereby decreasing the yield of BNPE. The problem was remedied by drying the 2-nitrophenol over phosphorous pentoxide and CaCl₂ in a desiccator. When this was done, the yield of H₂BAPE was increased to an amount close to the reported quantity. The H₂BAPE ligand was produced in good purity, which is evident from infrared, N.M.R., chromatography, and melting point data. The procedure for synthesizing the H₂BTAE ligand was fairly straightforward. Again however, obtaining a decent yield so that more than one complexation could be carried
Table 3.

Infrared Stretching Frequencies (cm⁻¹) for the Ligands. KBr Pellets.
(s = strong, m = medium, and w = weak; Ar = aromatic)

**H₂BAPE (see p. 59 for structure)**

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3460 (s), 3380 (s)</td>
<td>N-H (1° amine)</td>
</tr>
<tr>
<td>3070 (w)</td>
<td>Ar-H</td>
</tr>
<tr>
<td>1615 (s)</td>
<td>1,2-disubstituted benzene</td>
</tr>
<tr>
<td>1460 (s)</td>
<td>Ar-O-CH₂</td>
</tr>
<tr>
<td>1280 (m)</td>
<td>Ar-O</td>
</tr>
</tbody>
</table>

**H₂BTAE (see p. 59 for structure)**

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000 (w)</td>
<td>CH₃-C</td>
</tr>
<tr>
<td>1600 (s)</td>
<td>C=O, C=N (imine), C=C</td>
</tr>
<tr>
<td>1450 (m)</td>
<td>C=N (imine), C=C</td>
</tr>
<tr>
<td>1380 (m)</td>
<td>CH₃-C</td>
</tr>
<tr>
<td>1300-1100 (m)</td>
<td>-CF₃</td>
</tr>
<tr>
<td>770-700 (m)</td>
<td>-CF₃</td>
</tr>
</tbody>
</table>

**H₂BHBE (see p. 59 for structure)**

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3295 (s)</td>
<td>N-H (2° amine)</td>
</tr>
<tr>
<td>3010 (w)</td>
<td>Ar-H</td>
</tr>
<tr>
<td>2885 (w)</td>
<td>C-H</td>
</tr>
<tr>
<td>1600 (s)</td>
<td>N-H (2° amine), C=C (Ar)</td>
</tr>
<tr>
<td>1470 (s)</td>
<td>CH₂, C=C (Ar)</td>
</tr>
<tr>
<td>1280 (w)</td>
<td>C-N, Ar-O-</td>
</tr>
<tr>
<td>1260 (m)</td>
<td>Ar-O-, C-N</td>
</tr>
</tbody>
</table>

**H₂DSP (see p. 61 for structure)**

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3080 (w)</td>
<td>Ar-H</td>
</tr>
<tr>
<td>1620 (s)</td>
<td>C=N (imine)</td>
</tr>
<tr>
<td>1560 (s), 1480 (s)</td>
<td>C=C (Ar)</td>
</tr>
<tr>
<td>1275 (s)</td>
<td>Ar-O</td>
</tr>
<tr>
<td>1190 (s)</td>
<td>Ar-N</td>
</tr>
</tbody>
</table>

**8-HQ (see p. 45 for structure)**

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3030 (w)</td>
<td>Ar-H</td>
</tr>
<tr>
<td>1580 (s)</td>
<td>C=N (Ar), C=C (Ar)</td>
</tr>
<tr>
<td>1500 (s)</td>
<td>C=C (Ar)</td>
</tr>
<tr>
<td>1470 (m), 1435 (m)</td>
<td>C=C (Ar), C=N (Ar)</td>
</tr>
<tr>
<td>1280 (s)</td>
<td>Ar-O</td>
</tr>
</tbody>
</table>
### Table 4.

**Table of $^1$H N.M.R. shifts (200 MHz) relative to TMS in CDCl₃.**

(s = singlet, d = doublet, br = broad, and m = multiplet; M = multiplicity and I = integration)

<table>
<thead>
<tr>
<th>compound</th>
<th>shift (ppm)</th>
<th>M</th>
<th>I</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂BAPE</td>
<td>3.9</td>
<td>s</td>
<td>4</td>
<td>N-H</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>s</td>
<td>4</td>
<td>-O-CH₂CH₂-O-</td>
</tr>
<tr>
<td></td>
<td>6.9</td>
<td>s</td>
<td>8</td>
<td>Ar-H</td>
</tr>
<tr>
<td>8-HQ</td>
<td>7.1</td>
<td>s</td>
<td>1</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>m</td>
<td>3</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>8.2-8.3</td>
<td>m</td>
<td>1</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>8.8</td>
<td>m</td>
<td>2</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>-a</td>
<td></td>
<td></td>
<td>Ar-OH</td>
</tr>
<tr>
<td>yellow/green</td>
<td>0.8ₚ</td>
<td>m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.2ₚ</td>
<td>m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.7ₚ</td>
<td>m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.2ₚ</td>
<td>s</td>
<td>-</td>
<td>CH₃-CN</td>
</tr>
<tr>
<td></td>
<td>7.1-7.5</td>
<td>m</td>
<td>4</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>8.1</td>
<td>br</td>
<td>2</td>
<td>Ar-H</td>
</tr>
<tr>
<td>purple</td>
<td>1.4ₚ</td>
<td>m</td>
<td>-</td>
<td>Et₃N</td>
</tr>
<tr>
<td></td>
<td>2.0ₚ</td>
<td>s</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.2ₚ</td>
<td>s</td>
<td>-</td>
<td>CH₃-CN</td>
</tr>
<tr>
<td></td>
<td>3.2ₚ</td>
<td>m</td>
<td>-</td>
<td>Et₃N</td>
</tr>
<tr>
<td></td>
<td>7.2-7.5</td>
<td>m</td>
<td>4</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>8.1</td>
<td>s</td>
<td>2</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>12.0ₚ</td>
<td>br</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

ₚThis signal did not appear in CDCl₃, but was present in the spectrum using DMSO-d₆.  
ₚₚThese signals are due to solvent or other impurities.
out was initially a problem. However, by employing some standard synthetic techniques (the use of a reflux set up), a good yield of the ligand (50%) was obtained. The product that was isolated was of good purity after about five recrystallizations with benzene according to melting point and infrared data. A reason for a lower yield than expected can be due to the large number of recrystallizations done, and the subsequent loss of product from these. The H2DSP ligand was prepared previously by me in SCHI-765, the inorganic chemistry lab course. Its melting point and infrared spectrum were consistent with the literature values. The synthesis of the H2BHBE ligand also initially gave a low yield of product, but this problem was subsequently corrected by using the appropriate pressure of hydrogen (in p.s.i.) during the hydrogenation, which resulted in an increase in the yield of the ligand to about 56%. Both the melting point and infrared data confirmed the presence of the desired product. The H2BHBE ligand was not used for any attempted complexations, but it may be a potentially useful ligand for future studies. The infrared spectra and melting point's for the HBTA and 8-HQ ligands agreed closely with the literature.
C. Attempted Syntheses of Bis(quadridentate)niobium(IV) Complexes

A number of complexations were attempted using the majority of the above ligands and according to modified procedures which were published in the Kepert-Deutscher paper. All of the complexation reactions, with the exception of one, gave negative results (in terms of isolating a product with the desired paramagnetism), based on magnetic susceptibility measurements. The first series of complexations were conducted with the H₂BAPE ligand (starting on p.15). At this point, the techniques and apparatus used were in their infancy, as is apparent in the previously mentioned diagrams in the experimental section (also see Table 1). A number of different techniques and apparatus were used, but with negative results. In one instance (trial 3, p.33), a product which had a semblance of a green color was isolated, but decomposed to brown overnight. Still, that is not to say that this ligand cannot be complexed to niobium, because the complexations were not done under the purified nitrogen and with the procedural and technical improvements that have been made since that time. A single complexation reaction with the H₂DSP ligand (see p.34) was attempted out of curiosity to determine whether a Schiff base could form a complex with niobium. Since this reaction was done under similar conditions to that of the H₂BAPE complexations, it might
very well work if it was done under the latest conditions. The one complexation which was conducted that gave a paramagnetic product, was the reaction of the BTAE ligand with NbCl₄(NCMe)₃ (trial 2, p.36). It was at this time that the system was slightly more refined in terms of the apparatus and the redesign of the nitrogen purification system. The attempted complexation was done not, to isolate a pure product, but merely to isolate a paramagnetic product before it decomposed. This was done by conducting the reaction, omitting the filtration and washing steps, and immediately removing the solvent under vacuum, in order to isolate the product. The brown solid obtained tested to be paramagnetic,

\[ x_g = 1.77 \times 10^{-6} \text{ cgs} \]
\[ \text{M.W.} = 753 \text{ g/mole} \]
\[ x_m = 1.33 \times 10^{-6} \text{ cgs} \]
\[ u_{\text{eff}} = 1.78 \text{ BM} \]
\[ n = 1.05 \text{ electrons} \]

as desired. In order to prove that the NbCl₄(NCMe)₃ was not isolated, along with the unreacted ligand, a sample of NbCl₄(NCMe)₃ was synthesized, and was isolated as a brown solid. The solid starting material was found to be paramagnetic, but to a lesser degree than that of the complexation reaction product (see Table 2). However, the real test was the test of time; each of the samples was left out in the atmosphere in a magnetic susceptibility
tube. The isolated complex stayed paramagnetic overnight and well into the next day, whereas the starting material decomposed to a diamagnetic compound within hours after being isolated. Although the two compounds were obviously different with respect to their magnetic susceptibilities, in order to calculate the number of unpaired electrons (n) for the complexation product, it was assumed that the complex isolated was of the same composition and molecular weight as Nb(BTAE)₂. One must note that by making such an assumption, error was introduced into the calculation of the number of unpaired electrons in the sample since impurities such as zinc chloride, triethylammonium chloride, and unreacted starting materials were also isolated along with the complex. Even so, these results appeared to be somewhat promising, but were not immediately pursued. Two attempts were made to try to reproduce the previous result (p. 36), but no paramagnetic product was isolated. This is not to say that this reaction does not work, but might with some additional apparatus and procedural modifications. This synthesis could be included in a future project that is an extension of this thesis work.

D. Attempted Syntheses of Tetrakis(bidentate)niobium(IV) Complexes

After the majority of the complexation reactions
appeared to not be working, a different perspective on the research project was taken. It was felt that it was time to put the apparatus, procedures, and techniques being used up until this point, to a test. The test was that if the system truly worked, then it should be possible to reproduce one (or more) of the eight coordinate tetrakis(bidentate) systems reported by Deutscher and Kepert.\(^1\) Therefore, this working system could be used for the attempted syntheses of the desired niobium(IV) bis(quadridentate) complexes, with some degree of certainty. In addition, the tetrakis(bidentate) complex could conceivably be reacted with quadridentate ligands (1:2) to produce a bis(quadridentate) complex, since the reaction appears to be favored by entropy (the chelate effect). Therefore, the most stable complex of those synthesized, employing the HBTA ligand, was chosen as the first test complex. Once reaction trials for this complexation were begun, a number of shortcomings in the published procedure became apparent. The major problem in this procedure (and other procedures in that paper) is its lack of various details which would help in conducting the reaction. Firstly, observations of various color and physical changes during stages of the reaction are not present. Thus, one does not know if the reaction is proceeding correctly until almost its conclusion. Secondly, the authors do not indicate how the reaction
mixture was concentrated, prior to hexane addition, or the volume to which the solution was concentrated. Thirdly, the amount of hexane used to precipitate the product from the concentrated reaction mixture also remains unspecified. The last consideration, which is also absent from the paper, is why certain solvent systems were used for certain reactions, and not others. That is, were the solvents for particular complexations chosen arbitrarily, or was there a specific reason why they were used. These were and are still unanswered questions.

In any event, the complexation reaction with HBTA was attempted 13 times (pp.37-44, including trials and re-runs, and not including unreported failed attempts), with the most recent apparatus and procedural changes (which can be seen in the Experimental section). When this reaction was first carried out (trials 1-4, pp.37-40), evidence of the reaction proceeding (dark olive green color of reaction mixture) was only evident after allowing the mixture to reflux for the required time. For the trials (trials 5 and 6, pp.40-42) using an improved set of apparatus (Figs. 9-13), a dark green color was immediately obtained upon mixing the reactants, which was a very favorable sign. However, there were two major concerns with the apparatus and the procedure. The first was the presence of residual moisture on the glassware in the filtering apparatus.
(Fig.11), which was modified by rinsing the system with the dried solvents prior to use. The second concern was how to properly concentrate the filtered reaction mixture, prior to the addition of hexane to precipitate the product. In the past, a vacuum pump was used to do this job, but it was found that there may have been a problem with oxygen leaking in the system and destroying the product before it could be isolated. As an alternative to this method, the bubbling of nitrogen through the reaction mixture to reduce the solvent volume by induced evaporation was tried in trial 5. The problem with this technique is that toluene cannot be quickly removed in this manner due to its high boiling point. It was then thought that if benzene was substituted for toluene, as a solvent, the evaporation would be hastened (trial 6). As it turns out, the evaporation process was faster with benzene, but not quite fast enough. The proposed solution to this problem was to again use a vacuum distillation type system, but with the system containing the reaction mixture surrounded by a nitrogen atmosphere in the glovebag. Therefore, if leaks were present in the system, the product would be (in theory) safe due to the presence of the nitrogen atmosphere. This technique was first used in trial 7 (p.42), incorporating it into the procedure which was used in the sixth trial. As in trial 6, the same observations and results were obtained, with the formation of a green
oil, from which no solid was isolated. For trial 8 (p.43), the procedure was again unaltered, but with toluene being substituted for benzene. The observations and results for this trial were consistent with those from the previous two trials (6 and 7). A slightly modified apparatus was employed for trial 9 (p.43), with the main improvement being that the solvents were distilled under a positive pressure of nitrogen (Fig.15), rather than continuously purging the system, with the nitrogen exiting through a drying tube. Minor alterations were also made to the apparatus used for the attempted complexation (Figs. 16 and 17). The procedure used for this trial was basically unchanged from trial 8, with observations and results consistent with the previous trials; a green oil was formed, with no formation of solid precipitate upon addition of hexane. Trial 9 was repeated two additional times (p.44) with the sole modification being that a U-shaped steam heated tube was used to reduce the time involved for concentrating the filtrate, under vacuum, in the glovebag. The observations and results again proved to be reproducible, with the formation of a green oil, and no solid product.

After laboring over the attempted synthesis of Nb(BTA)₄ and obtaining the same results, regardless of changes in the apparatus and procedure, it was decided that another
approach to this project was necessary. Keeping in step with the idea of reproducing a complex from the Kepert-Deutscher paper¹, a second niobium complex, Nb(8-Q)₄, was selected for the next attempted synthesis. The Nb(8-Q)₄ complex was chosen for its relative stability, the simple nature of the reaction, and because its ligand, 8-hydroxyquinoline (8-HQ), has nitrogen and oxygen donor atoms (a desired feature for the proposed bis(quadridentate) complexes, according to the predictions of Orgel's orbital overlap model³). The reaction carried out in trial 1 (p.44), produced a yellow/green diamagnetic solid, which apparently is a single compound according to the elemental analysis (see below). Both the yellow/green color and the magnetism of the product were an oddity, because the reported complex was purple and paramagnetic. Trial 1 was repeated twice. The first time (p.46), no reaction was observed due to a problem with dissolving the NbCl₄ in acetonitrile. In the second re-run (p.46), the same problem was encountered. However, a reaction did take place to a small extent, which was denoted by the presence of a tiny amount of microcrystalline purple material on the reaction apparatus after filtration. Though the purple solid was not present in an amount large enough to be isolated, this observation was significant, due to the fact that the observed color was consistent with the color reported for the desired product. In trial 2 (p.46),
NbCl₄(NCMe)₃ was substituted for NbCl₄ in order to attempt to bypass its solubility problem, because it is prepared in solution by the reduction of NbCl₅ with aluminum powder (see Experimental Section under Starting Materials). The procedure used was similar to that of trial 1, with the same observations and results; the isolation of a yellow/green diamagnetic product. Trial 3 (p. 47) was yet another repeat of trial 1, with the main modification being that NbCl₄ was again used, but it was allowed to stir in acetonitrile for about 1.5 hours, in an attempt to dissolve it. As in the first repeat of trial 1, the NbCl₄ was not sufficiently dissolved for any reaction to occur. In the continuing effort to dissolve the NbCl₄, trial 3 was repeated (p. 48), but with the stirring time for the NbCl₄ being increased to approximately 2 days. The same procedure was used as in the previous trials, with the formation of a microcrystalline purple product, now in a sufficient amount to be isolated. The majority of the product was isolated (under nitrogen), and sealed inside an evacuated, flamed out glass tube. The remaining amount was tested to be diamagnetic, by magnetic susceptibility, and left exposed to the atmosphere. The magnetic susceptibility data for the reported purple complex (Nb(8-Q)₄) is listed below:

\[ x_g = 1.60 \times 10^{-6} \text{ cgs} \]

M.W. = 669 g/mole
\[ x_m = 1.07 \times 10^{-6} \text{ cgs} \]

\[ u_{\text{eff}} = 1.60 \text{ BM} \]

\[ n = 0.89 \text{ electrons} \]

It was observed that the purple product decomposed to the previously isolated yellow/green compound (based on similar infrared spectra), within hours of being exposed to the atmosphere. In order to further improve upon the chance for isolating the purple product again, in trial 4 (p.48) the NbCl\(_4\) was dissolved (under nitrogen) via a soxhlet extraction (Fig.20) with acetonitrile. Using the same procedure as in trial 3, a diamagnetic purple solid was again obtained and isolated. Trial 4 was repeated an additional time (p.49) with the same results obtained as before; a small amount of a diamagnetic purple solid was isolated. In all instances, the yield of the purple compound isolated could not be accurately determined due to its air sensitivity.

E. Analytical Methods Used to Characterize the yellow/green and purple compounds from the Attempted Synthesis of Nb(8-Q)\(_4\)

At this point, the attempted complexations yielded two diamagnetic products, yellow/green and purple, which differed from the reported Nb(8-Q)\(_4\) paramagnetic, purple product, with respect to their magnetism. The yellow/green product is obviously a decomposition product of the purple compound, since it was observed that it decomposed to the
yellow/green product when exposed to the atmosphere. The next step in the project was to analyze the differences between the desired purple product, and the isolated yellow/green and purple products. In order to do this, a number of qualitative and physical methods were employed.

1. **Pyrolysis.** After having driven off all of the organic species, only a white oxide (Nb₂O₅, which is the expected nonvolatile residue) remained in each case, demonstrating that both the yellow/green and the purple products were some type of niobium complexes.

2. **Thin Layer Chromatography (T.L.C.).** Since the 8-HQ ligand and other 8-HQ containing species streak on acidic T.L.C. mobile phases (such as silica gel), a neutral mobile phase was needed in an attempt to produce the desirable single moving spots for the 3 samples. In order to try to develop a T.L.C. solvent system which could be used for the simultaneous analysis of all 3 samples, a number of attempts using the ligand and the yellow/green samples via T.L.C. were made on cellulose, alumina, and reversed phase plates, using a variety of eluting and spotting solvents (including chloroform, methylene chloride, THF, DMF, DMSO, ether, and hexane). In each case, the ligand spot was able to be cleanly moved, while the yellow/green spot remained at the origin, suggesting that T.L.C. was not effective in
the analyses of 8-HQ and the yellow/green compounds, and that it also would not be useful in analyzing the purple compound (due to its similarities to the yellow/green compound). Therefore, T.L.C. of the yellow/green and purple compounds would indicate if 8-HQ was present, but it was not useful in determining if there was a mixture of complexes present in either sample.

3. Sodium Fusion. The sodium fusion tests which were carried out on both the yellow/green and the purple compounds showed no observable precipitate formation, only a slight clouding of each solution, which was not a conclusive indicator of the presence or absence of chlorine in either sample. The sample of NbCl₄, which was tested as a control, immediately gave a positive test result, thereby proving the validity of the experiment.

4. Electron Spin Resonance (E.S.R.). In an attempt to clarify the results of the sodium fusion test, an E.S.R. study of NbCl₄ was proposed. This experiment was undertaken to determine if NbCl₄ exists as discrete, paramagnetic entities in solution, or if it exists as an extended structure in solution. If the former case was true, then an E.S.R. signal should be observed due to the presence of the single d electron and should not be observed for the latter case. In order to determine which
case was true, a spectrum of the sample was obtained on Dr. Hornak's homebuilt, low field E.S.R. instrument. The result was that only a noisy baseline was obtained, with only a small pyrex glass signal being observed due to the sample container. The reason why no E.S.R signal was seen is that the instrument does not have the capability to distinguish between the two possible species of NbCl₄ due to its low magnetic field strength. Therefore, no particularly useful information was obtained from this experiment.

5. **Infrared.** Infrared spectra of 8-HQ, the yellow/green and the purple compounds were obtained (see Table 5) and their differences were interpreted as changes arising from the coordination of 8-HQ to niobium. That is, in the spectra for the yellow/green and the purple compounds, there should be noticable shifts for the corresponding aromatic C-O and C=N stretching frequencies upon coordination. First, one can observe a shift in the C=N stretching frequency in the spectra going from 8-HQ, to the yellow/green, to the purple compound (1580, 1575, 1570 cm⁻¹, respectively), denoting coordination of the nitrogen. Next, there is a corresponding shift observed for the C-O stretching frequency in comparing the 8-HQ spectrum to the spectra of the yellow/green and purple compounds (1280 to 1320 cm⁻¹, respectively), which denotes oxygen
Table 5.

Comparison of the Infrared Stretching Frequencies (cm⁻¹) for 8-HQ, yellow/green, and purple compounds, KBr pellets.

<table>
<thead>
<tr>
<th>compound</th>
<th>frequency (cm⁻¹)</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-HQ</td>
<td>3030 (w)</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>1580 (s)</td>
<td>C=N (Ar), C=C (Ar)</td>
</tr>
<tr>
<td></td>
<td>1500 (s)</td>
<td>C=C (Ar)</td>
</tr>
<tr>
<td></td>
<td>1470 (s), 1435 (s)</td>
<td>C=C (Ar), C=N (Ar)</td>
</tr>
<tr>
<td></td>
<td>1280 (s)</td>
<td>(Ar-O)-H</td>
</tr>
<tr>
<td></td>
<td>1235 (s)</td>
<td>?a</td>
</tr>
<tr>
<td>yellow/green</td>
<td>3080 (w), 2950 (w)</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>1575 (s)</td>
<td>C=N (Ar), C=C (Ar)</td>
</tr>
<tr>
<td></td>
<td>1500 (s)</td>
<td>C=C (Ar)</td>
</tr>
<tr>
<td></td>
<td>1470 (s)</td>
<td>C=C (Ar), C=N (Ar)</td>
</tr>
<tr>
<td></td>
<td>1320 (s)</td>
<td>(Ar-O)-Nb</td>
</tr>
<tr>
<td></td>
<td>1275 (s)</td>
<td>Ar-O (?)</td>
</tr>
<tr>
<td></td>
<td>1235 (w)</td>
<td>?a</td>
</tr>
<tr>
<td>purple</td>
<td>2950 (w)</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>1570 (s)</td>
<td>C=N (Ar), C=C (Ar)</td>
</tr>
<tr>
<td></td>
<td>1500 (s)</td>
<td>C=C (Ar)</td>
</tr>
<tr>
<td></td>
<td>1470 (s)</td>
<td>C=C (Ar), C=N (Ar)</td>
</tr>
<tr>
<td></td>
<td>1320 (s)</td>
<td>(Ar-O)-Nb</td>
</tr>
<tr>
<td></td>
<td>1275 (s)</td>
<td>Ar-O (?)</td>
</tr>
</tbody>
</table>

aNot yet assigned.
coordination. An additional C=O stretching frequency at 1275 cm⁻¹ also appears in the yellow/green and purple compound spectra. Lastly, as the purple compound decomposes to the yellow/green compound, a peak at 1235 cm⁻¹ emerges, not found in other complexes of 8-HQ¹³ (so it remains unassigned), which is in common with the spectrum of 8-HQ. Thus, shifts in the aromatic nitrogen and oxygen stretching frequencies in the infrared spectra, suggest complex formation has occurred in both the yellow/green and purple compounds, but also show the differences between the two compounds.

6. **¹H N.M.R.** As with the infrared spectra, one should observe changes in the N.M.R. spectra of the yellow/green and purple compounds which are consistent with the coordination of 8-HQ to niobium. That is, the aromatic protons (ortho and para to the nitrogen) on 8-HQ should shift upon complexation, and in addition, the aromatic OH proton signal should consequently disappear. The first set of spectra was obtained in CDCl₃ (Table 4, p.64), but the resolution of the aromatic region for the yellow/green and the purple compound spectra was not very good, due to solvent impurities. A second set of spectra, obtained in DMSO-d₆ (Table 6), also had similar solvent impurity signals, but they did not interfere with the resolution of the aromatic region. From the spectral data, one can first
Table 6.

Table of $^1$H N.M.R. shifts (200 MHz) for 8-HQ, the yellow/green compound and the purple compound in DMSO-$d_6$.

$s =$ singlet, $d =$ doublet, $br =$ broad, and $m =$ multiplet; $M =$ multiplicity and $I =$ integration.

<table>
<thead>
<tr>
<th>compound</th>
<th>shift (ppm)</th>
<th>$M$</th>
<th>$I$</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-HQ</td>
<td>2.5</td>
<td>s</td>
<td>-</td>
<td>CH$_3$ (DMSO)</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>m</td>
<td>1</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>7.4-7.6</td>
<td>m</td>
<td>3</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>m</td>
<td>1</td>
<td>Ar-H (para to N)</td>
</tr>
<tr>
<td></td>
<td>8.8</td>
<td>m</td>
<td>1</td>
<td>Ar-H (ortho to N)</td>
</tr>
<tr>
<td></td>
<td>9.8</td>
<td>s</td>
<td>1</td>
<td>Ar-OH</td>
</tr>
<tr>
<td>yellow/green</td>
<td>1.3$^a$</td>
<td>m</td>
<td>-</td>
<td>Et$_3$N</td>
</tr>
<tr>
<td></td>
<td>2.5$^a$</td>
<td>s</td>
<td>-</td>
<td>Et$_3$N, CH$_3$ (DMSO)</td>
</tr>
<tr>
<td></td>
<td>3.4$^a$</td>
<td>m</td>
<td>-</td>
<td>H$_2$O</td>
</tr>
<tr>
<td></td>
<td>7.1-7.5</td>
<td>m</td>
<td>4</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>br</td>
<td>1</td>
<td>Ar-H (para to N)</td>
</tr>
<tr>
<td></td>
<td>9.4, 9.7</td>
<td>br</td>
<td>1</td>
<td>Ar-H (ortho to N)</td>
</tr>
<tr>
<td>purple</td>
<td>1.0$^a$</td>
<td>m</td>
<td>-</td>
<td>Et$_3$N</td>
</tr>
<tr>
<td></td>
<td>2.1$^a$</td>
<td>s</td>
<td>-</td>
<td>CH$_3$-CN</td>
</tr>
<tr>
<td></td>
<td>2.5$^a$</td>
<td>m</td>
<td>-</td>
<td>Et$_3$N, CH$_3$ (DMSO)</td>
</tr>
<tr>
<td></td>
<td>3.3$^a$</td>
<td>m</td>
<td>-</td>
<td>H$_2$O</td>
</tr>
<tr>
<td></td>
<td>7.2-7.6</td>
<td>m</td>
<td>4</td>
<td>Ar-H</td>
</tr>
<tr>
<td></td>
<td>8.5, 8.7</td>
<td>br</td>
<td>1</td>
<td>Ar-H (para to N)</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>br</td>
<td>1</td>
<td>Ar-H (ortho to N)</td>
</tr>
</tbody>
</table>

$^a$These signals are due to solvent or other impurities.
observe the absence of the aromatic OH signal (which appears at approximately 9.8 ppm in the spectrum of 8-HQ) in both the spectra of the yellow/green and the purple compounds, indicating coordination in each case. In addition, it appears that the signals due to the aromatic protons ortho and para to the nitrogen (located at approximately 7.5 and 8.8 ppm in the ligand spectrum) are shifted down field and broadened in the spectra of the yellow/green and purple compounds. No differences between the the spectra of the two compounds, in comparison to each other and the 8-HQ spectrum, are apparent. Therefore, based on the N.M.R. spectral data, it appears that 8-HQ has been complexed to niobium in both the yellow/green and purple compounds.

7. $^{13}$C N.M.R.. The first set of spectra (summarized on Table 7), obtained on the 25 MHz instrument, did not provide any useful information, for the following reasons. First, only 6 peaks out of a possible 9 peaks were observed in the spectrum of 8-HQ, with the C-O carbon peak absent.$^{14}$ Next, both the yellow/green and the purple compound spectra suffered from a lack of observable peaks, due to baseline noise resulting from a low concentration of sample and a small number of scans (512). Therefore, additional $^{13}$C N.M.R. spectra (Table 8) were obtained on a higher field instrument (50 MHz), with a greater number of scans (9600),
Table 7.

$^{13}$C Spectra (25 MHz, 512 scans) of 8-HQ, the yellow/green compound, and the purple compound in CDCl$_3$.

<table>
<thead>
<tr>
<th>compound</th>
<th>obs. shift (ppm)</th>
<th>lit. shift (ppm)</th>
<th>carbon #</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-HQ</td>
<td>-</td>
<td>155.3</td>
<td>2</td>
</tr>
<tr>
<td>148</td>
<td>148.0</td>
<td>148.0</td>
<td>4$^a$</td>
</tr>
<tr>
<td>-</td>
<td>138.5</td>
<td>138.5</td>
<td>3$^a$</td>
</tr>
<tr>
<td>136</td>
<td>136.0</td>
<td>136.0</td>
<td>5</td>
</tr>
<tr>
<td>-</td>
<td>128.7</td>
<td>128.7</td>
<td>6</td>
</tr>
<tr>
<td>127</td>
<td>127.4</td>
<td>127.4</td>
<td>7</td>
</tr>
<tr>
<td>-</td>
<td>121.8</td>
<td>121.8</td>
<td>8</td>
</tr>
<tr>
<td>118</td>
<td>117.7</td>
<td>117.7</td>
<td>9</td>
</tr>
<tr>
<td>110</td>
<td>111.2</td>
<td>111.2</td>
<td>10</td>
</tr>
<tr>
<td>yellow/green</td>
<td>186</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>purple</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$The chemical shift for the para carbon should be further down field than the meta carbon (as in the proton spectra), which is the reverse of the assignments in reference 14.
Table 8.

$^{13}$C Spectra (50 MHz, 9600 scans) of 8-HQ and the yellow/green compound in DMSO-$d_6$.

<table>
<thead>
<tr>
<th>compound</th>
<th>obs. shift (ppm)</th>
<th>lit. shift (ppm)</th>
<th>carbon #</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-HQ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>153.02</td>
<td>155.3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>147.86</td>
<td>148.0</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>138.31</td>
<td>138.5</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>135.77</td>
<td>136.0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>128.57</td>
<td>128.7</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>127.27</td>
<td>127.4</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>121.56</td>
<td>121.8</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>117.52</td>
<td>117.7</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>110.95</td>
<td>111.2</td>
<td>10</td>
</tr>
<tr>
<td>yellow/green</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>210$^a$</td>
<td>-</td>
<td>-$^b$</td>
</tr>
<tr>
<td></td>
<td>156</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>148</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>142</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>138</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>129</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>122</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>114</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>112</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$This is an unspecified assignment which is probably an impurity, because it is the most remote signal on the spectrum (too large of a shift to be due to coordination) and it is the tenth signal out of a possible 9 carbon signals.  $^b$The assignments in this column are tentative (based on small changes that could possibly result upon coordination).
in an effort to combat these problems. Also, in order to at least duplicate the literature spectrum for 8-HQ\textsuperscript{14}, all of the spectra were obtained in DMSO-d\textsubscript{6}, since it was the solvent used in the 8-HQ reference. The only problem encountered with obtaining a new set of spectra using a greater number of scans was that no spectrum for the purple compound could be obtained due to its air sensitivity over the long time duration necessary to run a spectrum (overnight). The $^{13}$C spectrum of 8-HQ, in terms of the positions of the 9 carbons, matched exactly with the literature values\textsuperscript{14}, as can be seen in Table 8. It was thought that the spectrum for the yellow/green compound would provide information indicating that 8-HQ was coordinated to niobium, based on shifts of C-9, C-2, and C-4, which might be useful in determining its structure. In reality, the spectrum was able to supply some information consistent with complexation, but a noisy baseline (due to a low concentration of sample), made peak assignments very difficult.

\textbf{8. UV/Visible.} It was observed that 8-HQ was complexed to niobium in both the yellow/green and the purple compounds,
from the shift in the position of the ligand absorbance (ligand π-π* transition, in the UV region) from 312 nm in 8-HQ to 375 nm in the spectra of the complexes (see Table 9). An observable difference between the spectra of the yellow/green and the purple compounds was that a band at 514 nm (d-d transition), with an extinction coefficient approximately 0.1 of that of the band in the UV region, was present in the purple compound, denoting the presence of d electrons, and thus accounting for its color. Also notable, was that this absorbance at 514 nm disappeared when exposed to water, as the purple compound decomposed to the yellow/green compound (Table 10). Also note that the purple compound would not undergo the color change to yellow/green when stored in a desiccator (see p.49). Both of the absorbances which are present in the purple compound spectra (at 375 nm and at 514 nm) are also in common with the absorbances for the reported purple compound, Nb(8-HQ)₄. Therefore, the UV/visible spectra not only point up the fact that both the yellow/green and the purple compounds are niobium complexes, but they also show that d electrons are present in the purple compound (as evident from the d-d transition at 514 nm), and are absent in the yellow/green compound.
<table>
<thead>
<tr>
<th>compound</th>
<th>conc. (g/L)</th>
<th>lambda_{max} (nm)</th>
<th>Absorbance (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-HQ</td>
<td>0.029</td>
<td>312</td>
<td>1.40</td>
</tr>
<tr>
<td>yellow/green</td>
<td>0.052</td>
<td>312 (shoulder)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>375</td>
<td>1.17</td>
</tr>
<tr>
<td>yellow/green\textsuperscript{a}</td>
<td>0.075</td>
<td>375</td>
<td>1.67</td>
</tr>
<tr>
<td>purple</td>
<td>0.468</td>
<td>375 (off scale)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>514</td>
<td>1.53</td>
</tr>
</tbody>
</table>

\textsuperscript{a}This sample was washed with acetonitrile to remove traces of the ligand which were present.
Table 10.

UV/vis spectra showing the decomposition of the purple compound (conc. = 0.4680 g/L) to the yellow/green compound in methylene chloride.

<table>
<thead>
<tr>
<th>time</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Absorbance (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(initial)</td>
<td>375</td>
<td>(off scale)</td>
</tr>
<tr>
<td></td>
<td>514</td>
<td>1.53</td>
</tr>
<tr>
<td>15 min.</td>
<td>375</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>514</td>
<td></td>
</tr>
<tr>
<td>30 min.</td>
<td>375</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>514</td>
<td></td>
</tr>
<tr>
<td>45 min.</td>
<td>375</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>514</td>
<td></td>
</tr>
<tr>
<td>90 min.</td>
<td>375</td>
<td></td>
</tr>
<tr>
<td></td>
<td>514</td>
<td>-</td>
</tr>
<tr>
<td>24 hrs.</td>
<td>375</td>
<td>0.99$^a$</td>
</tr>
<tr>
<td></td>
<td>312 (shoulder)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$After 24 hours, the solution of the decomposed purple compound, which was now yellow/green in color, was diluted to a concentration of 0.0468 g/L, so that the band at 375 nm would be on scale.
9. **Elemental Analysis.** The percentages of C, H, N, O, and Nb were obtained from the elemental analysis of the yellow/green and purple compounds (Table 11). At this point, the goal was to determine the corresponding structures for each compound from the elemental analysis data. However, a problem was encountered with the purple sample, in terms of its purity. That is, the purple sample was obviously impure as shown by the presence of solvent impurities in the $^1$H N.M.R. spectra (Tables 4 and 6). The reason being was that the purple compound could not be washed and dried prior to analysis (due to its moisture sensitivity), as was the yellow/green sample.

10. **Vapor Phase Osmometry (V.P.O.).** V.P.O was attempted on the yellow/green compound in an effort to determine its molecular weight, but it did not work due to instrumental difficulties. That is, problems with the stabilization of the solvent signal (the reference) and clogging of the apparatus prevented any results from being obtained.

11. **Crystal Growth.** Attempts to grow suitable single crystals of the yellow/green compound in methylene chloride and tetrahydrofuran were not successful. In fact, after the solvents totally evaporated, a yellow/brown tar was observed in each case. Other attempts to grow crystals using solvent pairs of DMSO/pentane and DMF/pentane also have not yielded any crystals as of yet.
Table 11.

Elemental Analyses of the yellow/green and the purple compounds.

<table>
<thead>
<tr>
<th>sample</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% Cl&lt;sup&gt;a&lt;/sup&gt;</th>
<th>% Nb&lt;sup&gt;b&lt;/sup&gt;</th>
<th>% O&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>yellow/green</td>
<td>59.68</td>
<td>3.46</td>
<td>8.07</td>
<td>0.51</td>
<td>17.13</td>
<td>11.66</td>
</tr>
<tr>
<td>purple</td>
<td>54.53</td>
<td>8.36</td>
<td>9.64</td>
<td>16.36</td>
<td>10.69</td>
<td>0.42</td>
</tr>
</tbody>
</table>

<sup>a</sup>The % Cl was not included for the yellow/green sample, because it was a negligible amount.  
<sup>b</sup>% Nb = [(2 x F.W. of Nb)/(F.W. of Nb<sub>2</sub>O<sub>5</sub>)] x % Ash.  
<sup>c</sup>% O = (100 % - the sum of the percentages of the elements).
12. Analysis of the purple compound for HCl(g) Formation as the Sample Decomposes. The results from this test seemed to indicate that HCl(g) had indeed evolved as a result of the decomposition of the purple compound to the yellow/green compound. That is, for the 3 samples which were analyzed in the open vials, suggested the presence of acid (via orange/red spots on the indicator paper) being evolved as a result of decompositon. The remaining 3 samples (in the closed vials) showed no indication of acid having been evolved. However, the results for the controls also showed signs of the presence of acid. Therefore, the results were mixed, with regard to the evolution of HCl(g) as the purple compound decomposes to the yellow/green compound.

F. Structural Hypotheses for the yellow/green and the purple Compounds

At this point, all of the experimental and analytical data was now complete, and it was time to begin hypothesizing the probable structures for both the yellow/green and the purple compounds. The major piece of data which would be the deciding factor in determining the structures for each compound, was respective their elemental analyses. However, since the elemental analysis of the purple compound did not appear to be reliable (from
\(^1\text{H N.M.R. data})\), it would seem that the only alternative was to attempt to derive a logical structure for the yellow/green compound from its elemental analysis. That is, one should be able to determine a likely structure for the yellow/green compound by matching the calculated percentages of the elements (of the proposed structure), to the experimentally determined percentages obtained from the elemental analysis. Thus, once a logical structure for the yellow/green compound was deduced, it would be possible to work backwards from this structure and obtain a reasonable structure for the purple compound, based on the remaining analytical data. By using the aforementioned method, structures for the yellow/green compound that were arrived at are:

\[
\begin{align*}
\text{or} & \quad [\text{structure}]_n \\
\text{where} \quad \mathbf{Q} &= 8-
\end{align*}
\]

whose calculated percentages matched nearly perfectly with those from the elemental analysis (see Table 12). In addition, the polymeric structure is likely, owing to its similarities to NbOCl\(_3\). The previously obtained
Table 12.

Calculated Percentages of the Elements in the Proposed Structure of the yellow/green compound, with the Experimentally Determined Percentages in Parentheses.

<table>
<thead>
<tr>
<th></th>
<th># x F.W.</th>
<th>% of element</th>
<th># of moles</th>
<th>empirical #</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>C 648</td>
<td>59.89 (59.68)</td>
<td>4.99 (4.97)</td>
<td>26.97 (27.00)</td>
</tr>
<tr>
<td>36</td>
<td>H 36</td>
<td>3.33 (3.46)</td>
<td>3.33 (3.46)</td>
<td>18.00 (18.80)</td>
</tr>
<tr>
<td>6</td>
<td>N 84</td>
<td>7.76 (8.07)</td>
<td>0.55 (0.57)</td>
<td>2.97 (3.13)</td>
</tr>
<tr>
<td>8</td>
<td>O 128</td>
<td>11.83 (11.66)</td>
<td>0.74 (0.73)</td>
<td>4.00 (3.97)</td>
</tr>
<tr>
<td>2</td>
<td>Nb 186</td>
<td>17.20 (17.13)</td>
<td>0.18 (0.18)</td>
<td>1.00 (1.00)</td>
</tr>
</tbody>
</table>

Calculated Formula: \((C_{27}H_{18}N_3O_4Nb)_2\)

Experimental Formula: \((C_{27}H_{18}N_3O_4Nb)_2\)\(^{(19)}\)

Molecular Weight: 1082 g/mole
analytical data also point up the viability of the proposed structures. First, the proposed structures are diamagnetic, because Nb(V) has a $d^0$ electron configuration, which is in agreement with the diamagnetic magnetic susceptibility of the yellow/green complex. Next, the pyrolysis of the yellow/green compound shows that it contains niobium, which is consistent with these complexes. Next, the sodium fusion test for the yellow/green compound was inconclusive, but perhaps gave more of an indication that chlorine is not present in the sample for the amount of precipitate produced, which is also in line with the proposed structures. Next, both the infrared and N.M.R. data for the yellow/green compound denote oxygen and nitrogen coordination of the ligand to niobium, which is also present in the proposed structures. Lastly, the UV/visible data of the yellow/green compound indicates the absence of any $d$ electrons, which is also consistent with the proposed structures for the yellow/green compound, which are also devoid of $d$ electrons. In addition, the yellow/green compound is probably not a mononuclear niobium complex, because the corresponding Nb=O stretching frequency, which should appear at approximately 900 cm$^{-1}$, is not present in this region, as compared with the free ligand.

By using the analytical data (excluding the elemental
analysis) for the purple compound, the known structure of NbCl₄, and the assumed structures for the yellow/green compound, it was hypothesized that the purple compound is some type of dinuclear complex with bridging ligands. More specifically, two niobium atoms, each with 3 coordinated 8-HQ ligands, could form a spin paired complex bridged by a pair of chlorine atoms. The resulting complex,

![Diagram of NbCl₄ complex]

would of course be diamagnetic, owing to spin pairing of the single d electrons of each niobium atom, but it would also be a colored species due to the presence of d electrons. These facts for the proposed structure of the purple compound are consistent with purple compound's magnetic susceptibility (diamagnetic) and its color (purple), which was caused by the presence of d electrons (as proven by the d-d transition observed in the UV/visible spectrum of the purple compound). Further support for the hypothesized structure is the extended crystal structure of NbCl₄.
which possesses d electrons, but it exists as a diamagnetic species (due to spin pairing). If the extended structure of NbCl₄ is not completely broken up (into discrete paramagnetic entities), previous to its reaction with 8-HQ, then the proposed structure for the purple compound is plausible. Additional analytical data, such as infrared and ¹H N.M.R., indicate that coordination to niobium has occurred, also supporting the existence of the proposed structure for the purple compound. Now, in order to demonstrate the likelihood for the existence of the proposed structures (for the yellow/green and the purple compounds), a reasonable reaction showing the conversion (via decomposition) of one structure to the other had to be determined. It was previously observed that the purple compound decomposed to the yellow/green compound upon its exposure to moisture. Therefore, it is likely that the purple compound decomposes to the yellow/green compound via a hydrolysis step, followed by an oxidation step:
in which HCl(g) and H2(g) are the assumed by-products of the reaction. The last bit of data which would lend credence to this proposed reaction are the results of the test for HCl(g) evolution of the purple compound as it decomposes. As it turns out, the test results seemed to indicate that HCl(g) evolved from the purple compound upon decomposition. Therefore, this proposed reaction involving the decomposition of the purple compound to the
yellow/green compound was the most reasonable one which could be determined, based on the (limited) experimental evidence.

IV. Conclusion

Thus, the structures for both the yellow/green (p.92) and the purple (p.95) compounds, as well as the decomposition reaction (p.97) which converts one to the other, seem to be reasonable, based on consistencies with the experimental and analytical data. However, in light of these results, the question remains as to why the desired Nb(8-Q)₄ complex was not synthesized, and why was the synthesized purple compound obtained instead? Part of the answer to this question is available in the previous discussion section, but the remainder of the answer is sheer speculation at this point. That is, owing to differences in the apparatus and the experimental techniques used, as compared to those used in the major reference for this synthesis¹, it is possible that the desired Nb(8-Q)₄ was not able to form, because the reaction was not able to go to completion (owing to the extended structure of NbCl₄), thus producing the purple compound which was isolated. Therefore, the products obtained from the attempted synthesis of Nb(8-HQ)₄ were analyzed to the fullest extent possible, and the question of why the
desired product was not isolated, has potentially been explained.

In short, much progress in the way of improving experimental techniques, apparatus, and problem-solving abilities has been made over the course of this research project. Future extensions of this work, such as incorporating the newly refurbished glovebox into the project, the synthesis of a bis(quadridente)niobium(IV) complex using the H2BHBE ligand, as well as other novel complex syntheses remain to be explored. Though no completely desirable results were obtained from this research project, the experience and knowledge gained from these studies will benefit myself and persons working on similar projects in the future.
V. Appendix of Spectra

The collected infrared, $^1$H N.M.R., $^{13}$C N.M.R., UV/visible, and E.S.R. spectra of the ligands and complexes.

<table>
<thead>
<tr>
<th>Infrared spectra</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$BAPE</td>
<td>102</td>
</tr>
<tr>
<td>H$_2$BTAE</td>
<td>103</td>
</tr>
<tr>
<td>H$_2$BHBE</td>
<td>104</td>
</tr>
<tr>
<td>H$_2$DSP</td>
<td>105</td>
</tr>
<tr>
<td>8-HQ</td>
<td>106</td>
</tr>
<tr>
<td>yellow/green compound</td>
<td>107</td>
</tr>
<tr>
<td>purple compound</td>
<td>108</td>
</tr>
</tbody>
</table>

$^1$H N.M.R. spectrum in CDCl$_3$ obtained on the Perkin-Elmer R-600.

H$_2$BAPE                                             | 109  |

$^1$H N.M.R. spectra in CDCl$_3$ obtained on the Nicolet NT-200.

8-HQ                                                  | 110  |
| yellow/green compound                                  | 111  |
| purple compound                                        | 112  |

$^1$H N.M.R. spectra in DMSO-d$_8$ obtained on the Bruker WP-200.

8-HQ                                                  | 113  |
| yellow/green compound                                  | 114  |
| purple compound                                        | 115  |
$^{13}$C N.M.R. spectra in CDCl$_3$ obtained on the Bruker WP-100.

8-HQ ................................................................. 116
yellow/green compound ........................................ 117
purple compound ................................................... 118

$^{13}$C N.M.R. spectra in DMSO-d$_6$ obtained on the Bruker WP-200.

8-HQ ................................................................. 119
yellow/green compound ........................................ 120

UV/visible spectra in methylene chloride.

8-HQ ................................................................. 121
yellow/green (unwashed) ....................................... 122
yellow/green (washed) .......................................... 123
purple compound -initial ....................................... 124
  -after 15 min ................................................. 125
  -after 30 min ................................................. 126
  -after 45 min ................................................. 127
  -after 90 min ................................................. 128
decomposed purple (diluted) compound -after 24 hrs... 129

Attempted E.S.R. spectrum in acetonitrile.

NbCl$_4$ (approximately 0.1 M) ............................... 130
Infrared spectrum of H₂BAPE.
Infrared spectrum of H₂BHBE.
Infrared spectrum of 8-HQ.
Infrared spectrum of yellow/green compound.
Infrared spectrum of purple compound.
$^1$H N.M.R. spectrum of 8-HQ.
$^1$H N.M.R. spectrum of yellow/green compound.
1H N.M.R. spectrum of purple compound
$^{1}H$ N.M.R. spectrum of yellow/green compound.
$^1$H N.M.R. spectrum of purple compound.
$^{13}$C N.M.R. spectrum of yellow/green compound.
$1^3$C N.M.R. spectrum of purple compound.
13C N.M.R. spectrum of yellow/green compound.
UV/visible spectrum of 8-HQ.
UV/visible spectrum of yellow/green compound (unwashed).
UV/visible spectrum of yellow/green compound (washed).
UV/visible spectrum of purple compound (after 90 minutes).
UV/visible spectrum of decomposed purple compound (after 24 hours and diluted).
E.S.R. spectrum of NbCl₄ in acetonitrile.

1 V

LF ESR SIGNAL

NbCl₄ ~ 0.1 M in NCM2
Modo= 2
Gain= 0.02
NPTS= 500
NAVC= 1
DATE 04-28-1989

0 V

Sweep= 111 G
SW ST= 17 G
RF At= 17 dB

-1 V
VI. References


