

THE REACTIONS OF TRANSITION METAL IONS WITH
AN AROMATIC TETRAMINE AND SOME
CONDENSATION PRODUCTS

Thesis for the Degree of M. S.

MICHIGAN STATE UNIVERSITY

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1971

100-100-100



ABSTRACT

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By

Thomas Carl Creitz

A nickel(II) complex of 1,2,4,5-tetraminobenzene (TAB) has been prepared in which TAB functions as a bridging ligand. Elemental and infrared analyses confirmed the bridging donor behavior of TAB.

A nickel(II) complex of the Schiff base $\alpha, \alpha', \alpha'', \alpha'''$ -(1,2,4,5-benzenetetrayltetranitrilo)tetra-o-cresolato has been synthesized by either of two methods: 1) In situ condensation of salicylaldehyde with TAB in the presence of nickel(II); 2) The direct reaction of $\alpha, \alpha', \alpha'', \alpha'''$ -(1,2,4,5-benzenetetrayltetranitrilo)tetra-o-cresol with nickel(II). Analogous metal(II) Schiff base complexes with zinc and copper have been prepared by Method 2. All these compounds were characterized by elemental and infrared techniques.

The syntheses of polymeric nickel(II) macrocyclic complexes were attempted by the condensation of 2,3-butanedione or acetone with TAB in the presence of nickel(II). The infrared spectra of the proposed macrocyclic complexes could not be clearly interpreted.

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Thomas Carl Creitz

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1971

To
Mom, Dad, and Judy

ACKNOWLEDGMENTS

The author is deeply indebted to Dr. Gordon A. Melson for his inspiration, competent guidance, and friendship throughout the course of this research.

The author wishes to express his gratitude to the Department of Chemistry, Michigan State University and the Inorganic Faculty members for the financial aid and experience gained as a Graduate Teaching Assistant while attending this university.

Special appreciation is also expressed to Miss Cynthia L. Drew for her helpful assistance in the typing of the drafts of this work.

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I. INTRODUCTION

In the last two decades, research endeavors in polymer chemistry have been directed toward the synthesis of coordination polymers due to the growing need for polymers of high thermal stability.¹ It was hoped that a coordination polymer could be prepared that would exhibit stability at elevated temperatures and yet meet the required specifications of purely organic polymers—flexibility and elasticity.²

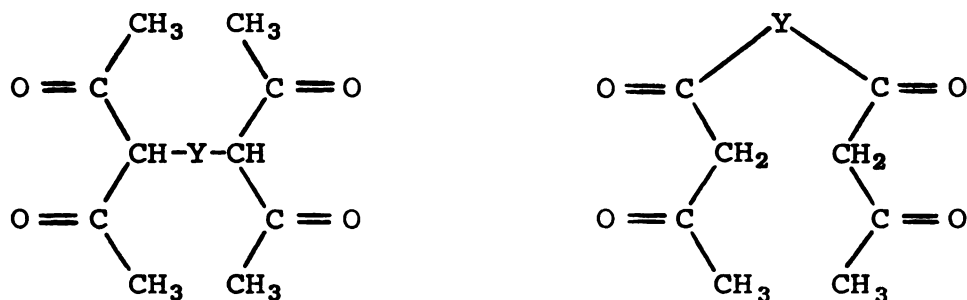
A coordination polymer is defined as a substance with repeating units containing metal ions in the backbone acting as acceptors in coordinate-covalent bonds.³ Coordination polymers can be synthesized in three general ways:¹ 1) polymerization through coordination; 2) polymerization through the functional groups of monomers containing coordinated metal ions; 3) metallization of purely organic polymers which contain suitably situated donor groups. This thesis concerns only the synthesis of coordination polymers by Method 1.

With a few exceptions, the work that has been done on coordination polymers has been concerned with linear polymers in which chelation is incorporated into the polymeric backbone.² This emphasis on chelation stems from the thermodynamic stability associated with the "chelate effect".⁴

Other properties may be affected by the inclusion of coordinated metal ions into the polymer chain. There are examples known where an organic ligand coordinated to a metal ion is stabilized toward hydrolysis,⁵ but this is not always the case.

In applying the chelate effect to synthesizing a long chain coordination polymer by Method 1, ligands have been used in which there are two chelating sites so related that both cannot chelate to the same coordination center. Reacting these bis-chelating ligands with metal ions in a one-to-one molar ratio should yield a long chain polymer.

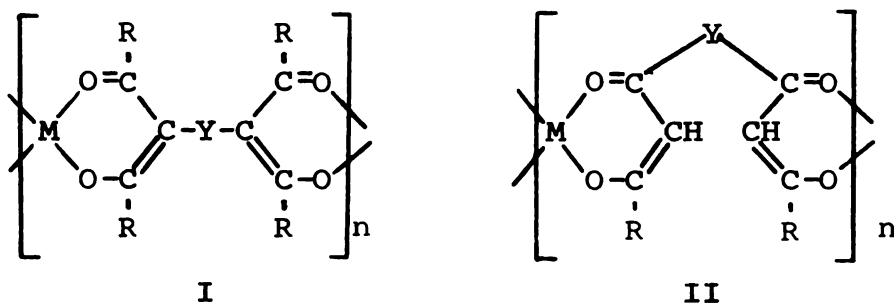
Most success was attained in the development of plastic coordination polymers with the bis-(β -diketones), in which the two chelating sites were not rigidly bound to one another.² β -diketones can be linked together to form bis-chelating groups in either of two ways: through the methylene groups or through the end groups of the ketone.



where Y = alkyl, aryl, or substituted alkyl substituents. Both types of bis-(β -diketones) have been investigated.

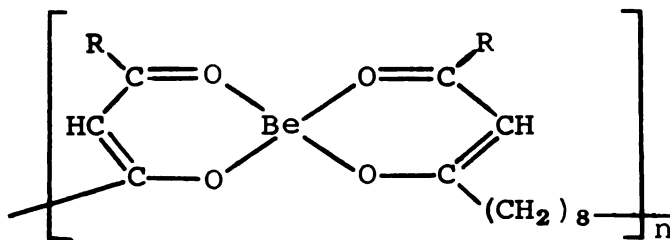
Wilkins and Wittbecker⁶ were the first to prepare polymeric bis-(β -diketone) complexes by allowing a

bis-(β -diketone) to react with various bivalent metal ions, namely nickel(II), copper(II), zinc(II), cobalt(II), and beryllium(II). In those cases where the β -diketone functions were directly bonded, or Y was a simple rigid group such as methylene or phenylene, the products were insoluble and intractable. However, where Y was a polymethylene chain, moldable products with fiber-forming properties were produced. In all cases, the degrees of polymerization were low. They proposed the polymeric species to have structures I or II depending upon the bis-(β -diketone) used.



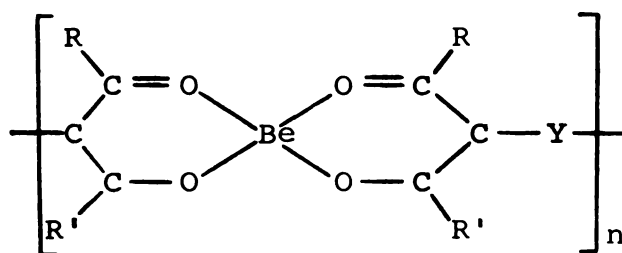
However, Oh and Bailar⁷ have shown by elemental analysis of the same bis-(β -diketone) polymers that they contained hydroxyl groups, either as ol bridges or as chain ends.

Kluiber and Lewis⁸ prepared polymers of high molecular weight with beryllium(II) having the following polymeric unit:



These polymers were flexible at room temperature and had high tensile strength characteristic of high molecular-weight, linear polymers. However, one would not expect them to show high thermal stability, since a beryllium atom cannot stabilize a long methylene chain.

Klein and Bailar⁹ synthesized beryllium complexes of the general formula $\text{Be}(\text{H}_3\text{CCOXCOCH}_3)_2$, where X was a reactive group such as $\text{C}(\text{O})\text{OC}_2\text{H}_5$, OH, or NH_2 . These complexes have been shown to react through their functional groups with appropriate difunctional organic molecules to produce polymers of the type shown below:

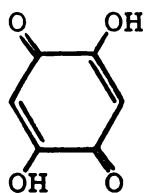


for $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_6\text{H}_5$; $\text{Y} = \overset{\text{O}}{\parallel}\text{CO}(\text{CH}_2)_2\overset{\text{O}}{\parallel}\text{OC}$, $\overset{\text{O}}{\parallel}\text{CNH}(\text{CH}_2)_6\overset{\text{O}}{\parallel}\text{NHC}$, and $\overset{\text{O}}{\parallel}\text{C}(\text{m-C}_6\text{H}_4)(\text{NH}_2)_2\overset{\text{O}}{\parallel}\text{C}$; for $\text{R} = \text{CH}_3$, $\text{R}' = \text{CH}_3$, $\text{Y} = \text{OSi}(\text{C}_6\text{H}_5)_2\text{O}$, $\text{p-C}_6\text{H}_4(\text{COO})_2$, $\text{p-C}_6\text{H}_4(\text{HFCOO})_2$, $\text{NHSi}(\text{C}_6\text{H}_5)_2\text{NH}$, $\text{p-C}_6\text{H}_5(\text{CONH})_2$, and $\text{p-C}_6\text{H}_5(\text{NHCONH})_2$. They were very similar in physical appearance to their organic analogs with weights of 1000 or less. Some were glasses at room temperature and could be drawn into fibers when molten.

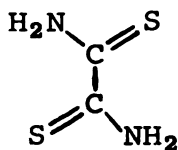
A number of other bis-chelating ligands quite similar to bis-(β -diketones) have been studied, but not as fully as the bis-(β -diketones). Less effort has been devoted to the

study of polymeric metal derivatives of bis(Schiff bases),¹⁰ bis(hydroxyquinolines),^{11,12} bis(amino acids),² bis(thio-picolinamides),¹³ bis(dicarboxylic acids),^{14,15} bis(hydroxy acids),¹⁴ bis(hydroxy-aldehydes),¹⁶ bis(aminophenols),² bis(dithiocarbamic acids),¹⁷ bis(thiosemicarbazones),² bis-(ketoimides),² bis(dioximes),¹¹ bis(dithiocarboxylic acids),² and poly(hydroxyphenyl)triazines.² In almost all cases, characterization was very difficult because of their insolubility and resistance to melting. In general, the metal ions used in the studies just mentioned have been those with a characteristic coordination number of four, namely nickel(II), copper(II), zinc(II), and cobalt(II). Use of these metals eliminated the possibility of crosslinking.

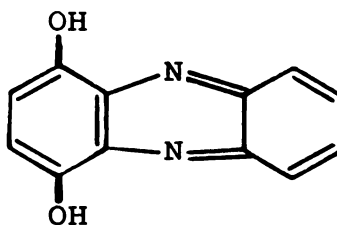
Very little research has been done in the area of bis-chelating ligands in which the chelating sites are joined very rigidly to one another.² Some ligands which would act as bis-chelating agents are the anions derived from compounds such as 2,5-dihydroxy-p-benzoquinone (a), dithiooxamide (b), 1,4-dihydroxyphenazine (c), and 5,8-dihydroxy-1,4-naphthoquinone (d).²



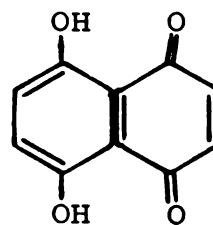
(a)



(b)

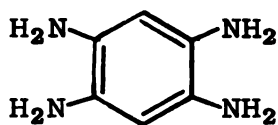


(c)



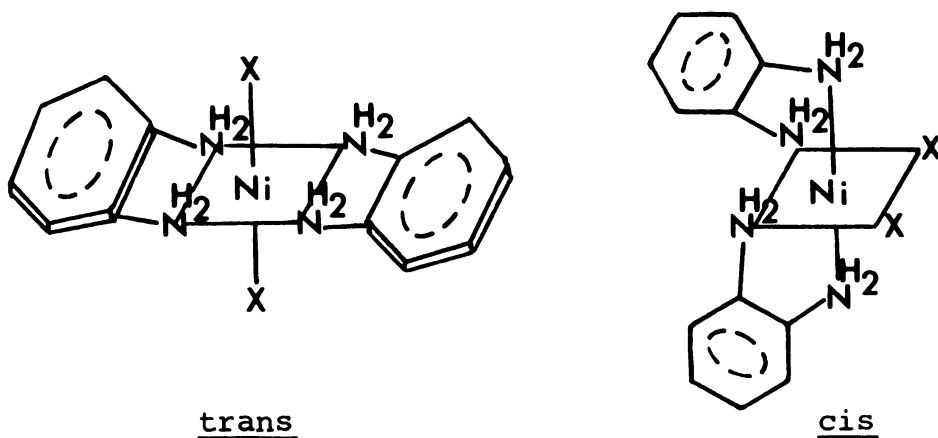
(d)

The neutral ligand, 1,2,4,5-tetraminobenzene shown below



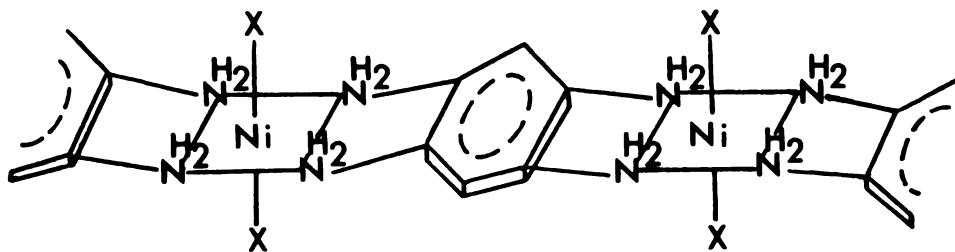
should also function as a bis-chelating ligand, since its structure is such that it could act as a bridging ligand between two metal ions. In this case, all four amino groups would be coordinated, however, not to the same metal ion. This thesis concerns the attempted synthesis of coordination polymers containing this ligand.

Kakazai and Melson¹⁹ have shown by far infrared spectra that six-coordinate complexes of the type $\text{Ni}(\text{opda})_2\text{X}_2$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}$ and $\text{opda} = 1,2\text{-diaminobenzene}$, had the trans (D_{4h}) stereochemical configuration in preference to the cis (C_{2v}) configuration.



Based on this evidence, one may extrapolate to the case of 1,2,4,5-tetraminobenzene, where one would also expect a

D_{4h} environment about the nickel(II) ion. However, because there are two chelating sites per ligand, each tetramine molecule is not only able to occupy two coordination sites in one octahedrally coordinated metal species, but also two coordination sites in an adjacent octahedrally coordinated species. Acting as a bridging ligand, 1,2,4,5-tetraminobenzene will link metal ions together and produce a coordination polymer. Thus for the reaction of 1,2,4,5-tetraminobenzene with nickel(II) halide in a one-to-one molar ratio, a long chain coordination polymer is expected to form, composed of a linear sheet-like plane consisting of alternate nickel(II) ions and ligand groups. The halide ions will be coordinated to the nickel(II) ions in trans positions. (See figure below.)



The formation of two five-membered chelate rings about each nickel(II) ion in the proposed coordination polymer should provide considerable thermodynamic stability. However, it is expected that this coordination polymer would be very easily hydrolyzed in aqueous solution, since 1,2,4,5-tetraminobenzene is anticipated to be a weak

coordinating ligand. Linking together of the coordinated amine groups by a two or three carbon bridge to produce a macrocyclic ring about each nickel(II) ion would not only make it more resistant to hydrolysis, but would provide additional thermodynamic stability. This could be accomplished by the condensation reaction of the (tetramino)-nickel(II) polymeric species with 2,3-butanedione or acetone. Curtis has shown that macrocyclic complexes formed by the condensation of (diaminoethane)nickel(II) complexes with acetone are very resistant to hydrolysis.²⁰

The final condensation product should exhibit enhanced stability, both kinetic and thermodynamic, due to the infinite array of macrocyclic rings each coordinated strongly to a nickel(II) ion.

II. EXPERIMENTAL

A. Reagents and Solvents

1,2,4,5-Tetraminobenzene tetrahydrochloride (98% Aldrich), sodium hydroxide (97.7% Baker), anhydrous sodium acetate (99.0% MC & B), salicylaldehyde (MC & B), acetone (reagent grade, MC & B), and 2,3-butanedione (99% Aldrich) were used as purchased. Anhydrous nickel(II) chloride was prepared by the vacuum drying of nickel(II) chloride hexahydrate (98% Mallinckrodt) at 161° for 24 hours.

Reagent grade methanol was dried over molecular sieves and deoxygenated by bubbling nitrogen through the solvent for 30 minutes. Reagent grade ethyl ether was dried and deoxygenated over sodium metal. Nitrogen, which was used as a purging agent and the inert atmosphere, was "Hi-Pure" nitrogen purchased from the Liquid Carbonic Division of General Dynamics. The nitrogen was dried by passing it through a magnesium perchlorate drying column.

Preparation of the methanolic solution of anhydrous nickel chloride and the methanolic solution of free base, TAB, was performed in the nitrogen-atmosphere glovebox.

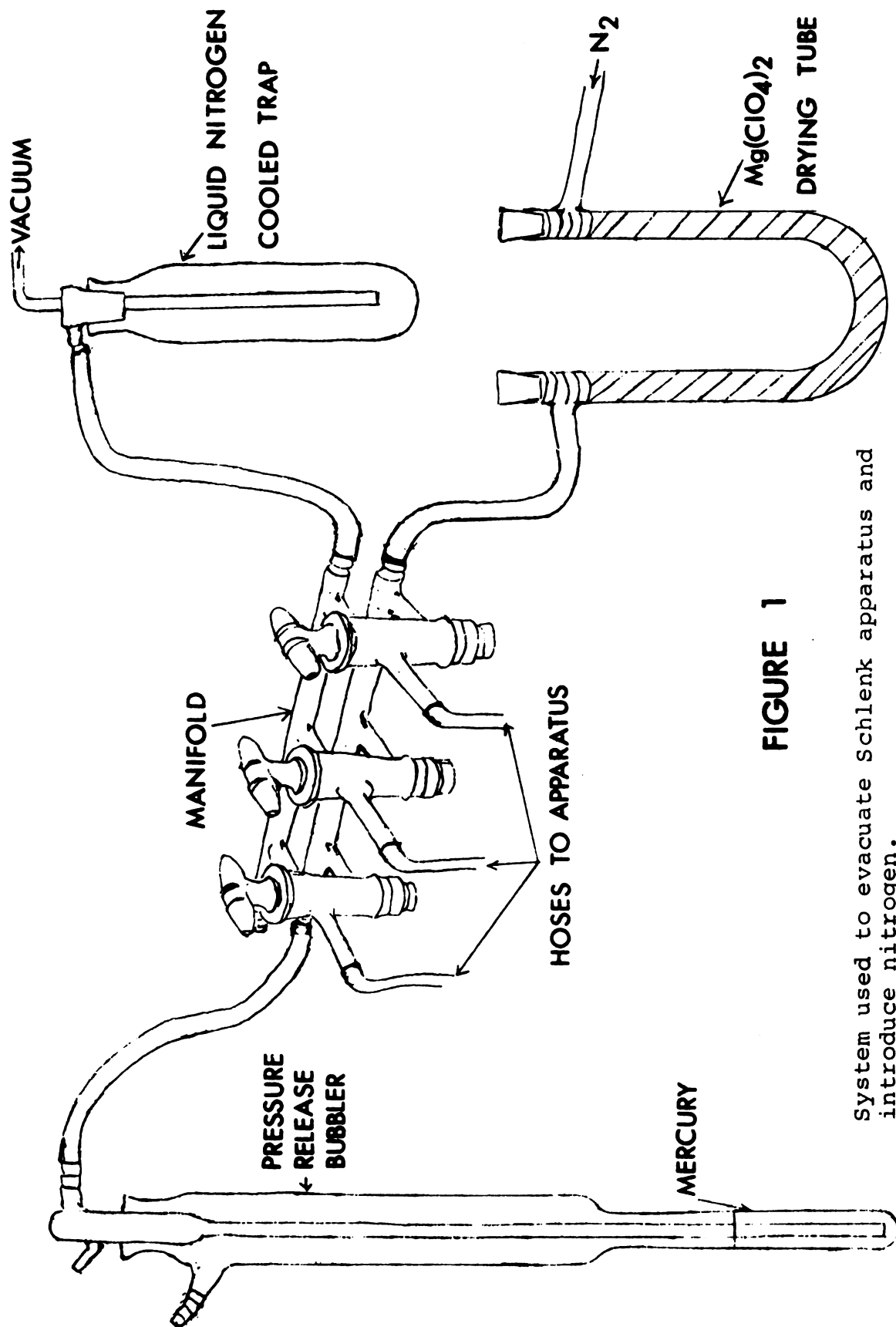
1,2,4,5-Tetraminobenzene tetrahydrochloride and its free base, 1,2,4,5-tetraminobenzene are abbreviated herein

as TAB·4HCl and TAB, respectively. $\alpha,\alpha',\alpha'',\alpha'''$ - (1,2,4,5-benzenetetrayltetranitrilo)tetra-o-cresol and $\alpha,\alpha',\alpha'',\alpha'''$ - (1,2,4,5-benzenetetrayltetranitrilo)tetra-o-cresolato are abbreviated BTCH₄ and BTC, respectively.

B. General Techniques

Since the free base, TAB, is readily oxidized by air and anticipated to be a weak coordinating ligand, all operations involved in the synthesis and reactions of the free base were conducted in the presence of nitrogen under anhydrous conditions. Schlenk-type glassware designed for bench-top operation in conjunction with a nitrogen-atmosphere glovebox made possible the desired experimental conditions. The Schlenk-type glassware was purchased from Kontes Glass Company in Vineland, New Jersey.

The essential feature of most of the Schlenk apparatus was a sidearm fitted with a stopcock. Through this sidearm the equipment was evacuated to eliminate air and nitrogen was introduced. A high vacuum was not necessary because the purge cycle was repeated at least three times. Because of the multiple operations involved in handling the apparatus, a small manifold equipped with a series of two-way stopcocks was employed (Figure 1). Attached to the lower section of the manifold was a source of purified nitrogen and to the upper section a mechanical vacuum pump, protected by a liquid nitrogen-cooled trap. Also attached to the lower section of the manifold was a pressure-release bubbler, which

**FIGURE 1**

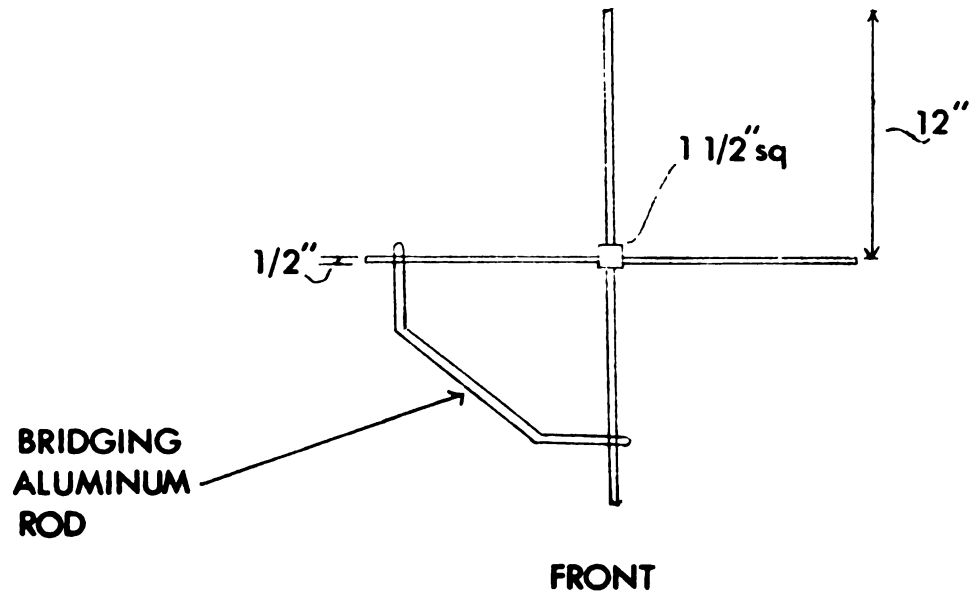
System used to evacuate Schlenk apparatus and introduce nitrogen.

was used to monitor the pressure of the Schlenk system.

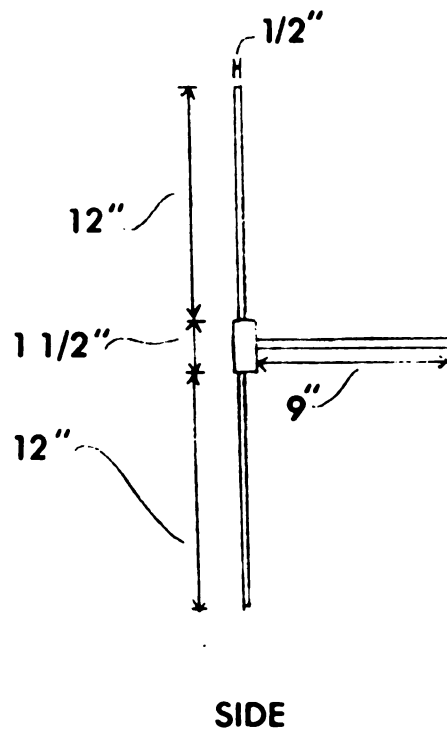
To reduce the chance of breakage when inverting a complex Schlenk assembly, a Schlenk cross (Figure 2) was constructed of four twelve-inch rods one-half inch in diameter attached to a five-eighth-inch thick $1\frac{1}{2}$ inch square steel block. Inserted perpendicular to these rods was a nine-inch aluminum rod one-half inch in diameter. A bridging aluminum rod was attached between two of the adjacent aluminum extensions and served as an additional point of attachment for the Schlenk assembly. The Schlenk assembly was attached to the Schlenk cross by clamping two of the central pieces firmly. All other pieces were held together at the joints by Kem-Klamps.

A purge cycle consisted of evacuation to eliminate air and introduction of nitrogen. To purge a system efficiently the purge cycle was repeated at least three times. Purging a system was accomplished by attaching a vacuum from the aforementioned manifold to one sidearm and stopcock on the system. With all the other sidearm stopcocks closed, the two-way valve was turned to the vacuum line. After pumping for five minutes, the two-way valve was turned to the nitrogen line while simultaneously turning the outlet valve on the nitrogen tank. Nitrogen was introduced until atmospheric pressure was attained as monitored by the pressure-release bubbler. This procedure was repeated at least two more times. The system was then ready for use.

FIGURE 2



Schlenk cross, to which the Schlenk apparatus was attached.



To attach a Schlenk flask to the Schlenk assembly, the male joint to receive the Schlenk flask was closed with a female cap and the Schlenk assembly was purged at least three times. Then with all the stopcocks closed, one vacuum hose was attached from the manifold to a sidearm on the purged Schlenk assembly and another hose from the manifold to the sidearm on the Schlenk flask. Before opening any stopcocks, each vacuum hose was purged three or four times. Then with both of the two-way stopcocks open to the nitrogen line, the stopcocks adjoining the hoses were opened. The outlet valve on the nitrogen tank was opened and the stopper on the Schlenk flask was slowly eased out of the joint. The outlet valve was opened even more to allow for a rapid flow of nitrogen. The female cap on the complex Schlenk assembly was then removed, and the flask was quickly joined to the assembly. The entrance of air was minimized by the rapid flow of nitrogen out of the two pieces while they were momentarily open. The stopcocks on the assembly and on the manifold were closed and the vacuum hoses removed. The apparatus was now ready for use.

C. Synthesis

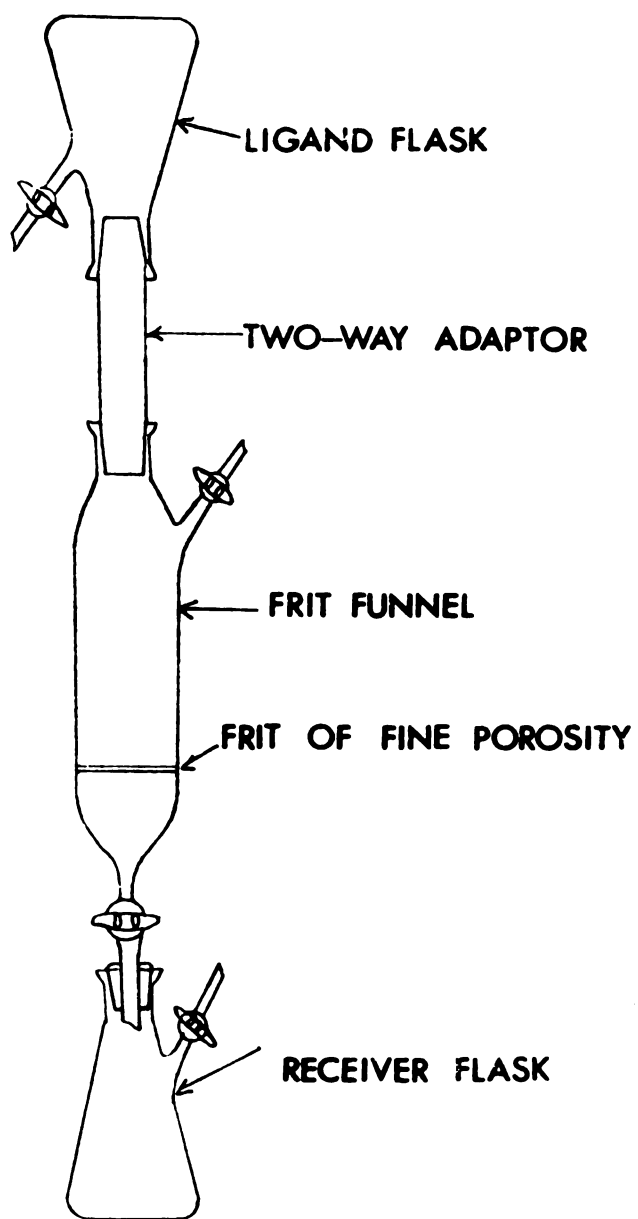
1. Preparation of 1,2,4,5-Tetraminobenzene

A solution containing 0.16 gram (0.004 mole) of sodium hydroxide in 50 ml of methanol was added to 0.284 gram (0.001 mole) of TAB•4HCl and stirred for 15 minutes. Fifty milliliters of ethyl ether was then added and stirring was

continued for five more minutes. The precipitated sodium chloride was removed by filtration (Figure 3) and washed with 10 ml of ethyl ether introduced into the fritted funnel from a 10 ml syringe. The solvent was removed from the filtrate by vacuum distillation at room temperature. The tan amorphous solid was dried in vacuo at room temperature for 12 hours. Obtained was 0.126 gram of the free base, TAB; yield, 90%.

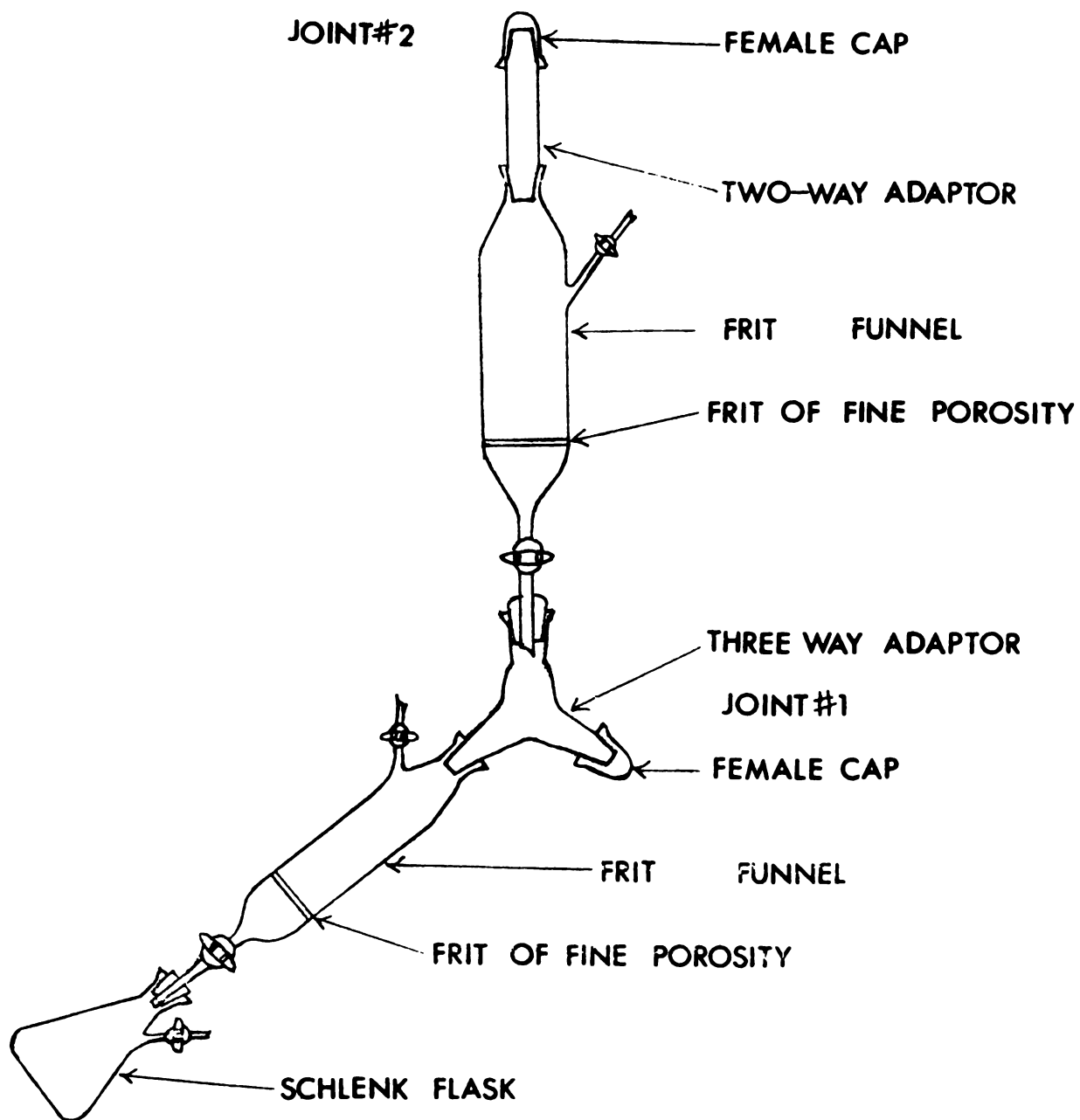
2. The Reaction of 1,2,4,5-Tetraminobenzene with Nickel(II) Chloride

A Schlenk flask containing a solution of 0.13 gram (0.001 mole) of anhydrous nickel(II) chloride in 50 ml of methanol was attached to joint #1 (Figure 4). The Schlenk cross was then inverted and a Schlenk flask containing a methanol-ethyl ether solution of TAB, prepared as described previously, was attached to joint #2. The Schlenk cross was returned to its original position and the TAB solution was filtered into the methanolic solution of nickel(II) chloride by partial evacuation of the lower Schlenk flask. After stirring for 3 hours, the precipitate was removed by filtration which was accomplished by a 45° counterclockwise rotation of the Schlenk cross and partial evacuation of the lower Schlenk flask. The precipitate was washed by the introduction of 10 ml of anhydrous deoxygenated methanol into the frit funnel from a 10 ml syringe while maintaining a positive nitrogen pressure. After washing the

FIGURE 3

Apparatus used for the preparation of 1,2,4,5-tetraminobenzene.

FIGURE 4



Apparatus used for the reaction of 1,2,4,5-tetraamino-benzene with nickel(II) chloride.

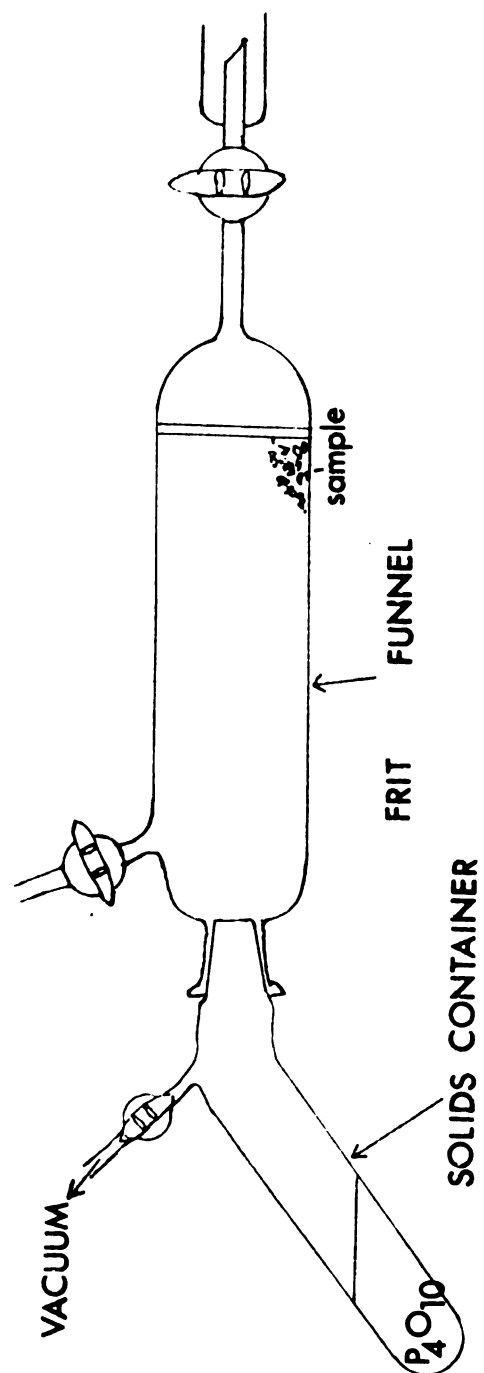
precipitate, a hooked stopper was inserted into the top joint of the frit funnel and the lower funnel stopcock was closed. Phosphorus pentoxide was placed in the solids container (Figure 5), which was then capped and purged at least three times. This vessel was connected under nitrogen flush to the frit funnel and a vacuum was drawn on the assembly (Figure 5) for 12 hours. The gray amorphous powder (0.006 gram) was obtained.

Anal. Calcd for $\text{Ni}(\text{C}_6\text{N}_4\text{H}_{10})\text{Cl}_2$: C, 26.91; H, 3.77; N, 20.92;
 Found: C, 25.28; H, 3.89; N, 18.30.

3. The Preparation of $\alpha, \alpha', \alpha'', \alpha'''$ - (1,2,4,5-Benzene-tetrayltetranitrilo)tetra-o-cresol

To 0.70 gram (0.0025 mole) of $\text{TAB} \cdot 4\text{HCl}$ were added 1.2 grams (0.015 mole) of anhydrous sodium acetate in 25 ml of methanol followed by addition of 1.05 ml (0.01 mole) of salicylaldehyde. The resulting mixture was stirred and refluxed for 7 hours under nitrogen. The residue was removed by filtration, washed with 50 ml of methanol, and dried in vacuo over P_4O_{10} for 12 hours. One gram of the orange amorphous powder was obtained; yield, 75%.

Anal. Calcd for $\text{C}_{34}\text{H}_{26}\text{N}_4\text{O}_4$: C, 73.63; H, 4.73; N, 10.10.
 Found: C, 71.01; H, 4.67; N, 11.28.

**FIGURE 5**

Apparatus used to dry a solid sample in vacuo.

4. The Reactions of $\alpha, \alpha', \alpha'', \alpha'''$ - (1,2,4,5-benzenetetrayltetranitrilo)tetra-o-cresol with Transition Metal Ions

- a. The Preparation of $[\mu - [\alpha, \alpha', \alpha'', \alpha''' - (1,2,4,5\text{-benzenetetrayltetranitrilo})\text{tetra-}\underline{o}\text{-cresolato}]]\text{-dizinc(II)}$.

Five one hundredths gram (0.0009 mole) of BTCH_4 was added to a solution of 0.0395 gram (0.00018 mole) of zinc(II) acetate dihydrate in 100 ml of a 50:50 mixture of acetone and methanol at the reflux temperature (Figure 6). After 26 hours, the precipitate was removed by filtration, washed with methanol, and dried in vacuo over P_4O_{10} for 12 hours. Obtained was 0.049 gram of an orange amorphous powder; yield, 80%.

Anal. Calcd for $\text{Zn}_2(\text{C}_{34}\text{H}_{22}\text{N}_4\text{O}_4)$: C, 59.94; H, 3.26; N, 8.22.

Found: C, 55.06; H, 3.71; N, 8.59.

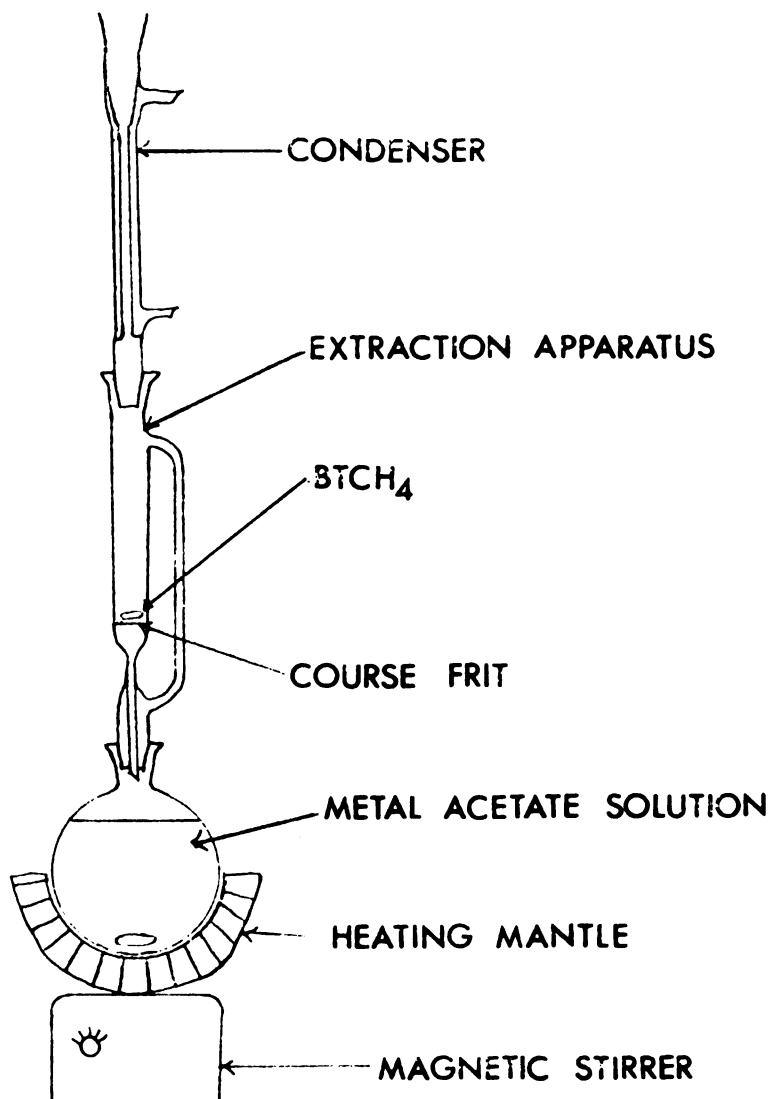
- b. The Preparation of $[\mu - [\alpha, \alpha', \alpha'', \alpha''' - (1,2,4,5\text{-benzenetetrayltetranitrilo})\text{tetra-}\underline{o}\text{-cresolato}]]\text{-dicopper(II)}$.

The procedure was analogous with that for the zinc(II) complex with the exception that copper(II) acetate monohydrate was used and 0.058 gram of the red-brown amorphous powder was obtained; yield, 95%.

Anal. Calcd for $\text{Cu}_2(\text{C}_{34}\text{H}_{22}\text{N}_4\text{O}_4)$: C, 60.26; H, 3.27; N, 8.27.

Found: C, 55.73; H, 3.51; N, 8.31.

FIGURE 6



Appartus used to prepare $\text{M}_2(\text{BTC})$ complexes, where $\text{M} =$ zinc(II), copper(II), and nickel(II).

- c. The Preparation of $[\mu - [\alpha, \alpha', \alpha'', \alpha'''] - (1, 2, 4, 5 - \text{benzenetetrayltetranitrilo}) \text{tetra-}\underline{\text{o}}\text{-cresolato}]] - \text{dinickel(II)}.$

The procedure was analogous with that for the zinc(II) complex with the exception that nickel(II) acetate tetrahydrate was used and 0.045 gram of the brown amorphous powder was obtained; yield, 75%.

Anal. Calcd for $\text{Ni}_2(\text{C}_{34}\text{H}_{22}\text{N}_4\text{O}_4)$: C, 61.13; H, 3.32; N, 8.39.

Found: C, 57.16; H, 3.48; N, 8.10.

5. The Condensation of Salicylaldehyde with 1,2,4,5-Tetraminobenzene in the Presence of Nickel(II)

A solution of 1.24 grams (0.005 mole) of nickel(II) acetate tetrahydrate in 100 ml of methanol was added to a mixture of 0.70 gram (0.0025 mole) of $\text{TAB} \cdot 4\text{HCl}$ and 1.2 grams (0.015 mole) of anhydrous sodium acetate in 100 ml of methanol. This was followed by addition of 1.05 ml (0.01 mole) of salicylaldehyde. The resulting mixture was stirred and refluxed for 3 hours under nitrogen. The residue was removed by filtration, washed with methanol, and dried in vacuo over P_4O_{10} for 12 hours. Obtained ~~were~~ 1.33 grams of the brown amorphous powder; yield, 75%.

Anal. Calcd for $\text{Ni}_2(\text{C}_{34}\text{H}_{22}\text{N}_4\text{O}_4)$: C, 61.13; H, 3.32; N, 8.39.

Found: C, 58.24; H, 3.42; N, 8.03.

6. The Condensation of 2,3-Butanedione with 1,2,4,5-Tetraminobenzene in the Presence of Nickel(II)

A solution of 0.32 gram (0.0025 mole) of anhydrous nickel(II) chloride in 100 ml of methanol was added with stirring to a mixture prepared by adding 0.40 gram (0.01 mole) of sodium hydroxide in 100 ml methanol to 0.70 gram (0.0025 mole) of TAB·4HCl. To this mixture was added 0.88 ml (0.01 mole) of 2,3-butanedione and stirring under nitrogen atmosphere at room temperature was continued for 4 days. The residue (0.41 gram) was removed by filtration, washed with methanol, and dried in vacuo over P₄O₁₀ for 12 hours. The gray residue was identified by mass spectrometry to have a molecular formula of C₁₀H₁₄N₄. The solvent was removed from the filtrate under reduced pressure and the remaining solid was dried in vacuo over P₄O₁₀ for 12 hours. The fine brown powder (1.13 grams) was found to contain nickel(II) by igniting a sample of the powder, digesting it with concentrated hydrochloric acid, adjusting the pH of the solution between 7 and 8, and precipitating the nickel(II) ions with dimethylglyoxime.

7. The Condensation of 2,3-Butanedione with 1,2,4,5-Tetraminobenzene

The procedure was analogous to the above with the exception that nickel(II) chloride was excluded and the solution was refluxed for 3 hours. The precipitate was removed by filtration, washed with methanol, and dried in vacuo

over P_4O_{10} for 12 hours. The tan product (0.22 gram) was identified by mass spectrometry to have a molecular formula of $C_{10}H_{14}N_4$.

8. The Condensation of Acetone with 1,2,4,5-Tetraminobenzene in the Presence of Nickel(II)

The procedure was analogous with the aforementioned (see 6) 2,3-butanedione condensation with the exception that 7.35 ml (0.01 mole) of acetone were used in place of 2,3-butanedione and the reaction was run for only 24 hours. The resulting orange solution was filtered to remove insoluble impurities and divided into aliquots of 25 ml (A), 25 ml (B), 50 ml (C), and 100 ml (D) in an attempt to isolate the product from solution. Addition of an aqueous solution of sodium perchlorate to solution (A) produced a color change from orange to dark red and no precipitation occurred. Meanwhile, solutions (B), (C), and (D) changed to the same dark red color from exposure to the air. A saturated aqueous solution of zinc(II) chloride was added to solution (B), however, no precipitation resulted. Upon addition of ethyl ether to solution (C), a small amount of gray solid was precipitated, removed by filtration, and dried over P_4O_{10} for 12 hours. The solvent from solution (D) was removed under reduced pressure and the remaining solid was dried in vacuo over P_4O_{10} for 12 hours. The fine brown powder (0.060 gram) obtained was found to contain nickel(II) by igniting a sample of the brown powder, digesting it with concentrated

hydrochloric acid, adjusting the pH of the solution between 7 and 8, and precipitating the nickel(II) ions with dimethylglyoxime.

D. Physical Measurements

Infrared spectra in the region $4000\text{--}250\text{ cm}^{-1}$ were recorded with a Perkin-Elmer Model 457 grating infrared spectrophotometer. Solid spectra were run as Nujol mulls between CSI plates, Visible and ultraviolet spectra were obtained with a Unicam Sp.800B spectrophotometer. Mass spectra were determined with a Hitachi-Perkin-Elmer RMU-60 Spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

III. RESULTS AND DISCUSSION

A thorough study of nickel(II) complexes with aromatic diamines was reported recently by Kakazai and Melson.¹⁹ However, no one has investigated the reactions of aromatic tetramines with nickel(II). This may be due to the fact that in the past most research problems have been carefully selected to avoid complications due to polymer formation.²¹ There is now a growing trend toward the synthesis of inorganic coordination polymers. The neutral ligand, 1,2,4,5-tetraminobenzene, is of such structure that it could act as a bridging ligand between two metal ions. This thesis concerns the investigation of the possibility of forming inorganic coordination polymers with 1,2,4,5-tetraminobenzene.

The free ligand, TAB, was prepared by neutralization of its salt, TAB·4HCl, with sodium hydroxide in a 50:50 methanol-ethyl ether solution to precipitate the sodium chloride and remove it by filtration. On exposure of the yellow ligand solution to air, the solution became dark purple. This color change to purple is common for nearly all aromatic amines and has been ascribed to oxidation.²² It was therefore necessary to perform all operations under oxygen-free conditions to ensure that the species coordinated to the metal ion was a tetramine and not an oxidized species.

If TAB behaves as a bridging ligand, reaction of TAB with nickel(II) chloride in a 1:1 molar ratio should produce a polymeric nickel(II) complex. However, should it function as a bidentate ligand, various stereochemistries would be expected depending upon the metal-to-ligand ratio. For a 1:1 metal-to-ligand molar ratio, a square planar or tetrahedral complex may result. For a 1:2 metal-to-ligand molar ratio, an octahedral complex may result with either cis or trans arrangement of the coordinated chlorides about the nickel(II) ion. For a 1:3 metal-to-ligand molar ratio, an octahedral complex may also result, however, with ionic chlorides.

Experimentally, the addition of a methanol-ethyl ether solution of TAB to a methanolic solution of anhydrous nickel(II) chloride in a 1:1, 10:1 or a 1:5 metal-to-ligand molar ratio produced the same species. A 1:1 metal-to-ligand ratio was confirmed by elemental analyses and infrared spectra. All attempts to isolate a pure nickel(II) complex in its solid state were unsuccessful, since the infrared spectra of nearly all the products indicated the presence of hydroxyl groups by a broad band at 3200 cm^{-1} . These hydroxyl groups may be associated with water, methanol, or nickel hydroxide impurities. Only in a few of the products isolated was it possible to look at the N-H stretching region of their infrared spectra.

In general, it was observed that only slow crystallization of the nickel(II) complex from methanol solution by addition of a small volume of ethyl ether produced a species containing a miniscule amount of water or methanol. Addition of a large volume of ethyl ether to the methanol solution of nickel(II) complex resulted in rapid precipitation and a species containing a considerable amount of water or methanol. The nickel(II) complex containing only a miniscule amount of water was also prepared by addition of a methanolic solution of TAB, in which the sodium chloride had not been removed, to a methanolic solution of anhydrous nickel(II) chloride. In this case, the nickel-to-ligand, nickel-to-chloride, and nickel-to-water molar ratios were respectively, 1:1, 1:6, and 1:4. For this preparation, it is hypothesized that the smaller metal-to-chloride molar ratio compared to the metal-to-water molar ratio favors coordinated chlorides and not coordinated waters. However, this preparation had sodium chloride impurities in the final product.

Various attempts were made to remove the water produced from the neutralization reaction of $\text{TAB} \cdot 4\text{HCl}$ and sodium hydroxide. 2,2-Dimethoxypropane was added to the methanolic TAB solution in one attempt, while in another attempt, the TAB was prepared in methanol over molecular sieves. Evaluation of the success of these methods for eliminating water was difficult, since the O-H stretching frequency for water and methanol is almost identical.

Even by preparing the free ligand TAB by neutralization of its salt, $\text{TAB} \cdot 4\text{HCl}$, with sodium hydroxide in a 50:50 methanol-ethyl ether solution, removing the solvent under reduced pressure, and drying in vacuo for 12 hours, it was not possible to prepare a completely anhydrous or unsolvated free ligand. However, this practically anhydrous ligand was redissolved in methanol and this solution was added to a solution of nickel(II) chloride in a 1:1 metal-to-ligand molar ratio, but the infrared spectrum had a broad band at 3200 cm^{-1} . It was apparent from these observations that water was not the only contaminant, but also methanol. Attempts to find a non-coordinating solvent for the reaction of TAB with nickel(II) chloride were unsuccessful. TAB dissolved in slightly polar or polar organic solvents, however, anhydrous nickel(II) chloride dissolved only in very polar organic solvents, which are also good coordinating solvents.

The pH of the nickel(II) complex solution also presented problems. The pH of an aqueous solution of TAB prepared by neutralization of 0.001 mole of $\text{TAB} \cdot 4\text{HCl}$ with 0.004 mole of sodium hydroxide was 11, while the pH of anhydrous nickel(II) chloride in methanol was 5. Assuming the pH of the methanol-ethyl ether solution of TAB was close to 11, addition of this solution to the methanolic nickel(II) chloride solution lowered the pH. Since basic conditions produce nickel(II) hydroxide and acid conditions protonate the amino groups of TAB, a narrow pH range favors complex formation. This pH range is probably between 6 and 7 pH units,

where the amino groups will be reprotonated to some extent. However, coordination of nickel(II) is expected to change the pK_b of the base due to the polarizing power of the nickel(II) ion and the final nickel(II) complex will contain the tetramine.

A final procedure for the preparation of the nickel(II) complex of TAB was developed. A 50:50 methanol-ethyl ether solution of TAB was added to a methanolic solution of anhydrous nickel(II) chloride. After stirring for 3 hours, the precipitate was removed by filtration and dried in vacuo over P_4O_{10} for 12 hours. The yield of complex from this reaction was of such small quantity that only an infrared spectrum and elemental analyses for C, H, and N were possible. Assuming chloride ions were present in the complex, it was apparent from the elemental analyses that there was a 1:1 metal-to-ligand molar ratio. The low values for C and N and the high value for H is explained by a small amount of water contaminant in the complex. A molecular formula corresponding to $Ni(TAB)Cl_2$ is proposed. This suggests the ligand behaves as a bidentate or a bridging ligand.

It has already been shown^{23,24} that it is possible to distinguish between unidentate and bidentate diamines from a study of the vibrations due to the $\nu(N-H)$, $\delta(NH_2)$, and $\nu(C-N)$ regions of their infrared spectra. In complexes where the diamine functioned as a bidentate ligand with both groups coordinated to the metal ion, there was a

lowering of the position of the $\nu(\text{N-H})$, $\delta(\text{NH}_2)$, and $\nu(\text{C-N})$ when compared with the positions observed for the free ligand. For complexes where the diamine functioned as a unidentate ligand, coordinated and uncoordinated amino groups were present. In this case, in each region of the infrared spectrum, there was a band or bands near to those found in the free ligand indicative of the presence of uncoordinated amino groups and a band or bands of lower frequency corresponding to the coordinated amino groups.

The infrared absorption bands of $\text{Ni}(\text{TAB})\text{Cl}_2$ along with those of the free ligand, are given in Table I. In the complex $\text{Ni}(\text{TAB})\text{Cl}_2$, coordination of the tetramine to the nickel(II) ion resulted in a lowering of the position of the $\nu(\text{N-H})$, $\delta(\text{NH}_2)$, and $\nu(\text{C-N})$ with no bands near to those found in the free ligand. This indicates that all four amino groups are coordinated to nickel(II) ions and TAB behaves as a bridging ligand.

From the 1:1 metal-to-ligand ratio and the bridging behavior of the tetramine in the nickel(II) complex, it is concluded that a polymeric nickel(II) complex is produced. Based on the D_{4h} stereochemical configuration of $\text{Ni}(\text{opda})\text{X}_2$,¹⁹ the structure of $\text{Ni}(\text{TAB})\text{Cl}_2$ is proposed as shown below:

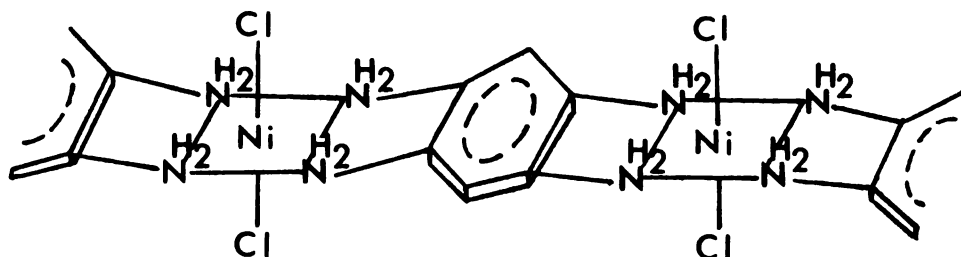
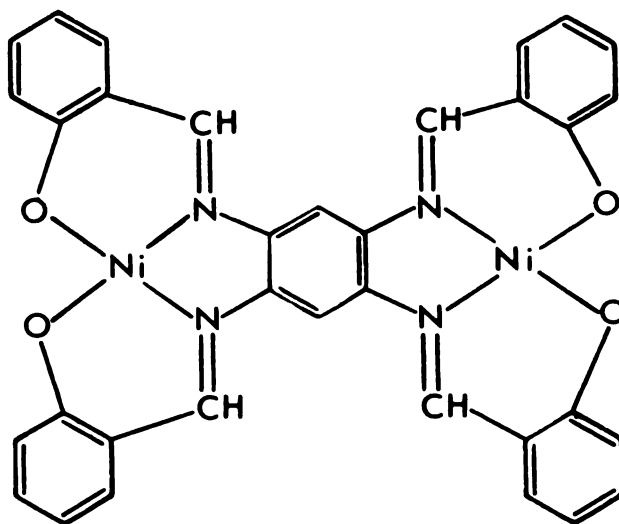


Table I. Infrared data for the free ligand 1,2,4,5-tetraaminobenzene and its nickel(II) complex. All values in cm^{-1} .

Compound	$\nu(\text{N-H})$	$\nu(\text{C-H})$	$\delta(\text{NH}_2)$	$\nu(\text{C-N})$
1,2,4,5-Tetraaminobenzene (TAB)	3360s, 3275s, 3190s	3030m	1605m	1261m
$\text{Ni}(\text{TAB})\text{Cl}_2$	3285s, 3155s, 3125s, 3000s	3030m	1580m	1243m

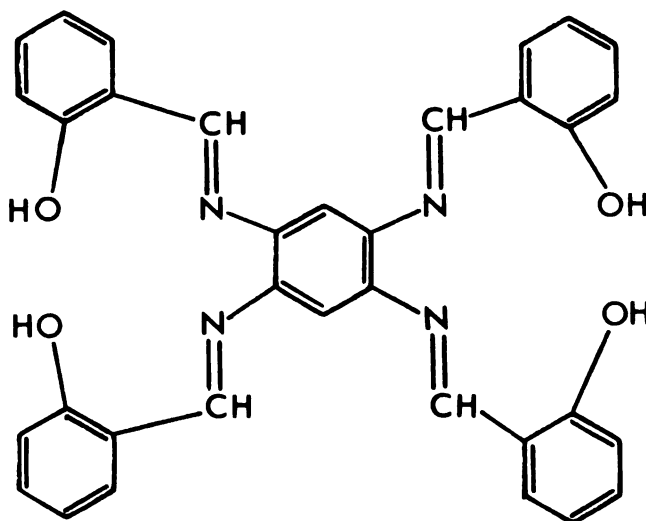
On addition of $\text{Ni}(\text{TAB})\text{Cl}_2$ to an aqueous solution, the solution became dark purple. This behavior is ascribed to hydrolysis of the complex, yielding the hexaaquonickel(II) ion and the free tetramine, which is oxidized. The kinetic stability of $\text{Ni}(\text{TAB})\text{Cl}_2$ could be increased by linking together the coordinated amino groups, since Curtis²⁰ has shown that macrocyclic complexes formed by the condensation of (diaminoethane)nickel(II) complexes with acetone are very resistant to hydrolysis.

In order to investigate the reactivity of the amino groups of TAB in condensation reactions with aldehydes and ketones, salicylaldehyde was added to a methanolic solution of TAB in the presence of nickel(II) acetate tetrahydrate in a 4:1:2 molar ratio. This in situ reaction produced the complex $[\mu\text{-}[\alpha,\alpha',\alpha'',\alpha''']\text{-}(1,2,4,5\text{-benzenetetrayltetra-nitrilo})\text{tetra-}\underline{o}\text{-cresolato}]]\text{dinickel(II)}$ shown below:



(Ni₂BTC)

Ni₂ (BTC) was also prepared by first preforming the ligand, $\alpha,\alpha',\alpha'',\alpha'''$ - (1,2,4,5-benzenetetrayltetranitrilo) - tetra-o-cresol (shown below) and adding this to a 50:50 methanol-acetone solution of nickel(II) acetate tetrahydrate, in a 2:1 metal-to-ligand molar ratio.

(BTCH₄)

Elemental analyses and infrared spectra confirmed that the product formed was identical with that prepared by the in situ reaction. The copper(II) and zinc(II) analogs corresponding to Ni₂(BTC) were also prepared by the direct reaction of the ligand, BTCH₄, with the metal acetates of copper(II) and zinc(II), respectively. The Zn₂(BTC) has been reported previously,²⁵ but the compound was only briefly characterized.

The ligand BTCH₄ and its complexes were characterized by elemental, infrared, UV-VIS, and mass spectral data. In all cases, the elemental analyses for carbon were consistently low, while the values for H and N were in agreement with the calculated values.

In Table II are recorded the infrared absorption bands for the ligand, BTCH_4 , and the complexes $\text{M}_2(\text{BTC})$ where M = zinc(II), copper(II), and nickel(II). The disappearance of the $\nu(\text{O-H})$ observed in the ligand together with the lowering of the $\nu(\text{C=N})$ and $\nu(\text{C-N})$ compared with those found in the ligand indicate coordination of the anionic form of the ligand to each of the respective metal ions.

Table II. Infrared data for the protonated ligand, BTCH_4 , and its metal complexes $\text{M}_2(\text{BTC})$. (All values in cm^{-1} .)

Compound	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{C-N})$
BTCH_4	3325m	1570m	1275m
$\text{Zn}_2(\text{BTC})$	none	1522m	1245m
$\text{Cu}_2(\text{BTC})$	none	1523m	1247m
$\text{Ni}_2(\text{BTC})$	none	1532m	1243m

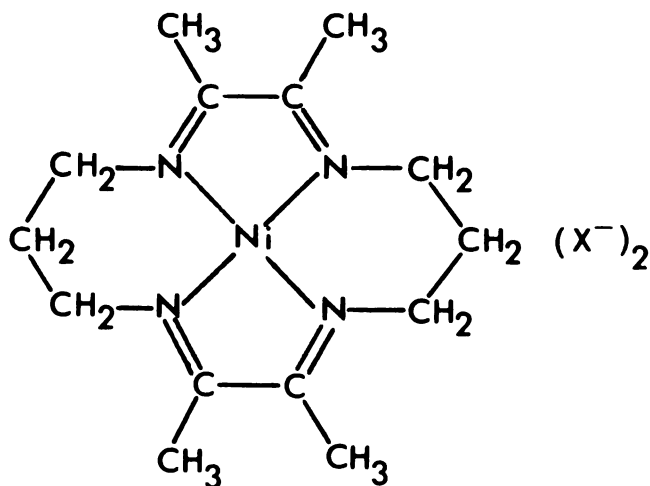
Mass spectral data were only obtained for BTCH_4 , which was volatilized at 330° . The parent peak was recorded at 554 a.m.u. Mass spectra of the metal complexes $\text{M}_2(\text{BTC})$, where M = zinc(II), copper(II), and nickel(II), were not obtained since the metal complexes could not be volatilized even at 380° .

The UV-VIS spectra for BTCH_4 and the metal complexes $\text{M}_2(\text{BTC})$, where M = zinc(II), copper(II), and nickel(II), in n-butanol had three characteristic bands in the region 338-374 nanometers, which were assigned as ligand absorptions or

possibly as charge transfer bands. No information was obtained as to the stereochemistry about the metal ions.

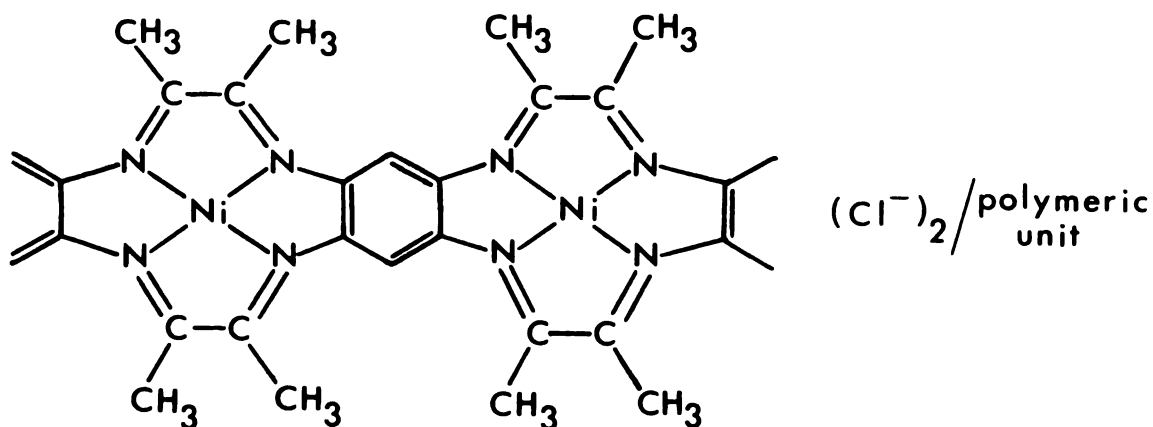
From the investigation of the complexes M_2 (BTC) where M = zinc(II), copper(II), and nickel(II), it is evident that the amino groups of TAB will condense with a carbonyl compound to form Schiff base links in the presence of a metal ion.

Baldwin and Rose²⁶ have utilized a condensation reaction in synthesizing macrocycles of the type shown below, in which two moles of 2,3-butanedione condense with two moles of 1,3-diaminopropane in the presence of nickel(II).

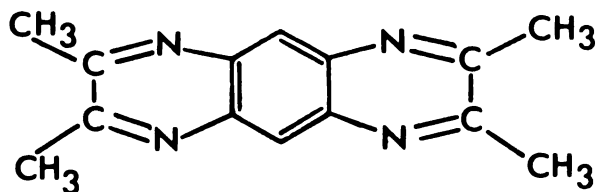


where $X^- = 0.5 \text{ ZnCl}_4^{2-}, \text{PF}_6^-, \text{NCS}^-$

An attempt was made to synthesize a macrocyclic nickel(II) polymeric complex containing a similar environment about the nickel(II) ion. The structure is shown below.



2,3-Butanedione was added to a methanolic solution of TAB in the presence of nickel(II) chloride in a 2:1:1 molar ratio and stirring was continued at room temperature for four days. The gray residue filtered from the reaction mixture was identified by mass spectrometry to have a molecular formula of $\text{C}_{10}\text{H}_{14}\text{N}_4$ (parent peak at 238 a.m.u). Infrared data obtained for this compound showed a strong $\nu(\text{C-H})$ at 3025 cm^{-1} , a medium $\nu(\text{C=N})$ at 1519 cm^{-1} , and a strong $\nu(\text{C-N})$ at 1266 cm^{-1} . Based on this evidence, the following structure is proposed:

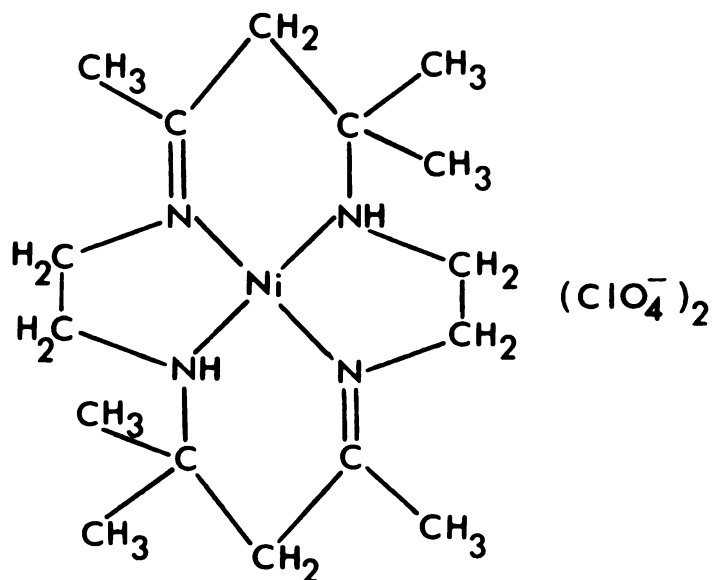


The brown powder isolated by removing the solvent from the filtrate under reduced pressure was found to contain

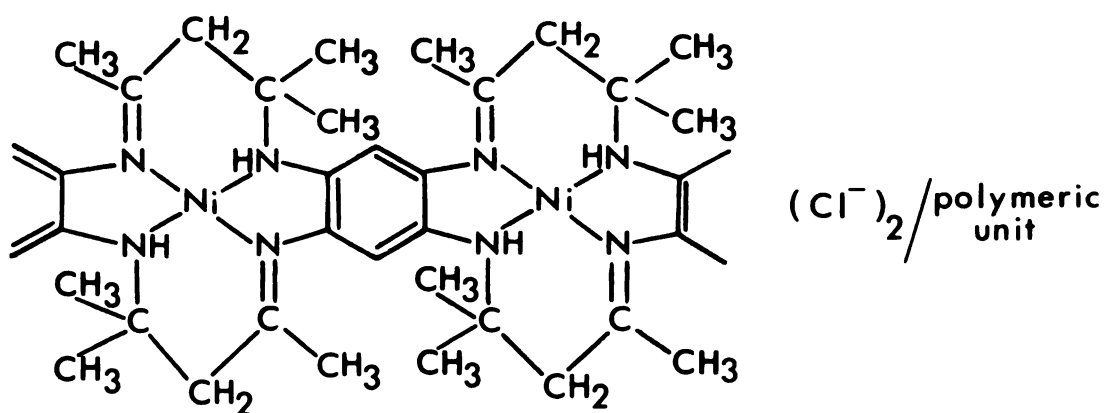
nickel(II) ions by the standard dimethylglyoxime test for nickel(II). The infrared spectrum of the amorphous brown powder indicated the presence of hydroxyl groups associated with water or methanol and the presence of C=O groups associated with 2,3-butanedione. The infrared spectrum also indicated that the brown powder was a different compound than the gray residue filtered from the reaction mixture. This implies that the nickel(II) ion is acting as a template in the synthesis of the brown powder, which is possibly a macrocyclic nickel(II) polymeric complex.

To ensure that the gray residue filtered from the reaction mixture was not a complex of nickel(II), 2,3-butanedione was added to a methanolic solution of TAB in a 2:1 molar ratio and refluxed for three hours. Infrared and mass spectral data confirmed that the tan product isolated in the absence of nickel(II) ions was identical with the gray residue formed in the presence of nickel(II) ions. Attempts to recrystallize the brown powder from methanol, ethanol, and isopropyl alcohol, were unsuccessful, since brown tars were produced.

Curtis²⁰ has shown that a macrocyclic nickel(II) complex of the type shown below forms by the condensation of (diaminoethane)nickel(II) complexes with acetone.



On this basis, an attempt was made to synthesize a polymeric complex with the following structure:

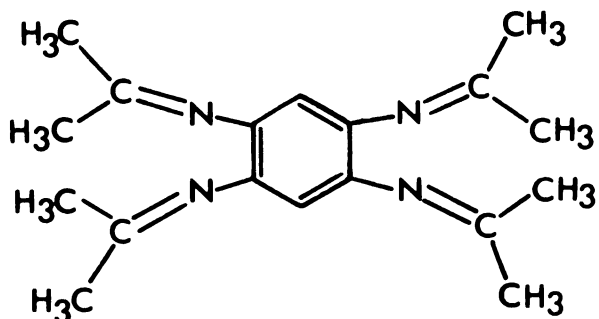


Acetone was added to a methanolic solution of TAB in the presence of nickel(II) chloride in a 4:1:1 molar ratio, respectively. After 24 hours, an orange solution was obtained. On exposure to air or addition of an aqueous solution

of sodium perchlorate, a color change from orange to red resulted. The addition of aqueous solutions of sodium perchlorate and zinc(II) chloride to different aliquots of the reaction mixture resulted in no precipitation. Addition of ethyl ether to a third aliquot resulted in precipitation of a gray product, however, the infrared spectrum indicated the presence of water or methanol. Removal of the solvent from the fourth aliquot under reduced pressure produced a fine brown powder found to contain nickel(II). It is anticipated that this product is the macrocyclic nickel(II) polymeric complex, although little information was obtained from the infrared spectrum of this product, other than the presence of water or methanol.

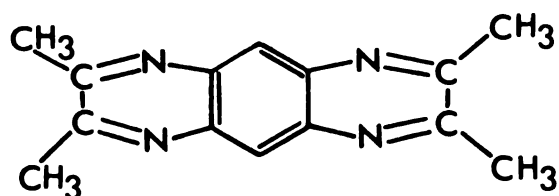
The products from the acetone condensation with TAB in the presence of nickel(II) must be compared with the products from the 2,3-butanedione condensation with TAB in the presence of nickel(II).

The macrocyclic nickel(II) polymeric complex containing acetone residues shown on the previous page should be more thermodynamically favored, due to the chelate effect,⁴ than the organic moiety (shown below) predicted to form as a byproduct.



The formation of this organic product is also hindered by the steric interaction of the methyl groups.

In the case of the 2,3-butanedione condensation with TAB in the presence of nickel(II), the macrocyclic nickel(II) polymeric complex is competing with the formation of a very thermodynamically favored aromatic system in the compound shown below.



To decide which system is more thermodynamically favored is not plausible at this time.

IV. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

On the basis of the data presented in this thesis, the following can be concluded:

1. The tetramine, 1,2,4,5-tetraminobenzene functions as a bridging ligand in the $\text{Ni}(\text{TAB})\text{Cl}_2$ complex. Because of the bridging behavior of TAB, $\text{Ni}(\text{TAB})\text{Cl}_2$ is a polymeric nickel(II) complex with D_{4h} symmetry and can be classified as a coordination polymer. It is proposed that this coordination polymer is composed of a linear sheet-like plane consisting of alternate nickel(II) ions and tetramine molecules. The chloride ions are coordinated to the nickel(II) ions in trans positions above and below the sheet-like plane.
2. The amino groups of TAB condense with salicylaldehyde to form Schiff base links in the presence of nickel(II). This reaction is an example of an in situ reaction. On this basis, it is expected that the amino groups of TAB will condense with other carbonyl compounds, such as 2,3-butanedione or acetone, to form Schiff base links in the presence of nickel(II).
3. Preliminary studies were carried out on the condensation of 2,3-butanedione with TAB in the presence of

nickel(II) and the condensation of acetone with TAB in the presence of nickel(II). In the 2,3-butanedione condensation, two different products were isolated, which indicates that a metal-ion template may be in operation. Very little information was obtained from the acetone condensation. Further studies on the condensation of 2,3-butanedione and acetone with TAB in the presence of nickel(II) are needed to determine whether macrocyclic nickel(II) complexes are formed. The condensation reactions of TAB with propionaldehyde, n-butyraldehyde, methyl ethyl ketone, 2,4-pentanedione, 1,2-cyclohexanedione, 3-hydroxy-2-butanone, diacetone alcohol, and mesityl alcohol in the presence of nickel(II) are also recommended, since these compounds have been shown^{20,27,28,29,30} to form new chelate compounds and macrocyclic complexes by their condensation with polyamines.

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