

THE PREPARATIONS OF N²-METHYLDIETHYLENETRIAMINE
AND ITS PLATINUM (II) COMPLEX

THESIS

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By

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CHAPTER I

INTRODUCTION AND RELATED WORK

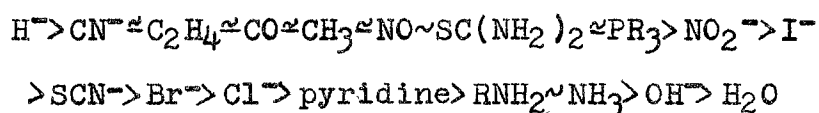
Certain ligands have been recognized as exhibiting directive effects in the substitution reactions of square planar complexes of metal ions.¹ Of these compounds, the most stable are those in which platinum (II) is the metal ion.² Substituents which most strongly direct substitution trans to themselves have partially filled π orbitals. The hydride ion, H^- , has no π orbitals; however, it strongly directs substitution in the trans-position thus indicating that factors other than π bonding are also important. The trans-effect associated with chlorine is weak because the 3d orbitals have rather high energies. The trans-effects for coordinated ammonia and water are weaker than that for chlorine. The importance of π bonding is shown in these square metal complexes by the influence of one coordination ligand upon the lability of another ligand in the same coordination complex.³ As mentioned previously, well known

¹J. V. Quagliano and L. Schubert, Chem. Revs., 50, 201 (1952).

²F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 1958, Chapter 4.

³C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. II, 1966, p. 442.

is the fact that certain ligands favor rapid substitution of other ligands which are in a trans-position relative to them. Also, the rate of increase is relatively independent of the nature of the entering ligand. The relative order of coordinated ligands in their decreasing trans-labilizing influence in platinum (II) compounds is:

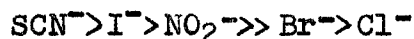


A different order is observed for platinum (IV) and other metals.

Palmer and Basolo have shown that the trans-effect should influence ligand bonds other than the metal-ligand bond.⁴ They recognized that for square complexes of metal ions, the rates of hydrogen exchange of metal amines increase with a decrease in the charge of the cation. However, they observed two rates of exchange for ions of the general formula $[\text{Pt}(\text{dien})\text{X}]^+$, where dien = diethylenetriamine and X = ligands with a single negative charge. Plots of the data therefore indicated nonequivalent hydrogens. The rate curve for the more rapid exchange corresponded to roughly 20% of the hydrogens. Of the five amine hydrogens in diethylenetriamine, the unique

⁴J. W. Palmer and F. Basolo, J. Phys. Chem., 64, 778 (1960).

hydrogen is apparently that one bonded to the nitrogen trans to the ligand X. Since the secondary amine with its single hydrogen is located trans to the ligand X in the $[\text{Pt}(\text{dien})\text{X}]^+$ complex, Palmer and Basolo interpreted the results as an example of the trans-effect. The rates of exchange of $[\text{Pt}(\text{dien})\text{X}]^+$ decrease in the order as follows:



This is essentially the same order as for the decreasing trans-effect of these X groups.

The physical evidence suggests that bonds on a coordinated atom are affected as a consequence of the changes in the central metal ion-coordinated atom bond when the ligand X, located trans to the coordinated atom, is changed. Palmer and Basolo proposed a secondary trans-effect, but the basis for this proposal was data which were obtained indirectly and were then subjected to further mathematical analysis. Watt and Cude apparently confirmed the existence of this secondary trans-effect in platinum (II) complexes.⁵ They used a direct chemical

⁵G. W. Watt and W. A. Cude, J. Am. Chem. Soc., 90, 6382 (1968).

method in the deprotonation of the $[\text{Pt}(\text{dien})\text{X}]^+$ ions and subsequent methylation of $[\text{Pt}(\text{dien-H})\text{X}]$, where dien-H = diethylenetriamine from which a proton has been removed and $\text{X} = \text{I}^-$, SCN^- , and NO_2^- . The methylation of the deprotonated species proceeded at differing rates which indicated that the order of the base strength of the deprotonated species for the ligand X was as follows:



Watt and Klett had predicted that the deprotonation site of $[\text{Pt}(\text{dien-H})\text{X}]$ could be found by use of infrared spectra after the compounds had been isolated.⁶ However, Watt and Cude found that the infrared spectra of the deprotonated species could not ultimately indicate where deprotonation occurred. They empirically made assignments previously made for $[\text{Pd}(\text{dien})\text{I}]\text{I}$ because there was almost a 1:1 correlation between the spectra of the Pt and Pd complexes.⁷

Comparison of the spectra of $[\text{Pt}(\text{dien})\text{I}]\text{I}$ and $[\text{Pt}(\text{dien-H})\text{I}]\text{I}$ suggested that deprotonation occurred on the center nitrogen of diethylenetriamine. However,

⁶G. W. Watt and D. S. Klett, Spectrochim. Acta, **20**, 1053 (1964).

⁷Ibid.

because the NH_2 stretching bands in the deprotonated species were broad and ill-defined in nature, the absence of the NH stretching band could not be confirmed. Also, the absorption band attributable to out-of-plane deformation for the NH group found in the spectrum of $[\text{Pt}(\text{dien})\text{I}]^+$ could have been obscured in the spectrum of $[\text{Pt}(\text{dien-H})\text{I}]$ by the broadening of a CH_2 vibrating band. In an effort to locate the deprotonation site, $[\text{Pt}(\text{dien-H})\text{I}]$ was treated with methyl iodide which produced $[\text{Pt}(\text{n-mdien})\text{I}]\text{I}$, where n-mdien = methyldiethylenetriamine in which no specification is made as to the nitrogen to which the methyl group is bonded. However, the infrared spectrum of $[\text{Pt}(\text{n-mdien})\text{I}]\text{I}$ did not clearly indicate the position of the methyl group. They further attempted to identify the deprotonation site by synthesizing $[\text{Pt}(\text{l-mdien})\text{I}]\text{I}$, where l-mdien = methyldiethylenetriamine with the methyl group attached to the first nitrogen, by an independent method and then comparing the infrared spectra of $[\text{Pt}(\text{l-mdien})\text{I}]\text{I}$ and $[\text{Pt}(\text{n-mdien})\text{I}]\text{I}$. The infrared spectra of $[\text{Pt}(\text{l-mdien})\text{I}]\text{I}$ and $[\text{Pt}(\text{n-mdien})\text{I}]\text{I}$ had noticeably different features. Therefore, they were led to the conclusion that the compound produced by the deprotonation of $[\text{Pt}(\text{dien})\text{I}]^+$ and the methylation of

$[\text{Pt}(\text{dien-H})\text{I}]$ was $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$, where 2-mdien = methyl-diethylenetriamine with the methyl group attached to the second nitrogen.

Because of the desirability of proving more conclusively that the compound which Watt and Cude prepared by the deprotonation of $[\text{Pt}(\text{dien})\text{I}]^+$ and the methylation of $[\text{Pt}(\text{dien-H})\text{I}]$ was $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$, it became of interest to attempt the synthesis of $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$ by a known method. A promising method to accomplish this end was to employ the Gabriel synthesis of a primary amine which was used by Mann to prepare N^2 -methyl-diethylenetriamine as a first step.⁸ The subsequent synthesis of $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$ would be done by a method similar to that used by Watt and Cude to produce $[\text{Pt}(\text{dien})\text{I}]\text{I}$.⁹ Inasmuch as the route employed by Mann produced only N^2 -methyldiethylenetriamine, the reasonable conclusion was made that the platinum (II) complex thus made could be only $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$. This would allow the identification of properties of $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$ by infrared spectra and by other analytical data.

⁸F. G. Mann, J. Chem. Soc., 461 (1934).

⁹G. W. Watt and W. A. Cude, Inorganic Chemistry, 7, 335 (1968).

CHAPTER II

EXPERIMENTAL METHODS

A. Preparation of Platinum (II) Iodide, $\text{PtI}_2 \cdot \text{H}_2\text{O}$

Ammonium Hexachloroplatinate (IV), $(\text{NH}_4)_2\text{PtCl}_6$.--

A 5.0-g. sample of platinum was dissolved in hot aqua regia. The dark-red solution was heated at 90° until the brown fumes of the nitrate and reduced forms of nitrogen were removed and droplets on the cover glass changed from yellow to colorless. The solution was cooled to about 5° , and a 50% excess of ammonium chloride was added giving a bright yellow precipitate of ammonium hexachloroplatinate (IV). The product was separated with a fritted glass filter and washed with three 20-ml. portions of water. The product was air-dried for 24 hours at room temperature. The yield of ammonium hexachloroplatinate (IV) was 11.0 g. or 96.6% based on platinum.

Ammonium Tetrachloroplatinate (II), $(\text{NH}_4)_2\text{PtCl}_4$.--

The procedure followed for the preparation of ammonium tetrachloroplatinate (II) was a proven method.¹ A suspension was made by the addition of 11.0 g. of

¹N. G. Kluchnikov and R. N. Savel'eva, Z. Neorgan. Khim., 1, 2764 (1956).

$(\text{NH}_4)_2\text{PtCl}_6$ to 250 ml. of water. A stoichiometric amount (1.3 g.) of hydrazine dihydrochloride, $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$, was added to the suspension; and these ingredients were stirred at room temperature for one hour. After this period, the components had changed to a dark-red solution with a small amount of the yellow precipitate of ammonium hexachloroplatinate (IV) still unreacted. The mixture was then stirred at 90° for two hours and was changed to a homogeneous solution with a dark-red color. After cooling to 5° , it was filtered; and a very small amount of metallic platinum was found, showing that the reaction was not quantitative. The literature indicated that the reaction is exact; however, the metal found was undoubtedly due to a small excess of hydrazine dihydrochloride in the initial reaction mixture.

Platinum (II) Iodide, $\text{PtI}_2 \cdot \text{H}_2\text{O}$.--The solution containing dissolved ammonium tetrachloroplatinate (II) was heated to about 90° , and an excess of potassium iodide was added with stirring. The black precipitate immediately formed was platinum (II) iodide and was dried overnight in an oven at 110° . The yield of platinum (II) iodide was 9.32 g.

Throughout this synthesis, all residues and washings were saved; and the platinum was recovered. Ashless

filter paper was used in all filtrations except for the filtration of ammonium hexachloroplatinate (IV) when a fritted glass crucible was used. After the dried ammonium hexachloroplatinate (IV) had been removed, water was allowed to drip through the filter removing all platinum residues.

B. Preparation of N^2 -methyldiethylenetriamine, $C_5H_{15}N_3$

Potassium Phthalimide, $KC_8H_4NO_2$.--The procedure followed for the preparation of potassium phthalimide was a proven method.² A 90-g. portion of phthalimide and 1800 ml. of absolute alcohol were placed in a beaker, and the mixture was boiled on a steam bath for 30 minutes. A solution of potassium hydroxide was prepared by dissolving 68.72 g. of the solid in 70 ml. of water and then adding 210 ml. of absolute alcohol. The hot solution of phthalimide and alcohol was decanted from any solid into one half of the potassium hydroxide solution. A precipitate of potassium phthalimide resulted, which separated immediately. The mixture containing the potassium phthalimide was cooled to room temperature by use of an ice bath and

²A. H. Blatt, "Organic Syntheses," Collective Vol. I, 1941, p. 119.

was stirred continuously. The precipitate was then filtered with suction being used as an aid. Another 90 g. of phthalimide was added to the filtrate, and the entire procedure was repeated. During filtration, part of the first crop of potassium phthalimide was removed from the funnel; and the second crop was then filtered in the same funnel with the same piece of filter paper. After filtration, the two crops of potassium phthalimide were placed in the funnel and washed with 500 ml. of acetone to remove any unchanged phthalimide. The potassium phthalimide was air-dried. The yield of potassium phthalimide was 146.6 g. or 79.1% based on phthalimide.

Bis-(2-chloroethyl)-amine, $C_4H_9Cl_2N$.--The procedure followed for the preparation of bis-(2-chloroethyl)-amine and the subsequent preparation of N^2 -methyldiethylene-triamine was a given method.³

A 100-g. portion of powdered bis-(2-chloroethyl)-amine hydrochloride and 160 ml. of 20% potassium hydroxide solution were added successively to 50 g. of ice. Bis-(2-chloroethyl)-amine rapidly separated. The amine

³F. G. Mann, J. Chem. Soc., 461 (1934).

was extracted in ether and was dried with potassium hydroxide pellets. The oily bis-(2-chloroethyl)-amine was recovered by bubbling dry nitrogen through the ether solution. The yield of bis-(2-chloroethyl)-amine was 56.01 g. or 70.4% based on bis-(2-chloroethyl)-amine hydrochloride.

Bis-(2-phthalimidoethyl)-amine, $C_{20}H_{17}N_3O_4$.--

A 56.01-g. portion of bis-(2-chloroethyl)-amine was slowly and thoroughly mixed with 146.6 g. of potassium phthalimide. The mixture was pressed into a round-bottomed flask and was heated. At about 145°, a vigorous exothermic reaction took place; and the temperature quickly rose to 200°. The contents of the flask were well stirred, and the temperature returned to 150° within 20 minutes. The flask was then heated at 145-150° for one hour. The product formed a solid mass after being heated for 20 minutes. After the product had been cooled, it was powdered and thoroughly washed with water; and the washed product was dried overnight in an oven at 110°. The amine was recrystallized three times from about 3 l. of boiling alcohol. The yield of pure bis-(2-phthalimidoethyl)-amine was 11.4 g. or 7.96% based on bis-(2-chloroethyl)-amine.

Bis-(2-phthalimidoethyl)-methylanine, $C_{21}H_{19}N_3O_4$.--

Silver oxide, Ag_2O , was prepared by the action of sodium hydroxide on silver nitrate. Both 6 g. of silver oxide and 3.55 ml. of methyl iodide, CH_3I , were added in turn to a suspension of 11.4 g. of powdered bis-(2-phthalimidoethyl)-amine in 713 ml. of hot acetone. The mixture was boiled under reflux for three hours. Before cooling, it was filtered; and the acetone was removed by distillation. After the acetone had evaporated and the residue cooled, the product was a brittle solid. This crude material was powdered and extracted with a small quantity of boiling alcohol. After recrystallization from alcohol, the extract of bis-(2-phthalimidoethyl)-methylanine deposited crystals which were pale in color. The yield of bis-(2-phthalimidoethyl)-methylanine was 0.3 g. or 3% based on bis-(2-phthalimidoethyl)-amine.

N^2 -methyldiethylenetriamine Trihydrochloride,

$C_5H_{18}Cl_3N_3$.--A mixture of 0.29 g. of bis-(2-phthalimidoethyl)-methylanine, 17 ml. of concentrated hydrochloric acid, and 7 ml. of water was boiled under reflux for two hours. The clear red solution was cooled causing phthalic acid to crystallize. The phthalic acid was separated by filtration, and the filtrate was evaporated

on a steam bath to a very small volume. The remaining filtrate was cooled and stirred. An almost solid mass was formed which was redissolved in hot concentrated hydrochloric acid. This solution, which contained the N^2 -methyldiethylenetriamine trihydrochloride, was cooled; and a very small quantity of the trihydrochloride and phthalic acid crystallized. These crystals were separated by filtration, and the cold filtered solution was treated dropwise with alcohol. A fine emulsion separated which was converted into a fine crystalline product by stirring. After more alcohol had been added, the trihydrochloride crystallized. The N^2 -methyldiethylene-triamine trihydrochloride was separated by filtration and was washed with 5 ml. of absolute alcohol and 5 ml. of ether in turn. The pale-pink crystalline trihydrochloride was air-dried. The yield of N^2 -methyldiethylene-triamine trihydrochloride was 0.3 g. or 172% based on bis-(2-phthalimidoethyl)-methylamine. The N^2 -methyldiethylenetriamine trihydrochloride was found to have a composition of 27.1% carbon, 7.91% hydrogen, and 16.1% nitrogen. This analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. The N^2 -methyldiethylenetriamine trihydrochloride was calculated to have 26.2% carbon, 8.01% hydrogen, and 18.5% nitrogen.

N²-methyldiethylenetriamine, C₅H₁₅N₃.--Both 0.3 g. of powdered N²-methyldiethylenetriamine trihydrochloride and 1.5 ml. of 20% potassium hydroxide solution were added successively to 5 g. of ice. Liquid N²-methyldiethylenetriamine immediately separated. The amine was extracted in ether and was dried with potassium hydroxide pellets. The oily N²-methyldiethylenetriamine was recovered by bubbling dry nitrogen through the ether solution. The yield of N²-methyldiethylenetriamine was 0.156 g. or 100% based on N²-methyldiethylenetriamine trihydrochloride.

C. Preparation of Iodo(N²-methyldiethylenetriamine)-
platinum (II) Iodide, PtC₅H₁₅I₂N₃

The preparation of iodo(N²-methyldiethylenetriamine)-platinum (II) iodide was done by a synthesis similar to that used by Watt and Cude in the preparation of [Pt(dien)I]I.⁴

A thick paste was made by adding a small amount of water to 1.0 g. of platinum (II) iodide. A 0.156-g. portion of N²-methyldiethylenetriamine was added dropwise

⁴G. W. Watt and W. A. Cude, Inorganic Chemistry, 7, 335 (1968).

with stirring to the platinum (II) iodide paste. The mixture was allowed to bake to dryness on a steam bath overnight. To extract the $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$, the dark gray product was placed in a beaker containing 500 ml. of water and was heated at 90° for one hour. The solution was filtered; and the platinum (II) iodide, which was collected as a residue, was processed to recover the platinum metal. The clear red filtrate was evaporated by directing a stream of air over the solution. This produced a yield of bright-yellow crystals of $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$ which amounted to 0.6 g. or 80% based on N^2 -methyldiethylenetriamine.

CHAPTER III

RESULTS AND DISCUSSION

The purpose of this research was to prove conclusively by a chemical reaction that the secondary trans-effect did occur in the work done by Watt and Cude.¹ They had proposed that the compound synthesized by the deprotonation of $[\text{Pt}(\text{dien})\text{I}]^+$ and the subsequent methylation of $[\text{Pt}(\text{dien-H})\text{I}]$ was $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$. However, they had suggested this on the basis that the infrared spectra of $[\text{Pt}(1\text{-mdien})\text{I}]\text{I}$ and their proposed $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$ were unlike.

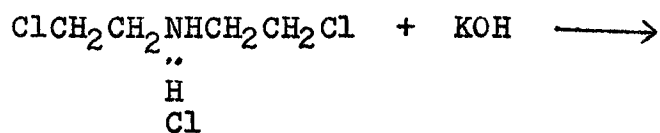
The synthesis of $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$ was attempted and accomplished. The compound was prepared by a two-step process, each step of which has been described previously. In the following discussion, the preparations of the individual compounds in each step will be given; and the preparation will be followed by the appropriate reaction.

The first and longest step was the preparation of N^2 -methyldiethylenetriamine with a procedure described by Mann being used.² His method was based on the Gabriel

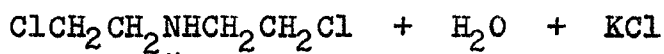
¹G. W. Watt and W. A. Cude, J. Am. Chem. Soc., **90**, 6382 (1968).

²F. G. Mann, J. Chem. Soc., 461 (1934).

synthesis of a pure primary amine, which is a well-known method.³ There has also been a recent review of the various methods which utilize the Gabriel synthesis of a pure primary amine.⁴ In the synthesis by Mann, the bis-(2-chloroethyl)-amine hydrochloride of unknown purity was the starting compound; and it was allowed to react with a 20% solution of potassium hydroxide.



bis-(2-chloroethyl)- potassium hydroxide
amine hydrochloride



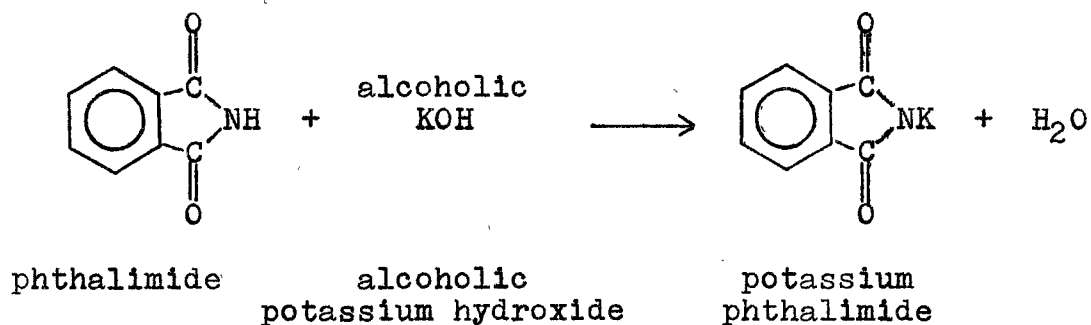
bis-(2-chloroethyl)-
amine

Potassium phthalimide was synthesized by a known method and was prepared by treating phthalimide with an alcoholic solution of potassium hydroxide.⁵

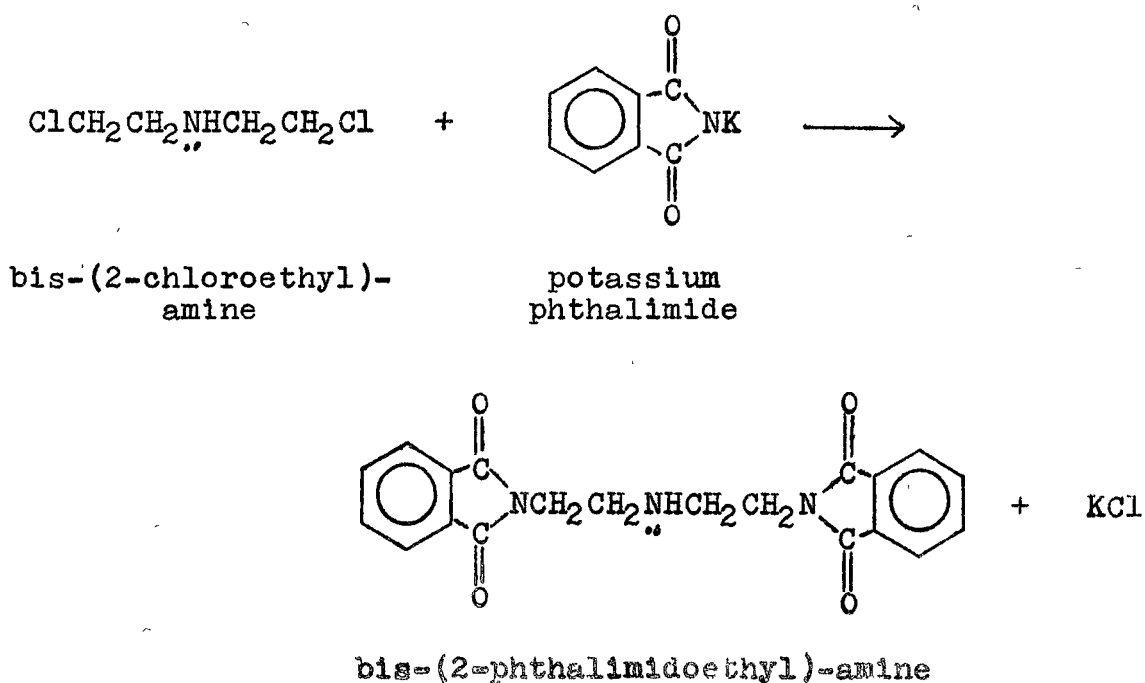
³R. T. Morrison and R. M. Boyd, "Organic Chemistry," 2nd ed., 1966, p. 916.

⁴M. S. Gibson and R. W. Bradshaw, Angewandte Chemie, 7, 919 (1968).

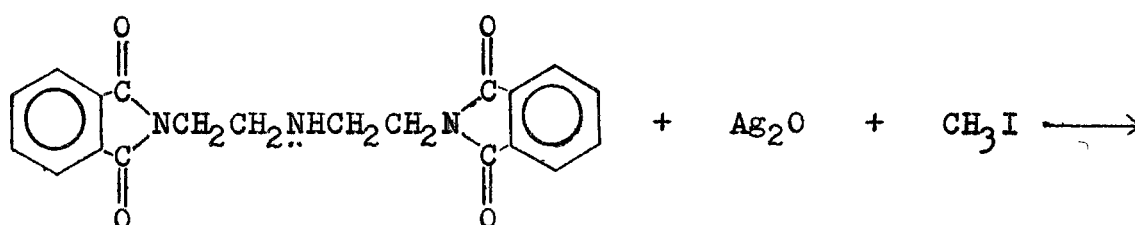
⁵A. H. Blatt, "Organic Syntheses," Collective Vol. I, 1941, p. 119.



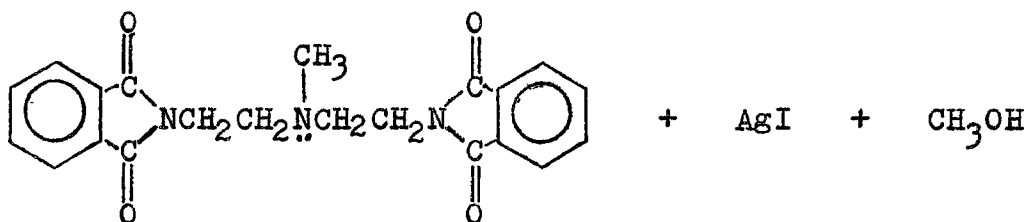
The free bis-(2-chloroethyl)-amine was treated with the potassium phthalimide. The bis-(2-phthalimidoethyl)-amine was formed by this reaction in a noticeably low yield. This reaction was very exothermic and hard to control, and it has been recommended that this procedure be revised or a completely different procedure be used in future research. No alternate procedure has been proposed because the search for an improved synthetic procedure was beyond the scope of this investigation.



The bis-(2-phthalimidoethyl)-amine was treated with silver oxide and methyl iodide in boiling acetone. The product of bis-(2-phthalimidoethyl)-methylamine was also in a very low yield, and again revision of this procedure or the use of a completely different procedure has been recommended.



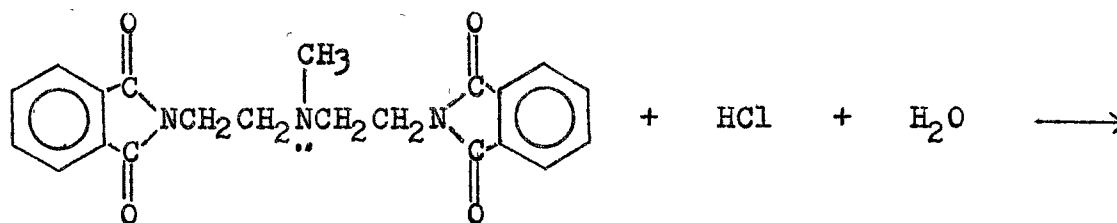
bis-(2-phthalimidoethyl)-amine
silver oxide
methyl iodide



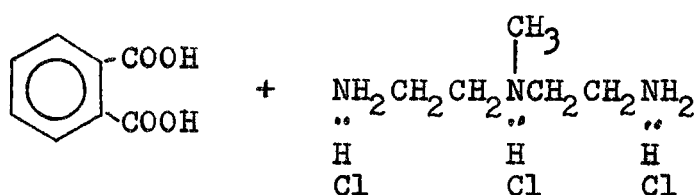
bis-(2-phthalimidoethyl)-
methylamine

The bis-(2-phthalimidoethyl)-methylamine was heated with hydrochloric acid, which caused rapid hydrolysis to occur. The very high yield of N^2 -methyldiethylenetriamine trihydrochloride based on bis-(2-phthalimidoethyl)-methylamine suggested the presence of impurities in the

product. The impure sample of N^2 -methyldiethylenetriamine trihydrochloride was analyzed for carbon, hydrogen, and nitrogen. Further purification of the compound was not attempted because only a small amount was produced. Mann stated that the N^2 -methyldiethylenetriamine trihydrochloride which he prepared was in the form of colorless leaflets while the same material prepared in this laboratory was in the form of very pale-pink leaflets. This difference in color likewise suggested the presence of impurities. The extent of the impurities was indicated by the difference between the calculated elemental percentages and those found, both of which were stated above in Chapter II. The difference was tolerable in hydrogen, but it was barely acceptable in carbon and unsatisfactory in nitrogen. The elemental analysis indicated that the impurities in the sample were primarily due to substances of high nitrogen content. A positive identification of the impurities was not attempted. However, the N^2 -methyldiethylenetriamine trihydrochloride may have partially decomposed, forming a secondary amine and a compound such as ammonium chloride which would have accounted for the high nitrogen content.

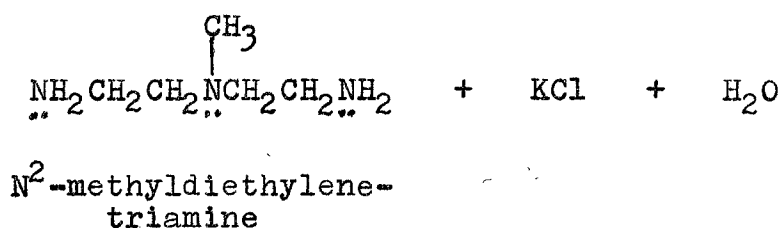
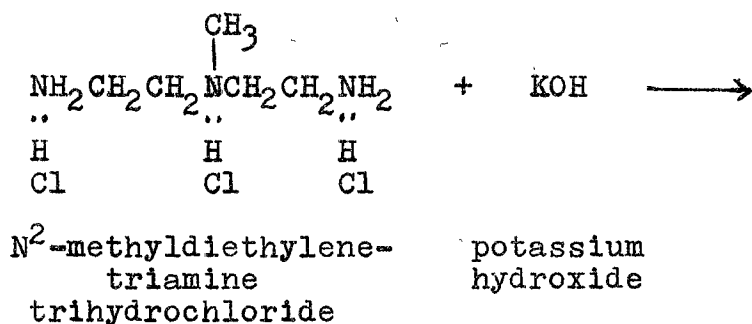


bis-(2-phthalimidoethyl)-methylanine hydrochloric acid water

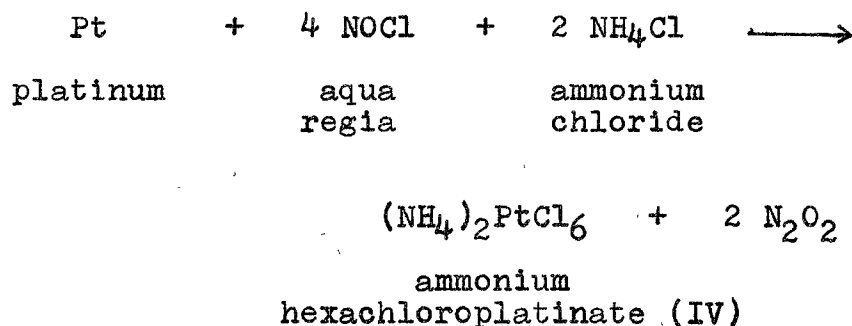


phthalic acid N²-methyldiethylenetriamine trihydrochloride

The free N²-methyldiethylenetriamine was formed by treating N²-methyldiethylenetriamine trihydrochloride with a 20% solution of potassium hydroxide. This yield was 100% based on the trihydrochloride. Since an analysis indicated that the N²-methyldiethylenetriamine trihydrochloride was slightly impure, it was assumed that the ether used in the separation of N²-methyldiethylenetriamine from the aqueous solution was not completely evaporated.

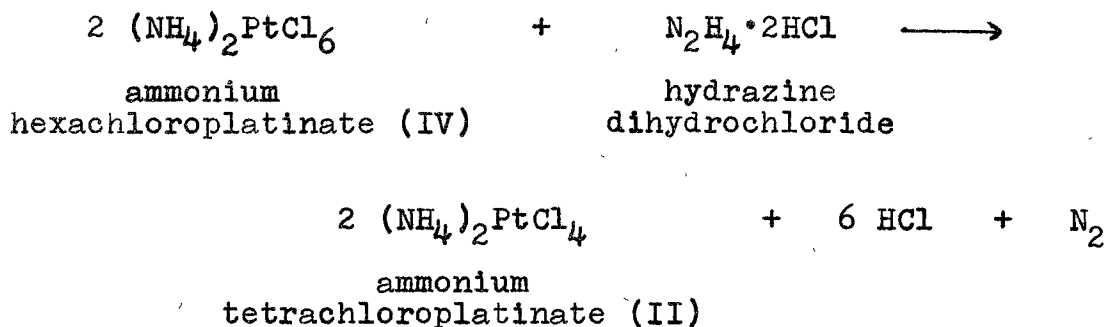


Platinum (II) iodide was treated with N^2 -methyldiethylenetriamine. Platinum (II) iodide was produced as previously described.⁶ In this method, platinum metal was dissolved in aqua regia. After this solution had cooled, an excess of ammonium chloride was added; and the bright-yellow precipitate of ammonium hexachloroplatinate (IV) was formed.

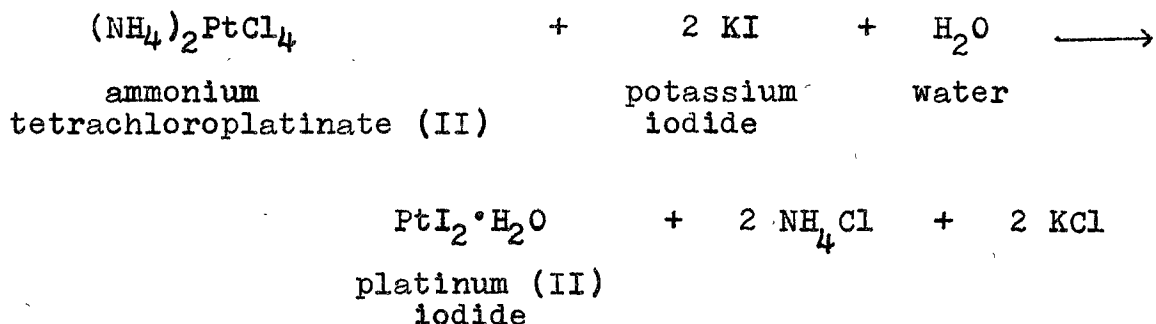


⁶G. W. Watt and W. A. Cude, Inorganic Chemistry, 7, 335 (1968).

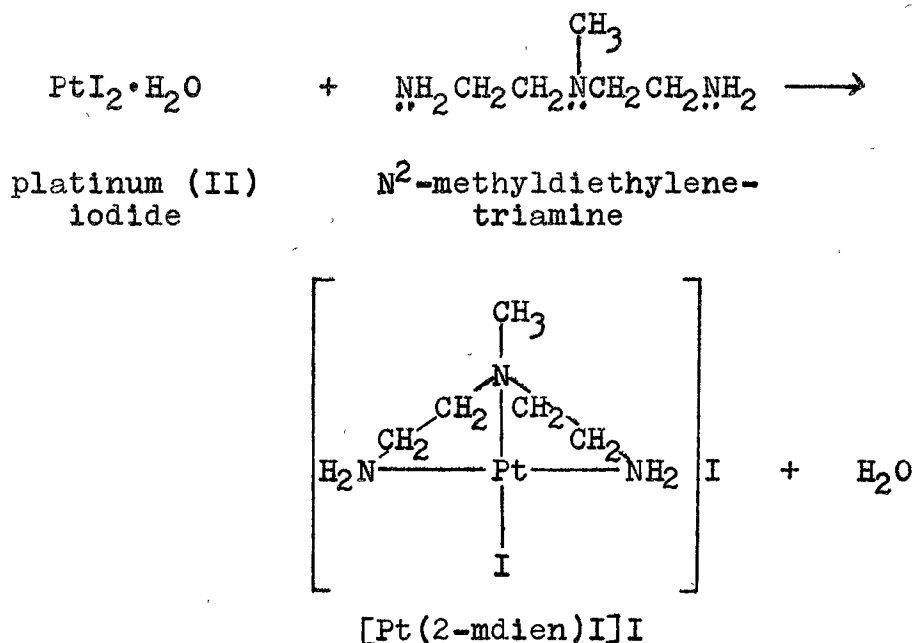
The dried ammonium hexachloroplatinate (IV) was suspended in water and was treated with hydrazine dihydrochloride.



The ammonium tetrachloroplatinate (II) was formed and was allowed to react with potassium iodide to form the black precipitate of platinum (II) iodide.



The reaction of platinum (II) iodide and N²-methyldiethylene-triamine produced [Pt(2-mdien)I]I.



The platinum (II) complex of N²-methyldiethylene-triamine was synthesized twice. This synthesis was also a known method given by Watt and Cude which they used in their syntheses of [Pt(dien)I]I and related compounds.⁷ The infrared spectra of samples from each of the syntheses of [Pt(2-mdien)I]I were identical. However, the infrared spectrum indicated an impure compound which most likely contained decomposition products. There were significant peaks at 3400 cm.⁻¹, 1540 cm.⁻¹, and 1390 cm.⁻¹ while the infrared spectrum of the proposed [Pt(2-mdien)I]I synthesized by Watt and Cude had a greater number of peaks with different wavenumbers.

⁷Ibid.

The purification of the platinum (II) complex of N^2 -methyldiethylenetriamine was considered. However, there was evidence that the platinum (II) complex was unstable. When the recrystallization of $[Pt(2\text{-mdien})I]I$ was attempted, the complex decomposed producing platinum (II) iodide, $PtI_2 \cdot H_2O$. The following method was used in the attempted recrystallization of the platinum (II) complex. The gray solid, which was produced by heating the paste containing platinum (II) iodide and N^2 -methyldiethylenetriamine on a steam bath, was placed in a large amount of water, heated on a steam bath, and stirred continuously. At this point, the unreacted platinum (II) iodide was removed by filtration leaving a clear red filtrate containing no solid particles. The filtrate was placed on the steam bath in order to evaporate the filtrate and to produce crystals of $[Pt(2\text{-mdien})I]I$. Within three hours, black particles of platinum (II) iodide appeared in the filtrate. This indicated that the yield of the platinum (II) complex may have been greatly reduced when the paste containing platinum (II) iodide and N^2 -methyldiethylenetriamine was heated. There was no way to be sure of decomposition during this heating or of failure of reaction in the first step of this preparation. Since there was an

indication that the compound was heat sensitive, the platinum (II) iodide was removed by filtration; and the filtrate was evaporated by directing a stream of air over the liquid.

Since there was evidence that the platinum (II) complex of N²-methyldiethylenetriamine was heat sensitive, then the complex synthesized by Watt and Cude in their deprotonation work was probably [Pt(1-mdien)I]I.⁸ Since there are five available hydrogens on the platinum (II) complex of diethylenetriamine, then the deprotonation could have occurred at one of five sites. However, there are nonequivalent hydrogens on this complex, one hydrogen being in the secondary amino group located trans to the ligand I and the other four equivalent hydrogens being in the two primary amino groups. Therefore, the methylation of the deprotonated species could have produced a mixture of the two compounds, [Pt(1-mdien)I]I and [Pt(2-mdien)I]I. If no secondary trans-effect occurred, then 80% of the mixture was [Pt(1-mdien)I]I; and 20% of the mixture was [Pt(2-mdien)I]I. However, if there was a secondary trans-effect, the composition of the mixture was not known. Watt and Cude believed that the secondary trans-

⁸G. W. Watt and W. A. Cude, J. Am. Chem. Soc., 90, 6382 (1968).

effect occurred and that the sole compound produced was $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$. Their proposal that $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$ was the only compound produced was suggested by the fact that the infrared spectrum of their proposed $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$ and the infrared spectrum of the $[\text{Pt}(1\text{-mdien})\text{I}]\text{I}$ which they produced from commercially prepared N^1 -methyldiethylenetriamine trihydrochloride were not identical. If the deprotonation work produced a mixture of $[\text{Pt}(1\text{-mdien})\text{I}]\text{I}$ and $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$, then the $[\text{Pt}(2\text{-mdien})\text{I}]\text{I}$ evidently did not survive because of its sensitivity to heat and perhaps its ability to decompose upon standing. The discovery of these properties was the single most important finding made during the course of this research. This fact adequately explained why purification of the product produced by deprotonation led to a compound having an infrared spectrum identical to that of $[\text{Pt}(1\text{-mdien})\text{I}]\text{I}$ rather than that which had been expected.⁹

⁹W. A. Cude, Unpublished Work (1968).

CHAPTER IV

SUMMARY

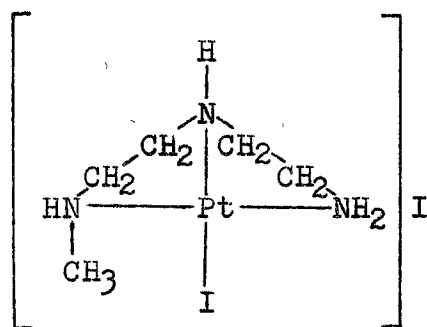
The secondary trans-effect which was reported by Watt and Cude apparently was not complete.¹ Palmer and Basolo had reported results which suggested that the secondary trans-effect was observable not only in the metal-ligand bonds but also in the bonding of atoms attached to a coordinated ligand atom.² Watt and Cude attempted to provide direct chemical evidence that a secondary trans-effect did extend beyond the metal-ligand atom bond to atoms attached to the coordinated ligand atom. They synthesized $[\text{Pt}(\text{dien})\text{I}]^+$, an ion of the same type used by Palmer and Basolo, which was treated with NH_2^- in liquid ammonia solution in an attempt to determine if selective deprotonation could occur. They then methylated the deprotonated species, $[\text{Pt}(\text{dien-H})\text{I}]$, with methyl iodide and produced $[\text{Pt}(\text{n-mdien})\text{I}]\text{I}$. Watt and Cude could not positively identify their product by use of an infrared spectrum because of their inability

¹G. W. Watt and W. A. Cude, J. Am. Chem. Soc., **90**, 6382 (1968).

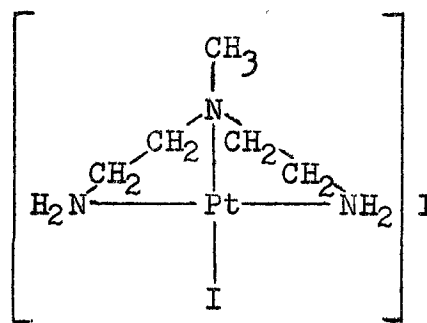
²J. W. Palmer and F. Basolo, J. Phys. Chem., **64**, 778 (1960).

to determine the position of the methyl group by indirect methods. They synthesized $[\text{Pt}(\text{l-mdien})\text{I}]\text{I}$ from commercially prepared N^1 -methyldiethylenetriamine trihydrochloride and compared the infrared spectra of $[\text{Pt}(\text{n-mdien})\text{I}]\text{I}$ and $[\text{Pt}(\text{l-mdien})\text{I}]\text{I}$. Because the spectra were not identical, they concluded that they had prepared $[\text{Pt}(\text{2-mdien})\text{I}]\text{I}$ in their deprotonation work and that there was an observable secondary trans-effect.

Further research has proven that Watt and Cude apparently did not isolate $[\text{Pt}(\text{2-mdien})\text{I}]\text{I}$ because of its high instability and also because of the possibility that a mixture of $[\text{Pt}(\text{l-mdien})\text{I}]\text{I}$ and $[\text{Pt}(\text{2-mdien})\text{I}]\text{I}$ actually existed in the deprotonation work. The work of Palmer and Basolo also showed that there was a great possibility of producing a mixture of $[\text{Pt}(\text{l-mdien})\text{I}]\text{I}$ and $[\text{Pt}(\text{2-mdien})\text{I}]\text{I}$ with the structures as follow:



$[\text{Pt}(\text{l-mdien})\text{I}]\text{I}$



$[\text{Pt}(\text{2-mdien})\text{I}]\text{I}$

The analysis of N²-methyldiethylenetriamine trihydrochloride for carbon, hydrogen, and nitrogen presented a good indication that the compound was actually prepared. The deviations found were tolerated because the N²-methyldiethylenetriamine trihydrochloride was impure when submitted for analysis, and purification would have resulted in too little yield to analyze or no yield whatsoever. The complex, [Pt(2-mdien)I]I, was formed when the relatively pure N²-methyldiethylene-triamine was treated with platinum (II) iodide.

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