

AN ABSTRACT OF THE THESIS OF

Thomas Alfred Lane for the degree of Master of Science  
in Chemistry presented on August 26, 1925

Title: THE OXIDATION OF TRIMETHYLAMINE BY COPPER(II)

CHLORIDE

Abstract approved:

*Redacted for Privacy*

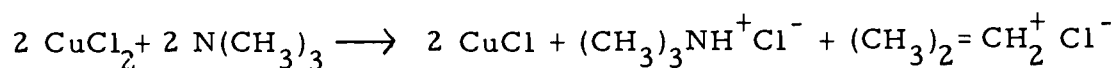
John T. Yoke III

This research was on the irreversible oxidation of trimethylamine by copper(II) chloride, which takes place at temperatures of about  $75^{\circ}$  and higher. The coordination of trimethylamine by copper(II) chloride, which is a preliminary reaction to the oxidation, was studied at  $0^{\circ}$ . The coordination of trimethylamine by the potential reduction product, copper(I) chloride, was also studied at  $0^{\circ}$ .

High vacuum and dry nitrogen glovebox techniques were used in studying the coordination reactions, the stoichiometry of the oxidation-reduction reaction, and the hydrolysis of the redox reaction products.

Complexes in the copper(II) chloride-trimethylamine system at  $0^{\circ}$  are a blue-green solid, presumably  $\text{CuCl}_2 \cdot 2 \text{N}(\text{CH}_3)_3$ , with a dissociation pressure of several hundred torr, and the yellow-brown solid  $\text{CuCl}_2 \cdot \text{N}(\text{CH}_3)_3$ , which has a negligible dissociation pressure. The latter, which had been reported previously, exhibits normal paramagnetism at room temperature. Copper(I) chloride and trimethylamine at  $0^{\circ}$  form the stable complex  $\text{CuCl} \cdot \text{N}(\text{CH}_3)_3$ .

The following reaction can be written for the irreversible thermally induced oxidation-reduction reaction.



When the reactants were present in equimolar amounts the reaction stoichiometry was approximately 1:1. The dimethylmethylen ammonium and trimethylammonium cations were identified by their characteristic infrared frequencies. The presence of the former was also indicated by the identification of its hydrolysis products, formaldehyde and dimethylamine.

When trimethylamine was present in excess, the amine: copper(II) chloride reaction stoichiometry was variable, in the range 1.1 to 1.4:1. This is attributed to various complex equilibria involving copper(I) chloride, and to the reaction of trimethylamine with the dimethylmethylen ammonium cation to give a polymeric product.

The results on the trimethylamine coordination complexes of copper(I) and copper(II) chloride differ from some previous reports in the literature. The oxidation of trimethylamine by copper(II) chloride closely resembles its previously described oxidation by vanadium(IV) chloride.

The Oxidation of Trimethylamine by  
Copper(II) Chloride

by

Thomas Alfred Lane

A THESIS

submitted to

Oregon State University

in partial fulfillment of  
the requirements for the  
degree of

Master of Science

Completed August 1975

Commencement June 1976

APPROVED:

*Redacted for Privacy*

\_\_\_\_\_  
Professor of Chemistry  
in charge of major

*Redacted for Privacy*

\_\_\_\_\_  
Chairman of Department of Chemistry

*Redacted for Privacy*

\_\_\_\_\_  
Dean of Graduate School

Date thesis is presented

Aug 26, 1975

Typed by Mary Jo Stratton for Thomas Alfred Lane

## ACKNOWLEDGEMENTS

I would like to thank my research advisor, Dr. John T. Yoke, whose guidance and encouragement was available when it was needed.

I would also like to thank the donors to the Oregon State University Foundation for the summer fellowships extended to me. I also thank the Department of Chemistry, Oregon State University, for the teaching assistantship granted to me.

To my wife, Shirley, a special thanks because without her love and understanding this thesis could not have been undertaken.

## TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
II. HISTORICAL	3
Coordination Compounds	3
Oxidation of Aliphatic Amines	6
General	6
Oxidation of Aliphatic Amines by	
Copper(II) Chloride	7
Oxidation of Trimethylamine	10
Dialkylmethylenammonium Compounds	12
III. EXPERIMENTAL	15
Manipulative Techniques	15
Materials	16
Trimethylamine	16
Dimethylamine	17
Methylamine	17
Methanol	17
Ethanol	17
Water	18
Copper(II) Chloride	18
Copper(I) Chloride	18
Instrumental Methods	18
Gas Chromatography	18
Infrared Spectra	19
Magnetic Susceptibility	19
The System Copper(II) Chloride-Trimethylamine	19
Complex Formation	19
Oxidation-Reduction	20
Hydrolysis	21
The System Copper(I) Chloride-Trimethylamine	22
IV. RESULTS	23
Copper(I) Chloride-Trimethylamine System	23
Coordination of Copper(II) Chloride	
by Trimethylamine	23
Oxidation-Reduction of Copper(II) Chloride	
with Trimethylamine	24

	<u>Page</u>
V. CONCLUSIONS	27
BIBLIOGRAPHY	30

## LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Formulas of Reported Complexes.	4
II	Infrared Spectral Data.	25



# THE OXIDATION OF TRIMETHYLAMINE BY COPPER(II) CHLORIDE

## I. INTRODUCTION

Previous work in this research group has shown that primary, secondary, and tertiary aliphatic amines are first coordinated and then irreversibly oxidized by copper(II) chloride. The oxidation-reduction reaction involves one-electron reduction of copper(II) to copper(I), and two-electron oxidation of an alkyl group to an olefinic group followed by polymerization to a polyvinyl amine. The protons liberated in the oxidation serve to protonate the polymeric amine, as well as additional unoxidized starting amine. The final products are a mixture of substituted ammonium dichlorocuprate(I) salts, which may engage in a series of additional complex equilibria involving copper(I) coordination complexes.<sup>11, 12, 14, 39, 43</sup>

The alkyl groups involved in the amines studied were ethyl, or longer; these were oxidized to vinyl or substituted vinyl groups. When an apparently similar oxidation of trimethylamine by copper(II) chloride was observed, no ready explanation for the course of the reaction could be given, since formation of an enamine is obviously impossible in this case.<sup>31</sup>

Further interest in this reaction developed when Kiesel and Schram described the oxidation of trimethylamine by vanadium(IV),

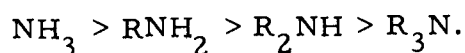
with partial characterization of the amine oxidation products.<sup>26,27</sup>

The purpose of this research was to reinvestigate the coordination and oxidation-reduction reactions of trimethylamine with copper(II) chloride, and to attempt to characterize the reaction products.

## II. HISTORICAL

### A. Coordination Compounds

The coordinating ability of alkylamines has been recognized to decrease in the sequence



Clifton<sup>13</sup> and Hatfield<sup>22</sup> have discussed the coordinating abilities of alkylamines with respect to Lewis basicity and steric factors.

A partial listing of coordination complexes of copper(I) chloride and copper(II) chloride with ammonia and the methyl and ethyl amines, which have been claimed in the literature, is given in Table I.

Later workers were unable to prepare some of the complexes listed in Table I. Simon<sup>36</sup> and co-workers noted the formation of species with stoichiometries of 3 1/3, 3, 2, and 1 mole of amine per copper from a series of plateaus in an isobaric (20 torr) temperature-composition study of the trimethylamine-copper(II) chloride system. Yoke and Nelson<sup>31</sup> in an isothermal (0°) pressure-composition study found only a sharp break at a 1:1 mole ratio, the pressure decreasing from a value greater than 600 torr to a negligible value at the composition  $\text{CuCl}_2 \cdot 0.75 (\text{CH}_3)_3\text{N}$ . At 0° and pressures of 20 torr or greater, the work of Simon et al. would have required  $\text{CuCl}_2 \cdot 2(\text{CH}_3)_3\text{N}$

Table I. Formulas of Reported Complexes (moles of coordinated amine per mole of copper chloride).

	CuCl	CuCl <sub>2</sub>
NH <sub>3</sub>	3, 1 1/2, 1 <sup>3</sup> 3, 1 1/2, 1, 1/2 <sup>29</sup>	6, 15, 17 2 <sup>15</sup>
CH <sub>3</sub> NH <sub>2</sub>	2 1/2, 1 1/2, 1 <sup>32</sup>	4, 1 <sup>37</sup> 7, 6, 4, 3 1/2, 2 <sup>36</sup>
(CH <sub>3</sub> ) <sub>2</sub> NH	3, 2, 1 <sup>32</sup>	1 <sup>34</sup> 4, 3 1/3, 2 <sup>36</sup>
(CH <sub>3</sub> ) <sub>3</sub> N	None <sup>32</sup>	1 <sup>37</sup> 3 1/3, 2, 1 <sup>36</sup>
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	3, 2, 1 <sup>12</sup>	8, 6, 5, 6, 3 1/3, 3, 2 <sup>36</sup> 4 <sup>42</sup> 6, 5, 4, 2 (1) <sup>14</sup>
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	2, 1 <sup>11</sup>	2, (1) <sup>14</sup>
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	1 <sup>43</sup>	2 <sup>34</sup>

or a higher complex to be the solid phase. Tronov and Sakharov<sup>37</sup> obtained materials approximately analyzing for the composition  $\text{CuCl}_2 \cdot \text{N}(\text{CH}_3)_3$  by crystallization from methanol solutions containing copper(II) chloride and trimethylamine in mole ratios of 1:1, 1:4, and 1:10. Also, the existence of the complex  $\text{CuCl}_2 \cdot 3.33\text{C}_2\text{H}_5\text{NH}_2$  reported by Simon et al. could not be confirmed by Clifton<sup>13</sup>.

The coordination of long chain primary alkylamines by copper(II) and copper(I) halides has been described by Broome et al.<sup>8</sup> and by Wilkins and Burkin,<sup>42</sup> respectively. Broome et al. found that only bis(amine) complexes were formed between copper(II) halides and long-chain primary alkylamines when the chain was 12 or more carbons long. Wilkins and Burkin found copper(I) chloride and copper(I) iodide formed only mono(amine) complexes with several long-chain alkylamines, whereas copper(I) bromide formed both bis- and mono(amine) complexes with the same amines. The bis(amine)-copper(I) complexes were found to be dimeric by cryoscopic molecular weight determination in benzene. Structures with bridging bromide ligands were posulated. The monoamine complexes were assumed to be tetrameric in structure.

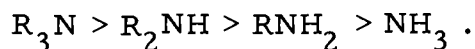
Clifton's<sup>11</sup> cryoscopic molecular weight determinations of  $\text{CuCl} \cdot 2(\text{C}_2\text{H}_5)_3\text{N}$  in nitrobenzene indicated a two-fold molecular weight. This complex may be formulated as a bridged dimer, di- $\mu$ -chlorotetrakis(diethylamine)dicopper(I). The 1:1 species was

presumed to be tetrameric because in diethylamine solution the solute species had a molecular weight four times that of the formula weight of copper(I) chloride. Tetrameric structures are well known for MXL compounds, where M is copper(I) or silver(I), X is halide ion, and L is a Group V ligand, e.g., an organic phosphine or arsine.<sup>10, 41</sup>

## B. Oxidation of Aliphatic Amines

### 1. General

The oxidation of aliphatic amines has been studied by several investigators, and has been reviewed by Arneson<sup>1</sup>. While many peroxides convert tertiary amines to the amine oxides, it is more generally found that the amine oxidation involves the loss of two electrons and two hydrogen ions, with the formation of enamines. These reactive intermediates often undergo secondary reactions yielding a variety of products, including substituted ammonium salts. The nature of these secondary products often depends on reaction conditions, the solvent and the nature of the reduced species. Studies have shown that tertiary amines are more easily oxidized than primary or secondary amines, and the usual tendency toward oxidation is in the order



It has been noted<sup>18</sup> that various metal ions in high valence states

oxidize aliphatic amines. Thus iron(III), tungsten(IV) and (V), vanadium(IV) and titanium(IV) are reduced by aliphatic amines. The emphasis in this work has been on characterization of complexes of the reduced metal species. In general, the amine oxidation products have been ignored.

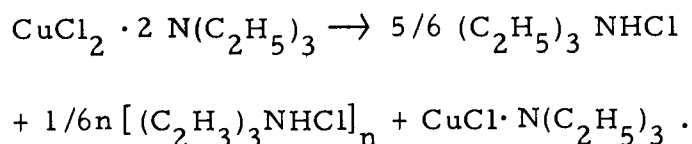
## 2. Oxidation of Aliphatic Amines by Copper(II) Chloride

Yoke and his students<sup>11, 12, 14, 39, 43</sup> have investigated the coordination and oxidation of the primary, secondary and tertiary ethylamines by copper(II) chloride. The systems were found to be very complicated, but in all cases coordination of the amines by copper(II) to give isolable complexes preceded the irreversible, thermally induced oxidation reaction.

The oxidation of triethylamine was somewhat different from the oxidation of ethyl- or diethylamine. This difference was attributed to a structural difference in the tertiary amine complex. When dichlorobis(triethylamine)copper(II), synthesized at a low temperature, was allowed to warm to room temperature, it was found that one-sixth of a mole of triethylamine was oxidized for each mole of copper(II) reduced to copper(I). At 0°C, a diamagnetic orange intermediate was observed, which at room temperature gradually changed to chloro(triethylamine)copper(I) and the hydrochlorides of

triethylamine and of a red-brown, tar-like, polymeric amine.

Hydrolysis of the orange intermediate yielded acetaldehyde and diethylamine. The postulated mechanism involves an initial one-electron oxidation of triethylamine, and disproportionation of the radical thus formed to give an enamine. Repeated steps lead eventually to a polymer of trivinylamine. The stoichiometry of the net reaction is

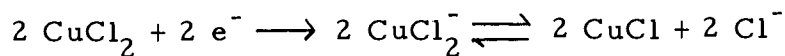


Clifton's<sup>13</sup> work on the copper(II) chloride oxidation of ethyl- and diethylamine showed significant differences in reaction behavior. In these cases, not only was a higher temperature necessary to induce oxidation-reduction, but the intermediate stages were quite different from triethylamine oxidation. Ethyl- and diethylamine also form dichlorobis(amine)copper(II) complexes, but the loss of one-half of the amine content to the gas phase is a prerequisite to the thermally induced oxidation-reduction reaction in these species. While the stoichiometry of triethylamine oxidation corresponds to dehydrogenation of all three ethyl groups, and that of ethylamine corresponds to dehydrogenation of the one ethyl group, the stoichiometry of diethylamine oxidation indicates dehydrogenation of more than one but less than two ethyl groups on the average.

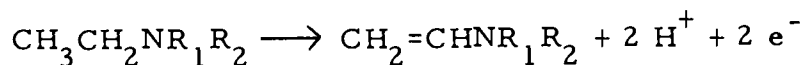


In all three cases, however, the key features of the overall reaction can be represented by the equations:

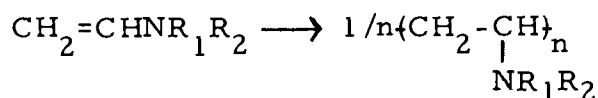
- (1) reduction of copper(II) to copper(I) species



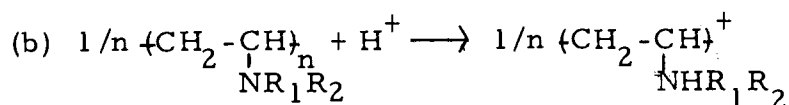
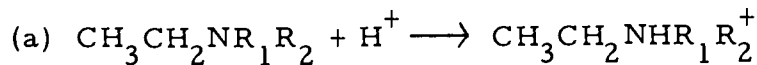
- (2) oxidation of an ethyl group to a vinyl group



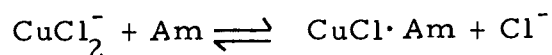
- (3) polymerization



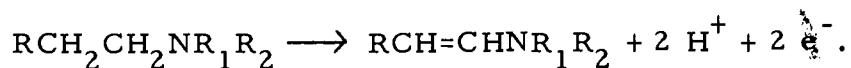
- (4) protonation



- (5) coordination of copper(I) by amine



The final products are chloride or dichlorocuprate(I) salts of protonated forms of both the starting amine and the amine oxidation product (which itself is a polymeric amine), as well as amine complexes of copper(I). Similar oxidation of higher molecular weight amines, e. g., tri-n-butylamine, was observed. Thus, step (2) above can be written generally as

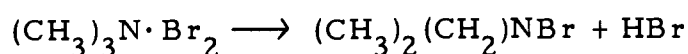
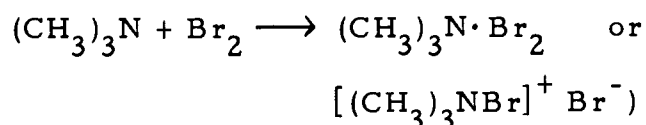


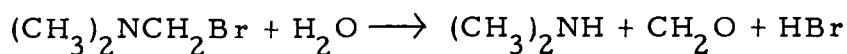
It is apparent, however, that this process would be impossible for an amine with only methyl ~~substituents~~.

### 3. Oxidation of Trimethylamine

The complexes of copper(II) chloride and trimethylamine prepared by Simon<sup>36</sup> and co-workers were observed to be unstable with respect to oxidation-reduction on heating. Yoke and Nelson<sup>31</sup> also observed reaction to give a dark tarry product, presumably due to oxidation-reduction, in the copper(II) chloride-trimethylamine system at temperatures above 68°C. The reaction products were not characterized.

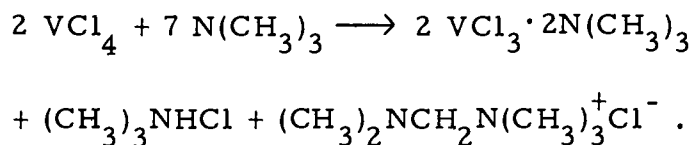
The oxidation of trimethylamine by halogens has been studied by Boehme and co-workers.<sup>5, 6, 7</sup> They suggest a reaction pathway that involves the formation of the addition product, e.g.,  $\text{R}_3\text{NBr}_2$ , and its decomposition upon heating. The stoichiometry for trimethylamine oxidation is one mole of amine oxidized per mole of bromine reduced. The reaction scheme postulated is:





Species involving the tribromide ion were identified when bromine was in excess.

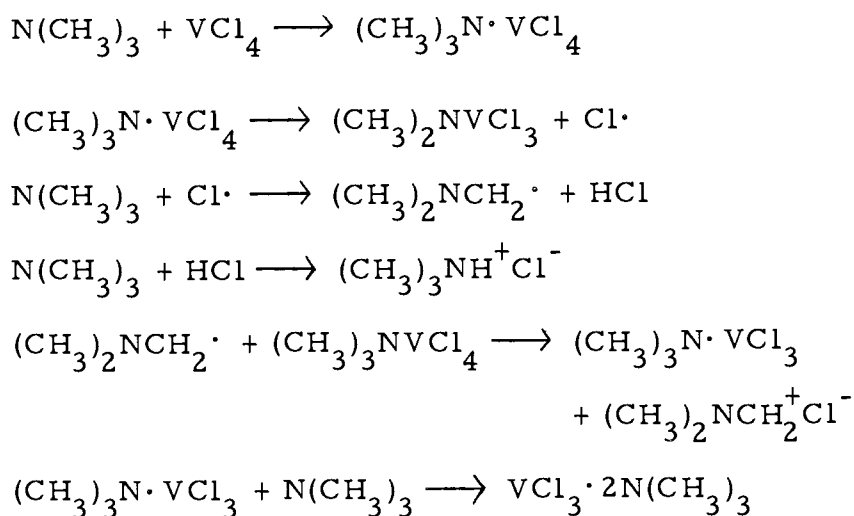
Kiesel and Schram<sup>26, 27</sup> have reported the stoichiometry of the oxidation-reduction reaction between vanadium(IV) chloride and trimethylamine as



The presence of trichlorobis(trimethylamine)vanadium(III) was established by its infrared spectrum following its extraction by trimethylamine from the red-brown reaction mixture. Similarly, trimethylammonium chloride was identified by infrared spectrophotometry as a component of the residual reaction mixture after extraction. The amine oxidation products were not isolated. The dimethylmethylenammonium ion,  $(\text{CH}_3)_2\text{N}=\text{CH}_2^+$ , was identified as an intermediate, in that its characteristic infrared frequencies were observed in the unseparated reaction mixture when a deficiency of trimethylamine was used. Kiesel and Schram write  $(\text{CH}_3)_2\text{NCH}_2\text{N}(\text{CH}_3)_3^+\text{Cl}^-$  as the final amine oxidation product when an excess of trimethylamine is present, by supposing that dimethylmethylenammonium chloride reacts with

additional trimethylamine to give this product. However, in the same report they show that such a reaction does not in fact occur (see Section II B 4).

Their proposed mechanism involves formation of an initial complex of vanadium(IV) and trimethylamine, with the subsequent elimination of atomic chlorine. This leads to formation of dimethylmethyleneammonium chloride.

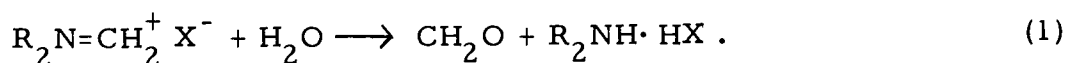


#### 4. Dialkylmethyleneammonium Compounds

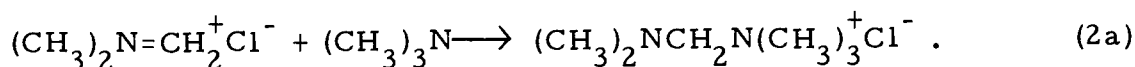
Volz and Kiltz<sup>38</sup> reported the formation of various  $\text{R}_1\text{R}_2\text{N}=\text{CH}_2^+$  salts, by hydride abstraction from methyl groups of tertiary amines. The infrared spectra of the perchlorate and hexachloroantimonate(V) salts had a characteristic peak in the range 1663 to 1675  $\text{cm}^{-1}$ , assigned to  $\nu(\text{C}=\text{N})$ . Eschenmoser et al.<sup>34</sup> have reported the synthesis, by thermal decomposition of trimethyliodomethylammonium iodide, of  $(\text{CH}_3)_2\text{N}=\text{CH}_2^+ \text{I}^-$  with  $\nu(\text{C}=\text{N})$  at 1682  $\text{cm}^{-1}$ . Both of these papers

also review previous work on the dialkylmethylen ammonium salts, especially by H. Boehme and co-workers, who showed that the equilibrium  $R_2NCH_2Cl \rightleftharpoons R_2N=CH_2^+Cl^-$  lies to the right. Kiesel and Schram<sup>26, 27</sup> prepared solid  $(CH_3)_2N=CH_2^+Cl^-$  and found  $\nu(C=N)$  at  $1696\text{ cm}^{-1}$ . The synthesis, involving the reaction of acetyl chloride with N, N, N', N'-tetramethylmethylenediamine, was first reported by Boehme and Haake.<sup>7</sup>

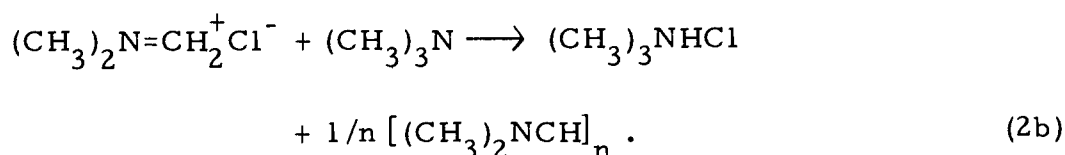
Various reactions of dialkylmethylen ammonium salts have been reported; those of particular relevance to this research are the reactions with water, trimethylamine, and copper(I) halides. Volz and Kiltz<sup>38</sup> showed that the hydrolysis of dialkylmethylen ammonium ions gives formaldehyde and the protonated dialkylamine,



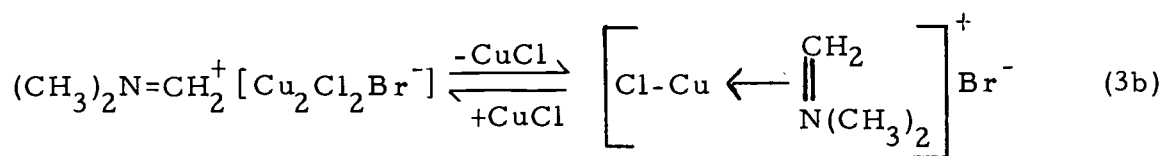
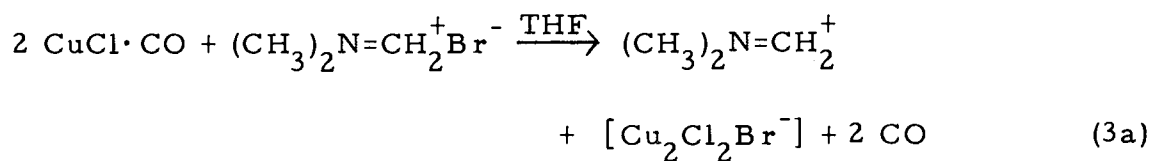
Kiesel and Schram were unsuccessful in three attempts under varying conditions to repeat a reaction previously reported by Boehme and Haake,



Instead, they found that trimethylammonium chloride was formed, and attributed this to deprotonation by trimethylamine of the dimethylmethylen ammonium ion, presumably to give a polymeric material,



In a communication with a paucity of experimental detail, Mason and Rucci<sup>28</sup> reported an interesting cationic complex of copper(I) chloride with the dimethylmethyleneammonium cation, supposedly formed by the reactions



### III. EXPERIMENTAL

#### A. Manipulative Techniques

A glass high vacuum system such as those described by Sanderson<sup>33</sup> and by Shriver,<sup>35</sup> with a pressure of  $< 10^{-5}$  torr, was used in the synthesis, oxidation-reduction and hydrolysis studies. Spectrovac Type I grease was used on the stopcocks and ground glass joints. Vapor pressures were measured using mercury manometers and a meter stick.

A stainless steel dry box was used; its nitrogen atmosphere was continuously circulated through an oxygen scrubbing tower containing BTS catalyst (BASF) and through two drying tubes. The bottom tube contained a mixture of Linde 5 A and 4 A molecular sieves; the top tube contained Linde 13X molecular sieves. Entrance to the dry box was through an evacuable port.

A sample of anhydrous copper(II) chloride was transferred in the nitrogen-filled dry box to a tared reaction assembly, consisting of a reaction flask containing a teflon coated magnetic stir bar, and fitted through ground glass joints with a connecting tube having a stopcock, permitting attachment to and removal from the vacuum system.

The procedure followed was to attach the empty reaction assembly to the vacuum system and to evacuate it. The assembly was then

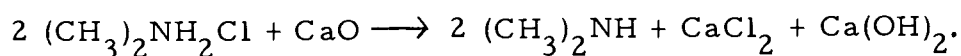
removed from the vacuum system, the inner connecting joint was wiped free of grease, and the assembly was weighed to obtain a tare weight. The evacuated assembly was then placed into the nitrogen-filled dry box and opened. A small amount of finely powdered anhydrous copper(II) chloride was transferred to the reaction flask. The connecting tube was replaced and the assembly was removed from the dry box and reattached to the vacuum system. The system was reevacuated for one hour. After this the stopcock was closed and the assembly removed from the vacuum system. The attachment tube joint was wiped free of grease and the evacuated assembly containing copper(II) chloride weighed. In this manner the exact amount of copper(II) chloride taken was determined.

## B. Materials

Trimethylamine. Anhydrous trimethylamine (Matheson) was purified using the vacuum line. The amine (b.  $3.5^{\circ}$ ) was condensed into an evacuated flask containing phosphorus oxide and stirred under its own pressure at  $0^{\circ}$  for several hours. The amine was then distilled through a trap at  $-23^{\circ}$  (carbon tetrachloride slush bath) into a liquid nitrogen cooled U tube connected to a manometer. The vapor pressure at  $0^{\circ}$  was 687 torr; this is in good agreement with literature values.<sup>23, 24, 40</sup>



Dimethylamine. Dimethylamine hydrochloride was recrystallized from absolute ethanol and dried in vacuo at  $65^{\circ}$ . Dimethylamine hydrochloride and freshly ignited calcium oxide powders were mixed in a 100 ml round bottomed flask. The mixture was covered with a layer of calcium oxide. The flask was attached to the vacuum line, evacuated at  $-196^{\circ}$ , and then heated moderately;



The dimethylamine and traces of water produced were condensed in a U trap at  $-196^{\circ}$ . The amine was then distilled through a  $-23^{\circ}$  trap into a tube containing anhydrous calcium chloride at  $-196^{\circ}$ . The contents of the tube were stirred at  $0^{\circ}$  for one-half hour. The dimethylamine was stored at  $-50^{\circ}$  as a liquid until used.

Methylamine. Similarly, methylamine was prepared from its hydrochloride and dried as described above. Methylamine was stored at  $-50^{\circ}$  as a liquid until used.

Methanol. Reagent grade methanol was refluxed over magnesium methoxide for two hours and distilled under nitrogen. The fraction boiling at  $65^{\circ}$  was collected and stored in a glass stoppered flask until used.

Ethanol. Similarly, ethanol was refluxed over magnesium ethoxide and distilled. The fraction boiling at  $78^{\circ}$ - $80^{\circ}$  was collected and stored in a glass stoppered bottle until used.

Water. Distilled water was boiled for one-half hour with nitrogen bubbling through it to remove dissolved oxygen. The water was cooled under nitrogen, and the flask was stoppered and stored until used.

Copper(II) Chloride. Copper(II) chloride dihydrate (Baker Reagent Grade) was dehydrated by heating at  $110^{\circ}$  until all of the blue dihydrate had become brown.<sup>14</sup> This material was stored in the dry nitrogen-filled dry box until used. Just prior to use the material was heated to  $100^{\circ}$  for 15 minutes under high vacuum.

Copper(I) Chloride. Copper(I) chloride was purified by the sulfite reduction method.<sup>25</sup> The white product was stored in a vacuum desiccator over phosphorous(V) oxide until used.

### C. Instrumental Methods

Gas Chromatography. A F & M Model 700 chromatograph with a thermal conductivity detector was used. Dual six foot stainless steel columns were packed (funnel coating method, solvent methylene chloride,  $\phi = 2.00$ )<sup>30</sup> with 5% tetraethylenepentamine (Aldrich) on Fluoropak 80. Helium was used as the carrier gas at a flow rate of 30 ml/min. With column temperatures in the range of  $60$ - $120^{\circ}$ , good separations were obtained of mixtures of trimethylamine, methanol and formaldehyde. However, the primary, secondary, and tertiary methylamines (boiling points -  $6.3^{\circ}$ ,  $7.4^{\circ}$  and  $3.5^{\circ}$  respectively) were not separated, eluting as a single sharp peak.

Preliminary tests with SE 30 and 10% polyethyleneimine on Porapak Q gave unsatisfactory results, with poor separation and severe tailing.

Infrared Spectra. A Beckman IR-8 spectrometer was used to obtain IR spectra. Samples were run in fluorolube and Nujol mulls as well as in potassium bromide pellets.

Magnetic Susceptibility. This was determined using a Gouy balance at room temperature, as described by Clifton.<sup>13</sup>

#### D. The System Copper(II) Chloride-Trimethylamine

Complex Formation. The typical procedure followed for studying complex formation was to use an evacuated reaction assembly loaded with a known amount of copper(II) chloride as described previously. A considerable excess of trimethylamine was transferred through the vacuum system into the assembly, which was cooled with liquid nitrogen. The stopcock in the connecting tube was then closed. The assembly was removed from the vacuum system and stored at  $-50^{\circ}$  for several days with magnetic stirring of the contents. The assembly was then reattached to the vacuum system. The excess of trimethylamine was distilled from the reaction assembly back into the storage vessel. With the temperature of the reaction assembly maintained at  $0^{\circ}$ , the pressure of the trimethylamine in equilibrium with the complex reaction product could be determined by opening the system to a

manometer. It was possible to remove the excess of amine from the complex and to measure the equilibrium pressures in this manner. It could be readily determined when all of the excess of trimethylamine had been removed from a complex, this being indicated by a sharp drop in the equilibrium pressure. At the point corresponding to the complete removal of the excess amine, the stopcock in the reaction assembly was closed, and the assembly was removed from the vacuum system and reweighed. The increase in weight representing combined trimethylamine was thus determined. The mole ratio of copper(II) chloride to amine retained so obtained represents the stoichiometry of the coordination reaction.

Oxidation-Reduction. The typical procedure followed for studying the oxidation-reduction reaction was to use an evacuated assembly loaded with a known amount of copper(II) chloride added as described previously. A considerable excess of trimethylamine was transferred through the vacuum system into a U trap which was cooled in liquid nitrogen. The U tube was closed off from the rest of the vacuum system and allowed to warm to  $0^{\circ}$  (ice bath). The U tube was then opened to the reaction assembly and the trimethylamine vapor was allowed to contact the copper(II) chloride. The reaction assembly was heated on a steam bath until reaction was complete, usually 2-4 hours. The bulk of the excess amine was then removed from the assembly by distillation into a liquid nitrogen cooled trap. Final traces of unreacted

trimethylamine were removed by opening the reaction assembly directly to the diffusion and mechanical pumps. After approximately two hours the connecting stopcocks were closed and the assembly removed from the vacuum system and reweighed. The increase in weight representing combined amine was thus determined. The mole ratio of copper(II) chloride to retained amine so obtained represents the stoichiometry of the oxidation-reduction reaction.

In one run a Parr Monel Bomb was used for the oxidation-reduction reaction. The procedure in this case was to cool the body of the bomb with dry ice in a nitrogen filled dry bag, and then transfer a measured amount of liquid trimethylamine into the bomb. The bomb was sealed, removed from the dry bag and heated on a steam bath.

Hydrolysis. The hydrolysis was conducted in the same assembly used for the oxidation-reduction reaction. An excess of degassed distilled water (2-5 ml) was transferred through the vacuum system into the assembly. The assembly was then closed off from the rest of the vacuum system and allowed to warm to room temperature. The solution was stirred magnetically for several hours and the most volatile portion was removed from the assembly by distillation into a liquid nitrogen cooled trap. This portion was then distilled through a  $-23^{\circ}$  (carbon tetrachloride slush bath) trap into a bulb containing a small amount of either methanol or ethanol. This solution was then removed for further tests.

### E. The System Copper(I) Chloride-Trimethylamine

The procedure for studying copper(I) chloride-trimethylamine complex formation was identical to that previously described for copper(II) chloride-trimethylamine complex formation, except that the reaction assembly was loaded with copper(I) chloride initially.

## IV. RESULTS

### A. Copper(I) Chloride-Trimethylamine System

The isothermal ( $0^{\circ}$ ) pressure-composition study showed only one break in which the pressure decreased from a value greater than 600 torr to a negligible value. The mole ratio as determined by weighing was 1.00:1.00  $\text{CuCl} \cdot (\text{CH}_3)_3\text{N}$ . The melting point was determined to be  $122-124^{\circ}$ .

### B. Coordination of Copper(II) Chloride by Trimethylamine

Several attempts were made to isolate coordination complexes of copper(II) chloride and trimethylamine. The formation of a mustard yellow solid, which is the 1:1 complex, and of an unstable blue-green complex, which is presumed to be the 2:1 mole ratio complex, was observed.

A sample of the mustard yellow complex with the nominal composition  $\text{CuCl}_2 \cdot 1.08 (\text{CH}_3)_3\text{N}$  was analyzed for C, H, N, and Cu with the following results:

	C	N	H	Cu
Calculated %	19.64	4.94	7.63	32.04
Found	19.76	5.09	7.69	31.92

The molar magnetic susceptibility of this material at  $21.5^{\circ}\text{C}$ , after diamagnetic corrections were made using Pascal's constants,

was found to be  $1.352 \times 10^{-3}$  cgs emu. The effective magnetic moment, calculated by the equation  $\mu_{\text{eff}} = 2.828 (X_M^{\text{cor}} T)^{1/2}$ , was 1.79 B.M.

In pressure-composition studies, samples of the blue-green complex gave mole ratios in a range greater than 1.3 trimethylamine: copper(II) chloride. The irreproducible results are due to the large dissociation pressure of  $\text{CuCl}_2 \cdot 2\text{Me}_3\text{N}$  under the experimental conditions.

#### C. Oxidation-Reduction of Copper(II) Chloride with Trimethylamine

Various reactions carried out in the manner previously described yielded similar red-black products that were tarry solids at  $25^\circ$  or less and oils at  $27^\circ$  and above. The products had mole ratios of trimethylamine:copper of 1.24-1.4 (on an original basis) when an excess of trimethylamine was present during the oxidation-reduction and from 0.96 to 1.01 when equimolar amounts of trimethylamine were used. The infrared spectra of the red-black tars had a sharp peak at  $1690 \text{ cm}^{-1}$  which is characteristic of (C=N). Further comparisons are given in Table II.

The most volatile portion of the solution after hydrolysis gave a positive Hinsberg test for secondary amines. The gas chromatogram showed not only the amine peak (unresolved di- and trimethylamines), but also showed another major peak which was identified as



Table II. Infrared Spectral Data ( $\text{cm}^{-1}$ ).

Oxidation-Reduction Product	Reported Values and Assignment <sup>27</sup>	
	<u><math>(\text{CH}_3)_2\text{NH}^+</math></u>	
2700-3150, 2480	2770, 2430	(N-H--Cl)
1600	1609	( $\text{NH}_2$ )
1015, 980	1010, 998	( $\text{NC}_2$ )
	883	( $\text{NC}_2$ )
	<u><math>(\text{CH}_3)_2\text{N}=\text{CH}_2^+</math></u>	
2700-3150	3118, 3020	( $\text{CH}_2$ )
1690	1695	(C=N)
1048, 1015, 980	1051, 1010, 998	( $\text{NC}_2$ )
825	820	$\rho_w$ ( $\text{CH}_2$ )

formaldehyde by comparison with an authentic sample. Further qualitative tests under aerobic conditions, on the non-volatile residue from hydrolysis indicated the presence of copper(I) and (II), formate ion and a polymeric amine, partly present as its hydrochloride as indicated by a positive chloride ion test.

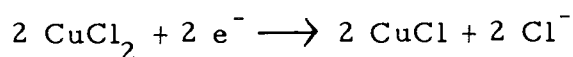
## V. CONCLUSIONS

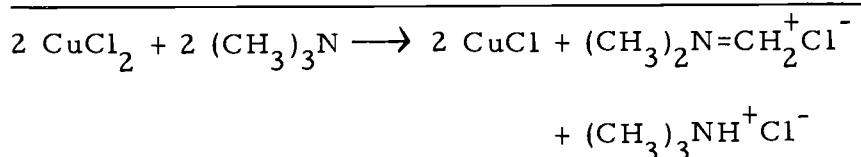
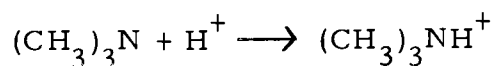
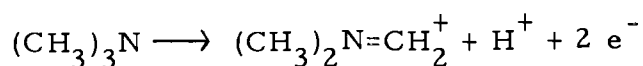
The study of the copper(I)-trimethylamine system indicated the formation of the complex  $\text{CuCl} \cdot \text{N}(\text{CH}_3)_3$ . This is not in agreement with the earlier report by Peters,<sup>32</sup> who found no complex in this system.

In the copper(II)-trimethylamine system two solids are identified: the mustard yellow 1:1 complex and the unstable blue-green 2:1 complex, which has a high dissociation pressure. In the same system Simon and co-workers<sup>36</sup> found a series of complexes. Their isobaric temperature-composition diagram shows that at 0° and 20 torr the stable complex should be  $\text{CuCl}_2 \cdot n\text{N}(\text{CH}_3)_3$  (where n is 2 or higher). The 1:1 complex was previously obtained by Tronov and Sakharov<sup>37</sup> by crystallization from methanol.

The oxidation of trimethylamine by copper(II) chloride resembles its oxidation by vanadium(IV) chloride.<sup>26, 27</sup> The presence of the dimethylmethyleneammonium cation,  $(\text{CH}_3)_2\text{N}=\text{CH}_2^+$ , is indicated especially by the absorption at  $1690 \text{ cm}^{-1}$ ;  $\nu (\text{C}=\text{N})$  has been assigned in the  $1663\text{-}1699 \text{ cm}^{-1}$  region in various salts of this cation.<sup>26, 27, 34, 38</sup> The hydrolysis products expected,<sup>38</sup> formaldehyde and dimethylamine, were identified.

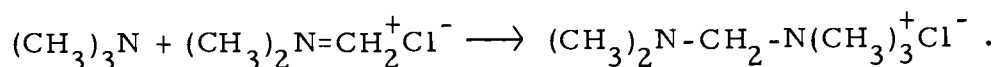
The reaction, when equimolar amounts of copper(II) chloride and trimethylamine are used, can be written



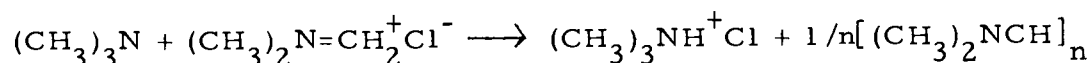


The actual state of the reaction products, and the variable stoichiometry reported in this work, are related to the complex interactions which may occur when excess trimethylamine is present, viz:

(1) Reaction of the dimethylmethyleneammonium ion with excess trimethylamine. Kiesel and Schram,<sup>26, 27</sup> following Boehme and Haake<sup>7</sup> write this reaction as



However, they also report failure in attempting this reaction with pure starting materials. Kiesel and Schram also write



and formation of such a polymer seems in better accord with the tarry nature of the reaction product.



between copper(I) chloride and the dimethylmethyleneammonium ion, which has been reported by Mason and Rucci.<sup>28</sup>

- (3) Formation of chlorocuprate complex anions, some of whose salts are oils at room temperature,<sup>2</sup> e.g;



- (4) Coordination of copper(I) chloride by excess trimethylamine.

## BIBLIOGRAPHY

1. Arneson, R., M.S. Thesis, Oregon State University 1974
2. Axtell, D.D., B.W. Good, W.W. Porterfield, and J.T. Yoke, J. Amer. Chem. Soc., 95, 4555 (1973)
3. Biltz, W., Z. Anorg. Chem., 130, 93 (1923)
4. Boehme, H., Chem. Ber., 90, 2008 (1957)
5. Boehme, H., Chem. Ber., 91, 340 (1958)
6. Boehme, H. and W. Krause, Chem. Ber., 84, 170 (1951)
7. Boehme, H. and M. Haake, Justus Liebigs Ann. Chem., 705, 147 (1967)
8. Broome, F.K., A.W. Ralston and M.H. Thornton, J. Amer. Chem. Soc., 68, 67 (1946)
9. Burkin, A.R., J. Chem. Soc., 122, (1950)
10. Churchill, M.R. and K.L. Kabra, Inorg. Chem., 13, 1065, 1427 (1974)
11. Clifton, J.R. and J.T. Yoke, Inorg. Chem., 5, 1630 (1966)
12. Clifton, J.R. and J.T. Yoke, Inorg. Chem., 6, 1258 (1967)
13. Clifton, J.R., Ph.D. Dissertation, Oregon State University 1967
14. Clifton, J.R. and J.T. Yoke, Inorg. Chem., 7, 39 (1968)
15. Distler, T. and P.A. Vaughan, Inorg. Chem., 6, 126 (1967)
16. Ephraim, F. and R. Linn, Chem. Ber., 46, 3742 (1913)
17. Ephraim, F., Z. Phys. Chem., 81, 513 (1913)
18. Fowles, G.W.A., Prog. Inorg. Chem., 6, 1 (1964)

19. Gemlin's Handbuch der Anorganischen Chemie, 8 Auflage, System No. 60 Kupfer, Gemlin Institute, Frankfurt am Main, Verlag Chemie GMBH, Weinheim, Bergstrasse, 1958, pg. 253.
20. Hanic, F. and I. A. Cakajdeva, Aeta Cryst., 11, 610 (1958)
21. Hanic, F. and I. A. Cakajdeva, Aeta Cryst., 12, 739 (1959)
22. Hatfield, W.E., Ph.D. Dissertation, University of Arizona 1962
23. Holmes, R.R. and E.F. Bertaut, J. Amer. Chem. Soc., 80, 2980 (1958)
24. Holmes, R.R., J. Phys. Chem., 64, 1295 (1960)
25. Jolly, W.L., "Synthetic Inorganic Chemistry," Prentice-Hall, Inc. Englewood Cliffs, New Jersey, 1960
26. Kiesel, R.F. and E.P. Schram, Inorg. Chem., 12, 1090 (1973)
27. Kiesel, R.F. and E.P. Schram, Inorg. Chem., 13, 1313 (1974)
28. Mason, R. and G. Rucci, J. Chem. Soc. Chem. Commun., 1132 (1971)
29. Muller-Litz, W., Z. Chem., 8, 389 (1968)
30. McNair, H.M. and E.J. Bonnell, "Basic Gas Chromatography," Varian Co., Walnut Creek, Calif., 1967 pp. 224-225, 230
31. Nelson, T. and J.T. Yoke, Unpublished results, University of Arizona 1964
32. Peters, W., Z. Anorg. Chem., 89, 191 (1914)
33. Sanderson, R.T., "Vacuum Manipulation of Volatile Compounds" J. Wiley and Sons, Inc., New York 1948
34. Schreiber, J., H. Magg, N. Hashimoto and A. Eschenmoser, Angew. Chem. Internat. Edit., 10, 330 (1971)
35. Shriver, D.F., "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York 1969

36. Simon, A., H. Haman and F. Arnold, Rev. Chim. (Bucharest), 7, 531 (1962)
37. Tronov, B.V. and A.P. Sakharov, Org. Kompleks. Soedin., 163 (1965)
38. Volz, H. and H. Kiltz, Justus Liebigs Ann. Chem., 752, 86 (1971)
39. Weiss, J.F., G. Tollin, and J.T. Yoke, Inorg. Chem., 3, 1344 (1964)
40. Weiss, J.F., Ph.D. Dissertation, University of Arizona 1964
41. Wells, A.F., "Structural Inorganic Chemistry," 3rd Ed., Oxford Univ. Press, London, 1962, p. 863
42. Wilkins, R.G. and A.R. Burkin, J. Chem. Soc., 127 (1950)
43. Yoke, J.T., J.F. Weiss and G. Tollin, Inorg. Chem., 2, 1210 (1963)