



A photochemical reaction of alkylammonium tetrachlorocuprates
by Kathleen Diane Mannila

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemistry
Montana State University
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Abstract:

A photochemical reaction has been observed in solutions of the alkylammonium tetrachlorocuprates, and three mechanisms have been postulated. According to experimental results, none of the three is precisely correct. It is believed, however, that copper (II) is reduced to copper(I) and that chloride is the species oxidized. These observations point to the necessity of excluding stray light from solutions of the tetrachlorocuprates prepared for quantitative spectral measurements, since a rapid decrease in absorbtivity occurs even in ordinary laboratory illumination.

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Date

September 25, 1969

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by

KATHLEEN DIANE MANNILA

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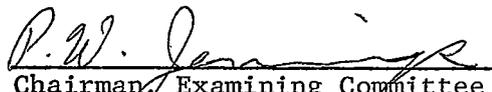
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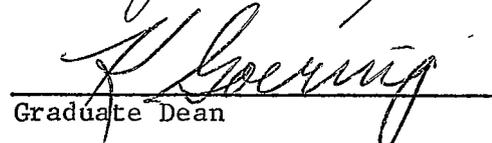
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TABLE OF CONTENTS

	Page
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
ABSTRACT.....	viii
INTRODUCTION.....	1
DISCUSSION.....	4
CONCLUSION.....	31
EXPERIMENTAL.....	35
Preparation of Compounds.....	35
Spectral Measurements.....	35
Decolorization of Tetrachlorocuprate Solutions With Light.....	35
Determination of Light Region Causing Decolorization.....	36
Determination of Change in Free Chloride and pH.....	36
Time Studies.....	37
LITERATURE CITED.....	42

LIST OF TABLES

	Page
I. Determination of Free Chloride.....	39
II. Determination of Change in Hydrogen Ion Concentration.....	39
III. Absorbance at 1200 m μ	40
IV. d Spacings for Precipitate Obtained from Irradiation of Acetamidinium Tetrachlorocuprate.....	41

LIST OF FIGURES

	Page
1. Squashed Tetrahedral Structure of CuCl_4^{--} Ions in Cs_2CuCl_4	1
2. Square Planar Arrangement of CuCl_4^{--} Ions in $(\text{NH}_4)_2\text{CuCl}_4$	1
3. Visible and Near Infrared Spectra of Red Filter Corning 2-59 and Blue-green Filter Corning 4-72.....	7
4. Ultraviolet Spectrum of Methylammonium Tetrachlorocuprate.....	8
5. Visible Spectrum of Methylammonium Tetrachlorocuprate.....	8
6. Ultraviolet Spectrum of Methylammonium Tetrachlorocuprate After Decolorization by Light.....	9
7. Visible Spectrum of Methylammonium Tetrachlorocuprate After Decolorization by Light.....	9
8. Ultraviolet Spectrum of Ethylammonium Tetrachlorocuprate.....	10
9. Visible Spectrum of Ethylammonium Tetrachlorocuprate.....	10
10. Ultraviolet Spectrum of Ethylammonium Tetrachlorocuprate After Decolorization by Light.....	11
11. Visible Spectrum of Ethylammonium Tetrachlorocuprate After Decolorization by Light.....	11
12. Ultraviolet Spectrum of Tetraethylammonium Tetrachlorocuprate.....	12
13. Visible Spectrum of Tetraethylammonium Tetrachlorocuprate.....	12
14. Ultraviolet Spectrum of Tetraethylammonium Tetrachlorocuprate After Decolorization by Light.....	13
15. Visible Spectrum of Tetraethylammonium Tetrachlorocuprate After Decolorization by Light.....	13
16. Near Infrared Spectrum of Methylammonium Tetrachlorocuprate Before and After Decolorization by Light.....	14
17. Near Infrared Spectrum of Ethylammonium Tetrachlorocuprate Before and After Decolorization by Light.....	15

18.	Near Infrared Spectrum of Tetraethylammonium Tetrachlorocuprate Before and After Decolorization by Light.....	16
19.	Ultraviolet Spectrum of Cuprous Chloride.....	18
20.	Visible Spectrum of Cuprous Chloride.....	18
21.	Near Infrared Spectrum of Cuprous Chloride.....	19
22.	Infrared Spectrum of $\text{ClCH}_2\text{CN} + \text{CuCl} + (\text{C}_2\text{H}_5)_4\text{NCl}$ After Light.....	23
23.	Infrared Spectrum of Chloroacetonitrile.....	24
24.	Infrared Spectrum of Tetraethylammonium Chloride.....	24
25.	Infrared Spectrum of Tetraethylammonium Tetrachlorocuprate Before Light.....	25
26.	Infrared Spectrum of Tetraethylammonium Tetrachlorocuprate After Light.....	25
27.	Infrared Spectrum of Chlorine in Acetonitrile After Light.....	28
28.	Infrared Spectrum of $\text{Cl}_2 + \text{CuCl} + (\text{C}_2\text{H}_5)_4\text{NCl}$ After Light.....	28
29.	Infrared Spectrum of Distillate from Tetrachlorocuprate Irradiation.....	29
30.	Visible Spectrum of Chlorine in Acetonitrile.....	30
31.	Decrease in Absorbance with Time.....	32
32.	Optical Diagram of a Cary 14 Spectrophotometer.....	34
33.	Standardization Curve for Determination of Chloride Ion Concentration.....	38

ABSTRACT

A photochemical reaction has been observed in solutions of the alkylammonium tetrachlorocuprates, and three mechanisms have been postulated. According to experimental results, none of the three is precisely correct. It is believed, however, that copper(II) is reduced to copper(I) and that chloride is the species oxidized. These observations point to the necessity of excluding stray light from solutions of the tetrachlorocuprates prepared for quantitative spectral measurements, since a rapid decrease in absorbtivity occurs even in ordinary laboratory illumination.

INTRODUCTION

The existence of the tetrachlorocuprate(II) anion, CuCl_4^{--} , has been reported for some time. A classification of the then known complex cupric chlorides (33 in all) by Remy and Laves in 1933 showed 22 tetrachlorocuprates.⁸ More recently, the study of the structure and spectra of copper(II) halide complexes has received considerable attention.

Two different geometries have been observed for the CuCl_4^{--} ion. It is known to exist as a distorted tetrahedron (Figure 1) in Cs_2CuCl_4 ,⁶ in molten chlorides,⁴ and in acetonitrile and nitromethane solutions of $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3]_2\text{CuCl}_4$ and of $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{CuCl}_4$.⁵ Spectral and X-ray measurements indicate a square planar ion in $(\text{NH}_4)_2\text{CuCl}_4$, in $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$, and in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ ^{9,10} (Figure 2). In general, M_2CuCl_4 compounds, where M represents a univalent cation, contain nonplanar CuCl_4^{--} ions provided the cations are large.³ Thus, monosubstituted ammonium salts contain square planar tetrachlorocuprate anions and tetrasubstituted ammonium salts contain tetrahedral anions.

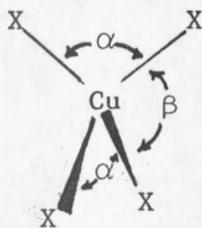


Figure 1. Squashed Tetrahedral Structure of CuCl_4^{--} ions in Cs_2CuCl_4 ($\alpha > \beta$)³

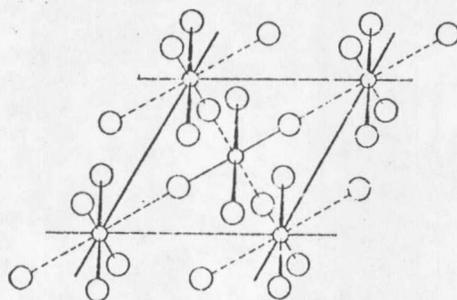


Figure 2. Square Planar Arrangement of CuCl_4^{--} ions in $(\text{NH}_4)_2\text{CuCl}_4$ ⁹

