



Synthesis and study of some new amidine transition metal complexes
by Leo Allan Bares

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
© Copyright by Leo Allan Bares (1966)

Abstract:

The syntheses of five new amidine-transition metal complexes are reported. Three of these complexes, acetamidinium tetrachlorocuprate, acetamidinium tetrachlorocobaltate and acetamidinium trichloronickelate, appear to be analogous to the corresponding cesium complexes. Copper (II) acetamidinate and copper (II) benzamidinate have also been prepared.

Solution and diffuse reflectance spectra have been determined for all five complexes. Magnetic data have been obtained for the chlorocuprate, acetamidinate and benzamidinate. These data suggest possible structures, but do not allow unequivocal structural conclusions.

144

SYNTHESIS AND STUDY OF SOME NEW AMIDINE
TRANSITION METAL COMPLEXES

by

LEO ALLAN BARES

A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree


of

MASTER OF SCIENCE

in

Chemistry


Approved:



Head, Major Department



Chairman, Examining Committee



Dean, Graduate Division

MONTANA STATE UNIVERSITY
Bozeman, Montana

June, 1966

ACKNOWLEDGEMENT

The author gratefully acknowledges the advice and encouragement given by Dr. Kenneth Emerson during the research on this project and during the writing of the thesis.

Appreciation is expressed to the United States Department of Health, Education, and Welfare for making graduate work possible through an N. D. E. A. Fellowship.

Finally, the author wishes to thank his parents, Mr. and Mrs. Norbert H. Bares, for their continued faith and encouragement.

TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	vii
INTRODUCTION	1
EXPERIMENTAL	
Preparation of Sodium and Potassium Amide	6
Attempts to Prepare Sodium and Potassium Acetamidinate	6
Synthesis of Acetamidinium Chloride	7
Attempts to Convert Acetamidinium Chloride to Sodium Acetamidinate	8
Synthesis of Acetamidinium Tetrachlorometallates	9
Preparation of Acetamidinium Trichloronickelate	17
Synthesis of Copper (II) Acetamidinate	19
Synthesis of Copper (II) Benzamidinate	22
DISCUSSION	
Acetamidinium Tetrachlorocuprate	29
Acetamidinium Tetrachlorocobaltate	30
Acetamidinium Trichloronickelate	31
Copper (II) Acetamidinate and Copper (II) Benzamidinate	31
SUMMARY	33
LITERATURE CITED	34

LIST OF TABLES

	Page
I. Spectral Bands and Intensities of Acetamidinium Tetrachlorometallates	14
II. Magnetic Data on Acetamidinium Tetrachlorocuprate	16
III. Spectral Bands and Intensities of Copper (II) Amidinates	27
IV. Magnetic Data on Copper (II) Amidinates	28

LIST OF FIGURES

	Page
1. Bidentate Configurations	1
2. Structure of Copper (II) Acetate Monohydrate	2
3. Copper (II) Formate Tetrahydrate	3
4. Ultraviolet Spectrum of Acetamidinium Tetrachlorocuprate	12
5. Visible Spectrum of Acetamidinium Tetrachlorocuprate	12
6. Ultraviolet Spectrum of Acetamidinium Tetrachlorocobaltate	13
7. Visible Spectrum of Acetamidinium Tetrachlorocobaltate	13
8. Diffuse Reflectance Spectrum of Acetamidinium Tetrachlorocuprate	15
9. Diffuse Reflectance Spectrum of Acetamidinium Tetrachlorocobaltate	15
10. Solution Spectrum of Acetamidinium Trichloronickelate	18
11. Diffuse Reflectance Spectrum of Acetamidinium Trichloronickelate	18
12. Ultraviolet Spectrum of Copper (II) Acetamidinate	23
13. Visible Spectrum of Copper (II) Acetamidinate	24
14. Reflectance Spectrum of Copper (II) Acetamidinate	24
15. Infrared Spectrum of Copper (II) Acetamidinate	25
16. Ultraviolet Spectrum of Copper (II) Benzamidinate	25
17. Visible Spectrum of Copper (II) Benzamidinate	26
18. Reflectance Spectrum of Copper (II) Benzamidinate	26

ABSTRACT

The syntheses of five new amidine-transition metal complexes are reported. Three of these complexes, acetamidinium tetrachlorocuprate, acetamidinium tetrachlorocobaltate and acetamidinium trichloronickelate, appear to be analogous to the corresponding cesium complexes. Copper (II) acetamidinate and copper (II) benzamidinate have also been prepared.

Solution and diffuse reflectance spectra have been determined for all five complexes. Magnetic data have been obtained for the chlorocuprate, acetamidinate and benzamidinate. These data suggest possible structures, but do not allow unequivocal structural conclusions.

INTRODUCTION

The ability of the acetate anion to function as either a monodentate or a bidentate ligand (for which there exist three possible configurations as shown in Figure 1) in complex formation with transition metals has been demonstrated (1-5). Complexes such as copper (II) acetate monohydrate, in which the bidentate nature of the acetate anion has been established (2), have evoked considerable interest in recent years. Much effort has been expended in attempting to elucidate the nature of the bonding involved in these complexes, particularly the bonding involved in the syn-syn bidentate complexes.

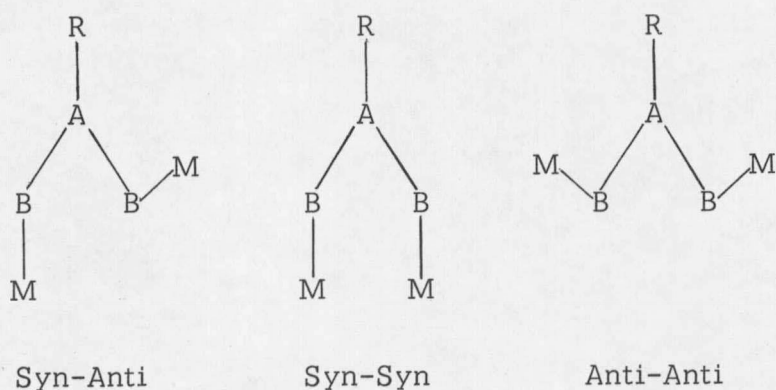


Figure 1. Bidentate Configurations

The structure of copper (II) acetate monohydrate has been determined crystallographically (2). The complex is dimeric and has a structure in which the Cu-Cu distance is 2.64 \AA (only slightly greater than the Cu-Cu distance of 2.56 \AA in metallic copper), the Cu-O distance is 1.97 \AA , and Cu is distorted out of the CuO_4 plane by 0.22 \AA .

Copper (II) acetate monohydrate exhibits an anomalously low magnetic moment of 1.42 Bohr Magnetons (compared to the spin-only value of

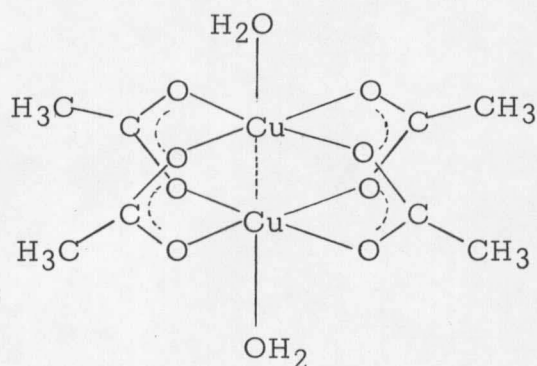


Figure 2. Structure of Copper (II) Acetate Monohydrate

1.73 B. M. normally observed for Cu (II) compounds) at room temperature and also displays an abnormal magnetic susceptibility versus temperature curve (6). Rather than decreasing with increasing temperature, as would be predicted by the Curie-Weiss law, the susceptibility increases with increasing temperature up to about room temperature. At this point the susceptibility begins to decrease. A definite maximum in the susceptibility curve, indicating antiferromagnetic behavior, is reached before adherence to the Curie-Weiss law begins. This maximum allows one to calculate a magnetic exchange energy between copper ions. The formation of a very weak δ bond between copper ions formed by $3d_{x^2-y^2}-3d_{x^2-y^2}$ orbital overlap has been postulated (6) to account for the observed exchange energy. Paramagnetic resonance spectrum studies (7) and a molecular orbital calculation (8) lend support to this type of direct exchange interaction hypothesis. Another direct exchange interaction postulate involving the formation of a strong σ bond formed by $3d_{z^2}-3d_{z^2}$ orbital overlap has also been advanced (9). Although the former explanation of the bonding involved in the copper (II)

