



<http://researchspace.auckland.ac.nz>

ResearchSpace@Auckland

Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.

<http://researchspace.auckland.ac.nz/feedback>

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form.

STRUCTURAL STUDIES OF

SOME COPPER(II)

COORDINATION COMPOUNDS

A Thesis Presented to
The University of Auckland
for the degree of
Doctor of Philosophy

by

Edward Neill Baker

July 1967

ABSTRACT

The crystal structures of four coordination compounds of copper(II) have been investigated by three-dimensional X-ray methods.

The structure of one crystalline form of bis-(N-ethyl-salicylaldiminato) copper(II) has revealed that the copper atom in such a compound may adopt a tetrahedrally-distorted coordination geometry under less severe steric conditions than had previously been supposed.

The structures of a methylamine perchlorate adduct of NN'-ethylenebis-(acetylacetoniminato) copper(II) and p-nitrophenol and chloroform adducts of NN'-ethylenebis-(salicylaldiminato) copper(II) have indicated that the bonding requirements of the copper atom can be modified by hydrogen bonding involving a ligand atom.

CONTENTS

CHAPTER		PAGE
I	Introduction	1
II	Chemical preparations and Crystal data	16
III	The Structure of the β -form of bis-(N-ethylsalicylaldiminato) copper(II)	26
IV	The Structure of the Methylamine Perchlorate Adduct of NN'-ethylenebis-(acetylacetoniminato) copper(II)	50
V	The Structure of the p-Nitrophenol Adduct of NN'-ethylenebis-(salicylaldiminato) copper(II)	84
VI	The Structure of the Chloroform Adduct of NN'-ethylenebis-(salicylaldiminato) copper(II)	108
VII	Discussion and Conclusions	132
APPENDICES		
A	Standard Deviations	151
B	The Ultra-Violet Absorption Spectra of NN'-ethylenebis-(salicylaldiminato) copper(II)	153
C	Symmetry and Translational Codes for Interatomic Distances	157
D	Tables of Observed Structure Amplitudes and Calculated Structure Factors	159
BIBLIOGRAPHY		173
ACKNOWLEDGEMENTS		178

ILLUSTRATIONS

<u>FIGURE</u>		<u>PAGE</u>
 β -FORM OF BIS-(N-ETHYLSALICYLALDIMINATO) COPPER(II)		
III. 1	Plot of $ F_o $ vs. $ F_c $ before correction for secondary extinction	46
III. 2	Bond lengths and angles	47
III. 3	Molecular distortion	48
IV. 4	Crystal packing	49
 METHYLAMINE PERCHLORATE ADDUCT OF NN'-ETHYLENEBIS- (ACETYLACETONEIMINATO) COPPER(II)		
IV. 1	Bond lengths and angles	81
IV. 2	The methylammonium nitrogen atom environment	82
IV. 3	Crystal packing	83
 p-NITROPHENOL ADDUCT OF NN'-ETHYLENEBIS-(SALICYL- ALDIMINATO) COPPER(II)		
V. 1	Bond lengths and angles	105
V. 2	Packing of the chelate molecules	106
V. 3	Packing of the chelate and p-nitrophenol molecules	107

FIGUREPAGECHLOROFORM ADDUCT OF NN'-ETHYLENEBIS-(SALICYL-
ALDIMINATO) COPPER(II)

VI. 1	Bond lengths and angles	129
VI. 2	The packing of the molecular "halves" of each dimer	130
VI. 3	Crystal packing of the adduct	131
VII.	Ultra-violet absorption spectra	156
