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-(acetylacetoneiminato) 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-(acetylacetoneiminato) copper(II)	50
V	The Structure of the p-Nitrophenol Adduct of NN'-ethylenebis-(salicyl-aldiminato) copper(II)	84
VI	The Structure of the Chloroform Adduct of NN'-ethylenebis-(salicyl-aldiminato) 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

FIGURE		PAGE
β-FORM OF BIS-(N-ETHYLSALICYLALDIMINATO) COPPER(II)		
III. 1	Plot of |Fo| vs. |Fc| 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

FIGURE		PAGE
CHLOROFORM 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