



<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.

STUDIES OF COPPER SYSTEMS  
INTERACTING WITH MOLECULAR OXYGEN

*A thesis presented to  
The University of Auckland  
for the degree of  
DOCTOR OF PHILOSOPHY*

*by*

KENNETH JOHN OLIVER

Department of Chemistry

November 1982

### ABSTRACT

This thesis describes the chemical, physico-chemical and structural studies of two types of copper compounds which interact with molecular oxygen in their formation.

The first type is an intensely coloured species based on the ligand oxalyldihydrazide. The divalent metal and the ligand react together with simple carbonyl compounds and molecular oxygen in basic conditions to form blue species the nature of which has been the subject of conjecture for many years. This work shows that the metal is trivalent in the highly coloured states and that it acts as an oxidative catalyst with ascorbic acid. The copper(III)/copper(II) potential has been established as +0.244 V by polarography. Compounds including acetaldehyde and acetone as the carbonyl component have been crystallized in monoclinic space groups. In both instances X-ray diffraction studies show that the metal is co-ordinated to a 6-5-6-5 macrocycle formed by a condensation reaction between two oxalyldihydrazide molecules and two carbonyl moieties. The co-ordination is *via* four deprotonated 'amide' nitrogen atoms and is of square-planar geometry. A structural study of oxalyldihydrazide has also been undertaken and comparisons are made with the co-ordinated species.

The second type of compound studied is a  $\text{Cu}_4\text{OX}_6\text{L}_4$  cluster. It was made from a copper(I) precursor and studies with oxygen-18 gas show that formation requires oxidation to copper(II) followed by hydrolysis. Infrared evidence based on the Cu-O stretch ( $500\text{--}580\text{ cm}^{-1}$ ) is presented. Attempts to include both fluorine and iodine as the halogen component suggest that only chlorine and bromine may fill such a role.

TABLE OF CONTENTS

	page
ABSTRACT	(i)
TABLE OF CONTENTS	(ii)
INDEX TO FIGURES	(v)
INDEX TO TABLES	(vii)
 CHAPTER I INTRODUCTION	 1
I.1 Copper in Biological Systems	1
I.2 'Blue' Copper Proteins	3
I.3 Haemocyanins	6
I.4 Mixed-Metal Copper Proteins	7
I.5 Galactose Oxidase	10
I.6 Trivalent Copper	14
I.7 Copper Complexes of Oxalyldihydrazide	18
 CHAPTER II X-RAY CRYSTALLOGRAPHIC METHODS	 24
II.1 Diffractometry	24
II.2 Initial Data Processing	28
II.3 Structure Solution	34
II.4 Structure Completion and Refinement	42
 CHAPTER IIIa OXALYLDIHYDRAZIDE COPPER(III) COMPOUNDS: THE BLUE COMPLEXES	 45
IIIa.1 Optimum pH	46
IIIa.2 Oxygen Cycle	47
IIIa.3 Molecular Oxygen Uptake	47
IIIa.4 Component Separation	48
IIIa.5 ESR Spectroscopy	49
IIIa.6 Oxidase Activity	50
IIIa.7 Oxidation Potential	51
IIIa.8 Related Chemical Investigations	52
IIIa.9 Crystallization of Blue Oxalyldihydrazide Copper(III) Compounds	55
 CHAPTER IIIb THE CRYSTAL AND MOLECULAR STRUCTURE OF OXALYLDIHYDRAZIDE	 67
IIIb.1 Preparation of Crystals and Determination of the Structure	67
IIIb.2 Description of the Structure	70

	(iii)
	page
CHAPTER IIIc THE CRYSTAL AND MOLECULAR STRUCTURE OF THE ACETONE DERIVATIVE	84
IIIc.1 Data Collection and Structure Solution	84
IIIc.2 Description of the Structure	90
CHAPTER IIId THE CRYSTAL AND MOLECULAR STRUCTURE OF THE ACETALDEHYDE DERIVATIVE	110
IIId.1 Data Collection and Structure Solution	110
IIId.2 Description of the Structure	116
CHAPTER IIIe THE CRYSTAL AND MOLECULAR STRUCTURE OF THE ACETALDEHYDE DERIVATIVE IN AN ORTHORHOMBIC SPACE GROUP	136
CHAPTER IV DISCUSSION	146
IV.1 The Oxalyldihydrazide Moiety	149
IV.2 Molecular Geometry of the Complexes	150
IV.3 Oxidation State of the Metal	156
IV.4 Mechanism of Ligand Formation	158
IV.5 Oxidation Potential and Electronic Absorption	161
IV.6 Oxidase Activity	165
IV.7 Proposals for Further Investigation	167
CHAPTER Va $\mu_4$ -OXO-HEXA- $\mu_2$ -HALO-TETRAKIS (LIGAND) TETRA-COPPER(II) COMPOUNDS - $\text{Cu}_4\text{OX}_6\text{L}_4$	171
Va.1 Occurrence and Preparation	171
Va.2 Spectral Studies	173
Va.3 Magnetic Studies	174
Va.4 Structural Studies	175
CHAPTER Vb STUDIES OF A NEW $\text{Cu}_4\text{OCl}_6\text{L}_4$ SYSTEM	177
Vb.1 Preparation of $\text{Cu}_4\text{OCl}_6(\text{DMI})_4$	178
Vb.2 X-ray Diffraction	180
Vb.3 Structure Solution and Refinement	181
Vb.4 Description of Structure	184
CHAPTER Vc ISOTOPIC OXYGEN STUDIES	186
Vc.1 Experimental	187
Vc.2 Results and Discussion	189
Vc.3 The Role of the Halogen	192
REFERENCES	
Chapter I	212
Chapter II	218
Chapter III	219
Chapter IV	221
Chapter V	222

STRUCTURE FACTOR APPENDICES

A	Oxalyldihydrazide	225
B	Blue Acetone Derivative	229
C	Blue Acetaldehyde Derivative ( $P2_1/a$ )	242
D	Blue Acetaldehyde Derivative ( $P_{bca}$ )	256
E	$Cu_4OCl_6(DMI)_4$	261

ACKNOWLEDGEMENTS

INDEX TO FIGURES

	page
CHAPTER IIIa	
IIIa.1 pH <i>vs.</i> Added Acid or Base	61
IIIa.2 Molecular Oxygen Cycle	62
IIIa.3 Oxygen Uptake <i>vs.</i> Time	63
IIIa.4 Differential Pulse Polarogram for Blue Acetaldehyde Compound	64
IIIa.5 Infrared Spectrum of Bismethyl- oxalyldihydrazide	65
IIIa.6 NMR Spectrum of Bismethyloxalyldihydrazide	66
CHAPTER IIIb	
IIIb.1 Oxalyldihydrazide Crystal	73
IIIb.2 ORTEP Representation of Oxalyldihydrazide	74
IIIb.3 <i>a, b</i> Projection of Unit Cell Contents	75
IIIb.4 Oxalyldihydrazide Hydrogen Bonding	76
CHAPTER IIIc	
IIIc.1 Acetone Derivative Crystal	93
IIIc.2 ORTEP Representation of Acetone Derivative	94
IIIc.3 <i>b, c</i> Projection of Anions in Unit Cell	95
IIIc.4 <i>b, c</i> Projection of Unit Cell Contents	96
IIIc.5 <i>a, b</i> Projection of Unit Cell Contents	97
IIIc.6 Hydrogen Bonding Network	98
CHAPTER IIId	
IIId.1 Geometrical Construction	119
IIId.2 Acetaldehyde Derivative Crystal 1	120
IIId.3 Acetaldehyde Derivative Crystal 2	121
IIId.4 ORTEP Representation of Acetaldehyde Derivative	122
IIId.5 <i>a, c</i> Projection of Unit Cell Contents	123
IIId.6 <i>b, c</i> Projection of Unit Cell Contents	124
IIId.7 Hydrogen Bonding Network	125
CHAPTER IIIe	
IIIe.1 Acetaldehyde Derivative Crystal ( $P_{bca}$ )	141
CHAPTER IV	
IV.1 Green and Purple Oxalyldihydrazide Compounds	169

## CHAPTER V

page

V.1	$\text{Cu}_4\text{OX}_6\text{L}_4$ Cluster	194
V.2	Distribution of $\text{Cu}_4\text{OCl}_6\text{L}_4$ Structural Parameters	195
V.3	$\text{Cu}_4\text{OCl}_6(\text{DMI})_4$ Crystal 1	196
V.4	$\text{Cu}_4\text{OCl}_6(\text{DMI})_4$ Crystal 2	197
V.5	$\text{Cu}_4\text{OCl}_6(\text{DMI})_4$ Crystal 3	198
V.6	ORTEP Representation of $\text{Cu}_4\text{OCl}_6(\text{DMI})_4$ Molecule	199
V.7	$a, b$ Projection of Unit Cell Contents	200
V.8	Isotopic Oxygen Apparatus	201
V.9	$\text{O}^{16}$ and $\text{O}^{18}$ Infrared Spectra	202



INDEX TO TABLES

	page
CHAPTER I	
I.1 Some Proteins Containing Copper	22
I.2 Copper Analysis of Copper-Containing Proteins	23
CHAPTER IIIf	
IIIf.1 Crystal Data	77
IIIf.2 Collection Parameters	78
IIIf.3 Final Positional Parameters	79
IIIf.4 Final Thermal Parameters	80
IIIf.5 Bond Distances in Å	81
IIIf.6 Bond Angles in °	82
IIIf.7 Least-Squares Planes	83
CHAPTER IIIf	
IIIf.1 Crystal Data	99
IIIf.2 Collection Parameters	100
IIIf.3 Final Positional Parameters	101
IIIf.4 Final Thermal Parameters	103
IIIf.5 Bond Distances in Å	105
IIIf.6 Bond Angles in °	106
IIIf.7 Least-Squares Planes	107
IIIf.8 Hydrogen Bonding Parameters	109
CHAPTER IIIf	
IIIf.1 Crystal Data	126
IIIf.2 Collection Data	127
IIIf.3 Final Positional Parameters	128
IIIf.4 Final Thermal Parameters	130
IIIf.5 Bond Distances in Å	131
IIIf.6 Bond Angles in °	132
IIIf.7 Least-Squares Planes	133
IIIf.8 Hydrogen Bonding Parameters	135
CHAPTER IIIf	
IIIf.1  F <sub>obs</sub>   for Standard Reflections	142
IIIf.2 Crystal Data	143
IIIf.3 Collection Parameters	144
IIIf.4 Final Atomic Parameters	145
CHAPTER IV	
IV.1 Oxalyldihydrazide Bond Distances	170

CHAPTER V

V.1	$\text{Cu}_4\text{OX}_6\text{L}_4$ Structural Parameters	203
V.2	Crystal Data	204
V.3	Collection Data	205
V.4	Final Positional Parameters	206
V.5	Final Thermal Parameters	208
V.6	Bond Distances in Å	209
V.7	Bond Angles in °	210