

CONTENTS

PREFACE TO THE SERIES	iii
PREFACE TO VOLUME 12	v
CONTRIBUTORS	xi
CONTENTS OF OTHER VOLUMES	xiii

Chapter 1

COORDINATION CHEMISTRY OF COPPER WITH REGARD TO BIOLOGICAL SYSTEMS	1
--	---

R. F. Jameson

1. Copper in Living Systems	1
2. Redox Properties of Copper	4
3. General Stereochemistry	8
4. Spectral and Magnetic Properties	13
5. Type III Copper	27
6. Epilogue	28
References	28

Chapter 2

COPPER(II) AS PROBE IN SUBSTITUTED METALLOPROTEINS	31
--	----

Ivano Bertini and Andrea Scozzafava

1. Introduction	32
2. ESR Spectra	33
3. Electronic Spectra	44
4. Nuclear Relaxing Properties of Copper(II)	46
5. Copper(II) as Probe in Carbonic Anhydrase	48
6. Copper Proteases	51
7. Copper-Substituted Iron Transport Proteins	53
8. Copper-Substituted Liver Alcohol Dehydrogenase	57
9. Copper Alkaline Phosphatase	60
10. Copper-Substituted Superoxide Dismutase	61

11. Further Considerations on the Copper-Protein Interactions	63
12. Experimental Procedures	64
Recent Developments	67
References	68

Chapter 3

COPPER(III) COMPLEXES AND THEIR REACTIONS	75
---	----

Dale W. Margerum and Grover D. Owens

1. Introduction	77
2. Copper(III) Intermediates in Organic Reactions	87
3. Evidence of Copper(III) in Peptide Complexes	92
4. Electrode Potentials of the Peptide Complexes	98
5. Amine Deprotonation of Copper(III) Peptides	106
6. Electron Transfer Reactions	109
7. Copper(III) Peptide Redox Decomposition: Thermal and Photochemical	116
8. Cu(III)-Peptide Substrate Oxidations	121
9. Copper(III) Catalysis of O ₂ Activation with Copper(II)-Tetraglycine	123
10. Biological Aspects of Copper(III)	124
Acknowledgment	126
Abbreviations	127
References	128

Chapter 4

COPPER-CATALYZED OXIDATION AND OXYGENATION	133
--	-----

Harald Gampp and Andreas D. Zuberbühler

1. Introduction	134
2. Copper-Catalyzed Oxidation (Dehydrogenation)	137
3. Copper-Catalyzed Monooxygenation	162
4. Copper-Catalyzed Dioxygenation	171
5. Conclusions: Models for Redox Enzymes (?)	175
Abbreviations	177
References	178

Chapter 5

COPPER AND THE OXIDATION OF HEMOGLOBINS	191
---	-----

Joseph M. Rifkind

1. Introduction	192
2. Oxidation of Hemoglobin by Copper	198

CONTENTS

ix

3. Binding of Copper to Hemoglobins	204
4. Location of the Copper-Binding Sites	210
5. Mechanism for Cu(II) Oxidation of Hemoglobin	215
6. In Vivo Oxidation of Hemoglobin	225
7. Conclusion	226
Abbreviations and Definitions	227
References	228

Chapter 6

TRANSPORT OF COPPER	233
---------------------	-----

Bibudhendra Sarkar

1. Introduction	234
2. Transport Through Gastrointestinal Tract	236
3. Transport in Blood	238
4. Transport Across Membrane	244
5. Transport Phenomena in Excretion	246
6. Transport Site on Albumin	248
7. Transport Mediated by Albumin-Cu(II)-Amino Acid Ternary Complex	263
8. Transport in Wilson's Disease	270
9. Transport in Menke's Disease	275
Abbreviations	276
References	277

Chapter 7

ROLE OF LOW MOLECULAR WEIGHT COPPER COMPLEXES IN THE CONTROL OF RHEUMATOID ARTHRITIS	283
---	-----

Peter M. May and David R. Williams

1. Introduction	283
2. Low Molecular Weight Complexes of Copper in Vivo	285
3. Copper Metabolism and Rheumatoid Arthritis	293
4. Conclusion	311
Abbreviations	311
References	311

AUTHOR INDEX	319
--------------	-----

SUBJECT INDEX	341
---------------	-----