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THE INTERACTION OF COPPER(II)

WITH LIGANDS CONTAINING NITROGEN AND

SULPHUR DONORS

A THESIS PRESENTED TO THE UNIVERSITY

OF AUCKLAND FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

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ABSTRACT

A study of the influence of several "soft donor" ligands on the cupric ion has been completed. Nitrogen and sulphur donors were chosen since these are considered to be present in "biological copper" situations, some of the conditions of which it was hoped to duplicate.

Complicated reactions were found with several different types of ligands. Those containing imine functions, when complexed to copper(II), were invariably found to cleave due to the presence of external nucleophiles and it was considered that for such donors to be important in "biological" situations they would need to be shielded by bulky ligand systems. The cleavage reactions were found to have their origin in electronic mechanisms and earlier suggestions based on steric interactions were criticised.

A study of sulphur donors showed that, whereas thioethers had a poor affinity for copper(II), thiols bonded very strongly. Reduction to copper(I) invariably took place, but with ligands containing π -delocalised aromatic thiols as well as amine donors mixed-valent complexes of copper were formed. The properties of most of these complexes were unusual and one, especially,

(N-(2-thiophenol)pyridine-2-aldiminato)copper(II) chloride, showed reactions and properties that suggested it may be a suitable model for cupro-enzymes.

Complexes with thiol donors were termed "anomalous" in view of their complicated physical properties, whereas compounds with other donors showed "normal" behaviour. Absorption spectral studies were undertaken in an attempt to understand the electronic states of the "soft donor" complexes; at the same time an assessment of a recent scheme for assigning stereochemistries from visible spectra as applied to "soft donor" systems was possible.

An X-ray structural determination of the complex μ -chloro-chlorobis(3,4-bis(3-amino-1-thiopropyl)toluene)dicopper(II) diperchlorate was undertaken, partly because of its unusual synthetic and physical character-

istics. Two copper centres, one five- and the other six- co-ordinate, were found to be linked by a bridging chloride ion. The geometries about each copper ion were considerably distorted from square-pyramidal and octahedral respectively; the ligand systems also showed unusual electronic effects. Comparison with other recent structural investigations suggested that five-co-ordination is favoured by the copper ion in "soft donor" environments, and this was thought to be significant in terms of oxygen-carrying ability, where an increase in co-ordination number must occur. Several attempts to oxygenate prepared complexes were made, but no conclusive results were obtained, although several somewhat unstable crystalline products were produced.