STUDIES OF COPPER SYSTEMS

INTERACTING WITH MOLECULAR OXYGEN

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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 $Cu_4OX_6L_4$ 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 (500-580 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.

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