

- exchange coupling of the hemocyanin active site depends mainly on the bridging tyrosine oxygen;
- asymmetric model complexes with increased bridging angle up to 140° are needed to obtain more information about the exchange coupling of the hemocyanin active site.

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PS4.18 — MO

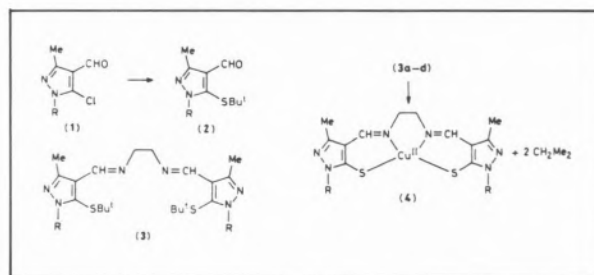
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BIOMIMETIC SYSTEMS FOR THE "VISIBLE" COPPER-SITE Cu_A IN CYTOCHROME *c* OXIDASE

Recent work on the structure of the Cu_A site of cytochrome *c* oxidase suggests that two cysteines and two histidines are ligated to the central copper ion. We have demonstrated that *t*-butyl sulfides are convenient sources of copper(II) thiolato complexes as Cu^{2+} is a sufficiently strong Lewis acid to cleave the sulfur *t*-butyl-bond. This method has been used to pre-

pare a series of S_2N_2 copper(II) complexes of Schiff-base ligands derived from 2-mercaptoaldehydes and diamines. From the spectral properties of these systems we have suggested that a red shift of the LMCT bands, as well as a decrease in A_{\parallel} , for the thiolato copper(II) complexes may be caused by two independent factors: either through an increase in the electron density at sulfur or through an increase in the tetrahedral distortion of the Cu(II) chromophore.

By variation in the molecules, we have prepared a number of ligands based on different heterocycles for the study of Cu(II) protein models. An example with pyrazole is shown in the scheme:



The β -chloroaldehydes as well as the protected β -mercaptoaldehydes are also useful as starting materials for the preparation of annelated heterocycles.

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PS4.19 — TU

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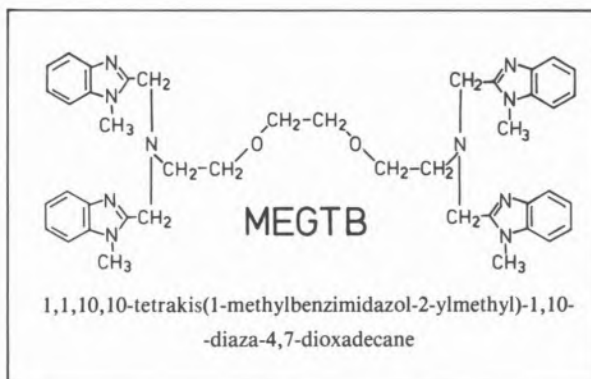
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COPPER CHELATES OF A DINUCLEATING BENZIMIDAZOLE-CONTAINING LIGAND AS MODELS FOR TYPE III COPPER PROTEINS

The active site in Type III copper proteins is generally believed to contain two copper ions close together and each coordinated by at least two imidazole groups of histidine residues [1]. The coordination geometry, imposed by the structure of the protein, is known to influence the specific properties, like O_2 transport or oxidative catalysis. To help elucidating the structures and understanding the reactivities of these proteins, low molecular weight compounds are studied as models. The steric constraints in polydentate ligands, *e.g.* the size of the bite and the presence of bulky substituents, are used as tools in tuning the model system. The incorporation of benzimidazole groups has the advantages of a biomimetic group being easily synthesized and having a bulky substituent.

The ligand megtb (see figure) has the potential to bind two metal ions with several possibilities for the metal-metal distances, both with and without exogeneous bridging ligands. The ligand has been prepared in two steps, *i.e.* a ring closure reaction by condensation of *o*-diaminobenzene with the polyaminocarboxylic acid EGTA (ethylene glycol bis-(β -aminoethyl ether) *N,N,N',N'*-tetraacetic acid), followed by *N*-methylation [2].

The coordination compounds with copper(II) appear to have two general formulae: a) $Cu_2LX_4 \cdot nH_2O$ with different kind of anions and



$Cu_2LX_2Y_2 \cdot nH_2O$ for X =halide and Y =a non-coordinating anion; b) $Cu_2LXY_3 \cdot nH_2O$ for X =1,3-azolate and Y =a non-coordinating anion. The crystal structures of $Cu_2(megtb)F_2(BF_4)_2 \cdot 3H_2O$ and $Cu_2(megtb)Cl_4 \cdot 6H_2O$ show a coordination geometry close to a square pyramid with 3 N atoms and the halide anion in the equatorial plane and an O ether atom on the apical position. The halide anion is also a sixth donor atom for a neighbouring Cu(II) ion at a larger, non-bonding distance. The resulting intermolecular Cu-Cu distance is slightly shorter than the intramolecular one. The magnetic exchange is weak in these compounds.

When bridging ligands are used in a sub-stoichiometric ratio, together with non-coordinating anions, intramolecular dicopper species can be obtained. They have a typical spin-triplet EPR spectrum both in the solid state and in solution, and *J*-values characteristic for copper dimers with bridging 1,3-azolates.

With Cu(I) both stable mononuclear compounds with non-coordinating anions, as well as dinuclear compounds with coordinating (pseudo)halides, are formed. Reaction with carbon monoxide results in a stable 1:1 (Cu:CO) product. The compounds react stepwise with dioxygen and are active in the oxidative coupling of 2,6-dialkylphenols. This reaction is used as a test reaction to investigate the catalytic properties of these and related systems.

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