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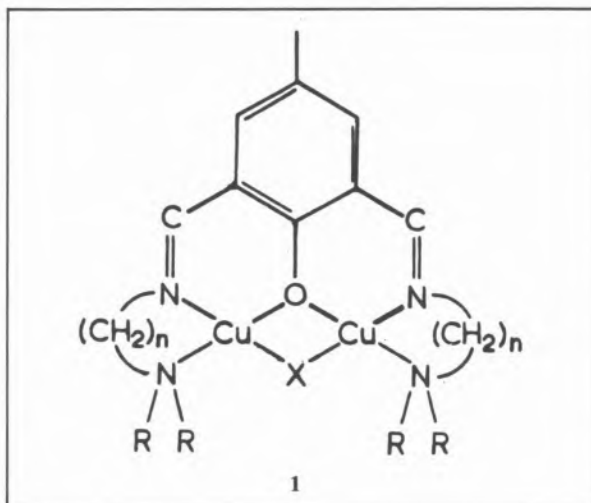
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MODELLING THE HEMOCYANIN ACTIVE SITE: A CONTRIBUTION TO MAGNETO-STRUCTURAL CORRELATIONS

The dioxygen carrying protein hemocyanin is the best investigated enzyme containing a binuclear Cu(II)-active site. In the oxidized form the Cu(II)-ions are tetragonally coordinated and bridged by an endogenous protein group for which authors [1] favour a phenolate group from tyrosine. For the oxy-form dioxygen is known to form an exogenous bridge, whereas azide, chloride, etc. are found in the artificial met-forms.

Magnetic investigations of these protein forms referred to strong antiferromagnetic coupling between the two Cu(II)-ions resulting in diamagnetism [2]. To understand this magnetic behaviour magneto-structural correlations for two particular features of the hemocyanin active site are needed. Model complexes containing (i) asymmetric bridged Cu(II)-ions and (ii) a large Cu-O-Cu bridging angle at the endogenous ligand have to be investigated. Because it is quite impossible to vary continuously the bridging angle in a single asymmetric bridged model system the problem has to be resolved separately and then correlated.

As a part of our investigations in the magnetic behaviour of the hemocyanin active site we present in this study different asymmetric bridged Cu(II)-dimers. For modelling the asymmetric bridging character of the active site we have synthesized a five-dentate macrocyclic ligand forming binuclear Cu(II)-complexes (1).



The structures of three complexes with an exogenous OH-bridge ($n=2$, $R=Et$ and $n=3$, $R=Me$) [3,4] and an exogenous N_3 -bridge ($n=3$, $R=Me$) [5], respectively, will be presented.

The copper coordination polyhedra in all complexes are similar. The 4+1 coordination can be described as a square planar basis plane with an additional ligand perpendicular to this plane and more elongated. In the azido-bridged dimer the azido-group is bound end-on. In this compound the bridging angles Cu-O-Cu and Cu-N-Cu are similar (103°) whereas in the OH-bridged complexes a significant difference of several degrees between the two Cu-O-Cu bridging angles has been observed.

A first attempt to obtain magneto-structural correlations for asymmetric bridged dimers will be discussed. We propose a model to relate the strong antiferromagnetic coupling found in all three asymmetric bridged complexes ($-500 \text{ cm}^{-1} > 2J > -900 \text{ cm}^{-1}$) to magneto-structural data from symmetric dimers. Exchange coupling has been found to depend mainly on the properties of that bridge (electronegativity, bridging angle) which would give the stronger antiferromagnetic coupling in symmetric dimers. The energy gap between the levels $S=0$ and $S=1$ can be described as having approximately the same magnitude as has been found for the corresponding symmetric complexes.

The magnetic behaviour of the discussed asymmetric bridged dimers leads to the following conclusions about exchange coupling in hemocyanin:

- 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.

REFERENCES

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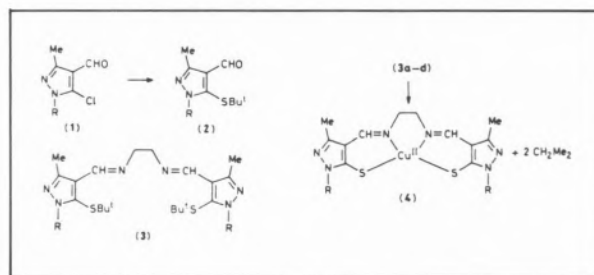
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BIOMIMETIC SYSTEMS FOR THE "VISIBLE" COPPER-SITE Cu_A IN CYTOCHROME *c* OXIDASE

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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