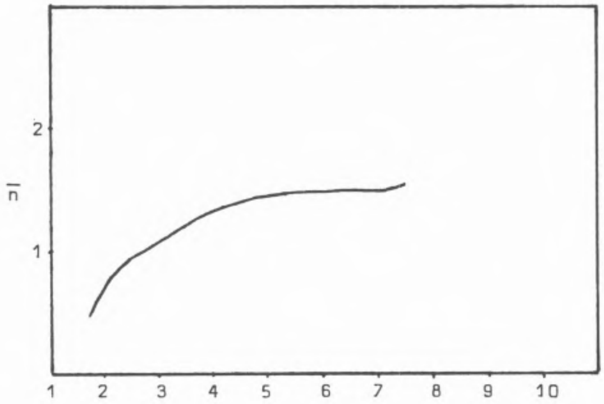

Fig. 2
Plot of $\bar{n}$ versus pH for the Fe(III)-glutaryl dihydroxamic acid system (n = 3)

xamate complexation of Fe(III). Further investigations are being carried out.

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PS4.16 — MO

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SYNTHETIC APPROACH TO THE MONONUCLEAR ACTIVE SITES OF MOLYBDOENZYMES

EXAFS results for several molybdoenzymes responsible for oxidation of substrates X/XO by oxygen atom transfer with concomitant changes of central molybdenum oxidation states from VI to IV (*via* V) indicate the minimal coordination spheres $Mo^{VI}O_2(SR)_{2,3}$ and $Mo^{IV}O(SR)_{3,4}$ for the oxidised and fully reduced forms, respectively. Numerous molybdenum-containing model complexes have been prepared to mimic the structural as well as the functional properties of the molybdoenzymes [1]. To date none of these model complexes appears to have all these properties very similar to the molybdoenzymes. We have synthesized some monomeric complexes of the general formula: $[MoS(S_2)(DTC)]$, $[MoO(DTC)(cat)]$ and $[MoO_2(DTC)(cat)]^-$ (DTC = dialkyldithiocarbamate, cat = catecholatedianion). These complexes catalyze the oxidation of xanthine and sulfite and can reduce molecular oxygen to superoxide. Typical EPR parameters for the complex $[MoOEt_2(DTC)(cat)]$ (g_{xx}, 1.951; g_{yy}, 1.979; g_{zz}, 1.995; $<g> = 1.975$; $<A>$, 31.0) suggest the structural closeness of this model compound to xanthine oxidase [2]. EPR and other spectral data along with C.V. results are presented and their relevance to enzymatic processes is discussed.

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PS4.17 — TH

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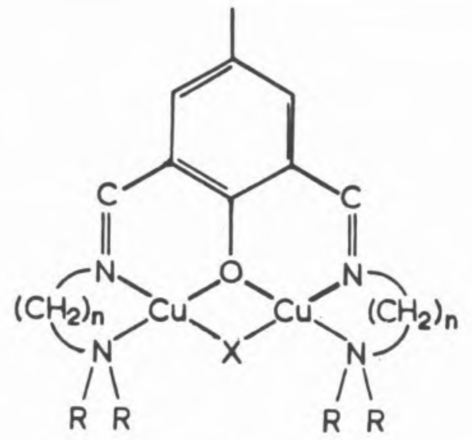
MODELLING THE HEMOCYANIN ACTIVE SITE: A CONTRIBUTION TO MAGNETO-STRUCTURAL CORRELATIONS

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**).



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 ($-500\ \mathrm{cm}^{-1} > 2J > -900\ \mathrm{cm}^{-1}$) 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: