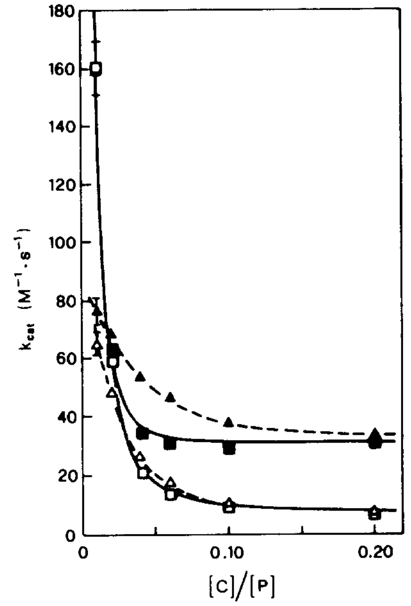

Fig. 2. Second-order rate constants for the electron transfer reaction between L-adrenaline (full lines) or L-dopa (broken lines) and FeL (empty symbols) or FeD (full symbols) as a function of [C]/[P] ratio of the catalytic systems. Experimental conditions as in Fig. 1; $[AH_2]_0 = 1 \times 10^{-4}$ (full lines) or 2×10^{-4} *M* (broken lines).

assistance from the coiled polypeptides [3]. This accounts for the lack of stereoselectivity in the oxidation reaction, which takes place at much higher rate however (Fig. 2).

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N2

Model Complexes for the Active Sites of Reduced and Oxidized Sites of Hemocyanin and Tyrosinase. Structures of Binuclear Cu(I) and Cu(II) Complexes and Characterization of a Model Copper Monooxygenase Reaction

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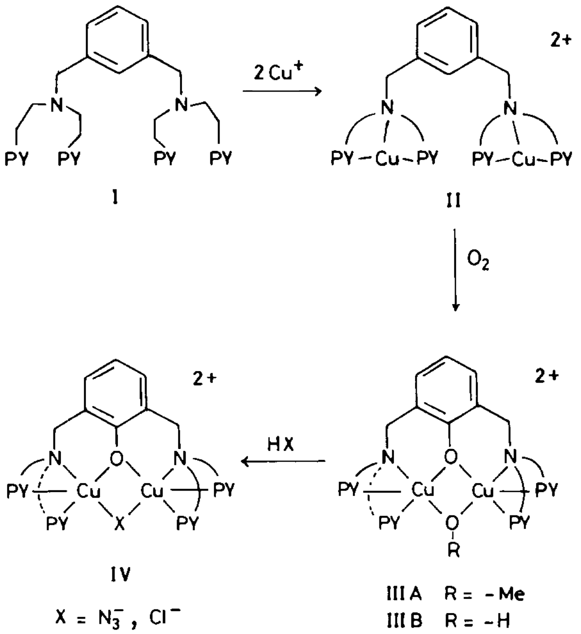
It has been established that the dioxygen carrying copper containing protein hemocyanin and the copper monooxygenase tyrosinase both contain electronically coupled binuclear copper centers. In the deoxy protein, copper centers are thought to be two or three coordinate, while in their oxidized form, tetragonally coordinated Cu(II) ions are bridged by an endogenous protein group which is thought to be phenolate from tyrosine. Coordinated dioxygen (as peroxide) is also known to bridge the two coppers. The binding of other exogenous ligands (azide, chloride, *etc.*) to the binuclear copper centers has been used to probe the active site structures and some of these may also bridge the Cu(II) ions in methemocyanin or tyrosinase derivatives [1].

Extensive coordination model studies are being carried out [2–4] in order to 1) determine the nature of the ligand donors and coordination geometries of these active site copper centers; 2) mimick and understand the coordination chemistry of relevant Cu(I) systems; 3) mimick the Cu(II) binuclear centers in order to relate the spectroscopic and chemical properties of these models and their derivatives (with appropriate probes) to those of the proteins and 4) understand those factors necessary and the mechanism(s) for reversible dioxygen binding and 'activation' of dioxygen (*i.e.* specific hydroxylation of substrates by the copper monooxygenases).

As part of our own extensive investigations into the chemistry of binuclear Cu(I) and Cu(II) moieties, we have employed the binucleating ligand m-XYLpy, *I* (py = 2-pyridyl), where two tridentate donor groups are separated by a meta-xylyl bridge [5]. A novel binuclear cuprous complex, *II*, *(See next column)* containing well separated trigonally coordinated Cu(I) ions is isolated by the reaction of *I* with two equivalents of $Cu(CH_3CN)_4PF_6$ [6]. The coordination geometry and the type of ligands in *II* makes it a good model complex for the deoxy-sites in the proteins. In addition, *II* reacts with O_2 in a manner analogous to the copper monooxygenase tyrosinase. Specific hydroxylation of the xylyl ligand occurs producing the phenoxy- and hydroxy- (R = H) doubly bridged binuclear Cu(II) complex *III*.

Manometric O_2 uptake experiments with *II* and mass spectrometric analyses of the oxidation product *III* utilizing isotopically labeled dioxygen demonstrate that both atoms of oxygen in *III* are derived from $^{18}O_2$ [6, 7]:



I II IIIA R = -Me IIIB R = -H IV X = N_3^-, Cl^-

The structures of compounds *II* and *III* have been proven by X-ray crystallographic studies [5–7]. Compounds *III* contain tetragonally coordinated Cu(II) ions which are phenolate bridged (Cu...Cu = ~3.1 Å), making them excellent structural models for the proposed active sites in hemocyanin and tyrosinase. Reaction of *III* (R = H) with HX (X = N_3^-, Cl^-) results in the replacement of the bridging ligand (-OH) by X with the formation of complexes *IV*. These have also been structurally characterized and they exhibit coordination geometries very similar to *III*. In the case of the azide complex (X = N_3^-), a novel μ-1,1-azido type of bridging is observed [7]. This mode of coordination has not been previously proposed to take place in the protein copper centers. Its possible occurrence should be considered in studies where azide ligand binding is used as a spectral probe of the protein copper centers.

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N3

Models for Hemocyanin

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Our attempts to understand oxygen binding at the active site of the binuclear copper protein hemocyanin (Hc) [1] encompass two strategies. The first of those is the investigation of the structures and reaction chemistry of Cu(I) complexes ligated by nitrogenous donors since the deoxy form of hemocyanin is of this form. Unfortunately, Cu(I) species have the d^{10} electron configuration, and direct spectroscopic observations of the metal ion environment are severely limited. The reaction of carbon monoxide with Cu(I) complexes circumvents this problem by generating a derivative which is spectroscopically observable. By comparing the physical and spectroscopic properties of synthetic Cu(I)–CO complexes with those for the carbonyl adduct of hemocyanin, we hope to confirm the proposed structure of the deoxy site in Hc [2].

This report reviews the synthesis and characterization of a series of two- and three-coordinate Cu(I) complexes ligated primarily by nitrogen heterocycles, especially pyrazole derivatives. The two-coordinate species are characterized by having a linear geometry with short Cu–N bond lengths (1.87 Å) [3, 4]. For the most part, such compounds are inert towards carbon monoxide unless an additional donor is added. The three-coordinate species adopt structures in which steric effects of the ligand distort the coordination geometry. All of the three-coordinate complexes bind carbon monoxide to varying degrees, depending on the nature of the ligating atoms [5]. The structures of some binuclear Cu(I) complexes are also reported, in addition to the results of their reaction with dioxygen [6].

Our second strategy for probing the nature of the active site in hemocyanin involves the study of binuclear Cu(II) complexes. Spectroscopic studies of oxyhemocyanin suggest an active site comprising two pentacoordinate Cu(II) ions bridged both by a phenolate and a peroxide ion [1]. The phenolate bridge promotes strong antiferromagnetic coupling between the two metal ions. We report the synthesis