of some binuclear Cu(II) complexes bridged by oxy anions. The ligands are prepared by a multistep route from phenol derivatives and provide tetracoordinate chelation in a manner that allows binding of an additional 'exogenous' ion to each copper. Magnetic susceptibility studies of the resulting bis(bridged) species show varying degrees of antiferromagnetic coupling including a strongly coupled system with a μ-hydroxy-μ-phenoxy ligand set [7].

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Synthesis and Oxygenation Studies of Monomolecular Hemoprotein Models

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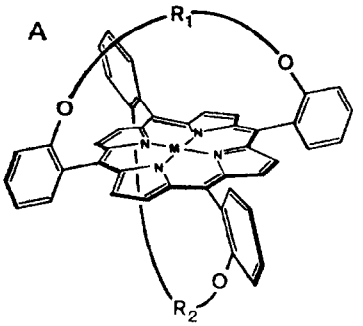
The preparation and properties of molecules modeling the active site of natural oxygen carriers have received considerable attention in recent years for the elucidation of the factors that control the binding reactions of molecular oxygen and carbon monoxide in some hemoproteins. Such compounds have been synthesized following three requirements which seem necessary in the biological functions of natural systems:

(a) pentacoordination of the iron(II) ion by a nitrogenous base on the proximal site;

(b) steric protection of the heme in order to prevent it from irreversible oxidation into μ-oxo iron(III) dimers;

(c) control of the dioxygen environment on the distal site.

Several groups have investigated these three problems separately [1]. As part of our studies of the stereochemical influences on the formation and stability of oxygenated model compounds, we have prepared two series of porphyrin derivatives which correspond to the three structural conditions mentioned above.

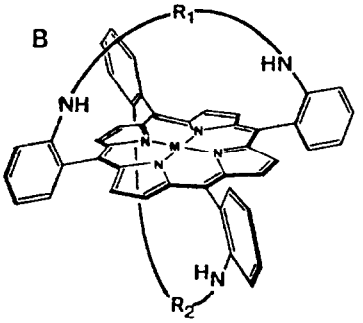


1 R_1 = $-(CH_2)_3$-(pyridine)-$(CH_2)_3-$ R_2 = $-(CH_2)_{10}-$

2 R_1 = " R_2 = $-(CH_2)_{12}-$

3 R_1 = " R_2 = $-(CH_2)_3$-(benzene)-$(CH_2)_3$

4 R_1 = " R_2 = $-(CH_2)_4$-(benzene)-$(CH_2)_4$



5 R_1 = $-CO-(CH_2)_2$-(pyridine)-$(CH_2)_2-CO-$ R_2 = $-CO-(CH_2)_8-CO-$

6 R_1 = " R_2 = $-CO-(CH_2)_{10}-CO-$

7 R_1 = $-CO-(CH_2)_3$-(pyridine)-$(CH_2)_3-CO-$ R_2 = "

8 R_1 = $-CO-(CH_2)_4-CH(N\text{-}CH\text{=}N)-(CH_2)_4-CO-$ R_2 = "

M = Fe^{II}

All the compounds were synthesized following the concept of both face hindered tetraphenylporphyrins ('basket handle' porphyrins) in which two opposite mesophenyl rings are bridged by a convenient chain [2, 3]. The proximal base (pyridine or imidazole) was inserted into one of the handles. The size and polarity of the cage on the distal side can be modified to some extent by suitable chemical changes of the second handle. The newly 'hanging base' porphyrins were prepared either from 5,10,15,20-tetrakis(*o*-hydroxyphenyl)porphyrin (series A, compounds *1–4*) or from 5,10,15,20-tetrakis(*o*-aminophenyl)-porphyrin (series B, compounds *5–8*). Thus the main structural difference between the two series lies in the presence of non polar ether groups in the former and of polar amide linkage in the latter [4].

Their iron(II) complexes have a magnetic high spin state (S = 2) characteristic of deoxymyoglobins and hemoglobins. Addition of O_2 and CO to these complexes results in the formation of hexacoordinated diamagnetic species (S = 0), as in oxy and carboxyhemoproteins, without any paramagnetic perturbations by low lying thermally excited states.

A systematic study of the O_2 and CO rates and equilibrium binding constants has been carried out in toluene by laser flash photolysis using a modified exchange rate law [5]. This clearly establishes the important role of factors such as the distal steric hindrance, the proximal base constraint and the polarity of the dioxygen environment in the control of the O_2 binding and of the stability of oxygenated complexes. The association rate constants of O_2 and CO are of the same order of magnitude in the two series, but a large variation in the dissociation rate constants is observed. The smaller dissociation rate constants are observed for the compounds having amide linkages as compared with their analogous ether bearing linkages. This results in an increase of the intrinsic stability of the oxygenated derivatives up to the values observed in the natural compounds.

The proton magnetic resonance spectra of the oxygenated complexes indicate that the bound dioxygen molecule lies preferentially in a plane oriented toward the distal amide groups in the B series, in contrast with series A in which four nearly equivalent orientations are observed. This preferential orientation of the oxygen molecule results from an hydrogen bonding interaction with the amide groups as shown by the chemical shift of the corresponding protons. The role of this bond in the stability and the bent geometry of the oxygenated complex is of the same type as those proposed for hemoproteins involving distal histidine [6, 7].

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The 'Pocket' Porphyrins: Hemoprotein Models with Lowered CO Affinities

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A new series of hemoprotein models, the iron(II) 'pocket' porphyrins [1], have been synthesized (Fig. 1). This series of congruent models has been designed so as to incorporate varying degrees of steric encumbrance at the gaseous ligand binding site. Throughout the series, the pockets are expected to accommodate the formation of unhindered, bent FeO_2 units, while providing, in differing degrees, steric hindrance sufficient to interfere with the binding of CO in a normal linear fashion. Dilute solutions of several iron(II) 'pocket' porphyrin complexes in toluene are five-coordinate in the presence of excess axial ligands (1-methylimidazole and 1,2-dimethylimidazole) and are sufficiently stable with respect to oxidation so as to allow determination of $P_{1/2}^{CO}$ and $P_{1/2}^{O_2}$ at room temperature under equilibrium conditions. Whereas the oxygen affinities of the ferrous 'pocket' systems are comparable to those of the 'picket fence' [2] compounds, the carbon monoxide affinities are significantly lowered and approach that of myoglobin (Table I). Kinetic data indicate that the lowered CO affinities in the 'pocket' complexes are primarily reflected in decreased association rates. By contrast, the 'pocket' models show both decreased O_2 dissociation and association rates as compared to the 'picket fence' analogues, FeTpivP(1,2-Me_2Im), *I*, and $FePiv_3$-5CIm, *II*. These results indicate that steric hindrance can selectively discriminate against CO binding in model compounds and support the hypothesis that the intrinsic CO affinities of hemes may be reduced by steric interaction with the binding pocket in hemoproteins [3].

A full account of this work is to be published elsewhere [1].

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