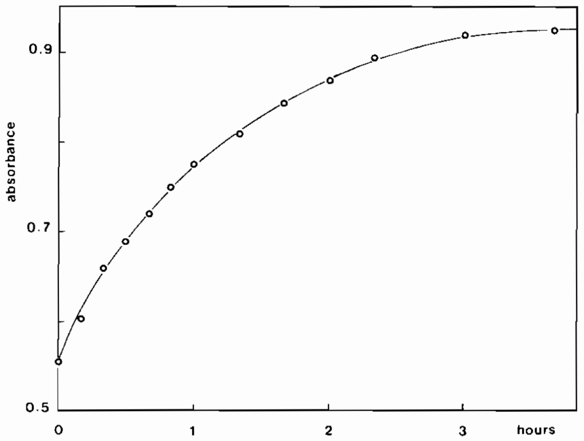
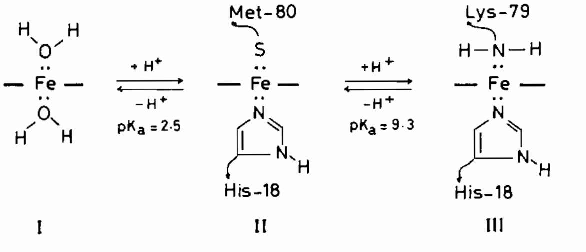


Fig. 2. Absorbance values at 548 nm of a 6.5 × 10^{-5} *M* deaerated aqueous solution of cytochrome *c*, as a function of irradiation time. Temperature 25 °C; pH = 7.

the absorbance *vs.* time observed at 548 nm (Fig. 2) shows that the photoreduction does not follow zero-order kinetics. Since the solution absorbs 100% irradiation light for the whole period of the photochemical run, the above behavior may be ascribed to a re-oxidation of the reaction product. The fact that no spectral changes were observed in the dark after irradiation suggests that the re-oxidation process occurs as a consequence of light absorption of the reduction product. This hypothesis is experimentally supported by the finding that irradiation of cytochrome *c* solutions, which were previously reduced by sodium dithionite, leads to spectral variations that are exactly opposite to those observed in the photoreduction experiments.

The photoreduction rate was observed to be strongly dependent on pH. The rate increases from pH 2 to pH 5, and then decreases from pH 8 to pH 11. It is known [1] that ferricytochrome *c* has five pH-dependent conformational states, which differ from one another depending on the nature of the axial ligands. An interpretation of three pH states of cytochrome *c* is illustrated in Scheme 1. The comparison of the equilibria shown in Scheme 1 with the observed dependence of the photoreduction on pH suggests that Species II, which contains methionine and histidine as iron axial ligands, is the only photoreducible species. This is an indication that an electron transfer from the sulfur of the methionine to the central iron should be responsible for the primary photoreduction.



Scheme 1.

The absorption spectrum of the photochemically reduced cytochrome *c* was found to be identical to that obtained for the chemically reduced hemeprotein, thus suggesting that both methionine and histidine are retained in the axial positions of central iron also after photoreduction. This conclusion gives rise to a question as to the fate of the hole on the sulfur atom after the electron transfer to iron. Studies aiming at the resolution of this problem are now in progress in this laboratory.

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Q10

Metal Ion Insertion into N-Alkylated and N,N′-Dialkylated Porphyrins

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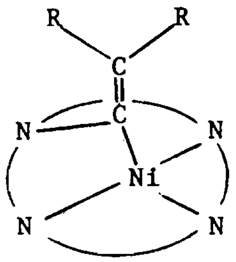
Addition of $FeCl_3/Fe$ to N-(2,2′-bis-p-chlorophenylethenyl)tetraphenyl porphyrin yields the iron(II) insertion product which has been characterized by extensive ^1H and ^2H NMR studies. The pyrrole protons of this and other N-alkyl porphyrin Fe(II) complexes show up as four equally intense resonances with chemical shifts at 25 °C of 28, 20, 8 and –6 ppm. The NMR spectra clearly distinguish between N-alkyl porphyrin complexes of Fe(II) and Fe(III) complexes of similar symmetry in which a carbene is inserted into the Fe–N bond. Treatment of N,N′-bis(2,2′-*p*-chlorophenylethenyl)tetraphenyl porphyrin with metal carbonyls can result in the rupture of one or both N–C bonds. Thus with $Fe_3(CO)_{12}$ the iron(II) carbene complex TPPFe (C = $C\{C_6H_4Cl\}_2$) is formed while $Ni(CO)_4$ nickel is inserted into one N–C bond to form I. (*See next column*).



Q11

Ligand Coordination Effects in the Spin State/Stereochemistry Relationships in Metalloporphyrins and Hemoproteins

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In order to elucidate the effects mentioned in the title we have developed a version of MO perturbation theory, which permits the solution of the problem of reagent geometry changes due to the interaction between them. In this version the sum of matrix elements of interreagent electronic and intrareagent vibronic interactions, which are nondiagonal in the basis of MO of free reagents, was considered as a perturbation.

The use of this approach to the interaction between metalloporphyrin (MeP) and axial ligands L_1 and L_2 gave the following expressions for the value of the out-of-plane metal displacement Q_{min}, and for the values of the energy differences $\Delta E_{h,i(1)}$ between the energies ^hE and ^iE (or ^1E) of the high-spin $^h\psi$ and intermediate-spin $^i\psi$ (or low-spin $^1\psi$) states:

$$Q_{min} = \frac{\sum_{f,n} (P_n - P_f)a_{nf}(A_{nf} + B_{nf})/\delta_{fn}}{\kappa - \sum_{f,n} (P_n - P_f)a_{nf}^2/\delta_{fn}} \tag{1}$$

$$\Delta E_{h,i(1)} = {}^hE(0) - {}^{i(1)}E(0) - \tfrac{1}{2}\Delta|Q_{min}^{h,i(1)}|\,| \times$$

$$\times \sum_{f,n} (P_n - P_f)a_{nf}(A_{nf} + B_{nf})/\delta_{fn}| \tag{2}$$

Here κ is the force constant for the A_{2u} out-of-plane displacement, a_{nf} is the constant of vibronic mixing of the n-th and f-th MO of MeP by A_{2u} displacements, P_n and P_f are the MO occupation numbers, $2\delta_{fn}$ is the energy gap between these MO, which is different from the appropriate energy gap in MeP due to the contribution of the diagonal matrix elements of the MeP-ligand interaction in zero hamiltonian, A_{nf} and B_{nf} are the corresponding matrix elements of the A_{2u} component of this interaction, $\Delta|Q_{min}^{h,i(1)}|$ is the difference between the $|Q_{min}|$ values in the $^h\psi$ and $^i\psi$ (or $^h\psi$ and $^1\psi$) states.

Consider first the complexes MeP (L) with one ligand ($B_{nf} = 0$). The greatest A_{nf} values correspond to the mixing of axially arranged MO: $a_{2u}(\pi)$ with $a_{1g}(d_{z^2})$, $a_{1g}(d_{z^2})$ with a_{2u} $(4p_z)$. On the other hand, the greatest softening of the A_{2u} force constant, as it may be concluded from eqns. (1) and (2), is realized in complexes with partially occupied a_{1g} (d_{z^2}) and $b_{1g}(d_{x^2-y^2})$ MO. Consequently, *ceteris paribus* Q_{min} values must be larger in the $^h\psi$ state, than in the $^1\psi$ and $^i\psi$ ones. The greatest Q_{min} values have to be expected in complexes with the greatest A_{nf} values, provided the vibronic softenings are not much different. The more the $3d_{z^2}$ and $4p_z$ orbitals are "elongated" in the axial direction, the larger are the A_{nf} values. In so far as the elongation of these orbitals decreases in the series of Mn, Fe, and Co atoms, an appropriate reduction of the Q_{min} values has to be expected in the corresponding MeP(L) with the same ligand L. This conclusion is confirmed by experimental data on the MeP(NO) and MeP (imidazole) systems. As far as the spin states are considered the ligand coordination, as it follows from eqns. (1) and (2), leads to the two effects: (1) enhances the Q_{min} value, promoting the lowering of ^hE value, and (2) enhances the δ_{fn} values and changes the $^hE(0) - {}^{i(1)}E(0)$ ones, in most cases opposing the lowering of the ^hE value. Therefore, the smaller the diagonal component of the MeP–L interaction and the larger the A_{nf} value, the more the formation of the MeP(L) system contributes to the realization of the high-spin state as the ground one.

The coordination of a second ligand favours the decrease of the Q_{min} value and the possibility of high spin ground state realization for the following two reasons: 1) $|A_{nf} + B_{nf}| < |A_{nf}|$, 2) the diagonal component of MeP–ligand interaction increases, enhancing the δ_{fn} values.

The above results explain, using the same point of view, both the spin state stereochemistry relationships in the heme in the process of T $\rightleftarrows$ R conformational transitions of hemoglobin and the essential in-plane position of the iron atom in cytochrome *c* independent of the oxidation state.