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Spin State/Stereochemistry Relationships in Metalloporphyrins: the Vibronic Approach

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Consider the pseudo Jahn–Teller instability [1] of the planar nuclear configuration of the MeP system with respect to the out-of-porphyrin plane displacement and to the change of hole diameter depending on the electronic state and the nature of the metal. The planar MeP has the D_{4h} symmetry, the out-of-plane metal displacement is of A_{2u} symmetry, and the change in hole diameter corresponds to the totally symmetric displacement. It may be concluded from selection rules and 3d MeP electronic structure calculations [2], that in $Fe^{II}P$ and $Mn^{II}P$ there are intermediate-spin ground, $^{i}\psi_0$, and excited, $^{i}\psi_1$, electronic states, which are mixed by A_{2u} displacements. The $^{i}\psi_1$ state can be constructed from the $^{i}\psi_0$ one by a one-electron excitation $a_{2u}(\pi) \rightarrow a_{1g}(d_{z^2})$.

The lowest high-spin states $^{h}\psi_0$ can be obtained from the $^{i}\psi_0$ one by electron $e_g(d\pi) \rightarrow b_{1g}(d_{x^2-y^2})$ excitations. These states are mixed by A_{2u} displacements with two near lying excited states. The first, $^{h}\psi_1$, can be obtained from the $^{h}\psi_0$ state by electron $a_{2u}(\pi) \rightarrow a_{1g}(d_{z^2})$ excitation, the mixing $^{h}\psi_0 - {}^{h}\psi_1$ being characterized by the same vibronic parameters as the $^{i}\psi_0 - {}^{i}\psi_1$ mixing. The second state $^{h}\psi_2$ is formed by the $b_{1g}(d_{x^2-y^2}) \rightarrow b_{2u}(\pi^*)$ excitation.

We have shown recently [3, 4] that in both cases the $\psi_0 - \psi_1$ mixing gives the main contribution to the instability of the planar MeP configuration, whereas the contribution of the $\psi_0 - \psi_2$ mixing per se is insufficient for the formation of such an instability (herefrom it may be concluded that in MeP with completely occupied $a_{1g}(d_{z^2})$ MO, *e.g.* in $Cu^{II}P$, $Zn^{II}P$, and diamagnetic $Ni^{II}P$, the in-plane position of the metal is stable due to the lack of low lying ψ_1 states).

On the other hand the occupation of the antibonding $b_{1g}(d_{x^2-y^2})$ MO in the $^{h}\psi_0$ state results, first, in the increase of the hole diameter due to the stronger interaction with the totally symmetric displacements and, second, in an additional reduction of A_{2u} force constant. Therefore, under the out-of-plane metal displacement the energy lowering in the $^{h}\psi_0$ state occurs more readily than in the $^{i}\psi_0$ one. As a result the intersection of the two terms takes place, provided the $\psi_0 - \psi_1$ vibronic mixing is strong enough (for the corresponding quantitative criterion see Ref. [4]). Thus for large enough out-of-plane displacements of the metal atom the $^{h}\psi_0$ state becomes the ground one, in contrast with the planar configuration case, where $^{i}\psi_0$ is the ground state and *vice versa,* if the MeP system is found in the high-spin state, it means that the size of the hole is greater and the out-of-plane metal displacement is larger, compared with $^{i}\psi_0$. Note, that as far as the out-of-plane displacement of the metal atom is determined by the $a_{2u}(\pi) - a_{1g}(d_{z^2})$ MO mixing, the essential influence of the environment of the MeP (both peripheral and axial) on the magnitude of this displacement and spin equilibrium has to be expected.

The results obtained are in qualitative agreement with the experimental data available [5].

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Catalytic Mechanisms and Reactivity of Peroxidases, Catalases and Iron–Porphyrin Model Systems

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Water-soluble iron(III)–porphyrins display both peroxidase and catalase-like properties [1, 2]. In both enzymic and model systems the basic catalytic mechanism is:

Catalyst + Oxidising Substrate →
Oxidised Catalyst Intermediate

Oxidised Catalyst + Reducing Substrate →
Catalyst + Oxidised Product

The kinetics of both phases of the catalytic cycles have been studied with the objective of elucidating the factors (steric, electronic, electrostatic) which influence reactivity, the natures of the intermediates and the mechanistic origins of enzymic reactivity and selectivity. The reactions of peroxidases (different proteins with the same iron-porphyrin prosthetic group) have been studied with a range of oxidising substrates (hydroperoxides) [3–5] and reducing substrates [6, 7]. Parallel studies have been made with protein-free, water-soluble iron(III)–porphyrins