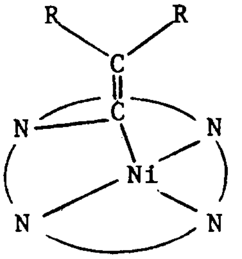

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Ligand Coordination Effects in the Spin State/Stereochemistry Relationships in Metalloporphyrins and Hemoproteins

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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:

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

$$\Delta E_{h,i(1)} = {}^hE(0) - {}^{i(1)}E(0) - \tfrac{1}{2}\Delta|Q_{min}^{h,i(1)}| \, |\times \sum_{f,n} (P_n - P_f)a_{nf}(A_{nf} + B_{nf})/\delta_{fn}| \quad (2)$$

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 ⇄ R conformational transitions of hemoglobin and the essential in-plane position of the iron atom in cytochrome *c* independent of the oxidation state.