

Orientations of Axially Coordinated Ligands in Model Systems of Cytochromes

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Many properties of cytochromes and model systems depend on orientations of axial ligands. In this work we elucidated role of substituents of porphyrin on orientation of axial ligands in model systems of cytochromes. The orientations of axially coordinated imidazoles and pyridines in crystal structures of model systems of cytochromes were analyzed and data were compared with previous quantum-chemical calculations.

The results show that eight ethyl groups on porphyrin ring strongly favor parallel orientation, hence, in all these complexes axial ligands, pyridines or imidazoles, are mutually parallel. Four phenyl or mesityl groups at *meso*-carbons also favor parallel orientation but less strong. Hence, in most of the bis-imidazole complexes orientation is parallel, while in bis-pyridine complexes orientation of pyridines depends on oxidation state of Fe.

In Fe(II) complexes orientation is parallel, in Fe(III) it is orthogonal. In Fe(III) complexes influence of the interaction of pyridine with porphyrin ring, dominates over influence of phenyl or mesityl groups on porphyrin ring, and the orientation is parallel. Namely, by previous quantum chemical calculations it was shown that in bis-pyridine Fe(III) porphyrinato complexes without substituents orthogonal orientation is favored by 16 kcal/mol.

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