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N43 MODEL SYSTEMS FOR IRON AND COPPER CONTAINING OXYGENASES

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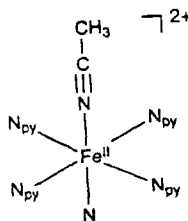
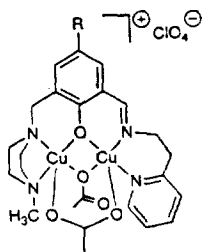
The activation of dioxygen in biological systems and the selective oxygenation of arenes, alkanes and alkenes is a challenging area of research. Recent emphasis is on functional modeling of metaloxxygenases to unravel molecular mechanisms of catalysis and on the design of new catalysts for oxygen atom transfer.¹ Structural and functional models for mono- and dinuclear metalloenzymes as well as new oxidation catalysts² will be presented.

New methodology for multidentate ligands, based on sequential aromatic Mannich reactions, allows the formation of non-symmetric dinuclear complexes,³ mimicking aspects of the binding of metal ions of dinuclear metalloenzymes (such as tyrosinase) in different environments.

The synthesis, structures and properties of non-symmetric dinuclear Cu(II)-complexes (e.g.1) with chemically or geometrically distinct copper-centers are described.⁴ The stepwise complexation of Cu(II) was determined by microcalorimetry. The molecular structure of a related dinuclear Fe(III) complex was also elucidated.

Our focus in mononuclear iron-oxygenase mimics is on nonheme iron centers in oxygen activation.

The synthesis and X-ray structure of the low-spin iron (II) complex $[\text{Fe}(\text{N}_4\text{py})\text{CH}_3\text{CN}](\text{ClO}_4)_2$ (**2**) of the new pentadentate ligand N_4py is reported. The complex reacts with hydrogen peroxide at room temperature to form a transient purple species, which exhibits low-spin Fe(III) EPR signals similar to those of activated bleomycin. The intermediate is formulated as an iron(III)hydroperoxide. Spectroscopy and catalytic activity in hydrocarbon oxidations are described.



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