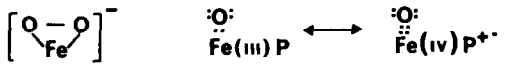
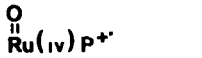


1 2 3

P-450 (Table I). We have extended this chemistry using ruthenium porphyrins [10] and find that a ruthenium (III) octaethylporphyrin and iodosylbenzene will catalyse epoxidation and hydroxylation in a similar fashion (Table I). In addition, a relatively stable complex, characterized as (4) has been isolated which exhibits an ESR signal at g = 2.0 confirming its porphyrin radical nature. This isolated complex performs the same oxidations as in the catalytic regime described in Table I. where the formation of,



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inter alia, cyclohexyl bromide from cyclohexene confirms the radical nature of the oxidation processes.

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B26

The Determination of Hydration Numbers of Metal Ions in Metalloenzymes by NMR

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Proton relaxation enhancement (PRE) was one of the first applications of NMR to biological systems [1]. It was successfully used to monitor changes in the hydration sphere of paramagnetic metal ions embedded in the active sites of enzymes, upon binding of substrates and inhibitors [2]. However, no unambiguous quantitative interpretation of PRE in terms of hydration numbers (q), exchange lifetimes (τ_M) and correlation times (τ_C) is available [3, 4].

The evaluation of these parameters on the basis of the frequency dependencies of the proton longitudinal relaxation times cannot be made in a unique manner mainly because of the invalidity of the relaxation equations at low magnetic fields, where, at least for Mn(II), the contribution of the zero field splitting cannot be ignored. Our approach was to evaluate all the parameters at one, high magnetic field strength, using the four relaxation times, T_{1p}^H, T_{2p}^H, T_{1p}^D and T_{2p}^D of the water protons and deuterons in the same solution. As a result, in addition to the three parameters, q, τ_M and τ_C, a contribution from the outer sphere relaxation could also be characterized.

For Mn(II) bovine carboxypeptidase and Mn(II) bovine carbonic anhydrase B, a hydration number of unity was obtained, and the exchange lifetimes $\tau_M = 1.0 \times 10^{-7}$ s and 0.75×10^{-7} s were found for the two enzymes respectively.

The same q and τ_M were obtained in independent measurements at different magnetic fields, and τ_M was found to be twice as long upon reducing the temperature from 20 °C to 0 °C, as expected.

The outer sphere relaxation could not be explained either by spin diffusion from the protein protons or by dipolar interaction between the Mn(II) ion and freely diffusing water molecules [5]. A good account of this contribution could be obtained by a mechanism involving water molecules which are bound outside the first hydration sphere and have an average exchange lifetime of about 3×10^{-10} s.

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B27

Role of the Protein in the B_{12}-dependent Enzymes: Steric Control of a Molecular Switch

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The initial step in the B_{12}-dependent isomerase and ribonucleotide reductase enzymes involves the reversible homolytic fission of the Co–C bond in