

Title: Probing Manganese (III) and (IV) Porphyrin Complexes with Different Coordination Numbers and Oxidation States by UV-Vis and $^1\text{H-NMR}$ Spectroscopy

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Titration of Mn^{3+} porphyrin complexes with several imidazole ligands is examined using UV-Visible absorption and $^1\text{H-NMR}$ spectroscopy. Mn^{3+} porphyrins have a d^4 electron configuration with two or more unpaired electrons, which makes Mn^{3+} porphyrin complexes paramagnetic and affects both their absorption and NMR spectra. Mn^{3+} porphyrins are isoelectronic with the catalytically important Fe^{4+} porphyrins present in redox active heme proteins that activate and reduce bound oxygen. Since these proteins funnel electrons into a distal oxygen ligand through the central metal, changes in the electron donating ability of the proximal ligand will affect the protein's reactivity. The spectral signature and reactivity of Mn^{3+} porphyrin complexes are studied because of their molecular similarities to biological systems.

The unusual split Soret and Q-band regions of the absorption spectra of $\text{Mn}^{3+}\text{PPDME}$ (protoporphyrin dimethyl ester) and Mn^{3+}OEP (octaethylporphyrin) are very sensitive to axial ligation changes upon displacement of weaker axial ligands with stronger field ligands. Ligand binding constants can be calculated from UV-Vis absorption spectra, to further describe the interaction between the metallo-porphyrin and its axial ligands. Imidazole (ImH) models the axial histidine ligand present in peroxidase heme proteins. Titration of Mn^{3+} porphyrins with increasing concentrations of imidazole in chloroform or methanol transforms the initial 5-coordinate (5C) mono-Cl or 6C bis-methanol species into mono-ImH then 6C bis-ImH complexes. Imidazoles with different steric, H-bonding and electron-donating capabilities show variation in the wavelength and intensity shifts that result from changes in the coordination number and geometry of the central metal. Binding of anionic methoxide ligands to Mn^{3+} porphyrins is also being studied. Beer's Law is used to determine molar absorptivity values. Several Mn^{4+} porphyrin complexes obtained by oxidation with meta-chloroperbenzoic acid show a collapsed single Soret band and different stabilities depending on the trans-axial ligand.

These complexes are also being examined by $^1\text{H-NMR}$ spectroscopy to further probe the structural and electronic changes that occur in the equatorial porphyrin ligand upon changes in axial ligation. Since Mn^{3+} and Mn^{4+} are paramagnetic, many of the porphyrin protons occur well outside the diamagnetic region, between +10 to +80 ppm and -1 to -10 ppm. Changes in chemical shifts are easier to observe than in diamagnetic coordination compounds. Experiments that illustrate spectral signature and reactivity of Mn^{3+} porphyrins can be used to understand Fe^{4+} porphyrin reactivity in redox active heme proteins, while Mn^{4+} porphyrins inform on high-valent Fe^{5+} catalytic intermediates.