Coordination of Methoxide Donor Ligands to Catalytic Manganese (III) and Manganese (IV) Porphyrins Probed by Paramagnetic NMR Spectroscopy

Gigi B. Ray, Bryan D. Cox, Ashley M. Ribera, and Cathy V. Tran

Department of Chemistry, University of West Georgia

The structural and electronic consequences of coordination of several different types of axial ligands to manganese(III) and manganese(IV) porphyrins have been examined by paramagnetic nuclear magnetic resonance and absorption spectroscopy. The interplay of interactions between the metal, its equatorial-porphyrin and axial ligands are probed by examining changes in porphyrin spin density distribution and electronic transitions. Solution characterization of Mn(III) porphyrin complexes with mono- and bis-coordination of the sigma- and pi-donor ligand methoxide (OCH_3^-), suggests an unusual spin state as measured by the Evans NMR method. Manganese tetra-aryl porphyrin (TPP) and octa-alkyl porphyrin (PPDME, OEP) adducts are compared. Paramagnetic ^1H-NMR spectra of weak field ligands (CH_3OH) and strong field ligands (imidazole, OCH_3^-, and CN^-) bound to Mn(III) and Mn(IV) porphryins indicate that the pyrrole and methine resonances are very sensitive to the coordination number and spin state of the metal. This information on biomimetic Mn-porphyrin model compounds helps elucidate the reactivity of catalytic manganese protein intermediates, in which the metal coordination environment and spin state are not well understood.