

EPR Spectroscopy of Transition Metallo-Proteins

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Continuous wave (cw), EPR spectroscopy has been used to structurally characterize metal binding sites in proteins containing specifically and non-specifically bound mononuclear Cu(II). Additionally, structural predictions have been made for ferric hemoproteins and for iron-sulfur proteins based on their EPR parameters.

More recently pulsed EPR investigations were the first to identify his-imidazole as a common equatorial ligand to the metal in all Cu(II) proteins. In addition, pulsed EPR has been used to identify weakly coupled protons arising from water bound to metal centers, as well as bound substrates, co-factors, and univalent cations that enter into the reaction mechanism of metalloenzymes. More recently, pulsed EPR investigations of Co(II)-substituted myoglobins and hemoglobins have been able to show how protein structure modulates O₂-binding properties.

Using a combination of cw and pulsed EPR methods we have recently identified the ligands to Cu(II) in the octapeptide repeats of the disordered N-terminal region of prion protein. The strategies for this structural identification, subsequently verified by x-ray crystallography of the octapeptide-Cu(II) complex, will be presented.