

Probing Fe-Substrate Orientation for Taurine/ α -Ketoglutarate Dioxygenase Using Deuterium ESEEM Spectroscopy

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The structural relationship between substrate taurine and the non-heme Fe(II) center of taurine dioxygenase (TauD), an α -ketoglutarate-dependent iron dioxygenase, was measured using Electron Spin Echo Envelope Modulation (ESEEM) spectroscopy. Studies were done on TauD samples treated with NO, co-substrate α -ketoglutarate, and either protonated or specifically deuterated taurine. Stimulated echo ESEEM data were divided to eliminate interference from ^1H and ^{14}N modulations and to accentuate modulations from ^2H . For taurine that was deuterated at the C-1 position (adjacent to the sulfonate group), ^2H ESEEM spectra show features that arise from dipole-dipole and deuterium nuclear quadrupole interactions from a single deuteron. Parallel measurements done for taurine deuterated at both C-1 and C-2 show an additional ESEEM feature at the deuterium Larmor frequency. Analysis of these data at field positions ranging from $g = 4$ to $g = 2$ have allowed us to define the orientation of substrate taurine with respect to the magnetic axes of the Fe(II)-NO, $S = 3/2$, paramagnetic center. These results will be discussed in terms of previous X-ray crystallographic studies and the proposed mechanism for this family of enzymes.