

# Characterization of a High-Valent Intermediate in the Reaction of Peroxide with Fe<sup>III</sup>-TAML in Aqueous Solution

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The reaction of Fe<sup>III</sup>-TAML (Tetra Amido Macrocyclic Ligand) with peroxide in an aqueous solution has been examined. The addition of one equivalent of H<sub>2</sub>O<sub>2</sub> to Fe<sup>III</sup>-TAML at pH = 11 yields an intermediate which we have characterized. X-band EPR spectroscopy shows a ground state  $S = 1/2$  signal with  $g = 2.14, 2.11, 1.99$  that broadens with <sup>57</sup>Fe enrichment. Mössbauer spectra at low temperature on the same samples show a new paramagnetic species. At high temperature this species collapses into a broadened doublet which can be fit with two doublets of equal area having isomer shifts of  $\delta = 0.00$  mm/s and  $\delta = -0.11$  mm/s indicating the formation of a mixed valence Fe<sup>III</sup> Fe<sup>IV</sup> species. A fit to the temperature dependence of the EPR signal finds an antiferromagnetic spin exchange coupling of  $J = 50\text{cm}^{-1}$ . The species has new optical bands above 500nm.

