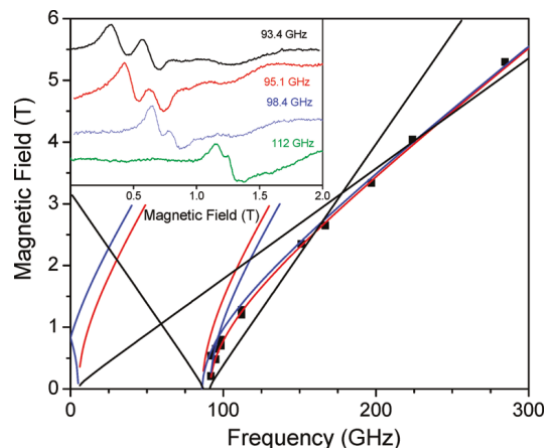
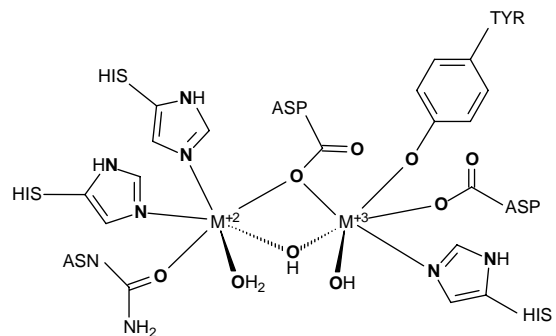




# Unsymmetrical Fe<sup>III</sup>Co<sup>II</sup> and Ga<sup>III</sup>Co<sup>II</sup> Complexes as Chemical Hydrolases.

## Biomimetic Models for Purple Acid Phosphatases (PAPs)

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This project, involving scientists from six institutions on four continents, had the goal of modeling an important class of enzymes (purple acid phosphatases, PAPs), structure shown at left, upper figure). PAPs catalyze the hydrolysis of phosphate esters and are found in animals and plants. The active site of PAPs comprises two metal ions:  $M^{3+} = \text{Fe}$ ,  $M^{2+} = \text{Mn, Fe, Zn}$ . Model complexes employing a novel dinuclear ligand and with metal ions:  $\text{Fe}^{3+}\text{Co}^{2+}$ ,  $\text{Fe}^{3+}\text{Zn}^{2+}$ , and  $\text{Ga}^{3+}\text{Co}^{2+}$  were studied by a variety of spectroscopic techniques including EPR, HF-EPR (done at NHMFL, spectra and field-frequency plot shown at left, lower figure), MCD, and x-ray diffractometry. These studies allowed characterization of the electronic structure of the PAP model, in particular the interaction between the two metal ions, which is crucial for enzyme function. In parallel chemical and biochemical studies, the kinetics of the phosphatase reaction were studied using both small molecules and DNA itself. Taken together, these studies allowed a detailed proposal to be made for the mechanism of enzymatic phosphate ester hydrolysis.

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