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H20 The Di-iron Center in Bovine Spleen Purple Acid Phosphatase

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The best characterized purple acid phosphatases (PAPs) have been isolated from porcine uterus (Uteroferrin, Uf) and bovine spleen (BSPAP). The enzymes contain an antiferromagnetically coupled, binuclear iron center and exist in two oxidation states (Fe(III)-Fe(III) and Fe(II)-Fe(III)).

Oxidized BSPAP is purple, has $\lambda_{\text{max}} = 560 \text{ nm}$, is catalytically inactive toward phosphate ester hydrolysis, has an $S = 0$ ground spin state and exhibits strong antiferromagnetic coupling reported to be $-2J = 80\text{--}300 \text{ cm}^{-1}$ [1].

Reduced BSPAP is pink, has $\lambda_{\text{max}} = 536 \text{ nm}$, is catalytically active toward phosphate ester hydrolysis, has an $S = 1/2$ ground spin state and exhibits weaker antiferromagnetic coupling ($-2J \sim 11 \text{ cm}^{-1}$) [1]. The reduced enzyme exists in variable percentages of two conformations, each exhibiting the classic EPR signal for an $S = 1/2$ ground spin state arising from an antiferromagnetically coupled high-spin ferric ion and an high-spin ferrous ion. The g values are at 1.94, 1.78, 1.64 and at 1.86, 1.74, and 1.58 for species A and B respectively.

While extensively studied, the details of the di-iron center have still to be elucidated. There is only indirect evidence to favor a μ -oxo structure over a μ -hydroxo structure based on the large magnetic coupling constant for the oxidized phosphate complex.

Paramagnetically shifted NMR resonances are consistent with one tyrosine and one histidine ligated to the ferric iron and one histidine ligated to the ferrous ion in BSPAP_{red} [2] and Uf_{red} [3]. However, the nature of the proposed carboxylate ligand(s) has yet to be determined and the identity of any remaining ligands to the cluster are to date unknown. Preliminary NMR evidence suggests the magnitude of J is smaller in oxidized BSPAP Vs Uf.

Through a combination of EPR and NMR spectroscopies we address the ligands of the catalytic di-iron site and the magnitude of the magnetic coupling constants for the enzyme in further detail. Additional analyses of the previously reported ternary complex [1] shall also be reported.

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