

Thiolester Hydrolysis by Zinc Hydroxide Complexes: Model Reactions for Glyoxalase II

Lisa M. Berreau¹, Amrita Saha¹, Atta M. Arif²

¹*Department of Chemistry and Biochemistry, Utah State University,* ²*Department of Chemistry, University of Utah*

The glyoxalase system, which is comprised of two metalloenzymes, catalyzes the conversion of 2-oxoaldehydes into α -hydroxy acids using glutathione as a required cofactor. Glyoxalase II (GLX II) catalyzes the second step of this pathway, hydrolysis of a thiolester moiety to yield free glutathione and lactic acid. The active site of GLX II from *Arabidopsis thaliana* contains a dinuclear metal center having primarily histidine ligation, with single bridging carboxylate and hydroxide ligands between the two metal centers.¹ In vivo, this enzyme incorporates Fe(II/III), Mn(II), and Zn(II) in variable dimetal combinations.² In this contribution, the synthesis and characterization of three new dinuclear zinc hydroxide complexes will be presented. A reactivity study of these complexes with a α -hydroxythiolester model substrate has yielded the first examples of thiolester hydrolysis mediated by zinc hydroxide complexes. Products identified for these reactions include a free thiol and zinc complexes having a coordinated α -hydroxycarboxylate ligand.

1. Cameron, A. D.; Ridderstrom, M.; Olin, B.; Mannervik, B. *Structure Fold Des.* **1999**, *7*, 1067-1078.
2. Wenzel, N. F.; Carenbauer, A. L.; Pfiester, M. P.; Schilling, O.; Meyer-Klaucke, W.; Makaroff, C. A.; Crowder, M. W. *J. Biol. Inorg. Chem.* **2004**, *9*, 429-438.