

# Coordination Chemistry of Mononuclear Ni(II) Complexes of Relevance to Acireductone Dioxygenase

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Acireductone dioxygenase (ARD) is the first reported example of a nickel dioxygenase. This enzyme catalyzes the oxidative breakdown of acireductone ( $\text{CH}_3\text{SCH}_2\text{CH}_2\text{C}(\text{O})\text{C}(\text{OH})=\text{CHOH}$ ) in a reaction that is a shunt out of the methionine salvage pathway in *K. pneumoniae* and results in the formation of methylthiopropionic acid, formate, and carbon monoxide.<sup>1</sup> In the resting state, the mononuclear Ni(II) center of ARD exhibits octahedral coordination with six O/N-donors, of which 3-4 are coordinated histidine residues<sup>2</sup>. In the enzyme/substrate complex, bidentate coordination of the acireductone substrate is suggested on the basis of X-ray absorption spectroscopic studies.

As an approach toward further elucidating the functional role of the Ni(II) center in ARD, we have undertaken a study focused on the preparation, characterization, and examination of the reactivity of synthetic mononuclear Ni(II) complexes. Initial studies yielded Ni(II) complexes of relevance to resting state ARD, which were characterized by several methods, including X-ray crystallography and paramagnetic <sup>1</sup>H NMR. Recent efforts have focused on the solid-state and solution characterization of enolate and carboxylate-bound mononuclear Ni(II) complexes with relevance to substrate- and product-bound forms of the Ni(II) center in ARD. Details of this work, with a particular emphasis on demonstrating the utility of paramagnetic <sup>1</sup>H NMR in monitoring reactions of synthetic mononuclear octahedral Ni(II) complexes, will be presented.

1. Dai, Y.; Pochapsky, T. C.; Abeles, R. H. *Biochemistry* **2001**, *40*, 6379-6387.
2. Al-Mjeni, F.; Ju, T.; Pochapsky, T. C.; Maroney, M. J. *Biochemistry* **2001**, *41*, 6761-6769.