Hydrogenase Models in a Proteic Environment

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The dithiolate cofactor of the Fe-hydrogenase active site has attracted much attention as one of the components that enables efficient catalysis. The dithiolate also represents a means by which diiron models can be functionalized, *e.g.* for the attachment of a Fe_4S_4 cubane, a photosensitizer, and surface-anchoring groups. In this report, we describe efforts to exploit the dithiolate to conjugate a synthetic diiron unit to a protein. Specifically, we have developed a maleimide-containing diiron carbonyl that adds to the free thiol within the heme-free pocket of a sperm-whale myoglobin mutant. Ligand substitution and related studies in aqueous solution will also be discussed. In general these studies elucidate for the first time the effects of a protein environment on the substitution and reactivity of the diiron unit.