Using X-ray Absorption Spectroscopy to Probe Metallocluster Biosynthesis in the Nitrogenase Enzyme System

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Ninety-percent of biological fixed nitrogen production, the process by which atmospheric nitrogen is reduced to ammonia, is catalyzed by the nitrogenase enzyme system. Two unique iron-containing metalloclusters, FeMoco and the P-cluster, have been identified as critical to nitrogenase activity. The assembly of these metalloclusters *in vivo* is a complex bioinorganic process of significant current interest. In *Azotobacter vinelandii*, the *ni*trogen *f*ixation (*nif*) genes control nitrogenase protein and metallocluster assembly. Genetic studies have targeted the specific *nif* genes involved in cluster biosynthesis; however, little is known about the molecular mechanisms by which these clusters are constructed. Using primarily x-ray absorption spectroscopy, we have determined the structures of metalloclusters at different stages in the biosynthetic pathway. These structures have lent new insights into the biosyntheses of this complex enzyme and its component clusters.