Assembly of the Metal Centre of [NiFe]-Hydrogenases

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The metal centre of [NiFe]-hydrogenases is coordinated to the large enzyme subunit via the thiolates of four cysteine residues from the protein backbone, two of them serving as bridging ligands. The Fe of the center carries three non-protein ligands, in the classical case one CO and two CN moieties. Synthesis and integration of the centre requires the activities of at least seven gene products (for rev. see ref.1). Six of them are designated as hyp genes. HypF and HypE synthesise cyanide from carbamoylphosphate. HypE which carries the cyanide as a thiocyanate delivers the cyanide to some acceptor group in a complex formed by the maturation proteins HypC and HypD. During this processes HypF interacts with HypE and HypE-CN undergoes transient complex formation with the HypCxHypD heterodimer. Based on the fact that HypC is also found in a complex with the precursor of the large subunit a putative role in the transfer of the cyanide group has been postulated. The source of the CO ligand is still unknown. Nickel incorporation requires the activities of the HypA and HypB proteins and, for optimal activity, the function of the SlyD protein (2). The seventh essential protein is an endopeptidase which removes an oligopeptide from the C-terminal end of the precursor of the large subunit once nickel has been inserted. The C-terminal cleavage of the precursor results in a conformational change and the closing und internalisation of the centre.

(1) M. Blokesch et al. (2002) Biochem. Soc. Transact. 30, 674-680.

(2) J. W. Zhang et al. (2005) J. Biol. Chem. 280, 4360-4366.