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Evidence for central carbon in nitrogenase FeMo cofactor

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The dissociation of the stable triple bond of atmospheric dinitrogen (N2) and the reduction to bioavailable ammonia (NH4+) is called nitrogen fixation. Biological nitrogen fixation is carried out by the nitrogenase1, an enzyme complex consisting under turnover condition of two metallo proteins, the MoFe- and the Fe-protein2. Nitrogen reduction takes place at the MoFe-protein, whereas the Fe-protein is the physiological and unique electron donor. The Azotobacter vinelandii MoFe-protein is a 230 kDa α2β2-heterotetramer and contains two metal clusters, the P-cluster [8Fe:7S] and the FeMo-cofactor [Mo:7Fe:9S:X:homocitrate] (FeMoco), per αβ-heterodimer. FeMoco is the active site for nitrogen binding and fixation. It is a highly symmetrical cluster and the most complex cluster known in nature. High resolution X-ray diffraction data revealed the presence of an interstitial light atom X (X = C, N or O) in FeMoco3. Due to its complexity, the actual site for nitrogen binding and the mechanism for nitrogen reduction are not understood in detail so far. A combination of X-ray crystallography and electron paramagnetic resonance spectroscopy evidences the central atom in the FeMoco to be a carbon4,5. This provides new insights towards understanding biological nitrogen fixation by nitrogenase.

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