Unique Structural Properties of a Chemotaxis Signal Transducer Protein DcrA Containing a *C*-Type Heme

Shiro Yoshioka, Katsuaki Kobayashi, Takeshi Uchida, Teizo Kitagawa, and Shigetoshi Aono

Okazaki Institute for Integrative Bioscience, National Institutes of Natural Sciences

A chemotaxis signal transducer protein DcrA from a sulfate-reducing bacterium *Desulfovibrio vulgaris* Hildenborough contains a *c*-type heme in its periplasmic domain (DcrA-N), which is the first example of a heme-based sensor protein that contains a *c*-type heme as a prosthetic group. We have characterized properties of DcrA-N using optical absorption and resonance Raman spectroscopies, and found that the heme *c* in DcrA-N shows redox-dependent ligand exchange (Fig. 1). Upon reduction, a water molecule that may be the sixth ligand of the ferric heme *c* is replaced by an unknown amino acid (L in Fig. 1). Though the reduced heme in DcrA-N is six-coordinate with two endogenous axial ligands, one of which is His-158 derived from the CXXCH motif typical for *c*-type cytochromes, CO can easily bind to the reduced heme to form CO-bound DcrA-N. Reaction of the reduced DcrA-N with molecular oxygen results in autoxidation to form the ferric state without any stable oxygen-bound form, which is probably due to the extremely low redox potential of DcrA-N (-250 mV vs. NHE). Given the present results, DcrA would act as a redox sensor, where the ligand exchange between a water and an endogenous amino acid may be a trigger for signal transduction.

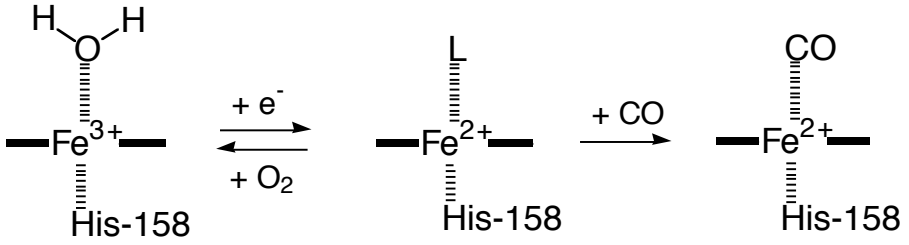

Figure 1. Proposed coordination structures of the heme *c* in DcrA-N. The unidentified sixth ligand of the ferrous form is indicated as L.