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Unifying Concepts in Catalysis

UniCat Colloquium

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Lecturer: **Prof. Russ Hille**, Alexander von Humboldt Research Prize, Department of Biochemistry, University of California, Riverside, USA

Title: **CO Dehydrogenase from *Oligotropha carboxidovorans***

Abstract: Carbon monoxide dehydrgenase (CODH) from *Oligotropha carboxydovorans* catalyzes the oxidation of carbon monoxide (CO) to carbon dioxide, providing the organism both a carbon source and energy for growth. We have investigated the reaction of reduced enzyme with various quinones, and find them to be catalytically competent. Benzoquinone has a k_{ox} of 125.1 s^{-1} and K_d of 48 µM; ubiquinone-1 has a k_{ox}/K_d value of 2.99 x 10^5 $M^{-1}s^{-1}$; 1,4-napthoquinone has a k_{ox} of 38 s^{-1} and K_d of 140 µM; and 1,2-napthoquinone-4-sulfonic acid a k_{ox}/ K_d of 1.30 x 10^5 $M^{-1}s^{-1}$. An extensive effort to identify a cytochrome that was reducible by CO/CODH was unsuccessful. The site of interaction between the quinone substrates and CODH is found to be the enzyme's FAD site. Our results strongly suggest that CODH donates reducing equivalents directly to the quinone pool without a cytochrome as an intermediary. The active site of the native enzyme is a unique binuclear molybdenum- and copper-containing center, and we have identified and characterized a Mo(V) species that exhibits strong coupling to the copper of the active center (I = 3/2) has been characterized by EPR. The signal is further split when [^{13}C]-CO is used to generate it, demonstrating that substrate (or product) is a component of the signal-giving species. Resonance Raman spectra of CODH reveal the presence of FAD, Fe/S clusters, and a [$CuSMoO_2$] coordination in the active site, consistent with earlier X-ray absorption and crystallographic results. We have also succeeded in replacing the copper in the binuclear center with silver. The characteristic hyperfine coupling of the I = ½ nucleus of Ag is evident in the EPR signal of the active site that is observed upon reduction with CO, indicating the incorporation of silver into the active site and retention of catalytic activity. The silver-substituted enzyme is reduced by CO with a limiting rate constant of 8.1 s^{-1}, as compared with the 51 s^{-1} seen with wild-type enzyme. This is apparently the first example of a silver-containing enzyme that retains catalytic activity.

Date: **Friday, August 26 , 2011**

Time: **12:15 pm**

Location: **Universität Potsdam;**
Institut für Biochemie und Biologie
Karl-Liebknecht-Straße 24-25, 14476 Potsdam-Golm
Haus 25 , Raum B0.01

Organiser: **Prof. Silke Leimkühler (TUB)**

Coffee and tea will be served thirty minutes prior to the lecture start.
Guests are cordially invited to attend!

Prof. Dr. Matthias Driess, Chair of the Cluster of Excellence UniCat