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Unifying Concepts in Catalysis

UniCat Colloquium

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Molybdoenzymes: new insights on their structure, reactivity and biogenesis gained from EPR spectroscopy and theoretical modelling

Mononuclear molybdo-enzymes are found in virtually all living organisms. In Prokaryotes, most of these enzymes harbour a large Mo-bis pyranopterin guanosine dinucleotide cofactor and catalyse a wide diversity of redox reactions involved in major biogeochemical cycles. In spite of the similarity of their Mo-bisPGD cofactor, these enzymes are able to use a broad diversity of substrates, but the molecular factors which trigger their reactivity remain largely unknown. During catalysis, the molybdenum ion cycles between the +IV and +VI redox states, the intermediate Mo(V) state being EPR-active (S=1/2). Several Mo(V) species have been identified, but in spite of numerous crystallographic and spectroscopic studies, their structure and catalytic relevance is still strongly debated.

To address these questions, we use various kind of bacterial nitrate reductases as model Mo-enzymes. By combining site-directed mutagenesis with EPR and DFT calculations, we brought new insights on the structure of the various spectroscopically detected Mo species and on their role in the catalytic process. Notably, by using specific isotope enrichment of the enzymes (^{98}Mo, ^{15}N) and high resolution EPR techniques (ESEEM, HYSCORE), the nuclear environment of the Mo ion could be studied in details, providing an accurate view of the Mo ion environment. The results emphasize the role of the second coordination sphere of the Mo ion in the stabilization of catalytic intermediates and provide some clues for the design of new bioinspired catalysts.

In addition, the analysis of magnetic coupling between Mo(V) ion and neighbor FeS cluster of the enzyme enable to monitor long range modifications of the Mo-cofactor during enzyme activation processes. The potential role of pyranopterin in these processes is clearly evidenced which emphasizes the need of a clear understanding of biogenesis steps leading to active enzymes.

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TU Berlin, Institute of Chemistry
Straße des 17. Juni 115, 10623 Berlin

Building C, Lecture Hall **C 264**

Prof. Dr. Leimkuehler (UP)
Organizer

Coffee and cake will be served 30 minutes before the lecture. Guests are cordially invited to attend!
Prof. Dr. Matthias Driess - Chair of the Cluster of Excellence UniCat - www.unicat.tu-berlin.de