

## **Colloquium**

### **Reactivity of molybdenum dependent enzymes, model chemistry, and non-covalent ligand-ligand cooperativity**

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The molybdenum (and tungsten) dependent enzymes, except for nitrogenase all bear one common structural motif: the molybdopterin ligand. The reactions they catalyse are oxygen atom transfer (OAT) and hydroxylations (OAT into a C-H bond) while water is the source or sink of the transferred oxygen atom. The back reactions are two proton coupled electron transfers to, e.g. NAD + or similar. Some enzymes are thought to be exceptional in this sense as they operate via distinct mechanisms. One example is the formate dehydrogenase (FDH) which catalyses the reversible oxidation of formate to CO<sub>2</sub> in a mechanism that was accepted to be a hydride transfer from formate to the active site. Recently we, in very close cooperation with the Leimkühler lab, have shown, that it is in fact also a common OAT that takes place. This finding has enormous implications for the respective model chemistry. Molybdopterin belongs, are non-innocent ligands which may in some cases directly participate in, and in others tune the redox activity of their complexes. This leads to some unusual behaviour in reactions and electrochemistry, which is typically not easy to decipher. We have developed a method with which it is possible to carry out and record, essentially in operando, UV-vis and IR-spectroelectrochemistry and to decompose the respective cumulative spectra into pure component spectra. With the support through DFT computations it is then possible to also characterise transient and non-isolable species. One particularly notable example, the complexes of which also exhibit ligand-ligand cooperativity, will be discussed. The seminar presentation comprises a potpourri of results and work in progress in the context of inorganic and organic syntheses, spectroscopy, mechanistic investigations, method development and the discovery of a peculiar phenomenon with implications for enzyme catalysis.

***Monday, Jul 22<sup>nd</sup> 2024***

***16:00 Hrs (Tea / Coffee 15:45 Hrs)***

***Auditorium, TIFR-H***