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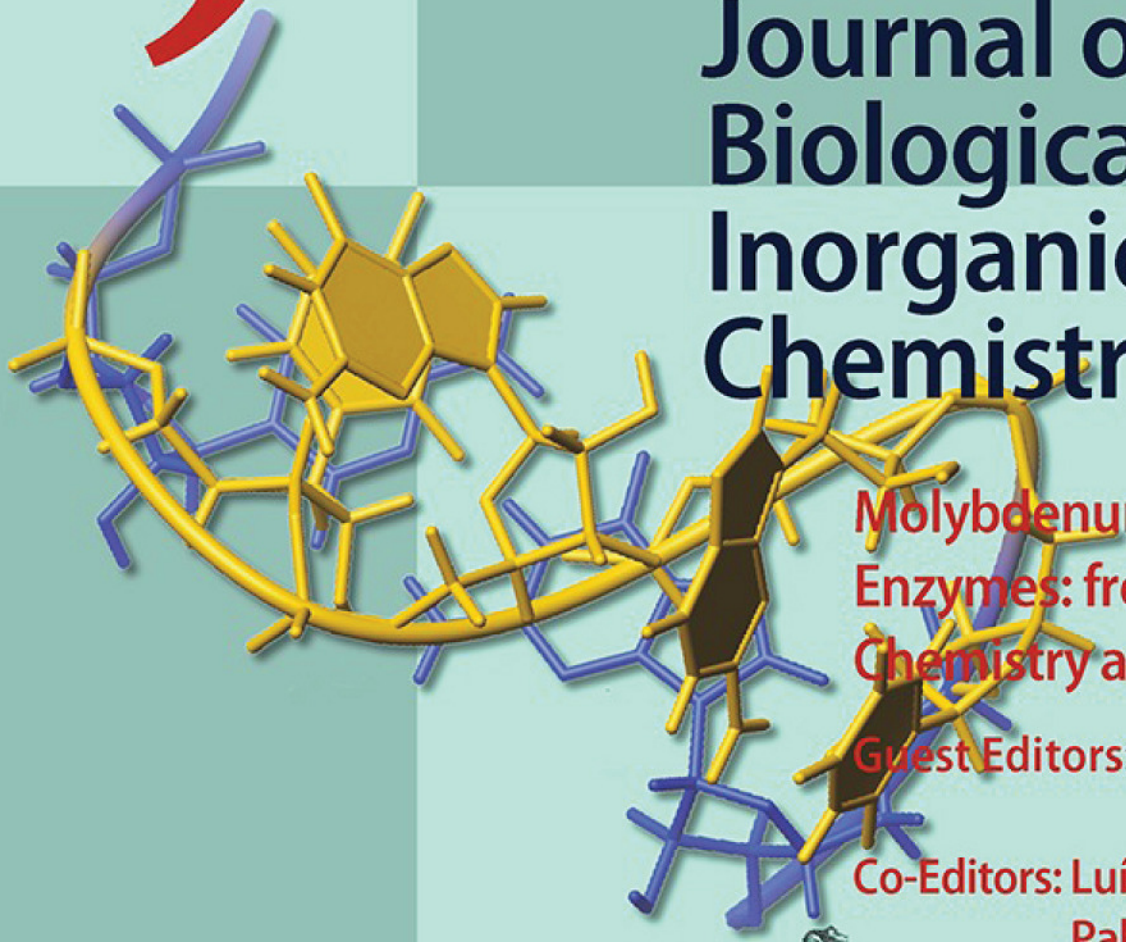

Molybdenum and Tungsten Enzymes: from Biology to Chemistry and Back

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INTRODUCTION

Molybdenum and tungsten enzymes: from biology to chemistry and back

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This special issue of JBIC was motivated by the *2013 Molybdenum & Tungsten Enzymes Conference*, held in Sintra, Portugal, following the 2011 conference in Edmonton, Canada, 2011, and several Gordon Research Conferences prior to that. The next meeting will be in 2015 in Hungary. This conference series is special in that it brings together an extremely broad cross section of scientists from areas including bioinorganic chemistry, enzymology, microbiology, biochemistry, crystallography and spectroscopy with a common interest in the structure, function and applications of Mo and W enzymes. Both Mo and W hold special places in bioinorganic chemistry as they are the only elements of their respective (2nd and 3rd) rows of the transition series found in nature.

The *Molybdenum & Tungsten Enzymes* conferences, in their early days, focused on the mononuclear molybdenum and tungsten-pterin-containing enzymes. Most recently, the conference themes have broadened to include contributors from nitrogenase field, where Mo is associated with Fe, in the FeMoco cluster and the papers in this issue reflect that greater breadth. This issue provides a comprehensive account of the field through the publication of several key minireviews, each summarizing the state-of-the-art knowledge and identifying outstanding questions and future directions. In addition, the issue includes a variety of original research articles spanning the entire Mo and W enzyme field.

The properties of the mononuclear enzymes have a comprehensive treatment including enzymes representative of the three different families. The xanthine oxidase family enzymes are thoroughly covered, with review and original works covering medical aspects, mechanistic features, substrate specificity, electronic structure as reactivity determinants and cofactor interactions within xanthine oxidoreductase, aldehyde oxidoreductase and CO dehydrogenase (Stein and Kirk, *Electronic structure contributions to reactivity in xanthine oxidase family enzymes*, doi: 10.1007/s00775-014-1212-8, Nishino and Okamoto, *Mechanistic insights into xanthine oxidoreductase from development studies of candidate drugs to treat hyperuricemia and gout*, doi: 10.1007/s00775-014-1210-x, Nuno et al., *Insights into the structural determinants of substrate specificity and activity in mouse aldehyde oxidases*, doi: 10.1007/s00775-014-1198-2, Correia et al., *Aromatic aldehydes at the active site of aldehyde oxidoreductase from* Desulfovibrio gigas*: reactivity and molecular details of the enzyme–substrate and enzyme–product interaction,* doi: 10.1007/s00775-014-1196-4 Gómez et al., *Isotropic exchange interaction between Mo and the proximal FeS center in the xanthine oxidase family member aldehyde oxidoreductase from* Desulfovibrio gigas *on native and polyalcohol inhibited samples: an EPR and QM/MM study*, doi: 10.1007/s00775-014-1204-8, Hille et al., *The aerobic CO*

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dehydrogenase from Oligotropha carboxidovorans, doi: 10.1007/s00775-014-1188-4).

The sulfite oxidase family is also reviewed in two distinct articles covering both the well-studied sulfite-oxidizing Mo enzymes (Kappler and Enemark, *Sulfite-oxidizing enzymes*, doi: 10.1007/s00775-014-1197-3) and the recently discovered mitochondrial amidoxime reducing component, which is only the fourth example of a Mo enzyme found in humans (Ott et al., *The mammalian molybdenum enzymes of mARC*, doi: 10.1007/s00775-014-1216-4). Original data on the regulation of plant nitrate reductase are also presented (Chi et al., *Dual binding of 14-3-3 protein regulates* Arabidopsis *nitrate reductase activity*, doi: 10.1007/s00775-014-1232-4).

A review is presented on formate dehydrogenases, and the induction/control of this activity by molybdate is also considered (Maia et al., *Molybdenum and tungsten-dependent formate dehydrogenases*, doi: 10.1007/s00775-014-1218-2, and Nair et al., *Changes in metabolic pathways of* Desulfovibrio alaskensis *G20 cells induced by molybdate excess*, doi: 10.1007/s00775-014-1224-4). In addition, the mechanistic aspects of these and other dimethylsulfoxide reductase family members are detailed and discussed (Cerqueira et al., *Theoretical studies on mechanisms of Mo enzymes*, doi: 10.1007/s00775-015-1237-7).

The biosynthesis of the molybdopterin cofactor, bound to the active site metal in every known mononuclear Mo and W enzyme, has been covered as well as its structural role in defining substrate selectivity across the entire enzyme family (Mendel and Leimkühler, *The biosynthesis of the molybdenum cofactors*, doi: 10.1007/s00775-014-1173-y, and Rothery and Weiner, *Shifting the metallocentric molybdoenzyme paradigm: the importance of pyranopterin coordination*, doi: 10.1007/s00775-014-1194-6).

From a synthetic chemistry perspective, relevant data on efforts to structurally or functionally mimic the mononuclear molybdenum active site are reviewed (Basu and Burgmayer, *Recent developments in the study of molybdoenzyme models*, doi: 10.1007/s00775-014-1228-0). Biotechnological applications of molybdoenzymes are also described, each utilizing electrochemistry, showing that the versatility of these enzymes can be employed for practical purposes (Kalimuthu et al., *A sensitive and stable amperometric nitrate biosensor employing* Arabidopsis thaliana *nitrate reductase*, doi: 10.1007/s00775-014-1171-0, and Chen et al., *Electrochemically mediated enantioselective reduction of chiral sulfoxides*, doi: 10.1007/s00775-014-1215-5). New catalytic reactions are also reviewed, clearly indicating that mononuclear molybdenum enzymes may be involved in biochemical pathways not yet identified (Maia and Moura, *Nitrite reduction by molybdoenzymes: a new class of nitric oxide-forming nitrite reductases*, doi: 10.1007/s00775-014-1234-2).

Last but not least, this special issue reports the latest developments in the nitrogenase field. The biosynthesis of unique cofactors present in nitrogenase is discussed (Hu and Ribbe, *Nitrogenase and homologs*, doi: 10.1007/s00775-014-1225-3) and insights into the oxidation state of molybdenum as well as the structural complexity of the metal core are addressed (Bjornsson et al., *The discovery of Mo(III) in FeMoco: reuniting enzyme and model chemistry*, doi: 10.1007/s00775-014-1230-6).

We trust that the papers in this issue will interest a wide range of readers, not only experts in the field but those yet to venture into this diverse and exciting area. This includes researchers and those who teach these topics, alerting them to the wide range of reactions carried out by these enzymes, their peculiar structural features and most exquisite mechanistic aspects that make Mo and W very "special" metals for bioinorganic chemists, widespread in biology and participating in most of the reactions associated with environmental cycling of the fundamental elements of life: carbon, oxygen, sulfur and nitrogen.