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Molybdate and Tungstate: Uptake, Homeostasis, Cofactors, and Enzymes

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Abstract Molybdenum (Mo) and tungsten (W) are trace elements that catalyze, upon binding to the appropriate cofactors, diverse and important redox reactions in the global carbon, nitrogen, and sulfur cycles. Mo is found in two forms of oxygen-labile metal cofactors, a pterin-based and a Fe – S-cluster-based scaffold, while W naturally only occurs in association with pterin cofactors and FeW-nitrogenases have been generated artificially. Both oxyanions enter the cell via an ABC-type high affinity uptake system and

are subsequently processed by a multistep biosynthetic machinery forming either Mo- and W-pterin cofactors (Moco or Wco) in a large variety of Mo- and W-containing enzymes or the FeMo cofactor (FeMo-co) in nitrogenase-catalyzed nitrogen fixation. The functional diversity of pterin-based Mo and W cofactors is reflected by a large number of enzymes such as nitrate reductase, dimethyl sulfoxide reductase, formate dehydrogenase, aldehyde oxidoreductase and CO dehydrogenase. In these enzymes Mo and W are bound via thiolates to one or two unique tricyclic pterin moieties, commonly referred to as molybdopterin but the term "metal binding pterin" (MPT) is more appropriate due to its association with both, Mo and W. It is commonly believed, but still not demonstrated, that Moco and Wco are synthesized by a similar and highly conserved pathway. Synthesis of the Moco can be divided into four major steps, according to the biosynthetic intermediates cyclic pyranopterin monophosphate, MPT, and adenylated MPT. Differences in the final metal insertion step(s) between Moco and Wco synthesis will be discussed. In contrast, FeMo-co biosynthesis is less understood in terms of reaction intermediate and mechanisms of different reactions catalyzed by the involved proteins. It starts with the formation of Fe – S cluster core structures that are assembled and arranged to a topology similar to mature FeMo-co. In the next steps, Mo and homocitrate are transferred before the mature cofactor is inserted into nitrogenase. Finally, a brief overview about Mo- and W-pterin enzymes as well as FeMo- and FeW-nitrogenases is given.

Abbreviations

AOR	Aldehyde oxidoreductase
cPMP	Cyclic pyranopterin monophosphate
DMSO	Dimethyl sulfoxide
DMSOR	Dimethyl sulfoxide reductase
FDH	Formate dehydrogenase
FeMo-co	FeMo cofactor
HVOR	(2*R*)-Hydroxy-carboxylate:viologen oxidoreductase
Mo	Molybdenum
Moco	Molybdenum cofactor
Mop	Molybdate-binding protein
MCD	MPT cytosine dinucleotide
MGD	MPT guanine dinucleotide
MPT	Molybdopterin/metal-binding pterin
MPT-AMP	Adenylated MPT
N_2	Dinitrogen
NR	Nitrate reductase
SAM	*S*-Adenosylmethionine
SO	Sulfite oxidase
TMAO	Trimethylamine-*N*-oxide
TMAOR	Trimethylamine-*N*-oxide reductase
V	Vanadium
W	Tungsten
Wco	Tungsten cofactor
XOR	Xanthine oxidoreductase