

## A Mini Review on Some Aspects of the Biochemistry of the Micronutrient Molybdenum (VI), (Mo<sup>6+</sup>)

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### ABSTRACT

This mini-review touches on some of the most important aspects of the biochemistry of the second row transition metal, micronutrient, molybdenum (VI) (Mo<sup>6+</sup>). Molybdenum can exist in metal complexes in a variety of oxidation states ranging from the metallic oxidation state of 0 to the most oxidized form of +6. To date, it is believed that molybdenum is taken up by living cells as the molybdate anion [MoO<sub>4</sub>]<sup>2-</sup>. There are not many reviews in the literature that cover the current topic. There are a total of about 50 Mo- Containing Enzymes/Proteins. Alongside the detailed literature review, we are also presenting the reactions of aqueous Mo<sup>6+</sup> with the organic ligand Malic Acid (MA). It appeared that, the reaction of Mo<sup>6+</sup> with MA in aqueous solutions at 25°C in 0.1 M ionic strength (NaNO<sub>3</sub>) formed a reaction mixture that released a large number of hydrogen ions, or protons (H<sup>+</sup>); 17 H<sup>+</sup> to be exact. This observation is not surprising for such complex behavior of such complex metal ion in aqueous solutions. This mini-review is a contribution to celebrate the 85th birthday of Professor Mostafa El-Sayed; at department of chemistry of the Georgia Institute of Technology, Atlanta, Georgia, USA.

Among all micronutrients, Molybdenum possesses very unique characters. It is the only second row

transition metal that has a tangible biological activity, it exists in a wide variety of oxidation states (ranging from 0 to +6) and it is a required cofactor for at least four dozen enzymes. There are a limited number of reviews or mini-reviews that have appeared with the biology/biochemistry of molybdenum in mind, particularly in aqueous solutions. However, the meticulous and thorough 75 page review by Hille et al. is a great reference for the biochemistry of molybdenum of which they cited 536 other biomolybdenum- related research articles.

Herein, we have conducted detailed literature research to prepare for this min-review and found the following three facts: (1) Not many research articles dealt with the reaction of Mo<sup>6+</sup> and aqueous solutions; (2) The chemistry of molybdenum is extremely complex; and (3) Billions of years ago, nature understood the uniqueness of molybdenum biochemistry that scientists only recently have recognized. It is noteworthy that there are a total of 44 journals within all ACS publication domains, which publishes thousands of research papers and reviews monthly.

There are at least four dozens known molybdenum-containing- enzymes and or proteins (molybdoenzymes); Nitrogenase being the most well-known among all of them within the biology and chemistry audience. Herein, we are going to

mention a dozen as example of these known molybdo-enzymes: (1) Nitrogenase, (2) Nitrate Reductase, (3) Xanthine Oxidase or Xanthine Dehydrogenase, (4) Pyrimidine Oxidase/Aldehyde Oxidase, (5) Trimethylamine Oxide Reductase, (6) Formate Dehydrogenase (7)

Carbon Monoxide Oxoreductase/Carbon Monoxide Dehydrogenase, (8) Pyridoxal Oxidase, (9) Sulfite Oxidase, (10) Biotin Sulfoxide Reductase, (11) Dimethyl Sulfoxide Redutase, and (12) Tetrathionite Reductase. Table 1 catalogues all of these enzymes. Some of these Molybdenumcontainingenzymes were isolated from bacteria (particularly cyanobacteria), fungi, yeast, plants, or mammals. For more details refer to references 1-3 and all 694 references mentioned therein. This current mini-review will focus on the discussion of the Molybdenum-containingenzymes “Nitrogenase”.

The detailed and the most trusted reviews of the molybdoenzymes by researchers stressed that the bi-dentate binding mode of the monohydroxyl poly-carboxylates, whether it is in the form of citrate or homocitrate, is the dominant mode of binding. Here in, we are stressing that the formed complex of  $\text{Mo}^{6+}$  with malic acid released a net of 17 proton equivalents which can only be accounted for by the binding of Malate in a bi-dentate or a tridentate fashion (the potentiometric titration is lacking supplying this information). The stoichiometry given in the equilibrium shown in equation (1) is only accounted for by the formation of a mixture of the two proposed molybdenummalate complexes depicted, i.e.,  $[\text{MoO}_2(\text{H1MA})(\text{OH})_2]^{3-} + [\text{MoO}_2(\text{H-1MA})_2]^{4-}$ . This mixture of the two complexes released a net of 17  $\text{H}^+$ . It is noteworthy that these two complexes are consistent with the ones identified by others.

**Keywords:** Aqueous solutions; Molybdenumcontaining- enzymes; Malic acid;  $\text{Mo}^6$