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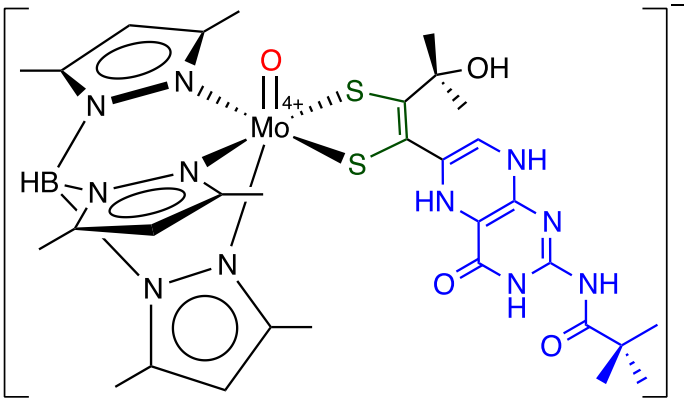
Summer Research Abstract: The Synthesis and Behavior of Molybdenum Pterin Dithiolene Complexes

Molybdenum-containing enzymes play important roles in nitrogen, sulfur, and oxygen metabolism in all forms of life. The catalytic center of Mo enzymes is a molybdenum-binding cofactor (Moco) composed of a pyranopterin dithiolene ligand. As proof of its significant role in medicine, a Moco precursor cPMP has been used to successfully treat a case of rare Moco deficiency type A. The combination of the functional groups is believed to contribute to an excellent electron-transfer relay that has rich redox properties. An investigation of the reactivity and conformation changes of the molybdenum pterin-dithiolene model complexes in different oxidation states offers a better understanding of the mechanism of Moco in biological systems.

The goal of this research project is to determine the structures of BMOPP [6-(3-butynyl-2-methnyl-2-ol)-2pivaloyl pterin] dithiolene complex $TEA^{+}[Tp^{*}Mo^{4+}(O)S_2BMOPP]^{-}$ and its oxidized form $Tp^{*}Mo^{5+}(O)S_2BMOPP$, as well as their behaviors in different solvents as shown in previous studies. The Burgmayer group has recently obtained the structure of model complex $Tp^{*}Mo^{5+}(O)S_2BMOPP$ via X-ray crystallography. However, the solid structure does not completely explain the reactivity of the complexes in solution. Therefore, other techniques are required to study the spectroscopic characteristics and structural information of its analogs. Further experiments are needed to optimize the isolation of these species, investigate the cyclization behavior using ^{1}HNMR and UV-visible spectroscopy, and identify other related complexes in this redox pathway.

The synthesis involves anaerobic conditions using dry-box and Schlenk line techniques to prevent deterioration of the compounds. ESI-MS, thin layer chromatography, and UV-vis are used throughout the experiment to monitor the reactions. FT-IR is also used to determine the characteristics of the complexes. ^{31}P NMR will be used to investigate the reaction mechanism.



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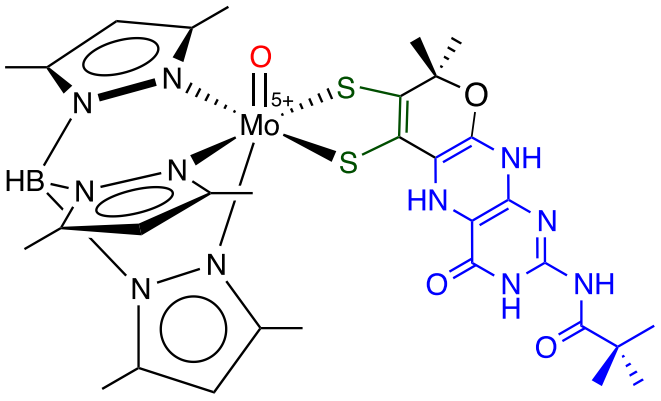

(2)

Figure 1. Two major compounds in the family of molybdenum BMOPP dithiolene complexes. **(1)** Proposed ring-open structure of $[Tp^*Mo^{4+}(O)S_2BMOPP]^-$. (Black=Tp*, Green=dithiolene, Blue=BMOPP) It needs further investigation to confirm this ring-open structure in different solvents. **(2)** The structure obtained via X-ray crystallography shows that the Mo(V) complex is in pyrano-cylized form.

References

McMaster, J.; Garner, C. D.; Stiefel, E. I. Molybdenum Enzymes. In *Biological Inorganic Chemistry: Structure and Reactivity*. Bertini, I.; Gray, H. B.; Stiefel, E. I.; Valentine, J. S., Ed.; University Science Books: Sausalito; 2007; pp518-530