

Synthesis and Characterization Different Models of the Molybdenum Cofactor

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The molybdenum cofactor (Moco) forms the active site of redox reactions in all eukaryotic molybdenum enzymes such as nitrate reductases and sulfite oxidase. Over 50 different pterin-containing molybdenum enzymes are known and classified on the basis of the coordination chemistry of molybdenum in their active site. The pterin group in Moco positions the catalytic molybdenum atom within the active center to control redox behavior and electron transfer to or from the Mo atom. The core structure of a pterin-based molybdenum cofactor consists of a 6 carbon substituted pyrano ring, a terminal phosphate and a unique dithiolate group coordinating to a molybdenum atom.

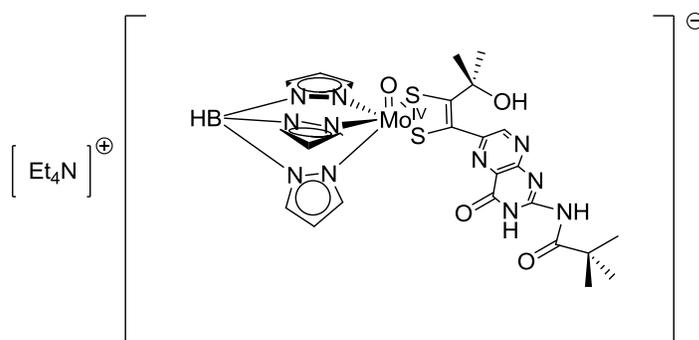


Figure 2. $[\text{Et}_4\text{N}]^+[\text{TpMo}^{4+}(\text{O})\text{S}_2\text{BMOPP}]^-$

One of the many focuses in the Burgmayer lab is to synthesize and study different analogs of the molybdenum cofactor. Pterin-dithiolene molybdenum complexes LMoS_2X [L = hydrotris(3,5-dimethylpyrazol-1-yl)borate(Tp^*), hydrotris(pyrazol-1-yl)borate(Tp) ; X = BMOPP] show redox behavior. We find that the nature of tris(pyrazolyl)borate ligands has significant impact on the modeling of molybdenum enzymes. Variations of the steric nature of the pyrazole ring substituent have shown interesting effects on the reactivity and synthesis of the model. The Tp ligand contains unsubstituted pyrazoles whereas the Tp^* ligand is methylated at positions 3 and 5 on the pyrazole rings.

The goal of this research project is to study the characteristics and effects of differently substituted pyrazole ligands in the synthesis of the BMOPP pterin molybdenum dithiolene analogs. The Tp ligand BMOPP dithiolene molybdenum model (Figure 2) is one of the newly synthesized models that requires further synthetic and characterization studies. The synthetic pathway derives from the more established synthesis of the Tp^* ligand BMOPP dithiolene molybdenum complexes in the Burgmayer lab. The synthesis of the Tp^* BMOPP dithiolene compound ($[\text{Et}_4\text{N}][\text{Tp}^*\text{Mo}^{4+}(\text{O})\text{S}_2\text{BMOPP}]$) begins with the formation of the sulfido intermediate ($[\text{Et}_4\text{N}][\text{Tp}^*\text{Mo}^{4+}(\text{S})\text{S}_2\text{BMOPP}]$). The sulfido intermediate is then oxidized to form Mo^{5+} BMOPP dithiolene complex ($[\text{Et}_4\text{N}][\text{Tp}^*\text{Mo}^{5+}(\text{O})\text{S}_2\text{BMOPP}]$). The Mo^{5+} BMOPP dithiolene complex is postulated to exist in two structural forms observed in different absorptions in the UV-Vis spectrum. Another goal of this research project is to pursue the synthesis and study of differently substituted pterin ligand molybdenum dithiolene complexes.