

# Synthesis and Electronic Structure Studies of Tp\*MoO(bds) “benzene diselenolate” Relevant to the Sulfite Oxidase Active Site

Antonio L. Williams<sup>1</sup> and Martin L. Kirk<sup>2</sup>

*University of New Mexico, Department of Chemistry*

Crystallographic and spectroscopic studies have led to the determination of structures for oxidized and reduced sulfite oxidase (SO). The oxidized active site of SO possesses coordination to a Mo by a pyranopterin ene-1,2-dithiolate linkage, two oxo groups and a cysteine sulfur. Site directed mutagenesis has shown that the cysteine residue is essential for catalysis. It has been hypothesized that the cysteine residue modulates the reduction potential of the Mo or acts as an electron transfer conduit; similar to its role in blue copper proteins. The exact role of the pyranopterin dithiolene has yet to be determined but may also be involved in electron transfer. Various model complexes, containing both Mo-thiolate and Mo-dithiolene donors have been synthesized and studied, however, deconvoluting the different contributions of thiolate and dithiolene donors to the underlying electronic structure of the Mo site in SO has proven to be a difficult task.<sup>1</sup> One way in which these differences might be illuminated is by selectively substituting Se for S in model complexes which possess multiple sulfur donor ligand environments.<sup>2</sup> We have synthesized and performed detailed spectroscopic studies on Tp\*MoO(bds), where bds is the selenium analogue of the dithiolene ligand benzene 1,2-dithiolate. A combined spectroscopic approach, utilizing magnetic circular dichroism, electronic absorption, resonance Raman and EPR spectroscopies, has provided additional insight into the role of the pyranopterin dithiolene in SO and related enzymes.

1. Kirk, ML; Peariso, K “Ground and excited state spectral comparisons of models for sulfite oxidase” *Polyhedron* **2004**, .23, 499-506
2. Peariso, K; Chohan, BS; Carrano, CJ; Kirk, ML “Synthesis and EPR characterization of new models for the one-electron reduced molybdenum site of sulfite oxidase” *Inorg. Chem.* **2003**,42,6194-6203