

Effects of Donor Substitution on Vibronic Instability in Oxomolybdenum Dichalcogenolenes

Jing Yang, Dominic Kofi Kersi, and Martin L. Kirk

Department of Chemistry and Chemical Biology, The University of New Mexico, MSC03 2060, 1 University of New Mexico, Albuquerque, NM 87131-0001

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ABSTRACT: Dithiolene distortions have long been suggested to play a critical role in electronically buffering the Mo active site of pyranopterin molybdenum enzymes against the large changes in charge that accompany Mo(IV)/Mo(V) and Mo(V)/Mo(VI) redox processes. In this work, we quantify the nature of dithiolene/diselenolene fold angle conformers via a combination of spectroscopy, bonding calculations, and the application of a vibronic coupling model. The structure of $\text{Tp}^*\text{MoO}(\text{bds})$ (**1**) (bds = benzene-1,2-diselenolate, Tp^* = hydrotris(3,5-dimethyl-1-pyrazolyl) borate) is very similar to its dithiolene analogue $\text{Tp}^*\text{MoO}(\text{bdt})$ (**2**) (bdt = benzene-1,2-dithiolate), but possesses longer Mo-E (E = Se, S) bonds (Mo-Se: 2.61 Å; Mo-S: 2.13 Å) and a greater metal-ligand envelope fold angle (**1**: 26.2°; **2**: 21.3°). Importantly, multifrequency EPR spectroscopy has revealed, for the first time, the presence of fold-angle conformers for the diselenolene ligand in **1**. The “fold up” and “fold down” conformers are populated in an approximate 80:20 ratio at room temperature. Resonance Raman spectroscopy and electronic structure calculations also provide strong evidence for the presence of these conformers in solution. We have employed a simple two-state vibronic coupling model to understand the electronic origin of the extremely soft ground state double potential well. These new results will be discussed in terms of the potential for fold angle conformers to modulate electron and atom transfer reactivity in pyranopterin molybdenum enzymes.