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Non-Innocent Dithiolene Ligands: A New Oxomolybdenum Complex Possessing a Donor-Acceptor Dithiolene Ligand

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The mono-oxomolybdenum dithiolene complex Tp*MoO(S_2BMOQO), **1**, has been characterized by X-ray crystallography, cyclic voltammetry, electronic absorption spectroscopy, and resonance Raman spectroscopy. The structure of **1** represents the first crystal structure determined for a Tp*Mo^{4+}O(dithiolene) complex. Compound **1** displays an unusual geometric and electronic asymmetry within the MoS_2C_2 chelate ring and a non-planar orientation within the dithiolene chelate where an ~14° fold angle is observed. Additionally, **1** is observed to possess an intense, low-energy absorption band that is unprecedented for a Tp*Mo^{4+}O(dithiolene) complex, and this band has been assigned as an intraligand dithiolene→quinoxaline transition involving the π system of the chromophore. This assignment is supported by the strong resonance enhancement of Raman vibrational modes associated with the quinoxaline component of the ligand, and bonding calculations that indicate a low-lying LUMO wavefunction possessing considerable quinoxaline character. The Mo(IV) d^2 electron configuration is also supported by the fact that the complex is diamagnetic and one-electron oxidization of **3** yields an EPR active Mo(V) species.

Systems that display rich metal-ligand redox interplay[1-4] or possess intraligand donor-acceptor interactions[5-7] have captured the attention of the chemical community due to their importance in enzymatic catalysis[2, 8, 9] and molecular electronics.[10-12] Dithiolene ligands facilitate complex redox chemistry[1, 8] and have been used as key components of donor-acceptor molecules.[13, 14] The pyranopterin molybdenum enzymes have been the subject of intense study since they possess a redox active Mo center bound by at least one pyranopterin dithiolene ligand (Fig. 1) and catalyze a variety of two-electron redox reactions coupled to the *formal* transfer of an oxo atom between the active site and substrate.[15, 16] The Mo active site cycles between the Mo(IV) and Mo(VI) redox states with the paramagnetic Mo(V) state representing an obligatory catalytic intermediate in the electron transfer regeneration of the active site. Although it is widely accepted that Mo-based redox processes dominate in the catalytic cycle of the enzymes,[15] it should be noted that both the dithiolene chelate and the pyranopterin contribute further redox possibilities through their highly non-innocent redox nature.[8] For example, reduced dithiolenes can be oxidized by one electron to a radical form,[17] or by two electrons to yield dithione or dithiete resonance forms of the oxidized ligand. Additionally, the pyranopterin itself can potentially store up to four redox equivalents via a combination of pyran ring opening and direct two-electron oxidation of the pterin ring.[8, 18] Thus the Mo-pyranopterin dithiolene ensemble represents one of the most redox non-innocent structures in biology and this drives our interest in studying Mo-dithiolene structure-property relationships in both enzymatic and model systems. In cases where such model systems display unusual spectroscopic features intimately associated with novel electronic structures, they may provide additional insight into the complex electron and atom transfer reactivity in this interesting class of metalloenzymes. Here we provide structural and spectroscopic evidence supporting a highly unusual electronic structure in the Tp*Mo^{4+}O(dithiolene) complex, Tp*MoO(S_2BMOQO) (**1**).

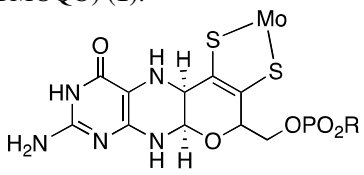

Figure 1. The pyranopterin dithiolene ligand coordinated to Mo as the reduced dianionic dithiolene.

Complex **1** (Fig. 2) was obtained as part of a larger study[19] directed at synthesizing molybdenum enzyme small molecule analogues that possess pterin- and quinoxaline-substituted dithiolene ligands. The dithiolene ligand in **1** is

generated in a coupling reaction of a quinoxalyl alkyne with a molybdenum tetrasulfide reagent, [TEA][Tp*Mo(S)(S_4)] (Fig. 2(a)). The coupling reaction at 70 deg C forms a dithiolene ligand and also results in an intramolecular ring closure that initially yields the molybdenum sulfido compound **2**. Treatment with triphenyl phosphine followed by column chromatography causes hydrolysis of the sulfido group of **2** to the oxo of **1** (Fig. 2(b)). Interestingly, compound **1** exhibits sharp resonances in the ^{1}H NMR spectrum consistent with a diamagnetic d^2 Mo(4+) center, and this is in marked contrast to the structurally related pentavalent oxomolybdenum dithiolene complex, Tp*Mo^{5+}O(qdt).[20] The cyclic voltammagram of **1** displays a reversible couple at + 0.250 V (vs. Ag/AgCl in ACN; Fc+/Fc +0.400 V) assigned to Mo(5+)/Mo(4+) reduction. This Mo(5+)/Mo(4+) reduction potential is strongly shifted (+300 mV) more positive than the corresponding potential in the related quinoxaline-1,2-dithiolene complex Tp*MoO(qdt), underscoring the highly electron withdrawing nature of the S_2BMOQO dithiolene and indicating a markedly more stabilized Mo(4+) state. As isolated, **1** sits at a resting potential of + 0.07 V, also consistent with a Mo(4+) oxidation state assignment. Ferrocenium oxidation of **1** yields the EPR active species **3** (Fig. 2(c)) that possesses typical Mo hyperfine structure, and this confirms that **3** is a d^1 Mo(V) species and not a ligand radical. One-electron oxidation of **1** forming **3** also results in a striking color change from blue to cherry red due to a large blue shift (2540 cm^{-1}) of the low-energy charge transfer band to 528 nm (18,940 cm^{-1}, ε = 6583 $M^{-1}L^{-1}$) without significant change in intensity. Blue **1** is not EPR active and there is no evidence for any resonances being paramagnetically shifted in the NMR spectra. Thus, the oxidation state of **1** is most consistent with a reduced d^2 Mo(IV) species.

Figure 2. Synthetic path to compounds **1** , **2** , and **3**: (a) acetonitrile, 70 °; (b) PPh_3, silica gel; (c) $[Fe(C_5H_5)_2][PF_6]$.

The X-ray crystal structure of **1** provides key evidence for its unusual electronic structure that derives from the nature of the quinoxalyl-dithiolene ligand. **1** crystallizes from methylene chloride and toluene in the triclinic $P\bar{1}$ space group with two molecules in the asymmetric unit. An ORTEP drawing of one molecule of **1** is displayed in Fig. 3. A striking aspect of the structure that points to a remarkable electronic asymmetry within the MoS_2C_2 dithiolene chelate ring is fact that the Mo-S2 distance is 0.04 Å longer than Mo-S1 while S2-C2 is 0.05Å shorter than S1-C1. Additionally, an average dithiolene fold angle of 13.3 deg (Fig. 3 bottom) is observed within the Mo-S1-S2-C1-C2 atoms of the dithiolene chelate.

Compound **1** is deep blue due to an intense absorption at 16,400 cm^{-1} (Band 2; 610 nm) with a molar extinction coefficient of 5,190 $M^{-1}L^{-1}$ (Fig. 4). Interestingly, intense low-energy charge transfer transitions are not observed in Tp*Mo^{5+}O(qdt)[20, 21] and are not anticipated for

Figure 3. ORTEP drawing of one molecule of **1** with 30% probability thermal ellipsoids. Selected bond distances (Å): Mo1-S1 2.4164(14), Mo1-S2 2.4565(14), Mo1-O1 1.688(3), Mo1-N3 2.214(4), Mo1-N5 2.222(4), Mo1-N7 2.395(4), S1-C1 1.748(5)-S2-C2 1.695(5), N1-C11 1.357(7). Calculated planes through Mo-S1-S2 and S1-S2-C1-C2 atoms measure a dihedral fold angle of 14.5 and 12.0 deg in the two independent molecules of **1**.

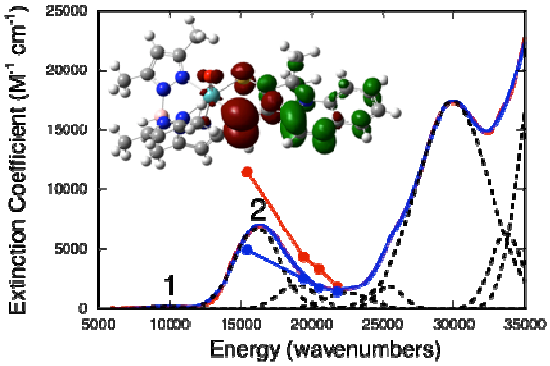

Figure 4. Gaussian resolved solution electron absorption spectrum of **1** in acetonitrile. Solid state resonance Raman excitation profiles for **1**. These vibrational modes have been assigned as intraligand modes that possess dominant quinoxoline character (1345 cm^{-1}, red circles) and C=C + quinoxaline character (1551 cm^{-1}, blue circles). (Inset) Electron density difference map that details the nature of the intraligand transition in **1** (red: electron density loss in transition, green: electron density gain in transition).

Tp*Mo^{4+}O(dithiolene) complexes since they possess low-spin $(xy)^2$ electronic configurations that preclude one-electron promotions to the low-lying Mo(xy) redox orbital. To our knowledge, such intense low-energy absorption features have never been observed in any Tp*MoO(dithiolene) complex, and therefore the presence of the 16,400 cm^{-1} band is additional evidence strongly supporting a novel electronic structure for **1**. Resonance Raman spectroscopy has identified a number of high frequency vibrational modes in **1** associated with the quinoxaline fragment of the dithiolene ligand. These modes are strongly resonantly enhanced with excitation into the 16,400 cm^{-1} charge transfer band and excitation profiles for the 1345 and 1551 cm^{-1} vibrations are presented in Fig. 4. These data are consistent with the quinoxaline fragment acting as an acceptor orbital in the one-electron promotion associated with this transition, and this is supported by both bonding and transition state calculations. As such, this CT band has been assigned as an *intraligand*

dithiolene(S)→quinoxaline CT transition (HOMO-1→LUMO) possessing a small degree of MLCT character, and its presence in **1** reflects the highly electron withdrawing nature of the quinoxaline fragment. The weak lower energy transition (Band 1; 9,763 cm^{-1}, $\varepsilon = 250\ M^{-1}L^{-1}$) is assigned as a Mo(xy)→quinoxaline (HOMO→LUMO) MLCT transition, in line with the acceptor nature of the quinoxaline fragment.

Two key resonance structures can be drawn for the dithiolene ligand in **1** (Fig. 5). Structure A represents a

Figure 5. Two contributing resonance structures for the S_2BMOQO dithiolene ligand in **1**. **A**: dithiol, **B**; thiol/thione.

reduced dianionic dithiolene as found in $Tp^*MoO^{5+}(qdt)$[20, 21] and other oxomolybdenum dithiolenes,[1] while structure B represents an induced internal redox reaction between the reduced dithiolene and the quinoxaline components of the ligand. The admixture of thiol/thione resonance structure B into structure A is reflected in the nature of the dithiolene(S)→quinoxaline intraligand CT transition and is responsible for the Mo-S bond asymmetry found in the X-ray structure of **1**. Together, these resonance forms underscore the remarkable non-innocence of this dithiolene ligand.

Our results illustrate how the nature of an N-heterocyclic substituent on a dithiolene ligand can markedly shift the Mo(IV/V) redox potential, stabilize the Mo(IV) oxidation state, and dramatically modify the electronic structure of the oxomolybdenum mono-dithiolene unit. This is clearly evident in the structure of **1**, where a relatively large S---S fold angle averaging 13.2° is observed. Dithiolene ligands in metallodithiolenes have been shown to electronically buffer the metal center against the large changes in electronic charge that accompany redox processes in model complexes and it has been suggested that this is one of the fundamental roles of the pyranopterin dithiolene in facilitating pyranopterin molybdenum enzyme catalysis.[22] As such, small (< 10 °) S---S fold angles are anticipated in electron-rich Mo(IV) systems in order to reduce dithiolene S^{op}→Mo(xy) (op = out-of-plane dithiolene sulfur orbital) charge donation. The S---S fold angles in **1** (14.5 and 12.0 °) are somewhat reduced from that observed in Mo(V) Tp*MoO(qdt) (29.5°) and Tp*MoO(bdt) (21.3°), but greater that that observed in Tp*MoO(bdt-Cl_2) (6.9°).[20] An explanation for the relatively large fold angle in **1** may result from the fact that the electron rich Mo(IV) center is coupled to a highly electron withdrawing dithiolene. Therefore, the S---S fold in **1** may function to facilitate a *backward* Mo(xy)→dithiolene charge donation that is mediated by the electron withdrawing nature of the quinoxaline. This is consistent with the MLCT character present in band 1 and the redox properties of **1** where the Mo(5+)/Mo(4+) potential is ~ +300 mV more positive than the Mo(5+)/Mo(4+) potential in Tp*MoO(qdt). In summary, a rare thiolate-thione ligand in compound **1** exhibits highly versatile donor-acceptor character that affects the Mo(IV/V) redox couple and points to a potentially non-innocent role of the pterin fragment (Fig. 1) in modulating molybdenum redox potentials during the course of pyranopterin molybdenum enzyme catalysis.

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SUPPORTING INFORMATION PARAGRAPH Synthetic, spectroscopic, computational, full crystallographic details. Resonance Raman spectrum of **1** at 514nm.

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A new monoanionic dithiolene ligand is found in Tp*MoO(S_2BMOQO). A combination of x-ray crystallography, electronic absorption and resonance Raman spectroscopies, and bonding calculations reveal that the monoanionic dithiolene ligand possesses considerable thiolate-thione character resulting from admixture of an intraligand charge transfer excited state into the ground state wavefunction. The unusual dithiolene exhibits a highly versatile donor-acceptor character that dramatically lowers the Mo(IV/V) redox couple and points to a potentially non-innocent role of the pterin fragment in pyranopterin Mo enzymes.