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Noninnocent Dithiolene Ligands: A New Oxomolybdenum Complex Possessing a Donor−Acceptor Dithiolene Ligand

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Systems that display rich metal−ligand redox interplay[1−4] and 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 possess a redox active Mo center bound by at least one pyranopterin dithiolene ligand (Figure 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] Although it is widely accepted that Mo-based redox processes dominate in the catalytic cycle of the enzymes,[15] both the dithiolene chelate and the pyranopterin contribute further redox possibilities through their highly noninnocent redox nature.[8] Reduced dithiolenes can be oxidized by one electron to a radical form[17] or by two electrons to yield dithione or dithiete resonance forms.[1] Additionally, the pyranopterin can potentially store up to four redox equivalents via a combination of pyran ring-opening and two-electron oxidation of the pterin ring.[8,18] Thus, the Mo−pyranopterin−dithiolene ensemble is one of the most redox noninnocent structures in biology. Here we provide structural and spectroscopic evidence supporting a highly unusual electronic structure in Tp*MoO(S_2BMOQO) (**1**) (Figure 2) that provides added insight into the complex electron and atom transfer reactivity in this interesting class of metalloenzymes.

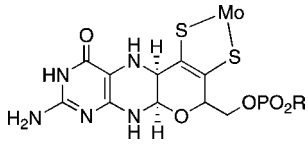

Figure 1. Pyranopterin dithiolene ligand bound to the active site molybdenum as the reduced dianionic dithiolene.

The synthesis of **1** is part of a larger study[19] directed toward synthesizing small molecule analogues that possess pterin- and quinoxaline-substituted dithiolenes. The dithiolene ligand in **1** is generated in a coupling reaction of a quinoxalyl alkyne with a molybdenum tetrasulfide (Figure 2a). This reaction initially yields the molybdenum sulfido compound **2** that hydrolyzes to **1** (Figure 2b). **1** exhibits sharp ^{1}H NMR resonances consistent with a diamagnetic d^2 Mo(4+) center, in marked contrast to the structurally related pentavalent oxomolybdenum dithiolene complex, Tp*Mo^{5+}O(qdt) (qdt = quinoxaline-2,3-dithiolate).[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 reduction potential is shifted 300 mV more positive than that observed for Tp*MoO(qdt), underscoring the highly electron-withdrawing nature of this dithiolene and indicating a markedly more stabilized Mo(4+) state. Ferrocenium oxidation of **1** yields the EPR active species **3** (Figure 2c) that possesses a typical Mo hyperfine structure confirming that **3** is a d^1 Mo(+5) species and not a ligand radical. Compound **1** is not EPR active and displays no paramagnetically shifted NMR resonances. Thus, the oxidation state of **1** is most consistent with a low-spin d^2 Mo(+4) species.

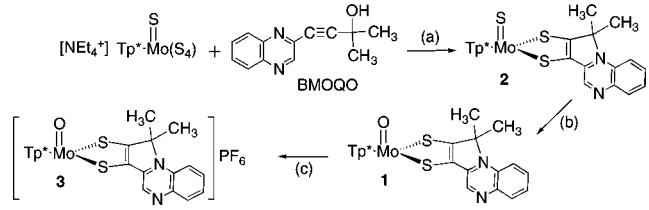

Figure 2. Synthetic path to compounds **1**, **2**, and **3**: (a) acetonitrile, 70°; (b) PPh_3, silica gel; (c) $[Fe(C_5H_5)_2][PF_6]$.

The X-ray structure of **1** (Figure 3) provides key evidence for an unusual electronic structure that derives from the nature of the quinoxalyl-dithiolene ligand. A striking aspect of the structure that

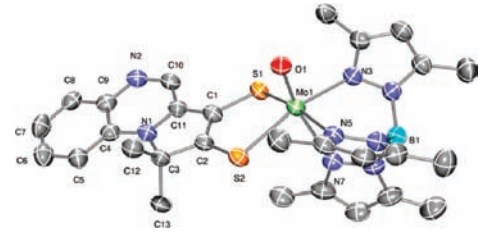

Figure 3. ORTEP drawing of one molecule of **1** with 30% probability thermal ellipsoids. Selected bond distances (Å): Mo1−S1 2.4164(14), Mo1−S2 2.4565(14), Mo1−O1 1.688(3), S1−C1 1.748(5), S2−C2 1.695(5), N1−C11 1.357(7).

points to a remarkable electronic asymmetry within the MoS_2C_2 dithiolene chelate ring is that the Mo−S2 distance is 0.04 Å longer than Mo−S1 while S2−C2 is 0.05 Å shorter than S1−C1, indicating some degree of thiol/thione character in **1**. Additionally, an average dithiolene fold angle of 13.3° is observed within the Mo−S1−S2−C1−C2 atoms of the dithiolene chelate.

Compound **1** is deep blue with an intense absorption at 16 400 cm^{-1} (ε = 5190 M^{-1} cm^{-1}) (Figure 4). Interestingly, intense low-energy charge transfer (CT) transitions are not observed in Tp*Mo^{5+}O(qdt)[20,21] and are not anticipated for Tp*Mo^{4+}O(dithiolene) complexes due to the low-spin $(xy)^2$ electronic configuration that precludes one-electron promotions to the Mo(xy) redox

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orbital. To our knowledge, intense low-energy CT features have never been observed in a Tp*MoO(dithiolene) complex, and therefore the presence of the 16 400 cm^{-1} band supports a novel electronic structure for **1**. Resonance Raman (rR) spectroscopy has identified a number of high frequency quinoxaline vibrational modes in **1** that are strongly resonantly enhanced with excitation into the 16 400 cm^{-1} CT band, and excitation profiles for the 1345 and 1551

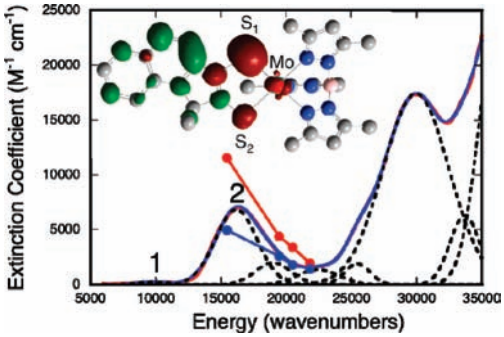

Figure 4. Gaussian resolved electron absorption spectrum of **1** in acetonitrile, and solid state rR excitation profiles. These vibrational modes have been assigned as intraligand vibrations that possess dominant quinoxaline character (1345 cm^{-1}, red circles) and C═C + quinoxaline character (1551 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; H-atoms omitted for clarity).

cm^{-1} vibrations are presented in Figure 4. The intensity of Band 2 and the dominant resonance enhancement of both quinoxaline and C═C modes are consistent with an electron-withdrawing quinoxaline fragment that acts as an acceptor in the 16 400 cm^{-1} transition. The rR and absorption data are consistent with the results of bonding and excited state calculations, allowing us to assign Band 2 as an *intraligand* dithiolene(S)→quinoxaline CT transition (HOMO-1→LUMO) possessing a small degree of MLCT character. The assignment of Band 2 allows the lower energy transition (Band 1) (9763 cm^{-1}, ϵ = 250 M^{-1} cm^{-1}) to be 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** (Figure 5). Structure A is a typical reduced dithiolene while B represents an induced internal redox reaction between the dithiolene and the quinoxaline components of the ligand. The admixture of resonance structure B into A is reflected in the nature of the

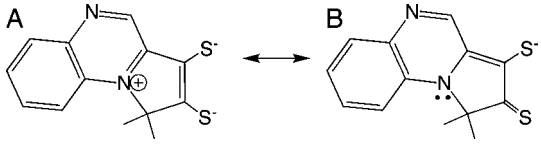

Figure 5. Two contributing resonance structures for the S_2BMOQO^- dithiolene ligand in **1**. **A**: dithiol, **B**; thiol/thione.

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 noninnocence of this dithiolene ligand. Our results illustrate how an N-heterocycle containing dithiolene can stabilize the Mo(+4) oxidation state and dramatically modify the electronic structure of the oxomolybdenum−dithiolene unit. Dithiolene ligands have been shown to electronically buffer the metal center against large changes in charge that accompany redox processes, and it has been suggested that this is one of the fundamental roles of the pyranopterin dithiolene in catalysis.[22] The S---S fold angles in **1** (14.5 and 12.0°) are intermediate between those observed in Tp*MoO(qdt) (29.5°) and Tp*MoO(bdt) (21.3°), and in Tp*MoO(bdt-Cl_2) (6.9°).[20] The relatively large fold angle in **1** may result from the fact that the electron-rich Mo(+4) center is coupled to a highly electron-withdrawing dithiolene which can facilitate a *backward* Mo(*xy*)→dithiolene charge donation. This is consistent with the nature of the low energy CT transitions and the redox properties of **1**. In summary, a rare thiolate−thione ligand in compound **1** exhibits highly versatile donor−acceptor character that affects the Mo(+4/+5) redox couple and points to a potentially noninnocent role of the pterin−dithiolene in modulating pyranopterin molybdenum redox potentials during the course of catalysis.

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Supporting Information Available: Synthetic, spectroscopic, computational, full crystallographic details. EPR specrtrum of **3** and rR spectrum of **1** at 514 nm. This material is available free of charge via the Internet at http://pubs.acs.org.

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