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A Valence Bond Description of Dizwitterionic Dithiolene Character in an Oxomolybdenum-bis(dithione)

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Abstract

Metallo-dithiolene non-innocence is explored in an oxomolybdenum-bis(dithione) complex, $[\text{Mo}^{4+}\text{O}(\textit{i}\text{-Pr}_2\text{Pipdt})_2\text{Cl}][\text{PF}_6]$ (where *i*-Pr₂Pipdt is N,N'-piperazine-2,3-dithione), that possesses a piperazine ring as an integral part of the dithiolene ligand. The title complex displays unusual spectroscopic features for a formally reduced Mo(IV) dithiolene complex, namely a low energy metal-to-ligand charge transfer band with appreciable intensity and C-C and C-S stretching frequencies that are markedly different from those of oxomolybdenum complexes coordinated to dianionic dithiolene ligands. The electronic structure of the ligand has been described in valence bond terms as a resonance hybrid of dithione and dizwitterionic dithiolene contributing structures.

Keywords

dithiolene; zwitterionic; electronic structure; molybdenum; Raman

Introduction

Metallo-dithiolenes display an extraordinarily rich metal-ligand redox interplay^[1] due to the inherent non-innocent redox behavior of the dithiolene.^[2] The fully reduced dianionic ene-1,2-dithiolate can be oxidized by one electron to a radical form,^[3] or by two electrons to yield the dithione/dithiete (Scheme 1). Additional possibilities for non-innocent behavior exist when the dithiolene is part of a larger ligand framework. Recently, unusual thiol/thione type dithiolene ligands have been incorporated into oxomolybdenum(IV)-mono(dithiolene) compounds and they were shown to possess low-energy *intra*ligand charge transfer transitions that resulted from the donor-acceptor character present in the extended dithiolene ligand.^[4] Dithiolenes are also found in the active sites of pyranopterin molybdenum enzymes^[1b, 2, 5]. These enzymes possess a redox active Mo center bound by one or two pyranopterin dithiolene ligands (Fig. 1) and catalyze two-electron redox reactions that are coupled to the formal transfer of an oxygen atom between the active site and substrate.^[6] It is believed that Mo-based redox processes are dominant in these enzymes,^[6a] with the Mo ion cycling between the Mo(IV) and Mo(VI) redox states. However, the pyranopterin possesses the potential to store up to four redox equivalents by accessing via tetrahydro, dihydro, and oxidized states of the pterin ring. Induced internal redox interconversions in the

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pyranopterin have been suggested to occur via a combination of pyran ring opening and direct two-electron oxidation of the pterin ring.^[2, 7] There is a dearth of experimental studies that have focused on the redox synergy within the coupled pyranopterin-dithiolene moiety or on the role of the pyranopterin-dithiolene in catalysis. In this manuscript, electronic structure calculations are evaluated in the context of electronic absorption and resonance Raman spectroscopies that probe the nature of the piperazine-dithiolene ligand in the oxomolybdenum-bis(dithiolene) complex $[\text{Mo}^{4+}\text{O}(\textit{i}\text{-Pr}_2\text{Pipdt})_2\text{Cl}][\text{PF}_6]$ (**1**, Figure 1) (where *i*-Pr₂Pipdt is N,N'-piperazine-2,3-dithione). Our studies reveal a considerable degree of dizwitterionic ligand character present in the ligands of **1**. As a result of this dizwitterionic character, **1** displays unusual spectroscopic features for a formally reduced Mo(IV) dithiolene complex.

Results and Discussion

Compound **1** possesses a low energy absorption feature at $\sim 13,500\text{ cm}^{-1}$ (Bands 1 and 2; Figure 2). Low-energy charge transfer transitions are not typically observed in oxomolybdenum (IV) mono- and bis-dithiolene complexes since they possess low-spin $(dx^2-y^2)^2$ electronic configurations that preclude LMCT transitions to this low-lying $\text{Mo}(dx^2-y^2)$ highest occupied molecular orbital (HOMO). To our knowledge, the only Mo(IV) bis-dithiolene complex to display similar low energy absorption features is $\text{Tp}^*\text{MoO}(\text{S}_2\text{BMOQO})$, **2**, which possesses a $16,400\text{ cm}^{-1}$ ($\epsilon = 5,190\text{ M}^{-1}\text{cm}^{-1}$) *intraligand* dithiolene(S) \rightarrow quinoxaline CT transition.^[4] The donor-acceptor nature of the S₂BMOQO ligand results from an admixture of thiol/thione and dithiol resonance structures, and is responsible for the intensity of the intraligand band in **2**.^[4] However, the origin of the low energy CT transition in **1** is different than that determined for **2**. The lowest unoccupied MOs in **1** (LUMO and LUMO+1) are bis-dithiolene ligand orbitals comprised of antisymmetric (LUMO) and symmetric (LUMO+1) linear combinations of a dithiolene S_{op}^{a} orbital (Fig. 3). The S_{op}^{a} orbital is doubly occupied in reduced dianionic dithiolenes, but is unoccupied in the two electron oxidized form of the ligand. Therefore, electronic transitions to the LUMO and LUMO+1 will directly probe the nature of the dithiolene in **1**. Time dependent DFT calculations^[8] have allowed for an assignment of Bands 1 and 2 as arising primarily from HOMO \rightarrow LUMO and HOMO \rightarrow LUMO+1 one-electron promotions. The MLCT character is clearly evident in the electron density difference map (EDDM) for Band 1, where the acceptor character is delocalized over the N₂C₂S₂ atoms of both dithiolenes (Fig. 2). The 647nm resonance Raman spectrum (Figure S1) of **1** displays bands at 1120, 1226, and 1516 cm^{-1} that correlate very well with calculated frequencies at 1119, 1224, and 1519 cm^{-1} , which have been scaled with a 2% frequency reduction factor. This has allowed for their respective assignments as $\nu(\text{C-C} + \text{C-S})$, $\nu(\text{C-C})$, and $\nu(\text{C-N})$, respectively. The C-C and C-S stretching frequencies for **1** are markedly different from those of oxomolybdenum complexes coordinated by dianionic dithiolene ligands, where $\nu(\text{C-S}) \sim 760 - 860\text{ cm}^{-1}$ and $\nu(\text{C-C}) \sim 1,450 - 1,600\text{ cm}^{-1}$ are typically observed.^[9]

The nature of the *i*-Pr₂Pipdt ligands can be further understood by examining the two key resonance structures in Figure 3. Structure **A** represents the neutral dithione form of *i*-Pr₂Pipdt while structure **B** represents a dizwitterionic form of the ligand. The nature of the low energy MLCT transitions and the Raman data suggest an admixture of resonance forms **A** and **B** in **1** with π delocalization that extends over the entire N₂C₂S₂ ligand framework. The low energy and appreciable intensity of the MLCT band in **1** directly results from the presence of low-lying ligand-based acceptor orbitals that possess extended π conjugation. Additionally, the observation of a high frequency 1519 cm^{-1} $\nu(\text{C-N})$ stretch (aliphatic amine $\nu(\text{C-N})$ 1020-1250 cm^{-1})^[10] is fully consistent with a significant contribution from the dizwitterionic resonance form **B**, which possesses C=N double bond character ($\nu(\text{C=N})$

1471-1689 cm^{-1})^[10]. The contribution of structure **B** is also clearly evident in the structure of the free ligand, which possesses *planar* sp^2 N atoms (Figure S2). The coefficients of the competing resonance forms of the free ligand can be calculated using a natural bond orbital (NBO) formalism.^[11] Our NBO calculations indicate very large donations from the piperazine N lone pairs of resonance form **A** into C-S π^* antibonding orbitals that lead to the formation of resonance structure **B**. The contributions of these two resonance structures to the ground state valence bond (VB) wavefunction can be approximated through use of NBO derived occupation numbers for the competing resonance forms. This analysis results in a 63:37 ratio of structures **A** and **B** contributing to the ground state VB description of the ligand. This is consistent with the spectroscopic data that show evidence for extensive $\text{N}_2\text{C}_2\text{S}_2$ π delocalization in the ligands. Thus, this VB description of the ligands in **1** nicely explains 1) the extended conjugation suggested by the Raman data and observed in the EDDMs of bands 1 and 2, 2) the electron withdrawing nature of the *i*-Pr₂Pipdt ligands that stabilize the Mo(IV) oxidation state, 3) the origin of the unusually low energy MLCT transitions in **1**, and 4) the planar sp^2 character of the piperazine N atoms.

Conclusions

In summary, our spectroscopic and electronic structure studies point to the *i*-Pr₂Pipdt ligands in **1** as a new type of dithiolene that can be described in VB terms as a resonance hybrid of dithione and dizwitterionic dithiolene contributing structures. This is of fundamental interest with respect to our understanding of the complex coordination chemistry of metallo-dithiolene complexes. In terms of applications, this electronic structure description may provide a guiding principle for designing molecule-based valence-delocalized materials, and for understanding electron transfer regeneration processes in molybdenum enzymes. With respect to the latter, it has been postulated that the piperazine ring component of the pyranopterin cofactor can electronically buffer the Mo center against changes in charge that accompany redox processes.^[12] The additional redox non-innocence of the pyranopterin suggests that zwitterionic forms of the cofactor may play a fundamental role in modulating its electron donor ability and facilitating pyranopterin molybdenum enzyme catalysis.^[12c]

Experimental Section

(General)

Synthesis of the molybdenum complex was carried out in oxygen-free dry argon atmospheres using dry degassed solvents. The ligand, diisopropylpiperazine-2,3-dithione (*i*-Pr₂Pipdt), was synthesized in air.^[13] Solvents were purchased either from Aldrich Chemical Co or Acros Organics and were purified by distillation as follows: acetonitrile from CaH₂, followed by Li₂CO₃-KMnO₄ and finally from P₂O₅; CH₂Cl₂ and CHCl₃ from CaH₂; diethyl ether and toluene from sodium benzophenone; methanol from sodium ethoxide. MoCl₅, N,N-dimethyl ethylene diamine, N,N-diisopropyl ethylene diamine and Lawesson's reagent were purchased from Aldrich and used without purification. Diethyl oxalate was purchased from Acros Organics and used as received.

Spectroscopic/Spectrometric Measurements

Routine UV-Visible spectra were recorded on a modified temperature-controlled Cary 14 spectrophotometer or a temperature controlled Cary 3 spectrophotometer. ¹H, and ¹³C NMR spectra were collected using either a Bruker 500 MHz or a 400 MHz spectrometer. IR spectra were recorded in reflection mode on a Thermo Electron corporation Nicolet 380 spectrometer with neat samples. Elemental analysis was performed by Midwest Microlab LLC, Indiana, IL. All mass spectra were collected in a Micromass ZMD quadrupole

spectrometer equipped with an electrospray ionization (ESI) source both negative and positive ion mode, using acetonitrile as the mobile phase. In order to get the molecular ion peak the capillary and the cone voltages were varied between 3.0-4.0 kV and 5-55 V respectively. The desolvation temperature was set at 100 °C and the source bath temperature was set at 80 °C.

Solid state resonance Raman (rR) spectra and associated rR excitation profiles were collected using a system comprised of an PI/Acton SpectraPro SP-2556 500 mm focal length imaging spectrograph with a triple grating turret and a PI/Acton Spec-10:100B back-illuminated 1340 × 100 pixel digital CCD spectroscopy system with a cryogenically cooled camera head. Coherent Innova Ar⁺ and Kr⁺ ion lasers were used as excitation source. Samples were mixed with either NaCl or a NaCl/Na₂SO₄ mixture with Na₂SO₄ as an internal calibrant. High resolution electronic absorption spectra were collected using a Hitachi U-3501 UV-Vis-NIR dual-beam spectrophotometer capable of scanning a wavelength region between 185 and 3200 nm. Spectral samples were dissolved in dry, degassed acetonitrile, and the electronic absorption spectra were measured in a 1 cm pathlength, 100 μL, black-masked, quartz cuvette (Starna Cells, Inc.) equipped with a Teflon stopper. All electronic absorption spectra were performed at room temperature and repeated at regular time intervals to ensure the structural stability and integrity of the complex in solution.

Electronic structure and vibrational frequency calculations were performed at the density functional level of theory using the Gaussian 03W^[8] and NBO 5.0^[11] software packages. All calculations employed the B3LYP hybrid functional and used a LANL2DZ basis set with an effective core potential for Mo. A 6-31G* basis set was used for all light atoms. Input files were prepared using the molecule builder function in the Gaussview software package. Electron density difference maps (EDDMs) were constructed using the GaussSum suite of programs.

Synthetic and characterization details for [(*i*-Pr₂Pipdt)₂MoOCl][PF₆]

160 mg (0.586 mmol) of MoCl₅ was dissolved in 3 mL of dry degassed methanol which led to a vigorous reaction and the reaction mixture turned green. To this mixture 300 mg (1.304 mmol) of *i*-Pr₂Pipdt was added and the color changed to blue green immediately. After stirring the reaction mixture for 15 min, 800 mg (4.74 mmol) of NaPF₆ in methanol (10 mL) was added, and stirred for 30 min. The solution was filtered and the precipitate was washed first with methanol to remove excess NaPF₆, and then with CHCl₃ to remove excess ligand. Drying of the precipitate resulted in analytically pure compound. Yield: 52% (212 mg, 0.306 mmol). Anal. Calcd (Experimental) for C₂₀H₃₆N₄S₄MoOClPF₆: C, 31.89 (31.67); H, 4.82 (4.75); N, 7.44 (7.34); S 17.03 (16.94). IR (neat, cm⁻¹): 1505 (vs, C-N), 1365 (vs, C=S), 1258, 1185, 938 (vs, Mo=O) 831 (vs, PF₆), 588 (m), 566 (s). ESI-MS (MeCN): base peak, *m/z* 609 [M]⁺. ¹H NMR (CD₃CN): δ=5.57, 5.42 (sep, 2H, CH), 4.04, 3.48 (s, 4H, CH₂), 1.50, 1.25 (d, 12H, CH₃). ¹³C NMR (CD₃CN): δ=180.75 (C=S), 59.10 (CH), 43.16 (CH₂), 17.69 (CH₃). Conductivity in acetonitrile: 162 ohm⁻¹cm²mol⁻¹.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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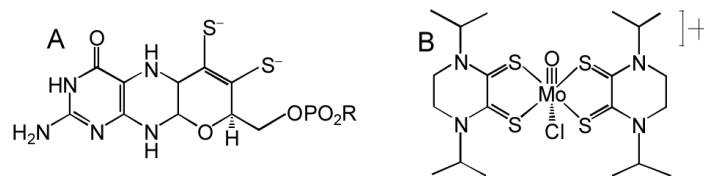


Figure 1.

A: Pyranopterin dithiolene coordinated to Mo as the dianion. B: *i*-Pr₂Pipdt ligand coordinated to Mo in **1** as the dithione. Note the presence of a piperazine ring in both structures.

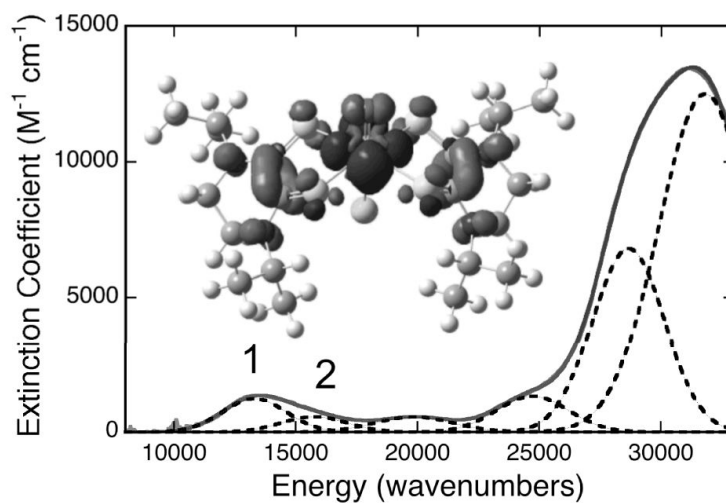


Figure 2. Gaussian resolved electronic absorption spectrum of **1** in acetonitrile. (Inset) Electron density difference map (EDDM) that details the nature of the low-energy MLCT transition (Band 1) in **1** (black: electron density loss in transition, gray: electron density gain in transition).

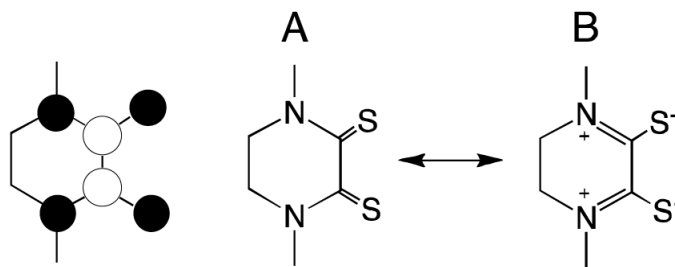
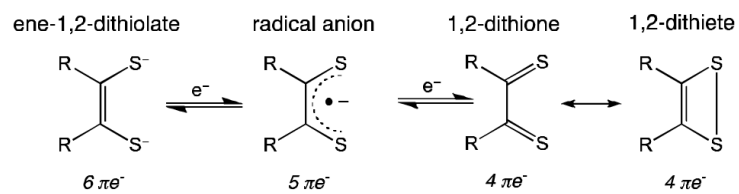


Figure 3.

The π delocalized S_{op}^a orbital. Right: Two contributing resonance structures for the *i*-Pr₂Pipdt ligand that lead to N₂C₂C₂ π delocalization. **A**: dithione, **B**: dizwitterionic dithiol.



Scheme 1.
Dithiolene ligand forms.