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A Valence Bond Description of Dizwitterionic Dithiolene Character in an Oxomolybdenum–Bis(dithione) Complex

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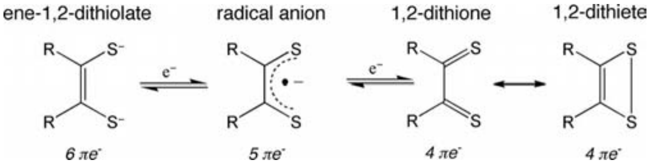
Metallodithiolene non-innocence is explored in an oxomolybdenum–bis(dithione) complex, $[Mo^{4+}O(i\mathrm{Pr_2Pipdt})_2Cl][PF_6]$ (where Pipdt is *N*,*N*′-piperazine-2,3-dithione), which has a piperazine ring as an integral part of the dithiolene ligand. The title complex displays spectroscopic features that are unusual 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 structures.

Introduction

Metallodithiolenes display an extraordinarily rich metal–ligand redox interplay[1] due to the inherent non-innocent redox behavior of the dithiolene group.[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 group 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 *intraligand* 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 (Figure 1) and catalyze two-electron redox reactions that are coupled to the formal transfer of an oxygen atom between the active site and the substrate.[6] It is believed that Mo-based redox processes dominate 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 the tetrahydro, dihydro, and oxidized states of the pterin ring. Induced internal redox interconversions in the pyranopterin have been suggested to occur by 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 pyranopterin–dithiolene in catalysis. In this manuscript, results of electronic structure calculations are evaluated in the context of electronic absorption and resonance Raman spectroscopy that probe the nature of the piperazine–dithiolene ligand in the oxomolybdenum–bis(dithiolene) complex $[Mo^{4+}O(i\mathrm{Pr_2Pipdt})_2Cl][PF_6]$ (**1**, Figure 1) (where Pipdt is *N*,*N*′-piperazine-2,3-dithione). Our studies reveal that a considerable degree of dizwitterionic ligand character is present in the ligands of complex **1**. As a result of this



Scheme 1. Forms of the dithiolene ligand.

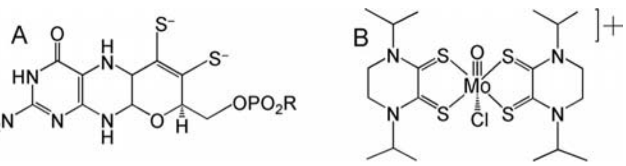


Figure 1. (A) Pyranopterin dithiolene coordinated to Mo as the dianion. (B) Ligand $i\mathrm{Pr_2Pipdt}$ coordinated to Mo in **1** as the dithione. Note the presence of a piperazine ring in both structures.

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dizwitterionic character, compound **1** displays spectroscopic features that are unusual for a formally reduced Mo^{IV}–dithiolene complex.

Results and Discussion

Compound **1** possesses a low-energy absorption feature at approximately 13500 cm^{-1} (bands 1 and 2; Figure 2). Low-energy charge-transfer transitions are not typically observed in mono- and bis(dithiolene) complexes of oxomolybdenum(IV), since they possess low-spin $(d_{x^2-y^2})^2$ electronic configurations that preclude LMCT transitions to this low-lying Mo($d_{x^2-y^2}$) highest occupied molecular orbital (HOMO). To the best of our knowledge, the only Mo^{IV}–bis(dithiolene) complex to display similar low-energy absorption features is Tp*MoO(S_2BMOQO) (**2**), which possesses a 16400 cm^{-1} (ε = 5190 M^{-1} cm^{-1}) *intraligand* dithiolene(S)→quinoxaline charge-transfer transition.[4] The donor–acceptor nature of the S_2BMOQO 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 charge-transfer transition in **1** is different from that determined for **2**. The lowest unoccupied MOs in **1** (LUMO and LUMO+1) are bis(dithiolene) ligand orbitals composed of antisymmetric (LUMO) and symmetric (LUMO+1) linear combinations of a dithiolene $S_{op}{}^{a'}$ orbital (Figure 3). The $S_{op}{}^{a'}$ orbital is doubly occupied in reduced dianionic dithiolenes, but it 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 enabled an assignment of bands 1 and 2 as arising primarily from HOMO→LUMO and HOMO→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 $N_2C_2S_2$ atoms of both dithiolenes (Figure 2).

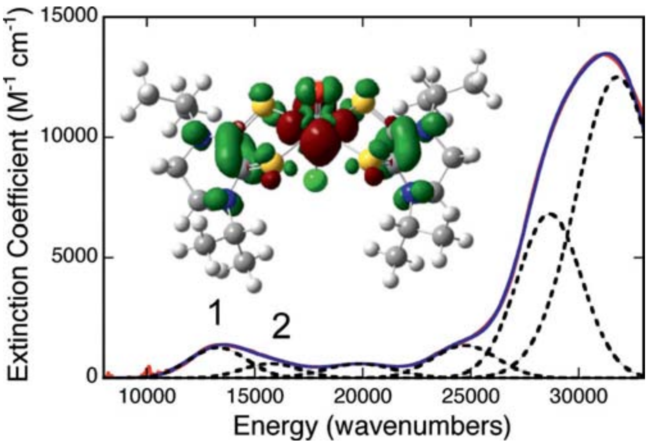

Figure 2. Gaussian resolved electronic absorption spectrum of **1** in acetonitrile. Inset: Electron density difference map (EDDM) that shows in detail the nature of the low-energy MLCT transition (band 1) in **1** (red: electron-density loss in transition; green: electron-density gain in transition).

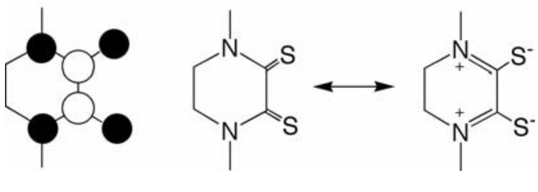

Figure 3. Left: the π-delocalized $S_{op}{}^{a'}$ orbital. Right: two contributing resonance structures for the R_2Pipdt ligand that lead to $N_2C_2C_2$ π-delocalization. **A**: dithione, **B**: dizwitterionic dithiol.

The 647 nm 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}, respectively, which have been scaled with a 2% frequency reduction factor. This has made possible their respective assignments as ν(C–C + C–S), ν(C–C), and ν(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 ν(C–S) ≈ 760–860 cm^{-1} and ν(C=C) ≈ 1450–1600 cm^{-1} are typically observed.[9]

The nature of the *i*Pr_2Pipdt ligands can be further understood by examining the two key resonance structures in Figure 3. Structure **A** represents the neutral dithione form of *i*Pr_2Pipdt, while structure **B** represents a dizwitterionic form of the ligand. The nature of the low-energy MLCT transitions and the Raman spectroscopic data suggest an admixture of resonance forms **A** and **B** in **1** with π-delocalization that extends over the entire $N_2C_2S_2$ 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 1516 cm^{-1} ν(C–N) stretch [aliphatic amine ν(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 [ν(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 by 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/B** contributing to the ground state VB description of the ligand. This is consistent with the spectroscopic data that provide evidence for extensive $N_2C_2S_2$ π-delocalization in the ligands. Thus, this VB description of the ligands in **1** nicely explains: (1) the extended conjugation suggested by the Raman spectroscopic data and observed in the EDDMs of bands 1 and 2, (2) the electron-withdrawing nature of the *i*Pr_2Pipdt 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*Pr_2Pipdt 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 metallodithiolene 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 pyranopterin dithiolene 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 under oxygen-free dry argon atmospheres by using dry degassed solvents. The ligand, diisopropylpiperazine-2,3-dithione (*i*Pr_2Pipdt), 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 CaH_2, followed by $Li_2CO_3/KMnO_4$ and finally from P_2O_5; CH_2Cl_2 and $CHCl_3$ from CaH_2; diethyl ether and toluene from sodium benzophenone; methanol from sodium ethoxide. $MoCl_5$, *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/Vis spectra were recorded with a modified temperature-controlled Cary 14 spectrophotometer or a temperature-controlled Cary 3 spectrophotometer. ^1H and ^{13}C NMR spectra were collected by using either a Bruker 500 MHz or a 400 MHz spectrometer. IR spectra were recorded in reflection mode with 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 with a Micromass ZMD quadruple spectrometer equipped with an electrospray ionization (ESI) source in both the negative-ion and the positive-ion mode, by 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 by using a system composed 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 $NaCl/Na_2SO_4$ mixture with Na_2SO_4 as an internal calibrant. High-resolution electronic absorption spectra were collected by 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 path length, 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 with 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 by using the molecule builder function in the Gaussview software package. Electron density difference maps (EDDMs) were constructed by using the GaussSum suite of programs.

Synthetic and Characterization Details for [(*i*Pr_2Pipdt)$_2$MoOCl]-[PF_6]: $MoCl_5$ (160 mg, 0.586 mmol) was dissolved in dry degassed methanol (3 mL). This led to a vigorous reaction, and the reaction mixture turned green. To this mixture was added *i*Pr_2Pipdt (300 mg, 1.304 mmol), and the color changed to blue-green immediately. After stirring the reaction mixture for 15 min, $NaPF_6$ (800 mg, 4.74 mmol) in methanol (10 mL) was added, and the mixture was stirred for 30 min. The solution was filtered, and the precipitate was washed first with methanol, to remove excess $NaPF_6$, and then with $CHCl_3$, to remove excess ligand. Drying of the precipitate resulted in an analytically pure compound. Yield: 52% (212 mg, 0.306 mmol). $C_{20}H_{36}ClF_6MoN_4OPS_4$ (753.1): calcd. C 31.67, H 4.75, N 7.34, S 16.94; found C 31.89, H 4.82, N 7.44, S 17.03. IR (neat): $\tilde{\nu}$ = 1505 (vs, C–N), 1365 (vs, C=S), 1258, 1185, 938 (vs, Mo=O) 831 (vs, PF_6), 588 (m), 566 (s) cm^{-1}. ESI-MS (MeCN): base peak, *m*/*z* = 609 $[M]^+$. ^1H NMR (CD_3CN): δ = 5.57, 5.42 (sep, 2 H, CH), 4.04, 3.48 (s, 4 H, CH_2), 1.50, 1.25 (d,12 H,CH_3) ppm. ^{13}C NMR (CD_3CN): δ = 180.75 (C=S), 59.10 (CH), 43.16 (CH_2), 17.69 (CH_3) ppm. Conductivity in acetonitrile: 162 $ohm^{-1}\,cm^2\,mol^{-1}$.

Supporting Information (see footnote on the first page of this article): Resonance Raman spectrum of **1** and X-ray structure of the free *i*Pr_2Pipdt ligand.

Acknowledgments

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