Published in final edited form as:

Inorg Chem. 2009 November 16; 48(22): 10581–10590. doi:10.1021/ic901112s.

Dioxo–Molybdenum(VI) Complexes with Ene–1,2–dithiolate Ligands: Synthesis, Spectroscopy, and Oxygen Atom Transfer Reactivity

Hideki Sugimoto^{*,†}, Susumu Tatemoto^{††}, Koichiro Suyama^{††}, Hiroyuki Miyake^{††}, Shinobu Itoh^{*,†}, Chao Dong[‡], Jing Yang[‡], and Martin L. Kirk^{*,‡}

[†] Department of Material and Life Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

^{††} Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sumiyoshi-ku, Osaka 558-8585, Japan

[‡] Department of Chemistry and Chemical Biology, The University of New Mexico, MSC03 2060, 1 University of New Mexico, Albuquerque, NM 87131–0001

Abstract

New dioxo–molybdenum(VI) complexes, $(\text{Et}_4\text{N})(\text{Ph}_4\text{P})[\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdt})]$ (**2**) and $(\text{Et}_4\text{N})(\text{Ph}_4\text{P})[\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdtCl}_2)]$ (**4**) ($\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2 = 1,2\text{-dicarbomethoxyethylene-1,2-dithiolate}$, $\text{bdt} = 1,2\text{-benzenedithiolate}$, $\text{bdtCl}_2 = 3,6\text{-dichloro-1,2-benzenedithiolate}$), that possess at least one ene–1,2–dithiolate ligand were synthesized by the reaction of their mono–oxo–molybdenum(IV) derivatives, $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdt})]$ (**1**) and $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdtCl}_2)]$ (**3**), with Me_3NO (Chart 1). Additionally, the bis(ene–1,2–dithiolate)Mo^{VI}O₂ complex, $(\text{Et}_4\text{N})(\text{Ph}_4\text{P})[\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2]$ (**6**), was isolated. Complexes **2**, **4**, and **6** were characterized by elemental analysis, negative–ion ESI mass spectrometry, and IR spectroscopy. X-ray analysis of **4** and **6** revealed a Mo^{VI} center that adopts a distorted octahedral geometry. Variable temperature ¹H NMR spectra of (CD₃)₂CO solutions of the Mo^{VI}O₂ complexes indicated that the Mo centers isomerize between Λ and Λ' forms. The electronic structures of **2**, **4**, and **6** have been investigated by electronic absorption and resonance Raman spectroscopy and bonding calculations. The results indicate very similar electronic structures for the complexes and considerable π –delocalization between the Mo^{VI}O₂ and ene–1,2–dithiolate units. The similar oxygen atom transfer kinetics for the complexes results from their similar electronic structures.

Introduction

The periplasmic DMSO reductases (DMSOR)^{1, 2} are pyranopterin molybdenum enzymes that contain the Mo active site as their only redox-active center and function as terminal

^{*}; Email: sugimoto@mls.eng.osaka-u.ac.jp; ; Email: shinobu@mls.eng.osaka-u.ac.jp, ; Email: mkirk@unm.edu.

Supporting Information Available: The ESI–mass spectra of **2**, **4**, and **6** (Figures S1 – S3). Crystal structures of **6b** and **7** (Figures S4 and S5). CIF files of **1a**, **4**, **6**, and **7**. Relevant molecular orbitals for **2** and **4** (Figures S6 and S7). This material is available free of charge via the Internet at <http://pubs.acs.org>.

electron acceptors during anaerobic growth of *R. sphaeroides* and *R. capsulatus* in the presence of DMSO. Consensus structures for the oxidized and reduced DMSOR family members are shown in Figure 1.³ The absence of additional chromophores in DMSOR has allowed for their characterization by resonance Raman (rR),⁴ electronic absorption⁵ and, for a glycerol inhibited form, magnetic circular dichroism (MCD) spectroscopy.⁶ The absorption spectra for the Mo^{VI} and Mo^{IV} forms of *R. sphaeroides* and *R. capsulatus* DMSOR display low energy absorption bands at 720 nm ($\sim 2000 \text{ M}^{-1}\text{cm}^{-1}$) and 640 nm ($\sim 1000 \text{ M}^{-1}\text{cm}^{-1}$) respectively, and their intensity implies significant charge transfer character.⁵ Additionally, rR spectroscopy⁷ provides evidence for vibrational modes that are sensitive to ³⁴S isotopic substitution. These data provide strong evidence that the observed low energy optical transitions possess considerable S(ene-1,2-dithiolate)→Mo charge transfer (CT) character.

It is therefore of interest to understand how bis(ene-1,2-dithiolate) coordination in members of the DMSOR family of enzymes affect electron and atom transfer reactivity during the course of catalysis. This interest arises from the fact that ene-1,2-dithiolates and dithiolenes are highly non-innocent ligands that have a dramatic effect on the electronic structure of their metal ion complexes.⁸ It has been suggested that the degree of π -delocalization within the dithiolene unit and charge donation to the metal can be monitored by the frequency of the $\nu(\text{C}=\text{C})$ stretching mode associated with the ene-1,2-dithiolate ligand ($-\text{S}-\text{C}=\text{C}-\text{S}-$).⁷ However, in some enzymes of the DMSOR family, the $\nu(\text{C}=\text{C})$ stretch is often difficult to observe or definitively assign by rR spectroscopy due to the intense absorption features of additional prosthetic groups such as flavins, Fe-S clusters, or hemes. Even in the absence of these chromophores, it can be difficult to unambiguously assign the $\nu(\text{C}=\text{C})$ stretch without an isotope perturbation. However, the $\nu(\text{C}=\text{C})$ stretch has been assigned in a number of DMSOR family enzymes using rR spectroscopy.⁷ In these studies, the $\nu(\text{C}=\text{C})$ stretch has been shown to range from 1525 to 1598 cm^{-1} in arsenite oxidase (AO)⁹, and from 1526 to 1576 cm^{-1} for DMSOR¹⁰ during their respective reaction catalytic cycles. The information gleaned from the $\nu(\text{C}=\text{C})$ stretching frequency, coupled with an understanding the electronic origins of the CT spectra in DMSOR family enzymes, can provide deeper insight into electronic structure contributions to the rich electron and atom transfer reactivity of DMSOR family enzymes. Structurally characterized model studies can serve as important benchmark systems for evaluating enzyme spectra and developing key structure-function relationships. Along these lines, more than two dozen $[\text{Mo}^{\text{IV}}\text{O}(\text{ene-1,2-dithiolate})]^{2-}$ complexes have been synthesized as analogues of reduced DMSOR family enzymes and characterized by IR and rR spectroscopies.¹¹⁻¹³ Recently, we reported a Mo^{IV}O complex which possesses both an ene-1,2-dithiolate ligand and an aromatic dithiolene ligand, $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdt})]$ (**1**) (Chart 1, $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2 = 1,2$ -dicarbomethoxyethylene-1,2-dithiolate, bdt = 1,2-benzenedithiolate).¹⁴ In contrast, Mo^{VI} complexes with one or two ene-1,2-dithiolate ligands have been considered to be unstable for isolation as a result of autoredox reactions that may be facilitated by π -delocalization between the metal and ene-1,2-dithiolate ligands.^{12, 15-18} Isolated Mo^{VI} $[\text{Mo}^{\text{VI}}\text{O}_2(\text{ene-1,2-dithiolate})_2]^{2-}$ complexes are limited to $[\text{MoO}_2(\text{mnt})_2]^{2-}$ (mnt = dicyanoethylene-1,2-dithiolate),¹⁹ which is believed to be stabilized by the very strong electron withdrawing nature of the CN substituents. Other Mo^{VI}O₂ or Mo^{VI}O(OR) bis(ene-1,2-dithiolate)

complexes have been generated *in situ*.^{15–18} Thus, there is a need for spectroscopic and electronic structure studies on structurally characterized model systems that do not have substituents in conjugation with the C=C unit of the ene-1,2-dithiolate ligand, since the pyranopterin cofactor is not believed to be conjugated to the ene-1,2-dithiolate moiety in the enzymes.^{1, 20}

In this manuscript, we describe the synthesis of $(\text{Et}_4\text{N})(\text{Ph}_4\text{P})[\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdt})]$ (**2**) and its chlorine substituted aromatic dithiolene derivative, $(\text{Et}_4\text{N})(\text{Ph}_4\text{P})[\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdtCl}_2)]$ (**4**). Additionally, the X-ray structure of **4** has been determined. These $\text{Mo}^{\text{VI}}\text{O}_2$ complexes possess one ene-1,2-dithiolate ligand in addition to an aromatic dithiolene ligand (Chart 1). A particular advantage of this mixed dithiolene ligand set is the ability to isolate stable d^0 dioxo $\text{Mo}^{\text{VI}}\text{O}_2$ complexes as well as their d^2 monooxo $\text{Mo}^{\text{IV}}\text{O}$ counterparts.^{21–27} We were also able to isolate and characterize the dioxo complex $(\text{Et}_4\text{N})(\text{Ph}_4\text{P})[\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2]$ (**6**) which had previously been considered too unstable for isolation.¹² Finally, we have used electronic absorption and resonance Raman spectroscopies to probe the basic electronic structure of the dioxo complexes, and this has provided insight into the relationship between their electronic structure properties and oxygen atom transfer reactivity.

Experimental Section

General

All reagents and solvents were used as received unless otherwise noted. All reactions were carried out under a dinitrogen atmosphere using standard Schlenk techniques. $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{IV}}\text{O}(\text{S}_4)(\text{bdtCl}_2)]$, $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdt})]$ (**1**), and $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2]$ (**5**) were prepared by following established literature procedures.^{14, 28}

Synthesis and Characterization of Complexes

$(\text{Et}_4\text{N})(\text{Ph}_4\text{P})[\text{Mo}^{\text{IV}}\text{O}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdt})]$ (**2**)

An acetonitrile solution of 1 mL containing Me_3NO (trimethylamine *N*-oxide, 4.8 mg, 0.064 mmol) was added to 3 mL of an acetonitrile solution containing **1** (23.2 mg, 0.032 mmol) and Ph_4PBr (41.2 mg, 0.098 mmol). The resultant deep-red solution was concentrated to ca. 1 mL. Addition of 25 mL of ethanol to the solution gave a red-black microcrystalline powder of **2**, which was collected by filtration and dried *in vacuo*. Yield: 22.9 mg (73%). Anal. Calcd for $\text{C}_{44}\text{H}_{50}\text{MoO}_6\text{NPS}_4 \cdot 3\text{H}_2\text{O}$ (mol wt. 999.09): C, 52.95; H, 5.66; N, 1.40. Found: C, 53.33; H, 5.27; N, 1.62. ^1H NMR (CD_3CN , 25°C, anionic part): δ 7.03 (m, 2H), 6.58 (m, 2H), 3.58 (s, 6H). UV-vis spectrum (CH_3CN): $\lambda_{\text{max}} = 362$ ($\epsilon = 8130$), 422 (sh, 4970), 530 nm ($1880 \text{ M}^{-1} \text{ cm}^{-1}$). ESI-MS (CH_3CN): $m/z = 606$ $\{[\text{M}]^{2-} + \text{Et}_4\text{N}^+\}^-$, 815 $\{[\text{M}]^{2-} + \text{Ph}_4\text{P}^+\}^-$. CV (CH_3CN): E_{pc} (irrev.) = -1.70 V vs. SCE. IR (KBr): ν 528 (vs), 691 (s), 723 (s), 759 (m), 836 (s), 870 (s), 997 (m), 1026 (s), 1077 (w), 1108 (vs), 1236 (vs), 1438 (vs), 1484 (s), 1586 (w), 1707 (s), 1716 cm^{-1} (s).

(Et₄N)₂[Mo^{IV}O(S₂C₂(CO₂Me)₂)(bdtCl₂)] (3)

This complex was synthesized using the same procedure as **1**,¹⁴ except (Et₄N)₂[MoO(S₄)(bdtCl₂)] (224 mg, 0.316 mmol) was used instead of (Et₄N)₂[MoO(S₄)(bdt)]. Yield: 166 mg (67%). Anal. Calcd for C₂₈H₄₈Cl₂MoN₂O₅S₄ (mol wt. 787.81): C, 42.69; H, 6.14; N, 3.56. Found: C, 42.83; H, 6.09; N, 3.53. ¹H NMR (CD₃CN, anionic part): δ 6.89 (s, 2H), 3.70 (s, 6H). UV–vis spectrum (CH₃CN): λ_{max} = 377 (ε = 3490), 431 (870), 531 nm (340 M⁻¹ cm⁻¹). ESI–MS (CH₃CN) : *m/z* = 264 [M]²⁻, 658 {[M]²⁻ + Et₄N⁺}⁻. CV (CH₃CN): *E*_{1/2}(rev.) = -0.11 V vs. SCE. IR (KBr): ν 784 (m), 807 (m), 909 (s), 999 (m), 1017 (m), 1055 (m), 1152 (m), 1172 (m), 1234 (vs), 1325 (m), 1394 (s), 1431 (m), 1454 (m), 1483 (s), 1528 (s), 1696 (s), 1711 cm⁻¹ (s).

(Et₄N)(Ph₄P)[Mo^{IV}O₂(S₂C₂(CO₂Me)₂)(bdtCl₂)] (4)

To 10 mL of an acetonitrile solution of **3** (50.9 mg, 0.065 mmol), 4 mL of an acetonitrile solution of Me₃NO (10.0 mg, 0.133 mmol) was added. The resultant deep-red solution was stirred for 5 minutes, and then Ph₄PBr (87.0 mg, 0.207 mmol) was added to the solution. A brown powder was precipitated by addition of ethanol to the solution, and this was collected by filtration and dried *in vacuo*. Yield: 50.5 mg (75%). Anal. Calcd for C₄₄H₄₈MoNO₆PS₄•H₂O (mol wt. 1030.95): C, 51.26; H, 4.89; N, 1.36. Found: C, 51.13; H, 4.76; N, 1.55. ¹H NMR (CD₃CN, 25 °C, anionic part): δ 6.73 (s, 2H), 3.59 (s, 6H). UV–vis spectrum (CH₃CN): λ_{max} = 329 (ε = 6670), 358 (5040), 417 (3000), 525 nm (1100 M⁻¹ cm⁻¹). ESI–MS (CH₃CN) : *m/z* = 674 {[M]²⁻ + Et₄N⁺}⁻, 883 {[M]²⁻ + Ph₄P⁺}⁻. CV (CH₃CN): *E*_{pc}(irrev.) = -1.66 V vs. SCE. IR (KBr): ν 528 (vs), 691 (s), 723 (s), 757 (m), 838 (s), 872 (s), 997 (m), 1027 (s), 1068 (s), 1109 (vs), 1154 (m), 1236 (vs), 1333 (m), 1394 (vs), 1437 (vs), 1483 (vs), 1585 (w), 1680 (s), 1715 cm⁻¹ (s).

(Et₄N)(Ph₄P)[Mo^{IV}O₂(S₂C₂(CO₂Me)₂)] (6)

An acetonitrile solution (1 mL) containing Me₃NO (6.6 mg, 0.084 mmol) was added to an acetonitrile solution (5 mL) containing **5** (31.3 mg, 0.040 mmol). An acetonitrile solution (2 mL) of Ph₄PBr (50.2 mg, 0.120 mmol) was immediately added to the reaction mixture and the resultant deep-red solution was concentrated to ca. 1 mL. When a solution comprised of 6 mL of ethanol and 10 mL of diethyl ether was added to the deep-red solution, a red-black microcrystalline powder (**6**) precipitated from the solution. This was collected by filtration and dried *in vacuo*. Yield: 28.2 mg (70%). Anal. Calcd for C₄₄H₅₂MoNO₁₀PS₄ (mol wt. 1010.75): C, 52.32; H, 5.19; N, 1.39. Found: C, 52.35; H, 4.99; N, 1.52. ¹H NMR (CD₃CN, 25 °C, anionic part): δ 3.60 (s, 12H). UV–vis spectrum (CH₃CN): λ_{max} = 358 (ε = 7630), 419 (5370), 536 nm (1840 M⁻¹ cm⁻¹). ESI–MS (CH₃CN) : *m/z* = 542 [M]⁻, 672 {[M]²⁻ + Et₄N⁺}⁻, 881 {[M]²⁻ + Ph₄P⁺}⁻. CV (CH₃CN): *E*_{pc}(irrev.) = -1.70 V vs. SCE. IR (KBr): ν 528 (vs), 692 (s), 724 (s), 763 (m), 838 (s), 869 (s), 997 (m), 1026 (s), 1076 (w), 1109 (vs), 1233 (vs), 1436 (vs), 1484 (s), 1685 (vs), 1708 cm⁻¹ (vs).

Physical Measurements

¹H NMR spectra were recorded with a JEOL Lambda 300, and TMS signal was adjusted to 0 ppm. ESI–MS spectra were measured with a JEOL JMS-700S. FT–IR spectra were recorded with a Perkin–Elmer Spectrum One spectrometer. Routine UV–vis spectra were

recorded on a Shimadzu–UV 2550 spectrometer. Additional solution electronic absorption spectra were collected using a Hitachi U-3501 UV–Vis–NIR dual-beam spectrometer capable of scanning a wavelength region between 185 and 3200 nm. Spectral samples were dissolved in dry, degassed dichloromethane, and the electronic absorption spectra were measured in a 1-cm pathlength, 100 μ L, 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. Solid state resonance Raman (rR) spectra and associated rR excitation profiles were collected using a system comprised of an PI/Acton SpectraPro SP-2500i 500mm 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. A Coherent Innova I305 Ar⁺ ion laser was the excitation source. Samples were mixed with either NaCl or a NaCl/Na₂SO₄ mixture with Na₂SO₄ as an internal calibrant.

Electrochemistry

Cyclic voltammetric measurements were performed under dinitrogen with a Hokuto Denko HZ–3000 potentiostat. A set of a glassy–carbon working electrodes (circular, 3 mm diameter), a SCE reference electrode, and a platinum counter electrode was employed in these experiments.

X-ray Crystallography

Single crystals of (Et₄N)(Ph₄P)[Mo^{IV}O(S₂C₂(CO₂Me)₂)(bdt)] (**1a**) were obtained from an acetonitrile solution of **1** in the presence of Ph₄PBr. Single crystals of **4** and **6** were obtained by diffusion of diethyl ether into each acetonitrile solution. Single crystals of (Et₄N)₂[MoO₂(S₂C₂(CO₂Me)₂)₂] (**7**) were obtained by diffusion of diethyl ether into an acetonitrile solution containing **5** and Me₃NO. Each single crystal obtained was mounted on a glass fiber, and all X-ray data were collected at –173 °C on a Rigaku CCD diffractometer with monochromatic MoK α radiation. The structures were solved by direct methods²⁹ and expanded using DIRDIF 99.³⁰ The non–hydrogen atoms were refined anisotropically by full–matrix least squares on F^2 . The hydrogen atoms were attached at idealized positions on carbon atoms and were not refined. All structures in the final stages of refinement showed no movement in the atom positions. The calculations were performed using Single–Crystal Structure Analysis Software, version 3.8.³¹ Crystallographic parameters are summarized in Table 1.

Electronic Structure Calculations

Spin restricted gas phase geometry optimizations and vibrational frequency calculations for compounds **2**, **4**, and **6** were performed at the density functional level of theory using the Gaussian 03W software package.³² All calculations employed the B3LYP hybrid functional. A LANL2DZ basis set with an effective core potential was used for Mo and 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. Frontier molecular orbitals were generated for the optimized ground states of **2**, **4**, and **6**, and the contributions of each M.O. were further

analyzed using the program AOMix.³³ Time-dependent DFT calculations were performed on the optimized ground state geometries, and the first 40 excited states were calculated. Electron density difference maps (EDDMs) were constructed using the GaussSum suite of programs

Kinetic measurements

For the oxygen atom transfer reactivity studies, CH₃CN:H₂O (3:2) solutions of the Mo^{VI}O₂ complexes and NaAsO₂ were prepared under dinitrogen. The progress of the atom transfer reactions from Mo^{VI}O₂ species to NaAsO₂ were performed at 20 °C, and the reaction progress was monitored spectroscopically using an HP 5453 diode array spectrometer. Each reaction was initiated by the injection of a CH₃CN:H₂O solution of NaAsO₂ through the septum cap of the quartz cell using a gastight syringe. The reactions were performed under pseudo-first-order conditions with 10 – 70 equiv. excess of NaAsO₂ over [MoO₂]₀ (1.5 × 10⁻⁴ M).

Results and Discussion

Preparation and Characterization of Mo^{IV}O/Mo^{VI}O₂ Complexes with S₂C₂(CO₂Me)₂

The complex (Et₄N)₂[Mo^{IV}O(S₂C₂(CO₂Me)₂)(bdtCl₂)] (**3**) (S₂C₂(CO₂Me)₂ = 1,2-dicarbomethoxyethylene-1,2-dithiolate) was synthesized by a method previously used for the synthesis of (Et₄N)₂[Mo^{IV}O(S₂C₂(CO₂Me)₂)(bdt)] (**1**). Complex **3** was then used as a precursor for the synthesis of the corresponding Mo^{VI}O₂ complex, **4**. The IR, ¹H NMR, and negative-ion ESI-mass spectra of **3** were indicative of a mono-oxo Mo^{IV}O center coordinated with one S₂C₂(CO₂Me)₂²⁻ and one bdtCl₂²⁻ ligand. Compound **3** exhibits a reversible redox wave for the Mo^V/Mo^{IV} redox process at -0.11 V vs. SCE in acetonitrile. The potential is shifted by +0.13 V relative to **1** (-0.24 V) and this is an indication of a weaker bdtCl₂²⁻ S→Mo charge donation when compared with the bdt²⁻ ligand.

The mono-oxo Mo(IV) compounds **1** and **3** were treated with Me₃NO to yield the corresponding isolable Mo^{VI}O₂ complexes via oxygen atom transfer. Upon addition of Me₃NO to an acetonitrile solution of **1** or **3**, the color was observed to change from orange to deep-red. Deep-red microcrystalline powders of (Et₄N)(Ph₄P)[Mo^{VI}O₂(S₂C₂(CO₂Me)₂)(L)] (**2**: L = bdt²⁻, **4**: L = bdtCl₂²⁻) were precipitated from the resulting solutions by addition of a slight excess of Ph₄PBr. The elemental analysis and negative-ion ESI-MS data (Figures S1 and S2) for these deep-red powders were consistent with the corresponding molecular formulae for these complexes. We note that compounds **2** and **4** are the first Mo^{VI}O₂ complexes to be synthesized that possess two different dithiolene ligands. Compound **6** was generated in acetonitrile from its precursor **5**, Me₃NO, and Ph₄PBr to yield a deep-red solution. A quick workup of this solution yielded a brown microcrystalline powder. The synthesis of **6** is important, since [Mo^{VI}O₂(S₂C₂(CO₂Me)₂)]²⁻ had been assumed to be unstable for isolation due to an autoredox reaction between the Mo^{VI} ion and S₂C₂(CO₂Me)₂²⁻ ligands.^{12, 18} Compound **6** was characterized in a manner similar to that of **2** and **4**, and its negative ESI-mass spectrum is given in Figure S3. The three Mo^{VI}O₂ complexes, **2**, **4**, and **6**, exhibit temperature dependent ¹H NMR spectra. The temperature dependent spectrum for **4** is shown in Figure 2 as representative of the spectra for **2** and **6**.

The ^1H NMR spectrum of **4** in $(\text{CD}_3)_2\text{CO}$ displays two singlets at $\delta = 6.73$ and 3.59 ppm, assigned to the bdtCl_2^{2-} and $\text{S}_2\text{C}_2(\text{CO}_2\text{CH}_3)_2^{2-}$ protons, respectively. These signals broadened as the temperature of the solution was decreased to -85°C , and each singlet was observed to split into two singlets at -90°C . Upon cycling the temperature back to 25°C , the original ^1H NMR spectrum was regenerated. The spectral changes observed for **4** were independent of concentration. These results indicate that **4** exhibits a structural isomerization between Λ and Λ forms (50% : 50%). Compounds **2** and **6** also exhibit an isomerization behavior similar to that observed for **4**. The equation $G = RT_c = 22.96 + \ln(T_c/\delta v)$ was used to calculate G for the isomerization process, and these values are found to be 40, 39, and 42 k J mol^{-1} , for **2**, **4**, and **6**, respectively.³⁴

Crystal Structures of $\text{Mo}^{\text{IV}}\text{O}$ and $\text{Mo}^{\text{VI}}\text{O}_2$ Complexes

Although the synthesis of **1** was reported previously,¹⁴ the crystal structure of the (Et_4N) (Ph_4P) salt (**1a**) was determined in this work. The complex anion is shown in Figure 3 and the selected bond distances and angles are listed in Table 2. The Mo1 atom possesses a distorted square pyramidal geometry, with a terminal oxo, two sulfur atoms of bdt^{2-} , and two additional sulfur atoms of $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$, found in other structurally characterized bis(dithiolene) $\text{Mo}^{\text{IV}}\text{O}$ complexes including $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2]$ (**5**) and $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{IV}}\text{O}(\text{bdt})_2]$.^{11-13,28,35}

The crystal structure of the anionic part in **4** is shown in Figure 4, and the selected bond distances and angles are listed in Table 3. The Mo1 atom of **4** is coordinated by two oxo oxygen atoms (O1 and O2), two sulfur atoms (S1 and S2) from bdtCl_2^{2-} , and two sulfur atoms (S3 and S4) from $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$. The S2–S1–S3–S4 torsion angle describing the twist of the two dithiolene ligands relative to one another is 94.1° , indicative of a distorted octahedral geometry about the Mo1 center.³⁶ Similar to the crystal structures of $(\text{Ph}_4\text{P})_2[\text{Mo}^{\text{VI}}\text{O}_2(\text{bdt})_2]$,²⁷ $(\text{Ph}_4\text{P})_2[\text{Mo}^{\text{VI}}\text{O}_2(\text{mnt})_2]$,^{19, 27} and $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{VI}}\text{O}_2(\text{bdtCl}_2)_2]$,²³ the Mo1–S2 and Mo1–S4 bond distances ($2.5537(19)$ and $2.6555(16) \text{ \AA}$) are longer than the Mo1–S1 and Mo1–S3 distances ($2.431(2)$ and $2.4059(18) \text{ \AA}$) due to the fact that S2 and S4 are oriented *trans* to the O1 and O2 oxo atoms. The structure of the bdtCl_2^{2-} ligand in **4** is very similar to those observed in $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{VI}}\text{O}_2(\text{bdtCl}_2)_2]$,²³ reflecting π -delocalization with the aromatic ring. Interestingly, the S3–C7 ($1.731(9) \text{ \AA}$) and S4–C8 ($1.720(7) \text{ \AA}$) bond distances for the $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$ ligand are remarkably similar and do not reflect whether the S–C bonds are oriented *trans* or *cis* relative to the O2 oxo atom. The two S–C bond distances are significantly shorter than those observed in the $\text{Mo}^{\text{IV}}\text{O}$ complex, **1** ($1.77 \text{ \AA}$ (average)). Large dihedral angles (30.3° and 75.7° for S3C7C8S3–O3C7O4 and S3C7C8S3–O5C11O6, respectively) are observed between the S3C7C8S3 and CO_2Me planes in **4**. This is indicative of a reduced conjugation between the ene-1,2-dithiolate and the CO_2Me substituents.

Two independent complexes (molecules a and b) are found in the unit cell of **6**. Crystal structures of **6a** and **6b** are indicated in Figures 5 and S4, respectively. The two complex anions are different in the orientation of their $-\text{CO}_2\text{Me}$ groups with respect to the S–C–C–S plane (see Table 3). The stereochemistry about Mo1a is described as a distorted octahedron, and this is reflected by a S2aS1aS3aS4a dihedral angle (95.1°) close to the 90° . The S2a–

C2a (1.715(5) Å) and S4a–C8a (1.720(4) Å) bonds oriented *trans* to O1a and O2a are short due to the *trans* influence of the oxo groups. By comparison, the S–C bonds oriented *cis* to O1a and O2a are 1.776(4) Å and 1.756(4) Å, respectively. Interestingly, the S2a–C4a and S4a–C8a bond distances are shorter than the four S–C bonds (average distance, 1.76 Å) of the corresponding Mo^{IV}O complex, **5**, and C1a–C2a and C7a–C8a (1.357(6) and 1.359(7) Å) bond distances are longer than the two C=C bonds (1.31(1) and 1.33 Å) of **5**.²⁸ Although these comparisons of the dimensions of **5** and **6** sometimes become unwarrantable due to the standard deviations, values of the $\nu(\text{C}=\text{C})$ stretching bands based on the $\text{S}_2(\text{C}_2\text{CO}_2\text{Me})_2$ units of **5** (1535 cm⁻¹)³⁷ and **6** (1510 and 1494 cm⁻¹, vide infra) in the Raman spectra supports the comparisons. On the contrary, the dimensions of the $\text{S}_2(\text{C}_2\text{CO}_2\text{Me})_2^{2-}$ ligands in molecule **6a** are similar to those observed in $(\text{Ph}_4\text{P})_2[\text{Mo}^{\text{IV}}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_3]$. The average S–C and C–C bond distances in $(\text{Ph}_4\text{P})_2[\text{Mo}^{\text{IV}}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_3]$ are 1.74 and 1.35 Å, respectively, indicative of a large π -delocalization between the Mo and $\text{S}_2(\text{C}_2\text{CO}_2\text{Me})_2^{2-}$ units.³⁷ Collectively, the structural results indicate that $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$ of **6a** possesses a greater contribution of the dithione resonance form than is observed for bdt^{2-} or bdtCl_2^{2-} .

The geometry about the molybdenum center (Mo1b) in **6b** is also best described as a distorted octahedron and possesses an S2bS1bS3bS4b torsion angle of ca. 100°. For one of the **6b** $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$ ligands, the S2b–C2b bond distance (1.714(5) Å) *trans* to O1b is noticeably shorter than the S1b–C1b bond distance (1.747(4) Å) *cis* to the oxo ligand, similar to what was observed for **6a**. The second $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$ ligand possesses a S4b–C8b bond distance (1.742(5) Å) *trans* to O2b, which is close to that observed in the *cis* position (1.728(4) Å), rather the former is slightly longer than the latter. These S–C bond distance differences are not as significant as those observed in **6a**. The four S–C bonds are shorter than those observed in **5**, while the two C=C bonds are longer. These comparisons suggest that the $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$ ligands of **6b** also possess some dithione character. Although both **6a** and **6b** possess $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$ ligands with some dithione character, the primary structural differences between **6a** and **6b** likely result from crystal packing forces. The metric parameters for $(\text{Et}_4\text{N})_2[\text{MoO}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)]$ (**7**) are close to those observed in molecule **6a** but not **6b** as indicated by the distinctive shorter S2–C2 (1.709(4) Å) and S4–C8 (1.731(5) Å) as compared with S1–C1 (1.759(5) Å) and S3–C7 (1.758(5) Å) of **7**.

Spectroscopy and Electronic Structure

Despite the different ligand sets in **2**, **4**, and **6**, the solution electronic absorption spectra of the complexes are remarkably similar and display three bands below 30,000 cm⁻¹ (Figure 6). The d⁰ nature of the Mo(VI) ion and the magnitude of the extinction coefficients (~2,000–8,000 M⁻¹cm⁻¹) for these three bands clearly identify the transitions in this energy range are ligand-to-metal charge transfer (LMCT) in nature. Due to the spectral similarity between complexes **2**, **4**, and **6**, we will focus our discussion on compound **6**, whose Gaussian resolved solution electronic absorption spectrum is presented in Figure 7.

Although **2**, **4**, and **6** possess no molecular symmetry, the dominant di-oxo ligand field principally dictates the nature of the Mo d orbitals. These vacant d molecular orbitals are the lowest energy acceptor orbitals and they are depicted in Figure 8 for compound **6**. The

orbital plots are shown in Figure 8 at an isodensity value of 0.05 a.u. in order to more clearly depict the nature of the Mo d orbital component in these low-lying virtual molecular orbitals. The five lowest energy acceptor orbitals (LUMO-LUMO+4) possess d orbital functions that are π antibonding with respect to the two oxo ligands. The LUMO and LUMO+1 are the lowest energy orbitals due to their weak π interactions with the oxo ligands. Their relative energy ordering is a function of the $O_{oxo}-Mo-O_{oxo}$ bond angle, with more acute angles leading to an orbital reversal between LUMO and LUMO+1. The LUMO+2, LUMO+3, and LUMO+4 orbitals possess Mo d orbital functions that are more strongly π antibonding with respect to the oxo ligands due to the increased directionality of the π bond along the Mo- O_{oxo} bond axes, and this leads to their higher energy. Additionally, the LUMO+2, LUMO+3, and LUMO+4 orbitals possess dithiolene C=C antibonding character, which is not present to a large degree in the LUMO and LUMO+1. Thus, one-electron promotions to LUMO+2, LUMO+3, and LUMO+4 acceptor orbitals should result in larger excited state distortions along the C=C and symmetric $O_{oxo}-Mo-O_{oxo}$ stretching coordinates. The LUMO+5 and LUMO+7 are at higher energy due to the fact they are σ antibonding with respect to the two *trans* dithiolene sulfur donors. Therefore, LMCT transitions to LUMO+5 and LUMO+7 not likely to be observed in at energies less than $\sim 25,000\text{cm}^{-1}$. The LUMO+16 orbital is found at very high energy since the Mo d orbital component of this LUMO is σ antibonding with respect to the two oxo ligands and the *cis* dithiolene sulfur donors.

The bonding calculations indicate that the two highest occupied molecular orbitals (HOMO's) of the bis-dithiolene ligand set are comprised of in-phase and out-of-phase combinations of out-of-plane symmetric dithiolene sulfur p orbitals (HOMO and HOMO-1 in Figure 8), and this is in agreement with earlier work on mono-oxomolybdenum dithiolene complexes.^{8, 38} The HOMO-2 function is at deeper binding energy and can be described as an out-of-phase linear combination of out-of-plane dithiolene sulfur p orbitals localized on the *cis* dithiolene sulfur atoms (Figure 8). Further inspection of the calculated orbital energies indicates that HOMO0 and HOMO-1 are relatively close in energy ($E = 3,300\text{ cm}^{-1}$), while LUMO0 and LUMO+1 are nearly isoenergetic ($E = 1,800\text{ cm}^{-1}$) (Figure 8). The near degeneracy of the LUMO and LUMO+1 orbitals in **2**, **4**, and **6** is markedly different from what is observed in the 5-coordinate dioxo active site of sulfite oxidase, where a large splitting between the LUMO and LUMO+1 is observed.^{39, 40} The relevant HOMO and LUMO orbitals for **2** and **4** are virtually identical to those of **6** and are provided in the Supplementary Information (Figures S5 and S7).

Having described an active space of metal and ligand frontier orbital functions, we can now begin to describe the nature of the lowest energy LMCT transitions in **2**, **4**, and **6**. Energy considerations indicate that the lowest energy LMCT excitations should occur between the HOMO-1, HOMO, LUMO, and LUMO+1. Thus, there are four possible one-electron promotions that can occur between these orbitals and they should dominantly contribute to the lowest energy band. This is supported by the results of time-dependent DFT (TDDFT) calculations where it is found that two LMCT transitions (T2 and T3) arising from a linear combination of HOMO $\rightarrow$ LUMO+1 and HOMO-1 $\rightarrow$ LUMO one-electron promotions possess the highest oscillator strengths and dominate in their contribution to Band 1. The nature of the LUMO and LUMO+1 indicate that one-electron promotions to these acceptor

orbitals will result in excited state distortions along the totally symmetric $O_{oxo}-Mo-O_{oxo}$ bend and weaker excited state distortions along the symmetric $O_{oxo}-Mo-O_{oxo}$ stretch. The mixing of these two one-electron promotions is clearly evident in the electron density difference maps (EDDMs) that are shown in Figure 9. Transitions 5, 7, 9 and 10 are the LMCT transitions that principally contribute to the absorption envelope of Band 2. The calculations indicate that HOMO-1 $\rightarrow$ LUMO+1 (T4) and HOMO $\rightarrow$ LUMO+3 (T5) one-electron promotions contribute to the low energy side of Band 2. The dominant transition (T7) that contributes to Band 2 is principally comprised of HOMO-2 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+2 one-electron promotions. Additional LMCT transitions, assigned principally assigned as HOMO-1 $\rightarrow$ LUMO+3 (T9) and HOMO $\rightarrow$ LUMO+4 (T10) complete the high energy envelope of Band 2. The nature of the dominant LMCT transitions that comprise Band 2 are summarized in the EDMs shown in Figure 9. The electronic origin of Band 3 is markedly more complex than Bands 1 and 2 due to the large density of excited states expected in this spectral region.

The resonance Raman spectrum of **6** using 458 nm excitation is presented in Figure 10. We have observed Mo-(S_{dt})₄ and $O_{oxo}-Mo-O_{oxo}$ metal-ligand stretching modes as well as ligand based ene-1,2-dithiolate C-S and C=C stretches, and their corresponding vibrational frequencies are listed in Table 4. The frequency assignments have been assisted by direct spectral comparison with previously published Raman data for various DMSO reductase family enzymes as well as data for relevant $[Mo^{VI}O_2(dithiolene)_2]^{2-}$ model complexes.⁷ In general, the experimental vibrational frequencies for **2**, **4**, and **6** are in reasonable agreement with the DFT calculated frequencies for these modes (Table 4). Resonance Raman excitation profiles have been constructed for the dithiolene C=C stretches and the symmetric and antisymmetric $O_{oxo}-Mo-O_{oxo}$ stretches in compound **6**. The excitation profiles are shown superimposed on the Gaussian resolved electronic absorption spectrum in Figure 7. Collectively, the resonance Raman enhancement profiles provide strong support for our LMCT assignments and the nature of the lowest lying Mo based acceptor orbitals. Specifically, the observed larger resonance enhancement of the symmetric $O_{oxo}-Mo-O_{oxo}$ stretch upon excitation into the low energy side of Band 2 is fully consistent with the population of acceptor orbitals (LUMO+2,+3,+4) being strongly π antibonding with respect to both oxo ligands. The resonance Raman excitation profiles for the two ene-1,2-dithiolate C=C stretches in **6** indicate that both of the ene-1,2-dithiolates are involved in LMCT transitions to the Mo center. As indicated previously, the electronic origin of Band 3 is considerably more complex, and calculations indicate that it is comprised of numerous transitions of varying oscillator strength. However, calculations indicate that the HOMO-1 $\rightarrow$ LUMO+5 one-electron promotion predominates in the transition that principally contributes to the intensity of this band.

Bands 1-3 result from $S_{dithiolene}\rightarrow Mo$ charge transfer transitions, and their intensities are a direct reflection of the degree of $S_{dithiolene}\rightarrow Mo$ charge donation present in $[MoO_2(dithiolene)_2]^{2-}$ complexes. It is this charge donation that reflects Mo(VI) contributions to the Mo(VI/V) redox couple by reducing the hard donor stabilization of the Mo(VI) oxidation state and facilitating reductive processes at the metal. Oxygen atom transfer from $[MoO_2]^{2+}$ centers to oxygen atom acceptors represents a two-electron

reductive process at the Mo site, and it has been observed by some groups that a linear correlation exists between $E_{1/2}$ and the rate of oxygen atom transfer to PPh_3 has been observed.⁴¹ The implication here is that the activation energy for oxygen atom transfer possesses a considerable contribution from partial electron occupancy of the Mo(VI) LUMO at the transition state. Therefore, Mo-dithiolene covalency can modulate the reduction potential of $[\text{MoO}_2]^{2+}$ complexes by reducing the hard donor stabilization of the Mo(VI) state, leading to an increase in the rate of oxygen atom transfer to oxygen atom acceptors. Additionally, electron occupation of the LUMO along the reaction coordinate will assist in the cleavage of the Mo=O bond in oxygen atom transfer reactions with oxo acceptors due to the O=Mo=O π^* character of the LUMO. Since both the low-energy LUMO and LUMO+1 are weakly O=Mo=O π antibonding in these pseudo C_2 symmetry dioxo complexes, electron occupation of the LUMO and LUMO+1 will not make a substantial contribution to lowering the activation energy for oxygen atom transfer to yield a Mo(IV) mono-oxo complex. This is in marked contrast to the situation proposed for the five coordinate active site found in sulfite oxidizing enzymes, where the LUMO is *strongly* π antibonding with respect to a single oxo ligand. The similar LMCT spectra for **2**, **4**, and **6** imply very similar ligand field splitting patterns and similar degrees of Mo-dithiolene covalency. In the next section, we use the nature of the LMCT transitions and the corresponding electronic structures for these $[\text{MoO}_2(\text{dithiolene})]^{2-}$ complexes to gain insight into their relative oxygen atom transfer rates.

Oxygen atom transfer reactivity of $\text{Mo}^{\text{VI}}\text{O}_2$ complexes

We investigated oxygen atom transfer reactions from the $\text{Mo}^{\text{VI}}\text{O}_2$ complexes, **2**, **4**, and **6**, to AsO_2^- , which is a native substrate of the DMSOR family enzyme arsenite oxidase.⁹ Compounds **4** and **6** transferred a single oxygen atom to AsO_2^- to yield the corresponding $\text{Mo}^{\text{IV}}\text{O}$ species, **3** and **5**, and AsO_3^- stoichiometrically. In contrast, **2** disproportionated into 0.5 equiv. of $[\text{Mo}^{\text{VI}}\text{O}_2(\text{bdt})_2]^{2-}$ and 0.5 equiv. of **6** to eventually yield the corresponding $\text{Mo}^{\text{IV}}\text{O}$ species after a prolonged reaction time. As a result, we determined the rates of reaction for **4** and **6** with AsO_2^- spectroscopically. The time course of reaction for **4** is illustrated in Figure 11a. Here, the characteristic bands at 418 and 525 nm were observed to decrease in intensity with time, obeying pseudo-first order kinetics. The observed rate constant (k_{obs} , s^{-1}) was proportional to the AsO_2^- concentration, and saturation kinetics was not observed even at high AsO_2^- concentration (Figure 11b). Thus, this oxygen atom transfer was analyzed as a second order reaction, $v = k[\text{MoO}_2][\text{AsO}_2^-]$, and the rate constant k was calculated to be $2.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. Oxygen atom transfer from **6** to AsO_2^- was also analyzed as a second order reaction and its rate constant k was determined to be $2.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. These two rate constants are identical. In molybdenum complexes that show a reversible Mo(VI)/Mo(V) process, the redox potential value is one of good indications for rate dependency and a reaction mechanism in oxygen atom transfer reactivity,⁴²⁻⁴⁴ however, the irreversible shape of the process of **4** and **6** and the little difference of the potential values prevent us further discussing the oxygen atom transfer reactivity. This result is consistent with the observation of similar LMCT spectra for these complexes as well as similar Mo=O bond strengths inferred from their $\text{O}_{\text{oxo}}\text{-Mo-O}_{\text{oxo}}$ stretching frequencies (873 cm^{-1} for **4** and 869 cm^{-1} for **6**).

Conclusions

We have shown that $\text{Mo}^{\text{VI}}\text{O}_2$ complexes with either one aliphatic ene-1,2-dithiolate ligand ($\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$) (**2** and **4**) or two aliphatic ene-1,2-dithiolate ligands (**6**) are isolable. This has enabled their structures to be determined by X-ray crystallography as well as detailed investigations of their solution structure, oxygen atom transfer reactivity, and electronic structure by variable-temperature ^1H NMR, electronic absorption, resonance Raman spectroscopies. The crystallographic, computational, and spectroscopic results indicate the presence of considerable π -delocalization between the $\text{Mo}^{\text{VI}}\text{O}_2$ and ($\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$) units. This is interpreted to result in a greater $\text{Mo}^{\text{VI}}\text{-S}$ bond covalency in **2**, **4**, and **6** as compared with $[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2]^{2-}$. Solution electronic absorption spectra and resonance Raman excitation profiles have allowed assignment of the lowest energy LMCT transitions in **2**, **4**, and **6**. Variable-temperature NMR spectra of the $\text{Mo}^{\text{VI}}\text{O}_2$ complexes indicated an isomerization between σ and Λ forms of an octahedral structure in $(\text{CD}_3)_2\text{CO}$. Finally, the kinetic studies of the $\text{Mo}^{\text{VI}}\text{O}_2$ complexes have provided insight into the relationship between their electronic structure and oxygen atom transfer reactivity.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgement

This work was partly supported by a grant for Scientific Research (No. 20550067 to H. S.) from the Japan Society for Promotion of Science. M.L.K. acknowledges the National Institutes of Health (GM-057378) for financial assistance.

References

1. Hille R. Chem. Rev. 1996; 96:2757–2816. [PubMed: 11848841]
2. Hille, R. Molybdenum enzymes containing the pyranopterin cofactor: An overview. Vol. 39. Marcel Dekker, Inc.; New York: 2002. p. 187-226.
3. Li H-K, Temple C, Rajagopalan KV, Schindelin H. J. Am. Chem. Soc. 2000; 122:7673–7680.
4. Garton SD, Temple CA, Dhawan IK, Barber MJ, Rajagopalan KV, Johnson MK. J. Biol. Chem. 2000; 275:6798–6805. [PubMed: 10702237]
5. Cobb N, Conrads T, Hille R. J. Biol. Chem. 2005; 280:11007–11100. [PubMed: 15649898]
6. Finnegan MG, Hilton J, Rajagopalan KV, Johnson MK. Inorg. Chem. 1993; 32:2616–2617.
7. Johnson MK. Prog. Inorg. Chem. 2004; 52:213–266.
8. Kirk ML, Helton ME, McNaughton RL. Prog. Inorg. Chem. 2004; 52:111–212.
9. Conrads T, Hemann C, George GN, Pickering IJ, Prince RC, Hille R. J. Am. Chem. Soc. 2002; 124:11276–11277. [PubMed: 12236735]
10. Garton SD, Hilton J, Oku H, Crouse BR, Rajagopalan KV, Johnson MK. J. Am. Chem. Soc. 1997; 119:12906–12916.
11. Sugimoto H, Tsukube H. Chem. Soc. Rev. 2008; 37:2609–2619. [PubMed: 19020675]
12. Enemark JH, Cooney JJA. Chem. Rev. 2004; 104:1175–1200. [PubMed: 14871153]
13. McMaster, J.; Tunney, JM.; Garner, CD. Chemical Analogues of the Catalytic Centers of Molybdenum and Tungsten Dithiolene-Containing Enzymes. Vol. 52. John Wiley and Sons, Inc; Hoboken, New Jersey: 2004. p. 539-584.

14. Sugimoto H, Suyama K, Sugimoto K, Miyake H, Takahashi I, Hirota S, Itoh S. *Inorg. Chem.* 2008; 47:10150–10157. [PubMed: 18826211]
15. Sugimoto H, Harihara M, Shiro M, Sugimoto K, Tanaka K, Miyake H, Tsukube H. *Inorg. Chem.* 2005; 44:6386–6392. [PubMed: 16124818]
16. Lim BS, Holm RH. *J. Am. Chem. Soc.* 2001; 123:1920–1930. [PubMed: 11456813]
17. Oku H, Ueyama N, Nakamura A. *Inorg. Chem.* 1997; 36:1504–1516. [PubMed: 11669732]
18. Oku H, Ueyama N, Nakamura A. *Inorg. Chem.* 1995; 34:3667–3676.
19. Das SK, Chaudhury P, Biswas D, Sarkar S. *J. Am. Chem. Soc.* 1994; 116:9061–9070.
20. Burgmayer, SJN. *Dithiolenes in Biology*. Vol. 52. John Wiley and Sons, Inc.; Hoboken, New Jersey: 2004. p. 491–538.
21. Wang JJ, Holm RH. *Inorg. Chem.* 2007; 46:11156–11164. [PubMed: 18044955]
22. Sugimoto H, Tarumizu M, Miyake H, Tsukube H. *Eur. J. Inorg. Chem.* 2006:4494–4497.
23. Sugimoto H, Tarumizu M, Tanaka K, Miyake H, Tsukube H. *Dalton Trans.* 2005:3558–3565. [PubMed: 16234938]
24. Partyka DV, Holm RH. *Inorg. Chem.* 2004; 43:8609–8616. [PubMed: 15606212]
25. Lim BS, Willer MW, Miao MM, Holm RH. *J. Am. Chem. Soc.* 2001; 123:8343–8349. [PubMed: 11516283]
26. Donahue JP, Goldsmith CR, Nadiminti U, Holm RH. *J. Am. Chem. Soc.* 1998; 120:12869–12881.
27. Ueyama N, Oku H, Kondo M, Okamura T.-a. Yoshinaga N, Nakamura A. *Inorg. Chem.* 1996; 35:643–650.
28. Coucouvanis D, Hadjikyriacou A, Toupadakis A, Koo SM, Ileperuma O, Draganjac M, Salifoglou A. *Inorg. Chem.* 1991; 30:754–767.
29. Burla MC, Camalli M, Carrozzini B, Cascarano GL, Giacovazzo C, Polidori G, Spagna R. *J. Appl. Crystallogr.* 2003; 36:1103–1103.
30. Beurskens, PT.; Admiraal, G.; Beurskens, G.; Bosman, WP.; de Gelder, R.; Israel, R.; Smits, JMM. *The DIRDIF-99 program system*, Technical Report of the Crystallography Laboratory. University of Nijmegen; The Netherlands: 1999.
31. *Crystal Structure Analysis Package*. Rigaku and Rigaku/MS; The Woodlands, TX, USA: p. 2000–2006.
32. *Gaussian 03*. R. C. G., Inc.; Pittsburgh, PA: 2003.
33. Molecular orbitals were analyzed using the AOMix program [a, b]. Gorelsky SI. AOMix: Program for Molecular Orbital Analysis. 1997 York University Toronto <http://www.sh-chem.net/> Gorelsky SI, Lever ABP. *J. Organomet. Chem.* 2001; 635:187–196.
34. Tc and $\delta\nu$ are the coalescence point and the frequency difference between sites in the exchange system, respectively. (Abraham, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy*, John Wiley and Sons Ltd., England, 1988.) Tc = 193, 188, 203 K and $\delta\nu$ = 25.3, 29.6, and 28.1 Hz for 2, 4, and 6, respectively, were employed.
35. Boyde S, Ellis SR, Garner CD, Clegg W. *J. Chem. Soc., Chem. Commun.* 1986:1541–1543.
36. Webster CE, Hall MB. *J. Am. Chem. Soc.* 2001; 123:5820–5821. [PubMed: 11403624]
37. Subramanian P, Burgmayer S, Richard S, Szalaki V, Spiro TG. *Inorg. Chem.* 1990; 29:3849–3853.
38. Inscore FE, McNaughton R, Westcott BL, Helton ME, Jones R, Dhawan IK, Enemark JH, Kirk ML. *Inorg. Chem.* 1999; 38:1401–1410.
39. Peariso K, McNaughton RL, Kirk ML. *J. Am. Chem. Soc.* 2002; 124:9006–9007. [PubMed: 12148977]
40. Hemann C, Hood BL, Fulton M, Hansch R, Schwarz G, Mendel RR, Kirk ML, Hille R. *J. Am. Chem. Soc.* 2005; 127:16567–16577. [PubMed: 16305246]
41. a Topich J, Lyon JT. *Inorg. Chem.* 1984; 23:3202–3206. b Hammes BS, Chohan BS, Hoffman JT, Einwachter S, Carrano CJ. *Inorg. Chem.* 2004; 43:7800–7806. [PubMed: 15554645] c Basu P, Nemykin VN, Senger RS. *Inorg. Chem.* 2009; 48:6303–6313. [PubMed: 19485389]

42. Izumi Y, Glaser T, Rose K, McMaster J, Basu P, Enemark JH, Hedman B, Hodgson KO, Solomon EI. *J. Am. Chem. Soc.* 1999; 121:10035–10046.
43. Sung K-M, Holm RH. *J. Am. Chem. Soc.* 2002; 124:4312–4320. [PubMed: 11960460]
44. Kail BW, Perez LM, Zaric SD, Milar AJ, Young CG, Hall MB, Basu P. *Chem. Eur. J.* 2006; 12:7501–7509. [PubMed: 16865754]

Chart 1.
Designation and Abbreviation of Complex Structures

$X = \text{O}, \text{OH}, \text{O}\cdot\text{Ser}, \text{S}\cdot\text{Cys}, \text{O}\cdot\text{Asp}, \text{etc.}$

Figure 1.
Structure of molybdenum center of oxidized ($n=1$) and reduced ($n=0$) DMSOR family.

Figure 2.
VT ^1H NMR spectra of **4** in $(\text{CD}_3)_2\text{CO}$. Asterisk indicates water or impurity

Figure 3.
Crystal structure of the anionic part of $(\text{Et}_4\text{N})(\text{Ph}_4\text{P})[\text{MoO}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdt})]$ (**1a**) shown with 50% ellipsoids. The hydrogen atoms were omitted for clarity.

Figure 4. Crystal structure of the anionic part of $(\text{Et}_4\text{N})(\text{Ph}_4\text{P})[\text{MoO}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bdtCl}_2)]$ (**4**) shown with 50% ellipsoids. The hydrogen atoms were omitted for clarity.

Figure 5.
Crystal structure of one of the two independent anionic parts (a and b) in $(\text{Et}_4\text{N})(\text{Ph}_4\text{P})[\text{MoO}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2]$ (**6**) shown with 50% ellipsoids. The hydrogen atoms were omitted for clarity.

Figure 6. Solution electronic absorption spectra for **2** (black), **4** (red), and **6** (blue). Extinction coefficients have been normalized to the 18,000 cm^{-1} band for comparative purposes.

Figure 7.

Gaussian resolved electronic absorption and resonance Raman excitation profiles for **6**.

Resonance Raman excitation profiles are shown for the 867 cm^{-1} symmetric $\text{O}_{\text{oxo}}\text{-Mo-O}_{\text{oxo}}$ stretch (red), 1494 cm^{-1} C=C stretch (green), 1510 cm^{-1} C=C stretch (blue), and 834 cm^{-1} asymmetric $\text{O}_{\text{oxo}}\text{-Mo-O}_{\text{oxo}}$ stretch (black).

Figure 8.

Calculated active space HOMO and LUMO wavefunctions for $[\text{MoO}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2]^{2-}$ depicted at an isodensity value of 0.05 a.u.

Figure 9.

Calculated electron density difference maps (EDDMs) for Transitions 2, 3, 4, 5, 7, 9, and 10 for $[\text{MoO}_2(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2]^{2-}$ depicted at an isodensity value of 0.005 a.u. Transitions 2 and 3 are the dominant contributors to Band 1 and Transitions 4, 5, 7, 9, and 10 are the dominant contributors to Band 2. Red regions indicate a loss of electron density in a transition to the excited state and green regions indicate a gain of electron density in a transition to the excited state.

Figure 10.

Low frequency (A) and high frequency (B) resonance Raman spectrum of **6** using 458 nm excitation. Raman bands for the Na₂SO₄ internal standard are indicated with black dots. Vibrational assignments are given in Table 4.

Figure 11.

(a) Spectral change of **4** (1.5×10^{-4} M) reacted with NaAsO₂ (7.5×10^{-3} M) in CH₃CN–H₂O (3:2) at 20 °C, recorded every 60 second. (b) Pseudo-first-order rate constants k_{obs} as a function of [NaAsO₂].

Table 1Crystallographic Data for **1a**, **4**, **6**, and **7**

	1a	4	6	7
formula	C ₄₄ H ₅₀ MoNO ₅ PS ₄	C ₄₄ H ₄₈ MoNO ₆ PS ₄ Cl ₂	C ₈₈ H ₁₀₄ Mo ₂ N ₂ O ₂₀ P ₂ S ₈	C ₂₈ H ₅₂ MoN ₂ O ₁₀ S ₄
fw	928.04	1012.93	2020.10	800.91
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pc</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	12.769(3)	18.557(4)	17.610(2)	16.367(7)
<i>b</i> , Å	19.816(4)	12.900(2)	13.596(1)	10.809(4)
<i>c</i> , Å	17.395(3)	19.479(5)	19.795(2)	21.510(9)
β , deg	94.392(3)	104.704(5)	103.658(3)	108.404(6)
<i>V</i> , Å ³	4388.4(15)	4510.4(17)	4605.3(8)	3611(3)
<i>Z</i>	4	4	2	4
ρ , g cm ⁻³	1.405	1.492	1.457	1.473
μ , mm ⁻¹	0.570	0.677	0.557	0.647
data	35262	44183	44597	32195
unique data	9950	9731	18153	10007
<i>R</i> 1 ^{<i>a</i>}	0.0450	0.0897	0.0470	0.0715
<i>wR</i> 2 (F ²) ^{<i>b</i>}	0.1318	0.1598	0.1265	0.2373
GOF	1.000	0.868	0.975	1.081

^{*a*} $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|.$

^{*b*} $wR2 = \{\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2\}^{1/2}.$

Table 2Selected Bond Distances (Å) and Angles (deg) of **1a**

1a			
Mo(1)–O(1)	1.696(2)	Mo(1)–S(1)	2.3785(8)
Mo(1)–S(2)	2.3905(8)	Mo(1)–S(3)	2.3863(8)
Mo(1)–S(4)	2.3988(8)	S(1)–C(1)	1.776(3)
S(2)–C(2)	1.774(3)	S(3)–C(7)	1.774(3)
S(4)–C(8)	1.753(3)	C(1)–C(2)	1.386(4)
C(7)–C(8)	1.356(4)	Mo(1)–4S plane	0.75
O(1)–Mo(1)–S(1)	108.75(8)	O(1)–Mo(1)–S(2)	107.05(8)
O(1)–Mo(1)–S(3)	109.98(8)	O(1)–Mo(1)–S(4)	107.24(8)
S(1)–Mo(1)–S(3)	141.26(2)	S(2)–Mo(1)–S(4)	145.70(2)
S(1)Mo(1)S(2)–S(1)C(1)C(2)S(2) ^a	8.097	S(3)Mo(1)S(4)–S(3)C(7)C(8)S(4) ^a	12.647

^a dihedral angle

Table 3Selected Bond Distances (Å) and Angles (deg) of **4**, **6**, and **7**.

	4	6a	6b	7
Mo(1)–O(1)	1.736(4)	1.725(3)	1.724(3)	1.732(3)
Mo(1)–O(2)	1.716(5)	1.719(3)	1.748(3)	1.739(3)
Mo(1)–S(1)	2.431(2)	2.4400(14)	2.4126(14)	2.4408(12)
Mo(1)–S(2)	2.5537(19)	2.6522(12)	2.6255(15)	2.6260(13)
Mo(1)–S(3)	2.4059(18)	2.4335(13)	2.4400(14)	2.4234(11)
Mo(1)–S(4)	2.6555(16)	2.6099(15)	2.5712(13)	2.6234(11)
S(1)–C(1)	1.747(10)	1.776(4)	1.747(4)	1.759(5)
S(2)–C(2)	1.740(9)	1.715(5)	1.714(5)	1.709(4)
S(3)–C(7)	1.731(9)	1.756(4)	1.728(4)	1.758(5)
S(4)–C(8)	1.720(7)	1.720(4)	1.742(5)	1.731(5)
C(1)–C(2)	1.394(11)	1.357(6)	1.377(7)	1.370(6)
C(7)–C(8)	1.355(11)	1.361(7)	1.359(6)	1.342(5)
O(1)–Mo(1)–O(2)	103.6(2)	104.48(17)	103.10(16)	102.93(16)
O(1)–Mo(1)–S(1)	82.78(19)	85.01(12)	82.74(11)	83.79(12)
O(1)–Mo(1)–S(3)	113.46(18)	105.79(11)	108.84(12)	109.05(13)
S(1)–Mo(1)–S(3)	161.13(8)	160.49(4)	160.18(4)	158.10(4)
S(2)S(1)S(3)S(4) ^a	94.1	95.1	99.7	99.4
S–C=C–S	30.3, 75.7	20.2, 62.8	4.09, 89.5	5.71, 79.0
–OCO ^b		20.4, 68.8	77.4, 18.8	2.4, 88.0
S(1)Mo(1)S(2)–S(1)C(1)C(2)S(2) ^b	21.5	5.5	6.4	6.4
S(3)Mo(1)S(4)–S(3)C(7)C(8)S(4) ^b	4.16	14.9	5.1	12.5

^aTorsion angle.^bdihedral angle

Table 4Summary of Resonance Raman Data for Compounds **2**, **4**, and **6**.

Compound 2	Frequency (cm ⁻¹) (observed)	Frequency (cm ⁻¹) (calculated)
Vibrational Mode		
Mo-(S _{dt}) ₄ (<i>sym</i>)	360	352
O _{oxo} -Mo-O _{oxo} (<i>sym</i>)	870	946
O _{oxo} -Mo-O _{oxo} (<i>anti</i>)	834	906
C-S stretch	764	764
C=C stretch	1497	1512
Compound 4		
Vibrational Mode		
Mo-(S _{dt}) ₄ (<i>sym</i>)	360	352
O _{oxo} -Mo-O _{oxo} (<i>sym</i>)	871	949
O _{oxo} -Mo-O _{oxo} (<i>anti</i>)	838	909
C-S stretch	765	765
C=C stretch ^a	1497	1516
Compound 6		
Vibrational Mode		
Mo-(S _{dt}) ₄ (<i>sym</i>)	360	353
O _{oxo} -Mo-O _{oxo} (<i>sym</i>)	867	944
O _{oxo} -Mo-O _{oxo} (<i>anti</i>)	838	922
C-S stretch	764	765
C=C stretch ^a	1494/1510	1510/1538

^aNote: there are two distinct molecules of **6** in the unit cell.