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A Model for Active-site Formation Process in DMSO Reductase Family Molybdenum Enzymes Involving Oxido-alcoholato- and Oxido-thiolato-molybdenum(VI) Core Structures

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Abstract

New bis(ene-1,2-dithiolato)-oxido-alcoholato-molybdenum(VI) and -oxido-thiolato-molybdenum(VI) anionic complexes, denoted as $[\text{Mo}^{\text{VI}}\text{O}(\text{ER})\text{L}_2]^-$ ($\text{E} = \text{O}, \text{S}$; $\text{L} =$ dimethoxycarboxylate-1,2-ethylenedithiolate), have been obtained from the reaction of the corresponding dioxido-moybdenum(VI) precursor complex with either an alcohol or a thiol in the presence of an organic acid (e.g. 10-camphorsulfonic acid) at low temperature. The $[\text{Mo}^{\text{VI}}\text{O}(\text{ER})\text{L}_2]^-$ complexes have been isolated and characterized, and the structure of $[\text{Mo}^{\text{VI}}\text{O}(\text{OR})\text{L}_2]^-$ has been determined by X-ray crystallography. The Mo(VI) center in $[\text{Mo}^{\text{VI}}\text{O}(\text{OR})\text{L}_2]^-$ exhibits a distorted octahedral geometry with the two ene-1,2-dithiolate ligands being symmetry inequivalent. The computed structure of $[\text{Mo}^{\text{VI}}\text{O}(\text{SR})\text{L}_2]^-$ is essentially identical to that of $[\text{Mo}^{\text{VI}}\text{O}(\text{OR})\text{L}_2]^-$. The electronic structures of the resulting molybdenum(VI) complexes have been evaluated using electronic absorption spectroscopy and bonding calculations. The nature of the distorted O_h geometry in these $[\text{Mo}^{\text{VI}}\text{O}(\text{EEt})\text{L}_2]^-$ complexes results in a LUMO wavefunction that possesses strong π^* interactions between the $\text{Mo}(\text{d}_{xy})$ orbital and the *cis* $\text{S}(\text{p}_z)$ orbital localized on one sulfur donor from a single ene-1,2-dithiolate ligand. The presence of covalent $\text{Mo}-\text{S}_{\text{dithiolene}}$ bonding interaction in these monooxido Mo(VI) compounds contributes to

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Supporting Information

Experimental details, Figures S1–S8 and Tables S1–S2. Additional computational data, including coordinates and energies for all described stationary structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

their low energy LMCT transitions. A second important d-p π bonding interaction derives from the $\sim 180^\circ$ O_{oxo}-Mo-*E*-C dihedral angle involving the alcoholate and thiolate donors, and this contributes to ancillary ligand contributions to the electronic structure of these species. The formation of [Mo^{VI}O(OEt)L₂][−] and [Mo^{VI}O(SET)L₂][−] from the dioxidomolybdenum(VI) precursor may be regarded as a model for the active-site formation process that occurs in the DMSO reductase family of pyranopterin molybdenum enzymes.

Graphical Abstract

Bis(ene-1,2-dithiolato)-oxido-alcoholato-molybdenum(VI) and -oxido-thiolato-molybdenum(VI) complexes are prepared by the reaction of the dioxido-molybdenum(VI) complex and either alcohols or hexanethiol in the presence of 10-camphorsulfonic acid. The complexes exhibit significant π -delocalization between the molybdenum(VI) atom and one of the ene-1,2-dithiolate ligands. The Mo(d_{xy}) and *cis* S(p_z) interactions are responsible for the lower energy charge transfer bands. The LUMO has little contribution of the alcoholate ligand whereas the thiolate ligand significantly contributes to the orbital.

INTRODUCTION

Pyranopterin molybdenum (Mo) enzymes are found in nearly all organisms and catalyze a wide variety of important chemical transformations that are involved in global carbon, nitrogen, and sulfur biogeochemical cycles.^{1–4} The most abundant form of Mo in Nature is the biologically active molybdate ion, MoO₄^{2−}. Molybdate enters the cell via active transport processes where it can be coordinated by the ene-1,2-dithiolate of molybdopterin (MPT). For enzymes of the dimethyl sulfoxide reductase (DMSOR) family, molybdate is converted to a mono-Mo-MPT form and, then, to a bis-Mo-MPT form, also referred to as Moco (MoO_n(MPT)₂ (n = 1 or 2)), by a MobA protein.^{5–8} Here, the Mo ion is ligated by the dithiolene chelates of two separate MPTs (Figure 1) and one or two terminal oxide ligands.^{5–8} Although the biosynthesis of MPT has been elegantly investigated,^{1–8} the insertion of Moco into DMSOR family apo-enzymes is still the subject of active investigation.^{9,10} It is known that specific Moco binding chaperones are required for insertion of Moco into apoenzymes of the DMSOR family in order to form catalytically competent holoenzymes. A sixth ligand is typically found to bind to the Mo ion in active enzyme forms, which may be a serine (-OH), cysteine (-SH), selenocysteine (-SeH), aspartate (-COOH), or hydroxide.^{11–14} Open questions remain regarding the nature of the core structure of the transferred Moco and how the sixth ligand is incorporated into the active site, although it is hypothesized that either a dioxidomolybdenum(VI) (Mo^{VI}O₂, n = 2) or a monooxidomolybdenum(IV) (Mo^{IV}O, n = 1) form (Figure 1, left) of bis-Mo-MPT represents the structure of the cofactor prior to coordination of the sixth ligand.^{9,10} Mo^{VI}O₂

($n = 2$) form will give a $\text{Mo}^{\text{VI}}\text{O}(\text{ER})$ ($E = \text{O}, \text{S}, \text{or Se}$) active site upon a reaction with $-\text{EH}$ of an apo enzyme whereas $\text{Mo}^{\text{IV}}\text{O}$ ($n = 1$) form will give a $\text{Mo}^{\text{IV}}(\text{ER})$ active site by a reaction with $-\text{EH}$ of an apo enzyme. Furthermore, full characterization of the resulting holo-enzyme active sites, particularly when in the $\text{Mo}(\text{VI})$ oxidation state, remains difficult due to the instability resulting from potential overoxidation of the MPT, thiolate, and/or selenate ligands as well as hydrolytic reactions at the $\text{Mo}(\text{VI})$ center.^{1–3} Thus, it is of fundamental importance to understand whether a $\text{Mo}-\text{ER}$ ($E = \text{O}, \text{S}, \text{or Se}$) bond can be formed by the reaction of a $\text{Mo}^{\text{VI}}\text{O}_2$ or $\text{Mo}^{\text{IV}}\text{O}$ center with either an alcohol, thiol, or selenol. In this manuscript, we use small molecule analogs to interrogate this reaction chemistry and probe electronic structure differences as a function of $-\text{SR}$ and $-\text{OR}$ ancillary ligation in well-defined model systems.

In modeling studies of pyranopterin molybdenum enzyme active sites, there have been no attempts reproduce the proposed formation step of the catalytically competent molybdenum sites found in DMSOR family enzymes.^{15–19} Although some excellent model compounds have been synthesized that mimic reduced DMSOR active sites, including *des*-oxido bis(ene-1,2-dithiolato)(ER)molybdenum(IV) complexes ($E = \text{O}, \text{S}, \text{Se}$; $\text{R} = \text{alkyl}$), their preparation methods are different from that proposed for the formation of the enzyme active sites (Figure 1).^{20–24} In this study, we have generated monooxido $\text{Mo}^{\text{VI}}\text{O}(\text{OR}/\text{SR})$ complexes by the reaction of a dioxido $\text{Mo}^{\text{VI}}\text{O}_2$ complex with an alcohol or a thiol, which can be regarded as a model reaction for active site formation in DMSOR family enzymes. Here, both $\text{Mo}^{\text{VI}}\text{O}_2$ and $\text{Mo}^{\text{IV}}\text{O}$ complexes ($\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2$ and $\text{Mo}^{\text{IV}}\text{OL}_2$) of dimethoxycarboxylate-1,2-ethylenedithiolate (L) were employed as the Moco models (see, Chart 1).^{25,26}

EXPERIMENTAL SECTION

General

All reagents and solvents were used as received unless otherwise noted. All reactions were carried out under a dinitrogen or an argon atmosphere using standard Schlenk techniques or a Miwa D80-1KP glovebox. Propionitrile was dried with CaH_2 and then P_2O_5 and distilled under dinitrogen atmosphere prior to use. $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]$ ($[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$) was prepared by following the established literature procedure.²⁶

Synthesis and Characterization of Complexes

$(\text{Ph}_4\text{P})[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]$ —Under an Ar atmosphere, 4 mL of ethanol was added to a 1 mL acetonitrile solution of $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]$ (60.7 mg, 75.8 μmol). This mixture was cooled to -40°C , and an acetonitrile solution of 10-camphorsulfonic acid (207 mM, 380 μL , 78.7 μmol) was added. The color of the brown solution then changed to purple. To the purple solution, 2 mL of an ethanol solution of Ph_4PBr (125.3 mg, 298.7 μmol) was added, and the solution was concentrated to ca. 500 μL to yield a deep-purple solid. The solid was collected by filtration and washed with ethanol and ether to yield a deep-purple solid product. Yield 48.5 mg, 53.4 μmol (70%). Anal. Calcd. for $\text{C}_{38}\text{H}_{37}\text{MoO}_{10}\text{PS}_4$ (MW = 908.88): C 50.22; H 4.10; N 0.00. Found: C 50.36; H 4.28; N 0.00%. ^1H NMR (CD_3CN , anionic part): δ 4.10 (q, $J = 6.8$ Hz, 2H), 3.72 (s, 12H), 1.33 (t, $J = 6.8$ Hz, 3H). UV-vis (acetonitrile): $\lambda_{\text{max}} = 539$ nm

(ε = 2380 M⁻¹ cm⁻¹), 742 (1470). CSI-MS (CH₃CN): 570.9 [M]⁻. IR (KBr): 890 cm⁻¹ (Mo=O). CV (0.1 V s⁻¹, CH₃CN): $E_{1/2}$ (quasi-rev.) = -0.52 V vs. SCE.

Generation of [Mo^{VI}O(SC₆H₁₃)L₂]⁻ Complex—A typical procedure is follows: 25 μ L of a propionitrile solution of 10-Camphorsulfonic acid (20.0 mM) was added to 5 mL of a propionitrile solution containing [Mo^{VI}O₂L₂]²⁻ (1.0 mM) and 1-hexanethiol (100.0 mM) at -80 °C through a septum cap of the quartz cell using a gastight syringe.

Electronic Structure Calculations—Gas-phase geometry optimizations, electronic structure, and spectroscopic calculations for [Mo^{VI}O(EEt)L₂]⁻ (E = O or S) were performed at the density functional level of theory (DFT) using the Gaussian 09 revision C. 01 software package.²⁷ The calculations utilized the PBE^{28,29} exchange-correlation functional with the def2-tzvp basis set³⁰ for all atoms and an effective core potential on Mo.³¹ The def2-tzvp basis set and effective core potential were obtained from the EMSL basis set exchange website.^{32,33} Orbital compositions were obtained using the Mulliken population analysis method as implemented in Gaussian 09.³⁴ Orbital compositions were analyzed utilizing AOMix Revision 6.51.^{35,36} Electronic transitions were computed using time dependent DFT (TD-DFT) methods as implemented in Gaussian 09.³⁷⁻⁴³ The Cartesian coordinates of [Mo^{VI}O(OEt/SEt)L₂]⁻ are listed in Tables S1 and S2.

Physical Measurements—FT-IR spectra were recorded using a Jasco FT-IR 4100 spectrometer. Resonance Raman data were collected using a He-Cd laser (Kimmon Koha, IK5651R-G) with an excitation wavelength of 441.6 nm. The scattered radiation was dispersed by a 1m single grating spectrograph (Ritsu Oyo Kogaku, MS-100DG) and the Raman scattered light was detected using a liquid nitrogen cooled CCD detector (Horiba Jobin Yvon, Symphony CCD-1024 256-OPEN-1LS). The resonance Raman measurements were collected with the sample in a spinning NMR tube cooled to -40 °C using flash cooled dinitrogen gas. ¹H NMR spectra were recorded on a JEOL Lambda 300 NMR spectrometer and the TMS signal was adjusted to 0 ppm. UV-vis spectra were recorded on an HP-8453 spectrophotometer equipped with a Unisoku thermostat cell holder (USP-203). CSI-MS (cryospray ionization mass spectra) data were collected using a BRUKER cryospray micrOTOFII.

Electrochemistry—Cyclic voltammetric measurements were performed under a dinitrogen atmosphere using a Hokuto Denko HZ-3000 potentiostat. The electrode set employed in these experiments consisted of a glassy-carbon working electrode (circular, 3 mm diameter), a SCE reference electrode and a platinum counter electrode.

X-ray Crystallography—A single crystal of (PPh₄)[Mo^{VI}O(OEt)L₂] $\cdot$ acetone was deep-purple and was obtained by vapor diffusion of diethyl ether into an acetone solution of the (Et₄N)[Mo^{VI}O(OEt)L₂] in the presence of slight excess of PPh₄Br at -40 °C. A single crystal of (PPh₄)[Mo^{VI}O(OEt)L₂] $\cdot$ acetone was mounted on a loop, and all measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-K α radiation at -180 °C. The structures were solved by direct methods (SIR2011) and refined anisotropically by full-matrix least squares on F^2 .⁴⁴ The OEt ligand (O2C13C14 atoms) was disordered with respect to the orientation of the O1 (oxide)-Mo1-

O2–C13 dihedral angles. The disorder was solved with occupancies of 0.86 (main) and 0.14 (minor). The data of the main structure was employed for discussion. 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 the Single–Crystal Structure Analysis Software, version 3.8.⁴⁵ Crystallographic parameters are summarized in Table 1.

RESULTS AND DISCUSSION

Formation and Characterization of Oxido-alcoholato- and Oxido-thiolato-molybdenum(VI) Complexes

The $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ complex is stable in an acetonitrile solution even in the presence of an excess amount of ethanol (EtOH). However, addition of a strong organic acid such as 10-camphorsulfonic acid (CSA) to a propionitrile solution of $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ (0.1 mM) containing 0.5 % ethanol (0.86 mM) at -60°C resulted in a color change from orange to purple.⁴⁶ The course of this reaction was followed by UV–vis spectroscopy, and the data that are presented in Figure 2a. The absorption bands at 360 and 423 nm due to $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ decrease in intensity with the concomitant appearance of the new absorption bands at 539 and 742 nm with a clear isosbestic point at 473 nm. The final spectrum exhibits absorption bands at $\lambda_{\text{max}} = 539\text{ nm}$ ($\varepsilon = 2430\text{ M}^{-1}\text{ cm}^{-1}$) and 742 nm (2130), which are close to those observed for the oxido-siloxido-molybdenum(VI) complex, $[\text{Mo}^{\text{VI}}\text{O}(\text{OSi}^{\text{iPr}}\text{Pr}_3)\text{L}_2]^-$ ($\lambda_{\text{max}} = 563\text{ nm}$ ($\varepsilon = 4301\text{ M}^{-1}\text{ cm}^{-1}$) and 729 (1280) in acetonitrile),^{47,48} suggesting the formation of the expected product $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$. The titration curves based on absorbance changes at 360, 539, and 742 nm are shown in the inset of Figure 2a, which clearly indicate the 1 : 1 stoichiometry of $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$: CSA. The CSI-mass spectrum of a propionitrile-ethanol (200 : 1) solution of $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ in the presence of one equiv of CSA taken at -60°C exhibited a peak cluster at $m/z = 570.9$ (Figure 2b). The isotope distribution pattern is consistent with the molecular formula of the oxido-ethanolato-molybdenum(VI) complex, $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ (Figure S1). On the basis of electronic absorption and CSI mass spectrometry data, we conclude that an oxido-ethanolato-molybdenum(VI) complex supported by two dithiolene ligands (L), $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$, has been generated from $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ by the reaction with ethanol in the presence of CSA at low temperature. This represents the first example of a bis(ene-1,2-dithiolato)oxido-alcoholato-molybdenum(VI) complex. Given the observed stoichiometry, the formation mechanism of $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ from $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ can be hypothesized as shown in Scheme 1. Protonation of one of the two oxide ligands in $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ yields an oxido-hydroxido-molybdenum(VI) center as an intermediate, from which a ligand exchange reaction takes place between OH^- and EtO^- to yield the observed $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ product. Since the UV-vis and CSI-mass spectra indicate that $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ remained intact in the absence of ethanol, the equilibrium between $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ and $[\text{Mo}^{\text{VI}}\text{O}(\text{OH})\text{L}_2]^-$ must lie far to the left, consistent with the general propensity for bis-dithiolene ligated Mo(VI) species to exist in a dioxidomolybdenum coordination environment.^{26, 49–51}

The PPh_4^+ salt of $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ was isolated as a black microcrystalline powder at -40°C by a cation exchange with PPh_4Br . The ^1H NMR spectrum and the elemental

analysis data are consistent with the expected molecular formula (see Experimental details). The $\text{Mo}^{\text{VI}} \equiv \text{O}$ stretch appeared at higher wavenumbers in the IR (KBr) spectrum when compared with those observed for the silyl alcoholate derivative (868 cm^{-1} , $(\text{Et}_4\text{N})[\text{Mo}^{\text{VI}}\text{O}(\text{OSi}^i\text{Pr}_3)\text{L}_2]$) and $(\text{Et}_4\text{N})[\text{Mo}^{\text{VI}}\text{O}(\text{OSi}^i\text{BuPh}_2)(\text{bdt})_2]$ (877 cm^{-1} , $\text{bdt} = 1,2$ -benzenedithiolate) and was observed at 890 cm^{-1} (Figure S2 (a)).⁵² The $\text{Mo}^{\text{VI}} \equiv \text{O}$ stretch was observed in the CH_3CN solution resonance Raman spectrum of $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ at 870 cm^{-1} (Figure S2 (b)). $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ displayed one quasi-reversible redox wave at -0.53 V vs. SCE in CH_3CN , which is assignable to the $\text{Mo}(\text{VI})/\text{Mo}(\text{V})$ redox couple. Bulk electrolysis at -0.65 V was used to reduce $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ to the corresponding $[\text{Mo}^{\text{V}}\text{O}(\text{OEt})\text{L}_2]^{2-}$, but this resulted in the formation of the $\text{Mo}^{\text{V}}\text{OL}_2$ complex with dissociation of the OEt^- ligand from the electrochemically generated molybdenum(V) center. Attempts to generate $[\text{Mo}^{\text{IV}}(\text{OEt})\text{L}_2]^-$ from the monooxido $\text{Mo}(\text{IV})$ complex, $[\text{Mo}^{\text{IV}}\text{OL}_2]^{2-}$, and ethanol in a manner similar to that employed for $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ were unsuccessful, and the molybdenum(IV) complex remained unchanged. These observations allow us to hypothesize that the bis-Mo-MPT transferred to apo DMSOR family enzymes may possess a bis(MPT)dioxidomolybdenum(VI) structure similar to that observed in $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$, with one of the two oxide donors being subject to protonation. This would yield a $[\text{Mo}^{\text{VI}}\text{O}(\text{OH})\text{L}_2]^-$ species with a more labile OH ligand that could bind to an apo-site serine residue with the aid of acid catalysis to yield the catalytically competent $[\text{Mo}^{\text{VI}}\text{O}(\text{OR})\text{L}_2]^-$ species in DMSOR. Since the ene-1,2-dithiolate ligand of $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ has $-\text{COOMe}$ electron-withdrawing substituents, a strong organic acid such as CSA may be requested for protonation to the one oxide ligand of $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$.

The reaction using $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ as a Moco model can be utilized to prepare other oxido-alcoholato-molybdenum(VI) derivatives. When 2-propanol and benzyl alcohol were employed in place of ethanol as the source of a monodentate ligand, the corresponding oxido-alcoholato-molybdenum(VI) derivatives, $[\text{Mo}^{\text{VI}}\text{O}(\text{OR})\text{L}_2]^-$, were obtained ($\text{R} = i\text{Pr}$ and CH_2Ph) at low temperature. These complexes were characterized by electronic absorption spectroscopy and CSI-mass spectrometry and are depicted in Figures S3 and S4, respectively. The solution ($\text{C}_2\text{H}_5\text{CN}$) absorption bands observed in the visible region of the spectrum are summarized in Table 2, where it can be seen that the two observed absorption bands vary slightly as a function of the nature of the alcoholato ligands. This overall similarity indicates that the electronic effects of the R groups are rather small.

In an effort to model relevant cofactor insertion chemistry in Type 1 DMSOR family enzymes (e.g. the periplasmic nitrate reductases, Nap) that possess a coordinated cysteine residue¹⁻⁴, we treated $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ with the organic acid CSA in the presence of a large excess of 1-hexanethiol in propionitrile at -80°C . This resulted in the formation of a deep-gray complex of $[\text{Mo}^{\text{VI}}\text{O}(\text{SC}_6\text{H}_{13})\text{L}_2]^-$ which we have characterized by electronic absorption spectroscopy and CSI-mass spectrometry (Figures 3 and S5). The absorption spectral changes from $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ to $[\text{Mo}^{\text{VI}}\text{O}(\text{SC}_6\text{H}_{13})\text{L}_2]^-$ proceeded with isosbestic points at 348, 461, 518, and 563 nm as shown in Figure S5 (a). The mass spectrum exhibited a peak cluster at $m/z = 642.9$ of which isotope distribution pattern is consistent with the calculated one as $[\text{Mo}^{\text{VI}}\text{O}(\text{SC}_6\text{H}_{13})\text{L}_2]^-$ (Figure S5 (b)). This complex is the first example of a bis(ene-1,2-dithiolato)oxido-thiolato-molybdenum(VI) complex. Many attempts to

isolate the thiolate complex were unsuccessful because of very high solubility of the complex due to the long $-C_6H_{13}$ chain. As shown in Figure 3, coordination of the hexanethiolate ligand in place of the alcoholate ligand at the molybdenum(VI) center results in a significant bathochromic shift of the absorption bands in the visible region ($\lambda_{\max} = 639$ and 774 nm). This suggests that the contribution of the thiolate ligand to the frontier orbitals is significant (*vide infra*).

Crystal Structure of Oxido-ethanolato-molybdenum(VI) and DFT Optimized Structure of Oxido-ethanthiolato-molybdenum(VI)

Single crystals of the oxido-ethanolato-molybdenum(VI) complex suitable for X-ray crystallography were obtained by recrystallization from acetone/diethyl ether at $-40\text{ }^{\circ}\text{C}$ in the presence of a slight excess amount of PPh_4Br . The asymmetric unit consists of one PPh_4^+ cation, one molybdenum(VI) complex anion, and one acetone molecule. The crystal structure of the anionic part is shown in Figure 4 (left). Selected bond lengths and angles are given in Table 3. The Mo1 atom is coordinated by one oxide oxygen atom (O1), one ethanolate oxygen atom (O2), and four sulfur atoms (S1 – S4) from the two dithiolene ligands (L^A and L^B). The S2–S1–S3–S4 torsion angle describing the twist of the two dithiolene ligands is 105° , indicating a distorted octahedral geometry around the Mo center, resulting in the two dithiolene ligands being symmetry inequivalent. The geometry around the Mo center is more distorted than the molybdenum(VI) center of $[\text{MoO}_2\text{L}_2]^{2-}$ and is similar to that of $(\text{Et}_4\text{N})[\text{Mo}^{\text{VI}}\text{O}(\text{OSi}^i\text{Pr}_3)\text{L}_2]$, which we have reported previously.^{26, 47} However, the Mo1–O2–C13 bond angle of $134.6(10)^{\circ}$ is significantly smaller than the Mo–O–Si bond angle of $164.04(16)^{\circ}$. Furthermore, the O1 oxygen atom interacts with one of the acetone methyl groups through a hydrogen bond ($3.16(3)\text{ \AA}$, Figure S7). This results in the Mo1–O1 bond length ($1.748(10)\text{ \AA}$) in $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$, being longer than that observed in $[\text{Mo}^{\text{VI}}\text{O}(\text{OSi}^i\text{Pr}_3)\text{L}_2]^-$ ($1.713(2)\text{ \AA}$). Similarly, in DMSOR the oxygen atom of the $\text{Mo}^{\text{VI}}\equiv\text{O}$ moiety interacts with Y114OH through hydrogen bonding.¹¹ The Mo1–S4 bond length of $2.521(3)\text{ \AA}$ is significantly longer than the other three Mo–S bonds ($2.396(3)$ for Mo1–S1, $2.464(4)$ for Mo1–S2, and $2.394(3)\text{ \AA}$ for Mo1–S3) due to the fact that S4 is oriented *trans* to the oxide oxygen atom, O1. The Mo1–S2 bond is also longer than the Mo1–S3 and Mo1–S3 bond due to *trans* influence of the ethoxide ligand. This asymmetric coordination mode of the four sulfur atoms is similar to that found in the crystal structure of DMSOR, where the two S atoms from one MPT ligand and one S atom from the another MPT ligand are at $2.4\text{ \AA}$ from the Mo center and the remaining Mo–S bond is at $3.1\text{ \AA}$.¹¹ The *trans* influence due to the O1 atom is responsible for the observed differences between the coordinating ligands L^A and L^B . The S4 atom on L^B is oriented *trans* to O1 and possesses a S4–C8 bond that is significantly shorter ($1.690(11)\text{ \AA}$) than that observed for the other three S–C bonds, which are oriented *cis* to O1 (S1–C1: $1.733(10)$, S2–C2: $1.724(12)$, and S3–C7: $1.750(10)\text{ \AA}$). As a result of the *trans* influence, the C7–C8 bond of L^B is longer ($1.374(16)\text{ \AA}$) than the C1–C2 C=C bond ($1.335(15)\text{ \AA}$) of the L^A ligand. Interestingly, the C7–C9 bond in the L^B ligand, $1.438(14)\text{ \AA}$, is shorter than that of the C8–C11 bond of $1.483(14)\text{ \AA}$. Regarding the orientation of the methyl ester moieties of L^B , the –C11–O9–O10–C12 group *trans* to the oxide oxygen atom possesses an 89.70° dihedral angle with respect to the chelating S3–C7–C8–S4 plane, while the dihedral angle consisting of the –C9–O7–O8–C10 group oriented *cis* to O1 atom and the S3–C7–C8–S4 plane is markedly

smaller (6.44 °). Thus, differences in Mo-S_{dithiolene} bond lengths appear to contribute to extended conjugation in L^B and to a lesser extent in L^A, as shown in Scheme 2. In general, the computed metric parameters for [Mo^{VI}O(OC₆H₁₃)L₂][−] are in agreement with those determined from x-ray crystallography.

We have not succeeded in obtaining single crystals of [Mo^{VI}O(SC₆H₁₃)L₂][−]. Thus, we have determined the molecular structure of this complex using DFT methods in order to make initial comparisons with the X-ray crystal structure of [Mo^{VI}O(OEt)L₂][−]. In these calculations, an ethanethiolate ligand has been used in place of the 1-hexanethiolate ligand and the optimized structure is presented in Figure 4 (right). The relevant bond lengths, bond angles, and the O1-Mo1-S5-C13 dihedral angle are given in Table 3 for comparison with [Mo^{VI}O(OEt)L₂][−]. The Mo center exhibits a distorted octahedral geometry as observed for structurally characterized [Mo^{VI}O(OEt)L₂][−]. The calculated Mo-S_{thiolate} bond length (Mo1-S5) of 2.42 Å is comparable to that observed in Tp^{*}Mo^{VI}O₂(SC₆H₅) (2.398 Å, Tp^{*} = Hydrotris(3,5-dimethyl-pyrazolyl)borate) and longer than the Mo-S_{thiolate} bond (2.380 Å) in the monooxido Mo(V) dithiolene compound [(L3S)MoO(bdt)] (bdt = benzene-1,2-dithiolate; L3SH = (2-dimethylethanethiol)-bis-(3,5-dimethylpyrazolyl)methane).^{53,54} The Mo(1)-S(4) distance is computed to be quite long (2.61 Å) and comparable to that observed experimentally in Mo^{VI}O₂(OEt)₂L₂.

Electronic Structure of Oxido-ethanolato- and Oxido-ethanthiolato-molybdenum(VI) Complexes

A key question remains regarding why specific amino acid ligands bind to certain classes of DMSOR family enzymes, particularly with respect to how this ligation contributes to the underpinning electronic structure that contributes to their unique reactivities. Our studies on the isostructural [Mo^{VI}O(OEt)L₂][−] and [Mo^{VI}O(SET)L₂][−] pair provides support for a hypothesis that states Mo-O_{serine} and Mo-S_{cysteine} ligation can result from the interaction of these amino acid donors with MoO(MPT)₂ Moco precursors, and further allows us to examine the effects of ancillary ligand (-OR, -SR) coordination on the electronic structures of these complexes at parity of the remaining coordination sphere.

The electronic absorption spectrum of [Mo^{VI}O(OEt)L₂][−] (742 nm and 539 nm) is remarkably similar to that of oxidized DMSO reductase (717 nm and 549 nm), and to what we have previously observed for [Mo^{VI}O(OBz)(cyclohexene-1,2-dithiolate)₂][−] (807 nm and 597 nm) and [Mo^{VI}O(OSi^{*i*}Pr₃)L₂][−] (739 nm and 568 nm).^{55,47} Our bonding calculations show that a *cis* S(p_z) orbital on L^B and an O(p) orbital from the alcoholate form d-p π bonding interactions with the Mo(d_{xy}) redox orbital which, for the Mo(VI) state, is the acceptor orbital (LUMO) in these low-energy LMCT transitions. The relevant Kohn-Sham orbitals for [Mo^{VI}O(OEt)L₂][−] are given in Figure S8. Using a combination of time-dependent DFT computations and our previous band assignments for [Mo^{VI}O(OSi^{*i*}Pr₃)L₂][−] and [Mo^{VI}O(OBz)(cyclohexene-1,2-dithiolate)₂][−], we can reasonably assign the lowest energy band as primarily arising from a HOMO → LUMO one-electron promotion (92%) with dominant L^A → (Mo d_{xy} + O2 π) charge transfer character. Band 2 primarily derives from a HOMO-1 → LUMO one-electron promotion (72%) and possesses dominant (L^A + L^B) → (Mo d_{xy} + O2 π) CT charge transfer character. The two LMCT bands in

$[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ are computed to occur at 755 nm and 511 nm, and the nature of these two ligand-to-metal charge transfer (LMCT) transitions is further illuminated in the calculated electron density difference maps (EDDMs) for Bands 1 and 2 (Figure 5).

As mentioned previously, the LMCT bands observed for $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ (774 nm and 639 nm) are red-shifted relative to $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$, indicating a significant contribution from the coordinated thiolate to these transitions. We tentatively assign the 774 nm band as primarily arising from a HOMO $\rightarrow$ LUMO one-electron promotion (90%) with dominant $\text{L}^{\text{A}} + \text{L}^{\text{B}} \rightarrow (\text{Mo } d_{xy} + \text{S3 } \pi)$ charge transfer character. Band 2 primarily derives from a HOMO-1 $\rightarrow$ LUMO one-electron promotion (71%) and possesses dominant $(\text{L}^{\text{A}} + \text{S3 } \pi) \rightarrow (\text{Mo } d_{xy} + \text{L}^{\text{B}})$ CT charge transfer character. The two LMCT bands in $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ are computed to occur at 790 nm and 557 nm, and the nature of these LMCT transitions is depicted in their respective calculated electron density difference maps (EDDMs) in Figure 6. The relevant Kohn-Sham orbitals for $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ are given in Figure S9.

The analysis of the electronic absorption spectra for $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ and $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ reveal key differences between alkoxide and thiolate ligation in these systems and allow for a critical analysis of the electronic structure differences between DMSOR family enzymes that possess cysteine or serine ligation. Namely, band 2 supports an increase in Mo-ER covalency for $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ compared to $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ due to (1) the markedly lower energy of the LMCT transition indicating an increase in $\text{EEt} \rightarrow \text{Mo}(\text{xy})$ LMCT character for $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$, (2) the increased oscillator strength for this transition, and (3) the $\text{EEt} \rightarrow \text{Mo}(\text{xy})$ electron donor character present in the EDDM for band 2 for $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ that is not present in $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$. The nature of the distorted O_h geometry in these $[\text{Mo}^{\text{VI}}\text{O}(\text{EEt})\text{L}_2]^-$ ($E = \text{O}, \text{S}$) compounds and in DMSOR is also of keen interest since this geometry results in a LUMO wavefunction that possesses strong π^* interactions between the $\text{Mo}(d_{xy})$ redox orbital and the *cis* $\text{S}(\text{p}_z)$ ene-1,2-dithiolate orbital localized on the equatorial L^{B} sulfur donor. The presence of covalent Mo-ene-1,2-dithiolate (S3) bonding interaction in these monooxido molybdenum(VI) compounds is reflected in the nature of their low energy LMCT transitions and this bonding interaction has previously been hypothesized to provide an ene-1,2-dithiolate mediated pathway for enzymatic electron transfer regeneration of the reduced enzyme involving only one of the pyranopterin ene-1,2-dithiolate.⁵⁵ A second important d-p π bonding interaction derives from the $\sim 180^\circ \text{O}_{\text{oxo}}\text{-Mo-}E\text{-C}$ dihedral angle involving the alcoholate and thiolate donors. In this geometry the in-plane $E(\text{p})$ orbital is properly oriented for good π overlap with the $\text{Mo}(\text{xy})$ orbital. For $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$, the $\text{O}_{\text{oxo}}\text{-Mo-O}_{\text{OEt}}\text{-C}$ dihedral angle is 171° , while for $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ the $\text{O}_{\text{oxo}}\text{-Mo-S}_{\text{SEt}}\text{-C}$ dihedral angle is computed to be 175° . Interestingly, the larger $\text{Mo-S}_{\text{thiolate}} \pi^*$ interaction relative to the $\text{Mo-O}_{\text{alkoxide}} \pi^*$ bonding interactions in the LUMOs of $[\text{Mo}^{\text{VI}}\text{O}(\text{EEt})\text{L}_2]^-$ and $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ do not appear to occur at the expense of the dithiolene contributions to these LUMOs (Table 4). There is an $\sim 50\%$ increase in the E contribution to the $[\text{Mo}^{\text{VI}}\text{O}(\text{EEt})\text{L}_2]^-$ LUMO as $E = \text{O}$ is replaced by $E = \text{S}$, an $\sim 500\%$ increase in the E contribution to the HOMO orbital, and an $\sim 400\%$ increase in the E contribution to the HOMO-1 orbital. This results in $\sim 36\%$ more SEt S character in the valence MOs of $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ relative to the OEt O character in $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$, and this derives from the greater electron donating ability of the thiolate

compared to the alkoxide. The dramatic increase in the thiolate character present in the $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ HOMO-1 and LUMO orbitals relative to the alkoxide character in $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ underscores a key difference in the contributions of these donors to the electronic structures of these $[\text{Mo}^{\text{VI}}\text{O}(\text{EEt})\text{L}_2]^-$ compounds. This clearly highlights the importance of serine and cysteine ligation in different DMSOR family enzymes for controlling the effective nuclear charge of the active site Mo ion and modulating the enzyme reduction potential.

CONCLUSION

In summary, we have demonstrated that the anionic bis(ene-1,2-dithiolato)dioxido-molybdenum(VI) complex, $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$, is smoothly converted to oxido-alcoholato- and oxido-thiolato-molybdenum(VI) complexes, $[\text{Mo}^{\text{VI}}\text{O}(\text{EEt})\text{L}_2]^-$ ($E = \text{O}, \text{S}$), by the reaction with the corresponding alcohol and thiol in the presence of an organic acid at low temperature. The oxido-ethanolato-molybdenum(VI) complex is the first crystallographically characterized example of a bis(ene-1,2-dithiolato)oxido-alcoholato-molybdenum(VI) complex. The substitution of one oxide ligand by the alcohol or thiol is initiated by the protonation of the terminal oxide ligand (Scheme 1). Importantly, the oxido-molybdenum(IV) complex possessing identical ene-1,2-dithiolate ligands is unreactive under the same conditions. We therefore suggest that the active sites of DMSOR family enzymes DMSO reductase and nitrate reductase may be generated by the acid catalyzed reaction of a $\text{Mo}^{\text{VI}}\text{O}_2$ from of the cofactor with an active site serine or a cysteine residue, respectively. The generated $\text{Mo}^{\text{VI}}\text{O}(\text{O}\cdot\text{Ser})$ and $\text{Mo}^{\text{VI}}\text{O}(\text{S}\cdot\text{Cys})$ species may be reduced by electron transfer proteins via a proton coupled electron transfer reaction to yield the *des*-oxidomolybdenum(IV) state, which is then poised to abstract an oxygen atom from DMSO or NO_3^- , respectively. We have also shown that there are potentially significant electronic structure differences that arise from thiolate (cysteine) and from alkoxide (serine) coordination to an oxomolybdenum(VI) site. Our spectroscopic and computational studies show that there is a markedly greater $S_{\text{thiolate}} \rightarrow \text{Mo}(\text{VI})$ charge donation in $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ compared to the $O_{\text{alkoxide}} \rightarrow \text{Mo}(\text{VI})$ charge transfer in $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$, as evidenced by the nature of the HOMO-1 $\rightarrow$ LUMO one-electron promotion contribution to Band 2 in $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$. These ancillary ligand interactions in DMSOR family enzymes are likely to play disparate roles in how effectively they can buffer the effective nuclear charge of the metal, leading to differences in how they contribute to redox potential modulation of the catalytic site during the course of catalysis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Proposed formation step of the active site of DMSO reductase family enzymes.

Figure 2.

(a) UV-vis spectral changes for the titration of $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ (0.10 mM) with 10-camphorsulfonic acid in propionitrile containing 0.5% ethanol (0.86 mM) at $-60\text{ }^{\circ}\text{C}$; (inset) plots of the absorbance at 360, 539, and 742 nm against the molar ratio of $[\text{CSA}]/[\text{Mo}]$, (b) CSI-mass spectrum of the final solution mixture taken at $-60\text{ }^{\circ}\text{C}$.

Figure 3. UV-vis spectral change for the conversion of $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ (black, 0.10 mM) to $[\text{Mo}^{\text{VI}}\text{O}(\text{SC}_6\text{H}_{13})\text{L}_2]^-$ (orange) by addition of 1 equiv. of 10-camphorsulfonic acid in propionitrile containing a large excess 1-hexanethiol (100 mM) at -80°C .

Figure 4.

Left: Crystal structure of the anionic part of $(\text{PPh}_4)[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]\cdot\text{acetone}$ with thermal ellipsoids at the 50% probability level. Right: DFT-optimized structure of $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ (def2-tzvp basis set).

Figure 5. Electron density difference map (EDDM) for the transition that is responsible for band 1 [HOMO → LUMO] in $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ (A) and $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ (B). The density value of the plot is 0.002. The oscillator strength for this transition is calculated to be $f = 0.0203$ and $f = 0.0266$ for (A) and (B), respectively. Red indicates a loss of electron density in the transition, and blue indicates a gain in electron density for the transition.

Figure 6.

Electron density difference map (EDDM) for the transition that is responsible for band 2 [HOMO-1 → LUMO] in $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ (A) and $[\text{Mo}^{\text{VI}}\text{O}(\text{SEt})\text{L}_2]^-$ (B). The density value of the plot is 0.002. The oscillator strength for this transition is calculated to be $f = 0.0631$ and $f = 0.0454$ for (A) and (B), respectively. Red indicates a loss of electron density in the transition, and blue indicates a gain in electron density for the transition.

Scheme 1.

Postulated Scheme for the Formation of $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt})\text{L}_2]^-$ from $\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2$ and Ethanol in the Presence of Acid.

Scheme 2.

π -Conjugation Involved in Ligand L^B Caused by *trans* Influence of Strong π -Donation of the Oxide Ligand.

Chart 1.
Structures of the Mo^{VI} and Mo^{IV} Model Complexes

Table 1Crystallographic Data for (PPh₄)[Mo^{VI}O(OEt)L₂]•acetone

formula	C ₄₁ H ₄₃ MoO ₁₁ PS ₄
Fw	966.94
size (mm)	0.04×0.03×0.01
temperature (K)	93
crystal system	monoclinic
space group	<i>P</i> 2 ₁ (#4)
<i>Z</i>	2
<i>a</i> , Å	11.0598(7)
<i>b</i> , Å	16.9292(11)
<i>c</i> , Å	11.8567(8)
α, deg	90
β, deg	100.879(8)
γ, deg	90
<i>V</i> , Å ³	2180.1(3)
μ, cm ⁻¹	50.785
no. reflns (<i>I</i> > 2σ(<i>I</i> _o))	7074
no. reflns (all data)	12615
no. variables	558
GOF	0.930
<i>R</i> _{<i>i</i>} % (<i>I</i> > 2σ(<i>I</i>))	0.0558
<i>wR</i> ₂ % (all data)	0.1335

$$R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|. \quad wR2 = \{\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2\}^{1/2}.$$

Table 2 λ_{max} Values in a Visible Region of $\text{Mo}^{\text{VI}}\text{O}(\text{ER})\text{L}_2$ in $\text{C}_2\text{H}_5\text{CN}$ at $-60\text{ }^\circ\text{C}$

<i>ER</i>	λ_{max} (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)
<i>OE</i> t	539 (2430), 742 (2130)
<i>OP</i> r	544 (2780), 732 (1610)
<i>OC</i> H ₂ Ph	535 (2860), 712 (1840)
<i>OSi</i> ^{<i>i</i>} Pr ₃ ^{<i>a</i>}	563 (4300), 753 (1280)
<i>SC</i> ₆ H ₁₃ ^{<i>b</i>}	639 (4120), 774 (1330)

^{*a*}R. T.^{*b*} $-80\text{ }^\circ\text{C}$.

Table 3Selected Bond Lengths (Å) and Angles (°) of $[\text{Mo}^{\text{VI}}\text{O}(\text{OEt}/\text{SEt})\text{L}_2]^-$

	$[\text{Mo}^{\text{VI}}\text{O}(\text{O Et})\text{L}_2]^-$	$[\text{Mo}^{\text{VI}}\text{O}(\text{O Et})\text{L}_2]^-$	$[\text{Mo}^{\text{VI}}\text{O}(\text{S Et})\text{L}_2]^-$
Mo(1)-O(1)	1.748(10) ^a	1.71 ^b	1.71 ^b
Mo(1)-O(2)/S(5)	1.875(13)	1.92	2.42
Mo(1)-S(1)	2.396(3)	2.42	2.42
Mo(1)-S(2)	2.464(4)	2.47	2.45
Mo(1)-S(3)	2.394(3)	2.41	2.41
Mo(1)-S(4)	2.521(3)	2.64	2.61
O(1)-Mo(1)-O(2)/S(5)	96.6(5)	98.6	88.9
O(1)-Mo(1)-S(4)	162.1(4)	159.3	156.1
O(2)/S(5)-Mo(1)-S(2)	160.2(5)	157.4	157.9
S(1)-Mo(1)-S(3)	157.86(9)	159.2	159.2
O(1)-Mo(1)-O(2)/S(5)-C(13) ^c	171.2(12)	169.0	174.8
Mo(1)-O(2)/S(5)-C(13)	134.6(10)	137.5	112.7
S(2)-S(1)-S(3)-S(4) ^c	105	101.3	104.2

^aData of X-ray structure.^bData for DFT optimized structures.^ctorsion angle

Table 4

Computed Atomic Orbital Compositions of $[\text{Mo}^{\text{VO}}(\text{EEt})(\text{L}_2)]^-$ ($E = \text{O}$ and S).

	% Composition of Fragment to the MO						
	Mo	DtA ^a	DtA(S) ^b	DtB ^c	DtB(S) ^d	Oxido	EEt
$E = \text{O} / \text{LUMO}+1$	49.01	20.4	4.9	8.13	5.44	18.52	3.26
$E = \text{O} / \text{LUMO}$	50.0	9.1	8.1	28.7	23.5	0.7	10.2
$E = \text{O} / \text{HOMO}$	4.4	53.4	35.3	37.1	24.2	2.9	1.5
$E = \text{O} / \text{HOMO}-1$	13.6	34.32	19.29	39.88	20.43	4.34	6.58
$E = \text{S} / \text{LUMO}+1$	51.59	14.52	2.89	6.73	3.98	21.6	5.37
$E = \text{S} / \text{LUMO}$	45.1	9.1	8.4	29.3	23.9	0.4	15.2
$E = \text{S} / \text{HOMO}$	3.3	43.2	29.0	42.1	27.4	1.9	8.6
$E = \text{S} / \text{HOMO}-1$	6.89	39.14	21.57	18.46	9.78	4.29	29.59

^aTotal dithiolene contribution on L^A.

^bSulfur contribution to L^A.

^cTotal dithiolene contribution on L^B.

^dSulfur contribution to L^B.