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Monodithiolene Molybdenum(V,VI) Complexes: A Structural Analogue of the Oxidized Active Site of the Sulfite Oxidase Enzyme Family

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Abstract: The active sites of the xanthine oxidase and sulfite oxidase enzyme families contain one pterin−dithiolene cofactor ligand bound to a molybdenum atom. Consequently, monodithiolene molybdenum complexes have been sought by exploratory synthesis for structural and reactivity studies. Reaction of $[MoO(S_2C_2Me_2)_2]^{1-}$ or $[MoO(bdt)_2]^{1-}$ with PhSeCl results in removal of one dithiolate ligand and formation of $[MoOCl_2(S_2C_2Me_2)]^{1-}$ (**1**) or $[MoOCl_2(bdt)]^{1-}$ (**2**), which undergoes ligand substitution reactions to form other monodithiolene complexes $[MoO(2\text{-}AdS)_2(S_2C_2Me_2)]^{1-}$ (**3**), $[MoO(SR)_2(bdt)]^{1-}$ (R = 2-Ad (**4**), 2,4,6-$Pr^i_3C_6H_2$ (**5**)), and $[MoOCl(SC_6H_2\text{-}2,4,6\text{-}Pr^i_3)(bdt)]^{1-}$ (**6**) (Ad = 2-adamantyl, bdt = benzene-1,2-dithiolate). These complexes have square pyramidal structures with apical oxo ligands, exhibit rhombic EPR spectra, and **3**−**5** are electrochemically reducible to $Mo^{IV}O$ species. Complexes **1**−**6** constitute the first examples of five-coordinate monodithiolene Mo^VO complexes; **6** approaches the proposed structure of the high-pH form of sulfite oxidase. Treatment of $[MoO_2(OSiPh_3)_2]$ with $Li_2(bdt)$ in THF affords $[MoO_2(OSiPh_3)(bdt)]^{1-}$ (**8**). Reaction of **8** with 2,4,6-$Pr^i_3C_6H_2SH$ in acetonitrile gives $[MoO_2(SC_6H_2\text{-}2,4,6\text{-}Pr^i_3)(bdt)]^{1-}$ (**9**, 55%). Complexes **8** and **9** are square pyramidal with apical and basal oxo ligands. With one dithiolene and one thiolate ligand of a square pyramidal $Mo^{VI}O_2S_3$ coordination unit, **9** closely resembles the oxidized sites in sulfite oxidase and assimilatory nitrate reductase as deduced from crystallography (sulfite oxidase) and Mo EXAFS. The complex is the first structural analogue of the active sites in fully oxidized members of the sulfite oxidase family. This work provides a starting point for the development of both structural and reactivity analogues of members of this family.

Introduction

In our recent investigations of the synthesis, structure, and reactivity of analogues of the active sites of molybdenum and tungsten enzymes of the oxotransferase/hydroxylase type,[1−4] we have concentrated on the desoxo and monooxo bis(dithiolene) complexes $[M^{IV}L(\text{dithiolene})_2]^{1-}$ and $[M^{VI}OL(\text{dithiolene})_2]^{1-}$ (M = Mo,[5−8] W[7,9−12]), respectively. In these species, the dithiolene (usually benzene-1,2-dithiolate or 1,2-dimethylethylenedithiolate) simulates the binding of the pterin−dithiolene cofactor ligand and L a protein-based ligand to the metal. The molybdenum complexes are minimal representations of the sites in the DMSO reductase enzyme family as classified by Hille.[1] In addition, the classification recognizes the xanthine oxidase and sulfite oxidase families of molybdoenzymes, which bind *one* pterin−dithiolene ligand at the active site. The sulfite oxidase family includes sulfite oxidase itself and assimilatory nitrate reductase. From the collective results of X-ray crystallography and X-ray absorption spectroscopy, the structural results for nitrate reductase[13] and sulfite oxidase[14−18] presented in Figure 1 have emerged.

We are particularly interested in the five-coordinate sites **a** and **b** (Figure 1), corresponding to the oxidized and reduced forms, respectively, of chicken liver sulfite oxidase. We seek analogues of these sites for structural and reactivity investigations. Monodithiolene Mo(IV,V) complexes have been reported,[19−27] the most thoroughly investigated of which is $[(HB(pz)_3)Mo^VO(bdt)]$.[24−27] Recently, the complexes

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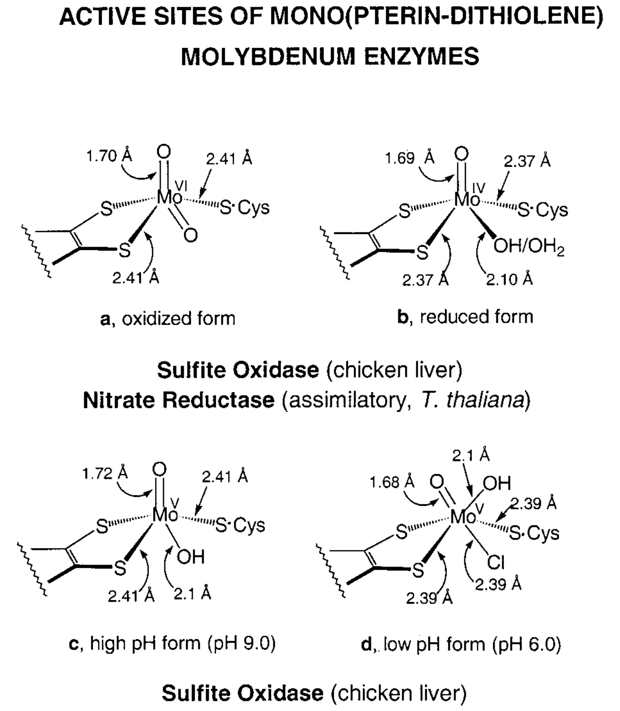

Figure 1. Schematic representations of the oxidized and reduced sites of sulfite oxidase and nitrate reductase, and the high- and low-pH forms of the sites in sulfite oxidase. The bond lengths were determined from EXAFS analysis and are those quoted by Hille.[1]

Chart 1. Designation of Compounds and Abbreviations

$[Mo^{V}OCl_2(S_2C_2Me_2)]^{1-}$	**1**
$[Mo^{V}OCl_2(bdt)]^{1-}$	**2**
$[Mo^{V}O(2\text{-}AdS)_2(S_2C_2Me_2)]^{1-}$	**3**
$[Mo^{V}O(2\text{-}AdS)_2(bdt)]^{1-}$	**4**
$[Mo^{V}O(SC_6H_2\text{-}2,4,6\text{-}Pr^{i}_3)_2(bdt)]^{1-}$	**5**
$[Mo^{V}OCl(SC_6H_2\text{-}2,4,6\text{-}Pr^{i}_3)(bdt)]^{1-}$	**6**
$[Mo^{V}_2O_2(\mu_2\text{-}O)_2(bdt)_2]^{2-}$	**7**
$[Mo^{VI}O_2(OSiPh_3)(bdt)]^{1-}$	**8**
$[Mo^{VI}O_2(SC_6H_2\text{-}2,4,6\text{-}Pr^{i}_3)(bdt)]^{1-}$	**9**

Ad	adamantyl
bdt	benzene-1,2-dithiolate(2-)
$HB(pz)_3$	hydrotris(pyrazolyl)borate(1-)
$L\text{-}N_2S_2$	*N,N'*-dimethyl-*N,N'*-bis(mercaptophenyl)ethylenediamine(2-)

$[(L{-}N_2S_2)Mo^{V}O(SR)]$ have been prepared and described as analogues of a Mo(V) state of sulfite oxidase.[28] (Abbreviations are given in Chart 1.) Like the enzyme site, these species possess three anionic sulfur ligands but do not contain a dithiolene ligand. These complexes, $[(HB(pz)_3)Mo^{V}O(bdt)]$, and others of the type $[(HB(pz)_3)Mo^{V}OLL']$ have been notably valuable in an elucidation of electronic properties of Mo(V) in controlled six-coordinate environments. We have been engaged in an investigation, by exploratory synthesis, of the scope of accessible five-coordinate monodithiolene Mo(V,VI) complexes with the intention of preparing close analogues of sites **a** and **b**. We describe here our initial results in monodithiolene molybdenum chemistry, which includes a structural analogue of oxidized site **a**.

Experimental Section

Preparation of Compounds. All reactions and manipulations were conducted under a pure dinitrogen atmosphere using either an inert atmosphere box or standard Schlenk techniques. Acetonitrile, ether, and THF were purified using an Innovative Technology solvent purification system and stored over 4-Å molecular sieves. In the following preparations, all volume reduction and evaporation steps were performed in vacuo.

(1) Mo(V) Complexes. $(Et_4N)[MoOCl_2(S_2C_2Me_2)]$. A solution of PhSeCl (25 mg, 0.13 mmol) in 1 mL of THF was added to a blue-violet solution of $(Et_4N)[MoO(S_2C_2Me_2)_2]$[6] (61 mg, 0.13 mmol) in 2 mL of acetonitrile. The mixture was stirred for 16 h to give a green solution and a black solid. The volume of the solution was reduced to half, and the solution was filtered. Several volume equivalents of ether were introduced into the filtrate by vapor diffusion. After 3 days, large dark-red crystals were obtained with white crystals and a yellow powder (neither of which was characterized). The dark red crystals were manually separated (17 mg, 30%). IR (KBr): ν_{MoO} 944 cm^{-1}. Absorption spectrum (acetonitrile): λ_{nm} (ϵ_M) 276 (5470), 320 (2040), 418 (590), 503 (320) nm. Anal. Calcd for $C_{12}H_{26}Cl_2MoNOS_2$: C, 33.42; H, 6.08; Cl, 16.44; N, 3.25; S, 14.87. Found: C, 33.36; H, 5.94; Cl, 16.35; N, 3.19; S, 14.92. The black solid, which was not soluble in acetonitrile, was confirmed as $[Mo(S_2C_2Me_2)_3]$[6,29] by its absorption and IR spectra.

$(Et_4N)[MoOCl_2(bdt)]$. This compound was prepared by the reaction of $(Et_4N)[MoO(bdt)_2]$[30,31] with 2 equiv of PhSeCl in a procedure analogous to the method for $(Et_4N)[MoOCl_2(S_2C_2Me_2)]$. The product was obtained as yellow-green crystals (67%). IR (KBr): ν_{MoO} 962 cm^{-1}. Absorption spectrum (acetonitrile): λ_{nm} (ϵ_M) 277 (10 200), 333 (3780), 422 (1280), 582 (sh, 204), 742 (sh, 248) nm. Anal. Calcd for $C_{14}H_{24}Cl_2MoNOS_2$: C, 37.09; H, 5.34; Cl, 15.64; N, 3.09; S, 14.15. Found: C, 37.03; H, 5.42; Cl, 15.07; N, 2.92; S, 14.25.

$(Et_4N)[MoO(2\text{-}AdS)_2(S_2C_2Me_2)]$. A solution of Li(2-AdS) (20 mg, 0.11 mmol; from adamantane-2-thiol[32] and BuLi) in 1 mL of THF was added to a solution of $(Et_4N)[MoOCl_2(S_2C_2Me_2)]$ (20 mg, 0.046 mmol) in 1 mL of acetonitrile. A dark red-violet color developed immediately. The resulting red-violet solution was stirred for 10 min. All solvents were removed, and the solid residue was dissolved in a minimum volume of acetonitrile. Several volume equivalents of ether were introduced to the filtrate by vapor diffusion. After 3 days, the product was obtained as large blocklike black crystals (18 mg, 56%). IR (KBr): ν_{MoO} 924 cm^{-1}. Absorption spectrum (acetonitrile): λ_{nm} (ϵ_M) 294 (6750), 437 (sh, 987), 532 (2380), 640 (sh, 533) nm. Anal. Calcd for $C_{32}H_{56}MoNOS_4$: C, 55.30; H, 8.12; N, 2.02. Found: C, 55.42; H, 8.03; N, 1.97.

$(Et_4N)[MoO(SC_6H_2\text{-}2,4,6\text{-}Pr^{i}_3)_2(bdt)]$. A solution of $(Et_4N)(SC_6H_2\text{-}2,4,6\text{-}Pr^{i}_3)$[6] (116 mg, 0.32 mmol) in 2 mL of THF was dropwise added to a solution of $(Et_4N)[MoOCl_2(bdt)]$ (100 mg, 0.32 mmol) in 2 mL of THF, generating a deep blue-violet solution. The reaction mixture was stirred for 6 h and filtered. Several volume equivalents of ether were layered onto the filtrate, and the mixture was kept overnight at −20

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Table 1. Crystallographic Data[a] for Monodithiolene Mo(V,VI) Complexes

	(Et$_4$N)[**1**]	(Et$_4$N)[**2**]	(Et$_4$N)[**3**]	(Et$_4$N)[**6**]	(Et$_4$N)$_2$[**7**]	(Ph$_4$P)[**8**]	(Et$_4$N)[**9**]·MeCN
formula	$C_{14}H_{24}Cl_2MoNOS_2$	$C_{14}H_{24}Cl_2MoNOS_2$	$C_{32}H_{56}MoNOS_4$	$C_{29}H_{47}ClMoNOS_3$	$C_{28}H_{48}Mo_2N_2O_4S_4$	$C_{48}H_{39}MoO_3PS_2Si$	$C_{31}H_{50}MoN_2O_2S_3$
fw	431.30	453.30	694.96	653.25	796.80	882.91	674.85
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
space gp	$C2/c$	$P2_1$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
Z	8	2	4	2	4	4	4
a, Å	9.2689(7)	7.924(4)	12.178(6)	9.9320(4)	8.504(3)	10.09(2)	15.7986(8)
b, Å	14.383(2)	14.434(7)	17.812(9)	10.1206(4)	15.536(5)	27.51(7)	15.8902(9)
c, Å	27.723(3)	8.619(4)	17.054(9)	19.0606(8)	27.298(9)	15.45(4)	14.3430(8)
α, deg				85.967(1)			
β, deg	94.046(7)	94.285(5)	109.132(7)	80.148(1)		92.70(3)	105.217(1)
γ, deg				60.860(1)		−	−
V, Å^3	3686.6(7)	983.0(9)	3495(3)	1648.5(1)	3607(2)	4280(20)	3474.5(3)
d_{calc}, g/cm^3	1.554	1.531	1.321	1.316	1.467	1.369	1.288
μ, mm^{-1}	1.221	1.149	0.639	0.690	0.959	0.510	0.586
θ range, deg	1.47−28.29	2.37−28.30	1.70−22.50	1.08−27.71	1.49−28.12	1.48−28.25	1.34−22.50
GOF (F^2)	1.074	1.071	1.054	1.024	1.106	1.002	1.078
R_1[b] (wR_2[c]), %	3.19 (7.85)	2.08 (5.43)	3.47 (8.74)	2.69 (7.39)	2.37 (6.23)	4.49 (9.51)	4.65 (10.72)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.710\,73$ Å) radiation. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

°C. Black crystals were collected, washed with ether (3 × 3 mL), and dried to obtain 120 mg (45%) of product. IR(KBr): ν_{MoO} 935 cm^{-1}. Absorption spectrum (acetonitrile): λ_{nm} (ϵ_M) 302 (22 300), 417 (1690), 532 (1760) nm. Anal. Calcd for $C_{44}H_{70}MoNOS_4$: C, 61.94; H, 8.27; N, 1.64; S, 15.03. Found: C, 62.08; H,8.20; N,1.68; S, 15.12.

(Et$_4$N)[MoO(2-AdS)$_2$(bdt)]. This compound was prepared with Li(2-AdS) in a procedure analogous to the method for (Et$_4$N)[MoO(SC$_6$H$_2$-2,4,6-Pr$^i_3$)$_2$(bdt)]. The product was isolated as dark violet crystals (40%). IR (KBr): ν_{MoO} 934 cm^{-1}. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 301 (10 200), 533 (3780) nm. Anal. Calcd for $C_{34}H_{54}MoNOS_4$: C, 56.95; H, 7.59; N, 1.95; S, 17.89. Found: C, 57.11; H, 7.55; N, 1.99; S, 17.95.

(Et$_4$N)[MoOCl(SC$_6$H$_2$-2,4,6-Pr$^i_3$)(bdt)]. A solution of (Et$_4$N)(SC$_6$H$_2$-2,4,6-Pr$^i_3$) (60 mg, 0.16 mmol) in 1 mL of THF was dropwise added to a solution of (Et$_4$N)[MoOCl$_2$(bdt)] (100 mg, 0.32 mol) in 2 mL of THF, generating a violet-brown solution. The reaction mixture was stirred for 6 h and filtered. Several volume equivalents of ether were layered onto the filtrate, and the mixture was kept overnight at −20 °C. Dark brown crystals were collected, washed with ether (3 × 3 mL), and dried to obtain 75 mg (36%) of product. IR (KBr): ν_{MoO} 939 cm^{-1}. Absorption spectrum (acetonitrile): λ_{nm} (ϵ_M) 300 (12 400), 414 (1090), 545 (707), 670 (sh, 405) nm. Anal. Calcd for $C_{29}H_{47}ClMoNOS_3$: C, 53.32; H, 7.25; Cl, 5.43; N, 2.14; S, 14.73. Found: C, 53.18; H, 7.24; Cl, 5.33; N, 2.17; S, 14.76.

(Et$_4$N)$_2$[Mo$_2$O$_2$(μ-O)$_2$(bdt)$_2$]. A solution of Et$_4$NOH (220 μL, 25% in MeOH, 0.32 mmol) was added dropwise to a mixture of (Et$_4$N)[MoOCl$_2$(bdt)] (100 mg, 0.32 mmol) and Et$_3$N (0.2 mL, 1.4 mmol) in 1 mL of THF. As the reaction proceeded, an orange-yellow powder was formed. The solid material was collected and dissolved in a minimal volume of acetonitrile to give a bright yellow solution. Several volume equivalents of ether were introduced by vapor diffusion. Large yellow crystals were collected and dried to afford 56 mg (44%) of product. IR (KBr): ν_{MoO} 943 cm^{-1}. Absorption spectrum (acetonitrile): λ_{nm} (ϵ_M) 278 (23 900), 305 (22 200), 399 (sh, 3240) nm. ^{1}H NMR (CD$_3$CN, anion): δ 7.40 (m, 2), 6.89 (m, 2). Anal. Calcd for $C_{28}H_{48}MoN_2O_4S_4$: C, 42.20; H, 6.07; N, 3.52; S, 16.10. Found: C, 42.14; H, 6.15; N, 3.50; S, 16.03.

(2) Mo(VI) Complexes. (Et$_4$N)[MoO$_2$(OSiPh$_3$)(bdt)]. A solution of Li$_2$(bdt) (0.250 g, 1.62 mmol) in 20 mL of THF was added dropwise to a solution of MoO$_2$(OSiPh$_3$)$_2$[33] (1.00 g, 1.47 mmol) in 20 mL of THF, resulting in a deep orange solution. A slurry of Et$_4$NCl (0.750 g, 3.26 mmol) in 20 mL of THF was added, and the mixture was stirred for 30 min and filtered. The orange filtrate was layered with hexane, causing separation of a solid which was collected, washed with methanol (2 × 15 mL) and ether (2 × 15 mL), and dried. The product was obtained as 0.567 g (57%) of an orange solid, which can be recrystallized from THF/benzene. IR (KBr): ν_{SiO} 960 cm^{-1}; ν_{MoO} 918, 885 cm^{-1}. Absorption spectrum (THF): λ_{max} (ϵ_M) 307 (4670), 341 (sh, 3110), 395 (1500), 495 (174) nm. FAB-MS: m/z 545 (M$^-$). ^{1}H NMR (CD$_3$CN, anion): δ 7.64 (d, 6), 7.40 (m, 9), 7.12 (q, 2), 6.83 (q, 2). Anal. Calcd for $C_{32}H_{39}MoNO_3S_2Si$: C, 56.88; H, 5.82; N, 2.07; S, 9.52. Found: C, 56.74; H, 5.83; N, 2.08; S, 9.60.

(Et$_4$N)[MoO$_2$(SC$_6$H$_2$-2,4,6-Pr$^i_3$)(bdt)]. To a solution of (Et$_4$N)[MoO$_2$(OSiPh$_3$)(bdt)] (50 mg, 0.074 mmol) in 2 mL of acetonitrile was added dropwise 2,4,6-Pr$^i_3$C$_6$H$_2$SH 34 (50 mL, 0.21 mmol). The reaction mixture was stirred for 1 h, generating a yellow-brown solution which was filtered. Several volume equivalents of ether were layered onto the filtrate, and the mixture was kept overnight at −20 °C. The product was obtained as 26 mg (55%) of yellow-brown platelike crystals. IR (KBr): ν_{MoO} 920, 885 cm^{-1}. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 341 (7430), 387 (sh, 3870), 566 (sh, 383) nm. ^{1}H NMR (CD$_3$CN, anion): δ 7.28 (m, 2), 7.01 (s, 2), 6.94 (m, 2), 3.90 (m, 2), 2.89 (m, 1), 1.25 (d, 6H), 1.20 (d, 12H). Anal. Calcd for $C_{29}H_{47}MoNO_2S_3$: C, 54.95; H, 7.47; N, 2.21;S, 15.18. Found: C, 55.08; H, 7.38; N, 2.24; S, 15.16.

X-ray Structure Determinations. The seven compounds listed in Table 1 were structurally characterized by X-ray crystallography. Component complexes are hereafter referred to by the numerical designations in the chart.

Crystals of (Et$_4$N)[**6**] were grown by standing a THF/ether (1:5 v/v) solution at −20 °C overnight. Crystals of (Et$_4$N)[**9**]·MeCN were grown similarly by standing a THF/MeCN/ether (5:1:25 v/v) solution at −20 °C overnight. Crystals of (Ph$_4$P)[**8**], obtained by cation exchange of Li[**8**] with Ph$_4$PBr in THF, were produced by vapor diffusion of ether into a THF solution. All other crystals ((Et$_4$N)[**1**], (Et$_4$N)[**2**], (Et$_4$N)[**3**], (Et$_4$N)[**7**]) were obtained by vapor diffusion of ether into saturated solutions in acetonitrile. Crystals were mounted on glass capillary fibers in grease and cooled in a stream of dinitrogen (−60 °C). Diffraction data were obtained with a Siemens (Bruker) SMART CCD area detector system using ω scans of 0.3°/frame, and 30-s frames such that 1271 frames were collected for a hemisphere of data. The first 50 frames were recollected at the end of the data collections to monitor for crystal decay; no significant decay was observed. Cell parameters were determined using SMART software. Data reduction was performed with SAINT software, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS. Space groups were assigned by analysis of symmetry and observed systematic absences determined by the program XPREP and by successful refinement of the structure. All structures were solved by direct methods with SHELXS and subsequently refined against all data by the standard technique of full-matrix least squares on F^2 (SHELXL-97).

Asymmetric units contain one formula weight for all compounds. Disordered atoms or groups were frequently found in the structures. One of the 2-adamantyl groups of (Et$_4$N)[**3**] was disordered over two different positions and refined with 0.57 occupancy factor. The MoS1S2S3O1 unit in (Et$_4$N)[**6**] was disordered over two sites and was refined with 0.97 occupancy factor. The sulfur atom and three isopropyl groups of the thiolate ligand in (Et$_4$N)[**9**]·MeCN were disordered over two sites and refined with occupancy factors 0.50, 0.48, 0.49, and 0.59, respectively. Methylene groups of the cations in (Et$_4$N)[**1**/**3**] were

Table 2. Mo−O Stretching Frequencies and Redox Properties of Monodithiolene Mo(V,VI) Complexes

complex	ν_{MoO}, cm$^{-1\ a}$	$E_{1/2}$, V (ΔE_p, mV)^b
$[Mo^VOCl_2(S_2C_2Me_2)]^{1-}$ (**1**)	962	−0.73,[c] 0.57 (92)
$[Mo^VOCl_2(bdt)]^{1-}$ (**2**)	944	−0.58[c]
$[Mo^VOCl(SC_6H_2-2,4,6\text{-}Pr^i{}_3)(bdt)]^{1-}$ (**6**)	939	−0.67[c]
$[Mo^VO(2\text{-}AdS)_2(S_2C_2Me_2)]^{1-}$ (**3**)	924	−1.00 (80)
$[Mo^VO(2\text{-}AdS)_2(bdt)]^{1-}$ (**4**)	934	−0.87 (77)
$[Mo^VO(SC_6H_2-2,4,6\text{-}Pr^i{}_3)_2(bdt)]^{1-}$ (**5**)	935	−0.73 (94)
$[Mo^{VI}O_2(OSiPh_3)(bdt)]^{1-}$ (**8**)	918, 885	−1.35 (180)
$[Mo^{VI}O_2(SC_6H_2-2,4,6\text{-}Pr^i{}_3)(bdt)]^{1-}$ (**9**)	920, 885	−1.26[c]

[a] In KBr. [b] Versus SCE. [c] Irreversible, E_{pc}.

Table 3. EPR Parameters for Chicken Liver Sulfite Oxidase[a] and Mono(dithiolene)Mo^VO Complexes[b]

complex	g_1	g_2	g_3	$A_1{}^c$	A_2	A_3
sulfite oxidase (low-pH form)	2.007	1.974	1.968	56.7	25	16.7
sulfite oxidase (high-pH form)	1.990	1.966	1.954	54.4	21	11.3
$[Mo^VOCl_2(S_2C_2Me_2)]^{1-}$ (**1**)	2.004	1.967	1.943	60	15	43
$[Mo^VOCl_2(bdt)]^{1-}$ (**2**)	2.006	1.968	1.943	60.8	14	43
$[Mo^VOCl(SC_6H_2-2,4,6\text{-}Pr^i{}_3)(bdt)]^{1-}$ (**6**)	2.017	1.978	1.963	58	12	39
$[Mo^VO(2\text{-}AdS)_2(S_2C_2Me_2)]^{1-}$ (**3**)	2.032	1.981	1.977	51	17	30

[a] Reference 25. [b] Measured in MeCN/DMF (1:1 v/v) at 4 K. [c] $A(^{95,97}Mo)$, $\times 10^{-4}$ cm^{-1}.

Table 4. Bond Distances (Å) and Angles (deg) for Monodithiolene Mo(V) Complexes

	1	**2**	**3**	**6**	**7**
Mo−Mo					2.614(1)
$Mo-O_{oxo}$	1.679(2)	1.677(2)	1.692(2)	1.681(1)	1.703(1)[a]
$Mo-O_{bridge}$					1.960(3)[a]
Mo−Cl	2.368(6)	2.36(1)		2.372(1)	
$Mo-S_{bdt}{}^a$	2.356(6)	2.360(5)	2.393(2)	2.37(2)	2.429(4)
$Mo-S_{thiolate}$			2.38(1)[a]	2.393(1)	
C−S[a,b]	1.765(5)	1.761(2)	1.765(3)	1.758(5)	1.762(3)
C−C[b]	1.333(4)	1.401(3)	1.327(5)	1.394(3)	1.411(9)
S1−Mo−S2[c]	82.15(3)	83.73(3)	81.34(5)	83.46(2)	82.44(8)
δ^d	0.712	0.714	0.790	0.747	0.711(1)[a]

[a] Mean values. [b] Chelate ring. [c] Bite angle of chelate ring. [d] Perpendicular displacement of Mo atom from S_4 least-squares plane.

disordered over two sites and were refined with site occupancy factors of 0.50 and 0.59, respectively. Two phenyl rings of the cation in (Ph_4P)-[**8**] were disordered over two positions and were refined with a site occupancy factor of 0.73. All non-hydrogen atoms were described anisotropically. In the final stages of refinement, hydrogen atoms were added at idealized positions and refined as riding atoms with a uniform value of U_{iso}. Final refined structures were examined for any overlooked symmetry with the checking program PLATON. Crystallographic and final agreement factors are included in Table 1. Metric parameters for the structures are collected in Tables 3 and 4. Because of the large quantity of data, mean values are given where feasible instead of individual data. (See paragraph at the end of this article for Supporting Information available.)

Other Physical Measurements. All measurements were made under anaerobic conditions. Absorption spectra were measured with a Cary 50 Bio spectrophotometer. ^1H NMR spectra were obtained with Varian Mercury 400/500 spectrometers. IR spectra were determined with a Nicolet Nexus 470 FT-IR spectrometer. Electrochemical measurements were performed with a PAR model 263 potentiostat/galvanostat using a platinum working electrode and 0.1 M $(Bu_4N)(PF_6)$ supporting electrolyte; potentials are referenced to the SCE. EPR spectra were obtained with a Bruker ESP 300 X-band spectrometer equipped with an Oxford Instruments variable-temperature accessory and a Hewlett-Packard 5350B frequency counter. Analysis of EPR spectra was carried out by simulation of frozen solution spectra with WIN-EPR Simphonia version 1.2. Anisotropic g values were first directly obtained from the experimental spectra and then simulated ($I = 0$ component) to obtain the best fit. The anisotropic $A(^{95,97}Mo)$ components were simulated separately ($I = {}^5/_2$ component only). Each simulated spectrum was integrated separately, and the contributions from the $I = {}^5/_2$ ($^{95,97}Mo$, 25% abundant) and $I = 0$ (75% abundant) components were summed.

Results and Discussion

Synthesis and Properties of Monodithiolene Complexes. (a) Mo(V). In seeking routes to these complexes, we have found that adjusting the reactant stoichiometry in systems known to produce bis(dithiolene) complexes[5,35,36] in order to favor monodithiolene products was not successful. In another approach, we note the nucleophilicity of sulfur atoms in coordinated dithiolenes, most recently demonstrated by the mono-S-alkylation of $[WO(S_2C_2Ph_2)_2]^{2-}$ in good yield.[10] This result is consistent with earlier demonstrations of S-alkylation in bis(dithiolene)Ni complexes.[37] The synthetic procedures used here to afford a family of Mo^VO complexes are outlined in Figure 2. Characterization data of complexes **1**−**7** are collected in Tables 2−4.

The key step is the conversion of a bis(dithiolene) to a monodithiolene by reaction 1 with the electrophile PhSeCl, which captures the dithiolate ligand as a selenosulfide and provides chloride to occupy the vacated coordination sites in the product **2**.

$$[MoO(bdt)_2]^{1-} + 2PhSeCl \rightarrow [MoOCl_2(bdt)]^{1-} + C_6H_4(SSePh)_2 \quad (1)$$

Because the yield of **2** (67%) is substantially higher than for **1** (30%), which is formed similarly, the majority of subsequent reactions is based on **2**. In the preparation of **1**, best results were obtained with 1 equiv of PhSeCl, while less than 2 equiv in the synthesis of **2** resulted in incomplete reaction. A consistent byproduct in the synthesis of **1** is $[Mo(S_2C_2Me_2)_3]$, a known complex[6,29] which forms green solutions and contributes to the lower yield. When the Mo(IV) complexes $[MoO(S_2C_2Me_2)_2]^{2-}$ and $[MoO(bdt)_2]^{2-}$ were treated with 1 equiv of PhSeCl in acetonitrile/THF, electron transfer rather than ligand replacement occurred, generating $[MoO(S_2C_2Me_2)_2]^{1-}$ and $[MoO(bdt)_2]^{1-}$, respectively. Quantitative formation of PhSeSePh (0.5 equiv/Mo) was detected by ^1H NMR.

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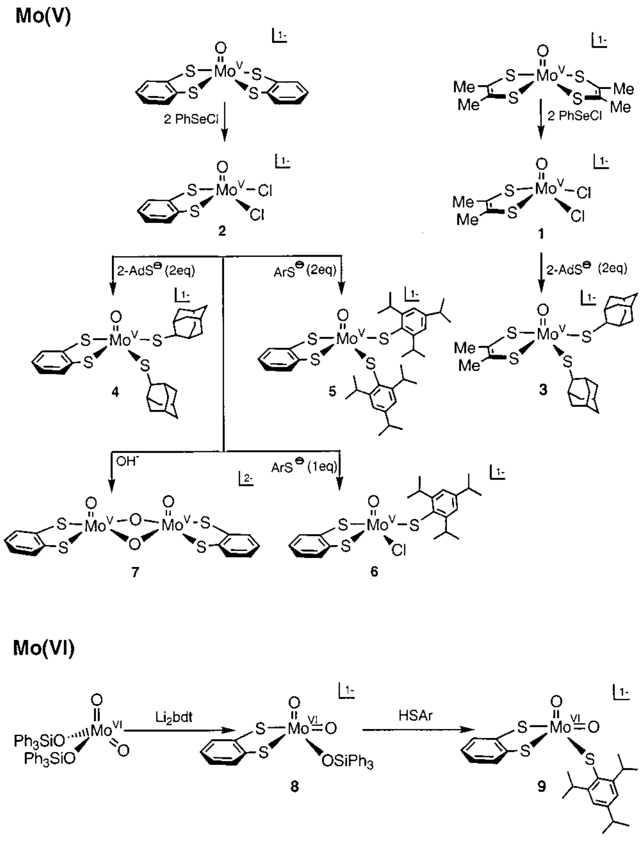

Figure 2. Synthetic schemes for monodithiolene complexes of Mo(V) (**1**−**7**) and Mo(VI) (**8**, **9**).

With complexes **1** and **2** in hand, substitution reactions with thiolate ligands were examined in view of the presence of cysteinate in the enzyme sites (Figure 1). Because mononuclear species were desired, sterically demanding adamantane-2-thiolate and 2,4,6-triisopropylbenzenethiolate were employed in reaction 2 ($n = 1, 2$). Two equivalents of thiolate afford

$$[\mathrm{MoOCl_2(bdt)}]^{1-} + n\mathrm{RS}^- \rightarrow [\mathrm{MoOCl}_{2-n}(\mathrm{SR})_n(\mathrm{bdt})]^{1-} + n\mathrm{Cl}^- \quad (2)$$

complexes **3**−**5** whereas 1 equiv of thiolate with **2** yielded **6**. The analogous complex $[\mathrm{MoOCl(2\text{-}AdS)(bdt)}]^{1-}$ proved difficult to isolate in pure form. Instead, red-orange binuclear $[\mathrm{Mo_2O_2}(\mu_2\text{-Cl})(\mu_2\text{-O})(\mu_2\text{-2-AdS})(\mathrm{bdt})_2]^{2-}$ was isolated and identified by an X-ray structure determination.[38] The structures of **1**−**3** are given in Figure 3 and that of **6** is shown in Figure 4. Selected bond distances and angles are contained in Table 4. The four complexes adopt a conventional square pyramidal geometry with the molybdenum atom displaced 0.71−0.79 Å from the least-squares basal plane toward the apical oxo atom. The C−C and C−S distances of **1** and **3** are consistent with the enedithiolate oxidation state, as is the case for Mo(IV,V,VI) complexes with the $\mathrm{Me_2C_2S_2}$ ligand.[6,8] These and other metric parameters are normal. With allowance for chloride in place of hydroxide, complex **6** is a structural representation of site **c** in the high-pH form of sulfite oxidase (Figure 1). Differences in Mo−O and Mo−S bond distances in **6** and site **c** are ≲0.04 Å.

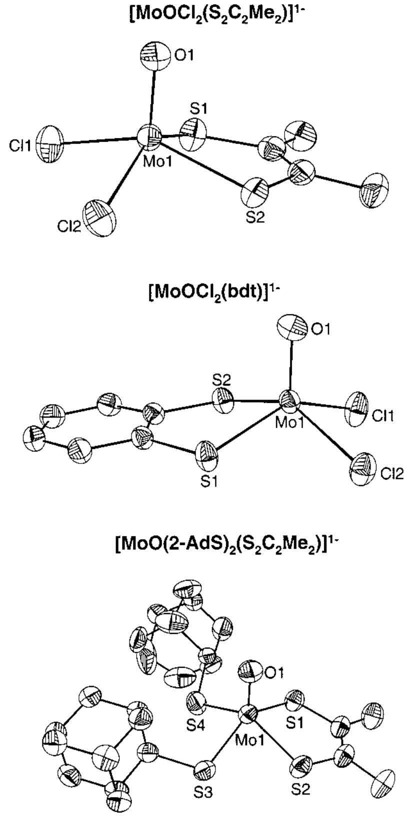

Figure 3. Structures of Mo(V) complexes **1** (upper), **2** (middle), and **3** (lower) showing 50% probability ellipsoids and partial atom labeling schemes.

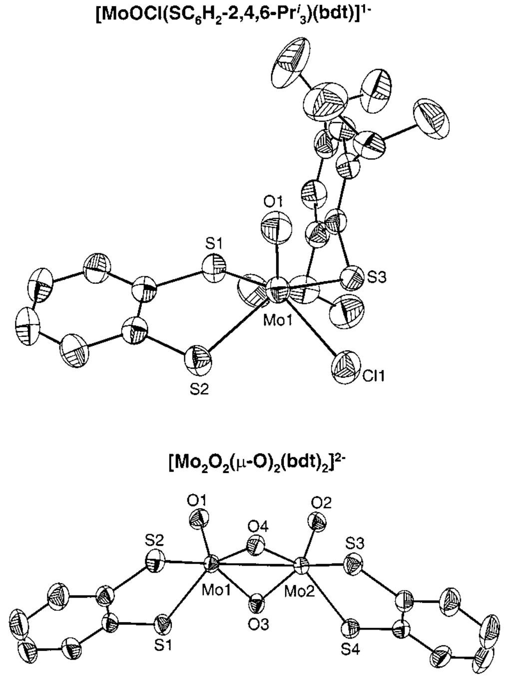

Figure 4. Structures of Mo(V) complexes **6** (upper) and **7** (lower) showing 50% probability ellipsoids and partial atom labeling schemes.

To investigate replacement of chloride by hydroxide, complex **2** was treated with 1 equiv of $\mathrm{Et_4NOH}$ in the presence of triethylamine. Reaction 3 ensued, affording the oxo-bridged dimer **7** rather than a mononuclear hydroxide complex. The reaction product was identified by an X-ray structure determi-

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[38] The compound $(\mathrm{Et_4N})_2[\mathrm{Mo_2}(\mu_2\text{-O})(\mu_2\text{-Cl})(\mu_2\text{-2-AdS})(\mathrm{bdt})_2]\cdot\mathrm{MeCN}$ crystallizes in monoclinic space group $P2_1/c$ with $a = 21.545(2)$ Å, $b = 9.758(1)$ Å, $c = 23.813(3)$ Å, $\beta = 112.77(1)°$, $Z = 4$, and $V = 4616(1)$ Å^3. Because this compound is not of direct interest in this work, it was not further characterized.

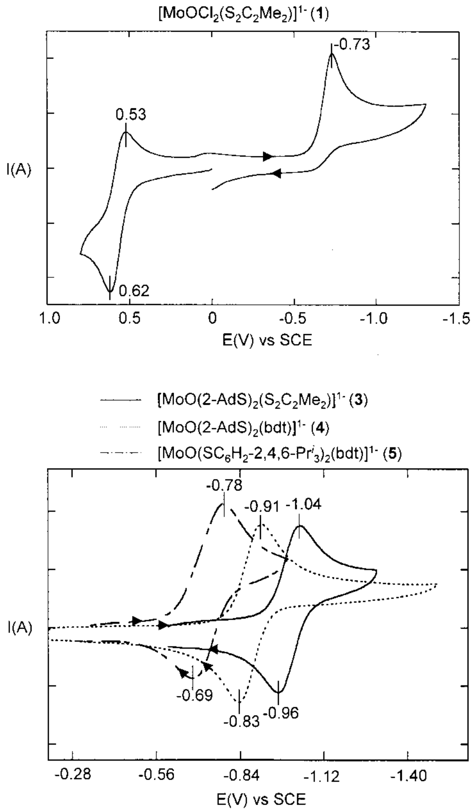

Figure 5. Cyclic voltammograms (100 mV/s) of **1** (upper) and **3**, **4**, and **5** (lower) in acetonitrile. Peak potentials vs SCE are indicated.

$$2[\mathrm{MoOCl_2(bdt)}]^{1-} + 2\mathrm{Et_4NOH} + 2\mathrm{Et_3N} \rightarrow [\mathrm{Mo_2O_2}(\mu_2\text{-}\mathrm{O})_2(\mathrm{bdt})_2]^{2-} + 2\mathrm{Et_4NCl} + 2\mathrm{Et_3NHCl} \quad (3)$$

nation (Figure 4), which reveals the pervasive $\mathrm{Mo^V{}_2O_4}$ grouping and an overall structure similar to $[\mathrm{Mo_2O_4(S_2CNEt_2)_2}]$[39] and $[\mathrm{Mo_2O_4(SPh)_4}]^{2-}$.[40]

The redox behavior of complexes **1**−**6** is summarized in Table 2; cyclic voltammograms of **1** and **3**−**5** are set out in Figure 5. Unlike bis(dithiolene) complexes, which often show a reversible $\mathrm{Mo^VO/Mo^{VI}O}$ couple,[5,6] only **1** exhibits a reversible oxidation, at 0.58 V. The cause of this behavior is very likely the electron-rich nature of the dialkyldithiolene ligand which reduces the potential for oxidation. Indeed, relative basicities of ligands are clearly reflected in potential trends for reversible $\mathrm{Mo^VO/Mo^{IV}O}$ reductions: **3** < **4**/**5**, **4** < **5**, and **5** < **6** (Table 2). By way of comparison with bis(dithiolenes), the $[\mathrm{MoO(S_2C_2Me_2)_2}]^{1-/2-}$ couple is 0.23 V lower than the $[\mathrm{MoO(bdt)_2}]^{1-/2-}$ couple.[5,6] The reduction of **6** approaches chemical reversibility ($i_{pc}/i_{pa} \sim 1$) only at high scan rate (400 mV/s); addition of excess chloride (>10 equiv) resulted in formation of dichloro complex **2**. In an attempt to obtain a $\mathrm{Mo^{IV}O}$ complex suitable for an oxo-transfer reaction to a monodithiolene $\mathrm{Mo^{VI}O_2}$ species, complex **5** was treated with $\mathrm{LiEt_3BH}$ in THF. A color change occurred and a noncrystalline solid was isolated. Reaction of the solid with $\mathrm{Me_3NO}$ resulted in several products as detected by IR spectroscopy, but only $[\mathrm{MoO(bdt)_2}]^{2-}$ could be isolated from the reaction mixture.

Frozen solution EPR spectra of complexes **1**−**3** and **6** (not shown) exhibit the expected rhombic line shapes. The parameters in Table 3 were determined by spectral fitting except for the hyperfine splitting A_2, which was evaluated from A_1, A_3, and the isotropic A value in fluid solution. Although the effect is small, g values increase with the number of coordinated sulfur atoms, reaching a maximum with **3**. This behavior conforms to the same trend established with a much larger set of complexes.[22] The EPR parameters of **1**, **2**, and **6** closely approach those of the high- and low-pH forms of sulfite oxidase (Table 3) except for the values of A_3, which are too high. Hahn et al.[41] described a model for the high-pH form on the basis of matching g values (1.992, 1.961, 1.953). However, this $\mathrm{MoNO_2S_3}$ complex is six-coordinate while the proposed structure (Figure 1) is five-coordinate. We note the caution raised by Dhawan and Enemark[25] about deducing active site structures, and, implicitly, structural similarities between or among protein sites and synthetic species, from g values alone. Complex **6** is one of few known five-coordinate $\mathrm{Mo^VO}$ complexes with three anionic sulfur ligands.[28] It is a close but not congruent spectroscopic model of ground-state electronic structure. The extent to which replacement of chloride with hydroxide, or other ligand changes, will cause these parameters to converge remains to be seen.

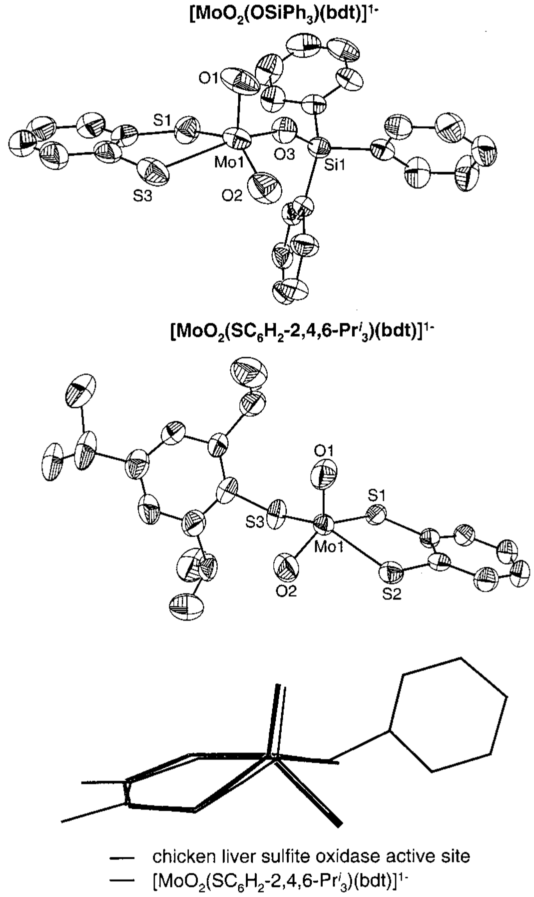

Figure 6. Structures of Mo(VI) complexes **8** (upper) and **9** (middle) showing 50% probability ellipsoids and partial atom labeling schemes. The lower figure is a superposition of the structures of complex **9** and the active site of sulfite oxidase determined crystallographically,[14] obtained using the OFIT routine of SHELXL-97.

(b) Mo(VI). Complexes **1**−**6** are the products of exploratory synthesis aimed at monodithiolene $\mathrm{Mo^VO}$ complexes. It is hoped that these species will serve as precursors for the synthesis of monodithiolene $\mathrm{Mo^{VI}O_2}$ complexes related to protein-bound sites

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Table 5. Bond Distances (Å) and Angles (deg) for Monodithiolene Mo(VI) Complexes

	8	**9**
Mo−O$_{ax}$	1.698(4)	1.686(3)
Mo−O$_{eq}$	1.710(4)	1.712(4)
Mo−S$_{oxo}$	2.467(5)	2.476(1)
Mo−S$_{OSi/SAr}$	2.452(4)	2.415(1)
Mo−O$_{OSi}$/S$_{SAr}$	1.916(4)	2.40(1)
C−S^{a,b}	1.75(1)	1.748(5)
C−C^{b}	1.413(6)	1.396(6)
O$_{ax}$−Mo−O$_{eq}$	109.2(2)	110.1(2)
S1−Mo−S2^{c}	79.9(1)	80.44(4)
δ^{d}	0.560	0.740

[a] Mean values. [b] Chelate ring. [c] Chelate ring bite angle. [d] Perpendicular displacement of Mo atom from S_2OX least-squares plane (X = O in **8**, X = S in **9**).

(Figure 1). Thus far, we have been unable to realize the desired complex by such means. Consequently, we turned to another approach (Figure 1) described by reactions 4 and 5 and based on tetrahedral $[MoO_2(OSiPh_3)_2]$,[33] a compound we have found susceptible to additional ligation.[42] Reaction 4 is conducted in

$$[MoO_2(OSiPh_3)_2] + Li_2(bdt) \rightarrow [MoO_2(OSiPh_3)(bdt)]^{1-} + LiOSiPh_3 \quad (4)$$

$$[MoO_2(OSiPh_3)(bdt)]^{1-} + 2,4,6\text{-}Pr^{i}_3C_6H_2SH \rightarrow [MoO_2(SC_6H_2\text{-}2,4,6\text{-}Pr^{i}_3)(bdt)]^{1-} + Ph_3SiOH \quad (5)$$

THF and is presumably aided by the formation of a stable lithium silyloxide, possibly $[Li_2(THF)_4(\mu_2\text{-}OSiPh_3)_2]$ by analogy with the 1,2-dimethoxyethane adduct.[43] The structure of product complex **8**, shown in Figure 6, is square pyramidal with axial and equatorial oxo ligands and the remaining ligands in the basal plane. Selected metric parameters are given in Table 5. Oxo ligand O2 exerts essentially no trans influence of the Mo−S1 bond, whose length is indistinguishable from Mo−S2.

Orange complex **8** is readily converted to yellow-brown **9** by reaction 5 in 55% yield, together with small amounts of byproduct **7**. Again, a hindered thiolate was used to promote mononuclear complex formation. Complex **9** has a square pyramidal structure (Figure 6) with the same ligand positions as in **8** and thiolate in place of silyloxide in the basal plane. The molybdenum atom is displaced 0.74 Å from this plane. Oxo ligand O2 has a trans influence of 0.06 Å on the Mo−S(1) bond. The other two Mo−S distances (2.415(1), 2.40(1) Å) are indistinguishable. The $Mo^{VI}O_2$ group geometry is virtually unchanged in passing from **8** to **9**. Complex **9**, with one dithiolene and one thiolate ligand in a square pyramidal $Mo^{VI}O_2S_3$ coordination unit, bears an obvious resemblance to site **a** of sulfite oxidase and nitrate reductase (Figure 1). It is the only complex with these attributes thus far prepared. The structure of **9** is compared in Figure 6 with that of chicken liver sulfite oxidase determined at 1.9-Å resolution.[14] Although the structure of the enzyme is not that of the fully oxidized form, as evidenced by one Mo−O bond of 1.7 Å and another of 2.3 Å (consistent with a water or hydroxide ligand), the geometry at the molybdenum center is square pyramidal with the oxo ligand in the apical position. Analysis of the positional deviations of the MoO_2S_3 coordination units of both structures affords a weighted rms deviation of 0.26 Å. Further, the Mo−S bond distance not subject to a trans influence and the two Mo−O bond distances of **9** occur within the ranges 2.40−2.43 and 1.68−1.74 Å, respectively, for oxidized sulfite oxidase[13,15−18] and assimilatory and dissimilatory nitrate reductase.[13,44−46,47]

We conclude that complex **9** is the most accurate synthetic representation of native site **a** currently available. As such, it serves as a *structural* analogue. The electronic and reactivity properties of it and related complexes are being examined in ongoing work. The X-ray absorption spectroscopy of the set of monodithiolene complexes will be reported elsewhere.[48]

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Supporting Information Available: X-ray crystallographic data for the seven compounds in Table 1. See any current masthead page for ordering information and Web access instructions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(47) The range of Mo−S distances does not include the value of 2.57 Å for one distance in the as-isolated form of *Arabidopsis thaliana*, where the pterin−dithiolene is apparently not symmetrically coordinated. In the nitrate-oxidized form, there are three Mo−S distances at 2.40 Å.[13]

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