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Oxygen/Sulfur Substitution Reactions of Tetraoxometalates Effected by Electrophilic Carbon and Silicon Reagents

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Reactions of $[MO_4]^{2-}$ (M = Mo, W) with certain carbon and silicon electrophiles were investigated in acetonitrile in order to produce species of potential utility in the synthesis of analogues of the sites in the xanthine oxidoreductase enzyme family. Silylation of $[MoO_4]^{2-}$ affords $[MoO_3(OSiPh_3)]^{1-}$, which with Ph_3SiSH is converted to $[MoO_2S(OSiPh_3)]^{1-}$. Reaction with $(Ph_3C)(PF_6)/HS^-$ yields the tetrahedral monosulfido species $[MO_3S]^{2-}$, previously obtained only from the aqueous system $[MO_4]^{2-}/H_2S$. Dithiolene chelate rings are readily introduced upon reaction with 1,2-$C_6H_4(SSiMe_3)_2$, leading to the square pyramidal trioxo complexes $[MO_3(bdt)]^{2-}$, a previously unknown dithiolene molecular type. Further ring insertion occurs upon reaction of $[WO_3(bdt)]^{2-}$ with 1,2-$C_6H_4(SSiMe_3)_2$, giving $[WO_2(bdt)_2]^{2-}$. Related reactions occur with $[ReO_4]^{1-}$. Treatment with 1 equiv of $(Me_3Si)_2S$ produces $[ReO_3S]^{1-}$; with 3 equiv of 1,2-$C_6H_4(SSiMe_3)_2$, $[ReO(bdt)_2]^{1-}$ is obtained with concomitant $Re^{VII} \rightarrow Re^{V}$ reduction. X-ray structures are reported for $[MO_3S]^{z-}$ (M = Mo, W, $z = 2$; M = Re, $z = 1$), $[MO_3(bdt)]^{2-}$, and $[WO_2(OSiPh_3)(bdt)]^{1-}$, a silylation product of $[WO_3(bdt)]^{2-}$. $[MoO_3(bdt)]^{2-}$ is related to the site of inactive sulfite oxidase, and $[WO_2(OSiPh_3)(bdt)]^{1-}$ should closely approximate the metric features of the [(dithiolene)MoO_2(OH)] site in inactive aldehyde/xanthine oxidoreductase. This work provides convenient syntheses of known and new derivatives of tetraoxometalates, among which is entry to a unique class of oxo-monodithiolene complexes.

Introduction

Molybdenum sites in the sulfite oxidase and xanthine oxidoreductase enzyme families[1] contain one pyranopterin-dithiolate ligand (S_2pd) bound to the metal, with the remaining ligands dependent on the family and state (active or inactive) of the enzyme. Oxidized sites of interest are schematically depicted in Figure 1. In functional sulfite oxidase, the site is $[Mo^{VI}O_2(S_2pd)(S_{Cys})]$; from EXAFS analysis, an inactive form of a mutant enzyme includes the $Mo^{VI}O_3$ group.[2] Inactive modifications of aldehyde and xanthine oxidoreductases feature protonated versions of this group with hydroxide or water ligands.[3,4] These desulfo forms lack the terminal sulfide atom essential for activity. This atom has been crystallographically located in the $[Mo^{V,VI}OS(S_2pd)(OH/OH_2)]$ sites of these enzymes.[5,6] The recent crystallographic determination of milk xanthine oxidoreductase

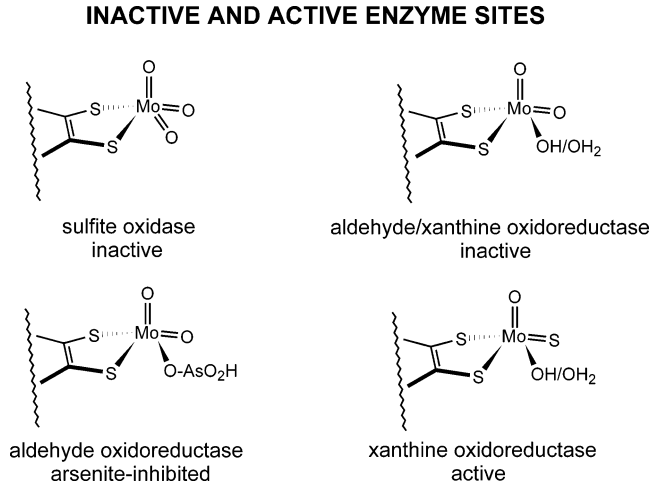

Figure 1. Schematic depictions of the sites in inactive mutant liver sulfite oxidase, inactive *Desulfovibrio gigas* aldehyde or milk xanthine oxidoreductase (oxidase), arsenite-inhibited *D. gigas* aldehyde oxidoreductase, and active milk xanthine oxidoreductase.

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places the sulfur atom in the equatorial plane of approximate square pyramidal stereochemistry.[6] It is probable that the same structure applies to the active form of oxidized aldehyde oxidoreductase.

We recently observed that the trigonal $M^{VI}O_3$ group (M = Mo, W) might serve as an actual or formal progenitor of the inorganic portions of the metal sites in Figure 1 and for any such sites in tungstoenzymes. Accordingly, we authenticated the nucleophilicity of oxo ligands in these groups by protonation and silylation reactions and also demonstrated oxo/sulfido substitution.[7] These experiments were performed with the six-coordinate complexes LMO_3 where L is a cyclic triaza ligand (1,3,5-tri-*tert*-butyl-1,3,5-triazacyclohexane, 1,4,7-trimethyl-1,4,7-triazacyclononane). Any route to the desired synthetic analogues of the active sites of xanthine and aldehyde oxidoreductases (Figure 1) requires the inclusion of an appropriate unsaturated 1,2-dithiolate (dithiolene) chelate ring in metal trioxo species following by sulfidation of the $M^{VI}O_3$ group, or the introduction of a ring in an $M^{VI}O_2S$ species. While bis- and tris(dithiolene) complexes of molybdenum and tungsten abound,[8,9] monodithiolene complexes potentially suitable for elaboration into active site analogues are uncommon. Several procedures were developed in the course of the synthesis of the sulfite oxidase analogue $[Mo^{VI}O_2(SR)(bdt)]^{1-}$, containing a single benzene-1,2-dithiolate chelate ring.[10] In this work, we report an efficient entry to certain mono- and bis-bdt complexes and the preparation of $[MO_3S]^{2-}$ species that may ultimately be useful in the synthesis of site analogues. Also included are several related reactions of $[ReO_4]^{1-}$.

Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen atmosphere using standard Schlenk techniques or an inert atmosphere box. Volume reduction steps were performed in vacuo. Acetonitrile, ether, and THF were purified with an Innovative Technology solvent purification system. Hexanes were distilled over sodium benzophenone ketal; acetonitrile-d_3 was stored over 4-Å molecular sieves. 1,2-Bis(trimethylsilylthio)benzene was prepared according to a literature procedure.[11] The known compound $(Et_4N)[ReO_4]$ was prepared by treatment of $AgReO_4$ with Et_4NCl in dichloromethane. All other reagents were commercial samples used as received. Compounds were identified by elemental analyses and crystal structure determinations.

$(Et_4N)[MoO_3(OSiPh_3)]$. This compound has been prepared previously in two steps from $[Mo_2O_7]^{2-}$ and Ph_3SiOH and isolated as the Bu_4N^+ salt.[12] We provide an alternative procedure not requiring preparation of the precursor molybdate salt. To a solution of 2.37 g (8.03 mmol) of Ph_3SiCl in dichloromethane was added 3.02 g (8.03 mmol) of Ag_2MoO_4. The suspension was stirred for 72 h, and 1.33 g (8.03 mmol) of Et_4NCl was added. The mixture was stirred overnight and filtered through Celite, and the solvent was removed. The residue was agitated in ether, and the ether was removed. The solid was extracted into 20−30 mL of dichloromethane, the solution was filtered, and the solvent was removed. These steps were repeated with the solid residue. The resultant solid was extracted with acetonitrile, and the extract was filtered through Celite. Ether was diffused into the filtrate, causing separation of 2.25 g of crystalline solid. The filtrate was taken to dryness and the residue similarly recrystallized, resulting in a total of 2.52 g (57%) of product as a white solid. IR (KBr): 712 (s), 880 (s, br, ν_{MoO}). ^1H NMR (CD_3CN, anion): δ 7.38 (m, 6), 7.43 (t, 3), 7.60 (d, 6). Anal. Calcd for $C_{26}H_{35}MoNO_4Si$: C, 56.82; H, 6.42. Found: C, 56.75; H, 6.37.

$(Et_4N)[MoO_2S(OSiPh_3)]$. To a solution of 209 mg (0.380 mmol) of $(Et_4N)[MoO_3(OSiPh_3)]$ in 10 mL of acetonitrile cooled to 0 °C in an ice bath was added 112 mg (0.383 mmol) of Ph_3SiSH in 2 mL of THF at 0 °C. The reaction mixture became bright orange within ca. 1 min, was stirred for 45 min at 0 °C, and was concentrated to 1.5 mL and filtered. Addition of ether followed by hexanes resulted in the separation of an orange solid. This material was collected, washed with ether, and dried to afford the product as 180 mg (84%) of orange solid. IR (KBr): 511 (s); 885, 905 (s, ν_{MoO}) cm^{-1}. ^1H NMR (CD_3CN, anion): δ 7.36−7.43 (m, ∼9), 7.57−7.60 (m, ∼6). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 255 (1850), 260 (1840), 314 (1440), 356 (sh, 463), 399 (sh, 272), 465 (sh, 96) nm. Anal. Calcd for $C_{26}H_{35}MoNO_3SSi$: C, 55.21; H, 6.24; N, 2.48; S, 5.67. Found: C, 55.39; H, 6.34; N, 2.46; S, 5.58. Mass spectrum: m/z 437.2 (M^+); also observed was a set of peaks at m/z = 431.2 to 440.4 with the correct isotope distribution for the indicated formulation.

$(Et_4N)_2[MoO_3S]$. Method A. To a solution of 156 mg (0.284 mmol) of recrystallized $(Et_4N)[MoO_3(OSiPh_3)]$ in 12 mL of acetonitrile and 2 mL of 2,6-lutidine cooled to −20 °C was added a solution of 47 mg (0.29 mmol) of $(Et_4N)(SH)$ in 6 mL of acetonitrile, also at −20 °C. The reaction mixture was stirred for 30 min at −20 °C and concentrated to ∼2 mL. Addition of ∼80 mL of cold ether caused separation of a light yellow solid. Ether was decanted, and the solid was washed three times with THF, dried, and dissolved into a minimal volume of acetonitrile. The solution was filtered, and ether was diffused into the solution. After 1 day, the product was collected as 86 mg (69%) of large yellow crystals. IR (KBr): 458 (s), 820, 868 (vs, ν_{MoO}) cm^{-1}. Anal. Calcd for $C_{16}H_{40}MoN_2O_3S$: C, 44.02; H, 9.24; N, 6.42; S, 7.35. Found: C, 43.27; H, 9.28; N, 6.26; S, 7.27.

Method B. To a solution of 104 mg (0.247 mmol) of scrupulously dried $(Et_4N)_2[MoO_4]$ in 7 mL of acetonitrile at 0 °C was added a solution of 96 mg (0.25 mmol) of $(Ph_3C)(PF_6)$ in 4 mL of acetonitrile, also at 0 °C. After being stirred for 5 min at 0 °C, the colorless solution was treated with a solution of 41 mg (0.25 mmol) of $(Et_4N)(SH)$ in 4 mL of acetonitrile. The lemon-yellow solution was stirred for 10 min at 0 °C, concentrated to half-volume, filtered through Celite, and concentrated to ca. 3 mL. Ether (80 mL) was added causing separation of a yellow solid. The ether was decanted, and the solid was stirred as a suspension in 30 mL of THF/propionitrile (3:2 v/v). The solvent was decanted, and the solid was

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washed with THF and dried, yielding the product as 95 mg (88%) of yellow solid. The IR and UV−vis spectra of this material are identical to the product of method A.

$(Et_4N)_2[MoO_3(bdt)]$. To a solution of 467 mg (1.11 mmol) of dry $(Et_4N)_2[MoO_4]$ in 20 mL of acetonitrile at −20 °C was added dropwise a solution of 319 mg (1.11 mmol) of 1,2-$C_6H_4(SSiMe_3)_2$ in 5 mL of acetonitrile at −20 °C. The solution assumed a red-orange color immediately and was stirred for 3 min. *N*,*N*-Dimethylacetamide (2 mL) in acetonitrile (2 mL) was added, and the reaction mixture was concentrated to the point of turbidity (∼2 mL). Addition of cold THF (80 mL) resulted in separation of the product as 427 mg (71%) of red solid. IR (KBr): 812 (s), 826, 878 (s, ν_{MoO}) cm^{-1}. ^1H NMR (CD_3CN): δ 6.52 (q, 2), 7.04 (q, 2). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 260 (13700), 325 (sh, 3700) nm. Anal. Calcd for $C_{22}H_{44}MoN_2O_3S_2$: C, 48.51; H, 8.14; N, 5.14. Found: C, 48.29; H, 7.96; N, 4.97.

$(Et_4N)_2[WO_3S]$. A solution of 190 mg (0.488 mmol) of $(Ph_3C)(PF_6)$ in 5 mL of acetonitrile was added dropwise to a solution of 248 mg (0.488 mmol) of dry $(Et_4N)_2[WO_4]$ in 10 mL of acetonitrile. The reaction mixture was stirred for 45 min and cooled to −20 °C. A solution of 80 mg (0.490 mmol) of $(Et_4N)(SH)$, also at −20 °C, was added over 3 min. The nearly colorless solution was stirred for 7 h, slowly warmed to room temperature, and concentrated to 1.5 mL. Sufficient ether was added to cause separation of a white solid, which was collected and washed with THF. The solid was slurried with 50 mL of THF/propionitrile (3:2 v/v) for 4 h to remove $(Et_4N)(PF_6)$, dried, and extracted into a minimal volume of acetonitrile. The extract was filtered through Celite. Vapor diffusion of ether into the filtrate afforded the product as 175 mg (68%) of colorless crystals. IR (KBr): 442 (m, ν_{WS}), 825, 898 (ν_{WO}) cm^{-1}. Anal. Calcd for $C_{16}H_{40}N_2O_3SW$: C, 36.64; H, 7.69; N, 5.34; S, 6.11. Found: C, 36.38; H, 7.54; N, 5.18; S, 6.15.

$(Et_4N)_2[WO_3(bdt)]$. A solution of 571 mg (1.12 mmol) of dry $(Et_4N)_2[WO_4]$ in 25 mL of acetonitrile was treated dropwise with a solution of 322 mg (1.12 mmol) of 1,2-$C_6H_4(SSiMe_3)_2$ in 5 mL of acetonitrile. By the end of the addition, the solution assumed a yellowish color. *N*,*N*-Dimethylacetamide (2 mL) was added, and the solution was concentrated to ca. 1.5 mL, at which point some yellow-orange precipitate formed. Addition of 80 mL of THF caused separation of more solid. The THF was decanted, and the solid was washed three times with small quantities of THF and dried. The product was obtained as 591 mg (83%) of yellow-orange solid. IR (KBr): 812 (s), 837, 902 (s, ν_{wo}) cm^{-1}. ^1H NMR (CD_3CN, anion): δ 6.54 (q, 2), 7.07 (q, 2). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 244 (20200), 247 (20300), 324 (2440) nm. Anal. Calcd for $C_{22}H_{44}N_2O_3S_2W$: C, 41.77; H, 7.01; N, 4.43. Found: C, 41.66; H, 6.94; N, 4.35.

$(Et_4N)[WO_2(OSiPh_3)(bdt)]$. A suspension of 202 mg (0.319 mmol) of $(Et_4N)_2[WO_3(bdt)]$ in 20 mL of THF containing 5 drops of 4-*tert*-butylpyridine was treated dropwise over 4−5 min with 99 mg (0.34 mmol) of Ph_3SiCl in THF. The suspension was stirred for 16 h and filtered through Celite, and the filtrate was taken to dryness. The residue was washed with ether and extracted into a minimum volume of acetonitrile; the extract was filtered through Celite. Addition of ether to the filtrate caused separation of a solid, which was collected and dried to afford the product as 71 mg (29%) of dark microcrystalline solid. IR (KBr): 895, 917 (s, ν_{WO}) cm^{-1}. ^1H NMR (CD_3CN, anion): δ 6.83 (q, 2), 7.16 (q, 2), 7.42 (m, 9), 7.66 (d, 6). Absorption spectrum (THF): λ_{max} (ϵ_M) 243 (57700), 261 (sh, 27900), 305 (10800), 529 (1790) nm. Anal. Calcd for $C_{32}H_{39}NO_3S_2SiW$: C, 50.46; H, 5.16; N, 1.84; S, 8.42. Found: C, 50.23; H, 5.11; N, 1.88; S, 8.31.

Chart 1. Designation of Complexes

$[MoO_3(OSiPh_3)]^{1-}$	**1**
$[MO_3S]^{2-}$	M = Mo **2**, W **6**
$[MoO_2S(OSiPh_3)]^{1-}$	**3**
$[MO_3(bdt)]^{2-}$	M = Mo **4**, W **7**
$[MO_2(OSiPh_3)(bdt)]^{1-}$	M = Mo **5**,[10] W **8**
$[WO_2(bdt)_2]^{2-}$	**9**[13,14]
$[ReO_3S]^{1-}$	**10**
$[ReO(bdt)_2]^{1-}$	**11**[15,16]

$(Et_4N)_2[WO_2(bdt)_2]$. The following preparation involves fewer steps than reported procedures.[13,14] To a solution of 40 mg (0.063 mmol) of $(Et_4N)_2[WO_3(bdt)]$ in 8 mL of acetonitrile was added dropwise a solution of 18 mg (0.063 mmol) of 1,2-$C_6H_4(SSiMe_3)_2$ in 2 mL of acetonitrile. The solution became violet and was stirred for 1 h, during which it assumed a brown-orange color. Solvent was removed; the residue was washed with THF and dissolved in a minimum volume of acetonitrile. The solution was filtered. Addition of THF and storage at −20 °C caused separation of the product as 46 mg (96%) of bright orange solid, whose spectroscopic properties are identical to those reported.[14]

$(Et_4N)[ReO_3S]$. To a solution of 170 mg (0.45 mmol) of $(Et_4N)[ReO_4]$ in 9 mL of acetonitrile was added dropwise a solution of 81 mg (0.45 mmol) of $(Me_3Si)_2S$ in 1 mL of acetonitrile. The reaction mixture was stirred for 2 days, over which the color slowly changed from colorless to yellow and then orange. The solution was concentrated to ca. 1 mL and filtered. Vapor diffusion of ether into the filtrate gave dark orange crystals, which were collected and dissolved in acetonitrile. Vapor diffusion of ether into the filtrate afforded the product as 125 mg (71%) of yellow-orange crystals. IR (KBr): 503 (s, ν_{ReS}); 901, 937 (s, ν_{ReO}). Anal. Calcd for $C_8H_{20}NO_3ReS$: C, 24.23; H, 5.08; N, 3.68; S, 8.09. Found: C, 24.32; H, 5.49; N, 3.45; S, 8.14.

$(Et_4N)[ReO(bdt)_2]$. The following procedure is simpler than previously reported methods.[15,16] To a solution of 124 mg (0.33 mmol) of $(Et_4N)[ReO_4]$ in 10 mL of acetonitrile was added a solution of 280 mg (0.98 mmol) of 1,2-$C_6H_4(SSiMe_3)_2$ in 5 mL of acetonitrile. The colorless solution slowly became yellow-orange. The reaction mixture was stirred overnight and filtered, and the filtrate was concentrated to ca. 10 mL and filtered through Celite to give a yellow filtrate and an orange solid. The solid was dissolved in 3 mL of DMF, and the solution was added to the filtrate. Vapor diffusion of ether into the filtrate gave the product as 160 mg (80%) of a bright orange solid. IR (KBr): 957 cm^{-1} (s, ν_{ReO}). ^1H NMR (CD_3CN, anion): δ 6.98 (q, 4), 7.78 (q, 4). This compound crystallizes in monoclinic space group $P2_1/c$ with $a = 7.722(2)$ Å, $b = 16.825(3)$ Å, $c = 26.827(5)$ Å, $\beta = 94.65(3)°$, and $Z = 8$. A truncated data set was collected and solved, identifying the compound. The square pyramidal stereochemistry of the anion has been previously demonstrated by the crystal structure of the Ph_4P^+ salt.[15]

In the sections that follow, complexes are numerically designated according to Chart 1.

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Table 1. Crystallographic Data[a]

	$(Et_4N)_2$[**2**]	$(Et_4N)_2$[**4**]	$(Et_4N)_2$[**6**]	$(Et_4N)_2$[**7**]	$(Et_4N)_2$[**8**]	$(Et_4N)_2$[**10**]
formula	$C_{16}H_{40}MoN_2O_3S$	$C_{22}H_{44}MoN_2O_3S_2$	$C_{16}H_{40}N_2O_3SW$	$C_{22}H_{44}N_2O_3S_2W$	$C_{32}H_{39}NO_3S_2SiW$	$C_8H_{20}NO_3ReS$
fw	436.50	544.65	524.41	632.56	761.70	396.51
cryst syst	monoclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	4	2	4	2	2	8
a, Å	13.699(3)	9.815(2)	13.644(3)	9.788(2)	10.070(2)	7.133(1)
b, Å	11.917(2)	10.689(2)	11.966(2)	10.673(2)	12.035(2)	21.366(4)
c, Å	13.252(3)	15.045(3)	13.245(3)	14.954(3)	14.978(3)	16.628(3)
α, deg		104.87(3)		104.76(3)	84.25(3)	
β, deg	94.53(3)	95.78(3)	94.38(3)	95.54(3)	88.57(3)	91.38(3)
γ, deg		116.56(3)		117.05(3)	65.48(3)	
V, Å^3	2156.8(7)	1321.7(5)	2156.2(7)	1303.9(5)	1643.0(6)	2533.5(9)
T, K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
R^b ($R_w{}^c$), %	5.41 (8.88)	4.49 (9.98)	6.58 (10.61)	2.09 (4.84)	2.90 (5.74)	9.70 (18.64)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation. [b] $R = \sum||F_o|/|F_c||/\sum|F_o|$. [c] $R_w = \{\sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]\}^{1/2}$.

X-ray Structure Determinations. All compounds were determined as Et_4N^+ salts and are referred to here by anion number. Crystals of **2**, **3**, and **8** were produced by vapor diffusion of ether into a saturated acetonitrile solution. Crystals of **4** were grown by vapor diffusion of ether into a saturated *N*,*N*-dimethylacetamide solution. Crystals of **6** were grown by diffusion of a 3:2 *tert*-butyl methyl ether/diethyl ether solution (v/v) into a saturated acetonitrile solution. Crystals of **7** were obtained by diffusion of ether into an acetonitrile/*N*,*N*-dimethylacetamide solution. Crystals of **10** were grown by diffusion of a 4:1 *tert*-butylmethyl ether/diethyl ether solution (v/v) into a saturated acetonitrile solution. Samples were coated in Paratone oil and mounted on glass capillary fibers on a Bruker CCD area detector instrument operated by the SMART software package. For each crystal, a hemisphere of data was collected at 213 K in 30 s frames and with ω scans of 0.3 deg/frame. Data reduction was performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS, and space groups were assigned using XPREP.

All structures were solved by Patterson methods with SHELXTL and refined against all data by full-matrix least squares on F^2. Hydrogen atoms were attached at idealized positions on carbon atoms and were refined as riding atoms with uniform isotropic thermal parameters. The cation of compound **10** was disordered and refined accordingly. All structures converged in the final stages of refinement, showing no movement in atom positions. Use of the checking program PLATON did not identify any missing or higher symmetry. Crystal data are presented in Tables 1 and 2.[17]

The compound (Et_4N)[**3**] crystallizes in triclinic space group $P\bar{1}$ with $a = 8.629(2)$ Å, $b = 9.226(2)$ Å, $c = 19.445(4)$ Å, α = 100.75(3)°, $\beta = 92.69(3)°$, $\gamma = 113.13(3)°$, and $Z = 2$ at 213(2) K. The structure was solved as above and refined to $R = 4.98\%$. Bond lengths indicated possible disorder of the MoO_2S portion; consequently, the structure is not reported in detail.

Other Physical Measurements. ^{1}H NMR spectra were obtained with Bruker AM 400N/500N/600N spectrometers. FT-IR spectra were taken on recrystallized solid samples in KBr on a Nicolet Nexus 470 FT-IR spectrometer, and UV−vis spectra were taken on a Varian Cary 50 Bio UV−vis spectrophotometer. Electrospray mass spectra were recorded on a Platform II quadrupole mass spectrometer (Micromass Instruments, Danvers, MA).

Results and Discussion

This work is an investigation of the reactions of certain carbon and silicon electrophiles with tetraoxometalate anions and several derivative complexes in order to obtain compounds of present or future utility in the synthesis of analogues of the protein-bound sites in Figure 1. Reactions are summarized in Figure 2; products were isolated as Et_4N^+ salts. Structures of selected reaction products are given in Figures 3 and 4. Reactions involving silicon electrophiles were largely based on the bond energy order Si−O (123−136) > Si−Cl (113) > Si−S (≲99) (kcal/mol) for Me_3Si compounds,[18] which proved of predictive value.

Table 2. Bond Distances (Å) and Angles (deg) in $[MO_3(bdt)]^{2-}$ (M = Mo (**4**), W (**7**)) and $[WO_2(OSiPh_3)(bdt)]^{1-}$ (**8**)

	4	**7**	**8**
M−O1	1.733(2)	1.752(2)	1.723(2)
M−O2	1.754(3)	1.774(2)	1.733(2)
M−O3	1.757(3)	1.769(2)	1.903(2)
M−S1	2.536(1)	2.521(1)	2.471(1)
M−S2	2.555(1)	2.538(1)	2.425(1)
O1−M−O2	107.8(1)	107.2(1)	107.3(1)
O1−M−O3	106.3(1)	106.0(1)	103.1(1)
O1−M−S1	105.7(1)	106.49(8)	111.33(7)
O1−M−S2	101.46(8)	101.87(7)	101.43(8)
O2−M−O3	103.8(1)	103.6(1)	99.6(1)
O2−M−S2	81.92(9)	81.75(7)	84.85(8)
O3−M−S1	80.41(9)	80.28(8)	78.97(7)
S1−M−S2	77.15(4)	77.75(4)	80.60(4)
O2−M−S1	143.28(1)	143.38(7)	140.67(9)
O3−M−S2	148.12(9)	148.41(7)	152.49(7)
MS_2/C_6S_2	165.90(8)	165.53(7)	

Monosulfido Derivatives of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$. The nucleophilic character of these anions has been demonstrated in numerous investigations. Here we show that reaction of $[MoO_4]^{2-}$ with Ph_3SiCl affords **1** (57%) in a procedure that does not require the prior preparation of $[Mo_2O_7]^{2-}$.[12] This species can be smoothly converted with Ph_3SiSH to the monosulfido complex **3** (84%), a new reaction for terminal oxo/sulfido conversion. The indicated tetrahedral structure of **3** was demonstrated by an X-ray structure determination, but because of apparent disorder, the structure is not presented in detail.

The classical method for the preparation of members of the series $[MO_{4-n}S_n]^{2-}$ (M = Mo, W; $n = 1-4$) has been the reaction of $[MO_4]^{2-}$ with H_2S in aqueous alkaline solution.[19,20] Indeed, this method dates back to the late 19th

(17) See paragraph at the end of this article for Supporting Information available.

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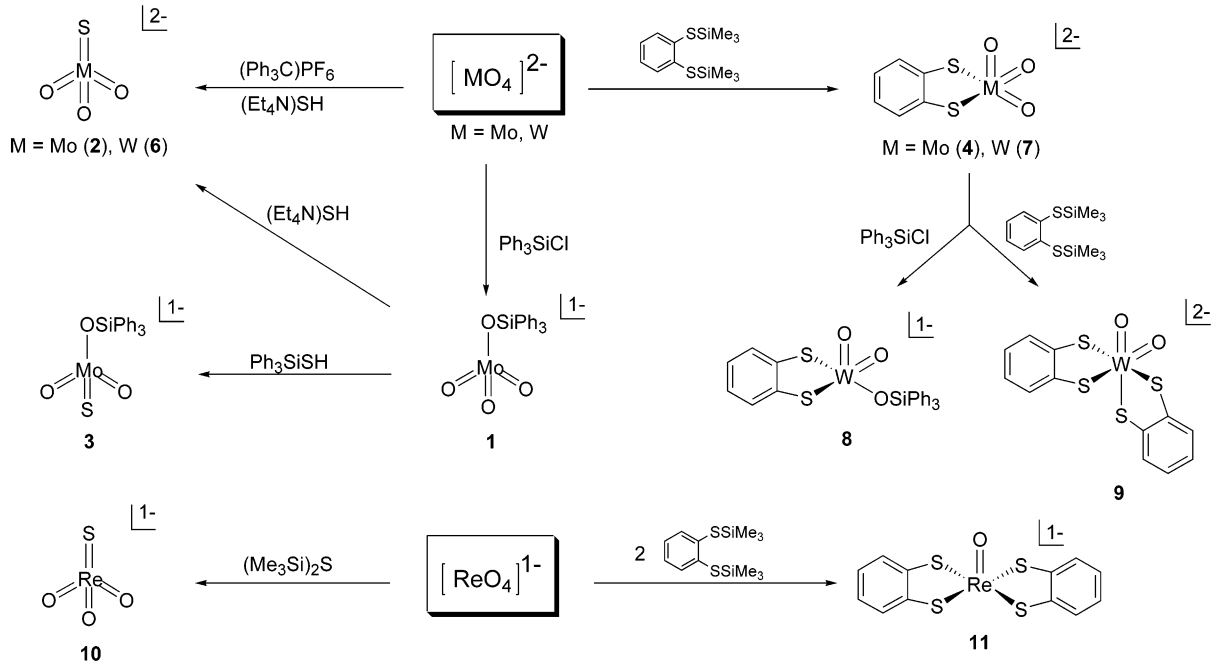

Figure 2. Reactions of molybdate, tungstate, and perrhenate ions with various carbon and silicon electrophiles leading to a silyloxide (**1**), monosulfido species (**2**, **3**, **6**, **10**), monodithiolene (**4**, **5**, **7**, **8**), and bis(dithiolene) complexes (**9**, **11**).

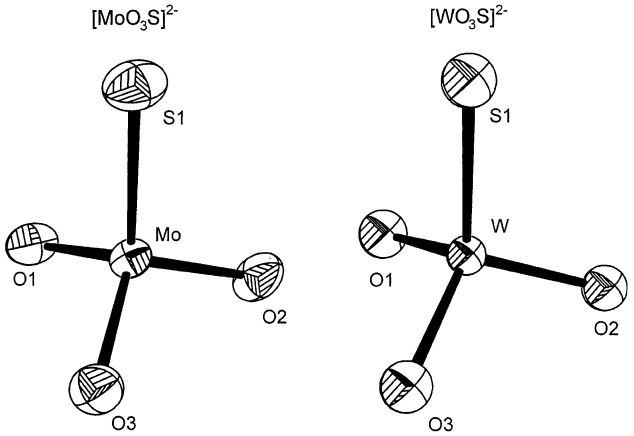

Figure 3. Structures of the monosulfido species $[MoO_3S]^{2-}$ and $[WO_3S]^{2-}$, showing the atom labeling schemes and 50% probability ellipsoids. Bond distances (Å) and angles (deg) for M = Mo/W: M−O1 1.780(3)/1.783(6), M−O2 1.753(3)/1.761(6), M−O3 1.764(3)/1.778(5), M−S 2.2236(1)/2.246-(2), O1−M−O2 108.8(2)/108.6(3), O1−M−O3 109.0(2)/109.0(3), O2−M−O3 108.6(1)/108.2(3), S−M−O1 109.1(1)/109.1(2), S−M−O2 110.3-(1)/110.8(2), S−M−O3 111.1(1)/111.2(2).

century when procedures were developed for isolation of specific ions by controlled reaction with H_2S and selective precipitation with an appropriate cation.[19,21−23] For the reaction $[MoO_{4-n}S_n]^{2-} + HS^- + H^+ \rightarrow [MoO_{3-n}S_{n+1}]^{2-} + H_2O$, rate constants decrease and equilibrium constants slightly increase as *n* increases.[24,25] At least in our hands, the most difficult species to isolate in relatively pure condition are salts of $[MoO_3S]^{2-}$ (**2**) and $[WO_3S]^{2-}$ (**6**). The sodium and potassium salts of **2**[21,26] and the potassium salt of **6**[22] have been reported; structure determinations are lacking. We have found that these ions are accessible in substantial purity by nonaqueous reactions. Reaction 1 affords **2** (69%) as yellow crystals. Reaction 2 likely proceeds by electrophilic attack of the carbocation to give $[MO_3(OCPh_3)]^{1-}$ (analogous to **1**) followed by nucleophilic displacement and proton transfer by hydrosulfide, yielding **2** (88%) or colorless **6** (68%). Compounds were identified by elemental analysis and crystal structure determinations (Figure 3).

$$[MoO_3(OSiPh_3)]^{1-} + HS^- \rightarrow [MoO_3S]^{2-} + Ph_3SiOH \quad (1)$$

$$[MO_4]^{2-} + Ph_3C^+ + HS^- \rightarrow [MO_3S]^{2-} + Ph_3COH \quad (2)$$

The ions have trigonally distorted tetrahedral stereochemistry with (mean) bond distances Mo−O = 1.76(1) Å and Mo−S = 2.236(1) Å and W−O = 1.77(1) Å and W−S = 2.246(2) Å. In reference to the few mononuclear oxo-sulfido structures known ($[MoOS_3]^{2-}$,[27] $[MoO_2S_2]^{2-}$,[28] $[WO_2S_2]^{2-}$ [29]), the M−O bond lengths are within 0.03 Å; M−S distances, for reasons unclear, are ca. 0.05 Å longer. Bond lengths in the limiting species $[MoS_4]^{2-}$ and $[WS_4]^{2-}$ are 2.18−2.19 Å.[30,31] The absorption spectrum of **2** in acetonitrile (Figure

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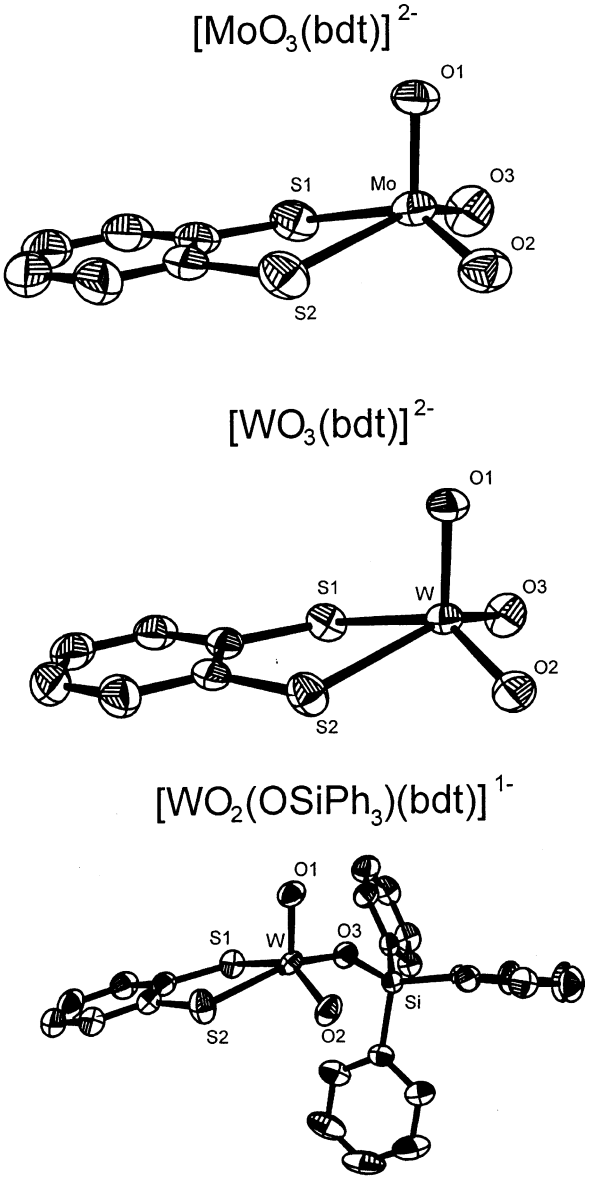

Figure 4. Structures of $[MoO_3(bdt)]^{2-}$ (upper), $[WO_3(bdt)]^{2-}$ (middle), and $[WO_2(OSiPh_3)(bdt)]^{1-}$ (lower), showing atom labeling schemes and 50% probability ellipsoids.

5), with bands at 289 and 391 nm in an ~30:1 intensity ratio, is in qualitative agreement with spectra ascribed to **2** generated in aqueous solution (λ_{max} = 288 or 292, 392−394 nm).[19,24,32,33] Other than λ_{max} (ϵ_M) = 292 (7400),[24] band intensities have not been reported, most likely because of the possible coexistence of $[MoO_2S_2]^{2-}$ (λ_{max} = 288, 320, 394 nm), also formed in the reaction with H_2S. The intense feature of **6** at 248 nm is found at 244 nm in aqueous solution where a second band 327 nm is evident. Our spectrum contains a corresponding band at 326 nm. The bands in the spectra of **2** and **6** have been assigned as S → M charge transfer transitions.[34,35] Although there is an apparent discrepancy in relative intensities for **2**, perhaps due in part to different solvents, we conclude that species generated in aqueous solution and our preparations by two methods are the same.

Monodithiolene Complexes. The first step in the synthesis of analogues of the sites in Figure 1 is the formation of a monodithiolene (ene-1,2-dithiolate) chelate ring. In seeking $[MoO_2(SR)(bdt)]^{1-}$,[10] an analogue of the active site of sulfite oxidase, one chelate functionality of $[Mo^{V}O(bdt)_2]^{1-}$ was removed with use of the selenium electrophile in reaction 3. Displacement of silyloxide by bdt and its subsequent stabilization as the lithium salt in THF in reaction 4 afforded a monodithiolene $Mo^{VI}O_2$ intermediate **5** that was converted to the desired product as a subsequent step. In these reactions, oxo ligands are retained. Reaction 5 with a disilylated version of bdt[11] and $[MO_4]^{2-}$ affords a simple route to monodithiolene $M^{VI}O_3$ complexes as red **4** (71%) and yellow-orange **7** (83%) with capture of one oxo ligand.

$$[MoO(bdt)_2]^{1-} + 2PhSeCl \rightarrow [MoOCl_2(bdt)]^{1-} + C_6H_4(SSePh)_2 \quad (3)$$

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

$$[MO_4]^{2-} + 1,2\text{-}C_6H_4(SSiMe_3)_2 \rightarrow [MO_3(bdt)]^{2-} + (Me_3Si)_2O \quad (5)$$

The Et_4N^+ salts of **4** and **7** are isomorphous, and the complexes are isostructural (Figure 4) and essentially isometric (Table 2), an expected property that applies to all molybdenum and tungsten dithiolenes with the same ligand set and oxidation level. The two complexes exhibit square pyramidal stereochemistry. Atom deviations are ±(0.05−0.06) Å from the least-squares O_2S_2 basal planes, and the Mo and W atoms are perpendicularly displaced by 0.54 Å from these planes toward axial ligand O1. The chelate rings are not exactly planar and are folded along the S···S direction by dihedral angles of 165−166° in the direction of the axial atom. Other dimensional features are unexceptional.

Several reactions of **7** were demonstrated. The complex can be monosilylated with Ph_3SiCl at a basal position to give **8** (29%, analogous to **5**) whose square pyramidal structure resembles **7** (Figure 4, Table 2). Silylation of O3 removes the trans influence of the oxo ligand, as reflected in a trans (W−S2) bond distance 0.11 Å shorter than in **7**. The cis (W−S1) distance is slightly shorter (0.03 Å) than in **7** but is also 0.05 Å longer than the trans bond. Similar effects on M−N bond distances have been observed with protonated and silylated $M^{VI}O_3$ groups bound to cyclic triaza ligands.[7] Additionally, reaction of **7** with 1 equiv of $1,2\text{-}C_6H_4(SSiMe_3)_2$ removes a second oxo ligand to form in nearly quantitative yield the bis(dithiolene)$W^{VI}O_2$ complex **9** (96%). This

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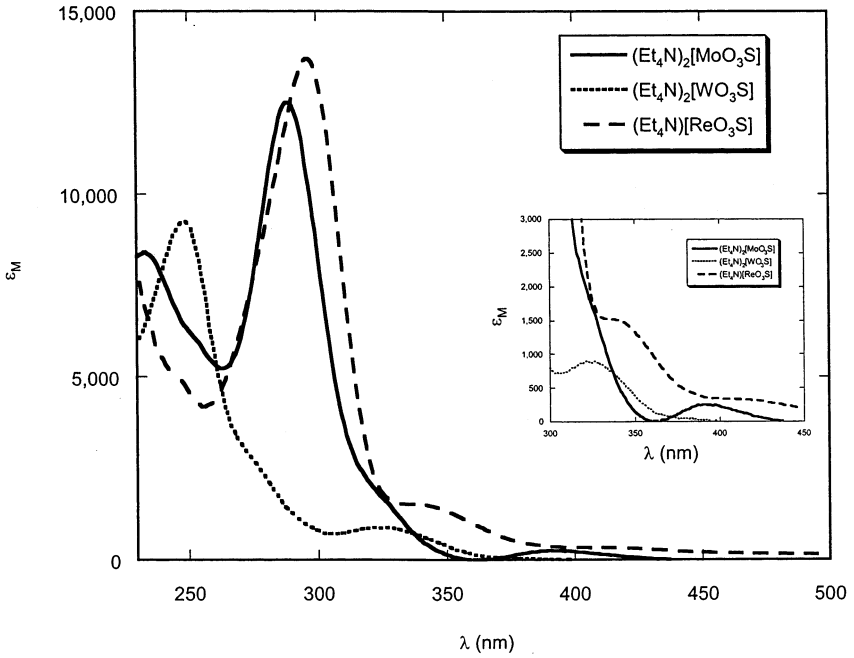

Figure 5. UV−vis absorption spectra (λ_{max} (ϵ_M)) of monosulfido species in acetonitrile solutions. $[MoO_3S]^{2-}$: 289 (12500), 391 (373) nm. $[WO_3S]^{2-}$: 248 (9280), 326 (893) nm. $[ReO_3S]^{1-}$: 296 (13700), 340 (1510) nm. In the spectrum of $[MoO_3S]^{2-}$, the weak shoulder near ~320 nm may arise from a slight amount of $[MoO_2S_2]^{2-}$.

complex was originally prepared by Ueyama et al.[13] in a multistep procedure; an improved method requires three steps.[14] The present two-step procedure based on tungstate is now the method of choice.

Rhenium Complexes. A brief investigation was carried out to see if certain of the preceding methods might be effective with metals other than molybdenum and tungsten. Members of the $[ReO_{4-n}S_n]^{1-}$ series have also been generated by the reaction of $[ReO_4]^{1-}$ with H_2S, with $[ReS_4]^{1-}$ being the most thoroughly characterized. However, unlike the molybdenum and tungsten series, the monosulfido member is rather easily accessible. This anion was first obtained in 1931 by controlled precipitation with monovalent cations.[36] Alkali metal salts were subsequently obtained in 1968 by metathesis of $TlReO_3S$,[37] and the tetrahedral structure of the anion, with Re−O = 1.75 Å and Re−S = 2.14 Å, was established a year later.[38] The procedures that afforded $[MO_3S]^{2-}$ are ineffective in the formation of monosulfido **10** from perrhenate. Instead, stoichiometric reaction 6 with $(Me_3Si)_2S$, a reagent of some utility in this laboratory[14,39−41] and elsewhere[42−45] for terminal oxo/sulfido substitution, proved effective. Complex **10** was isolated as yellow-orange crystals (71%). The tetrahedral structure of **10** (not shown) is essentially identical to **2** and **6**. (Et_4N)[**10**] crystallized with two anions in the asymmetric unit. For one of them, mean Re−O = 1.72(3) Å and Re−S = 2.129(5) Å, and for the other, mean Re−O = 1.731(5) Å and Re−S = 2.143(5) Å. The mean Re−S bond length in $[ReS_4]^{1-}$ is 2.123(5) Å.[46] Formation of the desired anion was further confirmed by its absorption spectrum (Figure 5), which is in good agreement with that in aqueous solution, for which λ_{max} = 298 and 340 nm, with an intensity ratio of ca.12:1.[47] Last, the utility of 1,2-$C_6H_4(SSiMe_3)_2$ as a dithiolene chelate ring precursor is further emphasized by formation of bis-complex **11** (80%) in a procedure more convenient than the published methods.[15,16] The reaction, performed with a 3:1 mol ratio of reactants, probably proceeds by the stoichiometry of reaction 7, in which the reductant of Re^{VII} is presumably (di)thiolate generated by Si−S bond cleavage. The sulfur-containing product would then be bis(*o*-phenylene)tetrasulfide[48] or a disulfide polymer.

$$[ReO_4]^{1-} + (Me_3Si)_2S \rightarrow [ReO_3S]^{1-} + (Me_3Si)_2O \quad (6)$$

$$[ReO_4]^{1-} + 3\ 1,2\text{-}C_6H_4(SSiMe_3)_2 \rightarrow [ReO(bdt)_2]^{1-} + 3(Me_3Si)_2O + \text{“}C_6H_4S_2\text{”} \quad (7)$$

Summary

This work provides simple, improved syntheses of known and new derivatives of tetraoxometalates of molybdenum,

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tungsten, and rhenium by reactions with carbon and silicon electrophiles. These include a monosilylated species (**1**), monosulfido anions (**2**, **3**, **6**, **10**), monodithiolene trioxo (**4**, **7**) and dioxo (**8**) complexes, and bis(dithiolene) dioxo (**9**) and monooxo (**11**) complexes. With reference to Figure 1, anions **2** and **6** are possible precursors to active site analogues in the xanthine oxidoreductase family by introduction of a dithiolene chelate ring, as are monodithiolenes **4** and **7** by oxo/sulfido substitution. Complex **4** is related to the site of inactive sulfite oxidase. The structure of **8** should reflect rather closely the dimensional features of a [(dithiolene)-$Mo^{VI}O_2(OH)$] group, as in the inactive form of aldehyde/xanthine oxidoreductase. Complexes **4**, **7**, **9**, and **11** demonstrate the introduction of dithiolene chelate rings by silylation of terminal oxo ligands. Extension of these methodologies for oxo/sulfido substitution and dithiolene ring insertion to other cases is readily conceived. Finally, a conspicuous advantage of these procedures is that the precursor metal sources, tetraoxometalates, are the cheapest and most accessible forms available for these metals.

Acknowledgment. This research was supported by NSF Grant CHE 0237419.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of the compounds in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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