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Silylation, Sulfidation, and Benzene-1,2-dithiolate Complexation Reactions of Oxo- and Oxosulfidomolybdates(VI) and -Tungstates(VI)

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The synthesis and structures of two types of molecules are presented: $[M^{VI}O_{3-n}S_n(OSiR_2R')]^{1-}$ (M = Mo, n = 0–3; M = W, n = 3) and $[M^{VI}O_2(OSiR_2R')(bdt)]^{1-}$ (M = Mo, W; bdt = benzene-1,2-dithiolate). For both types, R_2R' are Me_3, Pr^i_3, Ph_3, Me_2Bu^t and Ph_2Bu^t. The complete series of oxo/sulfido/silyloxo molybdenum complexes has been prepared. Complexes with n = 0 are readily prepared by the silylation of Ag_2MoO_4 and sustain mono- or disulfidation with Ph_3SiSH to form a species with n = 1 and n = 2, respectively. Complexes with n = 3 are accessible by the silylation of $[MOS_3]^{2-}$. Structures of the representative series members $[MoO_3(OSiPh_2Bu^t)]^{1-}$, $[MoO_2S(OSiPh_3)]^{1-}$, $[MoOS_2(OSiPr^i_3)]^{1-}$, $[MoS_3(OSiPh_2Bu^t)]^{1-}$, and also $[WS_3(OSiMe_2Bu^t)]^{1-}$, all with tetrahedral stereochemistry, are presented. Benzene-1,2-dithiolate complexes are prepared by the reaction of $[MoO_3(OSiR_2R')]^{1-}$ with the dithiol or by the silylation of previously reported $[MO_3(bdt)]^{2-}$. The structures of $[MoO_2(OSiPh_2Bu^t)(bdt)]^{1-}$ and $[WO_2(OSiPr^i_3)(bdt)]^{1-}$ conform to square-pyramidal stereochemistry with an oxo ligand in the apical position. The role of these complexes in the preparation of site analogues of the xanthine oxidoreductase enzyme family is noted. The sulfidation reactions reported here point to the utility of Ph_3SiSH and Pr^i_3SiSH as reagents for Mo^{VI}-based oxo-for-sulfido conversions.

Introduction

We are engaged in research on the biomimetic chemistry of molybdenum and tungsten directed at the attainment of structural and functional analogues of the catalytic centers of oxotransferase and hydroxylase enzymes. Results on oxotransferase analogues have been summarized[1] and are augmented by more recent developments.[2−4] Hydroxylases are members of the xanthine oxidoreductase enzyme family,[5] and utilize coordinated hydroxide as a nucleophile in reactions with purines, aldehydes, and other substrates of this family.[6,7] A critical structural and mechanistic feature of the apparently common, oxidized catalytic site is the presence of a basal sulfido ligand in the square-pyramidal unprotonated and protonated sites $[Mo^{VI}O_2S(S_2pd)]$ and $[Mo^{VI}O(OH)S(S_2pd)]$, respectively.[8] Appropriate structural analogues of these sites are shown in Figure 1, together with actual or projected methods of synthesis. In these molecules, benzene-1,2-dithiolate models the cofactor ligand and silylation simulates protonation. The approximate square-pyramidal geometry with axial and basal oxo and basal sulfido coordination follows from the X-ray structure of *Pseudomonas putida* quinoline 2-oxidoreductase.[9] Accurate bond distances are available from the molybdenum EXAFS analysis of bovine XO.[10]

The sulfidation method of synthesis has recently afforded, among others, the complexes $[WO_2S(bdt)]^{2-}$ and $[WOS(OSiPr^i_3)(bdt)]^{1-}$, which are the first structural analogues of the oxidized XO sites.[11] Tungsten is used without structural compromise to stabilize the M^{VI} state. In the course of this and recent work, we have investigated silylation and sulfidation reactions of oxomolybdates(VI) and oxotungstates-

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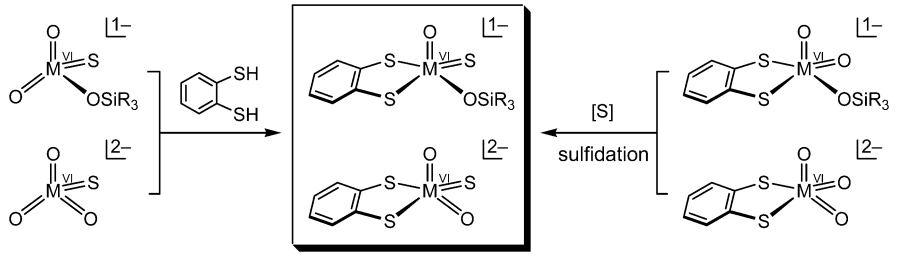

Figure 1. Synthetic analogues of the oxidized active sites in the xanthine oxidoreductase family of enzymes and their precursors.

(VI), leading to species of potential utility in the preparation of XO site analogues. For example, the ions $[MO_3S]^{2-}$ (M = Mo, W), difficult to obtain as pure R_4N^+ salts by the classical reaction of aqueous $[MO_4]^{2-}$ with H_2S, are readily prepared by the more easily controlled reactions 1 and 2.[12] Here, we describe the synthesis of a family of oxo/sulfido/silyloxo complexes of Mo^{VI} and W^{VI} comprised primarily of previously unreported or incompletely characterized types, and the structures of representative members. A later report will enlarge on the use of such complexes in the synthesis of oxo/sulfido site analogues.

$$[MO_4]^{2-} + Ph_3C^+ + HS^- \rightarrow [MO_3S]^{2-} + Ph_3COH \quad (1)$$

$$[MoO_3(OSiPh_3)]^{1-} + HS^- \rightarrow [MoO_3S]^{2-} + R_3SiOH \quad (2)$$

Experimental Section

Preparation of Compounds. All of the reactions and manipulations were performed under a pure dinitrogen atmosphere using either an inert atmosphere box or standard Schlenk techniques. Acetonitrile, diethylether, dichloromethane, and THF were freshly purified using an Innovative Technology solvent purification system and stored over 4 Å molecular sieves. Benzene-1,2-dithiol (H_2(bdt)) was prepared as described.[13] ^{1}H NMR data for salts refer to anions in CD_3CN solutions. IR spectra were recorded in KBr pellets and absorption spectra in acetonitrile solutions. All of the compounds were characterized by a combination of IR, ^{1}H NMR, UV−vis, mass spectroscopy, and elemental analysis. Negative-ion electrospray mass spectra of all of the complex salts reveal a prominent peak for the parent anion (M^-). Certain compounds not subjected to elemental analysis were identified by X-ray structure determinations.

Oxo/Sulfido/Silyloxo Complexes. $(Et_4N)[MoO_3(OSiR_2R')]$. These compounds were prepared on a 5−8 mmol scale, by a method analogous to that reported for $(Et_4N)[MoO_3(OSiPh_3)]$[12] but with the use of $R_2R'SiCl$. A solution of $R_2R'SiCl$ (1.0 equiv) in dichloromethane was added dropwise to a suspension of Ag_2MoO_4 (2−3 g) in dichloromethane. The reaction mixture was stirred for 72 h and 1.0 equiv of Et_4NCl was added. The mixture was stirred for 8 h, filtered through Celite, and the filtrate was taken to dryness, leaving a solid white residue. This material was dissolved in 20−30 mL of dichloromethane, the solution was filtered, and the filtrate solvent was removed. This step was repeated with the residue, the resultant solid was extracted with acetonitrile, and the extract was filtered through Celite. The filtrate was reduced to half-volume, several volume equiv of ether were layered on the filtrate, and the mixture was allowed to stand for 2 d. Products were isolated as crystalline white solids in the indicated yields.

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R = R′ = Me. Needlelike crystals, 49%. IR: 955, 902, 878 cm^{-1}. ES-MS: *m*/*z* 233 (M^-). ^{1}H NMR: δ 0.11 (s).

R = R′ = Pr^i. Platelike crystals, 59%. IR: 971, 906, 679 cm^{-1}. ES-MS: *m*/*z* 317 (M^-). ^{1}H NMR: δ 0.14 (sept, 3), 1.07 (d, 18). Anal. Calcd for $C_{17}H_{41}MoNO_4Si$: C, 45.62; H, 9.23; N, 3.13. Found: C, 45.48; H, 9.30; N, 3.09.

R = Me, R′ = Bu^t. Blocklike crystals, 55%. IR: 973, 907, 878, 678 cm^{-1}. ES-MS: *m*/*z* 275 (M^-). ^{1}H NMR: δ 0.06 (s, 6), 0.92 (s, 9).

R = Ph, R′ = Bu^t. Platelike crystals, 67%. IR: 972, 904, 885, 703 cm^{-1}. ^{1}H NMR: δ 1.03 (s, 9), 7.39 (m, 6), 7.74 (m, 4). ES-MS: *m*/*z* 399 (M^-). Anal. Calcd for $C_{24}H_{39}MoNO_4Si$: C, 54.43; H, 7.42; N, 2.64. Found: C, 54.38; H, 7.30; N, 2.69.

$(Et_4N)[MoO_2S(OSiPh_2Bu^t)]$. The procedure was performed at −20 °C. A solution of Ph_3SiSH (112 mg, 0.383 mmol) in 2 mL of THF was added dropwise to a solution of $(Et_4N)[MoO_3(OSiPh_2Bu^t)]$ (201 mg, 0.380 mmol) in 8 mL of acetonitrile. The reaction mixture turned bright orange within 3 min, and stirring was continued for 10 min. Solvents were removed, and the yellow-orange solid was washed with hexanes and dissolved in 1.5 mL of acetonitrile. The solution was filtered, and the filtrate was layered with 20 mL of ether. Over 8 h, a solid separated, which was washed with ether (2 × 3 mL) and dried, to afford the product as 171 mg (83%) of yellow-orange crystals. Absorption spectrum: λ_{max} (ϵ_M) 256 (5820), 311 (6780), 399 (sh, 770), 455 (sh, 1100) nm. ES-MS: *m*/*z* 415 (M^-). ^{1}H NMR: δ 1.04 (s, 9), 7.42 (m, 6), 7.75 (m, 4). Anal. Calcd for $C_{24}H_{39}MoNO_3SSi$: C, 52.83; H, 7.20; N, 2.57; S, 5.88. Found: C, 52.68; H, 7.10; N, 2.48; S, 5.86.

$(Et_4N)[MoO_2S(OSiPr^i_3)]$. The previous procedure was followed with the use of 0.40 mmol each of $(Et_4N)[MoO_3(OSiPr^i_3)]$ and Pr^i_3SiSH. The product was obtained as 168 mg (90%) of yellow-orange crystals. IR: 949, 901, 881, 500 cm^{-1}. Absorption spectrum: λ_{max} (ϵ_M) 255 (5370), 310 (4440), 350 (1860), 472 (280) nm. ES-MS *m*/*z* 333 (M^-). ^{1}H NMR: δ 1.09 (d) (CH not detected). Anal. Calcd for $C_{17}H_{41}MoNO_3SSi$: C, 44.04; H, 8.91; N, 3.02; S, 6.92. Found: C, 43.87; H, 9.02; N, 2.97; S, 6.85.

$(Et_4N)[MoOS_2(OSiR_2R')]$. To a solution of $(Et_4N)[MoO_3(OSiR_2R')]$ (0.38−0.40 mmol) in 6 mL of acetonitrile was added a solution of Ph_3SiSH (2.0 equiv) in 2 mL of THF. The reaction mixture turned bright orange within 1 min and was stirred for 10 min to give a deep-orange solution. The solution was filtered and the solvents were removed. The orange solid was washed with hexanes and ether and dissolved in 1.5 mL of acetonitrile. The solution was filtered, and the filtrate was layered with 20 mL of ether. The solid that separated over 8 h was washed with ether (2 × 3 mL) and dried to afford the products as orange platelike crystals in the indicated yields.

R = R′ = Pr^i. 84%. IR: 938, 899, 507 cm^{-1}. Absorption spectrum: λ_{max} (ϵ_M) 289 (4120), 300 (sh, 3950), 350 (4400), 404 (1260), 535 (190) nm. ES-MS: *m*/*z* 351 (M^-). ^{1}H NMR: δ 1.09

Table 1. Crystallographic Data for Compounds Containing $[MO_{3-n}S_n(OSiR_2R')]^{1-}$ (M = Mo, n = 0−3; M = W, n = 3)[a]

	(Et_4N)[**1d**]·CH_2Cl_2	(Et_4N)[**2b**]	(Et_4N)[**3a**]	(Et_4N)[**4e**]	(Et_4N)[**5c**]
formula	$C_{25}H_{41}Cl_2MoNO_4S_i$	$C_{26}H_{35}MoNO_2SSi$	$C_{17}H_{41}MoNO_2S_2Si$	$C_{24}H_{39}MoNOS_3Si$	$C_{14}H_{35}NOS_3SiW$
fw	614.52	565.64	479.66	577.77	541.55
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	2	2	4	4	4
a (Å)	9.830(2)	8.5965(8)	17.7637(14)	20.6752(16)	18.678(4)
b (Å)	10.660(2)	9.2168(9)	8.4492(7)	10.3777(8)	8.1799(16)
c (Å)	15.920(3)	19.4188(18)	16.5049(14)	14.4721(11)	16.724(3)
α (deg)	107.21(3)	100.911(2)			
β (deg)	103.20(3)	92.755(2)	90.732(2)	110.422(1)	110.59(3)
γ (deg)	93.31(3)	113.094(2)			
V (Å^3)	1537.3(5)	1376.9(2)	2477.0(4)	2910.0(4)	2392.0(8)
d_{calcd} (g/cm^3)	1.328	1.364	1.286	1.319	1.504
μ (mm^{-1})	0.667	0.622	0.756	0.723	5.141
θ range (deg)	1.39−27.90	1.08−25.00	1.15−25.00	1.05−28.28	1.16−27.89
GOF (F^2)	1.042	1.080	1.089	1.107	1.176
R1[b] (%)	3.10	4.90	4.79	3.50	3.22
wR2[c] (%)	8.33	13.47	10.31	8.95	8.36

[a] Mo Kα radiation, 193 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$.

(d) (CH not detected). Anal. Calcd for $C_{17}H_{41}MoNO_2S_2Si$: C, 42.57; H, 8.62; N, 2.92; S, 13.37. Found: C, 42.45; H, 8.76; N, 2.85; S, 13.44.

R = R′ = Ph. 88%. IR: 964, 906, 885, 510 cm^{-1}. Absorption spectrum: λ_{max} (ϵ_M) 260 (9280), 313 (6530), 352 (2830), 406 (sh, 1530) nm. ES-MS: m/z 453 (M$^-$). ^{1}H NMR: δ 7.43 (m, 9), 7.62 (m, 6).

R = Ph, R′ = Bu^t. The procedure was conducted at 0 °C.; 82%. IR: 972, 904, 885, 703 cm^{-1}. Absorption spectrum: λ_{max} (ϵ_M) 256 (8500), 302 (sh, 4020), 350 (4400), 404 (sh, 1300), 470 (660) nm. ES-MS: m/z 431 (M$^-$). ^{1}H NMR: δ 1.05 (s, 9), 7.42 (m, 6), 7.62 (m, 2), 7.76 (m, 2).

$(Et_4N)[MoOS_2(OSiMe_2Bu^t)]$. A solution of Me_2Bu^tSiCl (57 mg, 0.39 mmol) in 2 mL of THF was added to a suspension of $(Et_4N)_2[MoO_3S]$[12] (166 mg, 0.38 mmol) in 8 mL of THF. The reaction mixture became yellowish and then bright orange in 10 min and was stirred for 30 min, resulting in a deep-orange solution and a precipitate. The mixture was filtered, and the filtrate was taken to dryness. The solid residue was washed with ether (3 × 3 mL) and dissolved in 1.5 mL of acetonitrile. The solution was covered with 20 mL of ether, and the mixture was allowed to stand overnight. The product was isolated as 78 mg (43%) of orange platelike crystals. IR: 956, 882, 506 cm^{-1}. Absorption spectrum: λ_{max} (ϵ_M) 288 (4020), 301 (sh, 3890), 350 (4380), 406 (sh, 1240), 438 (780), 536 (140) nm. ES-MS: m/z 307 (M$^-$). ^{1}H NMR: δ 0.06 (s, 6), 0.92 (s, 9).

$(Et_4N)[MoS_3(OSiR_2R')]$. These compounds were prepared by a method and on a scale similar to the preceding preparation. A solution of $R_2R'SiCl$ (1.0 equiv) in THF was added to a suspension of $(Et_4N)_2[MoOS_3]$[14] (1.0 equiv) in THF. The reaction mixture became orange within 5 min and was stirred for 30 min. Workup was performed as in the preceding preparation, to afford the products as red blocklike crystals in the indicated yields.

R = R′ = Me. 49%. IR: 921, 510, 502 cm^{-1}. ES-MS: m/z 233 (M$^-$). Absorption spectrum: λ_{max}(ϵ_M) 290 (4800), 347 (sh, 1300), 408 (2570), 535 (450) nm. ^{1}H NMR: δ 0.13 (s). This compound can also prepared by the reaction of $(Et_4N)[MoO_3(OSiMe_3)]$ and ≥3 equiv of $(Me_3Si)_2S$ in acetonitrile.

R = R′ = Pr^i. 69%. IR: 922, 507 cm^{-1}. ES-MS: m/z 317 (M$^-$). Absorption spectrum: λ_{max} (ϵ_M) 287 (5000), 349 (sh, 960), 407 (2280), 440 (sh, 900), 534 (600) nm. ^{1}H NMR: δ 1.06 (d) (CH not detected). Anal. Calcd for $C_{17}H_{41}MoNOS_3Si$: C, 41.19; H, 8.34; N, 2.83; S, 19.40. Found: C, 41.31; H, 8.40; N, 2.76; S, 19.34. This compound can also be prepared by the reaction of $(Et_4N)[MoO_3(OSiPr^i_3)]$ and ≥3 equiv of Pr^i_3SiSH in acetonitrile.

Table 2. Crystallographic Data for Compounds Containing $[MO_2(OSiR_2R')(bdt)]^{1-}$ (M = Mo, W) and $[Mo_2O_3Cl_2(bdt)_2]^{2-}$ [a]

	(Et_4N)[**8d**]	(Et_4N)[**9b**]	$(Et_4N)_2$[**10**]
formula	$C_{30}H_{43}MoNO_3S_2S_i$	$C_{23}H_{45}NOS_2SiW$	$C_{28}H_{48}Cl_2Mo_2N_2O_3S_4$
fw	653.80	659.66	851.70
cryst syst	orthorhombic	triclinic	monoclinic
space group	$Pna2_1$	$P\bar{1}$	$P2_1/c$
Z	4	4	2
a (Å)	23.374(6)	8.4161(4)	8.3500(17)
b (Å)	8.965(2)	17.3262(9)	16.477(3)
c (Å)	15.057(3)	19.9065(11)	13.535(3)
α (deg)		84.9760(10)	
β (deg)		88.8130(10)	104.00(3)
γ (deg)		89.7990(10)	
V (Å^3)	3155.3(13)	2891.0(3)	1806.9(6)
d_{calcd} (g/cm^3)	1.376	1.516	1.565
μ (mm^{-1})	0.616	4.204	1.104
θ range (deg)	1.74−27.90	1.18−27.91	1.98−27.89
GOF (F^2)	0.993	1.089	1.046
R1[b] (%)	3.01	4.71	5.15
wR2[c] (%)	6.38	9.54	11.95

[a] Mo Kα radiation, 193 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$

R = R′ = Ph. 70%. ES-MS: m/z 467 (M$^-$). IR: 946, 518, 500 cm^{-1}. Absorption spectrum: λ_{max}(ϵ_M) 273 (4130), 291 (sh, 3900), 445 (2200) nm. ^{1}H NMR: δ 7.42 (m, 9), 7.63 (m, 6). This compound can also be prepared by the reaction of $(Et_4N)[MoO_3(OSiPh_3)]$ and ≥3 equiv of Ph_3SiSH in acetonitrile.

R = Me, R′ = Bu^t. 55%. IR: 924, 508 cm^{-1}. ES-MS: m/z 275 (M$^-$). Absorption spectrum: λ_{max} (ϵ_M) 285 (5500), 347 (sh, 1360), 405 (2770), 437 (sh, 1200), 535 (600) nm. ^{1}H NMR: δ 0.08 (s, 6), 0.92 (s, 9).

R = Ph, R′ = Bu^t. 68%. IR: 933, 508, 478 cm^{-1}. ES-MS: m/z 399 (M$^-$). Absorption spectrum: λ_{max} (ϵ_M) 271 (4060), 300 (sh, 2720), 382 (sh, 630), 448 (520) nm. ^{1}H NMR: δ 1.06 (s, 9), 7.42 (m, 6), 7.74 (m, 4).

$(Et_4N)[WS_3(OSiR_2R')]$. These compounds were prepared on a 5−8 mmol scale in a procedure analogous to the preceding preparations, but with $(Et_4N)_2[WOS_3]$,[14] and were isolated as yellow crystalline solids in the indicated yields.

R = R′ = Pr^i. 89%. IR: 936, 901, 490, 482 cm^{-1}. ES-MS: m/z 453 (M$^-$). Absorption spectrum: λ_{max} (ϵ_M) 254 (9000), 283 (sh,

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2460), 345 (3870), 434 (970) nm. ^{1}H NMR: δ 1.06 (d) (CH not detected). Anal. Calcd for $C_{17}H_{41}NOS_3SiW$: C, 34.94; H, 7.08; N, 2.40; S, 16.48. Found: C, 35.10; H, 7.02; N, 2.36; S, 16.34.

R = R′ = Ph. 77%. IR: 870, 484, 471 cm^{-1}. ES-MS: *m*/*z* 555 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 385 (4500), 439 (sh, 1200) nm. ^{1}H NMR: δ 7.45 (m, 9), 7.66 (m, 6).

R = Me, R′ = Bu^t. 75%. IR: 927, 486 cm^{-1}. ES-MS: *m*/*z* 411 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 254 (8600), 283 (sh, 2800), 341 (4120), 435 (1120) nm. ^{1}H NMR: δ 0.06 (s, 6), 0.92 (s, 9).

R = Ph, R′ = Bu^t. 82%. IR: 905, 514, 503 cm^{-1}. ES-MS: *m*/*z* 535 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 254 (10 200), 345 (4080), 438 (1070) nm. ^{1}H NMR: δ 1.03 (s, 9), 7.43 (m,6), 7.75 (m, 2), 7.82 (m, 2).

Oxo/Sulfido/Silyloxo-Benzenedithiolate Complexes. (Et_4N)-$[MoO_2(OSiR_2R')(bdt)]$. Method A. To a suspension of $(Et_4N)_2$-$[MoO_3(bdt)]$[12] (120 mg, 0.221 mmol) in 20 mL of THF was added a solution of $R_2R'SiCl$ (0.22−0.24 mmol) in 3 mL of THF. The reaction mixture was stirred for the specified time and the solvent was removed. The residue was washed with ether (3 × 3 mL), dissolved in 3 mL of acetonitrile, the solution was filtered, and the filtrate was layered with 20 mL of ether. After the mixture was allowed to stand overnight, the solid material was collected, washed with ether, and recrystallized from acetonitrile/ether to yield the product as an orange crystalline solid in the indicated yield.

R = R′ = Me. The procedure was performed at −20 °C, 10 min, 47%. IR: 946, 913, 884 cm^{-1}. ES-MS: *m*/*z* 357 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 299 (4310), 335 (sh, 3060), 401 (sh, 1100), 727 (230) nm. ^{1}H NMR: δ 0.16 (s, 9), 6.85 (dd, 2), 7.16 (dd, 2).

R = R′ = Pr^i. 50 min, 60%. IR: 944, 911, 884 cm^{-1}. ES-MS: *m*/*z* 441 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 301 (4500), 334 (sh, 2980), 399 (sh, 1070), 723 (240) nm. ^{1}H NMR: δ 0.15 (m, 3), 1.18 (s, 18), 6.84 (dd, 2), 7.15 (dd, 2). Anal. Calcd for $C_{23}H_{45}$-$MoNO_3S_2Si$: C, 48.31; H, 7.93; N, 2.45; S, 11.22. Found: C, 48.43; H, 7.90; N, 2.39; S, 11.31.

R = Me, R′ = Bu^t. 40 min, 48%. IR: 957, 908, 884 cm^{-1}. ES-MS: *m*/*z* 399 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 304 (4000), 338 (sh, 2870), 394 (1170) nm. ^{1}H NMR: δ 0.12 (s, 6), 0.93 (s, 9), 6.84 (dd, 2), 7.15 (dd, 2). Anal. Calcd for $C_{20}H_{39}MoNO_3S_2Si$: C, 45.35; H, 7.42; N, 2.64; S, 12.11. Found: C, 45.48; H, 7.47; N, 2.71; S, 12.04.

R = Ph, R′ = Bu^t. 60 min, 62%. IR: 952, 913, 883 cm^{-1}. ES-MS: *m*/*z* 523 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 300 (4930), 332 (sh, 3140), 399 (sh, 1430), 488 (sh, 540), 720 (500) nm. ^{1}H NMR: δ 1.08 (s, 9), 6.87 (dd, 2), 7.17 (dd, 2), 7.42 (m ,6), 7.83 (m, 4).

Method B. These compounds were prepared on a 0.20 mmol scale by the reaction of equimolar H_2(bdt) and $(Et_4N)[MoO_3$-$(OSiR_2R')]$ in acetonitrile. The orange reaction mixture was reduced in volume to 2 mL and was layered with 30 mL of ether, causing an orange precipitate. The solid was washed with ether and dried, affording the products (72−83%). Spectral properties are identical to those of the products of Method A.

$(Et_4N)[WO_2(OSiR_2R')(bdt)]$. To a suspension of $(Et_4N)_2[WO_3$-$(bdt)]$[12] (200 mg, 0.316 mmol) in 20 mL of THF was added a solution of 0.32−0.34 mmol of $R_2R'SiCl$ in 3 mL of THF. After the specified reaction times, the reaction mixtures were yellow or yellow-green. Solvent was removed and the residue was collected, washed with ether, and recrystallized from acetonitrile/ether.

R = R′ = Me. Green-brown crystalline solid, 2 h, 42%. ES-MS: *m*/*z* 445 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 302 (8510), 399 (350) nm. ^{1}H NMR: δ 0.l7 (m, 9), 6.84 (dd, 2), 7.20 (dd, 2).

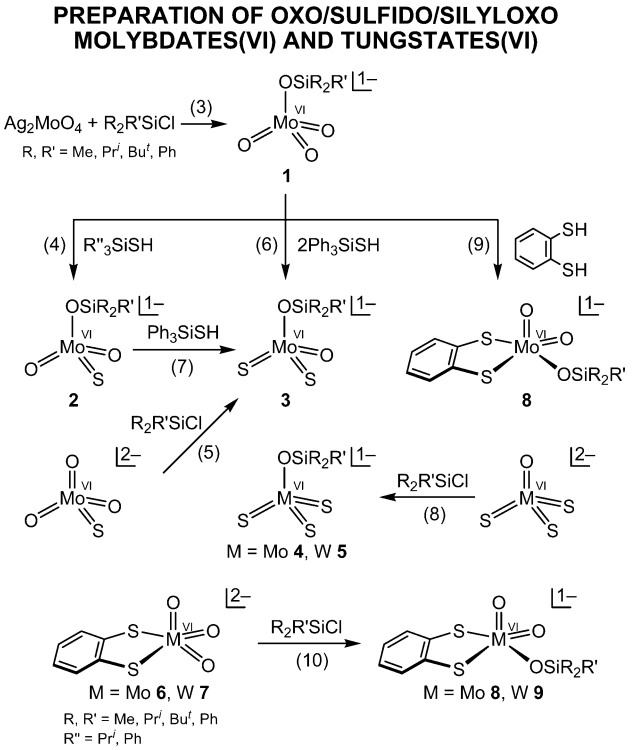

Figure 2. Synthetic scheme affording oxo/sulfido/silyloxo molybdates **1**−**4**, trisulfidosilyloxide tungstate **5**, and bdt complexes **8** and **9**.

R = R′ = Pr^i. Green-brown crystalline solid, 5 h, 68%. IR: 973, 920, 894 cm^{-1}. ES-MS: *m*/*z* 529 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 304 (8300), 397 (320) nm. ^{1}H NMR: δ 0.15 (m, 3); 1.13 (s, 18), 6.84 (dd, 2), 7.19 (dd, 2). Anal. Calcd for $C_{23}H_{45}$-NO_3S_2SiW: C, 41.88; H, 6.88; N, 2.12; S, 9.72. Found: C, 41.97; H, 6.81; N, 2.08; S, 9.52.

R = Me, R′ = Bu^t. Light-yellow crystalline solid, 5 h, 52%. IR: 977, 923, 895 cm^{-1}. ES-MS: *m*/*z* 487 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 303 (8150), 398 (360) nm. ^{1}H NMR: δ 0.13 (s, 6), 0.95 (s, 9), 6.84 (dd, 2), 7.20 (dd, 2).

R = Ph, R′ = Bu^t. Green-yellow crystalline solid, 10 h, 58%. IR: 977, 924, 890 cm^{-1}. ES-MS: *m*/*z* 611 (M^-). Absorption spectrum: λ_{max} (ϵ_M) 303 (8900), 397 (600) nm. ^{1}H NMR: δ 1.09 (s, 9), 6.87 (dd, 2), 7.21 (dd, 2), 7.42 (m, 6), 7.84 (m, 4). Anal. Calcd for $C_{30}H_{43}NO_3S_2SiW$: C, 48.58; H, 5.84; N, 1.89; S, 8.65. Found: C, 48.51; H, 5.89; N, 1.87; S, 8.47.

$(Et_4N)_2[Mo_2O_2Cl_2(bdt)_2(\mu_2\text{-}O)]$. To a suspension of $(Et_4N)_2$-$[MoO_3(bdt)]$ (120 mg, 0.221 mmol) in 20 mL of THF was injected dropwise a solution of Me_3SiCl (50 mg, 0.45 mmol) in 4 mL of THF. The reaction mixture become green-brown in 10 min and was stirred for an additional 10 min. Solvent was removed, the residue was washed with ether (3 × 3 mL), and was dissolved in 2 mL of acetonitrile. The solution was filtered, and the filtrate was covered with 20 mL of ether. The mixture was allowed to stand overnight, during which a red-brown crystalline solid separated. ^{1}H NMR: δ 6.97 (dd, 2), 7.59 (dd, 2). This compound was identified by an X-ray structure determination.

X-ray Structure Determinations. Structures of the eight compounds in Tables 1 and 2 were determined. Diffraction-quality crystals were obtained by layering several volume equiv of ether onto acetonitrile solutions that were maintained thereafter at 243−298 K for at least 12 h. Crystals were coated in paratone-N oil and mounted on either a Bruker SMART 1K or APEX CCD-based diffractometer equipped with a low temperature apparatus operating at 193 K. Data were collected with ω scans of 0.3°/frame for 30 s,

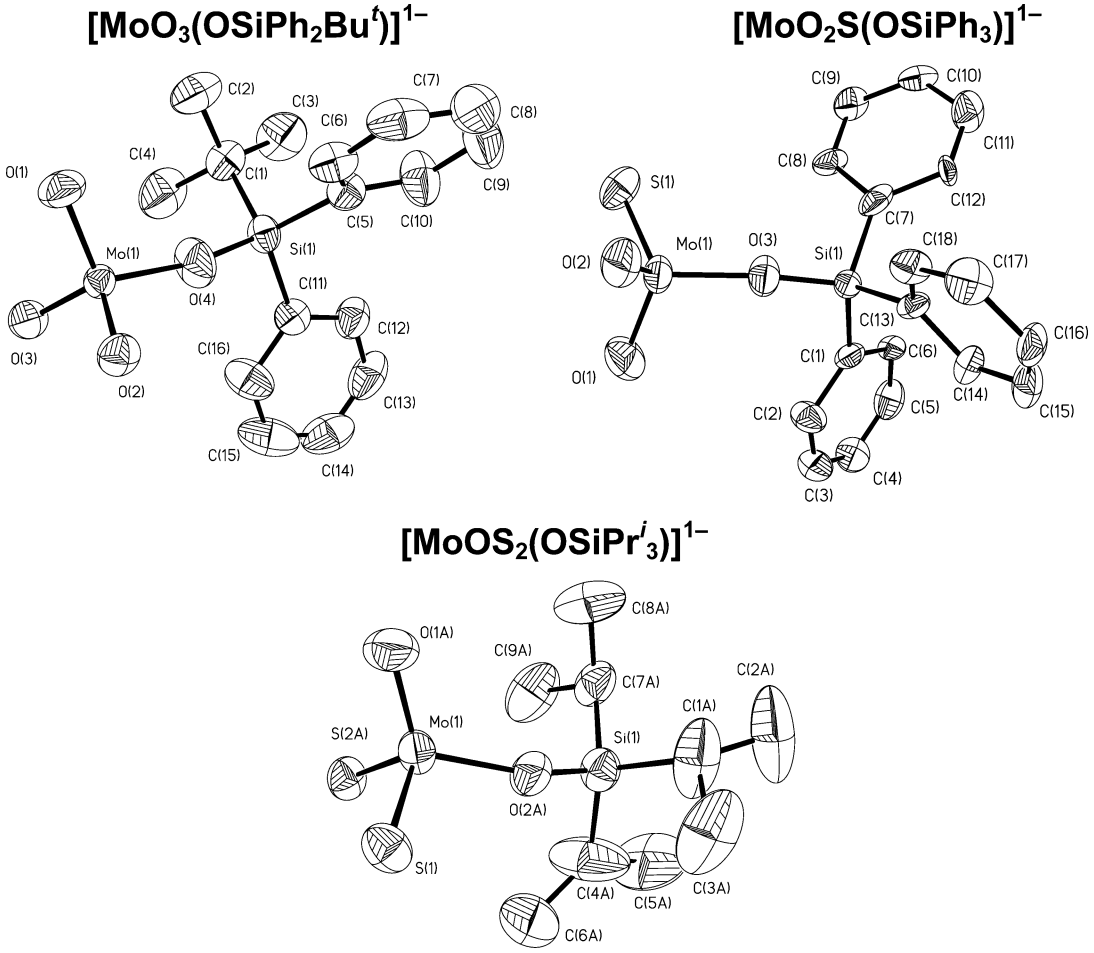

Figure 3. Structures of $[MoO_3(OSiPh_2Bu^t)]^{1-}$ (left), $[MoO_2S(OSiPh_3)]^{1-}$ (right), and $[MoOS_2(OSiPr^i_3)]^{1-}$ (center). In this and the following structural figures, 50% probability ellipsoids, the atom-labeling schemes, and selected (mean) bond distances (angstroms) and angles (degrees) are given. Left: mean Mo−O1,2,3 1.721(2), Mo−O4 1.876(2), O4−Si 1.622(2), Si−C 1.876(2); O1−Mo−O2 109.3(1), O2−Mo−O3 108.8(1), O1−Mo−O3 109.3(1), O1−Mo−O4 110.1(1), O2−Mo−O4 108.7(1), O3−Mo−O4 110.7(1), Mo−O4−Si 169.8 (1). Right: Mo−O1 1.792(4), Mo−O2 1.719(3), Mo−S1 2.104(2), Mo−O3 1.883(3), O3−Si 1.622(3), Si−C 1.865; O1−Mo−O2 108.0(2), O1−Mo−S1 108.8(2), O2−Mo−S1 108.5(2), O1−Mo−O3 110.7(2), O2−Mo−O3 107.7(2), S1−Mo−O3 113.0(1), Mo−O3−Si 161.2(2). Center: Mo−O1 1.70(2), Mo−S1 2.150(1), Mo−S2 2.06(1), Mo−O2 1.88(1), O2−Si 1.63(1), Si−C 1.87(1); S1−Mo−S2A 110.6(1), O1A−Mo−S1 105.6(4), O1A−Mo−S2A 111.6(5), O1A−Mo−O2A 118.8(5), S1−Mo−O2A 106.4(4), S2A−Mo−O2A 103.7(4), Mo−O2A−Si 156.3 (8).

such that 971−1647 frames were collected for a hemisphere of data. The first 50 frames were recollected at the end of the data collection to monitor for crystal decay; no significant decay was detected for any compound. Cell parameters were retrieved using *SAINT* software and refined with *SAINT* on all of the reflections. Data integration was performed with *SAINT*, which corrects for Lorentz polarization and decay. Absorption corrections were applied with *SADABS*. Space groups were assigned unambiguously by analysis of symmetry, and systematic absences were determined by *XPREP*. All of the crystals were checked with *PLATON* for the possibility of higher symmetry; none was found. Structures were solved by direct methods and refined against all of the data by full-matrix least-squares techniques on F^2 using the *SHELXL-97* package. All of the non-hydrogen atoms were refined anisotropically. Isopropyl groups in anions **3a**, **4b**, **5a**, **8b**, and **9b** were disordered. The disorder was modeled effectively in all cases except **3a**, for which no satisfactory description of the disorder was obtained. Hydrogen atoms were placed in idealized positions on carbon atoms and refined as a riding model. Crystal parameters and agreement factors are collected in Tables 1 and 2.[15]

In addition to the compounds in Tables 1 and 2, several other structures were determined. Owing to the close structural similarities of their complexes to those described in full, only crystallographic parameters are reported.[15] $(Et_4N)[MoS_3(OSiPr^i_3)]$: monoclinic, $P2_1/c$, $a = 17.990(4)$ Å, $b = 8.490(2)$ Å, $c = 16.505(1)$ Å, $\beta = 90.79(3)°$, $Z = 4$, $R_1(wR_2) = 0.1030(0.2617)$. $(Et_4N)[WS_3(OSiPr^i_3)]$: monoclinic, $P2_1/c$, $a = 18.061(2)$ Å, $b = 8.523(1)$ Å, $c = 16.662(2)$ Å, $\beta = 91.032(2)°$, $Z = 4$, $R_1(wR_2) = 0.0559(0.1242)$. $(Et_4N)[MoO_2(OSiPr^i_3)(bdt)]$: triclinic, $P\bar{1}$, $a = 8.400(2)$ Å, $b = 17.300(4)$ Å, $c = 19.860(4)$ Å, $\alpha = 85.08(3)°$, $\beta = 88.78(3)°$, $\gamma = 89.70(3)°$, $Z = 4$, $R_1(wR_2) = 0.0495(0.1057)$. $(Et_4N)[WO_2(OSiMe_2Bu^t)(bdt)]$: monoclinic, $P2_1/c$, $a = 19.940(4)$ Å, $b = 7.830(2)$ Å, $c = 34.290(7)$ Å, $\beta = 92.17(3)°$, $Z = 8$, $R_1(wR_2) = 0.0593(0.1329)$.

Other Physical Measurements. All of the measurements were made under anaerobic conditions. NMR spectra were recorded on a Varian Mercury 300 and 400 spectrometers. Infrared spectra were obtained on a Nicolet Nexus 470 FTIR spectrometer. Absorption spectra were measured with a Varian Cary 50 Bio spectrophotometer. Electrospray mass spectra were recorded on a Micromass

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

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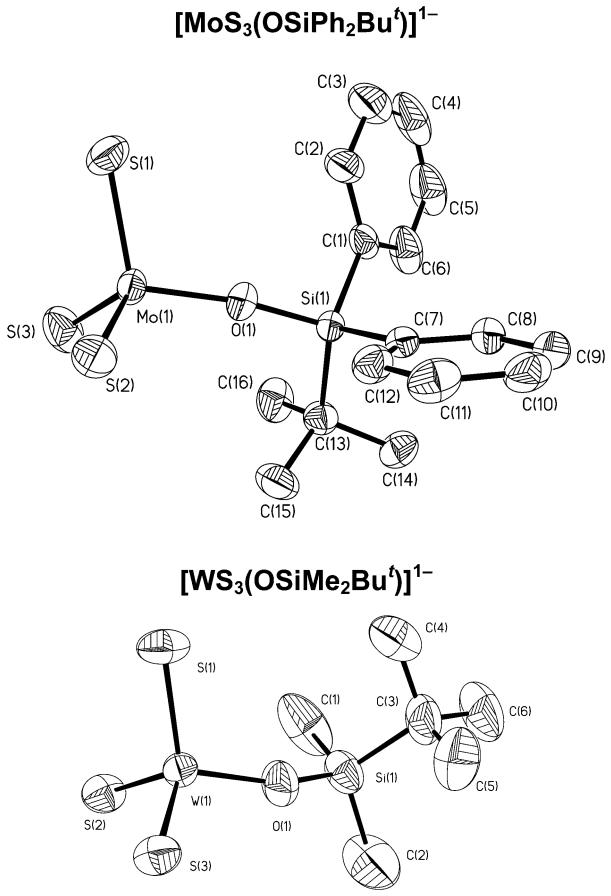

Figure 4. Structures of $[MoS_3(OSiPh_2Bu^t)]^{1-}$ (upper): mean Mo−S1,2,3 2.150(1), Mo−O1 1.857(1), O1−Si 1.636(2), Si−C 1.875(2); S1−Mo−S2 109.17(3), S1−Mo−S3 109.29(3), S2−Mo−S3 109.23(3), S1−Mo−O1 108.91(5), S2−Mo−O1 109.93(5), S3−Mo−O1 110.30(6), Mo−O1−Si 171.4(1). $[WS_3(OSiMe_2Bu^t)]^{1-}$ (lower): mean W−S1,2,3 2.154(1), W−O1 1.858(4), O1−Si 1.634(4), Si−C 1.861(8); S1−W−S2 109.33(5), S1−W−S3 109.33(6), S2−W−S3 109.40(6), S1−W−O1 110.0(2), S2−W−O1 110.4(1), S3−W−O1 108.4(1), W−O1−Si 155.2(3).

(Danvers, MA) Platform II quadrupole mass spectrometer. Elemental analyses were performed by H. Kolbe (Mülheim, Germany).

Results and Discussion

Reactions 3−8 leading to oxo/sulfido/silyloxo molybdates(VI) and tungstates(VI) are summarized by the scheme in Figure 2. All of the compounds were isolated as Et_4N^+ salts. Structures of representative complexes are presented in Figures 3 and 4 together with selected metric data. In the sections that follow, complexes are numerically designated, according to Chart 1. Complexes **1**−**4** constitute the series $[MoO_{3-n}S_n(OSiR_2R')]^{1-}$ ($n = 0-3$).

Oxosilyloxomolybdates. The scheme is initiated by the direct silylation reaction 3 of Ag_2MoO_4 in dichloromethane, affording colorless complexes $[MoO_3(OSiR_2R')]^{1-}$ as **1a**−**1d** in yields of 49−67%. **1e** was prepared recently by this method.[12] The first examples of this type were obtained by the silylation of $[Mo_2O_7]^{2-}$ with R_3SiOH.[18] Subsequently, it was shown that excess Ph_3SiCl with Ag_2MoO_4 yielded the doubly silylated product $[MoO_2(OSiPh_3)_2]$.[19] The method also succeeds with $AgMO_4$, resulting in $[Me_3SiOMO_3]$ (M = Tc,[20] Re[21]). The structure of **1d** (Figure 3) reveals the expected tetrahedral stereochemistry at the molybdenum atom (O−Mo−O angles of 108.9(1)−110.7(1)°), a mean Mo═O distance of 1.721(2) Å, a Mo−O_{Si} distance of 1.876(2) Å, and a nearly linear Mo−O−Si angle of 169.8(1)°. These complexes are precursors to monosulfido species. Despite repeated attempts under different conditions, no reaction was observed between Ag_2WO_4 and silylchlorides. A route to the complexes $[WO_3(OSiR_2R')]^{1-}$ remains to be developed.

Chart 1. Designation of Complexes and Abbreviations[a]

$[MoO_3(OSiR_2R')]^{1-}$	R_2R' = Me_3 **1a**, Pr^i_3 **1b**, Me_2Bu^t **1c**, Ph_2Bu^t **1d**, Ph_3 **1e**[12,18]
$[MoO_2S(OSiR_2R')]^{1-}$	R_2R' = Pr^i_3 **2a**, Ph_3 **2b**,[12] Ph_2Bu^t **2c**
$[MoOS_2(OSiR_2R')]^{1-}$	R_2R' = Pr^i_3 **3a**, Ph_3 **3b**, Me_2Bu^t **3c**, Ph_2Bu^t **3d**
$[MoS_3(OSiR_2R')]^{1-}$	R_2R' = Me_3 **4a**,[16] Pr^i_3 **4b**, Ph_3 **4c**, Me_2Bu^t **4d**, Ph_2Bu^t **4e**
$[WS_3(OSiR_2R')]^{1-}$	R_2R' = Pr^i_3 **5a**, Ph_3 **5b**, Me_2Bu^t **5c**, Ph_2Bu^t **5d**
$[MO_3(bdt)]^{2-}$ [12]	M = Mo **6**, W **7**
$[MoO_2(OSiR_2R')(bdt)]^{1-}$	R_2R' = Me_3 **8a**, Pr^i_3 **8b**, Me_2Bu^t **8c**, Ph_2Bu^t **8d**, Ph_3 **8e**[17]
$[WO_2(OSiR_2R')(bdt)]^{1-}$	R_2R' = Me_3 **9a**, Pr^i_3 **9b**, Me_2Bu^t **9c**, Ph_2Bu^t **9d**, Ph_3 **9e**[12]
$[Mo_2O_2Cl_2(bdt)_2(\mu_2\text{-}O)]^{2-}$	**10**

[a] bdt = benzene-1,2-dithiolate(2−); Bu^t_3tach = 1,3,5-*tert*-butyl-1,3,5-triazacyclohexane; Cp* = pentamethylcyclopentadienide(1−); S_2pd = pyranopterindithiolate(2−) cofactor ligand; Tp = tris(pyrazolyl)hydroborate(1−); XO = xanthine oxidoreductase.

$$Ag_2MoO_4 + R_2R'SiCl + Cl^- \rightarrow [MoO_3(OSiR_2R')]^{1-} + 2AgCl \quad (3)$$

Oxothiosilyloxomolybdates. Monosulfidation reaction 4a was first used to prepare **2b** from **1e**.[12] Application of this reaction to **1d** was successful, yielding **2c** (83%). However, this procedure was unsuccessful with the trialkylsilyloxides **1a**, **1b**, and **1c**, affording instead **2b** in good yield. This species was identified by mass spectrometry and a crystal structure determination (Figure 3). In these reactions, sulfidation occurs but with apparent protonation of the bound silyloxide group and its departure as the silanol, followed by the coordination of Ph_3SiS^-, nucleophilic attack of an oxo ligand at silicon, and Si−S bond breaking to generate the product. Such a sequence is avoided in the formation of **2c** because the capacious Ph_2Bu^tSiO group hinders the encroachment of also bulky Ph_3SiSH; additionally, the silyloxo group contains only one electron-releasing alkyl substituent. This situation can be avoided by the use of a less acidic silylthiol and/or the same silyl substituents, as in reaction 4b, which gives yellow-orange **2a** (90%). The structure of **2b** resembles that of **1d**, but with a Mo═S distance of 2.144(3) Å and a Mo−O−Si angle of 160.4(5)°.

$$[MoO_3(OSiR_2R')]^{1-} + Ph_3SiSH \rightarrow [MoO_2S(OSiR_2R')]^{1-} + Ph_3SiOH \quad (4a)$$

$$[MoO_3(OSiPr^i_3)]^{1-} + Pr^i_3SiSH \rightarrow [MoO_2S(OSiPr^i_3)]^{1-} + Pr^i_3SiOH \quad (4b)$$

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(19) Huang, M.; DeKock, C. W. *Inorg. Chem.* **1993**, *32*, 2287−2291.
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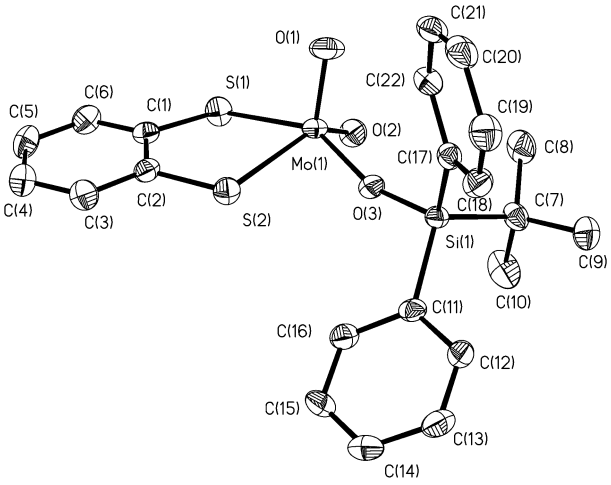
$[MoO_2(OSiPh_2Bu^t)(bdt)]^{1-}$



$[WO_2(OSiPr^i_3)(bdt)]^{1-}$

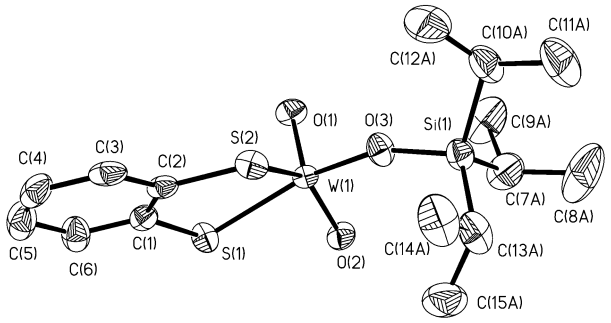


Figure 5. Structures of $[MoO_2(OSiPh_2Bu^t)(bdt)]^{1-}$ (upper): Mo−O1 1.700(2), Mo−O2 1.723(2), Mo−O3 1.911(2), Mo−S1 2.447(1), Mo−S2 2.472(1), S1−Mo−S2 79.47(2), $\theta = 132.1$, $\delta = 0.56$. $[WO_2(OSiPr^i_3)(bdt)]^{1-}$ (lower): W−O1 1.724(4), W−O2 1.731(4), W−O3 1.886(4), W−S1 2.434(2), W−S2 2.476(1), S1−W−S2 80.07(5), $\theta = 131.0$, $\delta = 0.57$.

$[Mo_2O_3Cl_2(bdt)_2]^{2-}$

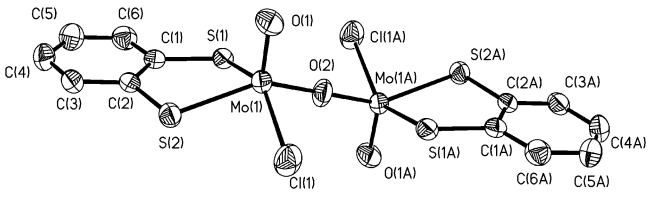


Figure 6. Structure of centrosymmetric $[Mo_2O_3Cl_2(bdt)_2]^{2-}$: Mo−O1 1.689(3), Mo−O2 1.877(1), Mo−Cl 2.395(1), Mo−S1 2.385(1), Mo−S2 2.393(1), S1−Mo−S2 83.14(4), $\theta = 130.7$, $\delta = 0.68$.

Attempts to prepare pure monosulfido **2** by the silylation of $[MoO_3S]^{2-}$ were not productive. In one case, reaction 5 with Me_2Bu^tSiCl (Figure 2) afforded the disulfido **3c** (43%). The course of this reaction is unclear. Subsequently, disulfido **3a**, **3b**, and **3d** were obtained by double-sulfidation reaction 6 as orange solids in 82−88% yield. The obvious intermediate is a monosulfido complex, as demonstrated by the clean conversions **2b** → **3b** and **2c** → **3d** with 1.0 equiv of Ph_3SiSH in reaction 7 (Figure 2). The structure of **3a** (Figure 3) closely resembles others in the series, with Mo═O and average Mo═S distances of 1.880(4) and 2.13 Å, respectively, and a Mo−O−Si angle of 159.1(4)°.

$$[MoO_3(OSiR_2R')]^{1-} + 2Ph_3SiSH \rightarrow [MoOS_2(OSiR_2R')]^{1-} + 2Ph_3SiOH \quad (6)$$

Trisulfido complexes are readily accessible by the silylation of the anions $[MOS_3]^{2-}$ (M = Mo, W) in reaction 8. Molybdenum complexes **4a**−**4e** were isolated as red crystals (49−70%) and tungsten complexes **5a**−**5d** as yellow crystals (75−89%). **4a**, **4b**, and **4c** were also prepared in high purity and yield by the reaction of the corresponding trioxo complexes with ≥3 equiv of $(Me_3Si)_2S$, Pr^i_3SiSH, and Ph_3SiSH, respectively, in acetonitrile. The first of these reactions is precedented by the reaction of $[Mo_2O_7]^{2-}$ with excess $(Me_3Si)_2S$ to afford **4a**.[16] The MS_3OSi fragments of **4e** and **5c** are isostructural and nearly isometric (Figure 4). Parameters of **4e** include a mean Mo═S bond length of 2.150(1) Å and a Mo−O−Si angle of 171.4(1)°. For **5c**, the mean W═S bond distance is 2.155(1) Å and the W−O−Si angle is 155.2(3)° because of the smaller steric bulk of the silyloxide substituents.

$$[MOS_3]^{2-} + R_2R'SiCl \rightarrow [MS_3(OSiR_2R')]^{1-} + Cl^- \quad (8)$$

Oxosilyloxobenzenedithiolate Complexes. Monobenzenedithiolate complexes were obtained by two related methods (Figure 2). In reaction 9, bdt is introduced with the elimination of an oxo ligand as water, to yield molybdenum complexes **8a**−**8d** as orange solids (72−83%). This reaction is similar to the preparation of $[MoO(bdt)(\mu_2\text{-}S)_2CuL]^{2-}$ from $[MoO_2(\mu_2\text{-}S)_2CuL]^{2-}$ and the dithiol.[22] Alternatively, trioxo complexes **6** and **7** are silylated to form **8a**−**8d** (47−62%) and tungsten complexes **9a**−**9d** (greeen-brown or light-yellow, 42−68%), respectively, in reaction 10.

$$[MoO_3(OSiR_2R')]^{1-} + H_2(bdt) \rightarrow [MoO_2(OSiR_2R')(bdt)]^{1-} + H_2O \quad (9)$$

$$[MO_3(bdt)]^{2-} + R_2R'SiCl \rightarrow [MO_2(OSiR_2R')(bdt)]^{1-} + Cl^- \quad (10)$$

The structures of **8d** and **9b** are set out in Figure 5 with selected dimensions. These complexes present isostructural $MO_3(bdt)$ fragments with distorted square-pyramidal coordination indicated by two basal angles S1−M−O3 and S2−M−O2 in the range of 138−152°, dihedral angles θ between MS1S2 and MO2O3 coordination planes, and displacements δ of the metal atom toward the apical oxo ligand O1. Values of the latter two parameters for **8d**/**9b** are $\theta = 132.1°/131.0°$ and $\delta = 0.56$ Å/0.57 Å. Other bond distances and angles are unexceptional. When trioxo complex **6** was treated with 2 equiv of Me_3SiCl in THF, the only isolable product was the Mo^V μ_2-oxo dimer **10**. The reaction proceeds with the initial formation of **8a**. The second equiv of the silyl chloride apparently removes the silyloxide as the siloxane with

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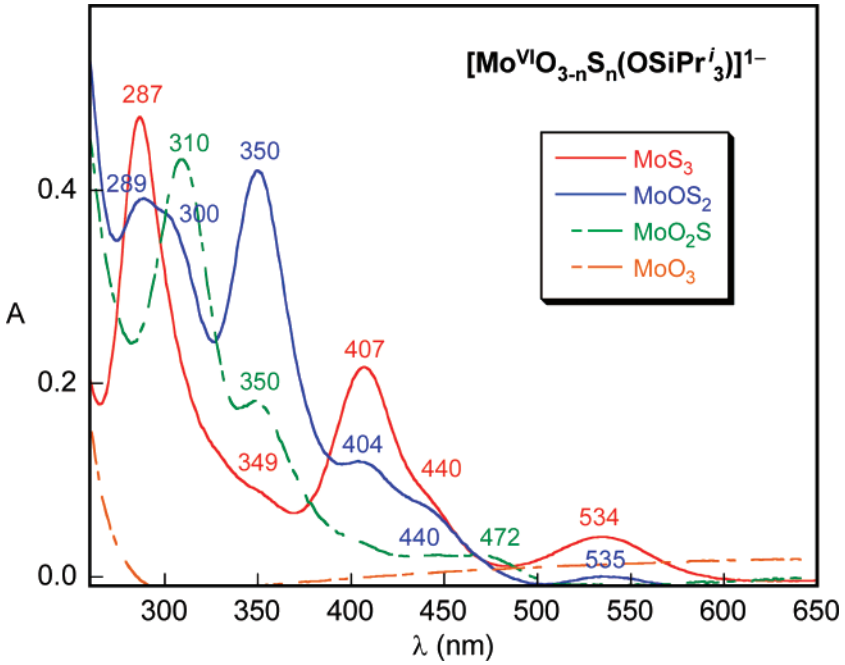

Figure 7. UV−vis absorption spectra of 1.0 mM $[Mo^{VI}O_{3-n}S_n(OSiPr^i_3)]^{1-}$ ($n = 3$, red solid line; $n = 2$, blue solid line; $n = 1$, green broken line; $n = 0$, brown broken line) in acetonitrile solutions.

coordination of chloride. The likely reductant is bdt. As seen in Figure 6, the complex is centrosymmetric and contains the ubiquitous $O{=}Mo^{V}{-}O{-}Mo^{V}{=}O$ fragment. Coordination at the molybdenum sites is approximately square pyramidal; other metric features are normal.

Summary. The principal results of this work are summarized in terms of two main classes of compounds. Multiple examples within each class are provided to support the generality of the synthetic procedures and the scope of the stable compounds.

•$[MO_{3-n}S_n(OSiR_2R')]^{1-}$. Examples of all of the members of the tetrahedral $[MoO_{3-n}S_n(OSiR_2R')]^{1-}$ series ($n = 0-3$) have now been isolated and structurally characterized. Colors range from nearly colorless ($n = 0$) to bright red ($n = 3$), as seen by the progressive low-energy shifts of the LMCT bands in Figure 7 as the sulfur content increases. The $n = 0$ complexes **1** are obtained by silylation of Ag_2MoO_4. These complexes undergo monosulfidation to give the $n = 1$ complexes **2**. These can be converted by further sulfidation to the $n = 2$ species **3**, one of which can be obtained by the silylation of $[MoO_3S]^{2-}$. Complexes **4** and **5** with $n = 3$ are accessible by the silylation of $[MOS_3]^{2-}$. The $n = 0$ and 3 members are precedented by three examples (**1e**,[12,18] $[MoO_3(OSiBu^t_3)]^{1-}$,[18] and **4a**[16]), two of which were prepared by different methods than employed here. The only previous example of an $n = 1$ complex is **2b**.[12] There has been no prior report of an $n = 2$ complex. Concerning the multiply bonded pyramidal fragment $MO_{3-n}S_n$ (M = Mo, W) in other molecular types but excluding members of the set $[MO_{4-n}S_n]^{2-}$,[12,23] there are no prior structurally characterized examples of $n = 1$ and of $n = 2$ other than $[Cp^*WOS_2]^{1-}$[24] and $[(Bu^t_3tach)WOS_2]$.[25] Pyramidal MS_3 units are more common, having been found in $[(Bu^t_3tach)MoS_3]$,[25] $[(Tp)WS_3]^{1-}$,[26] $[Cp^*MS_3]^{1-}$,[27,28] and $[WS_3(SR)]^{1-}$.[29−32]

•$[MO_2(OSiR_2R')(bdt)]^{1-}$. The complexes **8** are accessible from **1** by the reaction with H_2(bdt); silylation of trioxo complexes **6** and **7** affords **8** and **9**, respectively. They are square pyramidal with an oxo ligand in the apical position. As such, they are structural analogues of the inactive protonated sites $[MoO_2(OH)(S_2pd)]$ of the XO family. By sulfidation with Ph_3SiSH, they are immediate precursors to square-pyramidal $[WOS(OSiR_2R')(bdt)]^{1-}$ with apical oxo and basal sulfido ligation and are structural analogues of the active protonated sites $[MoOS(OH)(S_2pd)]$.[11,33] Further, **8** and **9** react with thiols to give $[MO_2(SR)(bdt)]^{1-}$,[33] which like the molybdenum complex with $R = C_6H_2$-2,4,6-Pr^i_3,[17] are analogues of the oxidized active site of sulfite oxidase.

The sulfidation reactions reported here call attention to the utility of silylthiols, here Ph_3SiSH and Pr^i_3SiSH, commercial compounds of moderate cost, as reagents for oxo-for-sulfido conversions. In the exhaustive compilation of such

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reactions by Donahue,[34] only one compound is cited for only one reaction, Ph_3SiSH in the conversion **1e** → **2b**. The minimal representation of these conversions is $M^{VI}{=}O + Ph_3SiSH \rightarrow M^{VI}{=}S + Ph_3SiOH$. On an enthalpic basis, the reaction is favored in part by the ca. 25−40 kcal/mol difference in Si−O versus Si−S bond dissociation energies.[35−37] Experimental M═O and M═S bond energies for M = Mo and W at constant structure and ligation are lacking. Density functional theory results for $[M^{VI}QCl_4]$ (Q = O, S) with optimized M═Q bond lengths close to those observed in the present compounds indicate bond energy differences for M═O versus M═S of 47 kcal/mol for M = Mo and 42 kcal/mol for M = W.[38] These results would appear to suggest that enthalpy changes for the minimal reaction based on bond energies are unfavorable. Experimental bond energies and reaction enthalpies would be helpful in resolving this issue.

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Supporting Information Available: X-ray crystallographic files in CIF format for the compounds in Tables 1 and 2.This material is available free of charge via the Internet at http://pubs.acs.org.

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