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Synthesis and Structures of Bis(dithiolene)−Tungsten(IV) Complexes Related to the Active Sites of Tungstoenzymes

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Recent protein crystallographic results on tungsten enzymes and primary sequence relationships between certain molybdenum and tungsten enzymes provoke interest in the generalized bis(dithiolene) complexes $[W^{IV}(QR)(S_2C_2R'_2)_2]^{1-}$ and $[W^{VI}O(QR)(S_2C_2R'_2)_2]^{1-}$ (Q = O, S, Se) as minimal representations of enzyme sites. The existence and stability of W(IV) complexes have been explored by synthesis. Reaction of $[W(CO)_2(S_2C_2Me_2)_2]$ (**1**) with PhO^- results in complete CO substitution to give $[W(OPh)(S_2C_2Me_2)_2]^{1-}$ (**2**). Reaction of **1** with PhQ^- affords the monocarbonyls $[W(CO)(QPh)(S_2C_2Me_2)_2]^{1-}$ (Q = S (**3**), Se (**5**)). The use of sterically demanding $2,4,6\text{-}Pr^i{}_3C_6H_2Q^-$ also yields monocarbonyls, $[W(CO)(QC_6H_2\text{-}2,4,6\text{-}Pr^i{}_3)(S_2C_2Me_2)_2]^{1-}$ (Q = S (**4**), Se (**6**)). The X-ray structures of square pyramidal **2** and trigonal prismatic **3**−**6** (with unidentate ligands cis) are described. The tendency to substitute one or both carbonyl ligands in **1** in the formation of $[M^{IV}(QAr)(S_2C_2Me_2)_2]^{1-}$ and $[M^{IV}(CO)(QAr)(S_2C_2Me_2)_2]^{1-}$ with M = Mo and W is related to the M−Q bond length and ligand steric demands. The results demonstrate a stronger binding of CO by W(IV) than Mo(IV), a behavior previously demonstrated by thermodynamic and kinetic features of zerovalent carbonyl complexes. Complexes **3**−**6** can be reversibly reduced to W(III) at approximately −1.5 V versus SCE. On the basis of the potential for **2** (−2.07 V), monocarbonyl ligation stabilizes W(III) by ~500 mV. This work is part of a parallel investigation of the chemistry of bis(dithiolene)−molybdenum (Lim, B. S.; Donahue, J. P.; Holm, R. H. *Inorg. Chem.* **2000**, *39*, 263) and −tungsten complexes related to enzyme active sites.

Introduction

All tungstoenzymes recognized thus far have been isolated from thermophilic bacteria and hyperthermophilic archaea and contain the pterin dithiolene cofactor depicted in Figure 1.[1−3] The enzymes have been organized into two principal families, AOR (aldehyde oxidoreductases) and F(M)DH (formate dehydrogenases, FDH, and *N*-formylmethanofuran dehydrogenases, FMDH). FDH functions in the first step of the conversion of carbon dioxide to acetate in acetogens, and FMDH is involved in the conversion of carbon dioxide to methane in methanogens. The crystal structures of two enzymes isolated from *Pyrococcus furiosus*, aldehyde oxidoreductase[4−6] and formaldehyde oxidoreductase,[7] have been determined by Rees and co-workers. The active sites of both enzymes contain a tungsten atom chelated by two cofactor ligands, with additional coordination thought to involve one or two oxygen atoms. Owing to the difficulty of locating light atom scatterers in the presence of tungsten and the possibility of site heterogeneity, the binding of oxygenous ligands is not well defined. The most recent EXAFS results for AOR, quoted by Johnson et al.,[2] are in substantial agreement with the X-ray structure and include one W−O interaction at 1.75 Å and possible W−O/N coordination at 1.97 Å.

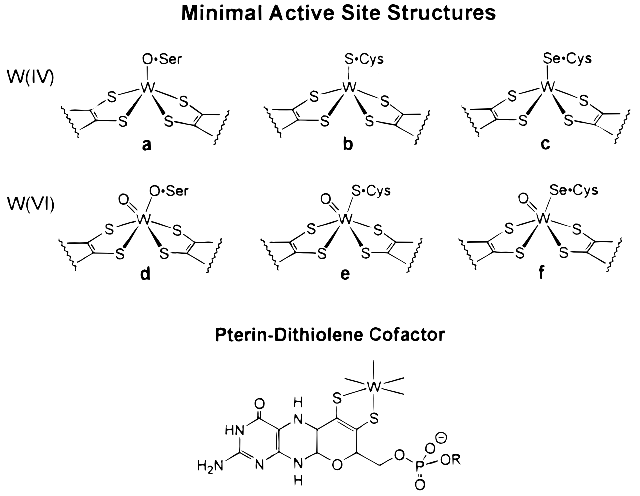

Figure 1. Structure of the pterin dithiolene cofactor ligand and putative minimal active site structures for members of the AOR (**a**,**d**) and F(M)DH (**b**,**c**,**e**,**f**) enzyme families.

In terms of primary sequences, there appears to be little relationship between the AOR and F(M)DH families.[2] However, there is substantial homology between the FM(D)H family and the molybdenum-containing DMSO reductases (DMSORs),[2,8] which are a structurally better defined family of enzymes. The possibility emerges that active FM(D)H enzymes resemble

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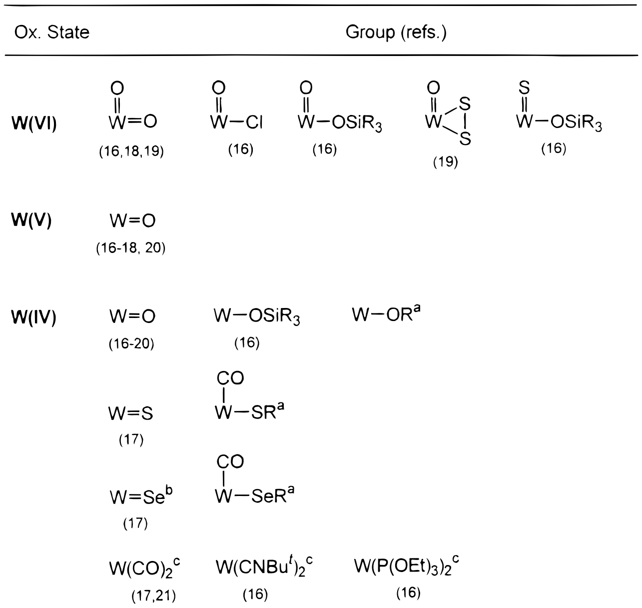
Rhodobacter sphaeroides DMSOR[9,10] by having two pterin dithiolenes and one endogenous protein ligand in the W(IV, VI) states and no oxo ligand in the W(IV) state. The protein ligands are serinate for DMSOR,[9,10] cysteinate for dissimilatory nitrate reductase,[11] and cysteinate or selenocysteinate for FDH[12−14] and FMDH. Under the Hille classification,[8] all of these enzymes are included in the Mo-DMSOR family. Putative minimal active site structures are shown as **a**−**f** in Figure 1. Consequently, the desoxo and monooxo complexes $[W^{IV}(QR)(S_2C_2R_2)_2]^{1-}$ and $[W^{VI}O(QR)(S_2C_2R_2)_2]^{1-}$ (Q = O, S, Se), respectively, are potentially relevant in determining intrinsic properties of active sites.

Interest in the foregoing species has led us to explore, rather generally, the types of mononuclear tungsten complexes accessible under the restriction of bis(dithiolene) ligation.[15−17] Currently known complexes[15−21] are summarized in Table 1 in terms of functional groups, that is, metal and nondithiolene ligands potentially subject to further reaction. The entries are limited to complexes that have been isolated in substance. Only the groups $W^{IV,V}O$, $W^{VI}O_2$, and $W^{VI}O(S_2)$ were characterized before the beginning of our investigation of the synthesis and structures of bis(dithiolene) complexes. None of the complete ligation modes in active site structures **a**−**f** (Figure 1) were represented prior to the inception of the present investigation. We herein describe the initial results from a synthetic search for the reduced sites **a**−**c**. Inasmuch as the corresponding molybdenum sites are of direct pertinence to the structure and function of members of the Mo-DMSOR family,[8] a similar synthetic exploration involving bis(dithiolene)Mo complexes has been undertaken and is described elsewhere.[22,23]

Table 1. Functional Groups in Bis(dithiolene)−Tungsten (IV, V, VI) Complexes



Ox. State	Group (refs.)				
W(VI)	$\overset{O}{\overset{\|}{W}}=O$ (16,18,19)	$\overset{O}{\overset{\|}{W}}-Cl$ (16)	$\overset{O}{\overset{\|}{W}}-OSiR_3$ (16)	$\overset{O}{\overset{\|}{W}}\overset{S}{\underset{S}{\|}}$ (19)	$\overset{S}{\overset{\|}{W}}-OSiR_3$ (16)
W(V)	W=O (16-18, 20)				
W(IV)	W=O (16-20)	W−OSiR$_3$ (16)	W−OR^a		
	W=S (17)	$\overset{CO}{\overset{\|}{W}}-SR^a$			
	W=Se^b (17)	$\overset{CO}{\overset{\|}{W}}-SeR^a$			
	W(CO)$_2{}^c$ (17,21)	W(CNBu^t)$_2{}^c$ (16)	W(P(OEt)$_3$)$_2{}^c$ (16)		

[a] This work; R = aryl. [b] Not proven by a structure determination. [c] Ambiguous oxidation state.

Experimental Section

Preparation of Compounds. All operations were carried out under a pure dinitrogen atmosphere using an inert atmosphere box or Schlenk techniques. Solvents were distilled and dried by the appropriate methods and stored over 4 Å molecular sieves in a drybox. $[W(CO)_2(S_2C_2Me_2)_2]$ was synthesized by ligand transfer from $[Ni(S_2C_2Me_2)_2]$ to $[W(CO)_3(MeCN)_3]$ and purified by column chromatography.[17] The compounds NaSPh and NaSePh were prepared by the reactions of NaOMe with benzenethiol and benzeneselenol, respectively, in methanol. Metathesis of these salts with Et_4NCl in acetonitrile afforded $(Et_4N)(SPh)$ and $(Et_4N)(SePh)$, which were recrystallized from acetonitrile/ether. The compound $NaSC_6H_2$-2,4,6-$Pr^i{}_3$ was prepared from 2,4,6-triisopropylbenzenethiol[24] by the method employed for NaSPh. Bis(2,4,6-triisopropylphenyl)diselenide was obtained by a published method.[25] The solvent removal and drying steps were performed in vacuo. The filtrations were through Celite; the compounds were isolated by filtration.

$(Et_4N)[W(OPh)(S_2C_2Me_2)_2]$. To a dark violet solution of 120 mg (0.25 mmol) of $[W(CO)_2(S_2C_2Me_2)_2]$ in 3 mL of THF was added 29.1 mg (0.25 mmol) of NaOPh. The reaction mixture, which became green-brown within 1 min, was stirred for 90 min, treated with 42.0 mg (0.25 mmol) of Et_4NCl, and stirred for an additional 10 min. The solvent was removed to leave a dark brown solid, which was dissolved in 1.5 mL of acetonitrile. The mixture was filtered and ether (15 mL) was layered on the filtrate, causing the separation of brown needlelike crystals over 1 d. This material was collected, washed with ether (3 × 1 mL), and dried to afford the product as 107 mg (66%) of brown crystals. ^1H NMR (CD_3CN, anion): δ 2.61 (s, 12), 6.42 (d, 2), 6.80 (t, 1), 7.01 (t, 2). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 250 (15 000), 299 (12 000), 319 (sh, 9500), 347 (sh, 4100), 394 (2100), 478 (sh, 610), 572 (290) nm. Anal. Calcd for $C_{22}H_{37}NOS_4W$: C, 41.05; H, 5.79; N, 2.18; S, 19.92. Found: C, 41.04; H, 5.96; N, 2.22; S, 19.77.

$(Et_4N)[W(CO)(SPh)(S_2C_2Me_2)_2]$. Method a. The compound PhSSPh (22.0 mg, 0.10 mmol) was treated with 0.20 mL of a 1.0 M solution of $LiBEt_3H$ in THF. The solution was transferred into a solution of 96.2 mg (0.20 mmol) of $[W(CO)_2(S_2C_2Me_2)_2]$ in 1 mL of THF, producing an immediate green color. The reaction mixture was stirred for 2 h, a solution of 34.2 mg (0.21 mmol) of Et_4NCl was added, and the mixture was stirred for an additional 10 min. The solvent was removed, the solid residue was treated with 1.5 mL of acetonitrile, and the mixture was filtered. Ether (60 mL) was layered onto the filtrate, causing the separation of dark green block-shaped crystals over 2 d. The solid was collected, washed with ether (3 × 4 mL), and dried to

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give the product as 82.1 mg (59%) of dark green crystals. IR (KBr): ν_{CO} 1933 cm^{-1}. ^{1}H NMR (CD$_3$CN, anion): δ 2.49 (s, 12), 7.02 (t, 1), 7.18 (t, 2), 7.48 (d, 2). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 273 (12 000), 334 (6700), 373 (sh, 6300), 436 (8200), 596 (3400) nm. Anal. Calcd for $C_{23}H_{37}NOS_5W$: C, 40.17; H, 5.42; N, 2.04; S, 23.31. Found: C, 39.98; H, 5.33; N, 1.94; S, 23.08.

Method b. To a solution of 78.7 mg (0.17 mmol) of [W(CO)$_2$(S$_2$C$_2$Me$_2$)$_2$] in 1 mL of THF was added a solution of 97.5 mg (0.41 mmol) of (Et$_4$N)(SPh) in 1 mL of acetonitrile. The dark green solution was stirred for 1 h, the solvents were removed, and the residue was dissolved in 2 mL of acetonitrile. The solution was filtered; 15 mL of ether was added to the filtrate, causing precipitation of a dark green crystalline solid over 3 d. This material was isolated, washed with ether (3 × 1 mL), and dried in vacuo, leading to 46.7 mg (41%) of product as a dark green solid. This material is spectroscopically identical to the product of the preceding method.

(Et$_4$N)[W(CO)(SC$_6$H$_2$-2,4,6-Pr$^i_3$)(S$_2$C$_2$Me$_2$)$_2$]. To a solution of 57.6 mg (0.22 mmol) of NaSC$_6$H$_2$-2,4,6-Pr$^i_3$ in 3 mL of acetonitrile was added 106 mg (0.22 mmol) of [W(CO)$_2$(S$_2$C$_2$Me$_2$)$_2$]. A green color developed immediately. The reaction mixture was stirred for 1 h, a solution of 37.4 mg (0.23 mmol) of Et$_4$NCl was added, and the mixture was stirred for an additional 10 min. The solvent was removed, and the dark green residue was dissolved in 2 mL of acetonitrile. The mixture was filtered, and 90 mL of ether was added. Dark green blocklike crystals separated over 3 d. The solid was collected by filtration, washed with ether (3 × 6 mL), and dried in vacuo to afford the product as 76.1 mg (42%) of green crystals. IR (KBr): ν_{CO} 1953 cm^{-1}. ^{1}H NMR (CD$_3$CN, anion): δ 1.00 (d, 12),1.23 (d, 6), 2.48 (s, 12), 2.89 (septet, 1), 3.16 (septet, 2), 6.95 (s, 2). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 291 (11 000), 344 (7200), 438 (6400), 590 (2800) nm. Anal. Calcd for $C_{32}H_{55}NOS_5W$: C, 47.22; H, 6.81; N, 1.72; S, 19.70. Found: C, 47.09; H, 7.02; N, 1.74; S, 19.48.

(Et$_4$N)[W(CO)(SePh)(S$_2$C$_2$Me$_2$)$_2$]. Method a. The procedure is analogous to method (a) for (Et$_4$N)[W(CO)(SPh)(S$_2$C$_2$Me$_2$)$_2$], but with the use of PhSeSePh instead. When conducted on a 0.18 mmol scale of [W(CO)$_2$(S$_2$C$_2$Me$_2$)$_2$], the product was isolated as a dark green crystalline solid in 41% yield. IR (KBr): ν_{CO} 1925 cm^{-1}. ^{1}H NMR (CD$_3$CN, anion): δ 2.53 (s, 12), 7.03 (t, 1), 7.09 (t, 2), 7.44 (d, 2). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 282 (14 000), 334 (sh, 7600), 373 (sh, 6600), 442 (8900), 591 (3600) nm. Anal. Calcd for $C_{23}H_{37}NOS_4SeW$: C, 37.60; H, 5.08; N, 1.91; S, 17.46; Se, 10.75. Found: C, 37.55; H, 5.12; N, 1.89; S, 17.38; Se, 10.84.

Method b. The procedure is analogous to method (b) for (Et$_4$N)-[W(CO)(SPh)(S$_2$C$_2$Me$_2$)$_2$] but with the use of (Et$_4$N)(SePh) instead. When conducted on a 0.22 mmol scale of [W(CO)$_2$(S$_2$C$_2$Me$_2$)$_2$], the product was isolated as a dark green crystalline solid in 68% yield. This material is spectroscopically identical to the product of the preceding method.

(Et$_4$N)[W(CO)(SeC$_6$H$_2$-2,4,6-Pr$^i_3$)(S$_2$C$_2$Me$_2$)$_2$]. Di-(2,4,6-triisopropylphenyl)diselenide (22.5 mg, 0.040 mmol) was added to 0.08 mL of a 1.0 M solution of LiBEt$_3$H in THF. The light yellow solution was transferred to a solution of 37.8 mg (0.080 mmol) of [W(CO)$_2$(S$_2$C$_2$Me$_2$)$_2$] in 1 mL of THF. A green color developed immediately. The reaction mixture was stirred for 1 h, a solution of 12.5 mg (0.075 mmol) of Et$_4$NCl in 1 mL of acetonitrile was added, and the mixture was stirred for an additional 10 min. The solvents were removed leaving a dark green residue, which was dissolved in 2 mL of acetonitrile. The solution was filtered, and 90 mL of ether was layered onto the filtrate. Over 3 d, dark green blocklike crystals deposited. This material was collected, washed with ether (3 × 6 mL), and dried in vacuo. The product was obtained as 38.9 mg (57%) of green crystals. IR (KBr): ν_{CO} 1953 cm^{-1}. ^{1}H NMR (CD$_3$CN, anion): δ 1.03 (d, 12), 1.25 (d, 6), 2.48 (s, 12), 2.89 (septet, 1), 3.18 (septet, 2), 6.97 (s, 2). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 298 (13 000), 339 (8700), 441 (8600), 610 (3800) nm. Anal. Calcd for $C_{32}H_{55}NOS_4SeW$: C, 44.65; H, 6.44; N, 1.63; S, 14.90; Se, 9.17. Found: C, 44.53; H, 6.51; N, 1.59; S, 14.11; Se, 9.12.

In the sections that follow, tungsten complexes are referred to by the numerical designations in Chart 1.

Chart 1. Designation of Bis(dithiolene)−Tungsten(IV) Complexes

[W(CO)$_2$(S$_2$C$_2$Me$_2$)$_2$]	**1**
[W(OPh)(S$_2$C$_2$Me$_2$)$_2$]$^{1-}$	**2**
[W(CO)(SPh)(S$_2$C$_2$Me$_2$)$_2$]$^{1-}$	**3**
[W(CO)(SC$_6$H$_2$-2,4,6,-Pr$^i_3$)(S$_2$C$_2$Me$_2$)$_2$]$^{1-}$	**4**
[W(CO)(SePh)(S$_2$C$_2$Me$_2$)$_2$]$^{1-}$	**5**
[W(CO)(SeC$_6$H$_2$-2,4,6,-Pr$^i_3$)(S$_2$C$_2$Me$_2$)$_2$]$^{1-}$	**6**

X-ray Structure Determinations. The five compounds listed in Table 2 were structurally identified by X-ray crystallography. Suitable crystals of (Et$_4$N)**[2]** (brown needles), (Et$_4$N)[**3**] and (Et$_4$N)[**5**] (thin dark green plates), and (Et$_4$N)[**4**] and (Et$_4$N)[**6**] (dark green blocks) were obtained by layering ether on the corresponding acetonitrile solutions and allowing the solutions to stand over 2−3 days. The crystals were coated in grease and mounted on a Siemens (Bruker) SMART CCD area detector instrument with Mo Kα radiation. The data were collected at 213 K with ω scans of 0.3° per frame, with 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 collection to monitor for decay; no significant decay was detected for any compound. Data out to 2θ of 56° were used for the compounds (Et$_4$N)[**2**,**4**,**6**], but for (Et$_4$N)[**3,5**], the data were used only out to 2θ of 45° because of the low-quality high-angle data. Cell parameters were retrieved using SMART software and refined using SAINT software on all observed reflections between 2θ of 3° and the upper thresholds. Data reduction was performed with the SAINT software, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS, as described by Blessing.[26] The space groups for all of the compounds were assigned unambiguously by analysis of symmetry and systematic absences determined by the program XPREP. The crystal parameters are listed in Table 2.

All of the structures were solved by the direct method with SHELXS-97 and subsequently refined against all data in the 2θ ranges by full-matrix least squares on F^2 using SHELXL-97. Asymmetric units contain one ((Et$_4$N)[**2**,**4**,**6**]), three ((Et$_4$N)[**3**]), and four ((Et$_4$N)[**5**]) formula weights. All of the methylene groups of the cation in (Et$_4$N)[**2**] and three methylene groups of one of the cations in (Et$_4$N)[**5**] in the asymmetric unit were disordered over two sites and were refined with site occupancy factors of 0.83 and 0.55, respectively. All non-hydrogen atoms, including those of the disordered cations, were refined anisotropically. Hydrogen atoms were attached at idealized positions on carbon atoms and were checked for missing symmetry by the program PLATON. The final agreement factors are given in Table 2. (See the Supporting Information.)

Other Physical Measurements. All measurements were performed under anaerobic conditions. Absorption spectra were recorded with a Varian Cary 50 Bio spectrophotometer. The ^{1}H NMR spectra were obtained with Bruker AM 400N/500N spectrometers. IR spectra were measured with KBr pellets in a Nicolet Impact 400 or a Nicolet Nexus 470 FT-IR instrument. Cyclic voltammograms and differential potential voltammograms were recorded with a PAR Model 263 potentiostat/galvanostat, using Pt disk working electrode and 0.1 M Bu$_4$NPF$_6$ supporting electrolyte in MeCN solution. Potentials were directly measured with and referenced to the saturated calomel electrode (SCE).

Results and Discussion

In seeking a convenient starting material for bis(dithiolene)-tungsten complexes, we have utilized the trigonal prismatic dicarbonyl complex **1**. This compound was first prepared by Schrauzer et al.[21] in low yield by means of a photochemical reaction between [W(CO)$_6$] and [Ni(S$_2$C$_2$R$_2$)$_2$] (R = Me, Ph). We have improved the synthesis by the use of [W(CO)$_3$(MeCN)$_3$];[27] the reaction system does not require irradiation and affords **1** in yields of ∼60−70%.[17] The lability of the carbonyl ligands was demonstrated by displacement with

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Table 2. Crystallographic Data[a]

	$(Et_4N)[\mathbf{2}]$	$(Et_4N)[\mathbf{3}]$	$(Et_4N)[\mathbf{4}]$	$(Et_4N)[\mathbf{5}]$	$(Et_4N)[\mathbf{6}]$
formula	$C_{22}H_{37}NOS_4W$	$C_{23}H_{37}NOS_5W$	$C_{32}H_{55}NOS_5W$	$C_{23}H_{37}NOS_4SeW$	$C_{32}H_{55}NOS_4SeW$
fw	643.62	687.69	813.92	734.59	860.82
cryst syst	monoclinic	triclinic	orthorhombic	triclinic	orthorhombic
space grp	$P2_1/n$	$P\bar{1}$	*Pbcn*	$P\bar{1}$	*Pbcn*
Z	4	6	8	8	8
a (Å)	8.7440(3)	10.1257(2)	25.4814(5)	19.2516(4)	25.5714(7)
b (Å)	24.2608(3)	16.1756(1)	16.9145(2)	19.2618(3)	16.8328(4)
c (Å)	12.7236(4)	25.8216(5)	17.1093(4)	19.3633(4)	17.2163(5)
α (deg)		88.915(1)		103.497(1)	
β (deg)	102.844(2)	82.50		104.794(1)	
γ (deg)		84.242(1)		116.170(1)	
V ($Å^3$)	2631.60(13)	4171.87(12)	7374.2(2)	5713.85(19)	7410.6(3)
d_{calc} (g/cm^3)	1.624	1.642	1.466	1.708	1.543
2θ range (deg)	3−56	3−45	3−56	3−45	3−56
$R_1{}^b$ ($wR_2{}^c$)	0.0360 (0.0687)	0.0386 (0.0742)	0.0612 (0.1132)	0.0479 (0.0716)	0.0286 (0.0728)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.710\,73$ Å) radiation at 213 K. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

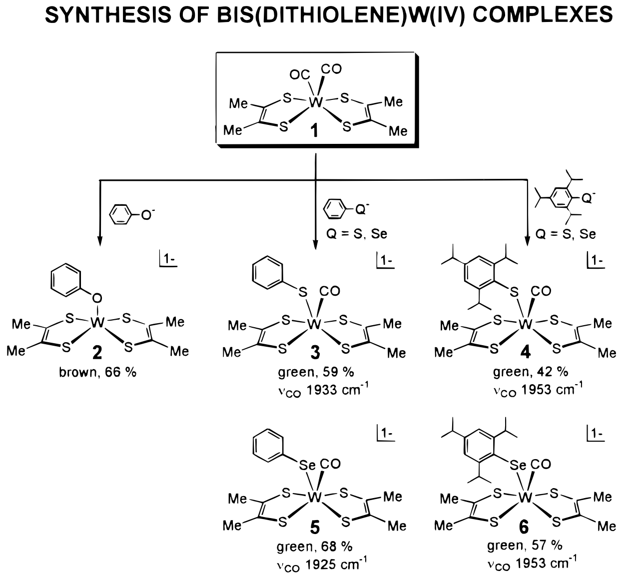

Figure 2. Synthesis of bis(dithiolene)W(IV) complexes **2**−**6** by ligand substitution of the dicarbonyl complex **1**.

hydroxide, sulfide, and selenide to form the series $[WQ(S_2C_2Ph_2)_2]^{2-}$ (Q = O, S, Se).[17] The corresponding complex $[Mo(CO)_2(S_2C_2Me_2)_2]$ is a versatile precursor for the formation of a large family of bis(dithiolene)Mo complexes with ligation modes resembling those of W(IV) in Figure 1.[23] Species derived from $[M(CO)_2(S_2C_2Me_2)_2]$ have the attractive feature of binding by a *dialkyl*dithiolene, in this sense, closely related to the cofactor ligand (Figure 1). Much of our previous work has utilized the ligand benzene-1,2-dithiolate.[16] Although it is of the dithiolene type and entirely suitable for structural studies, as in our recent X-ray absorption investigation,[28] this ligand should induce electronic properties including redox potentials that depart to an extent from those intrinsic to the cofactor ligand.

To examine the viability of molecules based on W(IV) sites **a**−**c** (Figure 1), reactions of **1** with arene oxide, sulfide, and selenide ligands have been investigated in THF or acetonitrile and are summarized in Figure 2. Reaction products **2**−**6** are diamagnetic. The structures of the five complexes are shown in Figures 3 and 4; metric data are collected in Table 3. Because dithiolene complexes are strongly colored, the usually highly featured absorption spectra provide a simple means of identification. For this purpose, UV−vis spectra are included in Figures 5 and 6.

Oxygen Ligation. Reaction of **1** in THF with NaOPh affords the phenolate complex **2** (66%), which manifests a square-pyramidal structure with the desired W−OPh ligation (Figure 3). As is typical of five-coordinate $[ML(S_2C_2R_2)_2]^{1-,2-}$ complexes (M = Mo,[22,23,29,30] W[16−20]), the two chelate rings are not coplanar and, in this case, are disposed at a dihedral angle $\theta_d = 127.3°$. The metal atom is displaced from the S_4 least-squares plane toward the axial ligand by $\delta = 0.78$ Å. The W−O bond length is 1.861(3) Å. The mean chelate ring bond distances of 1.321 Å (C−C) and 1.779(5) (C−S) Å indicate two enedithiolate ligands and thus the formulation $[W^{IV}(OPh)(S_2C_2Me_2)_2]^{1-}$, rather than a W(II) dithione/enedithiolate description. The molecule is structurally similar to $[Mo(OC_6H_3\text{-}2,6\text{-}Pr^i{}_2)(S_2C_2Me_2)_2]^{1-}$, for which $\theta_d = 125.7°$ and $\delta = 0.82$ Å.[23] The spectra of **2** and its molybdenum analogue (Figure 5) are quite distinct. The spectrum of **2** appears to be a blue-shifted version of the spectrum of $[Mo(OPh)(S_2C_2Me_2)_2]^{1-}$, but the exact band correlations require spectral assignments that are not yet available. Complex **2** is intended to be an approach to serinate-bound site **a**, the existence of which would be appear to be feasible. However, we note that **2** and its molybdenum analogue are extremely sensitive to small amounts of water. The hydrolysis product has not been characterized.

Sulfur and Selenium Ligation. Complex **1** in THF reacts instantly with benzenethiolate or benzeneselenolate in acetonitrile, when the latter is added to the reaction mixture as a salt or generated in situ by reduction of PhSSPh or PhSeSePh in THF. Green complexes **3** (59%) and **5** (68%) are obtained as monocarbonyls. These species exhibit characteristic absorption spectra, that of **5** being red-shifted compared to **3** (Figure 6). The compounds $[Mo(CO)(QPh)(S_2C_2Me_2)_2]^{1-}$ (Q = S, Se) are formed under comparable conditions.[23] In an attempt to prepare carbonyl-free complexes, the reactions of **1** and the sterically bulky ligands 2,4,6-triisopropylbenzenethiolate and 2,4,6-triisopropylbenzeneselenolate were examined. With ligand/**1** mol ratios in the range from 1:1 to 2.4:1 and reaction times of about 1 h, the green monocarbonyl complex **4** (42%) and **6** (57%) were obtained. Compared to **3** and **5**, the absorption spectra of these complexes are very similar; the ν_{CO} values are increased

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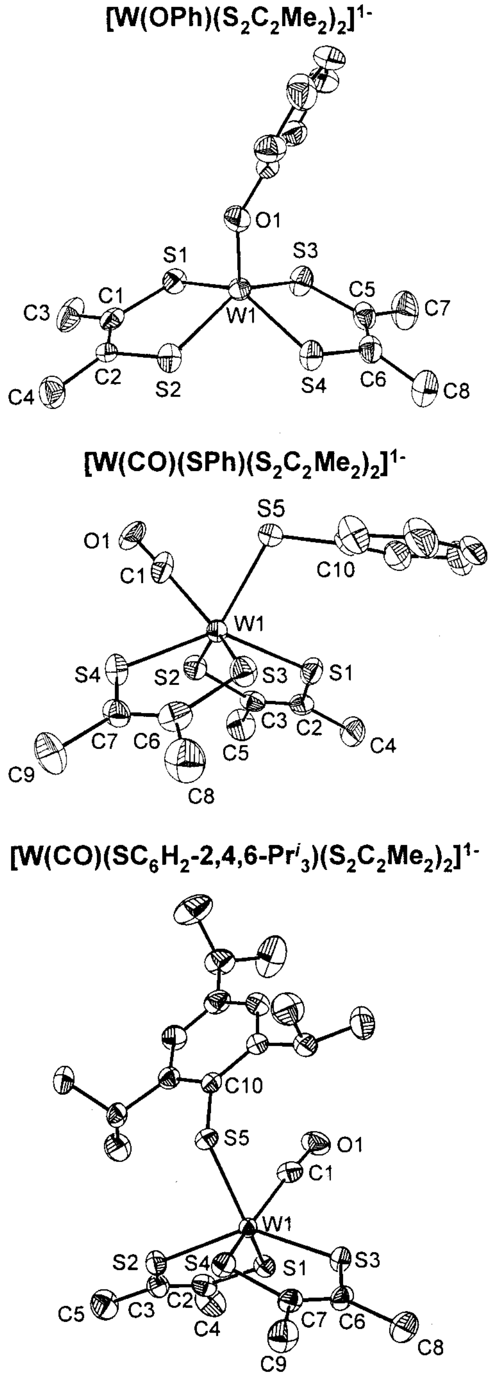


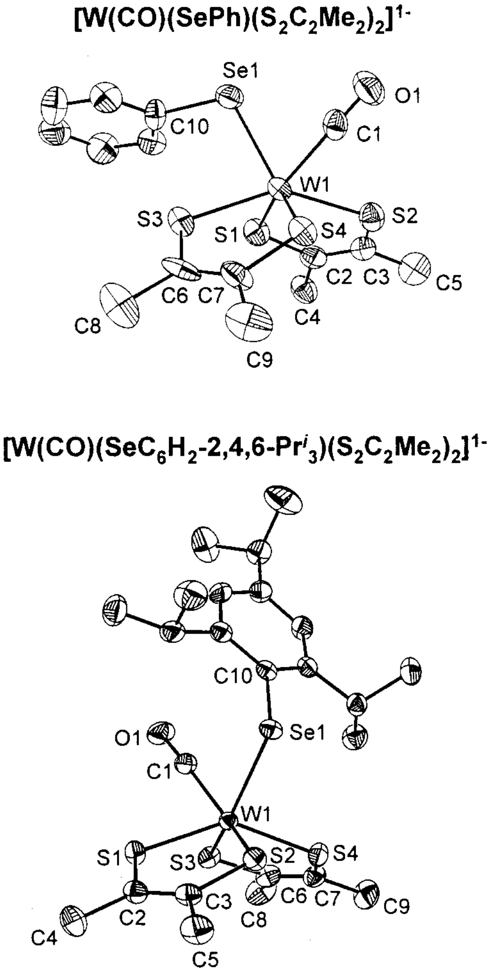
$[W(OPh)(S_2C_2Me_2)_2]^{1-}$

$[W(CO)(SPh)(S_2C_2Me_2)_2]^{1-}$

$[W(CO)(SC_6H_2\text{-}2,4,6\text{-}Pr^i_3)(S_2C_2Me_2)_2]^{1-}$

Figure 3. Structures of phenolate-ligated complex **2** and thiolate-ligated complexes **3** and **4**, showing 50% probability ellipsoids and atom labeling schemes.

by 20−28 cm^{-1}, presumably because of the higher basicity of the substituted ligands. Subsequently, reactions of the substituted ligands were conducted with the mol ratio ligand/**1** of 5:1 for 4 h in acetonitrile/THF. The solvent was removed in vacuo, and the absorption and IR spectra of the residue were examined. These are identical to those of **4** and **6**, prepared and isolated as described. Clearly, carbonyl-free complexes are not favored under these more forcing conditions.



$[W(CO)(SePh)(S_2C_2Me_2)_2]^{1-}$

$[W(CO)(SeC_6H_2\text{-}2,4,6\text{-}Pr^i_3)(S_2C_2Me_2)_2]^{1-}$

Figure 4. Structures of selenolate-ligated complexes **5** and **6**, showing 50% probability ellipsoids and atom labeling schemes.

Table 3. Selected Bond Distances (Å) and Angles (deg)

	2	**3**[a]	**4**	**5**[a]	**6**
W−Q[b]	1.861(3)	2.438(2)	2.450(2)	2.547(1)	2.568(1)
W−S1	2.329(1)	2.387(2)	2.382(2)	2.396(3)	2.331(1)
W−S2	2.331(1)	2.351(2)	2.374(2)	2.365(3)	2.403(1)
W−S3	2.311(1)	2.378(2)	2.336(2)	2.393(3)	2.378(1)
W−S4	2.319(1)	2.360(2)	2.410(2)	2.349(3)	2.368(1)
mean of 4	2.323(8)	2.37(1)	2.38(3)	2.38(2)	2.37(3)
W−C1		2.03(1)	2.022(7)	2.02(1)	2.017(3)
C1−O1		1.12(1)	1.154(8)	1.12(1)	1.139(4)
S−C[c]	1.779(5)	1.74(1)	1.756(5)	1.74(1)	1.751(6)
C−C[c,d]	1.321	1.341	1.341	1.354	1.337
W−Q−C[b]	146.7(3)	114.0(3)	110.3(2)	110.6(3)	108.2(1)
S1−W−S2[e]	81.98(5)	80.43(8)	79.67(6)	79.8(1)	82.21(3)
S3−W−S4[e]	82.34(5)	80.41(8)	82.10(6)	80.19(9)	79.81(3)
S1−W−S4[f]	141.82(4)	137.50(8)	147.3(2)	131.4(1)	142.08(3)
S2−W−S3[f]	139.99(5)	138.51(8)	141.28(6)	146.1(1)	137.57(3)
δ[g]	0.779	0.849	0.830	0.665	0.650
θ_d[h]	127.3	124.0	125.3	124.4	126.3

[a] One of three (**3**) or four (**5**) anions in the asymmetric; dimensions of other independent anions are not significantly different. [b] Q = O, S, or Se; unidentate ligand. [c] Mean value. [d] Chelate ring. [e] Chelate bite angle. [f] Transoid angle. [g] Perpendicular displacement of W atom from S_4 least-squares plane. [h] Dihedral angle between WS_2 planes.

The structures of complexes **3**/**4** (Figure 3) and **5**/**6** (Figure 4) are quite similar. The set of four possesses the following properties, evident from the data in Table 3: (i) The stereochemistry is distorted trigonal prismatic, as indicated by angles between coordination planes (θ_d = 124−126°) and transoid S−W−S angles, involving atoms of different ligands (131−147°). For a trigonal prism, θ_d = 120°, and the transoid angle is 136°. (ii) Ligand C−C and C−S bond distances point to an enedithiolate/W(IV) formulation. (iii) Mean W−S distances are essentially constant (2.37−2.38 Å) and are larger than the value for **2** (2.323(8) Å) because of the higher coordination number. They correspond closely to other five-coordinate W^{IV}−S(dithi-

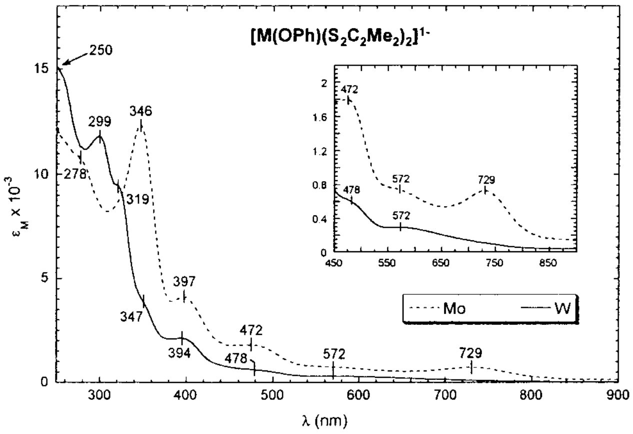


Figure 5. Absorption spectra of $[M(OPh)(S_2C_2Me_2)_2]^{1-}$ (M = Mo, W (**2**)) in acetonitrile solutions.

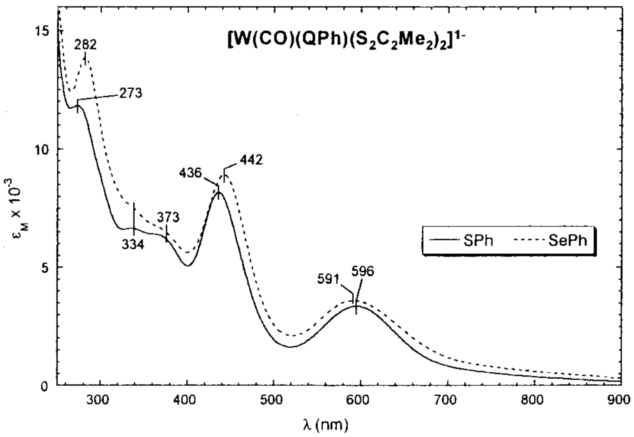


Figure 6. Absorption spectra of $[W(CO)(QPh)(S_2C_2Me_2)_2]^{1-}$ (Q = S (**3**), Se (**5**)) in acetonitrile solutions.

olene) values (2.33−2.39 Å[16−20]). (iv) The difference between W−SAr bond distances in **3** and **4** (0.01 Å) is not significant, and between W−Se bond distances in **5** and **6** (0.02 Å) is slight, indicating that the more voluminous triisopropylphenyl group does not significantly elongate these bonds. With the exception of certain conformational differences, analogous molybdenum[23] and tungsten complexes are isostructural and nearly isometric. The stereochemistry of six-coordinate complexes, such as **1** and **3**−**6**, places unidentate ligands in cis positions without exception. The trans isomer of either octahedral or trigonal prismatic geometry has never been observed.

In the context of active-site structural analogues, non-carbonyl complexes are obviously more desirable than monocarbonyls. Several interesting differences have emerged, thus far, in the comparative chemistry of molybdenum[23] and tungsten bis(dithiolenes) with arene oxide, thiolate, and selenolate (ArQ^-) ligands. Metal−ligand bond lengths for monocarbonyl and non-carbonyl complexes of molybdenum and tungsten are collected in Table 4, which makes evident the complexes that have not yet been prepared. We note certain dimensional factors that apparently contribute to the existence or nonexistence of the compounds included in Table 4. In the synthesis of oxygen-ligated complexes **2**, $[Mo(OPh)(S_2C_2Me_2)_2]^{1-}$, and $[Mo(OC_6H_3\text{-}2,6\text{-}Pr^i_2)(S_2C_2Me_2)_2]^{1-}$, no carbonyl intermediate or product has been detected. Passage of CO through an acetonitrile solution of **2** generates the extremely labile green chromophore $[W(CO)(OPh)(S_2C_2Me_2)_2]^{1-}$, whose formation is reversible. In comparison, sulfur-ligated **3** and $[Mo(CO)(SPh)(S_2C_2Me_2)_2]^{1-}$ are stable isolable compounds. However, $[Mo(CO)(SC_6H_2\text{-}2,4,6\text{-}Pr^i_3)(S_2C_2Me_2)_2]^{1-}$ (green-brown) has been observed only as an intermediate and reverts to five-coordinate $[Mo(SC_6H_2\text{-}2,4,6\text{-}Pr^i_3)(S_2C_2Me_2)_2]^{1-}$ (red-brown) upon workup, which includes solvent removal in vacuo. In contrast, selenium-ligated $[Mo(CO)(SeC_6H_2\text{-}2,4,6\text{-}Pr^i_3)(S_2C_2Me_2)_2]^{1-}$ (green-brown) is readily isolated under the same workup conditions. A carbonyl-free molybdenum selenolate complex has not been observed in the reaction system, nor has it been obtained by thermolysis or photolysis of the carbonyl complex. Similarly, tungsten complex **6**, with the triisopropylbenzeneselenoate ligand, is entirely stable.

Table 4. Metal−Oxygen/Sulfur/Selenium Bond Lengths (Å) (x = unknown compound)

	$[M(CO)(QAr)(S_2C_2Me_2)_2]^{1-}$		$[M(QAr)(S_2C_2Me_2)_2]^{1-}$	
^-QAr	Mo[a]	W	Mo[a]	W
OPh	x	x	*b*	1.861(3)
$OC_6H_3\text{-}2,6\text{-}Pr^i_2$	x	x	1.867(8)	*c*
SPh	2.469(1)	2.438(2)	x	x
$SC_6H_2\text{-}2,4,6\text{-}Pr^i_3$	*d*	2.450(2)	2.338(1)	x
SePh	2.585(1)	2.547(1)	x	x
$SeC_6H_2\text{-}2,4,6\text{-}Pr^i_3$	2.580(3)	2.568(1)	x	x

[a] Ref 23. [b] Not determined. [c] Not prepared. [d] Detected but not isolated.

Table 5. Tungsten (IV/III) Redox Potentials in Acetonitrile

complex	$E_{1/2}$, V[a] (ΔE_p, mV)
$[W(OPh)(S_2C_2Me_2)_2]^{1-}$	−2.07[b]
$[Mo(OPh)(S_2C_2Me_2)_2]^{1-}$	−1.78[b]
$[W(CO)(SPh)(S_2C_2Me_2)_2]^{1-}$	−1.45 (100)
$[W(CO)(SC_6H_2\text{-}2,4,6\text{-}Pr^i_3)(S_2C_2Me_2)_2]^{1-}$	−1.54 (166)
$[W(CO)(SePh)(S_2C_2Me_2)_2]^{1-}$	−1.45 (90)
$[W(CO)(SeC_6H_2\text{-}2,4,6\text{-}Pr^i_3)(S_2C_2Me_2)_2]^{1-}$	−1.57 (90)

[a] $E_{1/2} = (E_{pc} + E_{pa})/2$, 100 mV/s, vs SCE. [b] Irreversible; values from differential pulse voltammetry.

One likely factor affecting the stability of molybdenum carbonyl adducts is the length of the Mo−QAr bond. The short Mo−O bond and the multiple orientations of the diisopropylphenolate group by rotations about the Mo−O and C−O bonds should discourage carbonyl binding at a cis position. The longer Mo−S bond and similar orientational mobility do allow formation of a labile monocarbonyl but also enable the isolation of the carbonyl-free complex. The Mo−Se bond is 0.11−0.12 Å longer, and, even with the very bulky triisopropyl benzeneselenoate ligand, the carbonyl complex is stable. The same steric factors must apply to the isostructural tungten complexes. The stability of monocarbonyls **4** and **6**, containing the sterically demanding triisopropylphenyl group, reflects a larger intrinsic tendency of tungsten to bind carbon monoxide. This effect has been observed in other systems as both a thermodynamic and a kinetic property. For example, the bond dissociation energy of $[W(CO)_6]$ is ~5 kcal/mol larger than that found for $[Mo(CO)_6]$, as studied by laser pyrolysis.[31] Also, carbonyl subsitution reactions in M(0) complexes are usually markedly slower for tungsten than molybdenum.[32] We are unaware of additional comparative reactivity observations for Mo(IV) and W(IV) other than redox potentials.[33]

Tungsten(IV/III) redox potentials for complexes **2**−**6** are given in Table 5. The potential for **2** and its molybdenum counterpart are so negative as to preclude the formation of a

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bis(dithiolene)M(III) species under physiological conditions. The potential order W < Mo is observed without exception in constant coordination environments.[33] The retention of a carbonyl in the coordination sphere affords chemically reversible cyclic voltammograms ($i_{pc}/i_p \approx 1$, not shown) and stabilizes the W(III) state by ∼500 mV. The existence of bis(dithiolene) monocarbonyl complexes of both metals raises the interesting question as to whether reduced enzymes will bind carbon monoxide.

This work represents our initial exploration of the formation and stability of bis(dithiolene)W(IV) complexes related to sites **a**−**c** (Figure 1). Further development of structural and reactivity analogues of enzyme sites necessitates the examination of the oxidative chemistry, both the oxygen atom and the electron transfer, potentially leading to W(VI) sites **d**−**f**. Such studies, also involving bis(dithiolene)Mo(IV) complexes, are in progress.

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

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