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Tungsten Bioinorganic Chemistry: Synthesis, Structure, and Reactivity of *cis*-Oxothiotungsten(VI), *cis*-Bis(thio)tungsten(VI), and (Ene-1,2-dithiolato)tungsten(IV) Complexes

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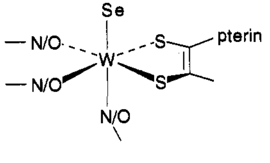
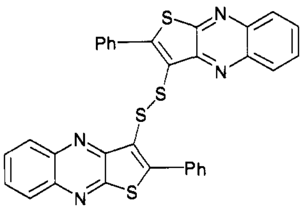
The partial characterization of a number of oxygen-sensitive, pterin-containing tungsten enzymes from thermophiles has stimulated a renewed interest in the bioinorganic chemistry of tungsten.[1,2] At present, the biological role of tungsten is unclear and the detailed structures of the tungsten centers are unknown. EXAFS of the selenocysteine-containing formate dehydrogenase from *Clostridium thermoaceticum* (CT-FD) is consistent with an active site devoid of terminal chalcogen ligands (**I**).[3] In contrast, EXAFS supports the presence of a $[WO_2]^{2+}$ center in an oxidized, inactive form of *Pyrococcus furiosus* aldehyde: ferredoxin oxidoreductase.[4a] For the active enzyme, there is evidence[4b] for a W–SH center and a case can be made for the involvement of thio–tungsten chemistry.[2] Advances in thio–tungsten model chemistry[2] are required to assess this possibility and ensure the accurate interpretation of enzyme behavior and spectroscopy. Recently, we described the novel complexes $\{HB(Me_2pz)_3\}W^{VI}OSCl$ (**1**) and $\{HB(Me_2pz)_3\}W^{VI}S_2Cl$ (**2**) [$HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethylpyrazol-1-yl)borate].[5] This paper reports the synthesis and structural characterization of $\{HB(Me_2pz)_3\}W^{VI}OS\{(-)\text{-mentholate}\}$ (**3**), $\{HB(Me_2pz)_3\}W^{VI}S_2(OPh)$ (**4**), and $\{HB(Me_2pz)_3\}W^{IV}(OPh)\{S_2C_2(CO_2Me)_2\}$ (**5**), the production of **II** (cf. urothione) upon aerial oxidation of $\{HB(Me_2pz)_3\}W^{IV}(SePh)\{S_2C_2(Ph)(2\text{-quinoxalinyl})\}$ (**6**, cf. **I**), and the electrochemical behavior of selected oxo– and thio–tungsten complexes. A new strategy for the synthesis of ene-1,2-dithiolate ligands is also reported.



(I)



(II)

Reaction of **1**[5] with sodium (1*R*,2*S*,5*R*)-(−)-mentholate in toluene results in two orange diastereomers of **3**.[6] These are chiral at tungsten and are assigned *R* and *S* configurations by taking the W···B vector as the imaginary, single binding point of the $HB(Me_2pz)_3^-$ ligand, which is assigned lowest priority. They exhibit strong ν(WO) (930 cm^{-1}) and ν(WS) (480 cm^{-1}) infrared bands and ^{1}H NMR spectra consistent with C_1 symmetry. The X-ray crystal structure of (*R*,*S*)-**3** has been determined (Figure 1);[7] the six-coordinate molecules exhibit distorted octahedral geometries with average W–O(1), W–S(1), and W–O(2) distances of 1.734(9), 2.118(6), and 1.850(7) Å, respectively. The O(1)–W–S(1) angles average at 102.9(5)°. Significantly different W–O(2)–C(1) angles are observed for the two diastereomers; 158(2)° for (*S*)-**3** and 135(1)° for (*R*)-**3**. Only one other octahedral *cis*-oxothiotungsten complex, viz., $[WOS(NCS)_4]^{2-}$, has been structurally characterized.[8] Intramolecular stabilization of the terminal thio ligand, as observed for $\{HB(Me_2pz)_3\}MoOS(S_2P^iPr_2)$,[9] is not a feature of any known oxothio–W(VI) complex.

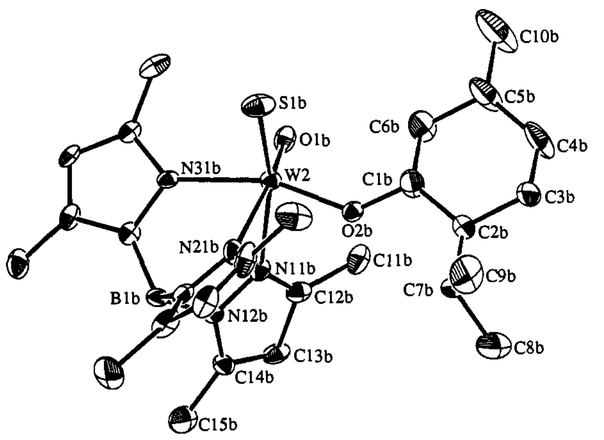


Figure 1. Structure of (*R*)-**3**. Selected bond legnths (Å) and angles (deg): W(2)–O(1b) 1.71(2), W(2)–S(1b) 2.132(8), W(2)–O(2b) 1.86(1), W(2)–N(11b) 2.26(2), W(2)–N(21b) 2.31(2), W(2)–N(31b) 2.18(1), O(2b)–C(1b) 1.40(2), O(1b)–W(2)–S(1b) 102.0(6), O(1b)–W(2)–O(2b) 100.7(6), S(1b)–W(2)–O(2b) 103.4(6), W(2)–O(2b)–C(1b) 135(1).

A series of $\{HB(Me_2pz)_3\}WS_2X$ (X = OPh (**4**),[10] SPh, SePh) complexes may be prepared from **2**.[5] These intensely colored, generally air-stable compounds exhibit $\nu_s(WS_2)$ and $\nu_{as}(WS_2)$ infrared bands at 495 and 475 cm^{-1}, respectively, and ^{1}H NMR spectra consistent with molecular C_s symmetry. The structure of **4**, determined by X-ray diffraction (Figure 2),[11] reveals two equivalent W=S bond distances [average 2.130(4) Å]. The S(1)–W–S(2) angle (102.9(1)°) and S(1)···S(2) separation [3.331(5) Å] confirm the presence of the *cis*-bis(thio)–W(VI) moiety. Structurally characterized *cis*-bis(thio)–metal complexes are extremely rare,[12] and **4** is the first to possess biologically relevant two-electron donor coligands and an octahedral geometry.

The dioxo complexes $\{HB(Me_2pz)_3\}WO_2X$ (X = Cl,[5] NCS,

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(6) Anaerobic reactions unless specified. Correct microanalyses were obtained. Synthesis of **3**: A suspension of **1** (0.15 g, 0.27 mmol) in toluene (10 mL) was treated with sodium (−)-mentholate (0.3 mmol) in THF (1.0 mL) and stirred for 24 h. The mixture was reduced to ca. 2 mL and then eluted on a silica column with toluene. The orange product was recrystallized from CH_2Cl_2/MeOH. Yield: 0.11 g (62%).

(7) Crystallographic data: **3**, $C_{25}H_{41}BN_6O_2SW$, fw 684.4, monoclinic space group $P2_1$ with a = 11.983(2) Å, b = 18.100(3) Å, c = 13.859(3) Å, β = 91.60(2)°, V = 3004.6(8) Å^3, and D_c = 1.513 g cm^{-3} for Z = 4. The structure was solved by direct methods and refined by a full-matrix least-squares procedure, using 4601 data, to a conventional R value of 0.038 (R_w = 0.046); the absolute configuration is determined by the conformation of (−)-mentholate.

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(10) Synthesis of **4**: A mixture of **2** (0.12 g, 0.21 mmol), NaOPh (0.10 g, 0.86 mmol), and 18-crown-6 (5 mg) was refluxed in toluene (10 mL) for 2.5 h and then reduced to dryness at 70 °C. The residue was redissolved and eluted on a silica column with 1:1 THF/hexanes and the product collected as the first orange band. Yield: 0.08 g (60%).

(11) Crystallographic data: **4**, $C_{21}H_{27}BN_6OS_2W{\cdot}CH_2Cl_2$, fw 723.2, orthorhombic space group *Pbca* with a = 16.961(4) Å, b = 33.098(7) Å, c = 9.554(2) Å, V = 5363(1) Å^3, and D_c = 1.791 g cm^{-3} for Z = 8. Analysis as for **3**, R = 0.049, R_w = 0.048 for 2922 data.

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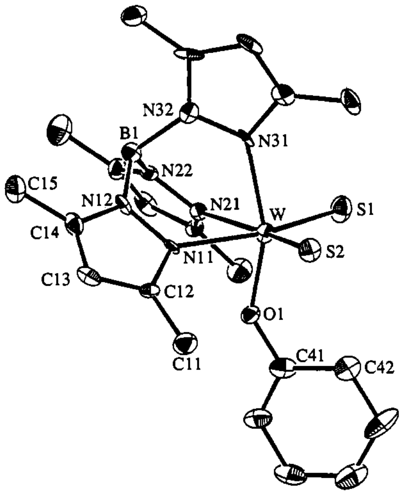


Figure 2. Structure of **4**. Selected bond lengths (Å) and angles (deg): W–S(1) 2.131(4), W–S(2) 2.129(4), W–O(1) 1.889(8), W–N(11) 2.268(8), W–N(21) 2.271(9), W–N(31) 2.161(9), O(1)–C(41) 1.36(1), S(1)–W–S(2) 102.9(1), S(1)–W–O(1) 100.5(2), S(2)–W–O(1) 99.5(3), W–O(1)–C(41) 137.3(9).

OPh, SPh, SePh) undergo generally irreversible, one-electron reductions in the range $E_{pc} = -1.08$ (X = NCS) to $E_{1/2} = -1.55$ V (X = OPh, reversible) vs SCE in acetonitrile. These reduction potentials are typically 470–740 mV more negative than the Mo(VI)/Mo(V) potentials of the analogous Mo complexes.[13] Oxothio complex **1** exhibits a reversible, one-electron reduction at $E_{1/2} = -0.84$ V, ca. 400 mV more positive than the corresponding dioxo complex. A slightly more positive (irreversible) reduction potential is observed for **2** ($E_{pc} = -0.82$ V). The complexes $\{HB(Me_2pz)_3\}WS_2X$ (X = OPh, SPh, SePh) exhibit reversible electrochemistry with reduction potentials $E_{1/2}$ in the range -0.99 to -0.86 V. Reduction potentials for the thio–W complexes are in the range of those established for related $[MoO_2]^{2+}$ complexes.[13] Terminal thio ligation at W(VI) clearly facilitates reduction and enhances reversibility on the cyclic voltammetric time scale. Moreover, these studies demonstrate that the oxothio– and bis(thio)-W(VI) complexes are reducible at biologically accessible potentials, whereas most of the dioxo–W(VI) complexes are not.

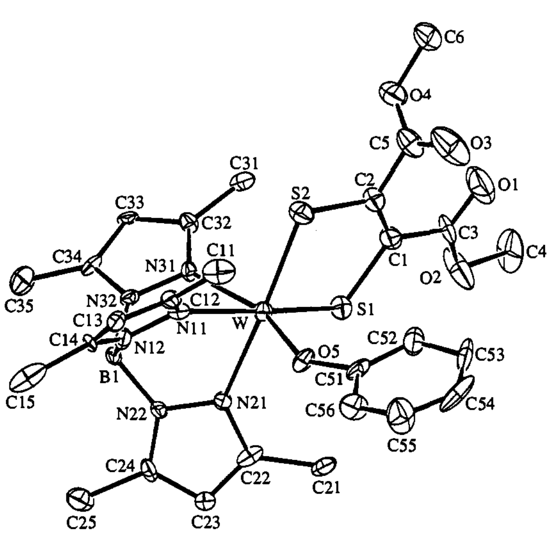
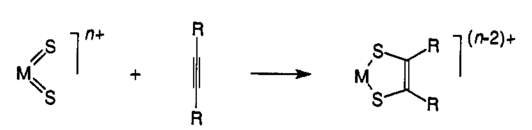


Figure 3. Structure of **5**. Selected bond lengths (Å) and angles (deg): W–S(1) 2.267(4), W–S(2) 2.279(4), W–O(5) 1.850(8), W–N(11) 2.19(1), W–N(21) 2.18(1), W–N(31) 2.19(1), S(1)–C(1) 1.77(2), S(2)–C(2) 1.74(2), C(1)–C(2) 1.33(2), O(5)–C(51) 1.34(2), S(1)–W–S(2) 85.0(2), S(1)–W–O(5) 101.1(3), S(2)–W–O(5) 97.9(3), W–O(5)–C(51) 146(1), W–S(1)–C(1) 107.8(6), W–S(2)–C(2) 106.6(6).



(1)

Solutions of $\{HB(Me_2pz)_3\}WS_2X$ react with alkynes[14] to form (ene-1,2-dithiolato)tungsten(IV) complexes, e.g., **5** and **6**, in a new strategy (eq 1) for the synthesis of ene-1,2-dithiolate complexes. The structure of orange, air-stable **5** is shown in Figure 3.[15] The W–S(1) and W–S(2) bond lengths of 2.267(4) and 2.279(4) Å, respectively, are considerably shorter (by 0.07 Å) than any previously reported[16e] for a tungsten enedithiolate; the average W–S distance for such compounds is 2.40 Å.[16] The W–S_{av} distance for CT-FD is virtually identical to this average at 2.39 Å.[3] The short W–S distances in **5** are indicative of considerable dπ–pπ bonding between the W and S atoms. The ene-1,2-dithiolate S_2C_4 framework is planar with a mean atom deviation of 0.035 Å and a C(1)–C(2) distance consistent with a double bond. The dihedral angle between this plane and the W–S(1)–S(2) plane is 8.7°. The W–O(5) distance of 1.850(8) Å and W–O(5)–C(51) angle of 146(1)° are consistent with dπ–pπ bonding between the W and O(5) atoms. Only one other mono(enedithiolate) complex of tungsten is known.[16b] Complex **6** provides a close model and potential structural and spectroscopic benchmark for the active site of CT-FD. Interestingly, methanolic solutions of **6** decompose rapidly in air to give $\{HB(Me_2pz)_3\}WO_2(OMe)$, diphenyldiselenide, and **II** (characterized by spectral comparison with an authentic sample[17]). Burgmayer et al.[17] reported that **II** is formed in the oxidative decomposition of $[Mo\{S_2C_2(Ph)(2\text{-quinoxalinyl})\}_3]^{2-}$ and related this reaction to the formation of urothione upon degradation of the molybdopterin-containing molybdenum cofactor. On the basis of our isolation of **II** upon oxidation of **6**, the degradation of molybdopterin-containing tungsten enzymes might also be expected to produce urothione.

Acknowledgment. We gratefully acknowledge the financial support of the Australian Research Council.

Supplementary Material Available: Electrochemical data and listings of fractional atomic coordinates, thermal parameters, H atom parameters, and all bond distances and angles for **3**–**5** (24 pages); structure factor amplitudes for **3**–**5** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) Synthesis of **5**: A solution of **4** (0.077 g, 0.12 mmol) in CH_2Cl_2 (10 mL) was treated with $CH_3CO_2C{\equiv}CCO_2CH_3$ (0.10 mL, 0.81 mmol) and then stirred in air for 0.5 h. The mixture was reduced to 3 mL and eluted on a silica column with 1:1 THF/hexane. The product was recrystallized from CH_2Cl_2/MeOH. Yield: 0.02 g (22%). Synthesis of **6**: A mixture of $\{HB(Me_2pz)_3\}WS_2(SePh)$ (0.080 g, 0.114 mmol) and 2-(phenylethynyl)quinoxaline (0.032 g, 0.139 mmol) in toluene (10 mL) was stirred for 1 h. The volume was reduced to 5 mL in vacuo, and dry *n*-hexane (10 mL) was added. The dark red, air-sensitive product was collected by filtration, washed with dry *n*-hexane (5 mL), and dried in vacuo. Yield: 0.06 g (57%).

(15) Crystallographic data: **5**, $C_{27}H_{33}BN_6O_5S_2W{\cdot}0.5CH_2Cl_2$, fw 822.8 orthorhombic space group *Pbcn* with $a = 29.826(6)$ Å, $b = 13.291(4)$ Å, $c = 16.078(4)$ Å, $V = 6373(5)$ Å^3, and $D_c = 1.715$ g cm^{-3} for $Z = 8$. Analysis as for **3**, $R = 0.049$, $R_w = 0.042$ for 2677 data.

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