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Synthesis and Structure of $W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)$: A Tungsten(II) Sulfur Dioxide Complex That Spontaneously Extrudes Sulfur To Form the Tungsten(VI) Dioxo Complex $W(phen)(SPh)_2(O)_2$

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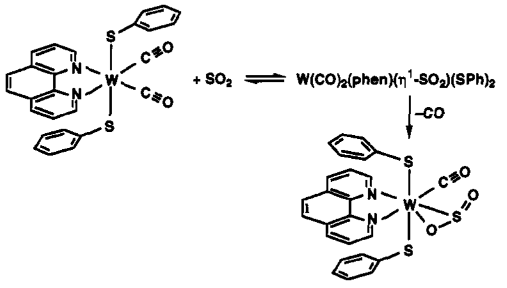
Sulfur dioxide can coordinate to transition metals in a variety of modes which include S-bound η^1-coplanar and η^1-pyramidal and η^2-S,O-bound geometries.[1-3] In addition to binding at the metal, coordination of SO_2 to ancillary ligands of metal complexes is well established.[4,5] The reactivity of SO_2 with transition metals is equally varied. Insertion into metal–carbon and metal–hydrogen bonds, oxygen atom transfer, disproportionation, and formation of sulfido and oxo complexes highlight the complexity of the reactivity of sulfur dioxide in the presence of metal complexes.[6] As part of our interest in the thermochemistry of group VI–sulfur complexes,[7] we recently reported synthesis and reversible ligand binding reactions of the 16-electron W(II) dithiolate complex $W(CO)_2(phen)(SPh)_2$. Over a 2-h period at room temperature, the red-brown dicarbonyl complex reacts with SO_2 in solution to give near quantitative conversion[8] to the dark red complex $W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)$. The crystal structure of this complex, the first example of SO_2 binding to W(II), is shown in Figure 1.

Reversible ligand binding and displacement reactions of the 16-electron complex, $W(CO)_2(phen)(SPh)_2$, proceed through 18-electron intermediates,[7] and we assume that binding of SO_2 occurs via a mechanism similar to that shown in eq 1. Attempts to detect the proposed intermediate complex $W(CO)_2(phen)(SPh)_2(\eta^1\text{-}SO_2)$ either in the forming reaction (eq 1) or by carbonylation of $W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)$ under pressure were unsuccessful. In addition, under 5 atm of ^{13}CO, no detectable isotopic exchange occurred after 20 h,[9] therefore discounting any establishment of a reversible equilibrium between η^1 and η^2 complexes as shown in eq 2. No evidence for coordination of SO_2 to the

$$\mathrm{W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)} \overset{^{13}\mathrm{CO}}{\Leftarrow X \Rightarrow} \mathrm{W(CO)(^{13}CO)(phen)(SPh)_2(\eta^1\text{-}SO_2)} \tag{2}$$

sulfur atom[5] of the coordinated thiolate was found, indicating preference for binding at the metal, but only in the η^2 form. These factors, as well as the rapid and quantitative[10] displacement of $P(OMe)_3$ by SO_2, shown in eq 3, indicate that SO_2 has a high bond dissociation energy in the W(II) complex.

$$\mathrm{W(CO)[P(OMe)_3](phen)(SPh)_2 + SO_2 \rightarrow W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2) + P(OMe)_3} \tag{3}$$



(1)

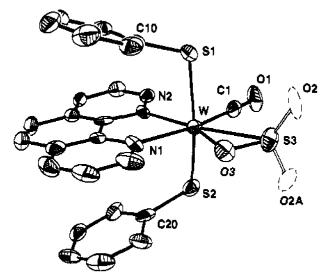


Figure 1. ORTEP representation with 50% probability ellipsoids (disordered atoms are drawn as dashed ellipsoids; hydrogen atoms are omitted for clarity) of $W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)$. Selected bond lengths and angles are given in footnote 11. Complete crystallographic data are available as supplementary material.

The crystal structure[11] of the SO_2 complex shown in Figure 1 is indicative of activation of the bond between the coordinated sulfur and oxygen (O_m) atoms. The S–O_m bond length of 1.588 (14) Å is long, relative to the other known η^2-SO_2 complexes (range = 1.468–1.550 Å),[12] indicating that the S–O_m bond is well on its way to oxidative addition. A higher effective oxidation

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(8) A solution of 1.5 g (0.0024 mol) of $W(CO)_2(phen)(SPh)_2$ in 100 mL of CH_2Cl_2 prepared under argon was reacted with excess SO_2 at atmospheric pressure. The reaction was quantitative after 2 h as determined spectroscopically. The product $W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)$ was recrystallized from CH_2Cl_2/heptane and yielded 0.60 g of a fine black crystalline solid (38% yield) that dissolves to give deep red solutions. Spectroscopic data: IR (Nujol mull) v_{CO} = 1913 cm^{-1}, ν(S–O) = 1135 cm^{-1}; NMR (CD_2Cl_2) 1,10-phenanthroline protons, 7.47 (d), 7.71 (d), 7.76 (m), 7.85 (m), 7.98 (d), 8.37 (d), 9.07 (d), 9.70 ppm (d); phenyl protons, 5.64 (d), 5.78 (d), 6.18 (m), 6.32 ppm (m).

(9) Continuous monitoring over a 20-h period of a solution of $W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)$ in THF under 104 psi of ^{13}CO showed gradual decay in the v_{CO} absorption of the starting material at 1920 cm^{-1} (due to formation of the oxo complex) and no concomitant formation of new bands assignable to $W(^{13}CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)$.

(10) Solutions of $W(CO)(phen)(SPh)_2[P(OMe)_3]$ in CH_2Cl_2 react quantitatively upon exposure to SO_2 at room temperature, forming $W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)$ as determined by IR and NMR analyses.

(11) Triclinic crystals of $W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)$ were obtained by slow cooling of a THF/heptane solution and crystallize in the $P\bar{1}$ space group: a = 9.974(8) Å, b = 10.679(12) Å, c = 13.417(12) Å, α = 73.59(8)°, β = 70.88(7)°, γ = 86.10(8)°, V = 1295 Å^3, Z = 2, d_{calc} = 1.812 g/cm^3; Enraf CAD4 diffractometer; 193 K; Mo Kα radiation (λ = 0.710 73 Å); scan method, 2θ–θ; data collection range, 4.0–50.0°; total number of data measured, 4828; number of independent reflections, 4543; number of observed reflections, 3344 [$F > (4.0)\sigma(F)$]. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to give final residuals of R = 0.0648 and R_w = 0.0791; GOF = 1.26. From final difference Fourier maps, residual electron densities of 4.03 and –4.41 e/Å^3 are present and are associated with the tungsten atom. The geometry around the W atom as shown in Figure 1 is distorted octahedral if the η^2-SO_2 group is considered to occupy one site on the metal. The oxygen atom on SO_2 not bound to the metal was disordered and found in two environments as shown, O(2) = 58%, O(2A) = 42%. Selected bond lengths (Å) and angles (deg): W–S(1) 2.380(5), W–S(2) 2.391(5), W–S(3) 2.486(4), W–C(1) 1.941(20), W–N(1) 2.190(13), W–N(2) 2.204(9), W–O(3) 1.985(9), S–O(3) 1.588(14), S–O(2) 1.444(21), S–O(2A) 1.416(27), C(1)–O(1) 1.176(25), S(1)–W–S(2) 164.4(1), S(1)–W–N(1) 91.8(3), S(1)–W–N(2) 83.8(3), S(1)–W–C(1) 86.3(5), S(2)–W–N(1) 91.7(3), S(2)–W–N(2) 82.5(3), S(2)–W–C(1) 86.6(5), S(3)–W–O(3) 39.7(4), W–O(3)–S(3) 87.4(5), O(A)–S(3)–O(3) 114.0(9), O(2A)–S(3)–O(3) 104.9(14). Complete crystallographic data are available as supplementary material.

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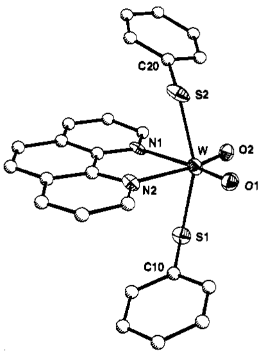
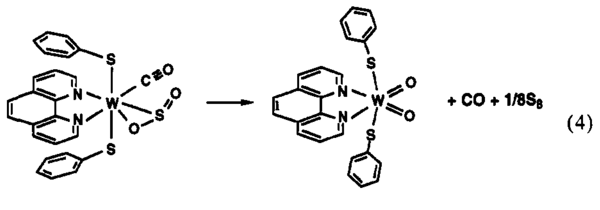


Figure 2. ORTEP representation with 50% probability ellipsoids (isotropically refined atoms are represented by shaded circles; hydrogen atoms are omitted for clarity) of W(phen)(SPh)$_2$(O)$_2$. Selected bond lengths and angles are given in footnote 20. Complete crystallographic data are available as supplementary material.

state for W in the SO$_2$ complex is confirmed by a shift of over 100 cm^{-1} for ν_{CO} for W(CO)(phen)(SPh)$_2$(η^2-SO$_2$) versus related complexes.[13]

Chemical evidence of S–O$_m$ bond activation in this complex is given by its spontaneous conversion[14] to the bright yellow W(VI) dithiolato dioxo complex shown in eq 4. Metal-induced elimination of S$_8$ from coordinated SO$_2$ has not been reported to date[15] and was unexpected by us on the basis of the stability of the W–η^2-SO$_2$ bond in this complex, and the favorable heat of formation of SO$_2$ itself.[16] The driving force for this reaction must be the formation of the strong tungsten oxo multiple bonds.[17]



(4)

Preliminary kinetic studies of reaction 4 indicate that the rate-determining step is first order in complex for 3–4 half-lives with $t_{1/2}$ = 18 h at 22 °C.[18] Two plausible first-order mechanisms would involve rate-determining steps of either (i) CO dissociation or (ii) S–O oxidative addition. Failure to observe a retarding influence on the reaction rate under a pressure of CO, or incorporation of ^{13}CO into the starting material at a rate comparable to that of formation of the oxo complex,[9] indicates that the rate-determining step is more likely to be S–O bond cleavage. Attempts to detect and characterize intermediates in this reaction are in progress.[19]

The structure[20] of W(phen)(SPh)$_2$(O)$_2$ is a distorted octahedral arrangement as shown in Figure 2. While several analogous structures have been reported, notably, Mo(Bpy)(X)$_2$(O)$_2$[21] and Mo(L-NS$_2$)(O)$_2$,[22] no strictly analogous dithiolato dioxo complex containing nitrogen donors in this geometry are known. In view of the interest in models for oxo transferases,[23] the preparation of this complex is novel since it is derived from low-valent starting materials.

Finally it is of interest to note that, in spite of the high thermodynamic stability of W(phen)(SPh)$_2$(O)$_2$ and a vacant site on the 16-electron complex W(CO)$_2$(phen)(SPh)$_2$, direct formation of the oxo complex at room temperature and 1 atm of O$_2$ did not occur after 5 days:[18]

$$\mathrm{W(CO)_2(phen)(SPh)_2 + O_2 \xrightarrow{X} W(phen)(SPh)_2(O)_2 + 2CO} \quad (5)$$

It is surprising to find that SO$_2$ is a kinetically more reactive oxidant than O$_2$ in this system. The complex W(CO)(phen)(SPh)$_2$(η^2-SO$_2$) and related complexes present a good opportunity to investigate the kinetics and thermodynamics of metal/sulfur interactions, and such work is in progress.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters, a summary of X-ray diffraction data, and completely labeled diagrams for W(CO)(phen)(SPh)$_2$(η^2-SO$_2$) and W(phen)(SPh)$_2$(O)$_2$ (17 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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(13) IR bands in the carbonyl regions as a function of L for the complexes W(CO)(L)(phen)(SPh)$_2$ in THF are PMe$_3$ = 1792, P(OMe)$_3$ = 1812, SO$_2$ = 1920 cm^{-1}.

(14) Solutions of W(CO)(phen)(SPh)$_2$(η^2-SO$_2$) in methylene chloride convert spontaneously to W(phen)(SPh)$_2$(O)$_2$ with a half-life of about 18 h at room temperature. CO, not COS or CO$_2$, is given off as a gas in the reaction as determined by FTIR spectroscopy. S$_8$ was determined by extraction with CS$_2$ with analysis of these solutions by GC/MS. Approximately 13% of the sulfur expected was produced as extractable S$_8$, and the balance is contained in precipitated nonextractable amorphous sulfur. FTIR spectroscopy was used to monitor the reaction by observing the decay of the ν_{CO} of starting material at 1926 cm^{-1} in CH$_2$Cl$_2$, and the emergence of the oxo bands of W(phen)(SPh)$_2$(O)$_2$ at 940 and 893 cm^{-1}. NMR data for W(phen)(SPh)$_2$(O)$_2$ in CD$_2$Cl$_2$: 1,10-phenanthroline resonances at 7.60 (m), 8.09 (s), 8.55 (d), and 9.14 ppm (d); phenyl resonances at 6.60 (m) and 6.86 ppm (m). The spectroscopic yield of the oxo complex is on the order of 70%. The low yield is attributed to the fact that the oxo complex itself undergoes slow decomposition in CH$_2$Cl$_2$.

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(20) Orthorhombic crystals of W(phen)(SPh)$_2$(O)$_2$ were obtained by slow cooling of a THF/heptane solution. The complex crystallizes in the *Pbca* space group: a = 8.569(3) Å, b = 16.706(6) Å, c = 30.019(10) Å, V = 4297 Å^3, Z = 8, d_{calc} = 1.902 g/cm^3; Enraf CAD4 diffractometer; 193 K; Mo Kα radiation (λ = 0.710 73 Å); scan method, ω; data collection range, 4.0–50.0°; total number of data measured, 5464; number of independent reflections, 3761; number of observed reflections, 2096 [$F > (4.0)\sigma(F)$]. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to give final residuals of R = 0.0520 and R_w = 0.0644; GOF = 1.48. From final difference Fourier maps, residual electron densities of 2.40 and –1.34 e/Å^3 are present and are associated with the tungsten atom. The geometry around the W atom as shown in Figure 2 is approximately octahedral with cis oxo and trans thiolato groups. Selected bond lengths (Å) and angles (deg): W–S(1) 2.440(5), W–S(2) 2.464(5), W–O(1) 1.724(11), W–O(2) 1.736(11), W–N(1) 2.294(13), W–N(2) 2.275(12), S(1)–W–S(2) 158.4(2), S(1)–W–N(1) 82.9(3), S(1)–W–N(2) 81.4(3), S(2)–W–N(1) 80.1(3), S(2)–W–N(2) 80.6(3), S(1)–W–O(1) 99.2(4), S(1)–W–O(2) 92.6(4), S(2)–W–O(1) 93.4(4), S(2)–W–O(2) 99.9(4), O(1)–W–O(2) 109.0(5). Complete crystallographic data are available as supplementary material.

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