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Redox Reaction of Bis(dithiolene)sulfidotungsten(IV) Complex with Elemental Sulfur: Functional Analogs of Polysulfide Reductase of Molybdoenzymes

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The reaction of bis(dithiolene)sulfidotungsten(IV) complex with elemental sulfur yielded bis(dithiolene)(tetrasulfido)tungsten(IV) complex. A labeling experiment using ^{34}S has indicated that the reaction is reversible and a sulfido(trisulfido)tungsten(VI) species is involved as an intermediate. The reaction represents a model reaction of polysulfide reductase of molybdoenzymes.

Redox reactions induced by transition-metal sulfides with elemental sulfur or sulfur–donor organic compounds are involved in sulfur metabolism and degradation in biological and industrial systems.[1–5] In biological systems, transition-metal sulfides also play important roles in electron transfer and small molecule activation events. In industry, they are central to hydrotreating catalysts for hydro-sulfurization, -nitrogenation, -oxygenation, and -metalation from petroleum fractions. Therefore, better understanding of the redox processes of transition-metal centers with sulfur has proven to be valuable in studies of enzymatic functions as well as in the design of next-generation catalysts.

Polysulfide reductase is a molybdoenzyme that participates in sulfur metabolism, catalyzing reduction of polysulfide $S_n{}^{2-}$ to $S_{(n-1)}{}^{2-}$ and H_2S (eq 1),[6–8] where the polysulfide reduction is coupled by disproportionation of $S_n{}^{2-}$ into $S_{(n-1)}/S^{2-}$ and two-electron reduction of $S_{(n-1)}$ to $S_{(n-1)}{}^{2-}$ at the molybdenum center.[6–8] In the polysulfide reductase, the presence of a mononuclear molybdenum reaction center coordinated by two pyranopterin dithiolenes has been suggested by DNA sequence comparison with other reductase molybdoenzymes, but the polysulfide reduction mechanism has yet to be elucidated.[9]

$$S_n{}^{2-} + 2H^+ + 2e^- \rightleftharpoons S_{(n-1)}{}^{2-} + H_2S \qquad (1)$$

In modeling studies of molybdenum enzyme reaction centers, few chemical analogs of polysulfide reductase have been reported. Sarkar et al. reported the conversion of polysulfide ion ($S_n{}^{2-}$) to sulfur ($S_{(n-1)}$) and H_2S by $[Mo^{IV}(C_6H_5S)_2(mnt)_2]^{2-}$ (mnt: 1,2-dicyanoethylene-1,2-dithiolate) in moist dichloromethane, although the mechanism of the polysulfide activation was not explored.[10,11] On the other hand, we have recently found that the disulfide-containing bis(dithiolene)oxotungsten(VI) complex of $(Et_4N)_2[W^{VI}O(S_2)(bdt)_2]$ (**$W^{VI}O(S_2)$bdt**, bdt: benzene-1,2-dithiolate) is easily generated from $(Et_4N)_2[W^{IV}O(L^{bdt})_2]$ (**W^{IV}Obdt**) and 2 equivalents of elemental sulfur (2/8 S_8).[12,13] This reaction stimulated us to examine a reaction of a sulfidotungsten(IV) complex possessing dithiolene ligands, L, with elemental sulfur to see whether $[W^{VI}S(S_n)L_2]^{2-}$ complexes could be generated and whether the redox reaction between S^{2-} (sulfide) and polysulfido ligands ($S_n{}^{2-}$) could occur on the metal center. Here we succeeded in developing such a system as an efficient functional model for polysulfide reductase.

The bis(dithiolene)sulfidotungsten(IV) complex of 1,2-diphenylethene-1,2-dithiolate (L^{Ph}), $(Et_4N)_2[W^{IV}S(L^{Ph})_2]$ (**$W^{IV}SL^{Ph}$**), was prepared as a starting compound by a literature procedure.[14] The reaction of **$W^{IV}SL^{Ph}$** with elemental sulfur (S_8) was investigated to see whether **$W^{VI}S(S_n)L^{Ph}$** could be generated under an Ar atmosphere.[15] Upon addition of a THF solution of elemental sulfur (S_8) into a CH_3CN solution of **$W^{IV}SL^{Ph}$** at room temperature, the known dinuclear complex, $(Et_4N)_2[\{W^V(L^{Ph})_2\}_2(\mu\text{-}S)_2]$,[14] was obtained. However, when the reaction was carried out at −40 °C, a different product was obtained as described below. Figure 1 shows UV–vis spectral changes for the titration of **$W^{IV}SL^{Ph}$** with S in CH_3CN at −40 °C. Three new broad absorption bands at 420, 550, and 613 nm increased in intensity upon treatment with S_8, resulting in a color change of the solution from pale-green to deep-purple. The spectral changes were completed when 3 equivalents of S (=3/8 S_8) were added to the CH_3CN solution of **$W^{IV}SL^{Ph}$** at −40 °C (Figure 1, inset). When the solution temperature was raised to room temperature, the known dinuclear complex formed.

The ESI-mass spectral change for the reaction of **$W^{IV}SL^{Ph}$** with 3 equivalents of S in CH_3CN at −40 °C is shown in Figure 2a → Figure 2b. **$W^{IV}SL^{Ph}$** exhibited a peak cluster at m/z 700 (Figure 2a) which corresponds to $[WSL^{Ph}]^-$ ion but not $[WSL^{Ph}]^{2-}$. Since **$W^{IV}SL^{Ph}$** displays a quasi-reversible

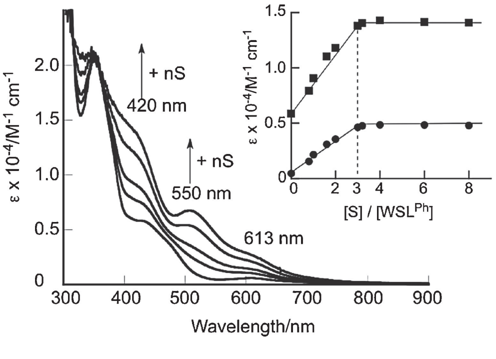


Figure 1. Titration of **$W^{IV}SL^{Ph}$** with S in CH_3CN at −40 °C (inset: plots of the molar extinction coefficients at 420 and 550 nm against molar ratio of $[S]/[WSL^{Ph}]$).

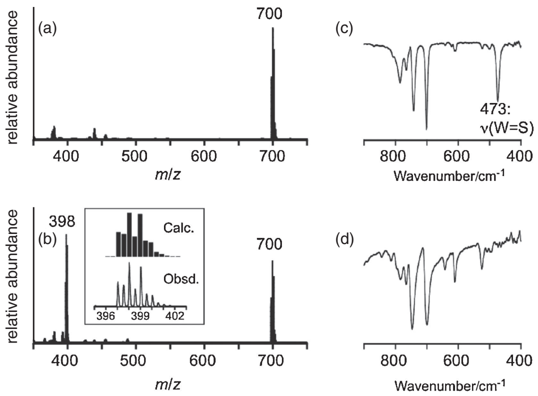


Figure 2. Negative-ion ESI-mass spectra of (a) $\mathbf{W^{IV}SL^{Ph}}$ (1.0 mM) in CH_3CN and (b) a reaction solution of $\mathbf{W^{IV}SL^{Ph}}$ + 3S in CH_3CN at −40 °C (inset: observed and calculated isotope patterns for $\{[WS(L^{Ph})_2]^{2-} + 3S\}^{2-}$; IR spectra of (c) $\mathbf{W^{IV}SL^{Ph}}$ (2.0 mM) in CH_3CN and (d) the microcrystalline black solid (KBr).

W(V)/W(IV) redox wave at −0.62 V vs. SCE in CH_3CN in the cyclic voltammetry measurement,[14] one-electron oxidation of $\mathbf{W^{IV}SL^{Ph}}$ might take place on the detector. In Figure 2b, a new peak cluster appears at *m/z* 398 together with *m/z* 700 due to $\{[W^{IV}S(L^{Ph})_2]^{2-} - e^-\}^-$. The peak cluster at *m/z* 398 appeared readily upon addition of elemental sulfur. The isotope distribution pattern at *m/z* 398 is consistent with the calculated isotope pattern of $[WS(L^{Ph})_2 + 3S]^{2-}$. The peak cluster at *m/z* 700 in Figure 2b is simulated as $\{[WS(L^{Ph})_2]^{2-} - e^-\}^-$ and may be a fragment of the generated complex.[15] A CH_3CN solution prepared from $\mathbf{W^{IV}SL^{Ph}}$ and 3 equivalents of S was ESR silent. A black microcrystalline solid was obtained by adding diethyl ether into a CH_3CN solution containing $\mathbf{W^{IV}SL^{Ph}}$ and 3 equivalents of S at −40 °C, which was stable for a few minutes. Data of the elemental analysis (C, H, N) of the isolated black powder are consistent with the calculated values for $\mathbf{W^{IV}SL^{Ph}}$ + 3S.[16] In the IR spectrum of $\mathbf{W^{IV}SL^{Ph}}$ (Figure 2c), there is a strong band at 473 cm^{-1} attributable to ν(W=S) stretch, whereas the black microcrystalline powder did not show such a strong band due to ν(W=S) stretch (Figure 2d). A CH_3CN solution of the powder at −40 °C exhibited the identical UV–vis spectrum with that of the in situ generated species. These results suggest that the black complex isolated at the low temperature is $(Et_4N)_2[W^{IV}(S_4)(L^{Ph})_2]$ ($\mathbf{W^{IV}(S_4)L^{Ph}}$) containing a bidentate S_4^{2-} ligand, rather than initially expected $(Et_4N)_2$-$[W^{VI}S(S_3)(L^{Ph})_2]$.[17]

The structure of $\mathbf{W^{IV}(S_4)L^{Ph}}$ was optimized by DFT calculation at (U)B3LYP level of theory (the calculation details are given in the Supporting Information[22]). Notably, a structure of singlet $[W^{VI}S(\eta^1\text{-}S_3)(L^{Ph})_2]^{2-}$ ($\mathbf{W^{VI}S(S3)L^{Ph}}$) was also optimized during the calculations as a singlet species, which was expected to be initially formed by the reaction of $\mathbf{W^{IV}SL^{Ph}}$ with 3 equivalents of S. The DFT structures of $\mathbf{W^{IV}(S_4)L^{Ph}}$ and $\mathbf{W^{VI}S(S_3)L^{Ph}}$ are shown in Figures 3a and 3b, respectively. Both of the tungsten centers adopt a distorted octahedral geometry. $\mathbf{W^{IV}(S_4)L^{Ph}}$ is lower in energy by 2.1 kcal mol^{-1} than $\mathbf{W^{VI}S(S_3)L^{Ph}}$, which is consistent with the fact that the isolated compound was $\mathbf{W^{IV}(S_4)L^{Ph}}$. The structure of $\mathbf{W^{IV}(S_4)L^{Ph}}$ has a twofold axis on the W atom and the dimensions of the $W(S_4)$ unit is similar to that of the $Cp_2W^{IV}(S_4)$.[18] In $\mathbf{W^{VI}S(S_3)L^{Ph}}$, one terminal sulfur atom of the S_3^{2-} ligand binds with the tungsten atom (2.400 Å) whereas another terminal sulfur atom located at distance of 5.529 Å from the tungsten atom, indicating η^1-coordination. The W=S bond distance is lengthened from that of $\mathbf{W^{IV}SL^{Ph}}$ (2.162(2) Å[14] → 2.201 Å).

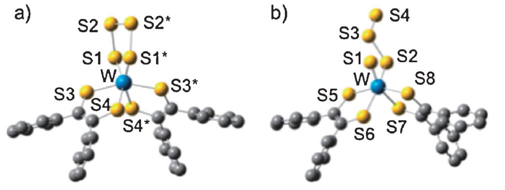


Figure 3. DFT optimized structures of a) $\mathbf{W^{IV}(S_4)L^{Ph}}$ and b) $\mathbf{W^{VI}S(S_3)L^{Ph}}$ calculated at the (U)B3LYP level of theory: W (blue), S (yellow), and C (gray).

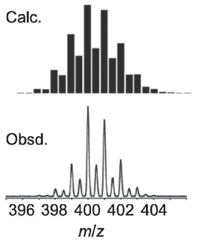
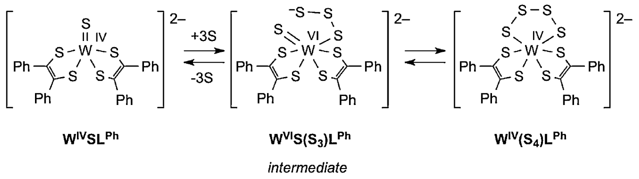


Figure 4. Negative-ion ESI-mass spectrum of a solution of $\mathbf{W^{IV}(S_4)L^{Ph}}$ mixed with 4 equivalent s of ^{34}S (=4/8 $^{34}S_8$): isopote pattern simulated as 1:4:6:4:1 mixture of $[W^{IV}(S_4)(L^{Ph})_2]^{2-} - {}^{32}S_4$, $[W^{IV}(S_4)(L^{Ph})_2]^{2-} - {}^{34}S^{32}S_3$, $[W^{IV}(S_4)(L^{Ph})_2]^{2-} - {}^{34}S_2{}^{32}S_2$, $[W^{IV}(S_4)(L^{Ph})_2]^{2-} - {}^{34}S_3{}^{32}S$, and $[W^{IV}(S_4)(L^{Ph})_2]^{2-} - {}^{34}S_4$ is indicated as Calcd.



Scheme 1. Proposed mechanism for the scrambling of sulfur atoms.

In order to get insights into the solution structure and formation mechanism of $\mathbf{W^{IV}(S_4)L^{Ph}}$, isotope labeling experiments were carried out using $^{34}S_8$. When 4 equivalent of ^{34}S (=4/8 $^{34}S_8$) was added to a CH_3CN solution of $\mathbf{W^{IV}(S_4)L^{Ph}}$ at −40 °C (4:4 stoichiometry of ^{32}S:^{34}S), the solution exhibited a peak cluster with a widely distributed isotope pattern around *m/z* 400 as shown in Figure 4.[20] The isotope distributed pattern was well simulated by assuming the existence of a mixture comprising $[W^{IV}(S_4)(L^{Ph})_2]^{2-} - {}^{32}S_4$, $[W^{IV}(S_4)(L^{Ph})_2]^{2-} - {}^{34}S^{32}S_3$, $[W^{IV}(S_4)(L^{Ph})_2]^{2-} - {}^{34}S_2{}^{32}S_2$, $[W^{IV}(S_4)(L^{Ph})_2]^{2-} - {}^{34}S_3{}^{32}S$, and $[W^{IV}(S_4)(L^{Ph})_2]^{2-} - {}^{34}S_4$ in a 1:4:6:4:1 ratio (Figure 4).[20] The result clearly indicates that $\mathbf{W^{IV}(S_4)L^{Ph}}$ exhibited a dynamic behavior accompanying a statistical scrambling of the sulfur atoms on the W center as indicated in Scheme 1. The tetrasulfide group (S_4^{2-}) in $\mathbf{W^{IV}(S_4)L^{Ph}}$ may be constructed from the three sulfur atoms added and original terminal sulfide group and exists in an equilibrium with $\mathbf{W^{VI}S(S_3)L^{Ph}}$ as an *intermediate* (Scheme 1).

Dissociation of the three sulfur atoms from $\mathbf{W^{VI}S(S_3)L^{Ph}}$ yields the original $\mathbf{W^{IV}SL^{Ph}}$. The repeated tetrasulfide group formation and dissociation of the sulfur atoms in the presence of ^{32}S and ^{34}S in a 4:4 ratio may provide $\mathbf{W^{IV}(^{32/34}S_4)L^{Ph}}$ with the statically scrambled sulfur atoms.[21] The conversion of the S_4^{2-} group to the S_3^{2-} and S^{2-} groups is coupled with the disproportionation of the S_4^{2-} group and reduction by the W^{IV} center, which mimic the reaction of polysulfide reductase.

In summary, this study demonstrated for the first time the redox reaction induced by the bis(dithiolene)sulfidotungsten complexes and elemental sulfur to yield a tetrasulfido group and monosulfido and trisulfido groups, providing an efficient model reaction of polysulfide reductase.

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16 $\mathbf{W^{IV}(S_4)L^{Ph}}$: A THF solution (0.2 mL) containing S_8 (3.0 mg, 0.012 mmol) was added to $\mathbf{W^{IV}SL^{Ph}}$[14] (30 mg, 0.031 mmol) in CH_3CN (2 mL) at −40 °C under an Ar atmosphere. The color of the solution was changed from pale green to red-purple by stirring for 10 min. Cold diethyl ether was gradually added to the solution using a dropping funnel. The resultant solution was kept for several days to yield a black microcrystalline powder, which was collected by filtration and dried under an Ar atmosphere. Anal. Calcd for $(Et_4N)_2[W(S_4)(L^{Ph})_2]$ ($Mr = 1057.32$): C, 49.98; H, 5.72; N, 2.65%, Found: C, 49.72; H, 5.74; N, 2.63%.

17 A monomeric tungsten(IV) structure with a bidentate S_4^{2-} ligand is found in $Cp_2W(S_4)$ (Cp: cyclopentadienyl)[18] and a similar sulfur donor ligand based internal redox is involved in $Tp^*W^{IV}O(pyS_2\text{-}N,S)$ and $Tp^*W^{VI}OS(pyS\text{-}S)$ (Tp*: hydrotris(3,5-dimethylpyrazol-1-yl)borate, pyS_2: pyridine-2-disulfanyl, pyS: pyridine-2-thiolate).[19]

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20 The peak cluster around m/z 700 in Figure 3b also changed to that around m/z 702, which is simulated as a mixture of $\mathbf{W^{IV}(^{32}S)L^{Ph}}$ and $\mathbf{W^{IV}(^{34}S)L^{Ph}}$ in a 1:1 ratio.

21 It seems that this scrambling completed within ca. 10 s. We were not able to observe any nonscrambled species such as $\mathbf{W^{32}S^{34}S_3}$ as main species.

22 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.