Electronic and Steric Effect of Bulky Triphenylsilyl Substituent in the Monooxobenzenedithiolatomolybdenum(V) Complex and the Tungsten Analog as Models of Molybdenum and Tungsten Oxidoreductases

Hiroyuki Oku, Norikazu Ueyama, and Akira Nakamura*†
Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560
†*Institute for Molecular Science, Okazaki, Aichi 444*

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Monooxotungsten(V) and Monooxomolybdenum(V) complexes with bulky dithiolato ligands, $(NEt_4)[M^VO(Ph_3Si\text{-}bdt)_2]$ (M = W (**1**) and Mo(**2**), Ph_3Si-bdt = 3-triphenylsilyl-1,2-benzenedithiolate) were synthesized as models of tungsten and molybdenum oxidoreductases.

Very recently, a crystallographic report by Rees et al. has revealed the two dithiolene coordination to tungsten ion in aldehyde ferredoxin oxidoreductase.[1] All of the tungsten and molybdenum oxidoreductases probably contain *one* or *two* pterin substituted tungsten (or molybdenum)-1,2-ene-dithiolate structure as an active site cofactor.[2] Some model complexes, $(PPh_4)[W^VO(bdt)_2]$ (**3**)[3] and $(NEt_4)[Mo^VO(bdt)_2]$ (**4**)[3,4] (bdt = 1,2-benzenedithiolate) have *two* dithiolene like ligands, bdt, which have been used to reveal the electronic properties of the tungsten and molybdenum cofactor. To evaluate the probable hydrophobic environment of the enzyme active sites, we have employed the aromatic bulky benzenedithiolate, 3-triphenylsilyl-1,2-benzenedithiolate (= Ph_3Si-bdt)[5] as a model ligand. Here, we describe the electronic and the steric effect of the aromatic bulky benzenedithiolato ligand in $(M^VO)^{3+}$ complexes and the structure of an air oxidized derivative, $(NEt_4)_2[\{Mo^{VI}O_2(Ph_3Si\text{-}bdt)\}_2(\mu\text{-}O)]\cdot 2DMF$ (**5**).

The complex, $(NEt_4)[M^VO(Ph_3Si\text{-}bdt)_2]$ (M = W (**1**)[6] and Mo(**2**)[7]) were prepared by the reaction of $(NEt_4)[M^VO(SPh)_4]$ (M = W (**6**) and Mo(**7**))[8] with the bulky dithiol, $Ph_3Si\text{-}bdtH_2$, (1:2) in DME (= 1,2-dimethoxyethane) suspension.

Some molybdenum oxidoreductases react with O_2 and H_2O when the enzymes catalyze the oxidation of substrates.[9] As a model reaction, the DMF (= *N,N*-dimethylformamide) solution of Mo(V) complex, **2**, (1 mmol dm $^{-3}$) was exposed to air. Within 5 min, the blue solution was changed to pale yellow gradually. The pale yellow color of the solution suggests the formation of polyoxomolybdate, $[Mo^{VI}_xO_y]^{n-}$.[10] To investigate the process of this oxidation reaction, we have examined the reaction of **2** with a trace amount of air (O_2 and H_2O).[11] The pale yellow crystal obtained in small yield was characterized by the X-ray crystallography. Figure 1 shows the anion part of the oxidized product, $(NEt_4)_2[\{Mo^{VI}O_2(Ph_3Si\text{-}bdt)\}_2(\mu\text{-}O)]\cdot 2DMF$ (**5**). The crystal structure of **3** contains an inversion center on the bridged oxygen atom (O11). The Mo(VI) ion has trigonal bipyramidal coordination with *cis*-di(terminal oxo), one bridged oxo, and one Ph_3Si-bdt ligand. Shibahara et al. and Bürger et al.[12] have reported similar binuclear complexes with non-thiolate ligands, $[\{Mo^{VI}O_2(dmso)_2(NCS)\}_2(\mu\text{-}O)]$ and $[\{Mo^{VI}O_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})\}_2(\mu\text{-}O)]$, respectively. The probable air oxidation process of **2** is described below.

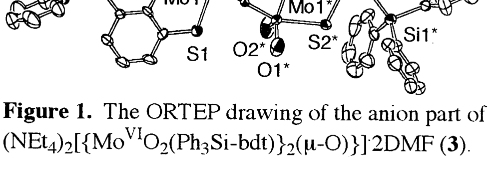

Figure 1. The ORTEP drawing of the anion part of $(NEt_4)_2[\{Mo^{VI}O_2(Ph_3Si\text{-}bdt)\}_2(\mu\text{-}O)\}]\cdot 2DMF$ (**3**).

$$2[Mo^VO(Ph_3Si\text{-}bdt)_2]^- + 2H_2O + 0.5O_2 \text{ ---->}$$

$$[\{Mo^{VI}O_2(Ph_3Si\text{-}bdt)\}_2(\mu\text{-}O)]^{2-} \ (+\ 2Ph_3Si\text{-}bdtH_2)$$

$$[\{Mo^{VI}O_2(Ph_3Si\text{-}bdt)\}_2(\mu\text{-}O)]^{2-} + \text{excess } O_2 \text{ ----> ---->} \text{ polyoxomolybdate}$$

Previously we reported the catalytic air oxidation of benzoin with the monooxomolybdenum(V) complex, **7**.[13] The complex, **5**, which has two thiolato ligands on each molybdenum atom, is a probable active species in the catalytic cycle. The reactivity of the binuclear complex, such as **5**, will be reported elsewhere. Compared with the two-bdt complex, $[Mo^{VI}O_2(bdt)_2]^{2-}$,[3,5,14] one-bdt coordination in **5** has an advantage in the access of the substrate to dioxomolybdenum(VI) center due to the coordinative unsaturation in **5**. Actually, some molybdenum oxidoreductases are expected to have monodithiolene coordination.[1]

Table 1 summarizes the UV/vis absorption maxima, the redox potentials, the Raman (IR) bands of $\nu(M^V{=}O)$ and $\nu(M^V\text{-}S)$. The substituent effect of Ph_3Si- group was observed in the Raman (IR) spectra and the electrochemical behaviors. The $\nu(M^V\text{-}S)$ bands shift to higher frequency (Δ(**1**-**3**) = 2 cm^{-1} and Δ(**2**-**4**) = 9 cm^{-1}), whilst the $\nu(M^V{=}O)$ bands shift to lower frequency (Δ(**1**-**3**) = -10 cm^{-1} and Δ(**2**-**4**) = -3 cm^{-1}). In addition,

Table 1. Raman (IR) bands of $\nu(M{=}O)$ and $\nu(M\text{-}S)$, UV/vis absorption maxima and redox potentials of benzenedithiolato complexes, **1**, **2**, **3** and **4**

	Raman (IR) band KBr disk		UV/vis absoprtion maxima in DMF	Redox potential in DMF
	$\nu(M{=}O)$ (cm^{-1})	$\nu(M\text{-}S)$ (cm^{-1})	λ_{max} (ε) (nm (mol dm^{-3} cm^{-1})	$E_{1/2}$ (V vs SCE)
1	944(943)	371	618 (3100) 462 (1200) 353 (sh, 3600)	-0.68
2	937(930)	365	618 (2400) 475 (840) 385 (1700) 322 (8000)	-0.38
3	954(953)	369	731 (7700) 515 (1800)	-0.64
4	940(934)	356	729 (4200) 550 (sh, 690)	-0.37

Table 2. X band ESR parameters for benzenedithiolato complexes, **1**, **2**, **3** and **4**, ([complex] = 1 mmol dm^{-3})

	1[a]	**2**[b]	**3**[c]	**4**[d]
g_{iso}	1.961	1.994	1.960	1.994
A_{iso} (mT)	5.3	3.06	5.8	3.09
g_1	2.050	2.023	2.044	2.023
g_2	1.913	1.986	1.911	1.986
g_3	1.932	1.977	1.931	1.997
A_1 (mT)	5.63	4.89	8.2	5.00
A_2 (mT)	3.9		4.16	
A_3 (mT)	4.0		4.4	

[a] At 285 K (for g_{iso} and A_{iso}) and at 115 K in DMF-CH_3CN (2:1) glass. [b] At 288 K (for g_{iso} and A_{iso}) and at 77 K in DMF-CH_3CN (1:1) glass. [c] At 285 K (for g_{iso} and A_{iso}) and at 115 K in DMF-CH_3CN (2:1) glass. [d] At 288 K (for g_{iso} and A_{iso}) and at 77 K in DMF-CH_3CN (1:1) glass.

the redox potentials were shifted to negative directions (Δ(**1**-**3**) = -0.04 V, and Δ(**2**-**4**) = -0.01 V (vs SCE). These spectroscopic changes are consistent with the increase of electron donation from the dithiolato to metal dπ orbitals. As a result of competition for a metal dπ orbital, stronger M-S π-bonding (higher frequency shift of $\nu(M^V\text{-}S)$) weakens M=O π-bonding (lower frequency shift of $\nu(M^V{=}O)$), in this case. The electron donative effect from sulfur atoms is caused by the interaction between phenyl (*Ph*$_3$Si-) pπ and sulfur pπ orbitals. The observed π-donation from phenyl (*Ph*$_3$Si-) pπ orbitals is consistent with the case of a Mo(IV) analog, $(NEt_4)_2[Mo^{IV}O(Ph_3Si\text{-}bdt)_2]$, as reported before.[5]

ESR parameters of **1** and **3** also reveal the electronic effect of Ph_3Si- group. Table 2 lists the ESR parameters. Compared with the unsubstituted complexes (**2** and **4**), Ph_3Si- substituted complexes (**1** and **3**) show smaller A values (ΔA_{iso}(**1**-**3**) = 0.6 mT, ΔA_{iso}(**2**-**4**) = 0.03 mT). The smaller A values are explained by the electron withdrawing from d_{xy} orbital of the central metal atom to the Ph_3Si- substituent through the benzenedithiolate.

The spectra of the Ph_3Si-bdt complexes, **1** and **3**, have indicated the enhanced π interaction between phenyl (*Ph*$_3$Si-) pπ and sulfur p orbitals. Two interaction mechanisms are probable. One is the direct overlap between phenyl pπ and sulfur pπ orbitals. The other is the through-bond interaction via the Si atoms and the bdt ligands. The direct π-π interaction is possible, because two of the three phenyl rings on the Ph_3Si- group can be located near the sulfur atoms (within 3.5 Å). Similar interactions have been observed in the model system of iron-sulfur proteins where π interaction (a sulfur atom to a phenyl ring) is thought to provide an electron transfer pathway.[15] Such phenyl-sulfur pπ interactions will be revealed in molybdenum enzymes in near future.

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6 The DME (70 cm^{-3}) suspension of **6** (1.75 g, 2.29 mmol) was added $Ph_3Si\text{-}bdtH_2$ (2.06 g, 5.41 mmol). The mixture was stirred for 72 h, the gray powder formed was collected and recrystallized from DMF-diethyl ether. Silver gray microcrystals. Yield 0.43 g (17%). Found: C, 57.69; H, 5.09; N, 1.62%. Calcd for $C_{56}H_{56}ONWS_4$: C, 59.66; H, 5.01; N, 1.24%. FAB-MS (negative), m/e 997 ([M+1]$^-$).

7 Similar to the synthesis of **1**, **2** was prepared from **7** (121 mg, 0.302 mmol) and $Ph_3Si\text{-}bdtH_2$ (102 mg, 0.151 mmol). Silver gray microcrystals were obtained. Yield 100 mg (32%). Found: C, 61.94; H, 5.41; N, 1.44%. Calcd for $C_{56}H_{56}ONMoS_4$: C, 64.71; H, 5.43; N, 1.35%. FAB-MS (negative), m/e 910 ([M]$^-$), 926 ([M+16]$^-$).

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11 DMF solution (1 cm^3) of **2** (5 mg, 5 × 10^{-3} mmol) was prepared under Ar atmosphere. To this solution, diethyl ether (5 cm^{-3}) vapor was diffused slowly during 7 days to precipitate crystals. During the crystal formation, a small amount of air was introduced through a small opening of the glass plug. Finally, almost all of **2** was recovered and 3 pieces of yellow plates (**5**) were formed. Yield 0.05 mg (0.05%). Crystal and refinement data for **5**: $P\bar{1}$ (triclinic), a = 9.73(1), b = 21.47(4), c = 9.12(2) Å, α =100.8(2), β = 109.8(1), γ = 88.0(1) °, V= 1759(5) Å^3, Z = 2, d_{calc} = 1.393 gcm^{-3}; unique reflections = 10381, used reflections = 3772 ($I_o > 3\sigma(I)$), R = 0.083, R_w = 0.071.

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