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Trans Influence of Oxo and Dithiolene Coordination in Oxidized Models of Molybdenum Oxidoreductase: Synthesis, Structures, and Properties of $Q_2[Mo^{VI}O_2(1,2\text{-benzenedithiolato})_2]$ ($Q = NEt_4$, PPh_4) and Related Complexes

Norikazu Ueyama, Hiroyuki Oku, Mitsuru Kondo, Taka-aki Okamura, Naoto Yoshinaga, and Akira Nakamura*

Department of Macromolecular Science, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan

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Three *cis*-dioxomolybdenum(VI) complexes with dithiolene-like benzenedithiolate ligands, $Q_2[Mo^{VI}O_2(1,2\text{-benzenedithiolato})_2]$ ($Q = NEt_4$ (**1a**), PPh_4 (**1b**)), $[Mo^{VI}O_2(3\text{-triphenylsilyl-1,2-benzenedithiolato})_2]^{2-}$ (**2**), and $[Mo^{VI}O_2(4\text{-methyl-1,2-benzenedithiolato})_2]^{2-}$ (**3**), were synthesized as models of oxidized sulfite oxidase and compared with the structure of $(PPh_4)_2[Mo^{VI}O_2(S_2C_2(CN)_2)_2]\cdot 2MeOH$ (**4**). The crystal data for **1b**, chemical formula $C_{60}H_{48}O_2P_2S_4Mo$, are $a = 13.938(6)$ Å, $b = 16.65(1)$ Å, $c = 22.645(5)$ Å, $\beta = 103.81(2)°$, $V = 5104(5)$ Å^3, $Z = 4$, and space group $P2_1/c$ and the data for **4**·2MeOH, chemical formula $C_{58}H_{48}O_2P_2S_4Mo$, are $a = 20.273(3)$ Å, $b = 15.632(5)$ Å, $c = 17.685(4)$ Å, $V = 5604(3)$ Å^3, $Z = 4$, and space group *Pbcn*. **1b** and **4** have a slightly distorted octahedral structure with two long Mo−S bonds (2.588(3) Å and 2.608(3) Å for **1b** and 2.635(2) Å for **4**) *trans* to each of the Mo═O groups and with two short Mo−S bonds (2.417(3) Å and 2.434(3) Å for **1b** and 2.440(2) for **4**) *cis* to them. The short S−C bond distances of the thiolate *trans* to the Mo═O groups in **4** suggest the presence of partial double bonding at the S−C (thioketone-like) bond, which contributes to the stabilization of the dioxomolybdenum(VI) species by weakening π-bonding in the Mo−S bonds *trans* to the Mo═O groups. The electron-donating or -withdrawing substituents, *e.g.* $4\text{-}CH_3$ or $3\text{-}SiPh_3$, on the 1,2-benzenedithiolate Mo(VI) complexes accelerate or retard its oxo-transfer reaction, respectively. The formation of any binuclear Mo(V) complex does not occur in the reaction between $[Mo^{VI}O_2(1,2\text{-benzenedithiolato})_2]^{2-}$ and $[Mo^{IV}O(1,2\text{-benzenedithiolato})_2]^{2-}$ when the *cis*-dioxomolybdenum(VI) complex is reduced by triphenylphosphine or benzoin.

Introduction

Recently, many studies have demonstrated the presence of a wide variety of dithiolene derivatives connecting pterin and phosphate groups as a molybdenum cofacter in xanthine oxidase,[1] sulfite oxidase,[1] trimethylamine *N*-oxide reductase[2] , dimethyl sulfoxide reductase[3] and various molybdenum oxidoreductase.[4−7] The X-ray absorption analysis of sulfite oxidase has shown the local structure of the active site with $(Mo^{VI}O_2)^{2+}$ surrounded by at least three sulfur ligands in the oxidized state.[8] If a dithiolene ligand coordinates to $(Mo^{VI}O_2)^{2+}$ in a regular octahedral geometry, one of the two sulfur ligands locates at the *trans* position to the Mo═O group. The dithiolene chelate structure in the molybdenum cofactor of dimethyl sulfoxide reductase has been demonstrated by the detection of an enhanced C═C and Mo−S Raman bands.[9] However, in the case of the active site of sulfite oxidase, the observation of a long Mo−X distance by the EXAFS analysis has led to a possibility that a methionine thioether ligand coordinates to the *trans* position of Mo═O.[10]

Numerous model complexes for the oxidized state of these molybdenum enzymes have been synthesized using a (thiolato, N), (thiolato, thioketone), or (thiolato, thioether) ligand, *e.g.* $[Mo^{VI}O_2(S,N\text{-cys-OR})_2]$ (R = Me, Et),[11] $Mo^{VI}O_2(S_2CNEt_2)_2$,[12] $[Mo^{VI}O_2(L)_2]$ (L = *N,N′*-dimethyl-*N,N′*-bis(2-mercaptophenyl)ethylenediamine),[13] $Mo^{VI}O_2(L\text{-}NS_2)_2$ ($L\text{-}NS_2$ = 2,6-bis(2,2-diphenyl-2-thioethyl)pyridinato), and $Mo^{VI}O_2(dttd)$ (dttd = 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane),[14] Many model reactions in the presence of dioxomolybdenum(VI) and monooxomolybdenum(IV) complexes have also been examined for the redox reaction of nitrate,[15] triphenylphosphine,[16−19] benzoin,[20,21] amine

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N-oxide,[22,23] and dimethyl sulfoxide.[24] Benzoin is one of the suitable biologically relevant substrates for the oxidation of the alcoholic C−H group. In fact, a molybdoenzyme isolated from *Proteus vulgaris* and *Proteus mirabilis* catalyzes a benzoin-related substrate, $\mathrm{RCH(OH)COO^-}$, to $\mathrm{RCOCOO^-}$.[25] Biomimetic oxidation of benzoin was studied in the presence of $[\mathrm{Mo^{VI}O_2(S,N\text{-}cys\text{-}OR)_2}]$ (R = Me, Et) and $\mathrm{Mo^{VI}O_2(S_2CNEt_2)_2}$.[20]

However, few reports on the synthesis of dioxomolybdenum(VI) or dioxotungsten(VI) complex having a dithiolene skeleton have been found.[23,26−28] This type of complex was thought to be unstable due to the *trans* influence by a Mo=O group toward one of the thiolate ligands.[29,30]

Boyde *et al*. have reported the synthesis and crystal structure of a reduced model complex, $[\mathrm{Mo^{IV}O(bdt)_2}]^{2-}$ (bdt = 1,2-benzenedithiolato) which has two dithiolene skeltons.[31] On the other hand, a single dithiolene complex, $\mathrm{Mo^{IV}O(bdt)}$[hydrotris(3,5-dimethyl-1-pyrazolyl)borate], has been reported.[32] We have studied the catalytic activity of the above $[\mathrm{Mo^{IV}O(bdt)_2}]^{2-}$ complex for the oxidation of benzoin by air or pyridine *N*-oxide. These Mo(IV) complexes are readily oxidized by trimethylamine *N*-oxide to give dioxomolybdenum(VI) complexes.[23,28] During the catalytic cycle the presence of a *cis*-dioxo species, $[\mathrm{Mo^{VI}O_2(bdt)_2}]^{2-}$, was suggested by spectroscopic methods.[26,33] This paper presents the synthesis, crystal structure and properties of $\mathrm{(NEt_4)_2[Mo^{VI}O_2(bdt)_2]}$ (**1a**) and the related complexes which were synthesized from the corresponding monooxomolybdenum(IV) complexes by an oxo-transfer reaction with trimethylamine *N*-oxide. Furthermore, the crystal structure of $\mathrm{(PPh_4)_2[Mo^{VI}O_2(S_2C_2(CN)_2)_2]\cdot 2CH_3OH}$ (**4**) containing an electron-withdrawing group has also been determined in order to study the electronic effect of the electron-withrawing group on dithiolene coordination. Recently, the synthesis and properties of $[\mathrm{Mo^{VI}O_2(S_2C_2(CN)_2)_2}]^{2-}$ have been independently reported by Sarkar *et al*.[34,35]

Experimental Section

All procedures were carried out under an argon atmosphere. *N*,*N*-Dimethylformamide (DMF), 1,2-dimethoxyethane (DME), acetonitrile, and acetonitrile-d_3 were purified by distillation before use. Benzoin and triphenylphosphine were recrystallized from ethanol and hexane, respectively.

Materials. 1,2-Benzenedithiol was prepared by the reported procedure.[36] Toluenedithiol was used as commercial grade. $\mathrm{(NEt_4)[Mo^{V}O(bdt)_2]}$ was prepared by the same method reported by Boyde *et al*.[31] $[\mathrm{Mo^{VI}O_2(S_2CNEt_2)_2}]$,[12] $[\mathrm{Mo^{IV}O(S_2CNEt_2)_2}]$,[17,37] and $[\mathrm{Mo^{VI}O_2(cys\text{-}OMe)_2}]$[38] were prepared by the reported methods.

$\mathbf{(NEt_4)_2[Mo^{VI}O_2(bdt)_2]}$ (1a). $\mathrm{(NEt_4)_2[Mo^{IV}O(bdt)_2]}$ was synthesized by a modified literature method.[31] To a DMF solution (40 mL) of $\mathrm{(NEt_4)_2[Mo^{IV}O(bdt)_2]}$ (207 mg, 0.32 mmol) was added a DMF solution (1.7 mL) of trimethylamine *N*-oxide (24 mg, 0.32 mmol) carefully at room temperature. The solution turned reddish-brown. Addition of diethyl ether (80 mL) to the solution resulted in formation of reddish-brown crystals. Yield: 78%. Mp: 130 °C dec. ^{1}H NMR (acetonitrile-d_3); 6.51 (br m, 4H), 7.45 (br s, 4H). Anal. Calcd for $\mathrm{C_{28}H_{48}O_2N_2S_4Mo}$; C, 50.28; H, 7.23 ; N, 4.78. Found; C, 50.38; H, 7.46; N, 4.35.

$\mathbf{(PPh_4)_2[Mo^{VI}O_2(bdt)_2]}$ (1b). The complex was obtained as reddish-brown crystals by the oxidation of $\mathrm{(PPh_4)_2[Mo^{IV}O(bdt)_2]}$ as described for the synthesis of **1a**.

$\mathbf{(NEt_4)_2[Mo^{VI}O_2(Ph_3Si\text{-}bdt)_2]}$ ($\mathbf{Ph_3Si}$-bdt = 3-(triphenylsilyl)-1,2-benzenedithiolato) (2). $\mathrm{(NEt_4)_2[Mo^{IV}O(Ph_3Si\text{-}bdt)_2]}$ was synthesized by a modified procedure reported previously.[23] To a DMF solution (10 mL) of $\mathrm{(NEt_4)_2[Mo^{IV}O(Ph_3Si\text{-}bdt)_2]}$ (181 mg, 0.16 mmol) was added a DMF solution (1 mL) of trimethylamine *N*-oxide (17 mg, 0.23 mmol) at room temperature. The solution became reddish-brown from pale-yellow. Reddish-brown microcrystals were obtained on addition of 80 mL of diethyl ether to the DMF solution. Yield: 70%. Mp: 170 °C dec. ^{1}H NMR (acetonitrile-d_3): d 7.52 (dd, 12H), 7.24 (tt, 6H), 7.20 (dd, 2H), 7.14 (t, 12H), 6.51 (t, 2H), 6.43 (dd, 2H). Anal. Calcd for $\mathrm{C_{64}H_{76}N_2O_2Si_2S_4Mo}$: C, 64.83; H, 6.46; N, 2.36. Found: C, 63.13; H, 6.58; N, 2.56. FAB MS(anion): *m/e*, 927.0 ($[\mathrm{Mo^{VI}O_2(Ph_3Si\text{-}bdt)_2}]^{2-}\cdot\mathrm{H^+}$).

$\mathbf{(NEt_4)_2[Mo^{VI}O_2(tdt)_2]}$ (tdt = 3,4-toluene-1,2-dithiolato) (3). The $\mathrm{(NEt_4)_2[Mo^{IV}O(tdt)_2]}$ was also prepared by a similar method reported previously.[23] $\mathrm{(NEt_4)_2[Mo^{VI}O_2(tdt)_2]}$ was synthesized by the careful oxidation of $\mathrm{(NEt_4)_2[Mo^{IV}O(tdt)_2]}$ (63.3 mg, 0.093 mmol) with a DMF solution (1.4 mL) of trimethylamine N-oxide (0.14 mmol). Addition of DME (20 mL) gave dark red microcrystals which were washed with DME (5 mL) and diethyl ether (5 mL) successively and dried under reduced pressure. Yield: 57%. Mp: 122 °C dec. ^{1}H NMR (acetonitrile-d_3): d 7.35 (dd, J = 7.51, 0.36 Hz, 2H), 7.33 (dd, J = 1.83, 0.36 Hz, 2H), 6.54 (dq, J = 7.51, 1.83, 0.73 Hz, 2H), 2.07 (d, J = 0.74 Hz, 6H). Anal. Calcd for $\mathrm{C_{30}H_{52}N_2O_2MoS_4}$: C,51.70; H, 7.52; N, 4.02. Found: C,51.30; H, 7.52; N, 4.03.

$\mathbf{(PPh_4)_2[Mo^{VI}O_2(S_2C_2(CN)_2)_2]\cdot 2CH_3OH}$ (4). The complex was synthesized by the following procedure, which is different from that reported by Sarkar and Das.[34] The stoichiometric oxidation of $\mathrm{(PPh_4)_2[Mo^{IV}O(S_2C_2(CN)_2)_2]\cdot EtCN}$ [28] (254 mg, 0.23 mmol) by a DMF/methanol solution of trimethylamine-N-oxide (16.0 mg, 0.21 mmol) gave reddish-brown crystals (48 mg, 19% yield).

Reaction of 1, 2, or 3 with Triphenylphosphine and Benzoin. A stoichiometric reaction of dioxomolybdenum(VI) complexes (1 mM) with benzoin (1 mM) in 5 mL of DMF was performed under an argon atmosphere at 29 °C. The reaction was monitored by the detection of benzoin and benzil using HPLC. ^{1}H NMR spectroscopy was also carried out on the reaction of a $\mathrm{(NEt_4)_2[Mo^{VI}O_2(bdt)_2]}$ solution (4 mM) with a benzoin solution (4 mM) in acetonitrile-d_3 (0.4 mL) at 30 °C. The observed rate constant was determined by the HPLC and ^{1}H NMR measurements. All errors are given as random errors with 99% a level (2.5σ) in parentheses after the observed rate constant.

In the case of the stoichiometric reaction between the dioxomolybdenum(VI) complex and triphenylphosphine, the reaction was monitored by ^{1}H NMR spectroscopy. To an acetonitrile-d_3 solution of triphenylphosphine (6.7 mg, 25.5 mM) was added $\mathrm{(NEt_4)_2[Mo^{VI}O_2(bdt)_2]}$ (3.1 mg, 4.6 mmol) at 29 °C. After the prescribed time, the yield of triphenylphosphine oxide was determined by the ratio of $\mathrm{OPPh_3}$ and $\mathrm{PPh_3}$ ^{1}H signals.

Physical Measurements. The absorption spectra were recorded on a Jasco U-best 30 using a 1 mm cell under an argon atmosphere. The ϵ value was given in $\mathrm{M^{-1}\ cm^{-1}}$. Raman and IR spectra (KBr disk) were taken on a Jasco R-800 spectrophotometer with 514.5- and 632.8-

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Table 1. Crystal, Data Collection and Refinement Data for $(PPh_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1b**) and $(PPh_4)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]\cdot 2CH_3OH$ (**4**·$2CH_3OH$)

	1b	**4**·$2CH_3OH$
chem formula	$C_{60}H_{48}O_2P_2S_4Mo$	$C_{58}H_{48}N_4O_4S_4P_2Mo$
fw	1087.17	1151.17
cryst shape	needle	needle
color	red brown	red brown
cryst syst	monoclinic	orthorhombic
lattice param		
a, Å	13.938(6)	20.273(3)
b, Å	16.65(1)	15.632(5)
c, Å	22.645(5)	17.685(4)
β, deg	103.81(2	
V, Å^3	5104(5)	5604(3)
space group	$P2_1/c$	$Pbcn$
Z	4	4
D_{calc}, g cm^{-3}	1.415	1.364
$F(000)$	2240	2368
radiation	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
μ(Mo Kα), cm^{-1}	5.12	4.89
scan type	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{max}$, deg	60.1	60.0
octants	$+h, +k, \pm l$ tot. 13 515 unique 12 943	$+h, +k, +l$ tot. 8914
no. of observs	4655 ($I > 2\sigma(I)$)	3323 ($I > 3\sigma(I)$)
no. of variables	620	330
residuals R, R_w values[a]	0.069, 0.069	0.082, 0.075

[a] $R = \sum \mid |F_o| - |F_c| \mid / \sum \mid F_o|$. $Rw = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

nm excitation lines and on a Jasco DS-402G spectrophotometer, respectively. ^{1}H NMR spectra were measured on a Jeol GSX-400 spectrometer. The cyclic voltammograms were measured on a Yanaco P-1100 with a three-electrode system consisting of a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel compartment. A DMF solution (1 mM) of the dioxomolybdenum(VI), **1**, **2**, or **3**, complex was used for the measurements which were carried out with 100 mV/s scan rate at room temperature. A solution of tetra-*n*-butylammonium perchlorate (0.1 M) was employed as a supporting electrolyte.

Crystallographic Data Collection and Structure Determination. A reddish-brown crystal of $(PPh_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1b**) or $(PPh_4)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]\cdot 2MeOH$ (**4**·2MeOH) having approximate dimensions of 0.4 × 0.1 × 0.7 mm^3 or 0.5 × 0.4 × 0.7 mm^3, respectively, was mounted in a glass capillary under an argon atmosphere. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angle of 20 carefully centered reflections in the range $24.0° < 2\theta < 28.2°$ for **1b**, corresponding to a monoclinic cell, and $26.9° < 2\theta < 27.5°$ for **4** corresponding to a primitive orthorhombic cell with dimensions listed in Table 1. On the basis of the systematic absence, the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ for **1b** and $Pbcn$ for **4**.

The intensities of three representative reflections which were measured after every 100 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). An emperical absorption correction based on azimuthal scans of three reflections was applied which resulted in transmission factors ranging from 0.91 to 1.00 for **1b** and from 0.96 to 1.00 for **4**. The data were corrected with Lorentz and polarization effects.

The positions of the molybdenum atoms were determined by the heavy atom method. Other non-hydrogen atom sites were located from successive Fourier maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed on the calculated positions. The final cycle of full-matrix least-squares refinement was based on 4655 observed reflections ($I > 2\sigma(I)$) and 620 variable parameters for **1b** and 3323 observed reflection ($I > 3\sigma(I)$) and 330 variable parameters for **4**. The unweighted and weighted agreement factors were refined with $R = 0.069$ and $R_w = 0.069$ for **1** and $R = 0.082$ and $R_w = 0.075$ for **4**. The standard deviations of an observation of unit weight were 1.48 for **1b** and 3.20 for **4**. Neutral atom scattering factors were taken from the literature.[39] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

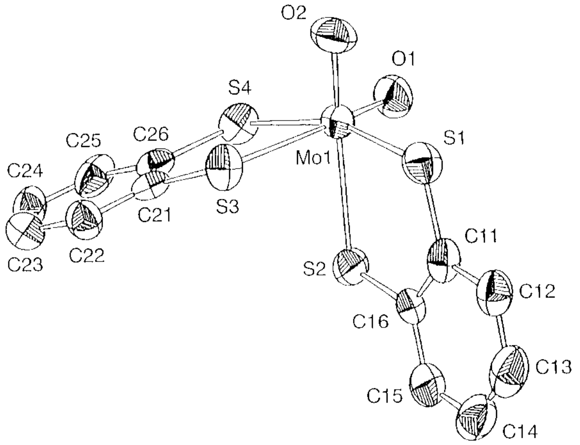

Figure 1. Structure of the anion part of $(PPh_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1b**).

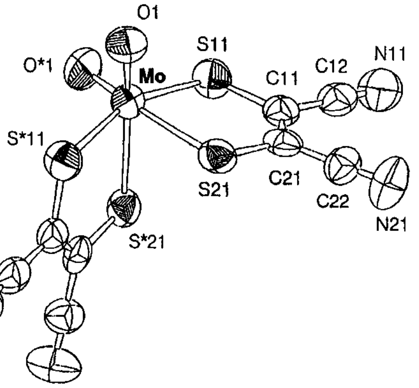

Figure 2. Structure of the anion part of $(PPh_4)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]$ (**4**)

Results

Crystal Structures of $(PPh_4)_2[Mo^{VI}O_2(bdt)_2]$ (1) and $(PPh_4)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]\cdot 2CH_3OH$ (4). Figures 1 and 2 show the perspective views of the anion part of $(PPh_4)_2[Mo^{VI}O_2(bdt)_2]$ and $(PPh_4)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]$, respectively. Each MoO_2S_4 core has an octahedral geometry with a *cis* location of the two terminal oxo ligands as other dioxomolybdenum(VI) complexes. The two thiolates of each bdt ligand in **1b** have a bite angle of 79.1(1) or 79.7(1)° and the S−Mo−S angles between the two bdt ligands are 83−90° as listed in Table 2. Table 3 lists the selected bond lengths and angles of **4** which has a similar S−Mo−S bite angle (79.78(8)°). An imposed two fold axis bisects the O−Mo−O angle in **4**. The selected structural parameters of both complexes were compared with those of the reported dioxomolybdenum(VI) complexes as listed in Table 4. The short Mo−S distances (2.417(3) Å and 2.434(2) Å for **1b** and 2.439(2) Å for **4**) *cis* to the oxo ligand are similar to those of two Mo−S bonds *cis* to the terminal oxo in $Mo^{VI}O_2S_2N_2$ complexes, *e.g.* $[Mo^{VI}O_2(S,N\text{-cys-OMe})_2]$ (2.414 Å)[40] and $[Mo^{VI}O_2[(CH_3)_2NCH_2CH_2N(CH_2CH_2S)_2]]$ (2.415(2) Å).[30] Of particular interest is the distances of the Mo−S bonds

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Table 2. Selected Bond Lengths and Bond Angles in $(PPh_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1b**)

Distances (Å)			
Mo−O1	1.724(7)	Mo−S4	2.417(3)
Mo−O2	1.730(7)	S1−C11	1.76(1)
Mo−S1	2.434(3)	S2−C16	1.76(1)
Mo−S2	2.608(3)	S3−C21	1.73(1)
Mo−S3	2.588(3)	S4−C26	1.75(1)
Angles (deg)			
O1−Mo−O2	103.0(4)	Mo−S3−C21	107.2(4)
S1−Mo−S2	79.1(1)	Mo−S4−C26	110.6(4)
S3−Mo−S4	79.7(1)	O1−Mo−S2	161.9(3)
S1−Mo−S3	83.6(1)	O2−Mo−S3	91.1(3)
S2−Mo−S3	83.5(1)	O1−Mo−S1	110.6(3)
S4−Mo−S2	89.7(1)	O1−Mo−S4	83.9(3)
Mo−S1−C11	111.2(4)	O2−Mo−S1	83.1(3)
Mo−S2−C16	106.3(4)	O2−Mo−S4	106.3(3)

Table 3. Selected Bond Lengths and Bond Angles in $(PPh_4)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]\cdot 2CH_3OH$ ($4\cdot 2CH_3OH$)

Distances (Å)			
Mo−O1	1.721(6)	S11−C11	1.763(9)
Mo−S11	2.439(2)	S21−C21	1.726(9)
Mo−S21	2.635(3)		
Angles (deg)			
O1−Mo−O*1	103.7(4)	O1−Mo−S*21	163.2(2)
S11−Mo−S21	79.78(8)	Mo−S11−C11	109.3(3)
S11−Mo−S*21	84.06(8)	Mo−S21−C21	104.9(3)
S11−Mo−S*11	158.3(1)	Mo−S11−C11−C12	−177.5(6)
S21−Mo−S*21	83.3(1)	Mo−S11−C11−C21	−0.6(8)
O1−Mo−S11	85.0(2)	Mo−S21−C21−C11	−2.3(8)
O1−Mo−S*11	108.6(2)	Mo−S21−C21−C22	178.1(6)
O1−Mo−S21	88.0(2)		

trans to the two oxo groups which are relatively long (2.588(3) and 2.608(3) Å for **1b** and 2.635(3) Å for **4**). The Mo−S distances *trans* to the oxo groups are comparable to Mo−thioether distances (2.690(6) and 2.684(6) Å) in $Mo^{VI}O_2(dttd)$ (dttd = 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane)[14] or to the Mo−thioketone distance (2.639(1) Å) in $Mo^{VI}O_2(S_2CNEt_2)_2$[41] rather than the ordinary Mo−S(thiolate) distances. A longer Mo−thioether distance (2.708(1) Å) has been reported for $Mo^{VI}O_2[(SCH_2CH_2)_2NCH_2CH_2SCH_3]$.[42] The four Mo−S distances in **1b** are longer than those (2.388(2), 2.377(1), and 2.376(6) Å) in $(NEt_4)_2[Mo^{IV}O(bdt)_2]$, $(PPh_4)[Mo^{V}O(bdt)_2]$, and $Mo^{VI}(bdt)_3$, respectively. Although the structures of these complexes have a $S_2C_6H_4$ plane bent from the MoS_2 planes,[31,43] that of $(PPh_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1b**) coincides with the MoS_2 plane, probably due to the release of stress by the rigid, small bite angle by the longer Mo−S bonds.

The two Mo═O bond distances (1.724(7) and 1.730(7) Å for **1b** and 1.721(6) Å for **4**) are similar to those (1.70−1.72 Å) of the reported dioxomolybdenum(VI) complexes having one or two thiolate ligands, *e.g.* $Mo^{VI}O_2(mercaptoquinolato)_2$,[44] $Mo^{VI}O_2[NMe_2C_2H_4N(C_2H_4S)_2]$,[30] $Mo^{VI}O_2(S,N\text{-}cys\text{-}OMe)_2$,[40] $Mo^{VI}O_2[(SC_2H_4NMe)_2C_2H_4]$,[45] $Mo^{VI}O_2[(SCH_2)_2py](OSC_4H_8)$,[46] $Mo^{VI}O_2(SCMe_2CH_2NHMe)_2$,[47] $Mo^{VI}O_2(NSC_6H_{12}O_2)_2$,[48] $Mo^{VI}O_2(S_2CNR_2)_2$ (R = Et, iPr),[41,49] and $Mo^{VI}O_2(dttd)$.[14] The Mo═O distance of **1b** is slightly longer than those of $(PPh_4)[Mo^{V}O(bdt)_2]$ and $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ (1.668(3) and 1.699(6) Å, respectively) due to the different geometries and Mo oxidation states.[31]

The observed O−Mo−O bond angle in **1b** or **4** is similar (103.0(4) or 103.7(4)°, respectively) to those (103−108°) found in other octahedral dioxomolybdenum(VI) complexes.[30,50] The structures of **1b** and **4** are slightly distorted octahedral and have a C_2 symmetry with the 2-fold axis bisecting the O−Mo−O, S_1−Mo−S_4 and S_2−Mo−S_3 angles. Large O−Mo−O angles (111 and 122.2°) have been reported for $Mo^{VI}O_2(dttd)$ and $Mo^{VI}O_2(SCMe_2CH_2NHMe)_2$, respectively.[14,47] In particular, the latter complex has a skew-trapezoidal bipyramid structure with a remarkably short S−S distance.

The S−C distances of the thiolate ligands *trans* to two of the other thiolate groups are 1.763(9) Å for **4**, whereas those of thiolate ligands *trans* to the oxo groups are 1.726(9) Å for **4** as listed in Table 2 and 3. The S−C distances are similar to the S-C distance (mean 1.727(6) Å) of the bdt ligand in $Mo^{VI}(bdt)_3$ even with the trigonal prismatic structure in the analogous Mo(VI) state.[43] The S—C bond of $Mo^{VI}(bdt)_3$ has been discussed to have some S═C double bond character, i.e. similar to a thioketone group.[43] In the case of the S—C bond at the sulfur *trans* to the oxo group in **4**, the slightly shorter S—C distances (1.726(9) Å) have similar S═C character. The longer S−C bond in **4** (1.763(9) Å) at thiolate sulfur atoms *trans* to the thiolate groups are close to the S−C distances for $(PPh_4)[Mo^{V}O(bdt)_2]$ and $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ (means,[51] 1.763(4) and 1.767(6) Å, respectively).[31]

A more pronounced *trans* influence was observed in the Mo—S—C angles of **1b** and **4**. The two Mo—S—-C angles (110.6(4) and 111.2(4)°) *cis* to the Mo═O group in **1b** are definitely larger than the two angles (106.3(4) and 107.2(4)°) *trans* to the Mo═O group. This trend is also observed for the larger Mo—S—C angle (109.3(3)°) *cis* to the Mo═O group and the small angle (104.9(3)°) *trans* to the Mo═O group in **4**. These two kinds of Mo—S—C angles correspond to the two types of Mo—S distances in both complexes. Thus, the strong Mo—S bond with the short distance is considered to promote the hybridization at S.

Charge repulsion between oxygen atoms of the two Mo═O groups causes the widening of the O—Mo—O angle. The crystal structure parameters for **1b** or **4** imply a relatively acute O—Mo—O angle (103.0(4) or 103.7(4)°, respectively) compared to the large O—Mo—O angle (111°) in $Mo^{VI}O_2(dttd)$ ascribed to a steric compactness of the dttd chelating ligand. The thioketone-like structure contributes to the increase of the π-interaction in Mo═O bonds with a decreasing Mo—S (thioketone-like) π-bonding. The resulting Mo═O π-interaction decreases the negative charge on the two oxygen atoms. Another possible explanation is the contribution of π-interaction from the filled oxygen p-orbitals to the empty metal d-orbitals. Recently, the presence of Mo═O triple bonding has been discussed in terms of such donative π-bonding for various dioxomolybdenum(VI) complexes.[52,53] Such an interaction between metal d-orbital and O p-orbital probably decreases the

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Table 4. Comparison of Structural Parameters in Dioxomolybdenum(VI) Complexes

	bond dist (Å)				
		Mo—X *trans* or *cis* to Mo═O		bond angle (deg)	
complex	Mo—O	trans	cis	O—Mo—O	ref
$[Mo^{VI}O_2(S,N\text{-cys-OMe})_2]$	1.714(4)	N 2.375(5)	S 2.414(2)	108.1(3)	40
$[Mo^{VI}O_2(S_2CNEt_2)_2]$	1.703(2)	S 2.639(1)	S 2.451(1)	105.8(1)	42
$Mo^{VI}O_2(dttd)$	1.72(2)	S 2.690(6)	S 2.393(7)	111.1(1)	14
	1.71(2)	S 2.684(7)	S 2.411(7)		
$(PPh_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1b**)	1.726(7)	S 2.596(3)	S 2.421(3)	102.6(3)	this work
	1.730(7)	S 2.612(3)	S 2.440(2)		
$(PPh_4)_2[Mo^{VI}O_2(S_2C_2(CN)_2)_2]\cdot 2MeOH$(**4**)$\cdot$2MeOH	1.721(6)	S 2.635(3)	S 2.439(2)	103.7(4)	this work

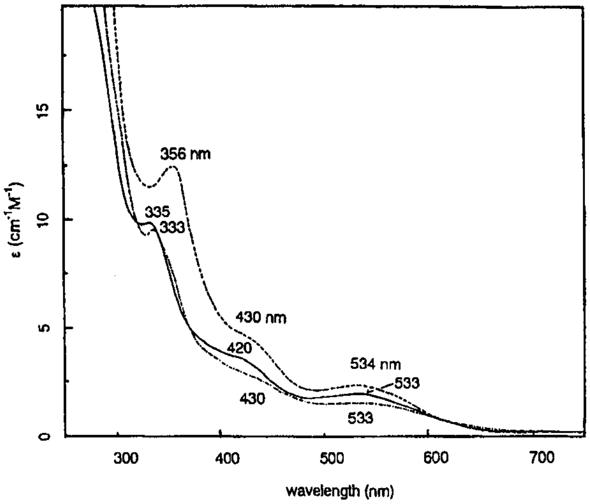

Figure 3. UV−visible spectra of (a) (—); $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1**), (b) (- -); $(NEt_4)_2[Mo^{VI}O_2(Ph_3Si\text{-bdt})_2]$ (**2**), and (c) (—•—) $(NEt_4)_2[Mo^{VI}O_2(tdt)_2]$ (**3**) in DMF.

negative charges on the two oxygen atoms and results in an acute O—Mo—O bond angle.

Electronic Spectra. Figure 3 shows the UV−visible spectra of $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1**), $(NEt_4)_2[Mo^{VI}O_2(Ph_3Si\text{-bdt})_2]$ (**2**), $(NEt_4)_2[Mo^{VI}O_2(tdt)_2]$ (**3**), and $(PPh_4)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]\cdot 2CH_3OH$ (**4**) in DMF. Three characteristic absorption maxima at 333−356, 420−430, and 533−534 nm for **1a**, **2**, and **3** in the visible region are due to O—Mo and S—Mo ligand-to-metal charge transfer (LMCT) bands since dioxomolybdenum(VI) has d^0 configuration. Similar maxima at 365, 425, and 525 nm in acetonitrile have been reported for $(Bu_4P)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]$.[34] The intense bands at 430 nm for **1a** and at 420 nm for **3** are associated with the O—Mo and S—Mo LMCT bands which were confirmed by the resonance Raman excitation profile as described later.

Subramanian *et al.* have assigned an absorption maximum in $Mo^{VI}O_2(dttd)$ at 410 nm (log ϵ, 3.72)[14] to an O—Mo LMCT band from the excitation profile of the resonance Raman spectra.[54] They have predicted the presence of a weak S—Mo LMCT band at *ca.* 480 nm from the observed maximum of the excitation profile at 520 nm and the skewed shape of the absorption spectra. The red-shifted bands detected clearly at 533−534 nm in **1a** and **3** are proposed to be due to S—Mo and O═Mo LMCT transitions as described later in the resonance Raman analysis. The present UV−visible spectroscopic results strongly suggest that the remarkably red-shifted S—Mo and O═Mo LMCT bands with a large magnitude of molar coefficient are realized by the strong π-interaction from S pπ or O pπ to the empty Mo d-orbital in the Mo—S or Mo═O bonds.

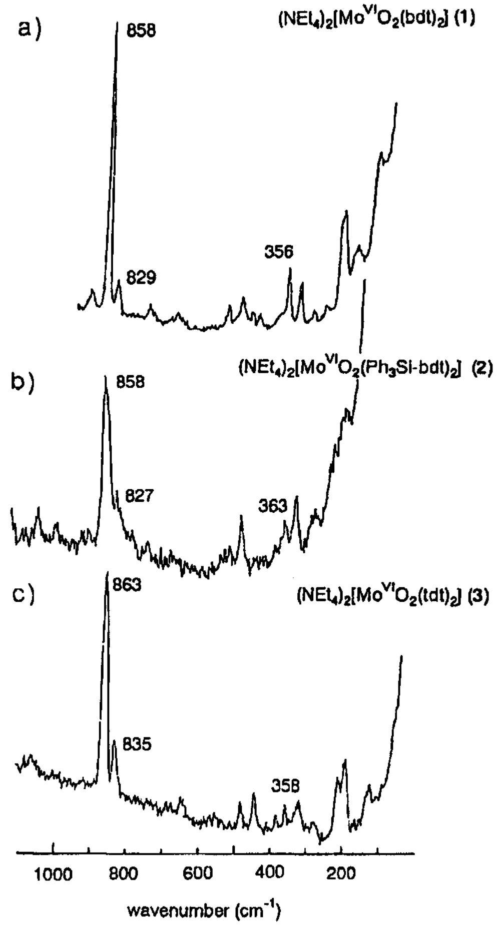

Figure 4. Raman spectra of (a) $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1**), (b) $(NEt_4)_2[Mo^{VI}O_2(Ph_3Si\text{-bdt})_2]$ (**2**), and (c) $(NEt_4)_2[Mo^{VI}O_2(tdt)_2]$ (**3**) in the solid state.

Raman Spectra. Figure 4 shows the resonance Raman spectra (RR) of **1a**, **2**, and **3** in the solid state with 514.5-nm excitation. Table 5 lists the RR and IR bands of **1a**, **2**, **3** and **4**. Two intense RR bands were observed at 858−863 and 827−835 cm^{-1} and assigned to ν_s and ν_a Mo═O stretchings for **1**, **2**, and **3**, respectively. **4** exhibits a considerably shifted Mo═O RR band at 881 and 851 cm^{-1}. The two Mo═O bands appear at a quite low wavenumber compared with the bands at 922 and 890 cm^{-1} for $Mo^{VI}O_2(dttd)_2$[54] and IR bands at 910 and 880 cm^{-1} for $[Mo^{VI}O_2(S_2CNEt_2)_2]$.[55] The ν(Mo−S) stretching bands for **1a**, **2**, **3**, and **4** are observed at 322, 328, 318 and 313 (or 330) cm^{-1}, respectively. The excitation profile indicates that absorption maxima at 420 nm and 533 nm in **3** are associated with both Mo═O LMCT bands and Mo—S LMCT bands. In the case of $Mo^{VI}O_2(dttd)$ the S—Mo LMCT absorption at *ca.* 480 nm which may be hidden under the shoulder of a broad intense maximum at 410 nm is due to O═Mo LMCT transition.[54]

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Table 5. Selected Resonance Raman (IR) bands (cm^{-1}) of $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1**), $(NEt_4)_2[Mo^{VI}O_2(Ph_3Si\text{-}bdt)_2]$ (**2**), $(NEt_4)_2[Mo^{VI}O_2(tdt)_2]$ (**3**) and $(PPh_4)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]\cdot 2CH_3OH$ (**4**·2CH$_3$OH) in KBr disk

assignments	ν_s(Mo=O)	ν_a(Mo=O)	ν(Mo−S)	
$(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ (1)	858 (858)	829 (831)	356 322	
$(NEt_4)_2[Mo^{VI}O_2(Ph_3Si\text{-}bdt)_2]$ (2)	858 (856)	827 (827)	363 328	ν(Si−C) 1425, 1093
$(NEt_4)_2[Mo^{VI}O_2(tdt)_2]$ (3)	863 (864)	835 (838)	358 318	
$(PPh_4)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]\cdot 2CH_3OH$(**4**·2CH$_3$OH)	885 (886)	851 (852)	354 330 313	ν(C=C) 1472 (1471)

Electrochemical Properties. Cyclic voltammograms in DMF solutions of **1a**, **2**, and **3** exhibit irreversible reduction peaks at −1.03, −1.40, and −1.15 V (concomitant with a −0.99 V irreversible peak) *vs* SCE, respectively, presumably assignable to the Mo(VI)/Mo(V) redox process and the successive O-atom releasing reactions when scanned in the cathodic direction. The order of the positively shifted reduction potentials obtained by the cyclic voltammograms is **3** > **1a** > **2**. The redox potentials correspond to the electron-donating tendency of the substituent on the benzenedithiolate ligand. Irreversible oxidation peaks were observed at 0.07, 0.05, and 0.02 V *vs* SCE for **1a**, **2**, and **3,** respectively, when scanned in the anodic direction. The results are in the similar range of the electrochemical reduction potentials of the related complexes, *e.g.* $E_{pc} = -0.87$ V *vs* SCE for $[Mo^{VI}O_2(S_2CNEt_2)_2]$[56] and $E_{pc} = -1.25$ V *vs* SCE for $[Mo^{VI}O_2(S,N\text{-}cys\text{-}OMe)_2]$[21] in DMF.

Oxo-Transfer Reactivity of 1a, 2, and 3. The stoichiometric reaction between **1a**, **2**, or **3** and benzoin was examined in DMF at 29 °C. The reaction proceeds as in the following equation.[20]

$$[Mo^{VI}O_2(bdt)_2]^{2-} + PhCH(OH){-}COPh \rightarrow [Mo^{IV}O(bdt)_2]^{2-} + PhCO{-}COPh + H_2O \quad (1)$$

The observed rates for **1**, **2**, and **3** at the initial stages are $k_{obs} = 4.0\ (\pm 0.7) \times 10^{-3}\ M^{-1}\ s^{-1}$, $1.5\ (\pm 0.4) \times 10^{-3}\ M^{-1}\ s^{-1}$, and $5.4\ (\pm 0.7) \times 10^{-3}\ M^{-1}\ s^{-1}$, respectively. The trend of the O-atom transfer reactivity is **3** > **1** > **2**, which is ascribed to the electron-donating subsituent effect.

A similar stoichiometric reaction of **1a** with triphenylphosphine in acetonitrile-d_3 at 27 °C was also kinetically studied. The reaction occurs according to the following stoichiometry.

$$(NEt_4)_2[Mo^{VI}O_2(bdt)_2] + PPh_3 \rightarrow (NEt_4)_2[Mo^{IV}O(bdt)_2] + OPPh_3 \quad (2)$$

At the initial stage, **1a** exhibits almost the same reactivity as $[Mo^{VI}O_2(S_2CNEt_2)_2]$ which however suffers a slow deactivation mainly due to the formation of a binuclear Mo(V) complex. The observed rate in the presence of **1a** is $3.9 \times 10^{-3}\ M^{-1}\ s^{-1}$ in acetonitrile although no reaction occurs in DMF. The poor solubility in acetonitrile due to the formation of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ probably facilitates the O-transfer reaction. Although $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ is soluble in acetonitrile up to 4 mM at 30 °C, the employed concentration (6.7 mM) is too high under our stoichiometric reaction conditions. The reaction between **1a** and triphenylphosphine was monitored by ^{1}H-NMR spectroscopy in acetonitrile-d_3 at room temperature. **1a** reacts with triphenylphosphine quantitatively to give $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ exhibiting two broad ^{1}H-NMR signals at 6.7 and 7.5 ppm (overlapped with triphenylphosphine signals). The other product, triphenylphosphine oxide, gives phenyl proton signals at 7.3 ppm distinguishable from the triphenylphosphine signal at 7.5 ppm. The contamination of a small amount of $(NEt_4)[Mo^{V}O(bdt)_2]$ causes the broadening of the bdt proton signals of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ with the fast electron exchange between these species.

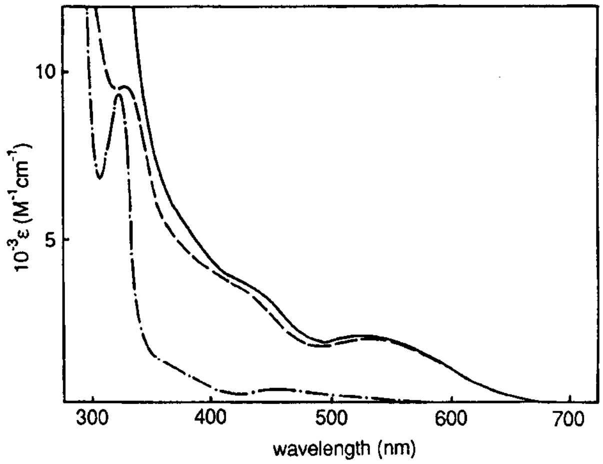

Figure 5. UV−visible spectra of (a) (—) a mixture of $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ and $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ (1:1), (b) (- -) $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$, and (c) (—•—) $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ in acetonitrile. Concentration: 1 mM for each molybdenum complex.

In these cases, the corresponding binuclear molybdenum(V) complex does not form during reduction of **1a** with triphenylphosphine. The reaction was also monitored using UV−visible spectra. In general, μ-oxobinuclear complexes, $[Mo^{V}_2O_3(L\text{-}L)_4]$, form when $[Mo^{VI}O_2(L\text{-}L)_2]$ (L-L = S$_2$CNEt$_2$, S,N-cys-OEt, S,N-cys-OMe) is reduced by triphenylphosphine[12,16] and also by other trialkylphosphines.[57,58]

Actually, the absence of the reaction between $[Mo^{VI}O_2(bdt)_2]^{2-}$ and $[Mo^{IV}O(bdt)_2]^{2-}$ in acetonitrile was established using the UV−visible spectroscopic analysis as shown in Figure 5. A mixture of $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ and $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ (1:1) in acetonitrile exhibits an additive spectrum by both components. The dinucleating reaction between $[Mo^{VI}O_2(L\text{-}L)_2]$ and $[Mo^{IV}O(L\text{-}L)_2]$ has been considered to be prevented by the bulky chelating ligand, *e.g. N,N′*-dimethyl-*N,N′*-bis(2-mercaptophenyl)ethylenediamine since the steric congestion hinders formation of a μ-oxo binuclear complex.[19,42,59] However, the steric hindrance is not conceivable for the present case of bdt ligand in **1a**.

In order to investigate origin for the absence of the formation of μ-oxodimolybdenum(V) complexes, the reaction between various Mo(VI) and Mo(IV) complexes was studied. $[Mo^{VI}O_2(S_2CNEt_2)_2]$ is known to react easily with $[Mo^{IV}O(S_2CNEt_2)_2]$ to

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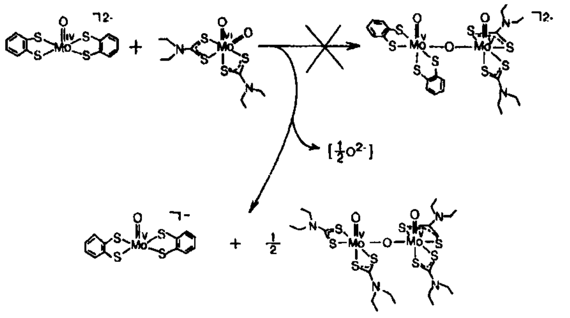

Figure 6. Scheme for formation of $[Mo^{V}O(bdt)_2]^-$ and $[Mo^{V}{}_2O_3(S_2CNEt_2)_4]$ in a reaction between $[Mo^{VI}O_2(S_2CNEt_2)_2]$ and $(NEt_4)_2[Mo^{IV}O(bdt)_2]$.

give $[Mo^{V}{}_2O_3(S_2CNEt_2)_4]$ and $(NEt_4)_2[Mo^{IV}O(bdt)_2]$, and it also reacts with $[Mo^{VI}O_2(S_2CNEt_2)_2]$ in acetonitrile to give a blue solution which exhibits strong absorption maxima at 510 nm and 730 nm. This result is interpreted by the absence of a μ-oxo binuclear complex, $(NEt_4)_4[(bdt)_2Mo^{V}({=}O){-}O{-}Mo^{V}({=}O)(S_2CNEt_2)_2]$. The maximum at 510 nm is assignable to a LMCT transition in $[Mo^{V}{}_2O_3(S_2CNEt_2)_4]$ and the other maximum at 725 nm is due to that for $[Mo^{V}O(bdt)_2]^-$. The solution exhibited ESR signals at $g_1 = 2.022$, $g_2 = 1.984$, and $g_3 = 1.976$ in acetonitrile/DMF (4:1) at 77 K. The observed signals are assignable to $(NEt_4)[Mo^{V}O(bdt)_2]$. The formation of $[Mo^{V}{}_2O_3(S_2CNEt_2)_4]$, which has a characteristic absorption maximum at 513 nm in benzene,[16] was detected by the observation of an absorption maximum at 508 nm in acetonitrile whereby its molar coefficient depends on the concentration at equilibrium. In the above reaction, $[Mo^{VI}O_2(S_2CNEt_2)_2]$ probably coordinates to the vacant axial position of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$, and then a one-electron transfer oxidation occurs as shown in Figure 6. It is likely that the strong covalency of the Mo−S bonds does not allow it to rearrange to form a stable μ-oxo binuclear complex. The reduced species of $[Mo^{VI}O_2(S_2CNEt_2)_2]$ finally releases one oxygen atom to an unknown acceptor. A similar reaction occurs upon the irreversible electrochemical reduction as reported for this complex.[56] The lack of any μ-oxo dimerization reaction occurring between $[Mo^{VI}O_2(bdt)_2]^{2-}$ and $[Mo^{IV}O(bdt)_2]^{2-}$ seems to be also caused by the poor reactivity of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$, although further study is required for the establishment of a detailed mechanism.

Discussion

The synthesis of an octahedral dioxomolybdenum(VI) complex having four thiolate ligands was considered to be difficult.[29,30] The thermal activation of the oxo-group *trans* to the thiolate ligands results in formation of $Mo^{VI}(bdt)_3$ when disodium benzene-1,2-dithiolate and MoO_2(acetylacetonato)$_2$ are mixed in methanol.[60] Only an extremely distorted dioxomolybdenum(VI) complex containing two thiolate ligands with an acute S−Mo−S angle has been known using the $CH_3NHCH_2C(CH_3)_2S^-$ ligand.[61] The synthesis of the complexes, **1a**, **2**, and **3**, was realized by the O-atom transfer reaction of trimethylamine *N*-oxide to $(NEt_4)_2[Mo^{IV}O(bdt)_2]$. Our results show the function of dithiolene-type thiolate as a chelating ligand capable to coordinate even at the *trans* position to the Mo=O groups of octahedral *cis*-dioxomolybdenum(VI) complexes.

The X-ray analysis data indicate that the MoO_2S_4 core of **1b** and **4** has an octahedral structure. The distances of the Mo=O and the Mo−S bonds *cis* to the Mo=O groups are similar to those of other dioxomolybdenum(VI) complexes having thiolate ligands. The Mo−S distances *trans* to the Mo=O groups are relatively long due to the *trans* influence which is greatly enhanced in d^0 Mo(VI) state.

The structural parameters of **1b** and **4** were compared with those of various molybdenum complexes having the dithiolene-like ligand. Bennett *et al.* have found a shorter S−C bond (1.727(6) Å) in $[Mo^{VI}(bdt)_3]$ than that of bdt-H_2.[62] The shorter bond corresponds closely to the S−C bond distance in the Mo−S(thioketone) bond which is presumably stabilized by π-conjugation in the phenyl ring. The Mo−S bond *trans* to the oxo group in **1b** and **4** may be approximated to a thioketone type double bond. On the other hand, the S−C distances for $(NEt_4)_2[Mo^{V}O(bdt)_2]$ and $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ have been reported to be 1.767(4) and 1.763(6) Å, which are similar to those of metal arenethiolates, *e.g.* 1.76(1) Å for $(NEt_4)[Mo^{V}O(SPh)_4]$.[59]

The thioketone-like structure is probably stabilized by the π-conjugation of its S=C bond with the CN groups especially in the dithiolene ligand of **4** although the observed crystal parameters in **1b** have a large standard deviation for the bond distances. Furthermore, the calculated negative charge is concentrated at the 6-position of the benzene ring. The introduction of an electron-donating group, *e.g.* 4-CH_3 in the benzene ring of **3** destabilizes the thioketonic structure and results in facilitation of the O-atom releasing reaction. On the contrary, the electron-withdrawing group assists the stabilization of the Mo=O bond *trans* to the Mo−S group since the increase of S−C pπ−pπ interactions results in the decrease of the Mo−S dπ−pπ component *trans* to Mo=O and then in the increase of the Mo−O d-p π-component.

The 3- or 4-substituted benzene-1,2-dithiolate dioxomolybdenum(VI) complexes show a significant difference in the reactivity of oxo-transfer. The reaction rates of the three complexes at the initial stages increases with a trend of **3** ($k_{obs} = 5.4\ (\pm 0.7) \times 10^{-3}\ M^{-1}\ s^{-1}$ > **1a** ($k_{obs} = 4.0\ (\pm 0.7) \times 10^{-3}\ M^{-1}\ s^{-1}$) > **2** ($k_{obs} = 1.5\ (\pm 0.4) \times 10^{-3}\ M^{-1}\ s^{-1}$) in the oxidation of benzoin in DMF at 29 °C. The trend corresponds to the electron-donating character in the substituted benzene ring. The electron-donating substituent causes activation of the O-atom releasing reaction from the Mo=O group. The above trend in the O-atom releasing reaction is consistent with the negative shift of the reduction potentials in Mo(VI)/Mo(V) from **3** to **1a** and **2**. If the electron transfer is predominant as in the case of a stoichiometric reaction between the dioxomolybdenum(VI) complex and benzoin, it is likely that the substrate initially transfers one-electron to the dioxomolybdenum(VI) complex to give a Mo(V) species and then releases the O-atom, which is activated by the electron-donating group on the benzenedithiolate ring.

Complexes **1a**−**3** react with benzoin or triphenylphosphine easily so that the above precise k_{obs} values are obtainable. This is due to the lack of a dimerization reaction to the μ-oxodimolyndenum(V) complex during the stoichiometric reaction. The dimerization reaction has also been prevented in systems containing sterically encumbered Mo(VI) and Mo(IV) complexes, *e.g.* $Mo^{VI}O_2$(2,6-bis-(2,2-diphenyl-2-mercaptoethyl)pyridine,[22,24] and $\{HB(Me_2pz)_3\}Mo^{VI}O_2\{S_2P(OEt)_2\}$.[63] Lack of the dimerization reaction in the bdt complexes is due to negative

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charges on both reactants and also to hinderance in required stereochemical change to the μ-oxo-*cis*,*cis*-bis[oxomolybdenum(V)] species rather than the steric congestion of the ligand.

In the stoichiometric reactions of **1a**, **2** and **3** with benzoin, the higher activity of **3** shows the facile Mo═O oxo-transfer with the decrease of the Mo═O π-components induced by the electron-donating CH_3 group in the benzene ring although it has a somewhat more negative reduction potential. It is noticeable that these dioxomolybdenum(VI) complexes having thiolate ligands *trans* to the Mo═O groups exhibit an irreversible reduction peak due to the O-atom release after reduction of the Mo(V) species as reported for $Mo^{VI}O_2(S_2CNR_2)_2$.[56] Since, in the LUMO of the octahedral structure, the Mo═O π-orbital is antibonding, the one-electron reduction of **1a** results in conversion from octahedral $[Mo^{V}O_2(bdt)_2]^-$ to square-pyramidal $[Mo^{IV}O(bdt)_2]^{2-}$ with an O-atom release. On the contrary, $Mo^{VI}O_2$(dttd) exhibits a reversible Mo(VI)/Mo(V) redox couple without release of one of the oxo ligands.[14] The difference is possibly due to strengthening of the Mo═O bond by the weakening of the Mo—S bond *trans* to Mo═O with a less electron-donating thioether ligand in $Mo^{VI}O_2$(dttd).

Biological Relevance

The X-ray absorption analysis of oxidized sulfite oxidase has demonstrated the presence of two terminal oxygen atoms at 1.68−1.70 Å, three sulfur atoms at 2.41 Å, one nitrogen atom and one oxygen atom at 2.05−2.19 Å, or one distal sulfur atom at 2.86 Å.[8,64] In the case of the model complexes, the Mo—S distances (2.421(3) and 2.440(2) Å for **1b** and 2.439(2) Å for **4**) *cis* to Mo═O are close to the short Mo—S bonds in the active center of the enzyme. The distal sulfur has been proposed to come from a single Mo—S(methionine thioether) interaction.[8] The presence of the two longer Mo—S bonds (*ca.* 2.60(1) Å for **1b** and 2.635(3) Å for **4**) *trans* to the Mo═O group makes it possibile for the long sulfur in native molybdooxidases to be assignable to one thiolate of molybdopterin dithiolene *trans* to the terminal oxo or sulfido group. The observed elongation of Mo−S distances by the *trans* influence in **1b** suggests that an electron-donating group, *e.g.* 4-methyl in the tdt ligand, conjugating with the sulfur coordination through the benzene ring increases the *trans* influence and that an electron-withdrawing group, *e.g.* 3-$SiPh_3$ in the Ph_3Si−bdt ligand decreases the *trans* influence.

A large variety of Mo cofactors containing pterin and phosphate groups have been isolated and characterized.[3−6,65] The redox-active pterin group was considered to be involved in the oxidation reaction.[66] Recently, S-protected pterin cofactor derivatives have been isolated from the oxidized forms of Mo cofactors in dimethyl sulfoxide reductase and formylmethanofuran dehydrogenase.[4,67] When the pterin dithiolene ligand coordinates as a pterin to Mo(VI) in the oxidized state,[46] for example, in sulfite oxidase, it is possible that the π-conjugation exists between the dithiolene C═C and the oxidized pterin ring. The electron-withdrawing effect through the possible pterin−dithiolene π-conjugation contributes to the *trans* influence to elongate the Mo—S bond with the formation of thioketone-like S—C bond. Therefore, the long Mo−S bond and the thioketone-like S—C bond presumably stabilizes the *trans* Mo═O group. This is suggested by the coordination of thioketone-like thiolate ligand to the dioxomolybdenum(VI) ion with the conjugated group in the benzene ring of **1b** and the cyano group of **4**. In fact, a recent study for Me_2SO reductase reported that addition of $K_3Fe(CN)_6$ to the isolated oxidized form did not change the absorption spectrum.[68]

Conclusions

The present *cis*-dioxomolybdenum(VI) complex with two benzenedithiolate ligands is the first to be synthesized as a model for the active site of oxidized sulfite oxidase. The complexes $(PPh_4)_2[Mo^{VI}O_2(1,2\text{-benzenedithiolato})_2]$ (**1b**) and $(PPh_2)_2[Mo^{VI}O_2\{S_2C_2(CN)_2\}_2]$ (**4**) have a slightly distorted octahedral structure with two longer Mo—S bonds located at the *trans* positions of the two Mo═O groups. The S—C bond distances in **4** of the thiolato ligands *trans* to the terminal oxo groups are shorter than those at the *cis* positions.

The thioketone-like bonding of S−C group by the π-conjugation weakens the π-bonding character of the Mo-S bonds *trans* to the oxo ligands and contributes to the stabilization of dioxomolybdenum(VI) group through the *trans* influence. In the case of molybdenum oxidoreductases, the dithiolene ligand possibly conjugates with the double bonds of pterin thereby enabling a stabilization of terminal oxo (or sulfide) ligands in the oxidized Mo(VI) state.

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Supporting Information Available: Tables of non-hydrogen atom anisotropic thermal parameters, complete geometric data, and atomic coordinates and a figure depicting the EHMO calculations (21 pages). Ordering information is given on any current masthead page.

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