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Synthesis, Molecular Structure, and Physical Properties of an Oxomolybdenum(IV) Complex with *p*-Chlorobenzenethiolate, $[\mathrm{Mo^{IV}O}(p\text{-}\mathrm{ClC_6H_4S})_4]^{2-}$, as a Model of Active Sites of Reduced Molybdo-Oxidases

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A monomeric oxomolybdenum(IV) complex with *p*-chlorobenzenethiolate, $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(p\text{-}\mathrm{ClC_6H_4S})_4]$ (**1a**), was synthesized as a relevant model of active sites of reduced molybdo-oxidases by reduction of $(\mathrm{NEt_4})[\mathrm{Mo^VO}(p\text{-}\mathrm{ClC_6H_4S})_4]$ (**2**) with $\mathrm{NEt_4BH_4}$. This complex was characterized by absorption, Raman, and ^{1}H NMR spectra and cyclic voltammograms, and compared with **2**. The complex $(\mathrm{PPh_4})_2[\mathrm{Mo^{IV}O}(p\text{-}\mathrm{ClC_6H_4S})_4]$ (**1b**), which was prepared by the cation exchange reaction of **1a**, crystallizes in the triclinic, space group $P\bar{1}$ with $a=21.131(18)$, $b=13.690(3)$, $c=13.490(5)$ Å, $\alpha=100.96(3)°$, $\beta=117.62(3)°$, $\gamma=78.77(5)°$, and $Z=2$. The average distances of Mo–S and Mo–O bonds of this complex are 2.415 and 1.690(9) Å respectively. The O–Mo–S–C torsion angles (θ) in **1b** range from 74° to 91°. EHMO calculation on $[\mathrm{Mo^{IV}O(SH)_4}]^{2-}$ showed that this conformation is thermally stable.

A molybdenum ion exists at the center of molybdenum cofactor in the active sites of the oxomolybdoenzymes such as sulfite oxidase, aldehyde oxidase, and xanthine oxidase.[1] Substrates are catalytically oxidized at these sites by a cycle between the oxidation states, Mo(VI) and Mo(IV), via an intermediate Mo(V) state during turnover.[2] EXAFS studies have shown that an $\mathrm{Mo^{IV}}$(=O) center in the reduced state, and $\mathrm{Mo^{VI}(=O)_2}$ or $\mathrm{Mo^{VI}}$(=O)(=S) centers in the oxidized state are present in the active sites. And these studies have also shown that two or three sulfur atoms coordinate to the molybdenum ion.[1,3] Chemical analysis of degradation products of the molybdenum cofactor has shown that a dithiolene ligand connected to a pterin derivative coordinates to the molybdenum ions.[4]

A number of dioxomolybdenum(VI) complexes with S(thiolato), N, or S(thioether or thioketone) ligans[5] and oxomolybdenum(V) complexes with S(thiolato) ligands[6,7] have been synthesized as models of active sites of the enzymes. For models of the active sites in reduced states, only a few syntheses of monomeric oxomolybdenum(IV) thiolate complexes have been reported because of the difficulty of the syntheses. We found a convenient synthetic method of an oxomolybdenum(IV) thiolate complex using $(\mathrm{NEt_4})[\mathrm{Mo^VO}(p\text{-}\mathrm{ClC_6H_4S})_4]$ (**2**)[8] as starting material.

In this paper, the synthesis, molecular structure, and physical properties of an oxomolybdenum(IV) complex having *p*-chlorobenzenethiolate, $[\mathrm{Mo^{IV}O}(p\text{-}\mathrm{ClC_6H_4S})_4]^{2-}$, are reported. This complex with arenethiolate ligands unconstrained by chelation serves as fundamental references to other oxomolybdenum(IV) thiolate complexes in consideration for their structures and physical properties.

Experimental

All syntheses and physical measurements were carried out under argon atmosphere. 1,2-Dimethoxyethane (DME), MeCN, diethyl ether, and MeCN-d_3 were dried over $\mathrm{CaH_2}$, distilled and deoxygenated before use. *p*-Chlorobenzenethiol, $\mathrm{NEt_4BH_4}$, and $\mathrm{PPh_4Br}$ used were of commercial grade obtained from Tokyo Kasei Co. **2** was prepared by the slight modified method of Boyd et al.[6] and Ellis et al.[8]

Synthesis of $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(p\text{-}\mathrm{ClC_6H_4S})_4]$ (1a). Complex **2** (3.27 g, 4.00 mmol) and $\mathrm{NEt_4BH_4}$ (0.616 g, 4.25 mmol) were mixed and stirred in DME (100 mL) for 5 h at room temperature. A precipitate obtained was collected with filtration and washed with DME until the filtrate were no longer colored. The green precipitate was dissolved in MeCN (30 mL). The solution was filtered and reduced in a volume to about 10 mL under reduced pressure. A blue microcrystalline product (0.70 g, 19%) was obtained by the addition of about 10 mL of diethyl ether to the solution, collected by filtration and dried in vacuo. Found: C, 50.16; H, 6.10; N, 2.86%. Calcd for $\mathrm{C_{40}H_{56}N_2OMoS_4Cl_4}$: C, 50.74; H, 5.96; N, 2.96%.

Synthesis of $(\mathrm{PPh_4})_2[\mathrm{Mo^{IV}O}(p\text{-}\mathrm{ClC_6H_4S})_4]$ (1b). Complex **1a** (0.163 g, 0.172 mmol) and $\mathrm{PPh_4Br}$ (0.176 g, 0.420 mmol) were dissolved in MeCN (14 mL). The solution was stood for overnight at ca. 10 °C. Microcrystals obtained were collected by filtration and washed with MeCN (2 mL, three times) and diethyl ether (2 mL), then dried under reduced pressure. Red microcrystals (0.06 g) were obtained in 25% yield. The crystals have MeCN as a crystalline solvent. Found: C, 62.55; H, 4.46; N, 0.98%. Calcd for $\mathrm{C_{74}H_{59}NOP_2MoS_4Cl_4}$: C, 63.20; H, 4.23; N, 1.00%.

Physical Measurements. Absorption spectra were recorded on a JASCO Ubest-30 spectrometer in MeCN solution with 1 mm matched silica cells. Raman spectra were obtained on a JASCO R-800 spectrometer in solid state with 514.5 nm excitation. The cyclic voltammograms were taken on a Yanaco P-1100 polarographic analyzer in MeCN solution (2 mM, 1 M=1 mol dm^{-3}) with a glassy carbon electrode working and $(n\text{-}\mathrm{Bu})_4\mathrm{NClO_4}$ (100 mM) as a supporting electrolyte. ^{1}H NMR spectra were measured on a JEOL JNH-GSX 270 spectrometer in MeCN-d_3 at 30 °C.

X-Ray Structure Determination. A single crystal of **1b** was sealed in a glass capillary under argon atmosphere for X-ray measurements. Diffraction experiment was performed with a Rigaku four-circle diffractometer using Ni-filtered Cu *Kα* radiation. Cell constants were determined by a least squares method based on setting angles of 24 reflections. Crystal data and experimental details are summarized in Table 1. Three intense reflections were recollected every 100 reflections and showed only 1.3% of decay of the intensities through data collections. Lorentz and polarization correction were applied, but no absorption correction was made. The structure was solved by using SHELX 86,[9] and refined by the block-diagonal least squares method.[10] All of the non-hydrogen atoms were refined with anisotropic temperature factors. Except the three hydrogen atoms of MeCN all hydrogen atoms were placed in idealized positions (C–H distance 1.08 Å) and added to the structure factor calculation, but their positions were not refined.

High R and R_w values and relatively large standard deviations of interatomic distances and angles are due to the poor quality of the crystal.

EHMO Calculation. As a simple model of **1b**, $[MoO(SH)_4]^{2-}$ in ideal C_4 symmetry was adopted for the calculations. The geometrical parameters used are: 1.690 Å for one Mo–O, 2.415 Å for four Mo–S, 1.08 Å for four S–H, 107.7° for O–Mo–S angle, 116.24° for Mo–S–H angle on the basis of the crystal structure of **1b**. The EHMO parameters for Mo were taken from a reported work,[11] and those for S, O, and H are the standard ones.

Results and Discussion

Synthesis. The air-sensitive, diamagnetic oxomolybdenum(IV) complex with monodentate thiolato ligands, **1a**, was synthesized by reduction of **2** with NEt_4BH_4. A DME solution was useful for this reaction because the product obtained gradually precipitates. Although yellow, diamagnetic byproducts are produced in this reaction process, these can be removed by washing with DME. Blue microcrystals were obtained by reprecipitation from MeCN/diethyl ether.

Table 1. Crystal and Refinement Data for $(PPh_4)_2[Mo^{IV}O(p\text{-}ClC_6H_4S)_4]$ (**1b**)

Formula	$C_{74}H_{59}NOP_2MoS_4Cl_4$
Formula weight	1406.25
Crystal system	Triclinic
a/Å	21.131 (18)
b/Å	13.690(3)
c/Å	13.490(5)
α/°	100.96(3)
β/°	117.62(3)
γ/°	78.77(5)
V/Å^3	3369(3)
Z	2
Space group	$P\bar{1}$
t/°C	20±1
D_{calcd}	1.39
Radiation	Cu *Kα*
$2\theta_{max}$/°	120
Scan mode	2θ–ω
No. of reflections measured	8207
No. of observns $I>3\sigma(I)$	7725
R[a]	0.094
R_w[b]	0.104

a) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. b) $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|)^2]^{1/2}$; $w=1/[\sigma^2(|F_o|)+0.34|F_o|+0.0048|F_o|^2]$.

Only a few reports on the syntheses of monomeric oxomolybdenum(IV) complexes with thiolate ligands are found, since synthetic methods of these complexes were limited. Mitchell and Pygall reported the syntheses of $K_2[Mo^{IV}O(edt)_2]$, (edt=1,2-ethanedithiolato), $K_2[Mo^{IV}O(tdt)_2]$, (tdt=3,4-toluenedithiolato), and $[Mo^{IV}O(dtc)_2]$, (dtc=diethyldithiocarbamato) by the reaction of $K_4[Mo^{IV}O_2(CN)_4]$ with 2 equiv of the corresponding ligands in H_2O,[12] and Boyde et al. synthesized $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ (bdt=1,2-benzenedithiolato) by their modified method.[13] Ellis et al. prepared $(NHEt_3)_2[Mo^{IV}O(SC_6F_5)_4]$ by the reaction of $[Mo^{IV}OCl_2(PPh_2Me)_3]$ with pentafluorobenzenethiol and NEt_3 in CH_2Cl_2.[10] However, this method could not be applied to other thiols. Coucouvanis et al. obtained $[Mo^{IV}O(S_2C_2(CO_2Me)_2)_2]^{2-}$ from the reaction between $[Mo^{IV}O(S_4)_2]^{2-}$ and dicarbomethoxyacetylene.[14]

The use of NR_4BH_4 for the reductant is convenient for the syntheses of oxomolybdenum(IV) complexes from the corresponding oxomolybdenum(VI or V) complexes. Subramanian et al. reported the synthesis of an oxomolybdenum(IV) complex having bulky ligands, $[Mo^{IV}O(3\text{-}t\text{-Bu-hbeH}_2)]$, ($3\text{-}t\text{-Bu-hbeH}_4$ = N, N'-bis-(2-hydroxy-3-*t*-butylbenzyl)-1,2-diaminoethane) by the reduction of $[Mo^{VI}O_2(3\text{-}t\text{-Bu-hbeH}_2)]$ with excess $(n\text{-Bu})_4NBH_4$ in MeOH.[15] The synthesis of homoleptic molybdenum(VI) thiolate complexes is difficult when the direct reaction of Mo(VI) ions with free thiols is attempted because Mo(VI) ions are readily reduced to Mo(IV) or Mo(V) states by free thiols.[16] Recently the successful synthesis of dioxomolybdenum(VI) complex with two conjugated dithiolate ligands, $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$, by the O-atom transfer oxidation of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ with Me_3NO was reported by Yoshinaga et al.[17]

Many oxomolybdenum(V) complexes with thiolate ligands were synthesized to date.[6,7] However, the reduction of oxomolybdenum(V) complexes with NR_4BH_4 is very difficult in most cases because of their negative Mo(V)/Mo(IV) redox potentials. Actually, it was difficult to complete the reduction of $(NEt_4)[Mo^{V}O(SC_6H_5)_4]$ to Mo(IV) state by NEt_4BH_4. Ellis et al. showed that the redox potential of $[Mo^{V}O(SAr)_4]^-$ complexes (Ar=aryl) shifted to the positive side by electron-withdrawing substituents on the benzenethiolate ligands.[8] The redox potential (−0.72 V vs. SCE) of $(NEt_4)[Mo^{V}O(SC_6H_5)_4]$ is more negative to the value of −0.66 V (vs. SCE) of **2**. Thus **2** is more readily reduced to the Mo(IV) state with NEt_4BH_4. Recently, Ueyama et al. reported the synthesis of an oxomolybdenum(IV) complex with monodentate thiolate ligands, $(NEt_4)_2[Mo^{IV}O(o\text{-}RCONHC_6H_4S)_4]$, by the NEt_4BH_4 reduction of the corresponding oxomolybdenum(V) complexes[18] which have a positive-shifted Mo(V)/Mo(IV) redox potentials (−0.2—−0.5 V) by the effect of NH–S hydrogen bond.

Description of Structure. The molecular structure of **1b** which was prepared by the cation exchange reaction of **1a** with PPh_4Br in MeCN was determined by a single-crystal X-ray analysis. This complex crystallizes in the space group $P\bar{1}$ and contains four cations, two anion, and two MeCN molecules in an asymmetric unit. This MeCN molecule does not coordinate to the molybdenum(IV) ion. Perspective view of the anion of **1b** is shown in Fig. 1. Positional parameters for the non-hydrogen atoms of **1b** are listed in Table 2 and the selected bond distances and bond angles are presented in Table 3.[19] The geometry of $MoOS_4$ core of **1b** is based on a square pyramid with C_{4v} symmetry, and this molecular structure is similar to that of $[Mo^{V}O(SPh)_4]^-$ reported by Bradbury et al.[20] In **1b** Mo atom lies 0.73(2) Å above a plane formed by four sulfur atoms. The Mo=O bond distance of 1.690(9) Å is in the range of the distances observed in oxomolybdenum(IV) thiolate complexes reported to date. For example, Mo=O bond distances of $[Mo^{IV}O(bdt)_2]^{2-}$, $[Mo^{IV}O(S_2C_2(CO_2Me)_2)_2]^{2-}$, and $(NEt_4)_2[Mo^{IV}O(S\text{-}o\text{-}CH_3CONH\text{-}C_6H_4)_4]$ are 1.699(6),[13] 1.686(6),[14] and 1.689(5) Å,[18] respectively. The average Mo–S distance (2.415 Å) of **1b** is nearly the same with the distance of $(PPh_4)_2[Mo^{IV}O(S\text{-}o\text{-}CH_3CONH\text{-}C_6H_4)_4]$ (av. 2.408(8) Å)[18] and is longer than that of $[Mo^{IV}O(bdt)_2]^{2-}$ (av. 2.388(2) Å)[13] and $[Mo^{IV}O(S_2C_2(CO_2Me)_2)_2]^{2-}$ (av. 2.380(2) Å).[14] The results show that the present monodentate benzenethiolate ligands more weakly coordinate to Mo(IV) ions than bdt or dithiolene chelate ligands. Although $[Mo^{IV}O(S_2CNPr_2)_2]$ has chelate ligands, the Mo–S distances are somewhat longer (av. 2.414(2) Å),[21] because of formal thioketone character of one of the two sulfur ligands, and a somewhat small metal-ligand overlap caused by narrow S–Mo–S bite angles (av. 72.4°) of the four-membered Mo–S–C–S ring.[22]

The O–Mo–S–C torsion angles of **1b** range from 74° to 91°. EHMO calculation of $[Mo^{IV}O(SH)_4]^{2-}$ showed that **1b** has a relatively stable structure in the torsion angles which are near 90° (vide infra), The Mo–S–C bond angles (av.116.2°) show that these sulfur atoms have a strong sp^2 character. However, the torsion angles between Mo–S–C plane and phenyl ring are far apart from 0° because of the steric effect among four phenyl rings. (Table 3) The O–Mo–S–C torsion angles in $[Mo^{V}O(SPh)_4]^-$ range from ca. −33° to −45°.[20]

The geometry around Mo(V) may be reflecting the d-electronic state, which has a singly occupied d_{xy} orbital. Then the repulsion between this d_{xy} orbital and $p\pi$ of sulfur atom is smaller than that of **1b** with a fully-occupied d_{xy} orbital. Actually the torsion angles of $[Mo^{V}O(SPh)_4]^-$ are far apart from 90°. This complex has a structure in which conjugation between Mo–S–C plane and phenyl ring is larger than **1b**.

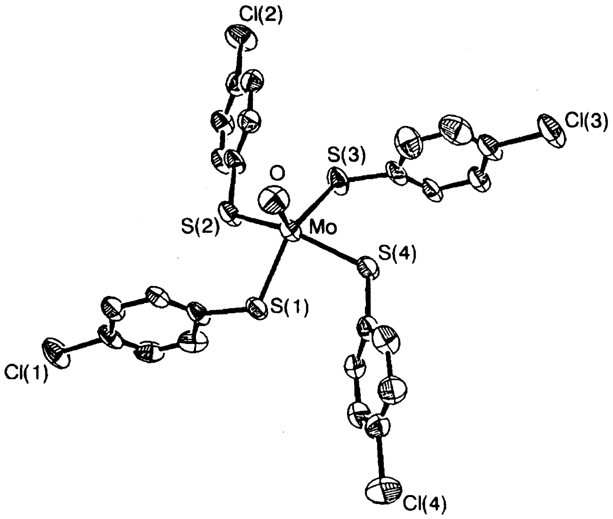

Fig. 1. Perspective view of the structure of the anion part of $(PPh_4)_2[Mo^{IV}O(p\text{-}ClC_6H_4S)_4]$ (**1b**). The atoms are drawn as 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Cleland et al. showed that $[LMo^{V}O(SPh)_2]$ (L=hydrotris(3,5-dimethyl-1-pyrazolyl)borate) has two quite different O–Mo–S–C torsion angles in solid state (−34° and −110°) and that the O–Mo–S bond angles depend on this torsion angle due to the $d\pi$–$p\pi$ repulsion between (Mo–O) and S atoms.[23] The O–Mo–S bond angles of **1b** does not depend on O–Mo–S–C torsion angles.

In order to elucidate the structure of **1b**, the EHMO calculations of $[Mo^{IV}O(SH)_4]^{2-}$ as a model (Fig. 2a) was carried out. In these calculations the O–Mo–S–C torsion angle (θ) was defined as Fig. 2b. The total energy of $[Mo^{IV}O(SH)_4]^{2-}$ has a minimum at $\theta=90°$ and has two maxima at $\theta=0°$ and 180° (Fig. 3). This is explicable by the orbital interactions. Thus, overlap of the anti-bonding d_{xy} orbital on Mo with $p\pi$ of sulfur atom in HOMO maximizes at $\theta=0°$ and 180° and minimizes at $\theta=90°$. (Fig. 4)

Physical Properties. The cyclic voltammograms (CV) of **1a** displayed a quasi-reversible Mo(V)/Mo(IV) redox couple at −0.65 V vs. SCE and irreversible oxidation to Mo(VI) at 0.54 V in MeCN. These redox potentials of **1a** were the same as those of **2** which showed a quasi-reversible Mo(V)/Mo(IV) couple at −0.65 V and irreversible oxidation to Mo(VI) at 0.54 V. The CV of **2** was remeasured to compare with **1** in the same condition. The i_{pa}/i_{pc} value of **1a** and **2** were 1.0 and 0.83, respectively.

The absorption spectra of **1a** and **2** in MeCN are shown in Fig. 5. The distinct absorption maxima of **1a** appeared at 265 nm (51000 $M^{-1}cm^{-1}$), 313 nm (30000), and 588 nm (480). **2** shows absorption maxima at 250 nm (55000), 290 nm (sh 25000), 330 nm (sh 16500), and 604 nm (6950). Generally monooxomolybdenum(V) complexes have a d–d transition in

Table 2. Atomic Coordinates of $(PPh_4)_2[Mo^{IV}O(p\text{-}ClC_6H_4S)_4]$ (**1b**)

Atom	x	y	z
Mo	0.72008(4)	0.98391(6)	0.56426(6)
Cl(1)	0.9043(2)	0.9619(2)	1.2207(2)
Cl(2)	0.6034(2)	0.4528(2)	0.4299(3)
Cl(3)	0.6206(2)	0.9443(3)	−0.0721(2)
Cl(4)	0.9419(3)	1.4291(3)	0.6941(4)
S(1)	0.8103(2)	1.0610(2)	0.7318(2)
S(2)	0.7431(2)	0.8519(2)	0.6773(2)
S(3)	0.7085(2)	0.8487(2)	0.4151(2)
S(4)	0.7593(2)	1.0663(2)	0.4614(2)
O	0.6381(4)	1.0441(6)	0.5444(7)
C(111)	0.8314(6)	1.0172(7)	0.8609(7)
C(112)	0.9023(6)	0.9763(8)	0.9261(10)
C(113)	0.9231(6)	0.9571(8)	1.0351(9)
C(114)	0.8762(6)	0.9793(7)	1.0788(7)
C(115)	0.8061(6)	1.0163(7)	1.0163(8)
C(116)	0.7849(5)	1.0349(7)	0.9075(8)
C(121)	0.7029(6)	0.7406(7)	0.6039(8)
C(122)	0.7395(6)	0.6501(8)	0.6409(8)
C(123)	0.7087(6)	0.5597(8)	0.5907(9)
C(124)	0.6401(6)	0.5646(8)	0.4985(9)
C(125)	0.6035(6)	0.6535(8)	0.4570(9)
C(126)	0.6341(6)	0.7431(8)	0.5130(9)
C(131)	0.6880(6)	0.8884(7)	0.2852(8)
C(132)	0.7351(6)	0.8652(8)	0.2393(7)
C(133)	0.7158(6)	0.8854(7)	0.1294(8)
C(134)	0.6452(7)	0.9252(8)	0.0673(8)
C(135)	0.5988(7)	0.9504(10)	0.1110(11)
C(136)	0.6198(7)	0.9307(10)	0.2192(11)
C(141)	0.8096(6)	1.1679(7)	0.5347(8)
C(142)	0.8823(6)	1.1536(8)	0.6163(8)
C(143)	0.9228(7)	1.2344(10)	0.6657(9)
C(144)	0.8910(7)	1.3274(9)	0.6319(10)
C(145)	0.8202(7)	1.3452(8)	0.5514(10)
C(146)	0.7808(6)	1.2636(8)	0.5051(9)
P(1)	0.1223(1)	0.6878(2)	0.7681(2)
P(2)	0.3565(1)	0.3968(2)	0.1055(2)
C(211)	0.2023(5)	0.7473(6)	0.8266(7)
C(212)	0.2553(6)	0.7281(7)	0.9356(9)
C(213)	0.3199(6)	0.7654(8)	0.9780(9)
C(214)	0.3335(6)	0.8204(7)	0.9163(10)
C(215)	0.2807(6)	0.8411(8)	0.8092(10)
C(216)	0.2141(6)	0.8047(7)	0.7641(9)
C(221)	0.1389(5)	0.5700(7)	0.6950(8)
C(222)	0.2057(6)	0.5340(8)	0.6988(9)
C(223)	0.2170(7)	0.4419(9)	0.6408(10)
C(224)	0.1622(7)	0.3822(9)	0.5814(11)
C(225)	0.0939(8)	0.4180(9)	0.5777(11)
C(226)	0.0825(6)	0.5099(8)	0.6338(9)
C(231)	0.0444(6)	0.7608(7)	0.6724(8)
C(232)	−0.0134(7)	0.8006(9)	0.6975(10)
C(233)	−0.0718(7)	0.8560(11)	0.6212(12)
C(234)	−0.0735(7)	0.8736(9)	0.5254(9)
C(235)	−0.0167(7)	0.8349(10)	0.4981(10)
C(236)	0.0433(7)	0.7765(9)	0.5721(9)
C(241)	0.1038(5)	0.6719(7)	0.8805(8)
C(242)	0.0866(6)	0.5811(8)	0.8873(9)
C(243)	0.0663(7)	0.5713(11)	0.9694(11)
C(244)	0.0687(8)	0.6520(11)	1.0507(10)
C(245)	0.0868(6)	0.7438(9)	1.0455(9)
C(246)	0.1043(6)	0.7520(9)	0.9618(9)
C(311)	0.4325(5)	0.3168(7)	0.1960(8)
C(312)	0.4880(7)	0.2754(8)	0.1704(10)
C(313)	0.5462(7)	0.2161(9)	0.2432(12)
C(314)	0.5465(7)	0.1941(8)	0.3375(10)
C(315)	0.4919(6)	0.2355(9)	0.3666(9)
C(316)	0.4335(6)	0.2974(8)	0.2962(8)
C(321)	0.3769(5)	0.4198(7)	−0.0022(8)
C(322)	0.3908(7)	0.5135(8)	−0.0049(10)
C(323)	0.4115(7)	0.5287(10)	−0.0842(11)
C(324)	0.4112(7)	0.4531(10)	−0.1663(10)
C(325)	0.3939(7)	0.3562(11)	−0.1682(10)
C(326)	0.3772(6)	0.3444(9)	−0.0858(8)
C(331)	0.2740(5)	0.3419(7)	0.0388(8)
C(332)	0.2582(6)	0.2840(7)	0.0985(8)
C(333)	0.1920(7)	0.2510(8)	0.0488(9)
C(334)	0.1395(6)	0.2744(8)	−0.0555(10)
C(335)	0.1566(6)	0.3295(8)	−0.1151(10)
C(336)	0.2234(6)	0.3640(7)	−0.0696(9)
C(341)	0.3452(6)	0.5112(7)	0.1884(8)
C(342)	0.2767(6)	0.5635(8)	0.1642(9)
C(343)	0.2702(7)	0.6555(10)	0.2261(10)
C(344)	0.3293(8)	0.6964(9)	0.3088(11)
C(345)	0.3963(8)	0.6427(11)	0.3361(12)
C(346)	0.4038(6)	0.5501(9)	0.2731(11)
N	0.5338(9)	1.2050(13)	0.7648(14)
C(411)	0.5324(9)	1.1294(14)	0.7199(14)
C(412)	0.5337(10)	1.0301(16)	0.6573(13)

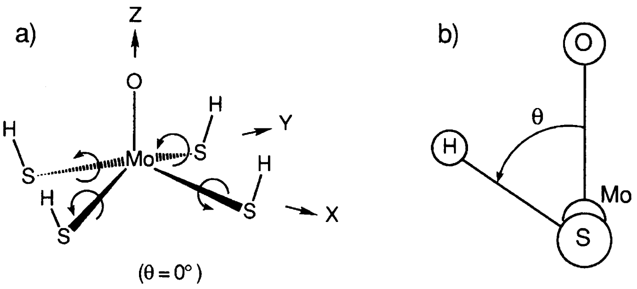

Fig. 2. a) Model used in EHMO calculation. b) The O–Mo–S–C torsion angle which was defined in these calculations.

low-energy region and CT transition in high-energy region. For example, $[Mo^VOCl_4]^-$ has a weak d–d transition at 604 nm.[24] Soft ligands such as thiolate shift the CT transition to lower-energy region.[24,25] Hanson et al. reported that $[Mo^VO(SC_6H_5)_4]^-$ have a strong absorption band at 598 nm. They assigned this band to an LMCT transition from sulfur ligands to Mo(V) ions from the following features: i) large extinction; ii) lower energy shift by electron-donating substituents on benzenethiolate ligand; iii) qualitative agreement with Jørgensen's theory.[26] A weak d–d transition in the oxomolybdenum(V) complexes, $[Mo^VO(S\text{-aryl})_4]^-$ is masked by the strong LMCT transition. Ellis et al. proposed that one-electron reduction of those oxomolybdenum(V) thiolato complexes causes a blue shift of the LMCT band to appear at the d–d transition

Table 3. Selected Bond Distances, Bond Angles, Torsion Angles, and Dihedral Angles of $(PPh_4)_2$-$[Mo^{IV}O(p\text{-}ClC_6H_4S)_4]$ (**1b**)

Bond distances/Å	
Mo–O	1.690(9)
Mo–S(1)	2.395(3)
Mo–S(3)	2.418(4)
Mo–S(3)	2.416(4)
Mo–S(4)	2.431(3)
Mean Mo–S	2.415
S(1)–C(111)	1.78(1)
S(2)–C(121)	1.78(1)
S(3)–C(131)	1.77(1)
S(4)–C(141)	1.77(1)
Bond angles/°	
S(1)–Mo–S(2)	85.0(1)
S(2)–Mo–S(3)	84.7(1)
S(3)–Mo–S(4)	83.1(1)
S(4)–Mo–S(1)	86.3(1)
S(1)–Mo–S(3)	140.6(1)
S(2)–Mo–S(4)	148.5(1)
O–Mo–S(1)	109.3(3)
O–Mo–S(2)	105.6(3)
O–Mo–S(3)	110.1(3)
O–Mo–S(4)	105.8(3)
Mo–S(1)–C(111)	116.9(4)
Mo–S(2)–C(121)	116.3(4)
Mo–S(3)–C(131)	114.1(5)
Mo–S(4)–C(141)	117.7(4)
Torsion angles/°	
O–Mo–S(1)–C(111)	86.9(6)
O–Mo–S(2)–C(121)	81.3(6)
O–Mo–S(3)–C(131)	74.6(6)
O–Mo–S(4)–C(141)	90.9(6)
Dihedral angles/°	
Mo–S(1)–C(111) and the phenyl ring	64.6(4)
Mo–S(2)–C(121) and the phenyl ring	35.0(4)
Mo–S(3)–C(131) and the phenyl ring	70.9(5)
Mo–S(4)–C(141) and the phenyl ring	69.9(4)

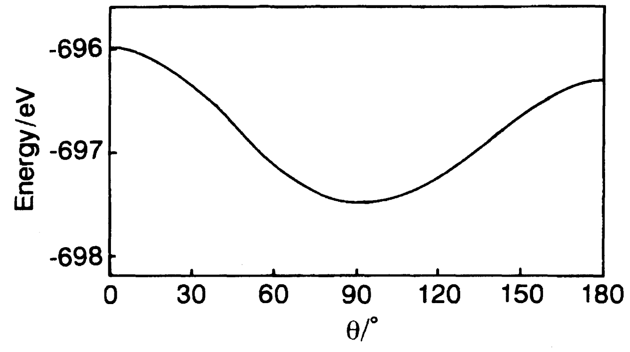

Fig. 3. Variation of the total energy of $[MoO(SH)_4]^{2-}$ with change in all O–Mo–S–H (θ) torsion angles.

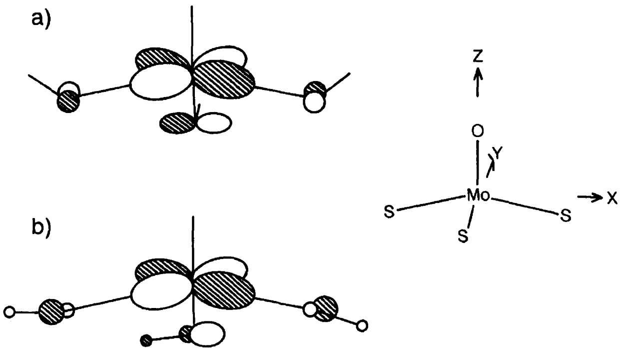

Fig. 4. Molecular orbitals of $[MoO(SH)_4]^{2-}$ a) at $\theta=0°$ and b) $\theta=90°$ in HOMO.

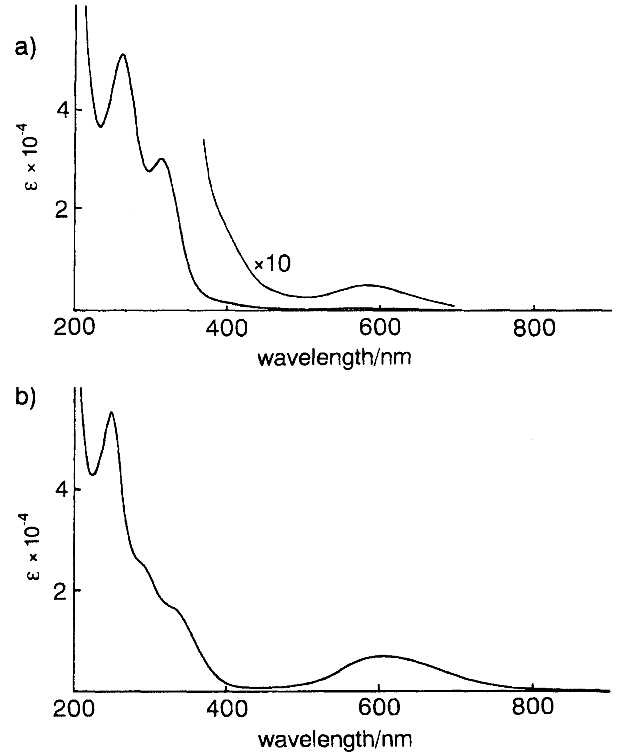

Fig. 5. Absorption spectra in MeCN of a) $(NEt_4)_2[Mo^{IV}O(p\text{-}ClC_6H_4S)_4]$ and b) $(NEt_4)[Mo^{V}O(p\text{-}ClC_6H_4S)_4]$.

region.12) The weak band at 588 nm near the LMCT region (604 nm) of **2** is thus assignable to a d_{xy}–d_{xz}, or d_{yz}, transition.

Raman spectra of **1a** and **2** showed ν(Mo=O) at 932 and 942 cm^{-1}, respectively. The difference (10 cm^{-1}) in ν(Mo=O) is not due to the structural change but due to the decrease of π-donation of O-pπ to Mo-dπ. Similar shift was observed between oxomolybdenum(IV and V) complexes having bdt or SC_6F_5 ligands. Thus, $[Mo^{IV}O(bdt)_2]^{2-}$ and $[Mo^{V}O(bdt)_2]^{-}$ show ν(Mo=O) stretching at 905 and 944 cm^{-1}, respectively.

^{1}H NMR (270 MHz) spectrum of **1** indicated diamagnetic d^2 configuration in MeCN-d_3. The proton signals of the benzene rings were observed as two doublets at 7.3 and 6.9 ppm ($J=8.3$ Hz), and the proton signals of counter cation, NEt_4^+, appeared at 3.1 (CH_2, q) and 1.1 ppm (CH_3, m). These proton chemical shifts of the p-chlorobenzenethiolate ligands were nearly the same with sodium p-chlorobenzenethiolate which has two doublets at 7.1 and 6.8 ppm.

1a (or **1b**) was found to be a useful starting material to produce various oxomolybdenum(IV) dithiolate complexes by a ligand exchange reaction because this complex was coordinated by only monodentate thiolate ligands. Similar methods have been developed for the syntheses of oxomolybdenum(V) dithiolate complexes, $[\mathrm{Mo^VO(bdt)_2}]^-$,[13] $[\mathrm{Mo^VO(edt)_2}]^-$,[7] and $[\mathrm{Mo^VO(\alpha\text{-tdt})_2}]^-$ (α-tdt=α'2-toluenedithiolato)[27] by a ligand exchange reaction between $[\mathrm{Mo^VO(SPh)_4}]^-$ and the corresponding dithiols. The details of these syntheses will be published elsewhere.

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