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Structure and Properties of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-toluenedithiolato})_2]$

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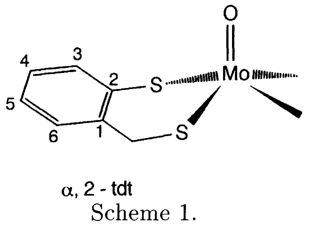
A novel oxomolybdenum(IV) complex, $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-toluenedithiolato})_2]$, was synthesized and characterized by visible, Raman and ^1H NMR spectroscopies. The complex crystallizes as $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-toluenedithiolato})_2]\cdot Et_2O$ in the space group *Cc* with $a=15.429(3)$, $b=16.618(2)$, $c=15.079(3)$ Å, $\beta=99.38(2)°$, $V=3815(2)$ Å^3, $Z=4$, and $D_{calcd}=1.315$ g cm^{-3}. The structure was solved and refinement based on 5975 reflections converged at $R=0.044$ and $R_w=0.052$. The complex has an apical oxo and *trans* bis(α,2-toluenedithiolato) structure with a tetragonal-pyramidal $MoOS_4$ core. Inertness of the complex to trimethylamine-*N*-oxide is due to the narrow S(alkane)–Mo–S(alkane) angle preventing from its coordination to the *trans* position of Mo=O, and/or two strong Mo–S(alkane) bonds preventing a rearrangement from *trans* dioxo to *cis* dioxo structure.

The molybdenum center of sulfite oxidase, trimethylamine-*N*-oxide and dimethylsulfoxide reductase has been considered to be bound to a bidentate dithiolene ligand connecting pterin and phosphate groups.[1—4] The EXAFS analyses of the reduced states have indicated that the molybdenum center has one or more Cys thiolate ligands besides the dithiolene ligand, which has been suggested to coordinate as a chelating dithiolene ligand to the Mo(IV) center.[5] The chemical properties of Mo(IV) thiolate complexes as a model of the reduced enzymes is still not clear.

The chemistry of monooxomolybdenum(V) thiolate complexes, e.g. $[Mo^VO(SPh)_4]^-$,[6] has been well established. Some monooxomolybdenum(IV) complexes having symmetrical dithiolate chelating ligands have been reported as the precursor model complexes for the reduced species of the active site of molybdoenzyme, e.g. $[Mo^{IV}O(SCH_2CH_2S)_2]^{2-}$,[7] $[Mo^{IV}O(bdt)_2]^{2-}$ (bdt=1, 2-benzenedithiolato),[8] $[Mo^{IV}O(S_2C_2(CO_2Me)_2)_2]^{2-}$,[9] $[Mo^{IV}O(SC_6H_4\text{-}p\text{-}Cl)_4]^{2-}$.[10] Novel model monooxomolybdenum(IV) complexes have been studied using a tridentate chelating ligand, e.g. sterically bulky tridentate monooxomolybdenum(IV) complexes,[11—13] and hydrotris(3,5-dimethyl-1-pyrazolyl)borate.[14,15]

The active center of sulfite oxidase and dimethylsulfoxide reductase has Mo(IV) species containing two or three thiolate ligands in the reduced state.[5] If the metal center has three thiolate ligands, one Cys thiolate besides two dithiolene sulfur ligands is involved. The complexation of two dithiolene-like ligands and two alkanethiolate to $(MoO)^{2+}$ ion in unsymmetrical dithiolate, α,2-toluenedithiolate (α,2-tdt), seems to furnish one of the relevant model complexes. Scheme 1 shows the structure of α,2-tdt ligand. Furthermore, the detailed structural comparison between Mo(V) and Mo(IV) complexes is of interest to obtain information on ligand addition process on tetragonal pyramidal complexes to an octahedral complexes associated with the number of thiolate ligands.



α, 2 - tdt

Scheme 1.

Experimental

All syntheses and physical measurements were performed under argon atmosphere. 1,2-dimethoxyethane (DME), acetonitrile, *N*,*N*-dimethylformamide (DMF), and diethyl ether were purified by distillation over calcium hydride under argon atmosphere before use. α,2-Toluenedithiol (α,2-tol-H_2) was prepared by the literature method.[16,17]

Synthesis of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$. The complex was synthesized by the ligand exchange method with $(NEt_4)_2[Mo^{IV}O(SC_6H_4\text{-}p\text{-}Cl)_4]$.[10]

A mixture of $(NEt_4)_2[Mo^{IV}O(SC_6H_4\text{-}p\text{-}Cl)_4]$ (1.1 g, 1.2 mmol) and α,2-toluenedithiol (0.37 g, 2.4 mmol) were stirred in 50 cm^3 of DME for 4 d at room temperature. A yellow-orange precipitate was collected with filtration and washed three times with 20 cm^3 of diethyl ether to remove free thiols, and dried in vacuo and dissolved in 35 cm^3 of acetonitrile. The solution was filtered and concentrated to 6 cm^3 volume under reduced pressure. Deep brown microcrystals were obtained by addition of 10 cm^3 of diethyl ether to the solution. The crude complex was recrystallized from acetonitrile/diethyl ether. Crystals contain one mole of diethylether per mol. Yield, 0.65 g (81%). The elemental analysis was carried out after removed diethyl ether under reduced pressure. Anal. Calcd for $C_{30}H_{52}N_2OMoS_4$: C, 52.92; H, 7.70; N, 4.11%. Found: C, 53.23; H, 8.02; N, 4.59%.

Reaction of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ with Dioxygen or Trimethylamine *N*-Oxide. To an acetonitrile solution (3 cm^3) of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ (0.057 g, 0.084 mmol) was added trimethylamine-*N*-oxide (8.7 mg, 0.11 mmol) with stirring vigorously at room temperature. The reaction was monitored by the change of ^1H NMR spectrum.

The reaction with dioxygen was carried out by bubbling dioxygen gas (27 cm^3, 0.0012 mmol) into an acetonitrile solution (0.6 cm^3) of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ (0.0012 mmol). The reaction was monitored by the characteristic absorption maxima of $(NEt_4)[Mo^VO(\alpha,2\text{-tdt})_2]$ using an absorption spectrophotometer.

Physical Measurements. Visible spectra were recorded in an acetonitrile solution of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ on a JASCO Ubest-30 spectrophotometer. Phase-sensitive 2D NOESY ^1H NMR spectra were measured on a JEOL JNM-GSX 400 spectrometer with 3.0 s mixing time determined by the T_1 measurements in acetonitrile-d_3 at 30 °C. A total of 8 FID's were recorded with the spectral range of 3333.3 Hz and the time domain of 512 data points. Raman spectrum was obtained on a JASCO R-800 spectrophotometer equipped with a HTV-R649 photomultiplier. A KBr disk sample sealed in a capillary was irradiated with a 514.5 nm argon laser excitation line. The frequency calibration of the spectrometer was carried out with the natural emission line of Ne lamp as a standard. Electrochemical measurements were carried out using a Yanaco P-1100 instrument in acetonitrile solution that contained 0.1 M tetrabutylammonium perchlorate ($1\ M=1\ mol\,dm^{-3}$) as a supporting electrolyte. $E_{1/2}$ value, determined as $(E_{p,a}+E_{p,c})/2$, was referenced to the SCE electrode at room temperature and a value uncorrected with junction potential was obtained. ESR spectra in DMF/acetonitrile (1/4 v/v) were recorded on a JEOL JES-FE1X spectrometer at room temperature and at ca. 80 K.

X-Ray Structure and Determination. A single crystal of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ was sealed in a glass capillary under argon atmosphere for the X-ray measurement.

X-ray measurement was performed at 23 °C on a Rigaku AFC5R diffractometer with graphite monochromated Mo $K\alpha$ radiation and a 12 kW rotating anode generator. Unit cell dimensions were refined with 25 reflections. Three standard reflections were chosen and monitored with every 100 reflections and did not show any significant change. The basic crystallographic parameters for $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ are listed in Table 1. An emperical absorption correction, based on azimuthal scans of three reflections, was applied which resulted in transmission factors ranging from 0.87 to 1.00 for the crystal. The structures were solved by the direct method using TEXSAN crystallographic software package. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed on the calculated positions. The final refinement was carried out using full-matrix least-squares techniques with non-hydrogen atoms. The refinement with anisotropic thermal parameters converged at $R=0.044$. Atom scattering factors and dispersion corrections were taken from the International Table.[18]

Results and Discussion

Synthesis. Only a few monooxomolybdenum(IV) thiolate complexes have been reported since methods for their direct synthesis are still limited. For example, $K_2[Mo^{IV}O(edt)_2]$ (edt=1,2-ethanedithiolato), $K_2[Mo^{IV}O(tdt)_2]$ (tdt = 3,4-toluenedithiolato), and $[Mo^{IV}O(\text{diethyldithiocarbamato})_2]$ were synthesized from the reaction between $K_4[Mo^{IV}O_2(CN)_4]$ and the corresponding ligands.[7] $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ (bdt = 1,2-benzenedithiolato) was also prepared by the above modified method.[8] Novel methods were adopted for the synthesis for $(NHEt_3)_2[Mo^{IV}O(SC_6F_5)_4]$ derived from $[Mo^{IV}OCl_2(PPh_2Me)_3]$ and $[Mo^{IV}O\{S_2C_2(CO_2Me)_2\}_2]^{2-}$ obtained from $[Mo^{IV}O(S_4)_2]^{2-}$.[9] Recently, $(NEt_4)_2[Mo^{IV}O(SC_6H_4\text{-}p\text{-}Cl)_4]$ has been isolated from $(NEt_4)[Mo^{V}O(SC_6H_4\text{-}p\text{-}Cl)_4]$[19] with a mild reductant, NEt_4BH_4, since the Mo(V) complex has a relatively positive-shifted redox potential due to the electron-withdrawing thiolate ligand.[10]

Table 1. Crystallographic Data for $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]\cdot Et_2O$

Chemical formula	$C_{34}H_{62}N_2O_2MoS_4$
Fw	755.08
Crystal system	Monoclinic
a/Å	15.429(3)
b/Å	16.618(2)
c/Å	15.079(3)
β/°	99.38(2)
V/Å^3	3815(2)
Z	4
Space group	*Cc*
t/°C	23
$D_{calcd}/g\,cm^{-3}$	1.315
Radiation	Mo $K\alpha$
$\mu(Mo\,K\alpha)/cm^{-1}$	5.7
$2\theta_{max}$/°	60.2
Scan type	ω–2θ
No. of reflections measured	5975
No. of observns with $I>3\sigma(I)$	3853
$R^{a)}$	0.044
$R_w{}^{b)}$	0.052

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

$(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ was synthesized from $(NEt_4)_2[Mo^{IV}O(SC_6H_4\text{-}p\text{-}Cl)_4]$ by the following ligand exchange method (Eq. 1).

$$(NEt_4)_2[Mo^{IV}O(SC_6H_4\text{-}p\text{-}Cl)_4] + 2\cdot\alpha,2\text{-tdt-}H_2 \longrightarrow (NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2] + 4\cdot HSC_6H_4\text{-}p\text{-}Cl \quad (1)$$

A direct synthesis of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ from $(NEt_4)[Mo^{V}O(\alpha,2\text{-tdt})_2]$ is unsuccessful since the Mo(V) complex has too negative Mo(IV)/Mo(V) redox potential (−0.73 V vs. SCE in acetonitrile)[20] to be reduced by a convenient reductant such as NEt_4BH_4. The successful synthesis was accomplished by the lower solubility of the product than that of the starting material during the ligand exchange reaction. From the above reaction only the *trans* isomer was obtained using unsymmetrical dithiolate ligands as that of $(NEt_4)[Mo^{V}O(\alpha,2\text{-tdt})_2]$.[20] The present Mo(IV) complex is thermally stable but extremely air sensitive.

Crystal Structure. The complex crystallizes in the space group *Cc* and contains four independent $[Mo^{IV}O(\alpha,2\text{-tdt})_2]^{2-}$ anions, eight cations, and four diethyl ether molecules in an unit cell. The ether molecule exists as a packing material in crystal. The perspective view of the $[Mo^{IV}O(\alpha,2\text{-tdt})_2]^{2-}$ anion having *trans* configuration for the two unsymmetrical dithiolate li-

Table 2. Atomic Coordinates of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]\cdot Et_2O$

Atom	x	y	z	$B(\mathrm{eq})/\text{Å}^2$
Mo(1)	0.0835	0.36648(2)	0.1653	3.01(2)
S(1)	−0.0649(1)	0.3282(1)	0.1000(1)	4.17(8)
S(2)	0.0552(1)	0.3154(1)	0.3040(1)	4.43(9)
S(3)	0.2329(1)	0.3297(1)	0.2309(1)	4.35(8)
S(4)	0.1042(1)	0.3099(1)	0.0261(1)	4.47(8)
O(1)	0.0817(8)	0.4679(2)	0.162(1)	4.1(2)
C(11)	−0.1361(5)	0.3524(4)	0.1706(6)	4.3(3)
C(12)	−0.2088(5)	0.3936(5)	0.1505(6)	4.6(3)
C(13)	−0.2672(5)	0.4073(5)	0.2165(7)	5.3(4)
C(14)	−0.2467(4)	0.3803(6)	0.3015(8)	7.6(6)
C(15)	−0.1760(6)	0.3334(6)	0.3280(8)	6.3(5)
C(16)	−0.1180(5)	0.3196(4)	0.2697(5)	3.9(3)
C(17)	−0.0467(5)	0.2679(4)	0.2992(5)	4.0(3)
C(21)	0.3090(5)	0.3490(4)	0.1498(5)	4.1(3)
C(22)	0.3836(6)	0.3998(6)	0.1912(9)	7.7(6)
C(23)	0.4486(6)	0.4195(7)	0.1449(8)	7.3(6)
C(24)	0.4393(6)	0.3830(6)	0.055(1)	7.7(6)
C(25)	0.3652(6)	0.3463(5)	0.0219(6)	5.5(4)
C(26)	0.3043(5)	0.3243(5)	0.0740(6)	4.9(4)
C(27)	0.2259(7)	0.2694(7)	0.0380(7)	7.4(6)
N(1)	0.4216(3)	0.1089(3)	0.2897(3)	3.2(2)
C(31)	0.3853(5)	0.1652(5)	0.3480(5)	4.6(4)
C(32)	0.2947(5)	0.1257(6)	0.3620(5)	5.7(4)
C(33)	0.4226(5)	0.0238(4)	0.3096(5)	4.4(3)
C(34)	0.4532(7)	0.0071(6)	0.4126(6)	6.0(4)
C(35)	0.5129(4)	0.1438(4)	0.2914(4)	3.5(3)
C(36)	0.5226(7)	0.2385(5)	0.2762(6)	5.9(4)
C(37)	0.3618(6)	0.1207(5)	0.1891(5)	5.4(4)
C(38)	0.4026(5)	0.0809(5)	0.1166(5)	4.8(4)
N(2)	0.2434(4)	0.3829(3)	0.5486(4)	3.6(2)
C(41)	0.1490(6)	0.3551(6)	0.5432(7)	6.1(5)
C(42)	0.1438(7)	0.2748(5)	0.5709(7)	6.3(5)
C(43)	0.2923(4)	0.3755(4)	0.6347(4)	3.6(3)
C(44)	0.2507(6)	0.4039(5)	0.7141(5)	5.6(4)
C(45)	0.2973(5)	0.3444(4)	0.4769(5)	3.5(3)
C(46)	0.3883(6)	0.3651(5)	0.4723(7)	5.3(4)
C(47)	0.2319(4)	0.4770(4)	0.5221(5)	3.7(3)
C(48)	0.2018(5)	0.4940(4)	0.4265(5)	3.6(3)
O(3)	0.119(1)	−0.076(1)	0.555(1)	8.1(4)
C(51)	0.103(2)	−0.030(2)	0.491(2)	10.2(7)
C(52)	0.062(4)	0.005(4)	0.379(5)	7(1)
C(53)	0.081(2)	−0.060(1)	0.602(2)	5.5(5)
C(54)	0.076(1)	−0.1133(7)	0.688(1)	7.0(3)

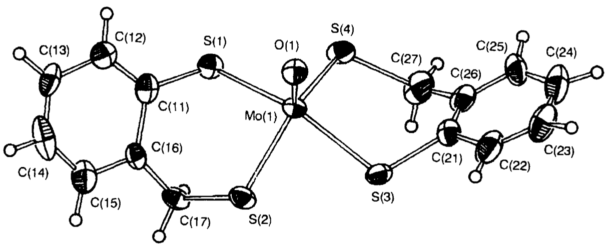


Fig. 1. Perspective view of $[Mo^{IV}O(\alpha,2\text{-tdt})_2]^{2-}$ anion showing the partial atom-labeling scheme.

gands is shown in Fig. 1. Table 2 lists the atomic coordinates of the non-hydrogen atoms and the estimated standard deviations. Selected bond distances and angles are listed in Table 3. The complex has an intermediate geometry between square-pyramidal and trigonal-bipyramidal with C_{2v} local symmetry. The ordinary $Mo^{IV}{=}O$ distance (1.686(4) Å) in $[Mo^{IV}O(\alpha,2\text{-tdt})_2]^{2-}$ is observed. The Mo^{IV}–S(alkanethiolate) distance is 2.366 Å (mean) similar to a mean distance (2.366 Å) for the Mo–S distance of $[Mo^{IV}O(SCH_2CH_2PPh_2)_2]$,[21] while the Mo^{IV}–S(arenethiolate) distance (2.430 Å) is longer than those of other Mo(IV) complexes.

The Mo=O distance of the Mo(IV) complex is similar to that of the corresponding Mo(V) complex, $(NEt_4)[Mo^VO(\alpha,2\text{-toluenedithiolato})_2]$, reported previously.[20] The same constancy of Mo(V)=O and Mo(IV)=O distances is also observed in $(NEt_4)[Mo^VO(S\text{-}o\text{-acetylamido-}C_6H_4)_4]$ and $(NEt_4)_2[Mo^{IV}O(S\text{-}o\text{-acetylamido-}C_6H_4)_4]$,[22] although the exceptional difference for those

Table 3. Selected Intramolecular Distances (Å) and Angles (deg) for $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-}tdt)_2]\cdot Et_2O$ Compared with Those of $(NEt_4)[Mo^{V}O(\alpha,2\text{-}tdt)_2]$[20)]

	$(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-}tdt)_2]\cdot Et_2O$	$(NEt_4)[Mo^{V}O(\alpha,2\text{-}tdt)_2]$
Distances (Å)		
Mo=O	1.686(4)	1.688(18)
Mo–S_1 (arenethiolato)	2.426(2)	2.406(7)
Mo–S_2 (alkanethiolato)	2.362(2)	2.368(7)
Mo–S_3 (arenethiolato)	2.433(2)	2.431(7)
Mo–S_4 (alkanethiolato)	2.369(2)	2.366(7)
Mean Mo–S (arenethiolato)	2.430	2.418
Mean Mo–S (alkanethiolato)	2.366	2.368
S_1–C_{11}	1.699(9)	1.771(23)
S_2–C_{17}	1.750(8)	1.881(27)
S_3–C_{21}	1.857(9)	1.811(26)
S_4–C_{27}	1.98(1)	1.881(24)
Angles (degree)		
S_1–Mo–S_2	88.10(7)	89.93(23)
S_2–Mo–S_3	81.37(7)	79.74(23)
S_3–Mo–S_4	90.29(7)	89.28(23)
S_4–Mo–S_1	77.91(7)	78.75(23)
S_1–Mo–S_3	150.28(7)	150.10(24)
S_2–Mo–S_4	135.46(7)	136.15(23)
O–Mo–S_1	103.9(4)	105.(34)
O–Mo–S_2	112.3(5)	112.92(64)
O–Mo–S_3	115.8(4)	104.53(64)
O–Mo–S_4	112.1(5)	110.92(64)
Mo–S_1–C_{11}	110.3(3)	
Mo–S_2–C_{17}	114.9(2)	
Mo–S_3–C_{21}	110.4(2)	
Mo–S_4–C_{27}	108.6(3)	
Torsion angles (degree)		
O–Mo–S_1–C_{11}	−69.9(6)	
O–Mo–S_2–C_{17}	109.5(5)	
O–Mo–S_3–C_{21}	−72.2(6)	
O–Mo–S_4–C_{27}	105.4(6)	
C_{15}–C_{16}–C_{17}–H_5	120.9	
C_{15}–C_{16}–C_{17}–H_6	2.1	
C_{11}–C_{16}–C_{17}–H_5	−52.5	
C_{11}–C_{16}–C_{17}–H_6	−171.4	
C_{25}–C_{26}–C_{27}–H_{11}	123.3	
C_{25}–C_{26}–C_{27}–H_{12}	8.7	
C_{21}–C_{26}–C_{27}–H_{11}	−58.4	
C_{21}–C_{26}–C_{27}–H_{12}	−173.0	
Displacement of Mo from S_4 plane (Å)	0.752	

between $(NEt_4)[Mo^{V}O(bdt)_2]$ and $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ has been reported.[8,23)] Thus, upon one-electron reduction from Mo(V) to Mo(IV), the Mo=O bonding does not change largely since the d_{xy} orbital sharing the electron is not influenced by the pπ-orbital of the O atom. Two electrons occupy the d_{xy} orbital in the low spin Mo(IV) state.[24)]

The Mo–S(arenethiolate) bond distance of $[Mo^{IV}O(\alpha,2\text{-}tdt)_2]^{2-}$ is longer than those of $[Mo^{V}O(\alpha,2\text{-}tdt)_2]^{-}$.[20)] The reduction to Mo(IV) results in elongation of the Mo–S bonds due to an antibonding HOMO between Mo(IV) d_{xy} and sulfur pπ orbitals. The Mo–S (arenethiolato) bond distance is longer than that of Mo–S (alkanethiolato) indicative of the stronger Mo–S (alkanethiolato) bonding. The conjugation of sulfur pπ and phenyl ring pπ orbitals weakens the π-interaction between Mo(IV) and sulfur. The angle, S_2(alkanethiolato)–Mo–S_4(alkanethiolato), is 135.46(7)° slightly smaller than 136.15(23)° in $[Mo^{V}O(\alpha,2\text{-}tdt)_2]^{-}$. The large deviation from 180° reflects a strong π-bonding of Mo–S as reported previously in the EHMO calculations of $[Mo^{V}O(\alpha,2\text{-}tdt)_2]^{-}$.[20)] The angle, S_1(arenethiolato)–Mo–S_3(arenethiolato), is 150.28(7)° which is similar to 150.10(24)° in $[Mo^{V}O(\alpha,2\text{-}tdt)_2]^{-}$. Actually, $[Mo^{IV}O(SC_6H_4\text{-}p\text{-}Cl)_4]^{2-}$ has two wide S–Mo–S angles (S_1–Mo–S_3 140.6(1)°, S_2–Mo–S_4 148.5(2)°) due to sole presence of arenethiolate ligands.[10] Other Mo(IV) complexes having chelating ligands, e.g. $[\mathrm{Mo^{IV}O(bdt)_2}]^{2-}$ and $[\mathrm{Mo^{IV}O(S_2CNPr^n_2)_2}]$ have relatively wide S–Mo–S angles (143.7°[8]) and 140°,[25]) respectively).

The above distortion in the Mo(IV) state has been found for $[\mathrm{Mo^{IV}O(SCH_2CH_2PPh_2)_2}]$[26]) and $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}$(S-*o*-acetylamido-$\mathrm{C_6H_4})_4]$.[22]) On the contrary, $[\mathrm{Mo^{IV}O(S_2CNPr^n_2)_2}]$ exhibits a local square-pyramidal structure having longer Mo–S bonds since one sulfur atom of the dithiocarbamate ligands serves as thioketone for the coordination.[25]) However, our results indicate that the long Mo–S(arenethiolato) bond distance of $[\mathrm{Mo^{IV}O}(\alpha,2\text{-tdt})_2]^{2-}$ as those (2.45 — 2.55 Å) of the dithiocarbamatomolybdenum(IV) complexes[25]) is ascribed to the variation of Mo–S π-bonding perturbed by the π-conjugation between sulfur and benzene ring, due to differences in the sulfur hybridization.

The short Mo–S(alkanethiolate) bond distance (mean 2.366 Å) is reasonable as the Mo–S (alkanethiolato) distance (mean 2.360 Å) as reported for $[\mathrm{Mo^{IV}O(SCH_2CH_2PPh_2)_2}]$.[26]) The strong π-interaction between Mo and sulfur atoms contributes to the short Mo–S (alkanethiolato) bond in the low energy MO levels although the doubly occupied HOMO antibonding with Mo d_{xy} and sulfur pπ-orbitals.

Electronic Spectrum of $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(\alpha,2\text{-tdt})_2]$. Figure 2 shows the UV-visible absorption spectra of $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(\alpha,2\text{-tdt})_2]$ and, for the comparison, $(\mathrm{NEt_4})[\mathrm{Mo^{V}O}(\alpha,2\text{-tdt})_2]$ in acetonitrile. Four distinct absorption maxima were observed at 250 (37700 $\mathrm{M^{-1}\,cm^{-1}}$), 287 (20700), 384 (5520), and 590 nm (370) in $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(\alpha,2\text{-tdt})_2]$. The weak maximum at 590 nm is assignable to d–d transition as those at 552 nm for $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}$(S-*o*-acetylamido-$\mathrm{C_6H_4})_4]$ in acetonitrile.[22]) The presence of the weak d–d transition band overlapping with a strong LMCT band at this region has been predicted by the detailed analysis of the electronic spectra of various Mo(V) benzenethiolate complexes.[6,19]) Furthermore, the presence of only weak d–d band of the Mo(IV) complex at 590 nm confirms that the four intense visible maxima of $(\mathrm{NEt_4})[\mathrm{Mo^{V}O}(\alpha,2\text{-tdt})_2]$ observed at 454, 520, 600, and 720 nm are ascribed to LMCT bands from sulfur p orbital to Mo d_{yz} or d_{zx} orbital.

Solution Structure of $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(\alpha,2\text{-tdt})_2]$ Determined by ^{1}H NMR Spectrum. The ^{1}H NMR signals of methylene protons, $\mathrm{CH_AH_B}$, in $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(\alpha,2\text{-tdt})_2]$ were observed separately with a doublet at 2.59 and 3.92 ppm ($J_\mathrm{gem}=10.8$ Hz) in acetonitrile-d_3 and Fig. 3 shows the NOESY spectrum. These clear spectra were obtained by the addition of tetraethylammonium tetrahydroborate (1%) to remove a small amount of paramagnetic $[\mathrm{Mo^{V}O}(\alpha,2\text{-tdt})_2]^-$ species which is responsible for the broadness of ^{1}H signals with fast electron exchange between the Mo(V) and Mo(IV) complexes. All of the assignable benzene ring protons are observed at $\delta=7.33$ (d) for 3-position, 6.80 (t) for 4-position, 6.89 (t) for 5-position, and 6.98 (d) for 6-position. Two possible explanations are considered for the origin of the difference in the chemical shift between $\mathrm{H_A}$ and $\mathrm{H_B}$. One is the different shielding for them by Mo=O group which influences like the ketonic double bonding or the alkyne triple bonding as has been recently discussed.[27]) Another is the shielding from the benzene ring of α,2-tol ligand. The results of NOE between 6-position H and $\mathrm{CH_B}$ ($\delta=3.92$) support the significance of the shielding of $\mathrm{CH_A}$ ($\delta=2.59$) by the benzene ring as shown in the Scheme 2.

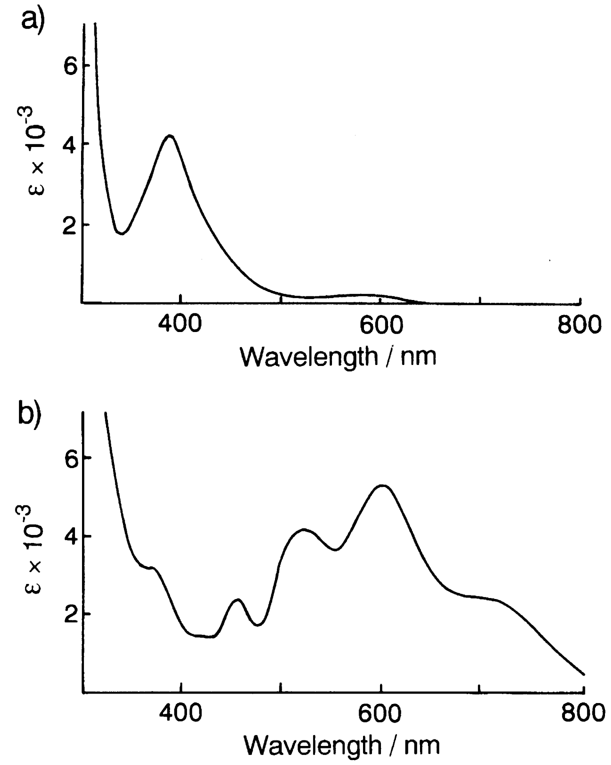


Fig. 2. UV-visible absorption spectra of a) $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(\alpha,2\text{-tdt})_2$ and b) $(\mathrm{NEt_4})[\mathrm{Mo^{V}O}(\alpha,2\text{-tdt})_2]$ in acetonitrile at 23 °C. Conditions; concentration, 1.0 mM.

No temperature dependence was observed in the range of −40—40 °C, indicative of a rigid structure of the six-membered chelating ring in $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(\alpha,2\text{-tdt})_2]$. Actually, the crystallographic data of the complex in solid state show the different environments for the two protons as one proton locates at torsion angle, 52.5° or 58.4°, of C(17)–C(16) from the benzene plane and then another proton locates at 2.1° or 8.7° from the benzene plane. H–H distances between 6-position H and $\mathrm{CH_A}$ ($\delta=2.59$) and $\mathrm{CH_B}$ ($\delta=3.92$ ppm) are approximately 3.4 and 2.3 Å, respectively.

Raman Spectrum of $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(\alpha,2\text{-tdt})_2]$ in Solid State. Figure 4 shows the Raman spectrum of $(\mathrm{NEt_4})_2[\mathrm{Mo^{IV}O}(\alpha,2\text{-tdt})_2]$ in solid state. The spectrum of the Mo(IV) complex is compared with that of $(\mathrm{NEt_4})[\mathrm{Mo^{V}O}(\alpha,2\text{-tdt})_2]$. The ν(Mo=O) stretching (940 $\mathrm{cm^{-1}}$) of Mo(V) complex shifts to 922

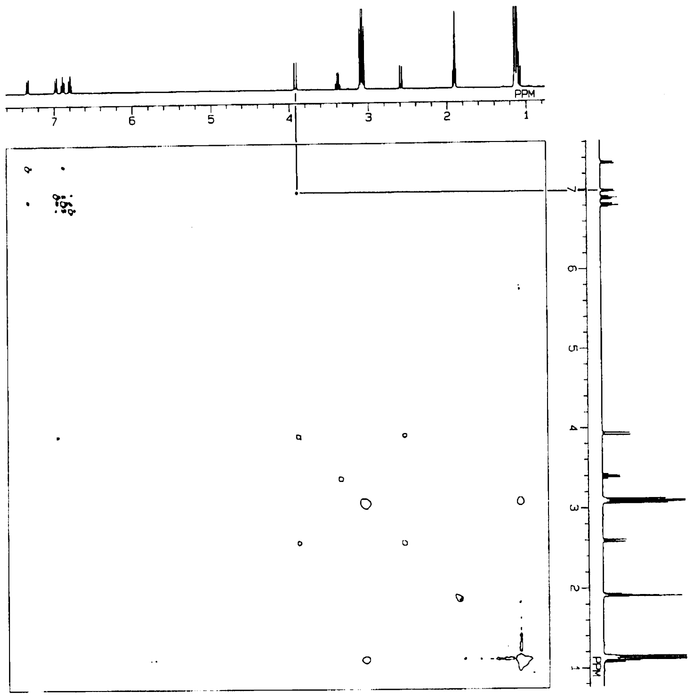


Fig. 3. ^1H-^1H-NOESY spectrum of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ in acetonitrile-d_3. Multiple signals at $\delta=3.39$ (CH_2, q) and 1.02 (CH_3, t) are due to concomitant diethyl ether. The signals for Et_4N^+ were observed at $\delta=3.09$ and 1.03.

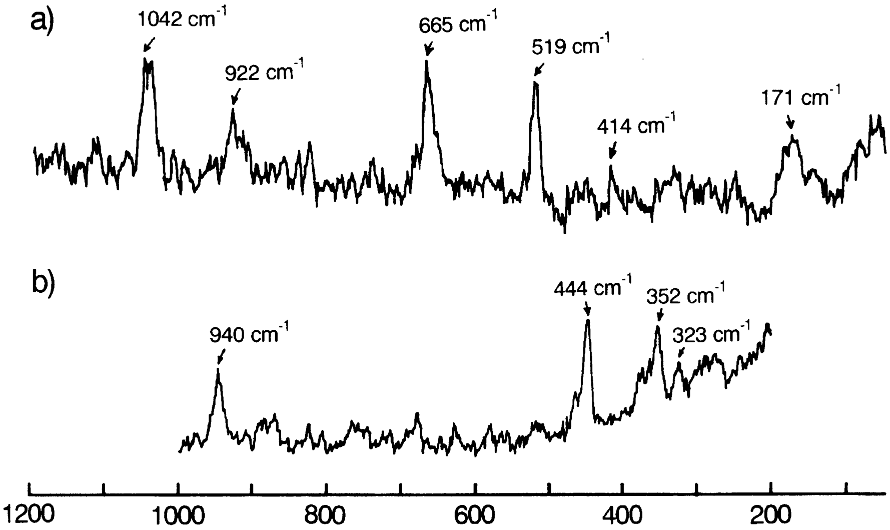
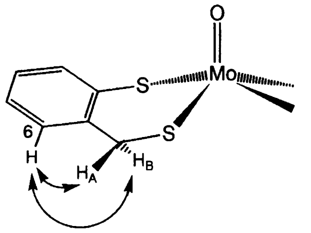


Fig. 4. Resonance Raman spectra of a) $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ and b) $(NEt_4)[Mo^{V}O(\alpha,2\text{-tdt})_2]$ in solid state.



Scheme 2.

cm^{-1} in the Mo(IV) complex. The relatively large shift (18 cm^{-1}) is similar to the IR shift (39 cm^{-1}) of ν(Mo=O) bands (905 and 944 cm^{-1}) in $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ and $(PPh_4)[Mo^{V}O(bdt)_2]$, respectively.[8] On the contrary, no shift between $(NEt_4)_2[Mo^{IV}O(S\text{-}o\text{-acetylamido-}C_6H_4)_4]$ and $(NEt_4)[Mo^{V}O(S\text{-}o\text{-acetylamido-}C_6H_4)_4]$ was observed as shown in the previous paper.[22] The Raman results of the Mo(IV) and Mo(V) complexes in the solid state indicate the large shift (18 cm^{-1}) of ν(Mo=O) although both complexes have almost the same Mo=O bond distances as shown the crystallographic data. On the basis of the isostructural parameters for the both Mo(IV) and Mo(V) complexes, the shift of ν(Mo=O) is caused by not only the change of

Mo=O bond character but also the geometry of $MoOS_4$ core. The trend is definitely different from those for $(NEt_4)[Mo^{V}O(bdt)_2]$ and $(NEt_4)_2[Mo^{IV}O(bdt)_2]$.

Electrochemical Property. Figure 5 shows the cyclic voltammogram of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ which exhibits a quasi-reversible redox couple of Mo(V)/Mo(IV) at −0.74 V vs. SCE ($i_{pa}/i_{pc}=0.98$) in acetonitrile. The redox value is almost the same as that (−0.73 V vs. SCE) of the corresponding $(NEt_4)[Mo^{V}O(\alpha,2\text{-tdt})_2]$ in acetonitrile[20] and is approximately middle between the values (−0.35 V vs. SCE and −1.18 V vs. SCE) of $(NEt_4)[Mo^{V}O(bdt)_2]$ in DMF[8] and $(NEt_4)[Mo^{V}O(SCH_2CH_2CH_2S)_2]$ in acetonitrile,[28] respectively.

Chemical Reactivity. The Mo(IV) complex in acetonitrile solution readily reacts with dioxygen and gives a dark blue solution. The product was identified as $(NEt_4)[Mo^{V}O(\alpha,2\text{-tdt})_2]$ by the observations of four intense visible maxima at 454, 520, 600, and 720 nm and of an ESR signal at $g_1=2.035$, $g_2=1.980$, and $g_3=1.976$ in acetonitrile/DMF (4/1 v/v) at 80 K which are the same as those reported for $(NEt_4)[Mo^{V}O(\alpha,2\text{-tdt})_2]$.[20] One electron transfer occurs between $[Mo^{IV}O(\alpha,2\text{-tdt})_2]^{2-}$ and dioxygen to produce superoxide anion as shown in the Eq. 2 because the complex has a suitable redox couple at −0.74 V vs. SCE.

$$[Mo^{IV}O(\alpha,2\text{-tdt})_2]^{2-} + O_2 \longrightarrow [Mo^{V}O(\alpha,2\text{-tdt})_2]^{-} + O_2^{-\bullet} \qquad (2)$$

This reaction commonly occurs for the Mo(IV) complex having many thiolate ligands, e.g. $K_2[Mo^{IV}O(SCH_2CH_2S)_2]$,[7] $[Mo^{IV}O(S_2CNEt_2)_2]$.[7,29]

Interestingly, $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ is inert to trimethylamine-*N*-oxide in acetonitrile at 30 °C, although the oxidant reacts slowly with $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ to give a dioxomolybdenum(VI) complex, $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$.[30] In general, monooxomolybdenum(IV) complexes having (S, N) or (S, S(thioketone)) ligand reacts readily with amine-*N*-oxide to give the corresponding dioxomolybdenum(VI) complexes because of its negative redox potential.[29] $[Mo^{IV}O(S_2CNEt_2)_2]$ also easily reacts with the oxidant and gives oxo-transfer product, $[Mo^{VI}O_2(S_2CNEt_2)_2]$.

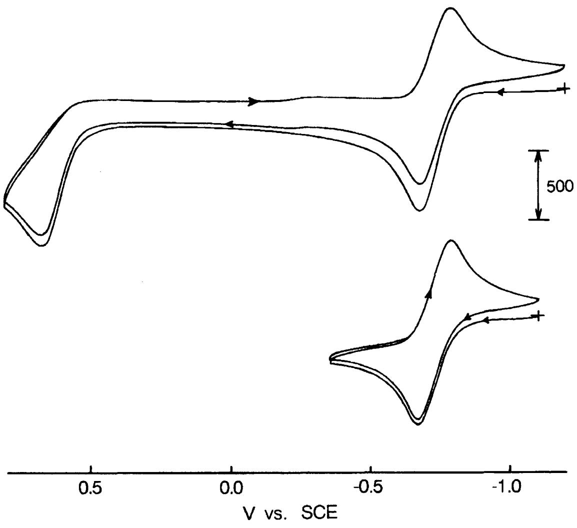
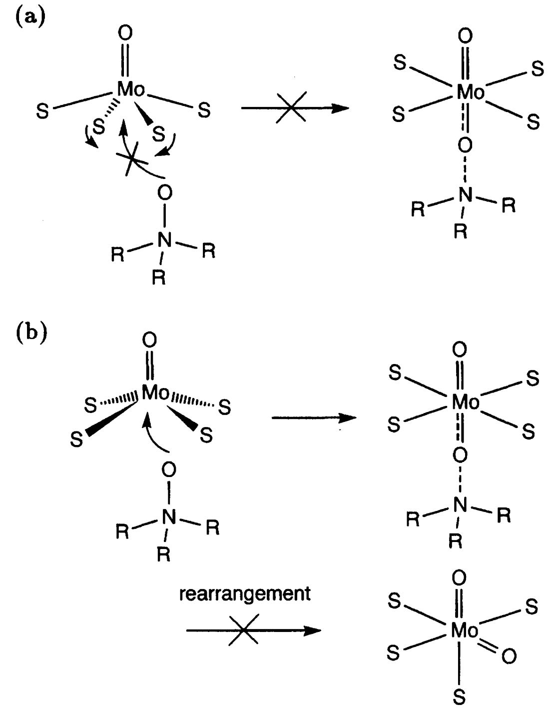


Fig. 5. Cyclic voltammogram of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ in acetonitrile at 23 °C. Conditions: concentration, [Mo(IV)], 2.0 mM; $[(n\text{-}Bu)_4NClO_4]$, 100 mM; scanning rate, 100 $mV\,s^{-1}$.

The inertness is attributed to the following two possibilities. One is the absence of the coordination of amine-*N*-oxide to the position of $[Mo^{IV}O(\alpha,2\text{-tdt})_2]^{2-}$ *trans* to Mo=O due to the narrow S(alkanethiolato)–Mo–S(alkanethiolato) angle as shown in Scheme 3a. Second is the slow rearrangement after coordination of amine-*N*-oxide. The two strong Mo–S(alkanethiolate) bonds in $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ prevent the complex from the interconversion of *trans* dioxo to *cis* dioxo since the formation of the *Oh* structure requires dissociation of Mo–S bond in the Mo(IV) complex having chelating ligands as shown in the Scheme 3b. The wide S–Mo–S(*trans*) angles of $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ and $[Mo^{IV}O(S_2CNPr^n_2)_2]$ as described before promote the rapid rearrangement to dioxomolybdenum(VI) complex since both complexes have weak, dissociative Mo–S bonds with π-conjugation between sulfur and benzene ring additionally.

Thus, although $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ has an ordinary square-pyramidal structure and relatively negative redox potential in acetonitrile, it is not oxidized by trimethylamine-*N*-oxide. A small amount of $[Mo^{V}O(\alpha,2\text{-tdt})_2]^{-}$ species is obtained in the reaction with di-



Scheme 3.

oxygen as other monooxomolybdenum(IV) complexes.

Holm et al. have studied on the reaction of $[Mo^{IV}O(LNS_2)(dmf)]$ (LNS_2 = 2,6-bis(2,2-diphenyl-2-mercaptoethyl)pyridine(2−); dmf = *N*,*N*-dimethylformamide) having a labile coordination site for a substrate, e.g. dimethylsulfoxide or nitrate ion and proposed the existence of a complex of Mo(IV) and substrate as an intermediate.[31,32] On the contrary, Enemark et al. have reported a dissociation mechanism for the reaction of $[HB(Me_2pz)_3]Mo^{IV}O[S_2P(OEt)_2]$ with dimethyl sulfoxide.[24] The *Oh* structure of the complex has no accessible site for the coordination of substrate.

The inertness of $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ against oxidant is unexpected since a negative redox potential causes high reductive reactivity. Furthermore, the formation of $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ from the oxidation of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ by trimethylamine-*N*-oxide has suggested the addition of the oxidant *trans* to Mo=O in the square-pyramidal Mo(IV) complex.[33] Thus, it is likely that the narrow S–Mo–S angle prevents the coordination of substrate.

Our results still remain a possibility of crucial coordination of substrate to a vacant site even if the active site of Mo(IV) in Mo-oxidases has at least three thiolate ligands. Also the presence of an evaluated mechanism can be considered for the oxidation by substrate in biological systems. For example, a fast reaction proceeds between $[Mo^{IV}O(S_2CNEt_2)_2]$ and substrate probably using a fast rearrangement by small S–Mo–S bite angles. Further study on the reactivity is in progress.

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