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Mononuclear Five-Coordinate Molybdenum(IV) and -(V) Monosulfide Complexes Coordinated with Dithiolene Ligands: Reversible Redox of Mo(V)/Mo(IV) and Irreversible Dimerization of $[Mo^{V}S]^{-}$ Cores to a Dinuclear $[Mo^{V}_{2}(\mu\text{-}S)_{2}]^{2-}$ Core

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A mononuclear five-coordinate molybdenum(IV) monosulfide complex, $(Et_4N)_2[MoS(L)_2]$ (L = cyclohexene-1,2-dithiolate) (**1**), was obtained and characterized by IR, UV–vis spectroscopic methods, and X-ray crystallography. **1** was oxidized by an equivalent ferrocenium cation to give the corresponding mononuclear molybdenum(V) complex, $(Et_4N)[MoS(L)_2]$ (**2**), which was stable for a few minutes under a lower concentration than 0.3 mM and then further dimerized to $(Et_4N)_2[Mo(L)_2]_2(\mu\text{-}S)_2$ (**3**).

One of the most challenging problems in molybdenum complex chemistry is the addition of a terminal sulfide group to a molybdenum atom because molybdenum(IV) and -(V) monosulfide complexes play key roles in industrial hydrogenation and hydrodesulfurization.[1,2] Furthermore, mononuclear molybdenum(IV) and -(V) monosulfide complexes with low coordination numbers are involved in catalytic cycles occurring at active sites of the xanthine oxidase family.[3] Although much effort has been devoted to preparing mononuclear molybdenum(IV) and -(V) monosulfide complexes,[4,5] most of the attempts were unsuccessful, and therefore examples of mononuclear molybdenum(IV) and -(V) monosulfide complexes are still limited. This is because redox and hydrolysis reactions cause structural changes of the molybdenum monosulfide complexes to yield polynuclear molybdenum−sulfur clusters.[6]

Young's and Enemark's groups have prepared a series of $[\{HB(Me_2pz)_3\}MoS(S_2CNR_2)]$ (R = Me, Et, ^{n}Pr, and ^{n}Bu) as mononuclear six-coordinate molybdenum(IV) complexes, a series of $[\{HB(Me_2pz)_3\}MoS(L)_n]$ ($n = 2$, L = Cl, OPh, etp, and pp; $n = 1$, L = cat, bdt, and tdt) as mononuclear six-coordinate molybdenum(V) monosulfide complexes, and $[HB(3\text{-}^{i}Prpz)_2(5\text{-}^{i}Prpz)MoS(S_2PR_2)]^{+/0}$ (R = ^{i}Pr and Ph) as a set of mononuclear six-coordinate molybdenum(IV) and -(V) monosulfide complexes, in which sterically hindered tridentate ligands effectively avoided polymerization.[7,8] On the other hand, only two examples, $[MoS(S_4)_2]^{2-}$ and $[MoS(CS_4)_2]^{2-}$, have so far been reported as mononuclear five-coordinate molybdenum(IV) monosulfide complexes.[9,10] Unfortunately, oxidation of the former complex did not yield $[MoS(S_4)_2]^{-}$ but gave a dinuclear $\{[(S_4)MoS]_2(\mu\text{-}S)_2\}^{2-}$ complex.[10−12] Thus, there is no example of a set of mononuclear five-coordinate molybdenum(IV) and -(V) monosulfide complexes.

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(8) Abbreviations of ligands: $HB(Me_2pz)_3$ = hydrotris(3,5-dimethylpyrazo1-1-yl)borate; $HB(3\text{-}^{i}Prpz)_2(5\text{-}^{i}Prpz)$ = hydrobis(3-isopropylpyrazo1-1-yl)(5-isopropylpyrazol-1-yl)borate; etp = 2-(ethylthio)-phenolate; pp = 2-(n-propyl)phenolate; cat = benzene-1,2-diolate; bdt = benzene-1,2-dithiolate; tdt = 4-methylbenzene-1,2-dithiolate; $S_2P^{i}Pr_2$ = diisopropyldithiophosphinate; S_2PPh_2 = diphenyldithiophosphinate; $S_2C_2Me_2$ = 1,2-dimethylethylene-1,2-dithiolate; $S_2C_2(CO_2Me)_2$ = 1,2-dicarbomethoxy-1,2-ethylenedithiolate.

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(12) $[(CS_4)MoS]_2(\mu\text{-}S)_2$ was obtained by a reaction of $\{[(S_4)MoS]_2(\mu\text{-}S)_2\}^{2-}$ with CS_2.[9]

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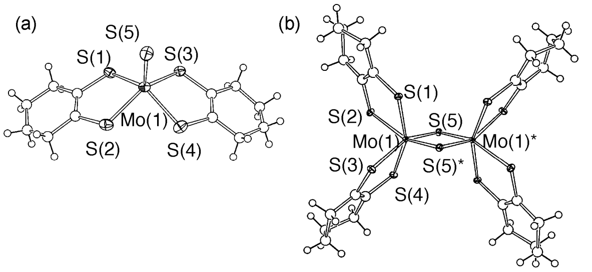


Figure 1. Crystal structures of anions of **1** and **3**−PPh_4.

Recently, we characterized high-valent mono-oxo molybdenum(VI), -(V), and -(IV), $[MoO(L)_2]^{0/-/2-}$ complexes (L = cyclohexene-1,2-dithiolate),[13] in which the aliphatic dithiolene ligands decreased the acidities of these molybdenum centers to stabilize these five-coordinate structures. Thus, it is expected that the five-coordinate molybdenum(IV) and -(V) monosulfide structures also are stabilized by the coordination of the aliphatic dithiolene ligand, L, to molybdenum centers, preventing the formation of six-coordinate structures. Here, we report the preparations and characterizations of a set of $(Et_4N)_2[MoS(L)_2]$ (**1**) and $(Et_4N)[MoS(L)_2]$ (**2**) complexes. The kinetics involved in the dimerization of **2** to $(Et_4N)_2[Mo(L)_2]_2(\mu\text{-}S)_2$ (**3**) are further discussed. Although dinuclear complexes of $(Et_4N)_2[Mo(S_2C_2Me_2)_2]_2(\mu\text{-}S)_2$ and $(Ph_4P)_2[Mo(S_2C_2(CO_2Me)_2)_2](\mu\text{-}S)_2$ have been previously characterized,[11,14] the dimerization mechanism and the intermediates involved in the dimerization have not been reported.

Treatment of $[Mo(CO)_2(L)_2]$[13] (L= cyclohexene-1,2-dithiolate) with 10 equiv of Na_2S in acetonitrile produced a green suspension. After the addition of Et_4NCl, Na_2S was removed by filtration. The solution was evaporated to dryness to obtain a green powder of **1**, which was recrystallized from acetonitrile/diethyl ether. Figure 1a shows the crystal structure of the anion in **1**. The molybdenum center is coordinated with one terminal sulfide and four sulfur atoms from two employed dithiolene ligands and adopts a square-pyramidal structure. The molybdenum atom is raised above the basal plane by 0.79 Å. The Mo(1)═S(5) distance (2.167(2) Å) is somewhat longer than those in $[MoS(S_4)_2]^{2-}$ (2.128(1) Å)[9] and $[MoS(CS_4)_2]^{2-}$ (2.126(3) Å),[10] and the value of the ν(Mo═S) stretching band of **1** (480 cm^{-1}) is lower than that of $[MoS(S_4)_2]^{2-}$ (525 cm^{-1}).[9] These comparisons indicate that the Mo═S bond of **1** is weaker than those of the above two complexes. Probably the strong electron-donating nature of the employed dithiolene ligand to the Mo center decreased S(terminal) → Mo electron donation.

1 exhibited remarkable electrochemical behavior. Within the cyclic voltammetry time scale, a reversible Mo(V)/Mo(IV) couple was observed at −0.75 V (vs SCE) in acetonitrile (Figure 2). Because, in contrast, five-coordinate $[MoS(S_4)_4]^{2-}$ and $[MoS(CS_4)_2]^{2-}$ produced irreversible oxidation waves,[9,10] the Mo(V) state can be stabilized by strong electron donation from the dithiolene ligand to the Mo center in the case of **1**.

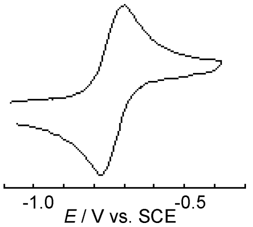
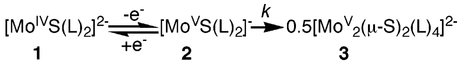


Figure 2. Cyclic voltammogram of $[MoS(L)_2]^{2-}$ (**1**): 1.0 mM of the complex in CH_3CN containing 0.1 M $TBAPF_6$; scan rate = 0.1 V s^{-1}.

Scheme 1



$$\underset{\mathbf{1}}{[Mo^{IV}S(L)_2]^{2-}} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \underset{\mathbf{2}}{[Mo^{V}S(L)_2]^{-}} \xrightarrow{k} \underset{\mathbf{3}}{0.5[Mo^{V}_2(\mu\text{-}S)_2(L)_4]^{2-}}$$

The reversible Mo(V)/Mo(IV) couple of **1** enabled us to observe the formation of the one-electron-oxidation product. By treatment with equivalent ferrocenium, **1** gave pink species that exhibited a strong absorption band centered at 760 nm. Furthermore, an aspect of the absorption spectrum is similar to those of $[MoO(L)_2]^-$ (**4**)[13] and $[\{HB(Me_2pz)_3\}MoSL]$ (L = Cl_2 and bdt, bdt = 1,2-benzenedithiolate).[7b,c] The ν(Mo═S) stretching band shifted from 480 to 495 cm^{-1} by oxidation. The observed value of the ν(Mo═S) stretching band (495 cm^{-1}) is also comparable to those of $[\{HB(Me_2pz)_3\}MoSL]$ (523 cm^{-1} for L = Cl_2 and 499 cm^{-1} for bdt).[7b,c] The electrospray ionization mass spectrum **(**ESIMS**)** of the oxidized complex measured in acetonitrile indicated only a peak cluster corresponding to a formula of $[MoS(L)_2]^-$ (Figure S1 in the Supporting Information).[15] Although **1** was ESR-silent, the pink complex showed ESR signals with a characteristic pattern of Mo(V) species at room temperature (Figure S2 in the Supporting Information). These results revealed that the pink species formed upon oxidation is a mononuclear five-coordinate molybdenum(V) monosulfide complex, **2**.[16]

2 generated in situ in acetonitrile was stable for a few minutes under a lower concentration than 0.3 mM, and then its pink solution changed to a deep-blue one. A result of ESIMS measurement of the deep-blue solution indicated the formation of a dinuclear species, **3**. Because a crystal structure of $(Ph_4P)_2[Mo(L)_2]_2(\mu\text{-}S)_2$ (**3**−PPh_4) was successfully determined, **2** turned out to gradually dimerize to **3** (Scheme 1). As illusrated in Figure 1b, **3** has two molybdenum centers bridged by two sulfur atoms, which are equivalent by an inversion center. Similar distorted octahedral structures were reported in $(Ph_4P)_2[Mo(S_2C_2(R)_2)_2]_2(\mu\text{-}S)_2$ (R = Me and CO_2Me) complexes.[11,14] Figure 3 shows the time-dependent spectral changes of **2** generated by the reaction of **1** with a ferrocenium cation. As the dimerization proceeded, the absorption band at 346 nm decreased in intensity and three absorption bands gradually increased at 460, 582, and 724 nm, which are characteristic bands of **3**. The half-life, $t_{1/2}$, value was inversely proportional to the initial concentration of **2**. These results indicate that the dimerization proceeded via second-order kinetics. As shown in the

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(15) ESIMS of **1** in acetonitrile gave a peak cluster of $\{[MoS(L)_2]^{2-} + Et_4N^+\}^-$.

(16) We have attempted to isolate **2** as a crystal but found that it was stable only for a few minutes.

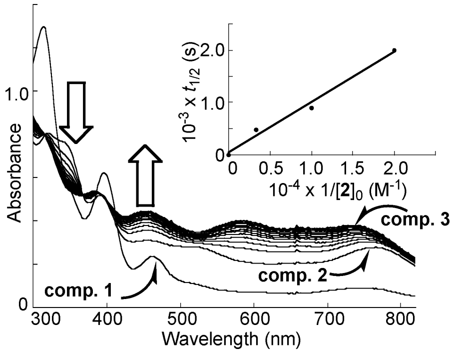

Figure 3. Spectral changes (720-s interval) observed upon the addition of ferrocenium (0.1 mM) into an acetonitrile solution of **1** (0.1 mM) at 25 °C under Ar. (inset) Plot of $t_{1/2}$ vs $1/[\mathbf{2}]_0$ ($=[\mathbf{1}]_0$).

inset of Figure 3, the second-order rate constant k was obtained as the reciprocal of the slope of the plot $t_{1/2}$ vs $1/[\mathbf{2}]_0$ ($k = 12 \pm 3$ M^{-1} s^{-1}). This is the first example of characterized dimerization from a mononuclear monosulfide complex to a dinuclear complex with a $M_2(\mu\text{-}S)_2$ core.

We have isolated a rare five-coordinate molybdenum(IV) monosulfide complex (**1**), which first gives a mononuclear five-coordinate molybdenum(V) monosulfide complex (**2**). These complexes provided the first example of a set of mononuclear five-coordinate molybdenum(IV) and -(V) monosulfide complexes with the same ligand. Dimerization of **2** to **3** was kinetically analyzed. These results offer a new possibility of the formation of $[Mo{=}S]^{2+/3+}$ cores with desired environments, and synthetic strategies are applied in the development of the catalysts for hydrogenation, hydrodesulfurization, and modeling of the xanthine oxidase family.

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Supporting Information Available: Synthetic procedures and characterization data and ESIMS of **2** (Figure S1), ESR of **2** (Figure S2), and crystallographic data of **1** and **3**−PPh_4 (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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