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The Stablization of Dioxomolybdenum(VI) Dithiolene Complex by the Electron Withdrawing Substituent on the Dithiolene Ligand: Comparison of Reactivities of Monooxomolybdenum(IV) Complex with $R_2S_2C_2$ (R = -CN and -COOMe) Ligands as Models of Molybdenum Oxidoreductases

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In the reaction between Me_3NO and $[Mo^{IV}O(mnt)_2]^{2-}$ (mnt = 1,2-Dicyanoethylene-1,2-dithiolate) in DMF, the oxidized complex, $[Mo^{VI}O_2(mnt)_2]^{2-}$ was isolated. On the contrary, in the case of the reaction of $[Mo^{IV}O(S_2C_2(COOMe)_2)_2]^{2-}$, the formation of the corresponding $(Mo^{VI}O_2)^{2+}$ complex was observed in the UV/vis spectra. Our model study suggest that the electron withdrawing effect by the substituent on dithiolene ligand modulates the reactivity of Mo=O group in the $(Mo^{VI}O_2)^{2+}$ state.

From many molybdenum2) and tungsten3) containing oxidoreductases, a variety of pterin cofacter containing dithiolene and pterin have been isolated. The EXAFS spectroscopic analyses of oxidized state enzymes, sulfite oxidase4) and aldehyde-ferredoxin oxidoreductase,5) have shown the presence of the active site with *cis*-$(Mo^{VI}O_2)^{2+}$ and *cis*-$(W^{VI}O_2)^{2+}$, respectively, surrounded by at least three sulfur ligands. The chelation by dithiolene ligand of pterin cofacter in molybdenum or tungsten oxidoreductase should place one of the thiolate ligands trans to Mo^{VI}(or W^{VI})=O when the $(Mo^{VI}O_2)^{2+}$ or $(W^{VI}O_2)^{2+}$ center is assumed to have an octahedral structure. The resonance Raman6) (Mo(VI) and (IV)) and variable temperature MCD7) (Mo(V)) studies on dimethyl sulfoxide reductase have suggested the chelating coordination of dithiolato to molybdenum center. However, no report of the structurally characterized $(Mo^{VI}O_2)^{2+}$ or $(W^{VI}O_2)^{2+}$ complex having the one thiolate ligand coordinated at the trans position to the Mo^{VI}(or W^{VI})=O group has been found except for bis(1,2-benzenedithiolato) dioxomolybdenum(VI)8) or tungsten(VI)9) complexes. This type of complex has been thought to be unstable due to trans influence by a Mo^{VI}=O group towards one of the thiolate ligands.10) From the study of benzenedithiolato complexes,8,9) the π-conjugated ligand and electron withdrawing substituent on the dithiolene ligand can both stabilize the terminal oxo ligands in the oxidized Mo(VI) and W(VI) state.

1,2-Dicyanoethylene-1,2-dithiolate (= mnt) ligands coordinated to oxomolybdenum(VI)11) or (IV)12) has been considered as a simple model of the active site of the enzymes. We synthesized $(PPh_4)_2[Mo^{VI}O_2(mnt)_2]\cdot 2MeOH$ (**2**·2MeOH)13) by the O-atom transfer reaction to $(PPh_4)_2[Mo^{IV}O(mnt)_2]$ (**1**)14,12) from trimethylamine *N*-oxide (= Me_3NO). **1** and **2**·2MeOH were both charactarized by X-ray crystallography. The structure of the anion part of $(Mo^{IV}O)^{2+}$ complex, **1**, is shown in Fig. 1. We will report elsewhere the structural details of $(Mo^{VI}O_2)^{2+}$ complex, **2**·2MeOH, which has an octahedral *cis*-$(Mo^{VI}O_2)^{2+}$ center surrounded by four thiolate ligands very similar to the structure of $[M^{VI}O_2(S_2C_6H_4)_2]^{2-}$ ($S_2C_6H_4$ =

1,2-benzenedithiolato) (M = Mo and W).8,9) The Mo^{IV}OS$_4$ core of **1** has an approximately square-pyramidal geometry (C_{2v} symmetry) with the oxygen atom at the apex and the molybdenum atom raised slightly above the basal (S$_4$) plane. Compared with another structure of a Mo(IV) complex having *cis*-1,2-di(methoxylcarbonyl)ethylene-1,2- dithiolato (= $S_2C_2(COOMe)_2$) ligand, $(NEt_4)_2[Mo^{IV}O(S_2C_2(COOMe)_2)_2]$ (**3**)15), the strong electron withdrawing effect of cyano group in **1** is observed at the larger Mo^{IV}-S distance (mean 2.423 (3) Å, 16) the difference of the mean Δ(**1** - **3**) = 0.026 Å) and the smaller angle of Mo^{IV}-S-C (mean 103.4 (4) °,16) the difference of the mean Δ(**1** - **3**) = - 2.9 °) suggests the presence of weaker π-interaction between Mo(IV) and sulfur.

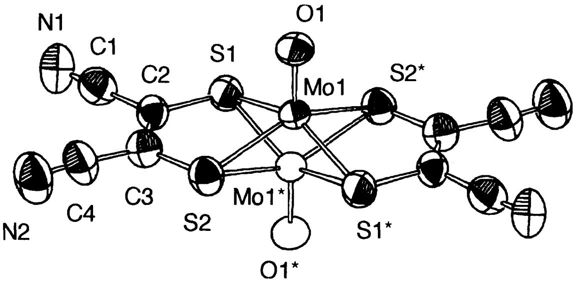

Fig. 1. Molecular structure of anion part of $(PPh_4)_2[Mo^{IV}O(mnt)_2]$ (**1**). (Each pair of Mo and O has 50% probability.)

In Fig. 2a, the spectroscopic time course of reaction between Mo(IV) complex, **1**, and Me$_3$NO at the ratio $[\mathbf{1}]_0 / [Me_3NO]_0 = 1 / 10$ (mol / mol) in DMF (*N*,*N*-dimethylformamide) is presented. As expected for the spectrum of the Mo(IV) complex, **1**, the maximum at 368 nm diminishes with time, showing tight isosbestic points at 358 and 375 nm. The final spectrum, with three bands at λ_{max} = 366, 420 and 522 nm, demonstrates the nearly quantitative formation (90%) of the Mo(VI) complex, **2**. Thus, we concluded that the reaction proceeds in the following way.

$$(PPh_4)_2[Mo^{IV}O(mnt)_2]\ (\mathbf{1}) + Me_3NO \dashrightarrow (PPh_4)_2[Mo^{VI}O_2(mnt)_2]\ (\mathbf{2}) + Me_3N$$

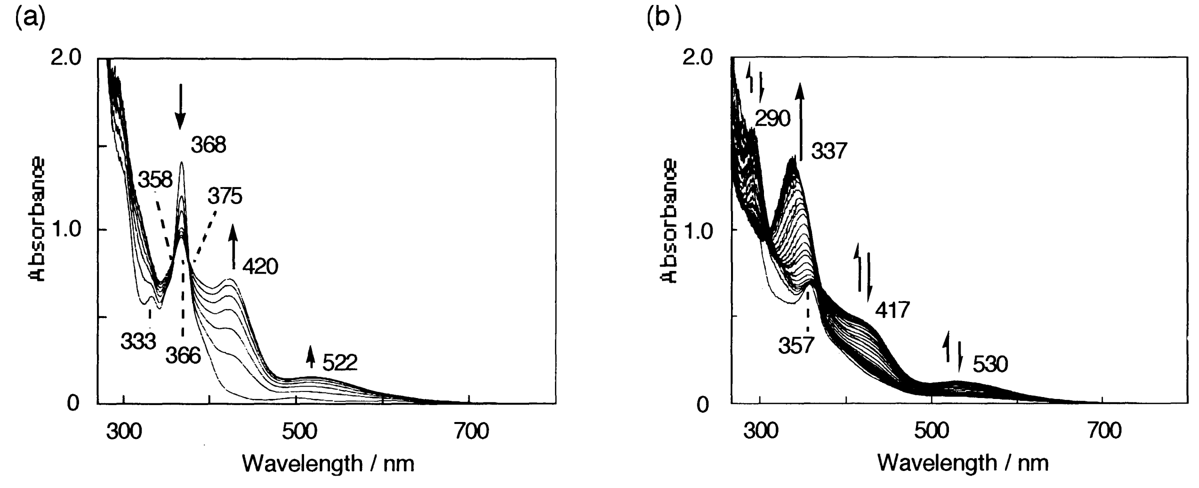

Fig. 2. UV/vis spectral change (measured every 1 h) in the oxidation of (a) $(PPh_4)_2[Mo^{IV}O(mnt)_2]$ (**1**) and (b) $(NEt_4)_2[Mo^{IV}O(S_2C_2(COOMe)_2)_2]$ (**3**) ([Mo] = 1 mM) with Me$_3$NO ([Me$_3$NO] = 10 mM) in DMF at 27 °C (cell length = 1 mm).

On the other hand, in the case of the $(Mo^{VI}O_2)^{2+}$ complex having the $S_2C_2(COOMe)_2$ ligand,

$(NEt_4)_2[Mo^{VI}O_2(S_2C_2(COOMe)_2)_2]$ (**4**), could not be isolated by the O-atom transfer method. Fig. 2b shows the spectrum of the reaction between Mo(IV) complex, **3**, and Me_3NO under the same conditions in the case of **1**. The absorption maxima of **3** increased in intensity at about 300 - 600 nm, showing an isosbestic point at 285 nm. In 10 h after the addition of Me_3NO, the spectrum, with λ_{max} = 390, 358, 417 and 530 nm, exhibits a typical feature for the dioxomolybdenum(VI) thiolato complex which resembles to those of $(NEt_4)_2[M^{VI}O_2(S_2C_6H_4)_2]^{2-}$ 8) (λ_{max} (in DMF) = 335 (sh, 2400), 430 (1400), and 533 nm (1400 $M^{-1}cm^{-1}$) and **2**. Each peaks at 390, 358, 417 and 530 nm, due to this intermediate species, decreased gradually. Finally, after 24 h, the reaction mixture gives only a maximum at 337 nm. Those spectral changes indicate that the further oxidation reaction at the thiolato part of Mo(VI) complex, **4**, different from the case of Mo(IV) complex, **1**, which yielded stable $(Mo^{VI}O_2)^{2+}$ thiolato complex, **2**. The isolated final product (after 24 h or later) in the reaction shows a clear ν(Mo=O) IR band at 914 cm^{-1} (KBr disk) which is assignable to Mo(IV) complex, **3**. The intermediate product (after 10 h) could not be isolated by the addition of THF and **3** was only obtained. In the case of the stoichiometric ([Mo] : [Me_3NO] = 1: 1) reaction, the same product, **3**, was isolated. A proposed reaction process is described in the following scheme.

$(NEt_4)_2[Mo^{IV}O(S_2C_2(COOMe)_2)_2]$ (**3**) + Me_3NO -------->
$(NEt_4)_2[Mo^{VI}O_2(S_2C_2(COOMe)_2)_2]$ (**4**) + Me_3N -------->
[thiolate ligand oxidation product] and **3**

These difference of reaction course between Mo(IV) complexes, **1** and **3**, suggest the electron withdrawing effect of dithiolene ligand in the stabilization of the $(Mo^{VI}O_2)^{2+}$ thiolato complex. In the case of the Mo(VI) complex, **2**, the trans influence from the trans positioned Mo^{VI}=O group can be modulated by the strong electron-withdrawing cyano group. Thus, the resulting Mo(VI) compound, **2**, is stable in the reaction mixture. On the contrary, in the case of the Mo(IV) complex, **3**, a relatively weak electron-withdrawing group, methoxylcarbonyl, could not modulate the trans influence between oxo and thiolate ligand. The further oxo transfer reaction probably proceeds between Mo(VI) complexes, **4**, in the labilized thiolate and activated oxo ligand. Thus, the major final product of this reaction between **3** and Me_3NO is the $(Mo^{IV}O)^{2+}$ complex, **3**. Under a combined effect of the weak electron-withdrawing property and the insufficient bulkiness of methoxycarbonyl group, the thiolate ligands in **4** could not escape from the attack of oxo ligand in **4**. Similar ligand oxidation has been prevented, when the bulky ligand is employed in the model systems of heme enzymes.18)

Our model study suggests that, in the active site of enzymes, the dithiolene coordination to the Mo(VI) ion can modulate the stability of the $(Mo^{VI}O_2)^{2+}$ thiolato center electronically by an electron-withdrawing effect which is expected, for example, in a large π-conjugated ligand system comprized of the pterin ring and the dithiolene chelate ring, and also suggests that the $(Mo^{VI}O_2)^{2+}$ center can be activated toward the oxo transfer reaction by the electron-donating effect from the thiolate ligand analogous to the case of the stability of model compound, **4**.

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13) The complex, **1**, was prepared by the following procedure different from Ref. 12. An MeCN (15 mL) soln. of $(PyH)_2[Mo^{V}OCl_5]$ 17) (0.64 g, 1.4 mmol) was added slowly to an MeOH (40 mL) soln. of MeONa (0.51 g, 9.3 mmol) and Na_2mnt (0.55 g, 2.95 mmol) in an ice bath. After filtration of the resulting soln, a MeOH (10 mL) soln. of PPh_4Br (1.73 g, 4.13 mmol) was added and cooled at -20 °C for 4 days. The red-green needle crystals were collected and recrystalized from EtCN - MeOH. **1**·EtCN (0.81 g, 0.75 mmol, 56% yield) was obtained. Anal. Found: C, 61.61; H, 4.06; N, 6.19%. Calcd for $C_{59}H_{45}N_5OS_4P_2Mo$: C, 62.92; H, 4.03; N, 6.22%. In the absence of MeONa, the tris(dithiolato) complex, $(PPh_4)_2[Mo^{IV}(mnt)_3]$, was formed (yield 4%). **1** was obtained by the recrystalization from DMF - MeOH. ^{13}C NMR (CD_3CN) δ 131.6 (ethylene group), 120.0 (cyano group). Anal. Found: C, 61.45; H, 3.94; N, 5.86%. Calcd for $C_{56}H_{40}N_4OS_4P_2Mo$: C, 62.80; H, 3.76; N, 5.23%. Raman (IR) (KBr): 1491 (1495) (ν(C=C)), 948 (937) (ν(Mo=O)), 344 (ν(Mo-S)) cm^{-1}. UV-visible absorption (in DMF): 295 (sh, 3000), 334 (5900), 356 (sh, 7000), 368 (13000), 387 (sh, 4800), 497(300), 606 nm (150 $M^{-1}cm^{-1}$). Crystallographic data for **1**: $P2_1/n$ (#14), $a =$ 11.196 (3), b = 15.468 (3), c = 14.587 (2), b = 96.88 (2), V = 2508 (2) $Å^3$, $Z = 2$, D_{calc}= 1.418 gcm^{-3}; 6026 unique reflections, 4114 ($I_o > 3\sigma(I)$) used reflections; R = 0.107, R_w = 0.154.

14) Different from Ref. 11, the complex, **2**·2MeOH, was obtained by the following method. To a DMF (0.3 mL) soln of **1**·EtCN (0.25 mg, 0.23 mmol) was added Me_3NO (0.016 g, 0.21 mmol). The deep red solution was formed in 30 min. After stirring for 5 h, MeOH (20 mL) was overlayed and stand at 3 °C for 2 days. Black needle crystals formed were collected, washed with diethylether and dried in vacuo (0.048 g, 0.041 mmol, 19% yield). Anal. Calcd for $C_{58}H_{48}N_4O_4S_4P_2Mo$: C, 60.51; H, 4.20; N, 4.87%. Found: C, 60.55; H, 4.07; N, 4.94%. ^{13}C NMR (CD_3CN) δ 124.0 (ethylene group), 118.3 (cyano group), 49.2 (CH_3OH). Raman (IR) (KBr) 1472 (1471) (ν(C=C)), 885, 852 (886, 851) (ν(Mo=O)), 354 (ν(Mo-S)) cm^{-1}. UV-visible absorption (in DMF): 291 (sh, 19000), 313 (sh, 13000), 366 (7600), 426 (7600), 522 nm (1600 $M^{-1}cm^{-1}$). Crystallographic data for **2**·2MeOH: $Pbcn$ (#60), a = 20.273 (3), b = 15.632 (5), c = 17.685 (4), V = 5604 (3) $Å^3$, $Z = 4$, D_{calc} = 1.364 gcm^{-3}; 8914 unique reflections, 3323 ($I_o > 3\sigma(I)$) used reflections; R = 0.082, R_w = 0.075.

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