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Bis(dithiolene) Molybdenum Complex that Promotes Combined Coupled Electron–Proton Transfer and Oxygen Atom Transfer Reactions: A Water-Active Model of the Arsenite Oxidase Molybdenum Center

Hideki Sugimoto,*[a] Makoto Tarumizu,[a] Hiroyuki Miyake,[a] and Hiroshi Tsukube[a]

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Combined CEPT (coupled electron–proton transfer)/OAT (oxygen atom transfer) reactions were accomplished in $(Bu_4N)_2[Mo^{IV}O(bdtCl_2)_2]$ (**1**) and $(Bu_4N)_2[Mo^{VI}O_2(bdtCl_2)_2]$ (**2**) complexes in aqueous media. The reaction mechanism of the CEPT reaction was analyzed electrochemically and the conversion of **1** to **2** was revealed to proceed by a two-proton two-electron oxidative process. The structural and reaction profiles provide a new model for the arsenite oxidase catalytic center.

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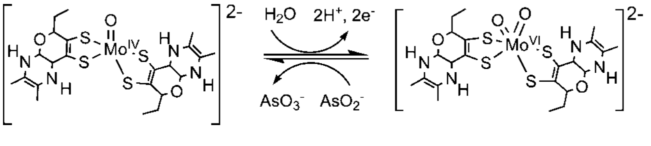
One of the most challenging themes in the field of bioinorganic chemistry is to develop active site models that work in aqueous media. The molybdenum-containing oxotransferases typically utilize water as the ultimate source or sink of oxygen in the overall catalytic reaction, and the reaction is combined with coupled electron–proton transfer (CEPT) and oxygen atom transfer (OAT) reactions.[1] Thus, a model of the catalytic centers is an intriguing target. Interestingly, in all members of the DMSO reductase family, the molybdenum center consists of reduced (Mo^{IV}) and oxidized (Mo^{VI}) states, and is essentially coordinated by two dithiolene ligands.[1]

A large number of OAT reactions from the enzymatic substrates, R_3NO, R'_2SO, or SeO_4^{2-}, to the Mo^{IV} complexes that have two dithiolene ligands have been used to model some reductases.[2] Furthermore, OAT reactions from Mo^{VI} complexes having two dithiolene ligands to substrates have also been extensively explored.[3] However, the CEPT process has yet to be accomplished with Mo complexes having dithiolene ligands. Even in the large number of mononuclear Mo^{VI} complexes reported,[4] only two complexes have been reported to promote CEPT processes. $[LMo^{IV}O(py)(SC_6H_5)]$ and $[LMo^{IV}(p\text{-}O\text{-}C_6H_4\text{-}OC_2H_5)_2]NO_3$ [L = hydrotris(3,5-dimethyl-1-pyrazolyl-borato)] were successfully converted to $[LMo^{VI}O_2(SC_6H_5)]$ and $[LMo^{VI}O(p\text{-}O\text{-}C_6H_4\text{-}OC_2H_5)_2]NO_3$, respectively, in water-containing solvents by two-step CEPT processes, and the resulting Mo^{VI} complexes exhibited OAT reactions.[5]

We report herein the first example of chemistry that combines CEPT/OAT reactions in molybdenum complexes having dithiolene ligands. The $(Bu_4N)_2[Mo^{IV}O(bdtCl_2)_2]$ complex (**1**) ($bdtCl_2$ = 3,6-dichloro-1,2-benzenedithiolate) is readily converted to $(Bu_4N)_2[Mo^{VI}O_2(bdtCl_2)_2]$ (**2**) in aqueous media (CH_3CN/H_2O, 5:7) by a CEPT process, and **2** further transfers the oxygen atom to arsenite. The structures and conversion process of **1**/**2** are very similar to those of the molybdenum center in arsenite oxidase (A.O.) (Scheme 1).[6] The reaction mechanism of the CEPT reactivity of **1** and a difference in the reactivity of **1**, **3** of bdt, and **5** of mnt are discussed (Figure 1: bdt = 1,2-benzenedithiolate and mnt = maleonitrile-1,2-ethylenedithiolate).



Scheme 1. Catalytic cycle mediated by the active site in arsenite oxidase.

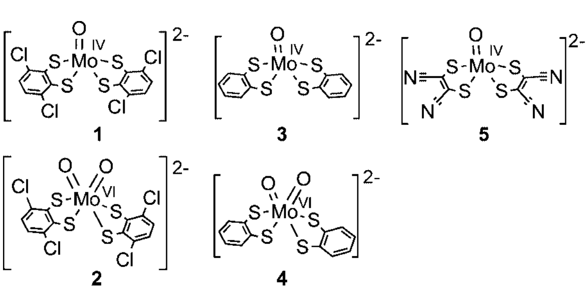


Figure 1. Structures of $[Mo^{IV}O(dithiolene)_2]^{2-}$ and $[Mo^{VI}O_2(dithiolene)_2]^{2-}$ complexes.

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[a] Department of Chemistry, Graduate School of Science, Osaka City University,
Sumiyoshi-ku 3-3-138, Osaka 558-8585, Japan
Fax: +81-6-6605-2522
E-mail: sugimoto@sci.osaka-cu.ac.jp

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We have newly synthesized **1** because the solubility of previously reported $(Et_4N)_2[MoO(bdtCl_2)_2]$[3e] in aqueous media is very low. Five coordinate complex **1** exhibited one reversible $Mo^{V/IV}$ redox couple at 0.04 V (versus SCE) in CH_3CN/H_2O (5:7) solution (pH = 9.0).[7] As the pH of the solution was increased from 9.0 to 12.5, the intensity of the current for the anodic process (E_{pa}) increased, whereas that of the cathodic process (E_{pc}) decreased (Figure 2, inset). This observation indicates that **1** is irreversibly oxidized at high pH. The electrolysis of the solution at pH = 12.0 and E = 0.2 V was monitored by electronic spectral changes (Figure 2). As the electrolysis proceeded, the band centered at 540 nm increased in intensity and the color of the solution changed from yellow to red. The final spectrum was consistent with the electronic spectrum of **2**. A coulometric measurement during the electrolysis confirmed this reaction to be a two-electron oxidative process.

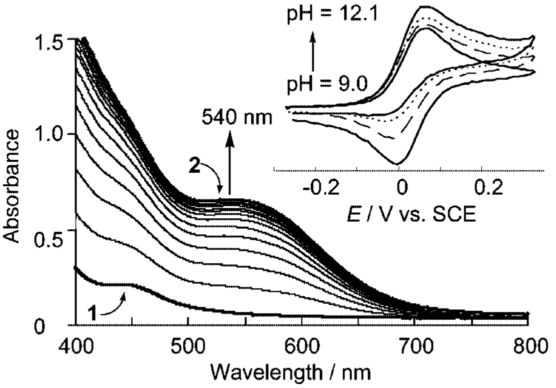


Figure 2. Electronic spectral changes during electrolysis of **1** ($3.5 \cdot 10^{-4}$ M) at 0.2 V (versus SCE) in CH_3CN/H_2O (5:7) pH = 12.0. Spectra were recorded every six minutes. (inset) pH-dependent cyclic voltammograms (pH = 9.0, 11.3, 11.8, and 12.1, scan rate = 100 mV s^{-1}) of **1** ($5.4 \cdot 10^{-4}$ M) in CH_3CN/H_2O (5:7).

Similarly, chemical oxidation of **1** with 2 equiv. of $K_3[Fe(CN)_6]$ in the presence of 2 equiv. of *t*BuOK in CH_3CN/H_2O (5:7) yielded $(Bu_4N)_2[MoO_2(bdtCl_2)_2]$ (**2**). Isolated **2** exhibited $\nu(Mo{=}O)_{asym}$ at 836 cm^{-1} (IR: solid) and an ESI-MS peak cluster attributed to $\{[Mo^{VI}O_2(bdtCl_2)_2]^{2-} + Bu_4N^+\}^-$ (in CH_3CN). When 98% $H_2{}^{18}O$ was used instead of H_2O, $(Bu_4N)_2[Mo^{VI}O^{18}O(bdtCl_2)_2]$ (**2a**) was stoichiometrically formed and isolated in 95% yield, which exhibited $\nu(Mo{=}O)_{asym}$ at 801 cm^{-1} (IR: solid) and gave an ESI-MS peak cluster attributed to $\{[Mo^{VI}O^{18}O(bdtCl_2)_2]^{2-} + Bu_4N^+\}^-$ (in CH_3CN, Figures 3 and S1).

In nonaqueous CH_3CN, **2** was obtained from **1** in the presence of Bu_4NOH by the CEPT process.[8] The reversible $Mo^{V/IV}$ couple at –0.07 V[3e] became an irreversible wave upon addition of Bu_4NOH to the CH_3CN solution of **1**, increasing and decreasing the current intensities of E_{pa} and E_{pc}, respectively. A plot of the ΔI_{pa} value against $[Bu_4NOH]/[\mathbf{1}]$ indicated that 2 equiv. of Bu_4NOH was consumed in the conversion of **1** to **2** (Figure S2). The coulometric and UV/Vis measurements (Figure S3) during the electrolysis at 0.2 V also supported that the conversion of **1** to **2** was a two-electron oxidative process.

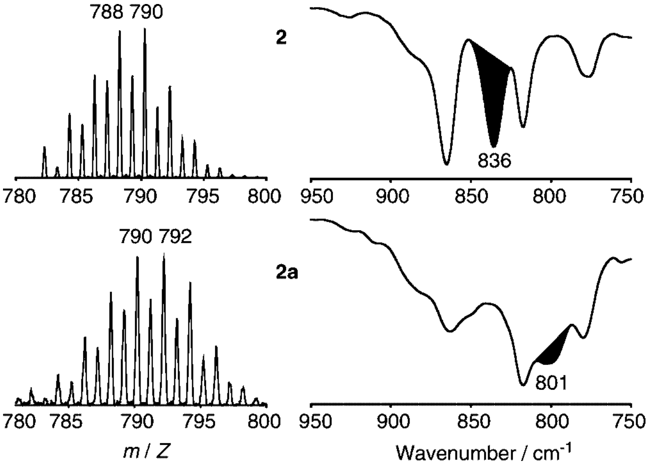


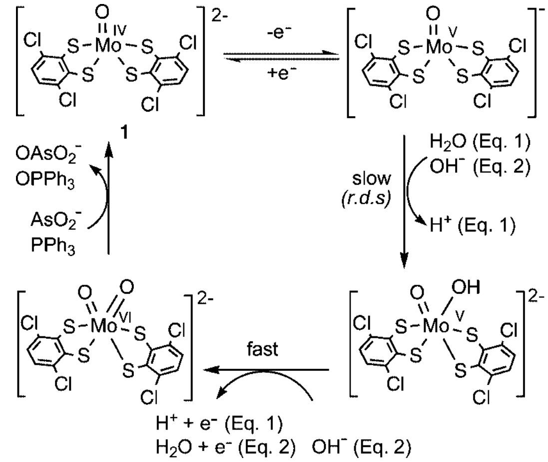
Figure 3. IR (solid) and ESI-MS (in CH_3CN) spectra of **2** (upper) with those of **2a** (lower).

The above results obtained in aqueous and CH_3CN solutions of **1** clearly indicate that the conversion of **1** to **2** occurs by a two-proton two-electron oxidative process. Because the irreversible structural change of **1** to **2** obeys the electrochemical *EC* mechanism, OH^- binding with $[Mo^VO(bdtCl_2)_2]^-$ is involved in the rate-determining step (Scheme 2).[9] Stoichiometries of the conversions from **1** to **2** in CH_3CN/H_2O (5:7) and CH_3CN solutions are described in Equations (1) and (2). The reaction mechanism from **1** to **2** is quite different from that of the pyrazolylborate system.[5] The MoO_2 core having two $bdtCl_2$ ligands is formed in the Mo^{VI} state and a Mo^V species was not detected during the CEPT process. However, both $[LMo^{VI}O_2(SC_6H_5)]$ and $[LMo^{VI}O(p\text{-}O\text{-}C_6H_4\text{-}OC_2H_5)_2]NO_3$ are formed by two-step CEPT processes, in which the MoO_2 and MoO cores, respectively, are formed in the Mo^V states; the intermediates $[LMo^VO_2(SC_6H_5)]^-$ and $[LMo^VO(p\text{-}O\text{-}C_6H_4\text{-}OC_2H_5)_2]$ have been characterized.[5,10] Furthermore, the coordination number of the molybdenum center changes from five to six when **1** is converted to **2** in our system, whereas the molybdenum centers maintain their six coordination structures in both the Mo^{IV} and Mo^{VI} complexes in the pyrazolylborate system. The electrochemical behavior of **1** is similar to that of the molybdenum center of arsenite oxidase; in both systems, five coordinate $Mo^{IV}O$ is converted to six coordinate $Mo^{VI}O_2$ by a two-proton two-electron process.[6]

$$[Mo^{IV}O(bdtCl_2)_2]^{2-}\ (\mathbf{1}) + H_2O \rightarrow [Mo^{VI}O_2(bdtCl_2)_2]^{2-}\ (\mathbf{2}) + 2H^+ + 2e^-\ (CH_3CN\text{-}H_2O) \quad (1)$$

$$[Mo^{IV}O(bdtCl_2)_2]^{2-}\ (\mathbf{1}) + 2OH^- \rightarrow [Mo^{VI}O_2(bdtCl_2)_2]^{2-}\ (\mathbf{2}) + H_2O + 2e^-\ (CH_3CN) \quad (2)$$

$[Mo^{IV}O(bdt)_2]^{2-}$ (**3**) and $[Mo^{IV}O(mnt)_2]^{2-}$ (**5**) exhibited markedly different reactivities in the CEPT process from that of **1** under the same conditions ([Mo] = 0.5 mM). Complex **3** was converted to $[Mo^{VI}O_2(bdt)_2]^{2-}$ (**4**) in CH_3CN by a CEPT process in the presence of 2 equiv. of Bu_4NOH; however, **3** did not afford **4** by the CEPT process in



Scheme 2. Proposed mechanism for the conversion of **1** to **2** by the CEPT process in CH_3CN/H_2O (5:7) [Equation (1)] and CH_3CN [Equation (2)] solutions, and further oxygen atom transfer.

CH_3CN/H_2O (5:7). An aspect of the reversible $Mo^{V}/^{IV}$ wave at –0.20 V in CH_3CN/H_2O (5:7) was intact up to pH = 14, and the electrolysis of the solution at 0.1 V resulted in the formation of $[Mo^{V}O(bdt)_2]^-$. On the other hand, **5** decomposed to $Mo_2O_7^{2-}$ by oxidative electrolysis at 0.55 V (versus SCE) both in CH_3CN/H_2O (5:7) and CH_3CN solutions.[11] The drastic difference in the reactivities observed among **1**, **3**, and **5** may be based on the electron donating properties of the dithiolene ligands employed, which controls the stability of each $Mo^{V}O$ center. The values of the $Mo^{V}/^{IV}$ couples (0.04 for **1**, –0.20 V for **3**,[2a] and 0.45 V for **5**[3a] in solutions of CH_3CN/H_2O) indicate that the electron donating properties of the dithiolene ligands increases in the order bdt > $bdtCl_2$ > mnt. The comparison of the CEPT reactivity of **1** with those of **3** and **5** suggests that $bdtCl_2$ offers a $Mo^{V}O$ center with suitable acidity to bind OH^- to afford a $Mo^{V}O(OH)$ complex which undergoes successive CEPT processes without decomplexation (Scheme 2).[12] The bdt ligand probably provides a weaker acidic $Mo^{V}O$ center. Thus, the $Mo^{V}O$ complex is stable, less reactive, and does not readily bind to OH^- in aqueous media, in where the activities of both the $Mo^{V}O$ center and the OH^- anion are decreased by the buffer action of H_2O. Therefore, $Mo^{V}O$ can bind the OH^- anion of Bu_4NOH in the CH_3CN solution, in where the activities of both the $Mo^{V}O$ center and the OH^- anion are increased by solvent effects. Conversely the mnt ligand provides a $Mo^{V}O$ center with high acidity. Because the $Mo^{V}O$ center is too unstable, it can be concluded that $Mo^{V}O(OH)$ decomposes by oxidative hydrolysis before the complex undergoes the CEPT process, although the decomplexation process is unclear at this stage.

It was found that **2** stoichiometrically oxidized AsO_2^- and PPh_3 to AsO_3^- and $OPPh_3$, respectively, and was converted to **1** in the CH_3CN/H_2O solution (Scheme 2).[13]

The present study has achieved, for the first time, a combination of CEPT/OAT reactions in aqueous media for molybdenum complexes having dithiolene ligands (Scheme 2). The $Mo^{IV}O$ complex of $bdtCl_2$, **1**, was converted into the $Mo^{VI}O_2$ complex, **2**, by a one-step CEPT process and the reaction mechanism was analyzed electrochemically. The similarity of the reaction profile of our system with that of the molybdenum center of the arsenite oxidase system suggests that this model can be very helpful in understanding the reaction mechanism occurring at the molybdenum center of the arsenite oxidase as well as to develop active site models that work in water.

Experimental Section

General: All reagents and solvents were used as received unless otherwise noted. CH_3CN was dried with CaH_2 and then P_2O_5 and distilled under an atmosphere of nitrogen prior to use. A dry 10% Bu_4NOH/CH_3OH solution was purchased from Tokyo Chemical Industry (TCI) and stored in the presence of molecular sieve. Each reaction was carried out under an atmosphere of argon in either a Schlenk tube or a Miwa DB0–1KP glove box.

Preparations: All complexes were synthesized under an atmosphere of nitrogen. Complexes **3** and **5** were prepared as described in the literature.[2a,3a]

$(Bu_4N)_2[Mo^{IV}O(bdtCl_2)_2]$ (**1**) was prepared in the same manner as $(Et_4N)_2[Mo^{IV}O(bdtCl_2)_2]$[3e] with the use of $(Bu_4N)_2[Mo^{VI}O_2(bdtCl_2)_2]$ (**2**) instead of $(Et_4N)_2[Mo^{VI}O_2(bdtCl_2)_2]$.[3e] $C_{44}H_{76}Cl_4MoN_2OS_4$ (1015.12): calcd. C 52.06, H 7.55, N 2.76; found C 51.99, H 7.53, N 2.76.

$(Bu_4N)_2[Mo^{VI}O_2(bdtCl_2)_2]$ (**2**): *Method A:* **1** (13.9 mg, 0.014 mmol), $K_3[Fe(CN)_6]$ (9.2 mg, 0.028 mmol), and *t*BuOK (3.1 mg, 0.028 mmol) were dissolved in CH_3CN/H_2O (5:7, 300–420 µL). The red solution was concentrated to about 300 µL. Red microcrystalline powder precipitated out of the solution, which was collected by filtration. Yield: 13.7 mg (95%). $C_{44}H_{76}Cl_4MoN_2O_2S_4$ (1031.11): calcd. C 51.25, H 7.43, N 2.72; found C 50.90, H 7.41, N 2.61. *Method B:* **2** was prepared in the same manner as $(Et_4N)_2[Mo^{VI}O_2(bdtCl_2)_2]$[3e] with the use of Bu_4NOH instead of Et_4NOH.

$(Bu_4N)_2[Mo^{VI}O^{18}O(bdtCl_2)_2]$ (**2a**) was prepared by method A as per **2** with the use of 98% $H_2{}^{18}O$ instead of H_2O. Yield: 13.7 mg (95%). $C_{44}H_{76}Cl_4MoN_2O^{18}OS_4$ (1033.11): calcd. C 51.15, H 7.41, N 2.71; found C 51.29, H 7.58, N 2.74.

Physical Measurement: FTIR spectra were recorded with a Perkin–Elmer Spectrum One. UV/Vis spectra were recorded with a Unisoku USP-801 spectrometer with an optical fiber attachment. Molar absorption coefficients were corrected by measuring $[Ru(2,2'\text{-bipyridyl})_3](PF_6)_2$ as an authentic sample. GC- and ESI-MS spectra were recorded with a Shimazu GC–MS-QP5050A and a JEOL JMS-700S, respectively. Cyclic voltammograms were recorded under an atmosphere of nitrogen with the use of a Hokuto Denko HZ-3000 potentiostat. A three-electrode configuration consisting of a glassy-carbon working electrode, a SCE reference electrode, and a platinum counter electrode was used.

Supporting Information (see footnote on the first page of this article): The isotope distribution pattern of the calculated mass spectrum as $\{[MoO^{18}O(bdtCl_2)_2]^{2-} + Bu_4N^+\}^-$ (Figure S1), cyclic voltammograms of **1** in CH_3CN in the presence of 0–2 equiv. Bu_4NOH and a plot of ΔI_{pa} versus $[Bu_4NOH]/[\mathbf{1}]$ (Figure S2), and electronic spectral changes during electrolysis of **1** in the presence of 2 equiv. Bu_4NOH at 0.2 V (versus SCE) in CH_3CN (Figure S3).

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[7] Because **1** still does not dissolve in H_2O, mixed solvent, CH_3CN/H_2O (5:7), was used instead. This ratio offered a maximized % volume of H_2O.

[8] A dry 10% Bu_4NOH/CH_3OH solution was used.

[9] The Mo^{IV} center of **1** does not bind H_2O or OH^- because the E_{pa} value of the $Mo^{IV}/^{V}$ couple and the electronic spectrum did not change at high concentrations of OH^-. $[Mo^VO(bdtCl_2)_2]^-$ that was characterized structurally and spectroscopically[3e] was stable only in aqueous media at pH < 9 and in CH_3CN.

[10] Recently, it was reported that $[Mo^{VI}(bdt)_3]$ was converted to $[Mo^{VI}OH(bdt)_3]^{2-}$ in the presence of H_2O, and the two $[Mo^{VI}(OH)(bdt)_3]^-$ oxidized one PPh_3 to give one $OPPh_3$, one H_2O, and two $[Mo^V(bdt)_3]^-$. In that case, the six coordination structure of $[Mo(bdt)_3]^{n-}$ may require a Mo^{VI} center of strong acidity to bind OH^-, whereas in the case of $[MoO(bdtCl_2)_2]^{n-}$, the Mo^V center can bind OH^- because of the five coordinate structure. A. Cervilla, F. Perez-Pla, E. Llopis, M. Piles, *Inorg. Chem.* **2005**, *44*, 4106–4108.

[11] $Mo_2O_7^{2-}$ was identified by ESI-MS of the solution. Sarkar et al. reported that the oxidation of $[MoO(mnt)_2]^{2-}$ resulted in the formation of MoO_4^{2-}.[3a] In solution, $Mo_2O_7^{2-}$ and MoO_4^{2-} are in an acid–base equilibrium.

[12] The $\nu(Mo^{IV,V}{=}O)$ stretching values (IR: solid) 910 and 941 cm^{-1} for the $bdtCl_2$ complexes, 905 and 935 cm^{-1} for the bdt complexes, and 928 cm^{-1} [$\nu(Mo^{IV}{=}O)$] for the mnt complex support that the order of acidity of the molybdenum centers is bdt < $bdtCl_2$ < mnt. The Mo^V complex of mnt is too unstable to be isolated and characterized.[3a]

[13] The stoichiometric oxidations of PPh_3 and AsO_2^- by **2** were confirmed by ^1H NMR, UV/Vis, and ESI-MS spectroscopy. However, the reaction mechanism of the oxidation of AsO_2^- by **2** could not be analyzed because the reaction was too fast to follow. The oxidation of PPh_3 by **2** was kinetically analyzed in ref.[3e]

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