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Communication

Selenidobis(dithiolene)metal(IV) Complexes (Metal M = Mo, W) Potentially Related to the Nicotinic Acid Hydroxylase Reaction Center: Redox Aspects in Electrochemistry and Oxygen Atom Transfer from Me_3NO to M^{IV} Centers

Hiroyuki Tano, Reiko Tajima, Hiroyuki Miyake, Shinobu Itoh, and Hideki Sugimoto*

Department of Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

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Selenidobis(dithiolene)molybdenum(IV) and -tungsten(IV) complexes were synthesized and characterized by several methods including X-ray crystallographic analysis. The five-coordinate M^{V}=Se species were accessed by one-electron oxidation of the M^{IV}=Se complexes. M^{VI}=Se complexes were suggested to be formed as an intermediate in oxygen atom transfer from Me_3NO to the M^{IV}=Se centers.

Molybdenum and tungsten complexes with one or two terminal chalcogenides are of great importance because of their relevance to reaction centers of molybdenum and tungsten enzymes.[1] Nicotinic acid hydroxylase has been proposed to include a Mo=Se reaction center coordinated with one or two molybdopterins, as shown in Figure 1, but its high oxygen sensitivity prevents clear characterization of the metal center.[1a,2] The above fact raises the importance of its modeling study. However, mononuclear Mo=Se complexes are extremely rare in contrast with M=O and M=S compounds (M = Mo, W),[3,4] resulting in only eight crystallographically characterized examples, $Mo^{VI}O(Se)$(piperidine *N*-oxide)$_2$,[5] $(Ph_4P)_2[Mo^{VI}Se_4]$,[6] $(Ph_4P)_2[Mo^{IV}Se(Se_4)_2]$,[6] $Mo^{V}Se$(*N*-^{t}Bu-3,5-dimethylanilido)$_4$,[7] and four *trans*-$Mo^{IV}Se_2$(phosphines)$_4$.[8−10] Because the ligands of the Mo=Se complexes reported are neither an S ligand nor dithiolene, selenido(dithiolene)molybdenum complexes are needed to clarify the roles of the enzyme reaction center. Here, we report the first selenidomolybdenum complex containing dithiolene ligands. The synthesis and characterization of its isostructural tungsten complex are also included in this Communication.

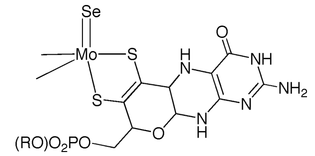

Figure 1. Proposed structure of a Mo=Se center in niconitic acid hydroxylase.

Treatment of $Mo(CO)_2(L)_2$ (L = cyclohexene-1,2-dithiolate)[11] with 3 equiv of Na_2Se and 2 equiv of Ph_4PBr in CH_3CN afforded a blue suspension. Repeated recrystallizations from CH_3CN/diethyl ether gave orange-green crystals of $(Ph_4P)_2[Mo^{IV}Se(L)_2]\cdot 2CH_3CN$ ($\mathbf{1}\cdot 2CH_3CN$). Its tungsten analogue, $(Ph_4P)_2[W^{IV}Se(L)_2]\cdot 2CH_3CN$ ($\mathbf{2}\cdot 2CH_3CN$), was prepared by a method similar to that of $\mathbf{1}\cdot 2CH_3CN$, except that $W(CO)_2(L)_2$[12] was employed instead of $Mo(CO)_2(L)_2$ (the detailed procedures are provided in the Supporting Information). Parts a and b of Figure 2 show the crystal structures of the anionic parts in $\mathbf{1}\cdot 2CH_3CN$ and $\mathbf{2}\cdot 2CH_3CN$, respectively. The molybdenum center (Mo1) is coordinated with one terminal selenido and four sulfur atoms from two

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[*] To whom correspondence should be addressed. E-mail: sugimoto@sci.osaka-cu.ac.jp.

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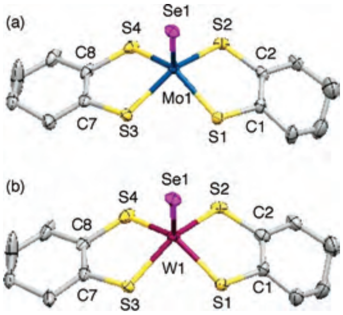

Figure 2. Crystal structures of anionic parts in **1**$\cdot$2CH$_3$CN (a) and **2**$\cdot$2CH$_3$CN (b) with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): (a) Mo1−Se1 2.3069(5), Mo1−S1 2.3517(12), Mo1−S2 2.3627(11), Mo1−S3 2.3618(11), Mo1−S4 2.3639(11), S1−C1 1.786(4), S2−C2 1.770(4), S3−C7 1.765(4), S4−C8 1.772(4); Se1−Mo1−S1 110.86(2), Se1−Mo1−S2 107.59(3), Se1−Mo1−S3 106.50(3), Se1−Mo1−S4 113.20(3), S1−Mo1−S4, 135.94(4), S2−Mo1−S3 145.90(3); (b) W1−Se1 2.3141(6), W1−S1 2.3468(17), W1−S2 2.3610(16), W1−S3 2.3592(15), W1−S4 2.3543(16); Se1−W1−S1 110.94(4), Se1−W1−S2 107.54(4), Se1−W1−S3 106.22(4), Se1−W1−S4 112.78(5), S1−W1−S4 136.28(6), S2−W1−S3 146.23(6).

dithiolene ligands. The Mo1 atom is raised above the basal plane comprising four sulfur atoms by 0.78 Å and adopts a distorted square-pyramidal structure with a dihedral angle between the S1−Mo1−S2 and S3−Mo1−S4 planes of 129°. The Mo1−Se1 bond distance at 2.3069(5) Å is somewhat longer than the Mo═Se distance of square-pyramidal $(Ph_4P)_2[MoSe(Se_4)_2]$ [2.270(4) Å][6] but significantly shorter than the Mo−Se bond distance of $(Et_4N)[Mo^{IV}(Se\text{-}Ad)(S_2C_2Me_2)_2]$ [2.439(1) Å; Se-Ad = 2-adamantylselenolate, $S_2C_2Me_2$ = 1,2-dimethylethylenedithiolate),[13] which indicates that the Mo1−Se1 distance has double-bond character. **2**$\cdot$2CH$_3$CN is isostructural with **1**$\cdot$2CH$_3$CN, and the W1 atom is displaced by 0.78 Å toward the Se1 atom from the basal plane consisting of four sulfur atoms, providing a dihedral angle between the S1−W1−S2 and S3−W1−S4 planes of 127°. The W1−Se1 bond distance at 2.3141(6) Å also indicates its double-bond character. Except these new two complexes, *trans*-$MSe_2(PMe_3)_4$ and $(Ph_4P)_2[MSe_4]$ complexes have been synthesized with both Mo═Se[6,8] and W═Se[6,14] units and crystallographically characterized.

^{77}Se NMR signals of **1** and **2** in $(CD_3)_2SO$ were observed at 1827.8 and 1275.7 ppm, respectively (Figure S1 in the Supporting Information),[15] which fall in the range for metal terminal selenido complexes (800−2300 ppm).[16] Distinct peak clusters assignable to $[\mathbf{1} - 2Ph_4P^+]^{2-}$ and $[\mathbf{2} - 2Ph_4P^+]^{2-}$ appeared at m/z = 464 and 552, respectively, in negative electrospray ionization mass spectra (negative ESI-MS) of **1** and **2** in CH_3CN (Figure S2 in the Supporting Information).[17] These observations indicate that the structures around the metal centers of **1** and **2** in a solid are retained in the solutions.

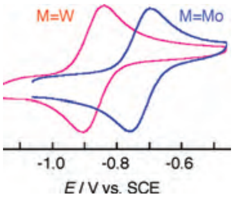

Figure 3. Cyclic voltammograms of $(Ph_4P)_2[MSe(L)_2]$ [M = Mo (**1**), blue; M = W (**2**), red]: 0.5 mM of the complexes containing 0.1 M TBAPF$_6$; scan = 0.1 V s^{-1}.

The two complexes exhibited one reversible M^V/M^{IV} redox couple [$E_{1/2}$ = −0.74 for **1** (ΔE = 61 mV) and −0.86 V vs SCE for **2** (ΔE = 61 mV)] in CH_3CN, as shown in Figure 3. Interestingly, the redox potentials for the Mo^V/Mo^{IV} process in the series of $[MoQ(L)_2]^{2-}$ (Q = O,[11] $E_{1/2}$ = −0.70 V; S,[18] $E_{1/2}$ = −0.74 V; Se, $E_{1/2}$ = −0.74 V) are scarcely influenced by the kind of terminal chalcogenido.[19] This suggests that the highest occupied molecular orbitals are hybridized with Mo d_{xy} and dithiolene orbitals. Similarly, in the series $[Mo^{IV}(Q\text{-}Ad)(S_2C_2Me_2)_2]^-$ (Q = O, S, Se; Ad = 2-adamantyl), the redox-active orbitals have characteristics of both the Mo d_{xy} and dithiolene orbitals.[20,21] For comparison, the Mo^{VI}/Mo^V redox potential in the series of MoQ(*N*-^{t}Bu-3,5-dimethylanilido)$_3$ (Q = O, S, Se), with no S ligand, significantly increases in the order of Q = O (−0.92) < S (−0.73) < Se (−0.64 V vs ferrocenium/ferrocene couple).[7] The Mo−S bonds in nicotinic acid hydroxylase also might have covalent character.

Good reversibility of the M^V/M^{IV} redox processes of **1** and **2** stimulated us to generate these M^V═Se species. By treatment with an equivalent ferrocenium tetrafluoroborate ($FcBF_4$), the CH_3CN solution of **1** once changed in color to gray and then to green. The green species was characterized as a dimolybdenum(V) complex of $(Ph_4P)_2[Mo^V(L)_2]_2(\mu\text{-}Se)_2$ by UV−vis spectroscopy and X-ray structural determination (Figure S3 in the Supporting Information). The structure around the two molybdenum atoms is similar to that of the $Mo^V{}_2(\mu\text{-}Se)_2$ complex of 1,2-dimethylethyleneditholate.[22] A gray complex derived from **1** at a lower concentration than 0.5 mM was stable within 30 min below −20 °C, and its UV−vis spectrum was featured by a strong absorption band centered at 753 nm, as indicated in Figure 4. Whereas **1** and $(Ph_4P)_2[Mo^V(L)_2]_2(\mu\text{-}Se)_2$ are EPR-silent, the gray species showed EPR signals with a characteristic pattern for the Mo^V ion at −35 °C (Figure 4, inset). These results indicate that the gray species formed upon oxidation of **1** is $(Ph_4P)[Mo^VSe(L)_2]$, and this dimerizes to $(Ph_4P)_2[Mo^V(L)_2]_2(\mu\text{-}Se)_2$ under a higher concentration or at a higher temperature, as indicated in Scheme 1. Similarly, oxidation of **2** by $FcBF_4$ in CH_3CN afforded a pink-gray species, $(Ph_4P)[W^VSe(L)_2]$,

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(15) Couplings of ^{95}Mo (I = $^5/_2$, 15.72%) and ^{97}Mo (I = $^5/_2$, 9.46%) and with ^{183}W (I = $^1/_2$, 14.4%) were not observed.

(16) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223.

(17) Because the m/z = 464 and 552 values correspond to these monoanionic states, one-electron oxidation of **1** and **2** may take place during the measurement.

(18) Sugimoto, H.; Sakurai, T.; Miyake, H.; Tanaka, K.; Tsukube, H. *Inorg. Chem.* **2005**, *44*, 6927.

(19) $[W^{IV}O(L)_2]^{2-}$ was reported in ref 12, but its sulfido analogue has not been prepared yet.

(20) The redox-active orbitals were calculated to be occupied with 69.0% of Mo and 30.6% of dithiolene orbitals for Q = O, 67.1% of Mo and 31.3% of dithiolene orbitals for Q = S, and 67.4% of Mo and 31.4% of dithiolene orbitals for Q = Se.

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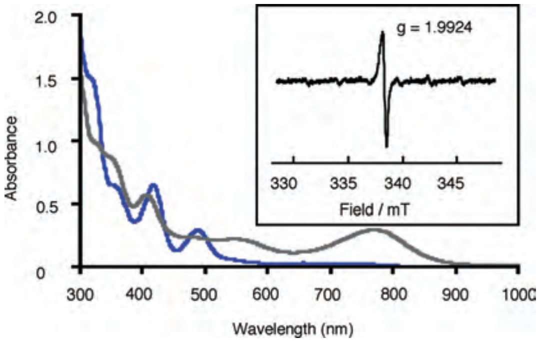
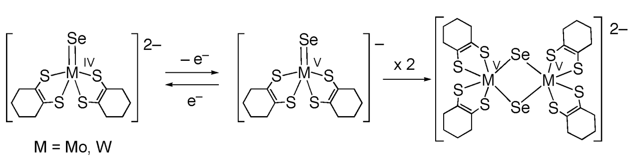


Figure 4. UV−vis spectra of **1** (blue line, 0.1 mM) and a gray species (gray line) generated by treatment of **1** (blue line, 0.1 mM) with 1 equiv of ferrocenium tetrafluoroborate at −35 °C. (inset) Electron spin resonance (ESR) spectrum of the gray species at −35 °C.

Scheme 1



of which the UV−vis spectral aspect was similar to that of $(Ph_4P)[Mo^{V}Se(L)_2]$.

Because it was found to be very difficult to generate the five-coordinate $[M^{VI}Se(L)_2]^0$ (M = Mo, W) complexes electrochemically from the cyclic voltammogram measurements of **1** and **2**, we attempted to generate $M^{VI}Se$ species in a six-coordinate $M^{VI}O(Se)$ form by oxygen atom transfer (OAT) from Me_3NO to **1** and **2**. Upon treatments with 1−10 equiv of Me_3NO, the ESI-MS peak cluster at $m/z = 464$, corresponding to **1**, decreased with concomitant appearance of a new peak cluster at $m/z = 402$ and a new IR band at 896 cm^{-1} appeared (Figure 5), which were identical with those of $(Ph_4P)_2[Mo^{IV}O(L)_2]$ prepared separately.[11] The conversion yield was calculated to be ca. 90% from the ratio of the original broad signal centered at 1.68 ppm and the newly appeared broad one centered at 1.54 ppm in the ^1H NMR change. In the case of **2**, its reaction with 1−10 equiv of the oxygen donor gave a dioxo complex $(Ph_4P)_2[W^{VI}O_2(L)_2]$, which was characterized similarly.[23] Although formation of the expected $M^{VI}O(Se)$ species was not confirmed in this study, the results obtained from OAT experiments suggest that the $M^{VI}O(Se)$ species might be generated once by OAT to the $M^{IV}Se$ center and the successive reductive elimination of Se from the $M^{VI}O(Se)$ unit gave the reduced $M^{IV}O$ complex, as shown in Scheme 2.[24] Further oxygen abstraction by the resulting $W^{IV}O$ complex from another Me_3NO might occur to give the $W^{VI}O_2$ form.[25,27]

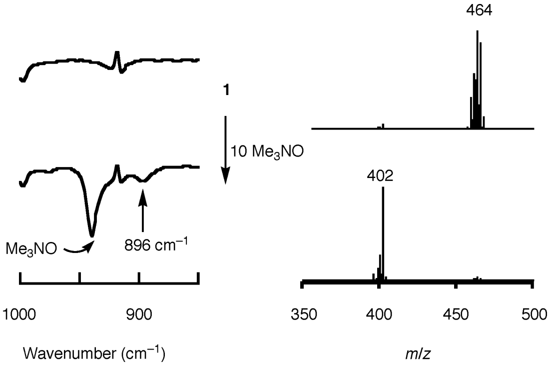
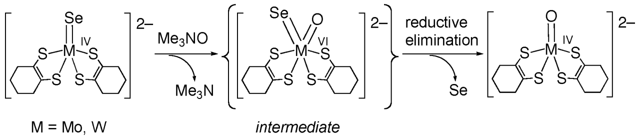


Figure 5. IR (left) and ESI-MS (right) changes of **1** (above) in CH_3CN upon treatment with 10 equiv of Me_3NO (below) at room temperature.

Scheme 2



In summary, this paper reported the first selenidomolybdenum complex coordinated with S coligands related to the reaction center of nicotinic acid hydroxylase of molybdenum enzymes. Its isostructural tungsten analogue was also synthesized. The selenidomolybdenum(V) and -tungsten(V) complexes were formed from their metal(IV) precursors with $FcBF_4$. Oxoselenidometal(VI) centers were suggested to be generated as intermediates in the conversion from the selenidometal(IV) complexes to the oxometal(IV) ones with Me_3NO. These results provide new synthetic strategies of $[M{=}Se]^{2+/3+/4+}$ complexes with desired environments for modeling of the molybdenum and tungsten enzyme reaction centers. Characterization of the $M^{VI}{=}Se$ species is in progress.

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Supporting Information Available: Synthetic procedures and characterization data of **1** and **2**, experimental details in measurements, ^{77}Se NMR spectra (Figure S1), ESI-MS spectra (Figure S2), ORTEP drawing of $(Ph_4P)_2[Mo^{V}(L)_2](\mu\text{-}Se)_2$ (Figure S3), crystallographic data of $1{\cdot}2CH_3CN$ and $2{\cdot}2CH_3CN$ (Table S1), and CIF files for $1{\cdot}2CH_3CN$, $2{\cdot}2CH_3CN$, and $(Ph_4P)_2[Mo(L)_2]_2(\mu\text{-}Se)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Concomitant formation of the dinuclear complex $(Ph_4P)_2[W^{V}(L)_2]_2(\mu\text{-}Se)_2$ was observed. Air oxidation of **2** might take place during the measurements because of its high air sensitivity.

(24) An alternative mechanism in which the selenido group becomes oxidized before it leaves the metal center is possible to consider.

(25) OAT from Me_3NO to bis(dithiolene)tungsten(IV) complexes was revealed to afford the corresponding dioxotungsten(VI) complexes.[3,26]

(26) Sugimoto, H.; Sugimoto, K. *Inorg. Chem. Commun.* **2008**, *11*, 77.

(27) In the Mo system, the corresponding $Mo^{VI}O_2$ species might be generated from the $Mo^{IV}O$ form and Me_3NO because $Mo^{VI}O_2$ complexes with aliphatic dithiolenes are not very stable and even under low ESI-MS energy fragmentation to show only the $Mo^{IV}O$ species is possible.[28]

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