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Syntheses and Properties of Oxomolybdenum(VI), -(V), and -(IV) Complexes with Ferrocenecarbodithioate

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A series of ferrocenecarbodithioato-oxomolybdenum(VI), -(V), and -(IV) complexes, $Mo^{VI}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (**1**), $Mo^{V}{}_2O_3(S_2CC_5H_4Fe^{II}C_5H_5)_4$ (**2**), and $Mo^{IV}O(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (**3**) have been prepared. Complex **2** undergoes a disproportionation reaction in solution and exists as an equilibrium mixture with **1** and **3**. Cyclic voltammograms of **1** and **3** display two and three sets of quasi-reversible couples, respectively, arising from stepwise redox reactions of the molybdenum and iron sites. Electronic spectra revealed that the oxidized species $[Mo^{VI}O_2(S_2CC_5H_4Fe^{III}C_5H_5)_2]^{2+}$, $[Mo^{V}O(S_2CC_5H_4Fe^{II}C_5H_5)_2]^{+}$, and $[Mo^{V}O(S_2CC_5H_4Fe^{III}C_5H_5)_2]^{3+}$ generated electrochemically are considerably stable owing to the electron-donating ability of the ferrocenecarbodithioate ligand.

Molybdenum in high oxidation states is known to be an essential component in six well-characterized enzymes; nitrogenase, nitrate reductase, xanthine oxidase, aldehyde oxidase, and sulfite oxidase.[1)] There exists a structural similarlity among the molybdenum sites of these enzymes except for nitrogenase.[2—4)] Recent EXAFS studies on sulfite oxidase[3)] and xanthine oxidase[4)] suggest that molybdenum in those enzymes has one or two oxo ligands in sulfide-rich environments. These results have further stimulated the syntheses of a variety of oxomolybdenum complexes with sulfur-containing ligand as possible model compounds to molybdoenzymes.[5—8)] Of the oxomolybdenum complexes with sulfur-containing ligands, which have been prepared so far, only the dithiocarbamate complexes have fully been characterized as a series of oxomolybdenum(VI), -(V), and -(IV) complexes.[9)] Thus, the stabilization of oxomolybdenum complexes in the three oxidation states, (VI), (V), and (IV), may be resulted from the electron-donating ability of the dithiocarbamate ligand. Recently, we have briefly reported the syntheses of oxomolybdenum(VI) and -(V) complexes with ferrocenecarbodithioate,[10)] which can stabilize the high oxidation states of molybdenum atoms. The present work reports the syntheses of a series of oxomolybdenum (VI), -(V), and -(IV) complexes with ferrocenecarbodithiocate, $Mo^{VI}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (**1**), $Mo^{V}{}_2O_3(S_2CC_5H_4Fe^{II}C_5H_5)_4$ (**2**), and $Mo^{IV}O(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (**3**), and their electrochemical properties.

Experimental

Materials and Methods. Dichlorodioxomolybdenum, $Mo^{VI}O_2Cl_2$,[11)] and diethylammonium ferrocenecarbodithioate, $[Et_2NH_2][S_2CC_5H_4Fe^{II}C_5H_5]$[12)] were prepared according to the literatures. All reactions and manipurations were carried out under nitrogen atmosphere and the solvents used for preparations and physical measurements were degassed by bubbling dry nitrogen for *ca.* 1 h or by distillation under nitrogen atmosphere prior to use.

Preparation of Complexes. Bis(ferrocenecarbodithioato)dioxomolybdenum(VI), $Mo^{VI}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (1). A methanol solution (20 cm³) of $Mo^{VI}O_2Cl_2$ (0.5 g, 2.5 mmol) was added dropwise to a stirred suspension of $[Et_2NH_2][S_2CC_5H_4Fe^{II}C_5H_5]$ (1.7 g, 5.0 mmol) in the same solvent (50 cm³) at −60 °C. The reaction mixture was stirred for further 2 h at the same temperature, followed by warming to 0 °C, which gave greenish blue precipitate. The precipitate was collected by filtration at 0 °C, washed with methanol (10 cm³×2 times), and dried *in vacuo*, 80% yield, mp>120 °C (dec). Anal. Calcd for $C_{22}H_{18}Fe_2MoO_2S_4$: C, 40.63; H, 2.79%. Found: C, 40.80; H, 2.99%. Molecular weight (MW) was measured in benzene cryoscopically: 628 (Calcd 650).

μ-Oxobis[bis(ferrocenecarbodithioato)oxomolybdenum(V)], $Mo^{V}{}_2O_3(S_2CC_5H_4Fe^{II}C_5H_5)_4$ (2). To a stirred aqueous solution (50 cm³) containing $Na_2Mo^{VI}O_4\cdot H_2O$ (1.2 g, 5.0 mmol) and $[Et_2NH_2][S_2CC_5H_4Fe^{II}C_5H_5]$ (3.4 g, 10 mmol) was added dropwise a 2 mol dm⁻³-HCl to adjust the pH of the solution to 5.5. The resulting dark blue precipitate was collected by filtration, washed with water and then diethyl ether, and dried *in vacuo*, 20% yield, mp>115 °C (dec). Anal. Calcd for $C_{44}H_{36}Fe_4Mo_2O_3S_8$: C, 41.14; H, 2.82%. Found: C, 41.49; H, 2.92%.

Bis(ferrocenecarbodithioato)oxomolybdenum(IV), $Mo^{IV}O(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (3). A benzene solution (50 cm³) containing **1** (1.1 g, 1.7 mmol) and PPh_3 (0.47 g, 1.8 mmol) was refluxed for 2 h. After cooled to room temperature, the solution was evaporated to dryness under reduced pressures. The resulting solid was triturated with ethanol (20 cm³×2 times), collected by filtration, washed with diethyl ether (20 cm³×2 times), and dried *in vacuo*, which gave dark blue microcrystals, 88% yield, mp>180 °C (dec.). Anal. Calcd for $C_{22}H_{18}Fe_2MoOS_4$: C, 41.66; H, 2.86%. Found: C, 41.36; H, 3.03%. MW in benzene 620 (Calcd 634).

Physical Measurements. Infrared and electronic spectra were recorded on a Shimadzu IR-400 and a MPS-5000 spectrophotometer, respectively. ESR spectra were measured at 9.52 GHz with a JEOL ME-1X spectrometer. Electrochemical experiments were performed by using a Hokuto-Denko Model HA-501 potentiostat/galvanostat, a HB-104 function generater, and a HF-201 coulomb/amperehour meter. Cyclic voltammograms were recorded on a National VP-6422A X-Y recorder. Tetrabutylammonium perchlorate, $[n\text{-}Bu_4N][ClO_4]$, was used as a supporting electrolyte, and a saturated calomel electrode (SCE) was employed as a reference electrode. A platinum disk (0.20 cm²) and a platinum plate (1×1 cm²) were employed as working electrodes for the cyclic voltammetry and the controlled-potential electrolysis, respectively. The controlled-potential electrolysis was

TABLE 1. INFRARED SPECTRA OF THE OXOMOLYBDENUM COMPLEXES WITH FERROCENECARBODITHIOATE

Complex	ν(Mo=O), cm^{-1} in Nujol	ν(Mo=O), cm^{-1} in CH_2Br_2
$Mo^{VI}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (**1**)	922	920
	889	885
$Mo^{V}_2O_3(S_2CC_5H_4Fe^{II}C_5H_5)_4$ (**2**)	940	955 br
		920
		885
$Mo^{IV}O(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (**3**)	960	962

performed at 110—180 mV more negative potentials than the cathodic peaks or more positive potentials than the anodic peaks of the complexes. Spectroelectrochemistry was accomplished by the use of an optically transparent thin-layer electrode (OTTLE) cell.[13]

Results and Discussion

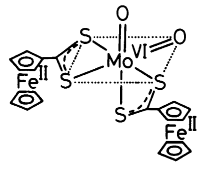
Infrared Spectra in the Solid State and in Solution. The infrared spectrum of **1** in Nujol mull shows two strong ν(Mo=O) bands at 922 and 889 cm^{-1} (Table 1), which are compared with those of the corresponding dithiocarbamate complexes, $Mo^{VI}O_2(S_2CNR_2)_2$ (R=Me, Et, n-Pr, n-Bu; 912—905 and 877—875 cm^{-1}) with the two oxo ligands in *cis*-positions to each other in the octahedral configuration.[14] Complexes **2** and **3** in Nujol mulls exhibit the ν(Mo=O) bands at 940 and 960 cm^{-1}, respectively (Table 1); the former and the latter fall in the same region as the ν(Mo=O) frequencies of $Mo^{V}_2O_3(S_2CNR_2)_4$ (R=Me, Et, i-Pr; 943—938 cm^{-1})[15] and $Mo^{IV}O(S_2CNEt_2)_2$ (962 cm^{-1}), respectively, as well.[16] These results indicate that the ferrocenecarbodithioate ligand is coordinated to molybdenum in a bidentate manner and the present oxomolybdenum complexes **1**, **2**, and **3** may assume the geometries **A**, **B**, and **C**, respectively, which are similar to those of the corresponding dithiocarbamate complexes which have been revealed by the X-ray crystallographic analysis.[17]

The infrared spectrum of **2** in CH_2Br_2, however, displayed three ν(Mo=O) bands at 955, 920, and 885 cm^{-1}, the latter two of which are nearly the same frequencies as those of **1** in the same solvent. This is suggestive of the occurrence of the disproportionation reaction of **2** into **1** and **3** in solution (Eq. 1). Thus, the ν(Mo=O) bands arising from **2** and **3** may be overlapped with each other to appear as a broad one at 955 cm^{-1}. This is consistent with the fact that an equimolar mixture of **1** and **3** in CH_2Br_2 exhibited an infrared spectrum quite similar to **2** in the same solvent. Disproportionation equilibria of Eq. 1 have been reported for some μ-oxodimolybdenum complexes of the $Mo^{V}_2O_3L_4$ type (L=S_2CNR_2, S_2CSR, and S_2PPh_2) in solution[18,19] though only the dithiocarbamate complexes have so far been fully characterized throughout three different oxidation states of molybdenum, (VI), (V), and (IV).[16]

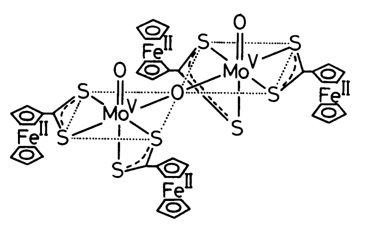
$$\begin{aligned} &Mo^{V}_2O_3(S_2CC_5H_4Fe^{II}C_5H_5)_4 \rightleftharpoons \\ &\quad Mo^{VI}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2 \\ &\qquad + Mo^{IV}O(S_2CC_5H_4Fe^{II}C_5H_5)_2 \end{aligned} \qquad (1)$$

Electrochemistry. Figure 1 illustrates the cyclic voltammograms of **1**, **2**, and **3** in CH_2Cl_2. As shown in Fig. 1a, the cyclic voltammogram of **1** in CH_2Cl_2 shows two well resolved quasi-reversible waves ($E_{1/2}=-0.89$ and $+0.77$ V *vs.* SCE) and no wave associated with liberated ligands[20] has been observed within the potential range -2.0 to $+2.0$ V (*vs.* SCE). The controlled-potential electrolysis of **1** in CH_2Cl_2 at -1.05 and $+0.95$ V (*vs.* SCE, a little more negative or positive potential than $E_{1/2}$) have consumed 0.94 and 1.89 electrons, respectively, per one mole of **1**. This result indicates that **1** undergoes one electron reduction at $E_{1/2}=-0.89$ V (*vs.* SCE) to produce the $[Mo^{V}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2]^-$ species, and two ferrocenecarbodithioate ligands are both oxidized at the potential $E_{1/2}=+0.77$ V (*vs.* SCE) to give $[Mo^{VI}O_2(S_2CC_5H_4Fe^{III}C_5H_5)_2]^{2+}$. Thus, the redox processes of **1** can formally be expressed as Scheme 1.

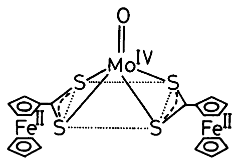
A CH_2Cl_2 solution of **3** displays three discrete redox couples ($E_{1/2}=-0.87$, $+0.60$, and $+0.98$ *vs.* SCE) without any peaks due to liberated ligands, as depicted in Fig. 1c. The controlled-potential electrolysis at a little more negative or positive potential (-1.10, $+0.80$, and $+1.25$ V *vs.* SCE) than $E_{1/2}$ has consumed 1.02, 0.94, and 1.93 electrons, respectively, confirming that the cathodic peak at -0.92 V (*vs.* SCE) and the anodic one at $+0.67$ V (*vs.* SCE) are both one-electron processes, whereas the anodic peak at $+1.12$ V (*vs.* SCE) is a two-electron process. Thus, the redox couple at $E_{1/2}=-0.87$, $+0.60$, and $+0.98$ V (*vs.* SCE) may be assigned to the Mo(IV)/Mo(III), Mo(IV)/Mo(V), and Fe(II)/Fe(III) processes, respectively. The assignment for the redox couple at $+0.60$ V (*vs.* SCE) is consistent with the fact that an oxidized species generated by the electrolysis of **3** at $+0.70$ V (*vs.* SCE) in CH_2Cl_2 gives an ESR signal with g=2.007 at room temperature, as shown in Fig. 2. This g-value is quite normal for molybdenum(V) com-



A



B



C

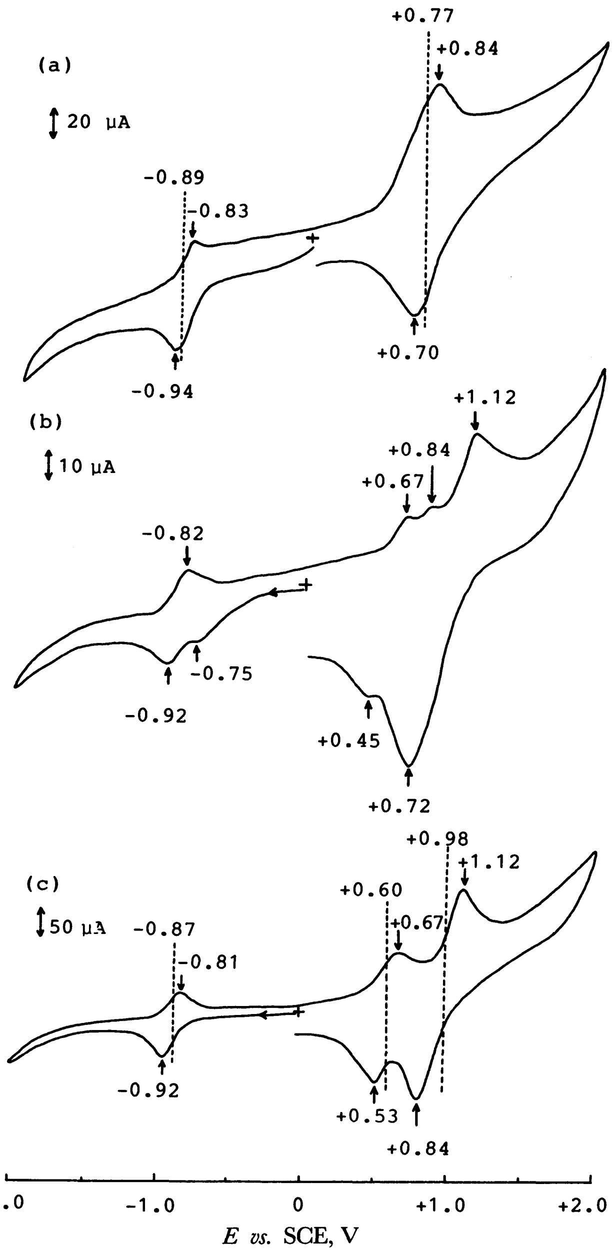


Fig. 1. Cyclic voltammograms of (a) $Mo^{VI}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (**1**)(1.0×10^{-3} mol dm^{-3}), (b) $Mo^{V}{}_2O_3(S_2CC_5H_4Fe^{II}C_5H_5)_4$ (**2**)(4.2×10^{-4} mol dm^{-3}), and (c) $Mo^{IV}O(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (**3**) (1.0×10^{-3} mol dm^{-3}) in CH_2Cl_2 containing 0.1 mol dm^{-3} [n-Bu_4N][ClO_4]; the scan rate 0.4 V s^{-1}.

$$[Mo^{V}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2]^- \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \underset{\mathbf{1}}{Mo^{VI}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2} \underset{+2e^-}{\overset{-2e^-}{\rightleftharpoons}} [Mo^{VI}O_2(S_2CC_5H_4Fe^{III}C_5H_5)_2]^{2+}$$

Scheme 1.

plexes which exhibit a signal in the range g=1.905 (K_2MoOF_5)[21] to 2.011 ([$Mo(S_2C_2Ph_2)_3$]$^-$),[22] whereas the ferricenium radical cations display quite different g-values from 2.0 ($g_{\parallel}$=4.35—3.62 and $g_{\perp}$=1.62—1.77)[23,24]

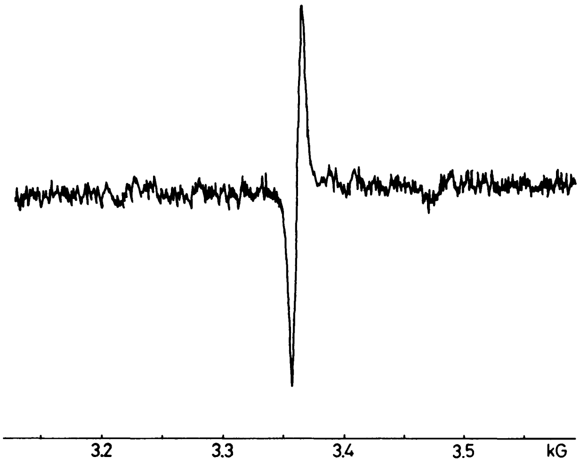


Fig. 2. Room temperature ESR spectrum of electrochemically generated [$Mo^{V}O(S_2CC_5H_4Fe^{II}C_5H_5)_2$]$^+$ in CH_2Cl_2 at 9.52 GHz.

at low temperatures; no ESR signal of the radical cations has been detected above 78 K[25] owing to very short relaxation times T_1.[26] In addition, the assignment of the redox process Fe(II)/Fe(III) for the couple at $E_{1/2}$=+0.98 V (*vs.* SCE) is consistent with a two-electron process of the anodic peak at +1.12 V (*vs.* SCE), where the two iron atoms of both ferrocenecarbodithioate ligands undergo simultaneous one-electron oxidation at the same potential, as in the case of **1**. The redox reactions of **3** can, therefore, be expressed as Scheme 2. Thus, complex **1** and **3** are considerably stable toward the electrochemical redox reactions, probably because of a large polarizability of the ferrocenecarbodithioate ligand with π-electron systems. This is in marked contrast to the corresponding dithiocarbamate and trithiocarbonate complexes, $M^{VI}O_2L_2$ and $Mo^{IV}OL_2$ (L=S_2CNR_2, S_2CSR), whose electrochemical redox reactions are followed by rapid irreversible chemical reactions resulting from the dissociation of the dithio ligands.[9,27]

As described above, **2** partly disproportionates into **1** and **3** in solution. The cyclic voltammogram of **2** in CH_2Cl_2, therefore, is rather complicated, as seen in Fig. 1b. A pair of cathodic and anodic waves at E_c=−0.92 V and E_a=−0.82 V (*vs.* SCE) may be an overlap of the redox couples of both **1** and **3**, since these potentials are almost the same as that of either **1** or **3** existing alone (See Fig. 1a and 1c). Thus, the cathodic peak at E_c=−0.75 V (*vs.* SCE, Fig. 1b) may be assigned to the reduction of **2**, whereas the corresponding anodic peak is not observed. The anodic wave at +0.84 V (*vs.* SCE) (Fig. 1b) is assigned to the oxidation of **1**, and those at +0.67 and +1.12 V (*vs.* SCE) (Fig. 1b) to the oxidation of the molybdenum and ferrocenyl moieties of **3**, respectively, both of which are resulted from the disproportionation of **2** (Eq. 1). The broad cathodic wave at +0.72 V (*vs.* SCE) may, therefore, be assigned to the reduction of the both Fe^{3+} ions of [$Mo^{VI}O_2(S_2CC_5H_4Fe^{III}C_5H_5)_2$]$^{2+}$ and [$Mo^{V}O(S_2CC_5H_4Fe^{III}C_5H_5)_2$]$^{3+}$. The

$$\begin{tikzcd}
\underset{\mathbf{3}}{\mathrm{Mo^{IV}O(S_2CC_5H_4Fe^{II}C_5H_5)_2}} \arrow[r, shift left, "-e^-"] \arrow[d, shift left, "+e^-"] & \mathrm{[Mo^{V}O(S_2CC_5H_4Fe^{II}C_5H_5)_2]^+} \arrow[l, shift left, "+e^-"] \arrow[d, shift left, "-2e^-"] \\
\mathrm{[Mo^{III}O(S_2CC_5H_4Fe^{II}C_5H_5)_2]^-} \arrow[u, shift left, "-e^-"] & \mathrm{[Mo^{V}O(S_2CC_5H_4Fe^{III}C_5H_5)_2]^{3+}} \arrow[u, shift left, "+2e^-"]
\end{tikzcd}$$

Scheme 2.

remaining cathodic wave at +0.45 V (*vs.* SCE) may constitute a redox couple, Mo(IV)/Mo(V) of **3**, with the anodic wave at +0.67 V (*vs.* SCE). These assignments may be supported from the fact that the cyclic voltammogram of **2** obtained upon an anodic scan from 0 V to +2.0 V (*vs.* SCE) followed by a reverse one to 0 V (*vs.* SCE) gave three anodic and two cathodic waves with the same potentials as Fig. 1b.

Electronic Spectra. It has been reported that both dioxomolybdenum(VI) and oxomolybdenum(IV) complexes with dithio chelate ligands exhibit the absorption band due to a molybdenum-oxygen transition around 380 nm[16] and μ-oxodimolybdenum(V) complexes with the dithio chelates display another characteristic absorption band around 510 nm as well as the 380 nm band.[16] The electronic spectra of **1**—**3**, however, show two absorption bands around 350 and 600 nm and their appearances resemble one another, irrespective of the oxidation state of the molybdenum atom. On the other hand, the ferrocenecarbodithioate anion exhibits two strong absorptions due to π-π^* (308 nm) and n-π^* (525 nm) transitions of the thiocarbonyl group, both of which are known to shift to higher wavelengths on coordination to metal atoms.[12] Thus, the bands due to transitions resulting from Mo=O and Mo-O-Mo bonds in the present complexes may be concealed by the strong absorptions of the ferrocenyl chromophore.

Table 2 lists the absorption maxima and the extinction coefficients in the electronic spectra of **1**—**3**, together with those of the electrochemical oxidized species of **1** and **3**, obtained by using a OTTLE cell. The absorption bands at 350 and 600 nm of **1** were shifted to 330 and 540 nm, respectively, on the electrochemical reduction at −1.05 V (*vs.* SCE) in CH_2Cl_2. Similarly, the reduction of **3** at −1.10 V (*vs.* SCE) in CH_2Cl_2 caused the movement of the 355 and 605 nm bands to 320 and 530 nm, respectively. Upon reoxidation of the both resulting solutions at −0.70 V (*vs.* SCE), however, neither original spectrum of **1** nor that of **3** has been recovered, suggesting that $[Mo^{V}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2]^-$ and $[Mo^{III}O(S_2CC_5H_4Fe^{II}C_5H_5)_2]^-$ decompose on the coulometric electrolysis time scale. In accordance with this, several attempts to detect the ESR signals of these reduced species generated under the controlled-potential electrolysis at −1.10 V (*vs.* SCE) of **1** and **3** in CH_2Cl_2 have been unsuccessful.

TABLE 2. ELECTRONIC SPECTRA OF THE OXOMOLYBDENUM COMPLEXES AND THEIR ELECTROCHEMICAL OXIDIZED SPECIES IN CH_2Cl_2

Entry	Complex	λ_{max}/nm	ε/cm^{-1} M^{-1}
1	$Mo^{VI}O_2(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (**1**)	350	24800
		600	8280
2	$[Mo^{VI}O_2(S_2CC_5H_4Fe^{III}C_5H_5)_2]^{2+}$	374	24200
		652	5000
3	$Mo^{V}_2O_3(S_2CC_5H_4Fe^{II}C_5H_5)_4$ (**2**)	350	42600
		600	14800
4	$Mo^{IV}O(S_2CC_5H_4Fe^{II}C_5H_5)_2$ (**3**)	355	25300
		605	5860
5	$[Mo^{V}O(S_2CC_5H_4Fe^{II}C_5H_5)_2]^+$	360	24100
		645	6900
6	$[Mo^{V}O(S_2CC_5H_4Fe^{III}C_5H_5)_2]^{3+}$	368	19000
		660	5170
7	$[Et_2NH_2][S_2CC_5H_4Fe^{II}C_5H_5]$	308	12700
		525	2220

On the other hand, the two absorption bands of **1** and **3** are shifted to higher wavelengths upon electrochemical oxidations (Compare Entries 1 with 2, and 4 with 5 and 6 in Table 2). This is consistent with the bathochromic shift of ferrocenyl derivatives with electron-attracting groups in the electronic spectra.[28] The oxidation of **1** at +0.95 V (*vs.* SCE) and the subsequent reduction at +0.60 V (*vs.* SCE) afforded the original electronic spectrum, suggesting that the oxidized species, $[Mo^{VI}O_2(S_2CC_5H_4Fe^{III}C_5H_5)_2]^{2+}$, is stable. Similarly, $[Mo^{V}O(S_2CC_5H_4Fe^{II}C_5H_5)_2]^+$ and $[Mo^{V}O(S_2CC_5H_4Fe^{III}C_5H_5)_2]^{3+}$ generated by the electrochemical oxidation of **3** at +0.80 and +1.25 V (*vs.* SCE), respectively, are stable, as confirmed from the fact that the electronic spectrum of **3** was recovered completely upon oxidation-reduction cycles. In contrast to the instability of the reduced species, the stability of electrochemically oxidized species of **1** and **3** may result from an electron-donating property of the ferrocenecarbodithioate ligand.

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