68539-08-2; $[Rh(NH_3)_5H]SO_4$, 19440-32-5.

Supplementary Material Available: Tables S-I (kinetic data) and S-II (variations of kinetic parameters with light intensity) (2 pages). Ordering information is given on any current masthead page.

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Kinetic Study on the Disproportionation Equilibrium of μ-Oxo-bis[oxobis(*N*,*N*-diethyldichalcogenocarbamato)molybdenum(V)]

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μ-Oxo-bis[oxobis(*N*,*N*-diethylthioseleno- and -diselenocarbamato)molybdenum(V)], $Mo^{V}_2O_3(XYCNEt_2)_4$ (XY = SSe, SeSe), were prepared. These compounds undergo a disproportionation reaction in solution to exist as an equilibrium mixture with $Mo^{IV}O(XYCNEt_2)_2$ and $Mo^{VI}O_2(XYCNEt_2)_2$, as reported for the dithiocarbamato analogue, $Mo^{V}_2O_3(S_2CNEt_2)_4$. Rates of the equilibration for these three systems were determined by the concentration-jump relaxation technique in 1,2-dichloroethane. The rate of disproportionation of the Mo(V) complexes increases in the order of XY = SS < SSe < SeSe, while that of the coupling reaction of the Mo(IV) complex with the Mo(VI) complex shows a reverse tendency. Activation parameters for the disproportionation and the coupling reaction of these systems suggest that the Mo–O–Mo linkage in the transition state of the disproportionation is greatly weakened. Enthalpy and entropy changes in the disproportionation were also obtained; the values in the diseleno complex are fairly smaller than those of the dithio and thioseleno analogues. A possible explanation for this is presented in terms of marked differences of the absorption intensity in their visible spectra.

Introduction

In recent years, much attention has been paid to molybdenum complexes containing sulfur ligands as model compounds for molybdenum-containing enzymes.[1,2] In this connection, dimeric μ-oxo-molybdenum(V) complexes of the $Mo_2O_3L_4$ type (L = dialkyldithiocarbamate, 1-piperidinecarbodithioate, diphenylphosphinodithioate, and related ligands) are well-known to undergo disproportionation in solution to exist as an equilibrium mixture with oxomolybdenum(IV), $MoOL_2$, and dioxomolybdenum(VI) complexes, MoO_2L_2, as follows:[3,4]

$$Mo_2O_3L_4 \overset{K}{\rightleftharpoons} MoOL_2 + MoO_2L_2$$

The equilibrium constant K for L = n-Pr_2NCS_2 was determined as 4×10^{-3} mol/L in chlorobenzene at 41 °C.[5] Newton and his co-workers have suggested that this sort of equilibrium

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Table I. $\nu(Mo{=}O)$ and $\nu(Mo{-}O{-}Mo)$ Frequencies of $Mo_2O_3L_4$ and Related Compounds (cm^{-1})

compound	medium	$\nu(Mo{=}O)$				$\nu(Mo{-}O{-}Mo)$
$Mo_2O_3(S_2CNEt_2)_4$	Nujol		936			750, 430
	CH_2Br_2	967	936	916	879	*a*
$MoO(S_2CNEt_2)_2$	CH_2Br_2	966				
$MoO_2(S_2CNEt_2)_2$	CH_2Br_2			916	879	
$Mo_2O_3(SSeCNEt_2)_4$	Nujol		937			740, 428
	CH_2Br_2	956	936	913	874	*a*
$Mo_2O_3(Se_2CNEt_2)_4$	Nujol		930			740, 420
	CH_2Br_2	961	931	907	882	*a*

[a] Not observed.

may exist also in Mo enzymes to play an important role in both Mo reductases and Mo oxidases.[3] Thus, the disproportionation equilibrium may have a significant meaning in molybdenum–sulfur complexes; however, no kinetic study has been carried out so far.

This paper reports a kinetic study on the disproportionation equilibria of three μ-oxo-bis[oxobis(*N*,*N*-diethyldichalcogenocarbamato)molybdenum(V)], $Mo_2O_3(XYCNEt_2)_4$ (XY = SS (**1**), SSe (**2**), and SeSe (**3**)), by the concentration-jump relaxation technique.[6] Complexes **2** and **3** are the first examples that Mo(V) complexes containing no 1,1-dithiolato ligands exhibit disproportionation equilibria.

Experimental Section

Materials and General Procedure. Dichlorodioxomolybdenum, MoO_2Cl_2, was prepared according to the literature method.[7] Sodium diethylthioseleno- and -diselenocarbamate, $Et_2NCSSeNa$[8] and Et_2NCSe_2Na,[9] were obtained as described elsewhere. All reactions and manipulations were carried out under dry nitrogen. Solvents used for the preparation and spectral measurements were deoxygenated by bubbling nitrogen before use.

Oxo- and Dioxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(IV) and -(VI), $MoO(S_2CNEt_2)_2$[4] and $MoO_2(S_2CNEt_2)_2$.[10] These compounds were prepared by the method described previously.

μ-Oxo-bis[oxobis(*N*,*N*-diethyldichalcogenocarbamato)molybdenum(V)], $Mo_2O_3(XYCNEt_2)_4$ (XY = SS (1), SSe (2), SeSe (3)). To a stirred and ice-cold aqueous solution of $Et_2NCSSeNa$ (5.23 g, 24 mmol) was added dropwise an aqueous solution of MoO_2Cl_2 (2.38 g, 12 mmol). A purple precipitate of **2** formed immediately and was collected by filtration, washed with water followed by ether, and dried in vacuo; 45% yield. Anal. Calcd for $C_{20}H_{40}N_4O_3S_4Se_4Mo_2$: C, 23.55; H, 3.93; N, 5.49. Found: C, 23.42; H, 3.95; N, 5.37. Dark purple **3** was similarly obtained by the reaction of MoO_2Cl_2 (2.0 g, 10 mmol) with Et_2NCSe_2Na (4.7 g, 20 mmol) in water; 40% yield. Anal. Calcd for $C_{20}H_{40}N_4O_3Se_8Mo_2$: C, 19.88; H, 3.34; N, 4.64. Found: C, 19.96; H, 3.39; N, 4.62. Purple complex **1** was prepared by the literature method.[3] Anal. Calcd for $C_{20}H_{40}N_4O_3S_8Mo_2$: C, 28.84; H, 4.84; N, 6.73. Found: C, 28.96; H, 4.92; N, 6.72.

Kinetic and Other Measurements. The concentration-jump experiments were carried out by mixing a 1,2-dichloroethane solution of $Mo_2O_3(XYCNEt_2)_4$ (0.2–1.9 mmol/L) with the same volume of 1,2-dichloroethane on a Union Giken stopped-flow spectrophotometer under an atmospheric pressure of dry nitrogen at four different temperatures in the 5–35 °C range. The reaction was followed by monitoring the decay of the absorption band of **1**, **2**, or **3** in the visible region. Changes of the absorbance with time after mixing were summed up at least 20 times with a Union Giken 71 kinetic data processor.

Visible and infrared spectra were recorded on Hitachi 124 and 215 spectrophotometers, respectively.

Results and Discussion

Disproportionation Equilibria. Table I lists the relevant infrared frequencies of **1**–**3** and $MoO_n(S_2CNEt_2)_2$ (n = 1, 2). Complex **1** in Nujol mulls exhibits only one $\nu(Mo{=}O)$ and two $\nu(Mo{-}O{-}Mo)$ bands, antisymmetric and symmetric. A dibromomethane solution of this complex, however, displayed three additional bands in the $\nu(Mo{=}O)$ region, whose frequencies are almost the same as those of $\nu(Mo{=}O)$ observed in $MoO(S_2CNEt_2)_2$ or $MoO_2(S_2CNEt_2)_2$ in dibromomethane. This is compatible with the result that **1** undergoes a part of disproportionation to exist as an equilibrium mixture with $MoO(S_2CNEt_2)_2$ and $MoO_2(S_2CNEt_2)_2$ in solution, as reported previously.[3] Infrared spectra of **2** and **3** in dibromomethane similarly show four $\nu(Mo{=}O)$ bands, whose frequencies are very close to those of **1** in the same solvent, while they display only a $\nu(Mo{=}O)$ band in the solid state (Table I). It is therefore suggested that **2** and **3** also undergo similar disproportionation reactions as follows:

$$Mo^{V}{}_2O_3L_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo^{IV}OL_2 + Mo^{VI}O_2L_2 \qquad (1)$$

$$L = Et_2NCS_2,\ Et_2NCSSe,\ Et_2NCSe_2$$

Binuclear μ-oxo-molybdenum(V) complexes containing the $Mo_2O_3{}^{4+}$ skeleton were reported to exhibit a characteristic strong band around 520 nm, which has recently been assigned to the electronic transition from the three-center Mo–O–Mo π-bonding orbital to the corresponding antibonding orbital.[2] This assignment is reasonable if one Mo–O–Mo skeleton is almost linear, as confirmed by the X-ray structure analysis of $Mo_2O_3(S_2CN\text{-}n\text{-}Pr_2)_4$,[11] $Mo_2O_3(S_2P(OEt)_2)_4$,[12] and $Mo_2O_3(S_2COEt)_4$.[13] Compounds **1** and **2** in 1,2-dichloroethane displayed the characteristic band at 512 and 526 nm at room temperature, respectively, while the corresponding band of **3** was concealed by an intense absorption in the higher energy region. At 6 °C, however, it appeared at 544 nm as a weak shoulder on the tail of the ligand absorption. This is because the equilibrium of eq 1 shifts to the left with lowering temperature, resulting in an increasing amount of the Mo(V) complex.

Kinetics. When a 1,2-dichloroethane solution of **1**, **2**, or **3** was mixed with the same volume of 1,2-dichloroethane, the intensity of the 512 nm (**1**), 526 nm (**2**), or 544 nm (**3**) bands of the complex decreases exponentially with half-lives of 0.1–1.8 s. The Guggenheim plots of the absorbance on the concentration jump gave a straight line (correlation coefficient of 0.999 over a period of 3τ), the slope of which gave the relaxation time τ ($\tau = 1/k_{obsd}$), as shown in eq 2, where A_t

$$\ln (A_{t+\alpha} - A_t) = -t/\tau + \ln (A_\infty - A_0)(1 - e^{-\alpha/\tau}) \qquad (2)$$

and $A_{t+\alpha}$ are absorbances at several times t and at a further set of times $t + \alpha$ and A_0 and A_∞ are those at the beginning and at the end of the reaction, respectively.

Newton et al. have reported that no ions were formed in solutions of **1** on the basis of conductance measurements, although the solvent was not specified.[3] No ionic dissociation may also be assumed to occur in solutions of **2** and **3**, because of similarity of the carbamato ligands among **1**–**3**. Thus, the τ value in the equilibrium reaction of eq 1 is written as[14]

$$1/\tau = k_1 + ([MoOL_2]_{eq} + [MoO_2L_2]_{eq})k_{-1} \qquad (3)$$

where $[MoOL_2]_{eq}$ and $[MoO_2L_2]_{eq}$ are the equilibrium concentrations of $MoOL_2$ and MoO_2L_2, respectively. From eq 3 is easily derived eq 4,[15] where $[Mo_2O_3L_4]_0$ stands for the

$$(1/\tau)^2 = 4k_1k_{-1}[Mo_2O_3L_4]_0 + k_1{}^2 \qquad (4)$$

concentration of $Mo_2O_3L_4$ when the equilibrium of eq 1 is assumed to shift to the left completely. Thus, plots of $(1/\tau)^2$ against $[Mo_2O_3L_4]_0$ should give a straight line with a slope of $4k_1k_{-1}$ and an intercept of $k_1{}^2$.

Figure 1 shows the plots of $(1/\tau)^2$ vs. $[Mo_2O_3L_4]_0$ at 25 °C, from which the rate constants k_1 and k_{-1} and then the equilibrium constants K were calculated. The results are summarized in Table II, which reveals the K value increases in the order **1** < **2** < **3**; the coordination of selenium displaces the equilibrium of eq 1 to the right more than that of sulfur. The large K value for **3** is compatible with the fact that the

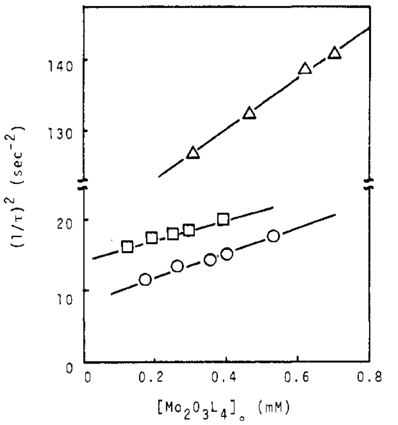

Figure 1. Plots of $(1/\tau)^2$ against $[Mo_2O_3L_4]_0$ in 1,2-dichloroethane at 25 °C: L = Et_2NCS_2 (○), Et_2NCSSe (□), Et_2NCSe_2 (△).

Table II. Rate and Equilibrium Constants of the Disproportionation of $Mo_2O_3L_4$ in 1,2-Dichloroethane at 25 °C[a]

$$Mo_2O_3L_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MoOL_2 + MoO_2L_2$$

L	k_1, s^{-1}	$10^{-2}k_{-1}$, s^{-1} M^{-1}	10^3K, M
Et_2NCS_2	2.93 ± 0.29	14.7 ± 0.2	2.0 ± 0.2
Et_2NCSSe	3.78 ± 0.11	9.0 ± 1.0	4.2 ± 0.5
Et_2NCSe_2	10.8 ± 0.1	8.3 ± 0.1	13.0 ± 0.2

[a] Errors were estimated at the 95% confidence level.

Table III. Activation Parameters[a] for the Disproportionation of $Mo_2O_3L_4$ and the Coupling Reaction of $MoOL_2$ with MoO_2L_2 (the Values for the Latter Reaction Are in Parentheses)

L	E_a, kJ/mol	$\Delta H^{\ddagger}_{298}$, kJ/mol	$\Delta S^{\ddagger}$, J/(mol K)	$\Delta G^{\ddagger}_{298}$, kJ/mol
Et_2NCS_2	73.8 ± 1.7	71.3 ± 1.7	0.6 ± 3.7	71.1 ± 2.1
	(23.9 ± 1.0)	(21.4 ± 1.0)	(−113 ± 2)	(55.2 ± 1.2)
Et_2NCSSe	81.3 ± 1.5	78.8 ± 1.5	30.5 ± 0.9	69.7 ± 2.4
	(18.2 ± 4.7)	(15.7 ± 4.7)	(−135 ± 32)	(56 ± 17)
Et_2NCSe_2	56.0 ± 4.6	53.5 ± 4.6	−45.5 ± 3.5	67.1 ± 7.7
	(31.1 ± 6.7)	(28.6 ± 6.7)	(−93 ± 27)	(56 ± 21)

[a] Errors were estimated at the 95% confidence level.

characteristic band of the binuclear μ-oxo-molybdenum complex was obscured by the tail of the ligand absorption at room temperature, as described above.

Garner et al. reported the kinetic study on oxo abstraction of $MoO_2(S_2CNEt_2)_2$ by $P(C_6H_5)_3$ in acetonitrile under the condition with greater than tenfold excess $P(C_6H_5)_3$ at 25 °C (eq 5),[16] where they have concluded that $MoO_2(S_2CNEt_2)_2$

$$MoO_2(S_2CNEt_2)_2 + P(C_6H_5)_3 \rightarrow MoO(S_2CNEt_2)_2 + OP(C_6H_5)_3 \quad (5)$$

is effectively reduced by $P(C_6H_5)_3$ before the equilibrium of eq 1 occurs, on the basis of the fact that no $Mo_2O_3(S_2CNEt_2)_4$ was detected in the reaction products under the conditions employed. The rate constant of this reaction (1.1 s^{-1} M^{-1}), however, is smaller by 3 orders of magnitude than that of the coupling reaction (k_{-1}) of $MoO(S_2CNEt_2)_2$ with $MoO_2(S_2CNEt_2)_2$ obtained in the present study. The rate constant of the oxo abstraction may therefore be acceptable only in the initial state of the reaction, because $MoO(S_2CNEt_2)_2$ formed by the oxo abstraction consumes $MoO_2(S_2CNEt_2)_2$ rapidly according to eq 1.

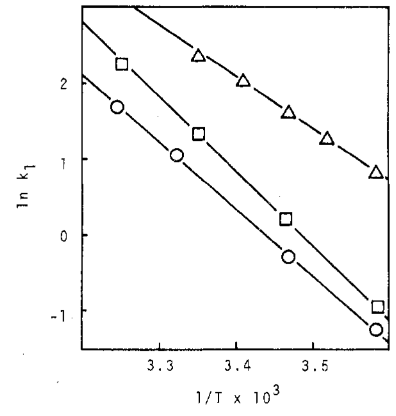

Figure 2. Arrhenius plots of the rate constants for disproportionation of $Mo_2O_3L_4$: L = Et_2NCS_2 (○), Et_2NCSSe (□), Et_2NCSe_2 (△).

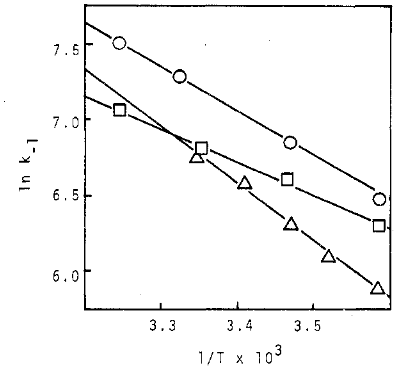

Figure 3. Arrhenius plots of the rate constants for the coupling reaction of $MoOL_2$ with MoO_2L_2: L = Et_2NCS_2 (○), Et_2NCSSe (□), Et_2NCSe_2 (△).

Table IV. Thermodynamic Quantities[a] for the Disproportionation of $Mo_2O_3L_4$

L	ΔH, kJ/mol	ΔS, J/(mol K)	ΔG_{298}, kJ/mol
Et_2NCS_2	50.5 ± 2.4	116 ± 14	15.9 ± 4.9
Et_2NCSSe	63.1 ± 4.8	166 ± 29	13.7 ± 6.8
Et_2NCSe_2	24.9 ± 2.7	47 ± 19	10.8 ± 4.4

[a] Errors were estimated at the 95% confidence level.

The Arrhenius plots for the rate constants of the forward and backward reactions of eq 1 obtained at various temperatures are shown in Figures 2 and 3, respectively, from which activation parameters were calculated. The results are collected in Table III. The activation enthalpies of the disproportionation of $Mo_2O_3L_4$ are fairly larger than those of the coupling reaction of $MoOL_2$ with MoO_2L_2. However, the activation entropies of the disproportionation reaction are small positive or negative values, and those of the coupling reaction are large negative values. These results suggest that the Mo–O–Mo bond is weakened to a great extent but the binuclear structure is still maintained in the transition state of the disproportionation of the Mo(V) complexes.

The molar extinction coefficient of **1** at 512 nm ($\epsilon_{512\ nm}$ 24 000 cm^{-1} M^{-1}) was determined from the equilibrium constant and those of $MoO(S_2CNEt_2)_2$ and $MoO_2(S_2CNEt_2)_2$ at 512 nm (90 and 75 cm^{-1} M^{-1}, respectively). This value is in good agreement with that reported previously (24 500 cm^{-1} M^{-1} in benzene).[17] The values of **2** ($\epsilon_{526\ nm}$ 23 000 cm^{-1} M^{-1}) and **3** ($\epsilon_{544\ nm}$ 8100 cm^{-1} M^{-1}) were similarly calculated from the equilibrium constants and the sum of the ε values of the corresponding Mo(IV) and Mo(VI) complexes obtained from the visible spectra.

Thermodynamic quantities for the disproportionation of Mo(V) complexes were obtained from plots of ln *K* against 1/*T*. The results are listed in Table IV, which shows fairly small Δ*H* and Δ*S* values for **3** compared with those for **1** and **2**. One possible explanation for this is that the Mo–O–Mo bond in **3** is bent and/or its dπ, pπ, and dπ orbitals are twisted to one another to decrease the contribution of the three-center

π bond. This assumption is consistent with a small ϵ value of **3** at 544 nm compared with those of **1** and **2** at 512 and 526 nm, respectively.

Registry No. $Mo_2O_3(Et_2NCS_2)_4$, 18539-11-2; $Mo_2O_3(Et_2NCSSe)_4$, 68539-98-0; $Mo_2O_3(Et_2NCSe_2)_4$, 68539-99-1.

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Resonance Raman Spectra of Tetrapyrrole Complexes of Oxomolybdenum(V)

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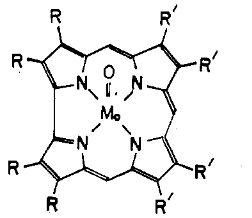
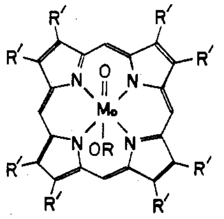
The resonance Raman spectra of MoO(MEC) and MoO(OEP)(OMe) have been measured in the solid state. Due to low symmetry of the tetrapyrrole core, the former exhibits about 2 times more bands than the latter in the 1650–400-cm^{-1} region. Excitation profile studies on MoO(MEC) show that some tetrapyrrole core vibrations give maxima at the α(O–O) band and that two bands at 950 cm^{-1} (Mo=O stretching) and 320 cm^{-1} are enhanced more than the core vibrations as the exciting frequency approaches the strong band at 455 nm. These results suggest that the 455-nm band is largely due to a ligand–metal charge-transfer transition and that the 320-cm^{-1} band is assignable to the Mo–N stretching vibration enhanced via such charge-transfer. The spectral change caused by laser irradiation of MoO(OEP)(OMe) in the solid state has been attributed to polymerization through the formation of the methoxy bridge between two metal atoms.

Recently, Murakami et al.[1] have prepared a novel molybdenum(V) complex with 2,3,17,18-tetramethyl-7,8,-12,13-tetraethylcorrole (abbreviated as MEC) and concluded from its ESR spectrum that the $MoON_4$ skeleton is close to a tetragonal pyramid. They also reported that MoO(OEP)(OMe) exists as a single monomeric species in dichloromethane or chloroform while more than one species is present in aromatic solvents.[2] The purpose of this paper is to report the resonance Raman spectra of MoO(MEC) and MoO(OEP)(OMe).





($R=CH_3$, $R'=C_2H_5$)

MoO(MEC) $MoO(OEP)OCH_3$

Although resonance Raman spectra of many metalloporphyrins have been reported, most of these compounds contain porphin cores of D_{4h} symmetry which severely limits the number of core vibrations observed in Raman spectra. The MEC complex is unique in that all the core vibrations are nondegenerate and Raman active due to its low symmetry (C_s or C_1). Thus, it is interesting to compare the number of Raman-active core vibrations between MoO(MEC) and MoO(OEP)(OMe). Secondly, metalloporphyrins of W(V), Cr(III), Mn(III), Mo(V), Re(V), etc. belong to "d-type hyperporphyrins",[3] which exhibit strong bands near 450 nm in addition to the α, β, and Soret bands. In the case of manganese(III) etioporphyrin I complexes, these extra bands near 460 nm (band V) have been assigned to the charge-transfer (CT) transition from the ligand ($a_{1u}(\pi)$ or $a_{2u}(\pi)$ orbital) to the metal ($e_g(d\pi)$ orbital)[3,4] or the ligand π–π* transition mixed with such a CT transition.[5] According to Gouterman,[3] the assignments of two bands at 500–440 nm (band V) and 350–340 nm (band VI) of the MoO(OEP)L type compounds depend upon the nature of L; when L is OCH_3, the stronger band (band V) at 443 nm is assigned to a Soret and a weaker band (band VI) at 342 nm is assigned to a CT transition. However, these assignments are reversed for L = Cl since band V at 500 nm is weaker than band VI at 350 nm. However, such an intensity criterion is by no means certain. Our excitation profile study may provide clues in elucidating the nature of these electronic bands.

Experimental Section

The compound MoO(MEC) was prepared by the method described previously.[1] The analogous MoO complex MoO(OEP)(OMe) was prepared by the literature method.[2] The resonance Raman spectra of these compounds were measured by using a Spex 1401 double monochromator. Detection was made with a cooled RCA C31034 photomultiplier tube and a Spex digital photometer. Excitation lines were provided by a Spectra-Physics Model 164 Ar-ion laser and a Spectra-Physics Model 375 CW dye laser (Rhodamine 6G) pumped by the Ar-ion laser. Calibration of frequency reading was made by using Ar-ion laser lines.

The resonance Raman spectra of MoO(MEC) (Figure 1) were measured in thin films cooled to 20 K using the apparatus described in our previous paper.[6] The excitation profile studies (Figure 4) were made in a K_2SO_4 pellet (2×10^{-3} molar ratio). The pellet was rotated during the measurement to avoid thermal decomposition. Using the 986-cm^{-1} band of K_2SO_4 as the internal standard, we estimated the relative intensity of the MoO(MEC) band from the band area or the peak height if the band is partially overlapped. The detector sensitivity and ν^4-law corrections were made on relative intensities thus obtained. The Raman spectrum of MoO(OEP)(OMe) was measured in a KBr pellet at room temperature. The electronic spectra of both compounds

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