Molybdenum(VI), -(V), and -(IV) Oxo Complexes with S-methyl 3-(2-hydroxyphenyl)methylenedithiocarbazate and Its Derivatives

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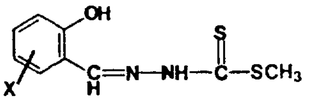
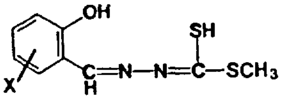
A number of molybdenum(VI), -(V), and -(IV) oxo complexes with S-methyl 3-(2-hydroxyphenyl)methylenedithiocarbazate and its derivatives as the ONS-donor metal-binding substrate are synthesized. The Mo(VI)-dioxo complexes are cis-dioxo $MoO_2L(D)$, where D is solvent molecules such as MeOH, DMF, Py(pyridine), DMSO, and γ-Pic(γ-picoline). The Mo(V)-oxo complexes are of the type $(PyH)[MoO(NCS)_2L]$ with an octahedral geometry. The Mo(IV)-oxo complexes, MoOL are derived from corresponding Mo(VI)-dioxo complexes by oxo abstraction with PPh_3. The complexes are characterized by IR, ^1H-NMR, UV-Vis spectroscopy and cyclic voltammetry. On the basis of ligand displacement reaction, the qualitative order of D binding for $MoO_2L(D)$ complexes is also discussed.

Introduction

Molybdenum oxo complexes have attracted considerable attention in the last two decades on account of their redox catalytic activity[1] and multielectron electrochemical behavior.[2] It is well-known[3] that catalytic reactions of the molybdoenzymes involve oxidation states Mo(VI) and Mo(IV). Recent EPR studies of such reaction have established[4] that the Mo(V) state coexists with Mo(VI) and Mo(IV) during the process of electron transfer to or from the redox centers. Furthermore, extended X-ray absorption fine structure (EXAFS) spectroscopic studies have also implicated the presence of a sulfur atom, besides oxygen and nitrogen, at the active sites of oxo-transfer molybdoenzymes.[5] In relation to these studies, we have taken up S-methyl 3-(2-hydroxyphenyl)methylenedithiocarbazate and its derivatives as a trifunctional (ONS) dianionic schiff base ligand. These ligands shown in thione and thiol form as A and B are of important because their complexes with the MoO_2^{2+} or MoO^{2+} core could be of the form MoO_2L or MoOL, possessing one or two "open" coordination sites that can be utillized for substrate binding. It has been also reported[6] that the phenyl substituents play a important role whether the isolated molybdenum(VI)-dioxo complexes are discrete monomers, $[MoO_2L(D)]$ (D=EtOH or MeOH) or polymeric species, $[(MoO_2L)_n]$, containing ⋯(O)Mo=O-Mo(O)=O⋯ chains in $[MoO_2(tridentate)]$ species.



A



B

	X
H_2L^1	H
H_2L^2	5-Me
H_2L^3	3-CH_3O
H_2L^4	5,6-Bz

Although a number of papers for the molybdenum(VI), -(V), and -(IV) oxo complexes of tridentate ONS donor systems have been reported, the related complexes of S-methyl 3-(2-hydroxyphenyl)methylenedithiocabazate or its derivatives have been little published. In this work, we report some new monomeric molybdenum(VI), -(V), and -(IV) oxo complexes of these ligands. Spectroscopic properties and the electrochemical behavior of the complexes have been discussed. On the basis of ligand displacement reactions, the qualitative order of D binding for $MoO_2L(D)$ (D=neutral monodentate ligands) complex have been also established.

Experimental

Meterials. Molybdenyl acetylacetonate, $[MoO_2(acac)_2]$ was obtained from Tokyo Kasei Chemical Industry Co., Ltd. Pyridinum oxoisothiocyanatomolybdate(V), $(PyH)_2[MoO(NCS)_5]$ was prepared by literature method.[7] Salicylaldehyde, 3-methoxysalicylaldehyde, and 2-hydroxy-1-naphthaldehyde were obtained from Tokyo Kasei or Fluka Chemical Co., Ltd. 5-Methylsalicylaldehyde[8] and S-methyldithiocabazate[9] were prepared by the method described in the literature. All other chemical used for preparative work were of reagent grade and were employed without further purification. Reagent grade solvents were dried and distilled before use.

Physical measurements. C. H. N. for the complexes were carried out by Kolon R and D center and Mo was analyzed by using a Labtaim ICP spectrometer (Model 8440). The M. P. measurements were performed by using a Haake melting point apparatus. The molar conductance of the complexes were measured by YSI conductivity bridge (Model 31). The IR spectra of solid samples in KBr were recorded on a Mattson Polaris FT-IR. The ^1H-NMR spectra in DMSO-d_6 were recorded on a Bruker AM 300 spectrometer and referenced to TMS (internal). Electronic spectra were obtained on a Shimazdu UV-160A uv-visible spectrophotometer. Cyclic voltammograms were recorded on a Electrochemical Research System 270/6/0 (EG & G) consisting of PAR 263 Potentiostat/Galvanostat and Electrochemical analysis software 270. The electrochemical studies were conducted in oxygen-free DMSO or DMF solution containing 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte. We empolyed a three-electrode cell configuration consisting of a gold working, platinium counter and a saturated calomel reference electrode.

Synthesis. Ligands.[10] H_2L^1-H_2L^4. The compounds were obtained by condensation of appropriate aldehydes with an ethanolic solution of S-methyldithiocabazate. Anal. Calcd for $C_9H_{10}N_2OS_2(H_2L^1)$: C, 47.76; H, 4.86; N, 12.28. Found: C, 48.12; H, 4.59; N, 12.13. Calcd for $C_{10}H_{12}N_2OS_2(H_2L^2)$: C, 50.00; H, 5.00; N, 11.67. Found: C, 49.95; H, 5.02; N, 11.72. Calcd for $C_{10}H_{12}N_2OS_2(H_2L^3)$: C, 46.88; H, 4.69; N, 10.94. Found: C, 47.09; H, 4.58; N, 10.80. Calcd for $C_{13}H_{12}N_2OS_2(H_2L^4)$: C, 56.52; H, 4.35; N, 10.14. Found: C, 56.73; H, 4.50; N, 10.21.

Complexes. $[MoO_2L^1(MeOH)]$ (1a). To a filtered solution of 0.326 g (1.0 mmol) of $MoO_2(acac)_2$ in 20 *ml* of methanol was added 0.226 g (1.0 mmol) of H_2L^1 in 15 *ml* of methanol. The resulting organe-red solution was refluxed for 2 h. The volume of the solution was then reduced to about 10 *ml* in rotavaporator. This was allowed to stand for 24 h in a refrigerator. The yellowish-brown compound that separated out was filtered, washed with cold methanol, and dried *in vacuum* oven. The compound was recrystallized from methanol; Yield 59%. mp. 248-250℃. Anal. Calcd for $C_{10}H_{12}N_2O_4S_2Mo$: C, 31.26; H, 3.15; N, 7.29; Mo, 25.91. Found: C, 30.55; H, 3.05; N, 7.1; Mo, 26.22.

$[MoO_2L^2(MeOH)]$ (1b) and $[MoO_2L^3(MeOH)]$ (1c). These were prepared similarly, by following the methods described above for the preparation of **1a**, with use of appropriate schiff base ligands instead of H_2L^1. **1b**: Yield 77%. mp. 255-256℃. Anal. Calcd for $C_{11}H_{14}N_2O_4S_2Mo$: C, 33.17; H, 3.54; N, 7.03. Found: C, 32.97; H, 3.24; N, 6.95. **1c**: Yield 63%. mp. 254-257℃. Anal. Calcd for $C_{11}H_{14}N_2O_5S_2Mo$: C, 31.89; H, 3.41; N, 6.76. Found: C, 32.50; H, 3.31; N, 6.72.

$[MoO_2L^4]$ (1d). This was prepared by following the method described above for the preparation of **1a**. The complex was not dissolved in methanol and couldn't be recrystallzed from methanol medium. Yield 92%. mp. 350℃ above. Anal. Calcd for $C_{13}H_{10}N_2O_3S_2Mo$: C, 38.81; H, 2.15; N, 6.96. Found: C, 39.68; H, 2.43; N, 6.88.

$[MoO_2L^1(DMF)]$ (1e). To a solution of 0.370 g (1.0 mmol) of **1a** in 25 *ml* of methanol was added dropwise with constant stirring a solution of 0.073 g (1.0 mmol) of dimethylformamide. The orange solution was refluxed for 4 h. The solution was kept for 24 h in refrigerator. The orange compound that seperated out was filtered, washed with diethylether, and dried *in vacuum* oven; Yield 64%. mp. 165-167℃. Anal. Calcd for $C_{12}H_{15}N_3O_4S_2Mo$: C, 33.89; H, 3.55; N, 9.88. Found: C, 33.09; H, 3.44; N, 9.36.

$[MoO_2L^1(Py)]$ (1f). This was prepared as an orange compound, by following the method described above for the preparation of **1e**, with use of 0.425 g (1.0 mmol) of **1e** and 0.079 g (1.0 mmol) of pyridine (Py), in a yield of 86%. mp. 247-248℃. Anal. Calcd for $C_{14}H_{13}N_3O_3S_2Mo$: C, 39.98; H, 3.04; N, 9.74; Mo, 22.24. Found: C, 39.90; H, 2.93; N, 9.90; Mo, 22.24.

$[MoO_2L^1(\gamma\text{-Pic})]$ (1g). This was prepared as an orange microcrystalline compound, by following the same procedure as mentioned above for the preparation of **1e**, with use of 0.431 g (1.0 mmol) of **1f** and 0.093 g (1.0 mmol) of γ-picoline (γ-Pic) in a yield of 84%. mp. 186-187℃. Anal. Calcd for $C_{15}H_{15}N_3O_3S_2Mo$: C, 40.45; H, 3.39; N, 9.44. Found: C, 39.47; H, 3.33; N, 9.45.

$[MoO_2L^1(DMSO)]$ (1h). This was prepared as a reddish-orange compound, by following the methods described above for the preparation of **1e**, with use of 0.445 g (1.00 mmol) of **1** g and 0.078 g (1.0 mmol) of dimethylsulfoxide, in a yield of 73%. mp. 181-183℃. Anal. Calcd for $C_{11}H_{14}N_2O_4S_3Mo$: C, 30.70; H, 3.28; N, 6.51. Found: C, 30.49; H, 3.20; N, 7.02.

The complexes **1e-1h** were also prepared by treating $[MoO_2L^1(MeOH)]$ with an equimolar of neutral monodentate donor ligands in methanol medium.

$(PyH)[MoO(NCS)_2L^1]$ (2a). To a suspension of 0.226 g (1.0 mmol) of H_2L^1 in 5 *ml* of methanol with stirring at 50℃ was added 0.56 g (1.0 mmol) of $(PyH)_2[MoO(NCS)_5]$ in 5 *ml* of methanol. After complete dissolution of H_2L^1 into the solution, 0.158 g (2.0 mmol) of pyridine in 2 *ml* of methanol was slowly added to the solution. The solution turned dark brown, and it was kept in a refrigerator for 5 days. The shinning black crystalline compound was precipitated out. This was filtered, washed with methanol, diethyl ether and dried *in vacuum* oven; Yield 78%. mp. 126-130℃. Anal. Calcd for $C_{16}H_{14}N_5O_2S_4Mo$: C, 36.09; H, 2.65; N, 13.15; Mo, 18.02. Found: C, 35.80; H, 2.74; N, 12.71; Mo, 18.02.

$(PyH)[MoO(NCS)_2L^2]$ (2b), $(PyH)[MoO(NCS)_2L^3]$ (2c), and $(PyH)[MoO(NCS)_2L^4]$ (2d). These were prepared similary, by following the method described above for the preparation of **2a**, with use of appropriate schiff base ligands. **2b**: Yield 67%. mp. 170-172℃. Anal. Calcd for $C_{17}H_{16}N_5O_2S_4Mo$: C, 37.36; H, 2.95; N, 12.81. Found: C, 36.89; H, 3.01; N, 11.33. **2c**: Yield 68%. mp. 180-182℃. Anal. Calcd for $C_{17}H_{16}N_5O_3S_4Mo$: C, 36.30; H, 2.85; N, 12.46. Found: C, 36.15; H, 2.85; N, 12.50. **2d**: Yield 67%. mp. 215-218℃. Anal. Calcd for $C_{20}H_{16}N_5O_2S_4Mo$: C, 41.23; H, 2.77; N, 12.02. Found: C, 40.70; H, 2.66; N, 12.25.

$[MoOL^1]$ (3a) and $[MoOL^3]$ (3b). To a refluxing solution of 1.0 mmol of the complexes **1a/1c** in 25 *ml* of degassed acetonitrile was added 0.392 g (1.5 mmol) of PPh_3 in 15 *ml* of acetonitrile. The green solution turned dark brown, and a brown compound separated out. This precipitate was filterd hot, washed well with hot acetonitrile, and dried *in vacuum* oven; **3a**: Yield 77%. mp. 238-239℃. Anal. Calcd for $C_9H_8N_2O_2S_2Mo$: C, 32.15; H, 2.40; N, 8.33; Mo, 28.53. Found: C, 31.52; H, 2.25; N, 7.63; Mo, 28.46. **3b**: Yield 88%. mp. 350℃ avobe. Anal. Calcd for $C_{10}H_{10}N_2O_3S_2Mo$: C, 32.79; H, 2.75; N, 7.65. Found: C, 31.98; H, 2.62; N, 7.43.

$[MoOL^1](Phen)]$ (3c). To a refluxing solution of 0.37 g (1.0 mmol) of **1a** in 25 *ml* of methanol was added 1.00 g (5.0 mmol) of phenanthroline. To the resulting solution was added dropwise 0.393 g (1.5 mmol) of PPh_3. The solution was refluxed for 2 h. The greenish-blue microcrystalline precipitated was collected by filtration of hot solution, washed well with methanol, diethyl ether, and dried *in vacuum* oven; Yield 47%. mp. 186-187℃. Anal. Calcd for $C_{21}H_{16}N_4O_2S_2Mo$: C, 48.84; H, 3.12; N, 10.85. Found: C, 47.57; H, 2.81; N, 9.49.

Results and Disscussion

Molybdenum(VI)-dioxo and Molybdenum(IV)-oxo complexes. Most of molybdenum(VI)-dioxo and molybdenum(IV)-oxo complexes with tridentate schiff base could be synthesized, in high yield, from methanol and acetonitrile solution. All complexes are air stable in the solid state. The complexes are moderately soluble in methanol, dichloromethane and dimethylsulfoxide, but highly soluble in dimethyl-

Table 1. Spectral and Conductivity Data for the Complexes

Complex	IR (cm^{-1})*			UV-Vis	Λ_M[d]
	ν(Mo=O)	ν(C=N)	Others	λ_{max} (logε dm^3 mol cm^{-1})	(mho cm^2 mol^{-1})
$MoO_2L^1(MeOH)$ (**1a**)	902, 931	1600 (1620)		410(3.48) 320(4.34)	4.0
$MoO_2L^2(MeOH)$ (**1b**)	906, 930	1611 (1623)		424(3.42) 322(4.33)	4.4
$MoO_2L^3(MeOH)$ (**1c**)	874, 942	1590 (1616)		397(3.59) 328(4.19)	3.2
MoO_2L^4 (**1d**)	818, 918	1618 (1622)		436(3.68) 346(4.30)	4.4
$MoO_2L^1(DMF)$ (**1e**)	896, 924	1597	1652[a] (1670)	417(3.50) 320(4.38)	4.1
$MoO_2L^1(Py)$ (**1f**)	901, 923	1598		414(3.51) 320(4.36)	4.3
MoO_2L^1(γ-Pic) (**1g**)	900, 919	1620		417(3.47) 320(4.32)	5.0
$MoO_2L^1(DMSO)$ (**1h**)	887, 899	1600	1008[b] (~1050)	414(3.53) 320(4.40)	4.0
$(PyH)[MoO(NCS)_2L^1]$ (**2a**)	933	1597	2042[c]	821(1.69) 447(3.41) 319(4.24) 267(4.17)	53.6
$(PyH)[MoO(NCS)_2L^2]$ (**2b**)	939	1609	2039[c]	689(2.13) 459(3.50) 316(4.18) 266(4.32)	84.7
$(PyH)[MoO(NCS)_2L^3]$ (**2c**)	935	1597	2038[c]	716(2.10) 400(sh) 313(4.18) 260(4.13)	54.6
$(PyH)[MoO(NCS)_2L^4]$ (**2d**)	938	1615	2037[c]	816(1.58) 446(3.65) 339(4.34) 267(4.41)	52.7
$MoOL^1$ (**3a**)	967	1602		697(0.59) 413(3.02) 319(4.30) 264(4.19)	20.7[e]
$MoOL^3$ (**3b**)	964	1599		719(1.08) 387(3.83) 327(4.41) 285(3.40)	18.2[e]
$MoOL^1(Phen)$ (**3c**)	943	1625			

*Free ligand vibration in parentheses, [a] ν(C=O) in dimethylformamide, [b] ν(S=O) in dimethylsulfoxide, [c] ν(N≡C-S) in thiocyanate, [d] 10^{-3} M in DMSO at 25℃, [e] 10^{-3} M in DMF at 25℃.

formamide. The values of molar conductance of the molybdenum(VI)-dioxo complexes are in the range 3.2 to 5.0 mho cm^2 mol^{-1} in DMSO solution. The molybdenum(IV)-oxo complexes show the values in the range 18.2 to 20.7 mho cm^2 mol^{-1} in DMF solution. These results indicate that the complexes are nonelectrolytes.[11] Also, the complexes (**1e-1h**) could be synthesized by the substitution reaction of the type $MoO_2(L)(D)+D' \rightarrow MoO_2(L)(D')+D$, where D and D′ are different donor molecules. On addition of the equimolar DMF to $MoO_2(L)(MeOH)$ in methanol, $MoO_2L(DMF)$ is formed. On addition of the equimolar pyridine to $MoO_2L(DMF)$ in methanol, $MoO_2L(Py)$ is formed. Each of other complexes, MoO_2L(γ-Pic) and $MoO_2L(DMSO)$ is also isolated by the same method. From experiments of this type the following increase in qualitative order of D binding could be established: MeOH<DMF<Py<γ-Pic<DMSO. This order of D binding is supported from the ν_{sym}, Mo=Ot (terminal oxygen) increase in the order: DMSO<γ-Pic<Py<DMF<MeOH, indicating that strong donor binding to molybdenum reduces the bond strength of trans-Mo=Ot to D binding position (Table 1).

Spectral properties. The schiff base ligands can act either in a monoanionic tridentate (thione form) or in a dianionic tridentate (thiol form) manner, but all physicochemical properties of the complexes support dianionic tridentate ONS chelation of the ligands. The ν(OH) band at ~3110 cm^{-1} of the free ligands disappears on complexation, indicating coordination through the deprotonated phenolic oxygen atoms. The intense bands at *ca.* 1620 cm^{-1} associated with the C=N stretching frequency of the free ligands are shifted to *ca.* 1600 cm^{-1}, respectively in the corresponding complexes, indicating the coordination of the azomethine nitrogen to the metal ion.[12] The free ligands exhibit a ν(C=S) vibrations at *ca.* 1050 cm^{-1} and ν(NH) vibrations at *ca.* 2975 cm^{-1} in their IR spectra,[13] indicating that they exist as the thione form *A* in the solid state. On complexation they are found in the dianionic thiol form, involving deprotonation of the phenolic and SH group of *B* as is apparent from the disappearance of their ν(OH) and ν(NH), as well as from the absence of any ν(SH) or ν(C=S) vibration. The IR spectra of the molybdenum(VI)-dioxo complexes, except the complex **1d**, all show two sharp intense bands at *ca.* 900 cm^{-1} and *ca.* 920 cm^{-1}. These bands are assigned to the molybdenum-oxygen terminal stretching vibration, ν(*cis*-MoO_2), by comparison with the spectra of the free ligands and previously reported data.[14] The complex **1d** exhibits a broad band at 818 cm^{-1} with the strong band at 918 cm^{-1} due to ν(*cis*-MoO_2). The appearance of this band indicates that complex **1d** is polymeric in nature, polymerization most probably taking place *via* Mo=O→Mo linkages.[14,15] The complexes of molybdenum(IV)-oxo all exhibit a single strong infrared vibration at *ca.* 935 cm^{-1}, which is characteristic of the Mo=O vibration in the MoO^{2+} group.[3a,6] The molybdenum(VI)-dioxo complexes, except the **1d**, all exhibit charactristic bands corresponding to the bond monodentate donor (CH_3OH). The complexes **1a-1c**, exhibit a broad bands at *ca.* 3400 cm^{-1} due to the presence of coordinated methanol molecule. The appearances of strong band at 1652 cm^{-1} due to ν(C=O) of **1e** and a medium intensity ν(S=O) band at 1008 cm^{-1} of **1h** represents that DMF and DMSO is coordinated to MoO_2 group in each complex.[14] The IR spectra for the Mo=Ot stretching vibrations of the complexes **1d**, **1f** and **3a** are shown in Figure 1.

The ^{1}H-NMR spectrum of the representative complex **1b** is shown in Figure 2. The ^{1}H resonances for the phenolic aromatic group appear in the range of 6.85-8.14 ppm as well-resolved doublets or triplets.[16] The azomethine, S-methyl, and 5-methyl proton resonances each show at 8.84, 2.59 and 2.30 ppm as intense singlet.[6] The ^{1}H resonances for CH_3 and OH group of methanol as neutral monodentate ligand each appear at 3.18 and 4.00 ppm as doublet and quartet.[17] The ^{1}H-NMR spectrum of complex **1b** exhibit integrated in-

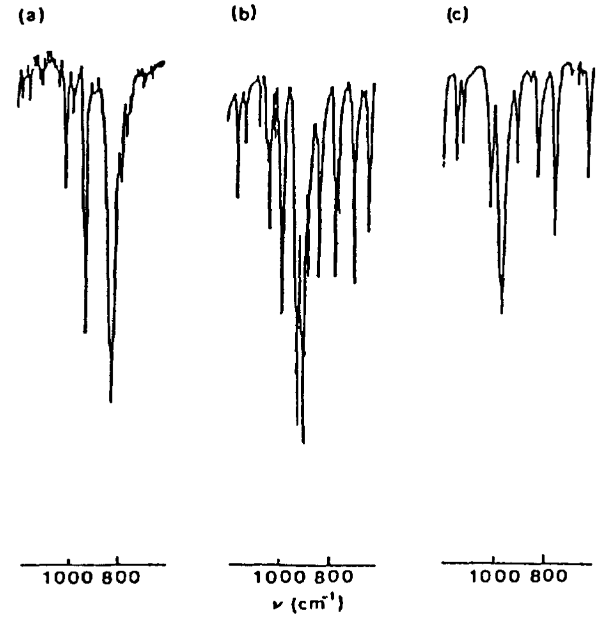


Figure 1. The Mo=O stretching frequencies of complexes (a) MoO_2L^4, (b) $MoO_2L^1(Py)$, and (c) $MoOL^1$.

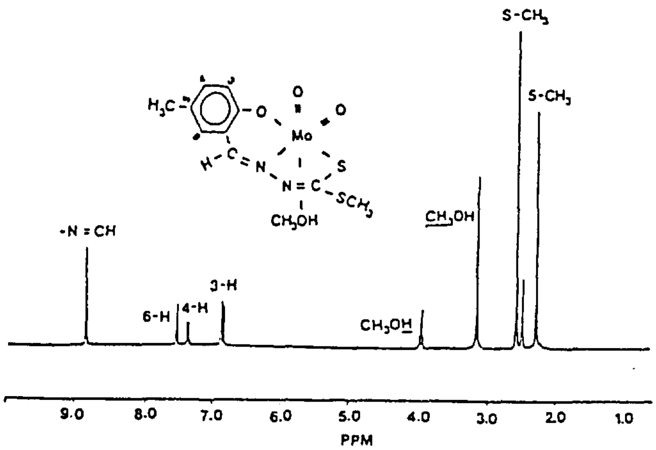


Figure 2. The ^{1}H-NMR spectrum of $MoO_2L^2(MeOH)$ in DMSO-d_6.

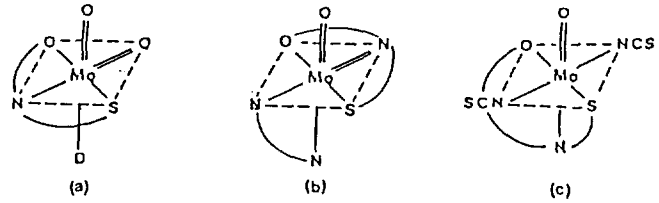


Figure 3. The structure of the complexes MoO_2LD (a), MoOL (N-N) (b), and $[MoO(NCS)_2L]^-$ (c).

tensities for 5-methyl, aromatic, azomethine, S-methyl protons in the ratio 3 : 3 : 1 : 3 consistent with the stoichiometry of schiff base ligand. The ratio of integrated intensities for the proton resonances of schiff base and methanol also show 3 : 1 consistent with the stochiometric ratio 1 : 1. The ^{1}H-NMR spectra of all complexes are similar to complex **1b** and can be divided into two regions, either side of a chemical shift of 5 ppm (downfield of Me_4Si). The phenolic, aromatic and azomethine proton resonances each appear as well-resolved singlets, doublets, or triplets in the low-field region; the high-field region comprises the resonances for the substituents (5-CH_3, 3-CH_3O) of schiff base ligands, neutral monodentate (MeOH, DMF, DMSO, etc), and intense singlet for the S-CH_3 group. The detailed assignments of the ^{1}H-NMR spectra for the complexes are summarized in Table 2. The OH and SH proton resonances of free schiff base ligand disappear on complexation and the azomethine proton resonances are shifted to downfield (from *ca.* 8.30 ppm to *ca.* 8.93 ppm) compared to those of free ligands. This confirms that the schiff base ligand is bonded to the molybdenum atom through the phenolic oxygen and azomethine nitrogen, besides the thiol sulfur as in the results of IR spectra. In all the complexes, the dianionic tridentate ligand spans three meridional positions. Isomeric facial spanning is sterically precluded by the ligand planarity.[3a] We propose the probable struc-

Table 2. ^{1}H-NMR Data for Complexes in DMSO-d_6[a]

Complex	ArH	N=CH	S-CH₃	Others
1a	6.95-7.77(m, 4H)	8.93(s)	2.60(s)	3.18(d, 3H, $\underline{CH_3}OH$) 4.02(q, 1H, $CH_3\underline{OH}$)
1b	6.85-7.54(m, 3H)	8.84(s)	2.59(s)	2.30(s, 3H, 5-CH_3) 3.18(d, 3H, $\underline{CH_3}OH$) 4.00(q, 1H, $CH_3\underline{OH}$)
1c	7.00-7.33(m, 3H)	8.90(s)	2.60(s)	3.18(d, 3H, $\underline{CH_3}OH$) 3.81(s, 3H, 5-CH_3) 4.00(q, 1H, $CH_3\underline{OH}$)
1d	7.19-8.41(m, 6H)	9.67(s)	2.67(s)	
1e	6.95-7.77(m, 4H)	8.93(s)	2.60(s)	2.74(s, 3H, $(\underline{CH_3})_2NC(O)H$) 2.89(s, 3H, $(\underline{CH_3})_2NC(O)H$) 7.96(s, 1H, $(CH_3)_2NC(O)\underline{H}$)
1f	6.95-7.76(m, 4H)	8.93(s)	2.60(s)	7.38(m, 2H, *m*-C_5H_5N) 7.80(s, 1H, *p*-C_5H_5N) 8.57(d, 2H, *o*-C_5H_5N)
1g	6.95-7.76(m, 4H)	8.93(s)	2.60(s)	2.31(s, 3H, $\underline{CH_3}C_5H_4N$) 7.20(d, 2H, *m*-C_6H_7N) 8.42(d, 2H, *o*-C_6H_7N)
1h	6.95-7.76(m, 4H)	8.93(s)	2.60(s)	2.54(s, 6H, $(\underline{CH_3})_2SO$)
2a	6.97-7.76(m, 4H)	8.94(s)	2.60(s)	7.99(t, 2H, *m*-C_5H_6N) 8.50(t, 1H, *p*-C_5H_6N) 8.89(d, 2H, *o*-C_5H_6N)
2c	7.02-7.32(m, 3H)	8.91(s)	2.59(s)	3.81(s, 3H, 3-CH_3O) 7.85(t, 2H, *m*-C_6H_6N) 8.34(t, 1H, *p*-C_5H_6N) 8.81(d, 2H, *o*-C_5H_6N)
3a	6.95-7.77(m, 4H)	8.93(s)	2.60(s)	
3b	7.00-7.34(m, 3H)	8.91(s)	2.60(s)	3.81(s, 3H, 3-CH_3O)

[a] Chemical shifts are given in ppm *vs.* Me_4Si.

Table 3. Cyclic Voltammetric Results[a] for Dioxomolybdenum(VI) Complexes at 25℃

Complex	E_{pc}, V (*vs* SCE)
1a	-0.84, -1.77
1b	-0.87, -1.76
1c	-0.86, -1.77
1d	-0.78, -1.78
1e	-0.85, -1.75
1f	-0.85, -1.76
1g	-0.84, -1.78
1h	-0.85, -1.76

[a] Solvent DMSO; solute concentration $\sim 10^{-3}$ M; working electrode gold; reference electrode SCE.

tures of the complexes as shown in Figure 3.

The electronic spectra of the molybdenum(VI)-dioxo complexes **1a**-**1h** display a single low-energy absorption band in the range 397-424 nm. On the basis of the d^0 electronic configuration of the metal, this transition is assigned to a S(pπ) $\rightarrow$ Mo(dπ) ligand to metal charge transfer (LMCT) transition.[18] The molybdenum(IV)-oxo complexes of in degassed dimethylsulfoxide solution exhibit two absorption maxima above 400 nm. The band at the longest wavelength is assigned to one of the *d-d* transitions in the d^2 systems.[19]

Electrochemical properties. The electrochemical behavior of the monomeric molybdenum(VI)-dioxo complexes has been examined in DMSO/0.1 M TEAP at a gold electrode by using cyclic voltammetric techniques. The complexes exhibit two successive reductive responses in the potential range 0.0 to -2.0 V (Table 3, Figure 4). The reductions of all complexes are irreversible. It has been reported[14,20] that the reduction of molybdenum(VI)-dioxo complexes in aprotic solvents are generally irreversible. On comparing the cyclic voltammograms of other monomeric Mo(VI)-oxo complexes[1a,3a,21] it appears that the initial reduction wave near -0.8 V is due to the reduction of Mo(VI) to Mo(V) species and a Mo(V)-oxo species generated electrochemically undergo a futher reduction to generate a Mo(IV)-oxo species near -1.8 V. It is observed here that the cyclic voltammograms of neutral monodentate derivatives (**1a**, **1e**-**1h**) in DMSO exhibit identical with that of the complex **1h**. This observation indicates that the monodentate bases are readily replaced by the solvent molecule. It is also noted that the reduction potentials (E_{pc}) are sensitive to the nature of the substituents on the salicyl phenyl ring. As the substituents become more electron withdrawing (Me<MeO<H<5,6-Bz) E_{pc} of the Mo(VI)-Mo(V) couple are shifted in the anodic direction, which means the Mo(VI) complexes become easier to reduce.

The redox behaviors of the molybdenum(IV)-oxo complexes is found to be irreversible. The Mo(IV) complexes can be reduced/oxidized to the corresponding monomeric molybdenum (III)/(IV)-oxo. However, the cyclic voltammograms of both complexes (**3a**, **3b**) each show only reductive wave at -0.85 and -0.87 V. The cathodic peak is found to be coupled to the broad anodic peak at -0.71 and -0.75 V. It is probably[3a,19] that the Mo(IV) complexes undergo reduction to the corresponding Mo(III) complexes and are reoxidized by one electron to a Mo(IV) complex.

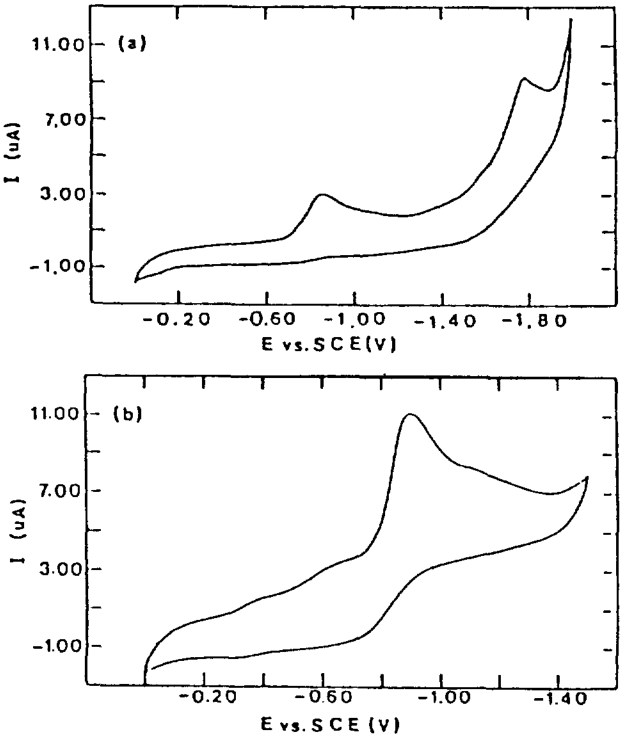


Figure 4. Cyclic voltammograms for (a) $\sim 1 \times 10^{-3}$ M MoO_2L^1(MeOH) and (b) $\sim 1 \times 10^{-3}$ M $[MoO(NCS)_2L^1]^-$ in 0.1 M TEAP-DMSO; scan rate 50 mV s^{-1}.

Molybdenum(V)-oxo complexes. All the complexes are moderately soluble in CH_3CN, MeOH, EtOH and DMSO but highly soluble in DMF. The complexes are air stable in the solid state. The values of molar conductance of the complexes are in the range 52.7 to 84.7 mho cm^2 mol^{-1} in DMSO solution indicating[12] that the complexes are 1 : 1 electrolytes.

Spectral properties. The ligands are found to act in a dianionic tridentate manner, coordinating through the deprotonated phenolic oxygen, the azomethine nitrogen, and the thiol sulfur atom in the relevant complexes, and this is supported by the analytical and all physicochemical data. All the complexes exhibit a strong sharp band at *ca.* 935 cm^{-1}. This band agrees with that usually observed for mono oxo complexes of molybdenum ions in octahedral, indicating the presence of Mo=Ot bond.[22] The ν(OH) and ν(NH) bands of the free ligands did not show in the corresponding complexes and the intense bands at *ca.* 1620 cm^{-1} associated with the C=N stretching vibration of free ligands are shifted to *ca.* 1600 cm^{-1}, respectively, on complexation. In regard to the NCS^- ligands, their characteristic absorption frequencies clearly indicate the coordination through the nitrogen atom. The strong band resulting from the C≡N stretching mode exhibit in the range 2037 to 2042 cm^{-1}, much lower than the value (*ca.* 2100 cm^{-1})[23] observed for the SCN^- ligand in the thiocyanato complex. This frequency lowering is characteristic for the N-bonded NCS-ligand. This C-S stretching vibration is also observed at relatively high frequencies, 835-866 cm^{-1}-a typical feature for isothiocyanates.[7]

The ^{1}H-NMR spectra of complex **2a** and **2c** all show strong

Table 4. Cyclic Voltammetric Results for Oxomolybdenum(V) Complexes in 0.1 M TEAP at 25℃

Complex	$E_{pc}{}^a$, V (*vs* SCE)
2a	−0.87 (−0.74)
2b	−0.96 (−0.83)
2c	−0.87 (−0.75)
2d	−0.84 (−0.70)

[a] Values in parentheses are coupled oxidation peaks observed with complete CV cycle, solvent; DMSO.

bands for the proton resonances of pyridinium ion and weak bonds for schiff base ligand protons. The aromatic protons of the pyridinium ion as a counter ion are easily distinguished from those of schiff base ligands by comparison of the spectra of the molybdenum(VI)-dioxo complexes prepared in this work and previously reported data.[12] The *ortho*-, *meta*-, and *para*-protons for the pyridinium ion of complex **2a** each appear at 8.89, 7.99 and 8.50 ppm as well-resolved doublet, triplet and triplet with relative intensity ratio of 2 : 2 : 1. The azomethine proton and S-methyl proton resonances each exhibit at 8.94 ppm and 2.60 ppm as singlet. The aromatic proton resonances of schiff base ligand show in the range from 6.94 to 7.76 ppm as very weak bands compared to pyridinium ion.

The electronic spectra of the molybdenum(V) complexes **2a**-**2d** display one absorption band in the ligand field reigon (716-821 nm) due to the first crystal field transition $^2B_2 \rightarrow {}^2E$, assuming the effective symmetry of C_{4v}.[7] The second crystal field transition $^2B_2 \rightarrow {}^2B_1$ is obscured by other charge-transfer transitions.[24]

The results of spectroscopic studies above support[12] that the structure of the oxomolybdenum(V) complex are the same as shown in Figure 3.

Electrochemical properties. The electrochemical behavior of the monoanionic molybdenum(V)-oxo complexes in DMSO/0.1 M TEAP has been studied by cyclic voltammetry at a gold working electrode and the data in the potential range 0.0 to −2.0 V (*vs*. S. C. E.) are summarized in Table 4. All complexes display a strong cathodic responses near −0.9 V (Figure 4).

This reduction wave is found to be coupled to a weak and broad anodic peak near −0.7 V. This indicates probably that the species reduced at −0.9 V is reoxidized near −0.7 V, and this oxidized product is found to be reduced again at −0.9 V.

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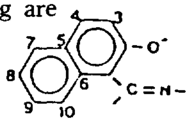
10. The labelings of the carbon atoms of the 2-hydroxylphenyl group and 5,6-benzo derivative ring are 

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