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Chemistry of Molybdenum with Hard–Soft Donor Ligands. 2.[1] Molybdenum(VI), -(V), and -(IV) Oxo Complexes with Tridentate Schiff Base Ligands

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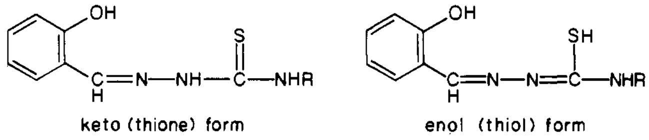
The synthesis and characterization of a number of oxomolybdenum(VI), -(V), and -(IV) complexes with salicylaldehyde thiosemicarbazones as the SNO-donor metal-binding substrates are described. The Mo(VI) complexes are *cis*-dioxo, $MoO_2(SNO)$, with one coordination site available for substrate binding. The Mo(V)–oxo complexes are of the type $MoO(SNO)X_2$ (X = Cl, Br) with a distorted-octahedral geometry. The Mo(IV)–oxo complexes, MoO(SNO), are derived from the corresponding Mo(VI)–dioxo complexes by oxo abstraction with PPh_3. The cyclic voltammograms for $MoO_2(SNO)$ complexes are typically irreversible, involving Mo(VI)/Mo(V) and Mo(V)/Mo(IV) reductive responses. The Mo(V)–oxo complexes display unique voltammograms exhibiting Mo(V)/Mo(IV), Mo(IV)/Mo(III), and Mo(V)/Mo(VI) couples. The Mo(IV)–oxo complexes are oxidized to Mo(V)–oxo complexes and undergo one-electron reduction to the corresponding Mo(III) species. EPR results indicate that the isotropic metal hyperfine coupling constant of Mo(V)–oxo complexes decreases with an increase of covalent character in going from chlorine to their bromine analogues. The spin–orbit coupling of bromide ligands appears to be the dominant factor contributing to the drastic change in isotropic *g* values.

Introduction

Because of their intrinsic relevance to the active sites of molybdoenzymes, the chemistry of oxomolybdenum complexes involving NS donor ligands has received the intense attention of the coordination chemist and the biochemist in recent years, which is evidenced by a flurry of papers published in this area.[3-8] It is well-known[9,10] that catalytic reactions of the molybdoenzymes involve oxidation states Mo(VI) and Mo(IV). Recent EPR studies of such reactions have established[9,11,12] that the Mo(V) state coexists with Mo(VI) and Mo(IV) during the process of electron transfer to or from the redox centers.

Although oxomolybdenum(VI), -(V), and -(IV) complexes of several bi-, tri-, and tetradentate NS, SS, and SNO donor systems are reported[3-8,13-20] to simulate many characteristic properties of the active sites of molybdoenzymes, a careful survey of the relevant literature has failed to locate any study on oxomolybdenum complexes of thiosemicarbazones acting as NS/SNO donors. Our interest in the chemistry of oxometal cations ligated to mixed hard–soft NS donors in general and modeling of the active sites of molybdoenzymes in particular has prompted us to pursue the present work, which reports a set of Mo(VI)–dioxo, Mo(V)–oxo, and Mo(IV)–oxo complexes with the dianionic/monoanionic tridentate ligands salicylaldehyde thiosemicarbazone (TSCsal) and salicylaldehyde 4-phenylthiosemicarbazone (4-PhTSCsal).



keto (thione) form　　enol (thiol) form

R = H: TSCsal (LH_2)
R = Ph: 4-PhTSCsal ($L'H_2$)

It is noteworthy that this is the first instance of the use of thiosemicarbazone ligands in the modeling of the molybdenum binding site of the molybdenum cofactor. These two ligands are of particular interest 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 utilized for substrate binding. The planar disposition of these ligands is a factor that makes them even more suitable for modeling the active sites, and the substitution of one of the two hydrogen atoms of the terminal NH_2 group creates a change in the hydrophobicity around the oxomolybdenum acceptor center. We have synthesized Mo(VI) complexes of the type MoO_2LB (where B is a neutral monodentate Lewis base) and Mo(IV) complexes of the MoOL(N-N) type (where N-N is a neutral bidentate donor). Oxo abstraction from Mo(VI)–dioxo complexes with use of PPh_3 has been successfully used in this study to generate the corresponding Mo(IV) species.

Although the chemistry of the Mo(V) state is dominated by oxo-bridged dimers, a good number of reasonably stable monomeric complexes have been reported. In this work we report some new monomeric oxomolybdenum(V) complexes with the monoanionic tridentate SNO ligands TSCsal and 4-PhTSCsal.

Spectroscopic properties and the electrochemical behavior of the complexes have been discussed in detail.

Experimental Section

Physical Measurements. Carbon, hydrogen, and nitrogen analyses were performed in a Perkin-Elmer 240C analyzer. Molybdenum was estimated gravimetrically by using 8-hydroxyquinoline (oxine) as the reagent. IR spectra were recorded with a Perkin-Elmer 783 spectrophotometer using the KBr wafer technique. Far-IR spectra were recorded as Polythene pellets with use of a Polytech FIR-30 FT-far-IR spectrometer. Electronic spectra of the compounds were recorded on a Pye-Unicam Model SP8-150 UV-vis spectrophotometer using spectral grade solvents. Electrical conductance data in solution were obtained on a Philips PR-9500 conductivity bridge fitted with a dip-type cell cali-

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brated with 0.02 M KCl solution. Static susceptibility measurements at room temperature were made with the help of a Princeton Applied Research Model 155 vibrating-sample magnetometer using $Hg[Co(SCN)_4]$ as the calibrant. Electrochemical studies were done with the help of a PAR Model 370-4 electrochemistry system: Model 174A polarographic analyzer, Model 175 universal programmer, Model RE 0089 and RE 0074 X-Y recorder. All the experiments were carried out under a dry nitrogen atmosphere with a three-electrode configuration. A planar Beckman Model 39273 platinum electrode was used as the working electrode. The results were collected at 298 ± 1 K and are referenced to a saturated calomel electrode (SCE). The reported potentials are uncorrected for junction contribution. Room-temperature EPR spectra of the compounds in powdered form as well as in solution were recorded at X-band frequency on a Varian E-112 X/Q-band spectrometer. DPPH was used as an internal field marker.

Materials. Ammonium paramolybdate was obtained from Aldrich Chemical Co. Ltd., Dorset, U.K. $MoO_2(acac)_2$ (acac = acetylacetonate anion) was prepared from ammonium paramolybdate by a known[21] method. $(NH_4)_2[MoOCl_5]$ and $(NH_4)_2[MoOBr_5]$ were prepared by following standard[22] methods. All other chemicals used for preparative work were of reagent grade and were employed without further purification. Reagent grade solvents were dried and distilled before use. Tetraethylammonium chloride ((TEA)Cl) was obtained from Fluka AG. It was recrystallized[23] from a chloroform–pentane mixture, dried at 110 °C in vacuo, and stored over P_2O_5. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Fluka AG) by following a standard[24] procedure. Dimethylformamide (DMF) used for electrochemical purposes was dried by distillation in vacuo over P_2O_5 and then stored over Linde AW-500 molecular sieves. Reactions and manipulations of compounds involving Mo(V) and Mo(IV) were carried out under purified dinitrogen.

Ligands. Salicylaldehyde Thiosemicarbazone (TSCsal). To a hot solution of 4.5 g (0.05 mol) of thiosemicarbazide (TSC) in 20 mL of ethanol was added 5.3 g (0.05 mol) of salicylaldehyde (sal) in 10 mL of ethanol and the mixture then slowly refluxed for 2 h. The mixture was then cooled down to room temperature, when a cream-colored crystalline compound separated out. The compound was collected by filtration, washed well with ethanol, and dried in vacuo. This product was recrystallized from hot absolute ethanol: yield 70%; mp 220 °C dec. Anal. Calcd for $C_8H_9N_3SO$: C, 49.23; H, 4.61; N, 21.54. Found: C, 49.01; H, 4.56; N, 21.34.

Salicylaldehyde 4-Phenylthiosemicarbazone (4-PhTSCsal). The compound 4-phenylthiosemicarbazide (4-PhTSC) was prepared from distilled aniline by a known method reported earlier.[1] A 4.2-g (0.025-mol) amount of 4-PhTSC was dissolved in 20 mL of hot ethanol, and to this was added 2.7 g (0.025 mol) of salicylaldehyde in 10 mL of ethanol over a period of 10 min with continuous stirring. Within 20 min, a white compound began to separate out. After the mixture was stirred at room temperature for about 4 h, the compound was filtered, washed thoroughly with ethanol, and then dried in vacuo. The compound was recrystallized from hot absolute ethanol: yield ~75%; mp 178 °C dec. Anal. Calcd for $C_{14}H_{13}N_3SO$: C, 61.99; H, 4.79; N, 15.49. Found: C, 61.87; H, 4.70; N, 15.35.

Complexes. MoO_2L (1a). To a filtered solution of 0.33 g (1.0 mmol) of $MoO_2(acac)_2$ in 20 mL of methanol was added 0.195 g (1.0 mmol) of TSCsal in 15 mL of methanol. The resulting orange-red solution was refluxed for 2 h. The volume of the solution was then reduced to about 10 mL in a rotavaporator. The yellowish brown compound that separated out was filtered, washed with cold methanol, and dried in vacuo; yield ~45%. The compound was recrystallized from 1:1 acetonitrile–benzene. Anal. Calcd for $C_8H_7N_3SO_3Mo$: C, 29.90; H, 2.18; N, 13.08; Mo, 29.90. Found: C, 29.87; H, 2.28; N, 12.93; Mo, 30.01.

MoO_2L' (1b) was prepared similarly with a yield of 50%. Anal. Calcd for $C_{14}H_{11}N_3SO_3Mo$: C, 42.31; H, 2.77; N, 10.58; Mo, 24.18. Found: C, 41.82; H, 2.75; N, 10.74; Mo, 23.18.

$MoO_2L(\gamma\text{-pic})$ (1c). To a stirred solution of 0.321 g (1.0 mmol) of MoO_2L in 25 mL of methanol was slowly added 0.093 g (1.0 mmol) of γ-picoline, upon which the solution turned deep red. The solution was refluxed slowly for ~4 h, and the volume of the solution was reduced to ~10 mL when a dark brown solid separated out. It was filtered, washed thoroughly with acetone, and then dried in vacuo; yield ~50%. Anal. Calcd for $C_{14}H_{14}N_4SO_3Mo$: C, 40.58; H, 3.38; N, 13.52; Mo, 23.19. Found: C, 40.15; H, 3.29; N, 13.30; Mo, 22.95.

$MoO_2L'(\gamma\text{-pic})$ (1d). This was prepared, by following the same procedure as mentioned above, in yields of 45%. Anal. Calcd for $C_{20}H_{14}N_4SO_3Mo$: C, 48.98; H, 3.67; N, 11.43; Mo, 19.59. Found: C, 48.23; H, 3.56; N, 11.20; Mo, 19.09.

$MoO_2L(imz)$ (1e) and $MoO_2L'(imz)$ (1f) were prepared similarly, by taking the ligand imidazole (imz) in 10 mL of methanol, with yields of 50–55%. Anal. Calcd for $C_{11}H_{11}N_5SO_3Mo$ (**1e**): C, 33.93; H, 2.83; N, 17.99; Mo, 24.68. Found: C, 34.15; H, 2.90; N, 17.81; Mo, 24.08. Calcd for $C_{17}H_{15}N_5SO_3Mo$ (**1f**): C, 43.87; H, 3.22; N, 15.05; Mo, 20.64. Found: C, 43.63; H, 3.25; N, 14.81; Mo, 19.79.

The complexes **1c–f** were also prepared in situ from $MoO_2(acac)_2$ in methanol by refluxing with the relevant ligands.

MoOL (2a). To a refluxing solution of 0.321 g (1.0 mmol) of MoO_2L in 25 mL of degassed acetonitrile was added 0.393 g (1.5 mmol) of PPh_3 in 15 mL of acetonitrile. The orange-red solution turned dark brown, and a brown compound separated within 10 min. This was filtered hot, washed well with hot acetonitrile, and dried in vacuo; yield ~80%. Anal. Calcd for $C_8H_7N_3SO_2Mo$: C, 31.47; H, 2.29; N, 13.77; Mo, 31.47. Found: C, 31.92; H, 2.35; N, 13.85; Mo, 31.80.

This compound was also prepared in situ from $MoO_2(acac)_2$ by refluxing with TSCsal and then with PPh_3 in methanol with a yield of 60%.

MoOL′ (2b). This compound was prepared, by following the methods described above for the preparation of MoOL, in a yield of 70%. Anal. Calcd for $C_{14}H_{11}N_3SO_2Mo$: C, 44.09; H, 2.89; N, 11.02; Mo, 25.19. Found: C, 43.53; H, 2.81; N, 11.06; Mo, 25.52.

MoOL(bpy) (2c). To a refluxing solution of 0.321 g (1.0 mmol) of MoO_2L in 25 mL of degassed acetonitrile was added 1.56 g (10.0 mmol) of 2,2′-bipyridyl (bpy), followed by a solution of 0.393 g (1.5 mmol) of PPh_3 in 15 mL of degassed acetonitrile. The solution turned green, and it was refluxed for about 2 h, after which a shining green crystalline compound precipitated out. This was filtered hot, washed well with dry acetonitrile, and dried in vacuo; yield 75%. Anal. Calcd for $C_{18}H_{15}N_5SO_2Mo$: C, 46.85; H, 3.25; N, 15.18; Mo, 20.82. Found: C, 46.88; H, 3.19; N, 14.81; Mo, 20.95.

MoOL(phen) (2d). This was prepared as a greenish brown microcrystalline compound, by following the same procedure as mentioned above, with use of 0.99 g (5.0 mmol) of 1,10-phenanthroline (phen) in a yield of 65%. Anal. Calcd for $C_{20}H_{15}N_5SO_2Mo$: C, 49.48; H, 3.09; N, 14.43; Mo, 19.79. Found: C, 49.38; H, 3.08; N, 13.98; Mo, 19.67.

MoOL′(bpy) (2e). To a refluxing solution of 0.397 g (1.0 mmol) of MoO_2L' in 30 mL of acetonitrile was added 1.56 g (10 mmol of 2,2′-bipyridyl in 15 mL of acetonitrile, followed by a solution of 0.393 g (1.5 mmol) of PPh_3 in 10 mL of acetonitrile. The solution immediately turned deep green. This was refluxed for 2 h, after which a green microcrystalline compound separated out. This compound was collected by filtration of the hot solution, washed well with acetonitrile, and dried in vacuo; yield 60%. Anal. Calcd for $C_{24}H_{19}N_5SO_2Mo$: C, 53.63; H, 3.54; N, 13.03; Mo, 17.87. Found: C, 54.57; H, 3.66; N, 13.68; Mo, 18.25.

The compound was also prepared from $MoO_2(acac)_2$ by refluxing with 4-PhTSCsal, and the resulting solution was then treated with PPh_3 (1.5 mmol) in the presence of 2,2′-bipyridyl (10 mmol); yield 70%.

MoOL′(phen) (2f). The compound was prepared, by following the methods employed for the corresponding bipyridyl compound **2e** described above, with a yield of 65%. Anal. Calcd for $C_{26}H_{19}N_5SO_2Mo$: C, 55.61; H, 3.38; N, 12.47; Mo, 17.11. Found: C, 55.15; H, 3.28; N, 12.09; Mo, 17.69.

$MoO(LH)Cl_2$ (3a). To a filtered solution of 0.325 g (1.0 mmol) of $(NH_4)_2[MoOCl_5]$ in 20 mL of dry and degassed methanol was slowly added 0.195 g (1.0 mmol) of TSCsal in 20 mL of dry methanol with stirring under a dry dinitrogen atmosphere at room temperature. The solution turned brownish green. After 4 h the volume of the solution was reduced to 10 mL under vacuum. The solid that separated out was filtered, washed with dry acetonitrile, and dried in vacuo. The olive green compound was recrystallized from dry acetonitrile under a dinitrogen atmosphere; yield 50%. Anal. Calcd for $C_8H_8N_3SCl_2O_2Mo$: C, 25.46; H, 2.12; N, 11.14; Cl, 18.83; Mo, 25.46. Found: C, 25.83; H, 2.09; N, 11.28; Cl, 17.91; Mo, 24.91.

$MoO(LH)Br_2$ (3b). This was obtained as a dark brown solid from $(NH_4)_2[MoOBr_5]$ by using the procedure described above; yield 45%. Anal. Calcd for $C_8H_8N_3SBr_2O_2Mo$: C, 20.60; H, 1.71; N, 9.01; Br, 34.33; Mo, 20.60. Found: C, 21.10; H, 1.81; N, 9.24; Br, 35.46; Mo, 21.76.

$MoO(L'H)Cl_2$ (3c). To a filtered solution of 0.325 g (1.0 mmol) of $(NH_4)_2[MoOCl_5]$ in 25 mL of dry and degassed methanol was slowly added 0.271 g (1.0 mmol) of 4-PhTSCsal in 15 mL of methanol with stirring under a dinitrogen atmosphere. The resulting solution turned yellowish green. Stirring was continued for 4 h at room temperature, and the greenish brown compound that separated out was filtered, washed well with dry methanol, and dried in vacuo; yield 60%. Anal. Calcd for

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Table I. Characteristic IR Bands (cm^{-1}) and Electronic Spectral Data (nm (dm^3 mol^{-1} cm^{-1}))^b for the Complexes

complex	ν(Mo=O)	ν(Mo—S)	ν(Mo—X)	λ_{max} (ϵ)
MoO_2L (**1a**)	930, 900, 810 (b)	370 (m)		400 (1265), 325 (30 149), 300 (25 649), 220 (w sh)
MoO_2L' (**1b**)	930, 920, 815 (b)	380 (m)		405 (2520), 335 (14 149), 310 (w sh), 250 (12 328)
MoO_2L(γ-pic) (**1c**)	945, 920	365 (m)		440 (8941), 320 (19 279), 250 (25 556)
MoO_2L'(γ-pic) (**1d**)	950, 920	360 (m)		445 (10 041), 330 (21 423), 250 (27 734)
MoO_2L(imz) (**1e**)	950, 920	370 (m)		400 (1478), 325 (36 000), 300 (34 941), 222 (w sh)
MoO_2L'(imz) (**1f**)	960, 935	385 (m)		405 (5452), 335 (25 323), 250 (26 710)
MoOL (**2a**)	970	355 (w)		650 (429), 455, 308
MoOL′ (**2b**)	960	380 (m)		650 (413), 420 (16 467), 335, 267
MoOL(bpy) (**2c**)	920	390 (w)		660 (3476), 575 (2236), 425 (7063), 340, 302
MoOL(phen) (**2d**)	930	390 (w)		650 (6421), 580 (4724), 430 (6940), 340, 305
MoOL′(bpy) (**2e**)	915	360 (w)		650 (6745), 570 (4911), 430 (18 106), 330, 300
MoOL′(phen) (**2f**)	925	365 (w)		640 (7825), 575 (6042), 440 (11 782), 330, 305
$MoO(LH)Cl_2$ (**3a**)	960	380 (m)	340, 310	545 (177), 400 (2409), 350 (6375), 323 (sh), 290
$MoO(LH)Br_2$ (**3b**)	960	375	267, 230	580 (288), 445 (1861), 365 (4750), 330 (sh), 285
$MoO(L'H)Cl_2$ (**3c**)	970	370 (m)	340, 320	600 (179), 400 (5149), 340 (15 412), 270 (sh), 240
$MoO(L'H)Br_2$ (**3d**)	965	365 (m)	265, 233	580 (168), 405 (4105), 325 (13 183), 286 (sh), 250

^{a} m = medium, w = weak, sh = shoulder. ^{b} **1a–f**, **3a–d** in dry CH_3CN, **2a–f** in DMF.

$C_{14}H_{12}N_3SCl_2O_2Mo$: C, 37.08; H, 2.65; N, 9.27; Cl, 15.67; Mo, 21.19. Found: C, 37.45; H, 2.73; N, 9.46; Cl, 16.35; Mo, 21.95.

$MoO(L'H)Br_2$ (3d). This compound was obtained as a yellowish brown solid from $(NH_4)_2[MoOBr_5]$ by using the same procedure employed for the analogous chloro compound (**3c**); yield 60%. Anal. Calcd for $C_{14}H_{12}N_3SBr_2O_2Mo$: C, 30.94; H, 2.21; N, 7.75; Br, 29.52; Mo, 17.71. Found: C, 31.74; H, 2.29; N, 8.02; Br, 29.90; Mo, 18.05.

Results and Discussion

A. Dioxomolybdenum(VI) and Oxomolybdenum(IV) Complexes. Most of the dioxomolybdenum(VI) (**1a–f**) and oxomolybdenum(IV) (**2a–f**) complexes could be synthesized by more than one method. All complexes are air stable in the solid state. Complexes of type **1** are moderately soluble in methanol and acetonitrile but highly soluble in DMF and DMSO. On the other hand, complexes of type **2** have poor solubilities in common organic solvents but are highly soluble in DMF and DMSO, and if left exposed to air, they are slowly oxidized in solution. These complexes are formulated on the basis of elemental analysis and a variety of physical measurements. It may be noted here that since four-coordinate Mo(IV)–oxo complexes are unlikely, the compounds **2a,b** are likely polymeric species in the solid state. Type **1** complexes are nonelectrolytes in dry acetonitrile, while type **2** complexes are nonelectrolytes in DMF. The Mo(VI) compounds, as expected for a d^0 Mo(VI) state, are diamagnetic. The Mo(IV) complexes, reported in this work, are also found to be diamagnetic at room temperature. It should be mentioned here that most of the previously reported[25–28] Mo(IV)–oxo complexes exhibit diamagnetic behavior and only a few compounds show temperature-independent paramagnetism with magnetic moment values lying in the 0.6–0.9 μ_B range.

IR Spectra. A few characteristic infrared absorption frequencies of the compounds are listed in Table I. The ligands can act either in a monoanionic tridentate (keto form) or in a dianionic tridentate (enol form) manner, depending on the conditions (e.g. pH of the medium, oxidation state of the metal ion). All physicochemical properties of the complexes support dianionic tridentate SNO chelation of the ligands. The ν(OH) band (3440 cm^{-1} for TSCsal, 3380 cm^{-1} for 4-PhTSCsal) of the free ligands disappears on complex formation and points to coordination from the deprotonated phenolic oxygen. The intense bands at 1610 and 1625 cm^{-1} for TSCsal and 4-PhTSCsal associated with the C=N stretching frequency of the free ligands are shifted to 1595 and 1605 cm^{-1}, respectively, in the corresponding complexes, indicating the coordination of the azomethine nitrogen[29,30] to the metal ion. The complexes exhibit a medium-intensity band around 380 cm^{-1}, which may be assigned[19] to ν(Mo—S). It is rather unlikely that **1a** and **1b** are monomeric with pentacoordinated Mo(VI). Dimerization or oligomerization can occur[16] through phenolic oxygen bridging or Mo=O→Mo bridging. The ligand band at 1540 cm^{-1} due to ν(C—O)[16a,29] is shifted to around 1555 cm^{-1} in the complexes, indicating the coordination of O^-. This band occurs almost at the same frequency in **1c–f**, where complexes are evidently monomeric. This indicates[16a] the absence of any bridging phenolic oxygen. Thus, it is likely that **1a** and **1b** are polymeric in nature, polymerization most probably taking place via Mo=O→Mo linkages. This proposal is further augmented by the presence of a broad band at ~810 cm^{-1} in the IR spectra of **1a** and **1b**, which can be assigned[16] to Mo=O---Mo grouping. This band, however, disappears on adduct formation with monodentate donors. The appearance of two strong bands at around 900 cm^{-1} is indicative of $\nu(Mo{=}O)_t$ frequencies not only in monomeric but also in polymeric complexes, suggesting a weak polymeric interaction in the latter complexes. This is in accordance with the assignments given in ref 16a. Also, there are structural proofs of ligated and polymeric dioxomolybdenum(VI)-tridentate complexes.[16b] The crystal structure of $MoO_2(LNS_2)$TMSO (where LNS_2 = pyridine-2,6-dimethanethiolate and TMSO = tetramethylene sulfoxide) confirms[16b] the presence of well-separated mononuclear molecules with a distorted-octahedral structure common to most dioxomolybdenum(VI) complexes,[11] with cis terminal oxo ligands. On the other hand, crystals of $[MoO_2(LNO_2)]_n$ (where LNO_2 = pyridine-2,6-dimethanolate) consist of polymeric chains of molybdenum complexes, each of which has a distorted-octahedral environment with an oxo group unsymmetrically bridging from an adjacent complex. The polymeric structure of $[MoO_2(LNO_2)]_n$ clearly supports the claim of a similar chainlike arrangement in unligated MoO_2(salicylaldiminato) complexes,[16a] and this may be extended to the complexes **1a** and **1b** also. No Mo=O---Mo bridging is observed in **2a** and **2b**. All the Mo(IV)–oxo complexes display their characteristic $\nu(Mo{=}O)_t$ frequencies in the 900–100-cm^{-1} region (Table I). Complexes **1c–f** exhibit characteristic bands corresponding to the bound monodentate donor (γ-picoline, imidazole). Characteristic strong bands at ~1440 and ~1220 cm^{-1} and a sharp band of medium intensity in the 1100–1000-cm^{-1} region confirm the presence[30] of a coordinated γ-picoline molecule in **1c** and **1d**. The imidazole complexes exhibit a sharp ν(NH) band at 3200 cm^{-1} for **1e** and at 3235 cm^{-1} for **1f** respectively. Several new bands appear in the region 400–500 cm^{-1} in the IR spectra of **1e** and **1f** that confirm the presence[31–33] of coordinated imidazole. It is revealed from the IR absorption frequencies for the $\nu(Mo{=}O)_t$ band of the Mo(IV)–oxo complexes that the coordination of the neutral bidentate donor ligands (bpy, phen), as expected,[34] has the effect of lowering the $Mo{=}O_t$ stretch from

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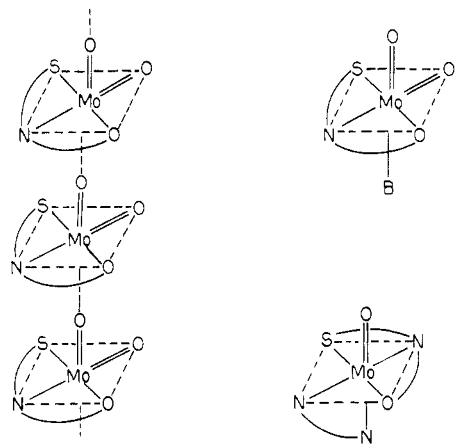

Figure 1. Structures of the compounds MoO_2L (**1a,b**; left), MoO_2LB (**1c–f**; right, top), and MoOL(N-N) (**2c–f**; right, bottom).

Table II. Cyclic Voltammetric Results[a] for Dioxomolybdenum(VI) Complexes at 298 K

complex	E_{pc}, V (vs SCE)	complex	E_{pc}, V (vs SCE)
1a	–0.84, –1.75	**1d**	–0.68, *b*
1b	–0.68, –1.75	**1e**	–0.89, –1.60
1c	–0.90, –1.62	**1f**	–0.66, –1.77

[a] Solvent DMSO; solute concentration ~10^{-3} M; working electrode platinum; reference electrode SCE. [b] Not clearly observed.

the value observed (Table I) for **2a** and **2b**.

In all the complexes, the dianionic tridentate ligand spans three meridional positions. Isomeric facial spanning is sterically precluded by the ligand planarity. We propose the probable structures of the compounds as shown in Figure 1.

Electronic Spectra. The complexes of type **1** exhibit one low-energy electronic absorption (in acetonitrile) in the region 400–450 nm (Table I) which may be assigned[19] a to S(pπ) → Mo(dπ) LMCT transition due to the promotion of an electron from the HOMO of sulfur to the LUMO of molybdenum. Electronic spectra of the Mo(IV)–oxo compounds are recorded in freshly prepared degassed DMF solutions, and the compounds are found to display (Table I) several absorption maxima in the range 300–650 nm. The complexes **2a** and **2b**, which produce brown solutions, exhibit one low-energy band around 650 nm ($\epsilon \approx 400$), but the bpy and phen derivatives (**2c–f**), which produce green solutions, exhibit two low-energy charge-transfer[34,35] bands around 650 and 570 nm, respectively.

Electrochemistry. Dioxomolybdenum(VI) Complexes (1a–f). The electron-transfer behavior of the Mo(VI) complexes has been examined in DMSO/0.1 M TEAP at a platinum electrode by using cyclic voltammetric techniques. The complexes exhibit two successive reductive responses in the potential range –0.7 to –1.75 V (Table II). Though no detectable oxidation wave is observed (Figure 2) in the cyclic voltammograms during reverse anodic scans, a second cycle yields the same trace and on multiple scan reversal the waves retain the original shapes, indicating high reproducibility of the electrode reactions. However, it is important to note here that the cyclic voltammograms of the picoline and imidazole derivatives in DMSO are identical with those of the corresponding parent compounds **1a** and **1b**. This observation[16a] indicates that the monodentate heterocyclic bases are readily replaced by the solvent molecules.

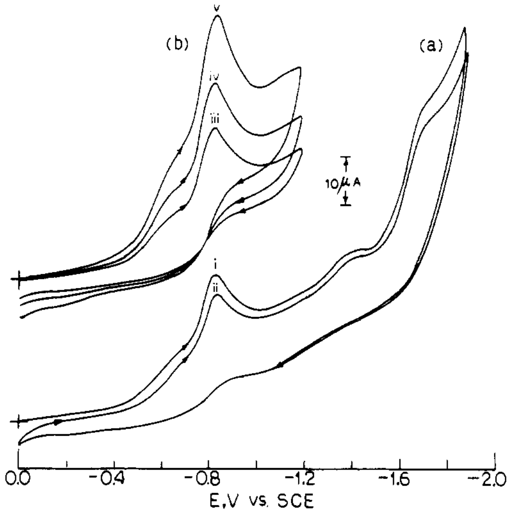

Figure 2. Cyclic voltammograms (~1 × 10^{-3} M in DMSO, 0.1 M TEAP) of MoO_2(TSCsal): (a) multiple scan reversal with an initial cathodic scan at a rate of 50 mV s^{-1}; (b) first reductive response at scan rates of 50, 100, and 200 mV s^{-1}.

It has been reported that the introduction of a sulfur atom in place of an oxygen donor (SNO instead of ONO) in the donor skeleton of the ligand results in a more facile[36] reduction of the molybdenum center. Since the reduction potential depends on the energy of the lowest unoccupied molecular orbital (LUMO), it appears from the electrochemical results of the complexes[5b,36] containing otherwise identical ligands that the energy of the LUMO, which is a sulfur pπ–dπ antibonding orbital in the S-ligated complexes, is less than that of an oxygen pπ–dπ antibonding orbital in the O-ligated analogues. Again, the degree of delocalization can also alter[36] the Mo(VI) cathodic reduction potential. The complexes, where the ligand systems are completely delocalized with extended π systems, are easier to reduce compared to others with less delocalized π systems. The ease of reduction of the present set of compounds suggests that the LUMO is better stabilized due to the presence of a sulfur donor atom in the ligand skeleton, and as both of the ligands have extended π systems, the incoming electron is easily accommodated in the redox orbital of the complexes, thus facilitating the reduction of the oxomolybdenum acceptor center. However, both of the reductions that are observed for all these compounds are irreversible. It may be noted here that the reductions of dioxomolybdenum(VI) complexes in aprotic solvents are generally irreversible.[5b,16a,36,37] This indicates that a chemical reaction follows the electrochemical reductions, and this may involve loss of an oxo group and/or dimer formation. It may be pointed out here that the isolated monomeric oxomolybdenum(V) complexes with these ligands are fairly stable in the solid state as well as in solutions. So, it is not unlikely that a monomeric Mo(V)–oxo species generated electrochemically is partially stabilized and undergoes a further one-electron reduction to generate a Mo(IV)–oxo species. It appears that the initial reduction product, $[MoO_2L(DMSO)]^-$, is partially stabilized[5b] by the addition of a proton/protons (probably the source of proton is the trace of water present in DMSO) to one of the terminal oxo groups (since the basicity of the reduced product is increased), forming either MoO(OH)L(DMSO) or $[MoOL(DMSO)]^+$, the latter being more likely as evidenced by the irreversible nature of the cyclic voltammogram. In any case, the further one-electron-reduction product is presumed to be MoOL(DMSO) with the ultimate loss of an oxo group, and a rapid chemical oxidation is highly likely for this species in DMSO medium, generating the *cis*-dioxomolybdenum(VI) complex.

Oxomolybdenum(IV) Complexes (2a–f). The electron-transfer behavior of the complexes **2a–f** has been examined in DMF by using cyclic voltammetry at a platinum electrode. TEAP and (TEA)Cl have been used separately as the supporting electrolyte. Cyclic voltammograms for all these complexes exhibit a reduction as well as an oxidation wave, the position of these waves being dependent on the nature of the supporting electrolyte. In the presence of (TEA)Cl, the redox behavior of the complexes is found

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Table III. Cyclic Voltammetric Results[a] for Oxomolybdenum(IV) Complexes in 0.1 M TEAP at 298 K

	Mo(V)/Mo(IV)				Mo(IV)/Mo(III)			
complex	E_{pa}, V	E_{pc}, V	ΔE_p, mV	$(E_{1/2})_1$, V	E_{pc}, V	E_{pa}, V	ΔE_p, mV	$(E_{1/2})_2$, V
2a	+0.46	+0.34	120	+0.40	−1.15	−0.75	400	−0.95
2b	+0.47	+0.34	130	+0.405	−1.10	*b*		
2c	+0.14	+0.08	60	+0.11	−1.68	−1.56	120	−1.62
2d	+0.19	+0.11	80	+0.15	−1.64	−1.53	110	−1.585
2e	+0.16	+0.10	60	+0.13	−1.62	−1.52	100	−1.57
2f	+0.20	+0.12	80	+0.16	−1.57	−1.48	90	−1.525

[a] Solvent DMF; solute concentration ~10^{-4} M; working electrode platinum; reference electrode SCE. $E_{1/2} = 0.5(E_{pa} + E_{pc})$; $\Delta E_p = E_{pc} - E_{pa}$. E_{pc} and E_{pa} are cathodic and anodic peak potentials, respectively. [b] Not clearly observed.

Table IV. Cyclic Voltammetric Results[a] for Oxomolybdenum(IV) Complexes in 0.1 M (TEA)Cl at 298 K

complex	E_{pc},[b] V	E_{pa}, V
2a	−1.34 (−0.40)	+0.20
2b	−1.34 (−0.40)	+0.19
2c	−1.38 (−0.44)	+0.11
2d	−1.36 (−0.42)	+0.14
2e	−1.40 (−0.44)	+0.08
2f	−1.34 (−0.42)	+0.16

[a] Solvent DMF; solute concentration ~10^{-4} M; working electrode platinum; reference electrode SCE. [b] Values in parentheses are coupled oxidation peaks observed with complete CVA cycle.

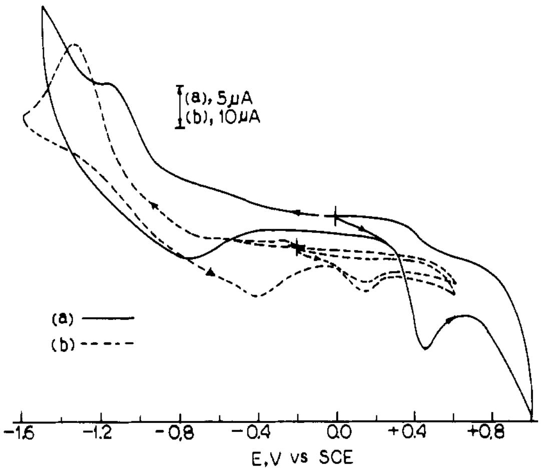


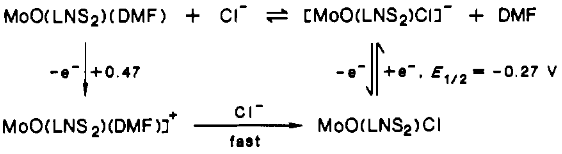
Figure 3. Cyclic voltammograms for ~1 × 10^{-4} M MoO(TSCsal) in DMF (scan rate 50 mV s^{-1}): (a) in 0.1 M TEAP; (b) in 0.1 M (TEA)Cl.

to be irreversible. It is presumed that the Mo(IV)–oxo complexes undergo one-electron reduction to the corresponding Mo(III) complex and are oxidized by one electron to a Mo(V) complex. Similar observations have been made by Boyd and Spence[34] for Mo(IV)–oxo complexes with dianionic tridentate ligands having ONO and SNO donor sites.

MoOL (2a) and MoOL′ (2b). The representative cyclic voltammogram of the complexes in DMF/0.1 M TEAP is shown in Figure 3a. For an initial negative scan at a scan rate of 50 mV s^{-1}, there is a reduction peak near −1.00 V (Table III); reversal of the scan gives two anodic peaks at −0.75 and +0.46 V, respectively. The oxidation wave at +0.46 V is also present in an initial anodic scan; reversal of this scan gives the cathodic peaks at +0.34 and −1.00 V, and a second reversal yields the same anodic and cathodic peaks. The cathodic peak at −1.00 V is found to be coupled to the broad anodic peak at −0.75 V, and the anodic wave at +0.46 V is coupled to the reductive response at +0.34 V, the latter being a quasi-reversible process. From the electrochemical results it appears that the oxidation wave at −0.75 V is due to the reoxidation of the reduced species (at −1.00 V) to the initial Mo(IV)–oxo complex and the oxidized species at +0.46 V is reduced back to the initial complex at +0.34 V.

When the same experiment is repeated with (TEA)Cl as the supporting electrolyte, a cathodic shift of both the cathodic and anodic peaks is observed (Figure 3b, Table IV). This is probably due to the fact that Cl^- ion(s) directly coordinates to the metal center of the coordinatively unsaturated complex MoOL before electrolysis; otherwise, a cathodic shift of the cathodic response would not be observed. The involvement of the chloride ion(s) facilitates the oxidation of the complex, thus causing the cathodic shift of the anodic response. However, the redox behavior of these two complexes is different from that of $MoO(LNS_2)$ (where LNS_2 = 2,6-bis(2,2-diphenyl-2-mercaptoethyl)pyridine) in DMF containing 0.1 M (TEA)Cl. The redox behavior of this compound includes[5b] a reversible oxidation at $E_{1/2} = -0.27$ V ($\Delta E_p = 80$ mV). Another irreversible oxidation wave is also observed at +0.47 V (vs SCE) which is coupled to the reversible redox step at lower potential. The overall process has been explained[5b] by the Scheme I, which clearly indicates the presence of two different species, one with halogen and another without, in the mother solution. Thus, two oxidative responses are obtained at −0.23 and +0.47 V, respectively, obviously showing the ease of oxidation of the chloro species. However, MoOL complexes (**2a**,**b**) exhibit only one oxidation wave due to the Mo(IV,V) couple and invariably this process is found to be irreversible in the presence of Cl^- ions. On the other hand, in the absence of Cl^-, the complex $MoO(LNS_2)$ in 0.1 M $(n\text{-}Bu_4N)(ClO_4)$ shows an irreversible oxidation at +0.52 V, indicating the instability of the oxidized species, while **2a**,**b** exhibit quasi-reversible Mo(IV,V) couples ($E_{1/2}$ = +0.40 V) in the presence of TEAP.

Scheme I



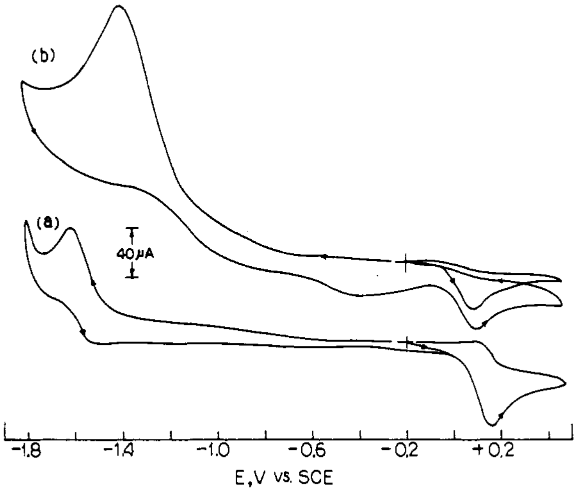


Figure 4. Cyclic voltammograms for ~1 × 10^{-4} M MoO(4-PhTSCsal)(bpy) in DMF (scan rate 100 mV s^{-1}): (a) in 0.1 M TEAP; (b) in 0.1 M (TEA)Cl.

MoOL(bpy) (2c), MoOL(phen) (2d), MoOL′(bpy) (2e), and MoOL′(phen) (2f). All the complexes (**2c**–**f**) exhibit quasi-reversible redox behavior in DMF/0.1 M TEAP with $(E_{1/2})_1$ and $(E_{1/2})_2$ values around +0.15 and −1.60 V, respectively. For an initial anodic scan at a rate of 100 mV s^{-1}, an oxidation wave near

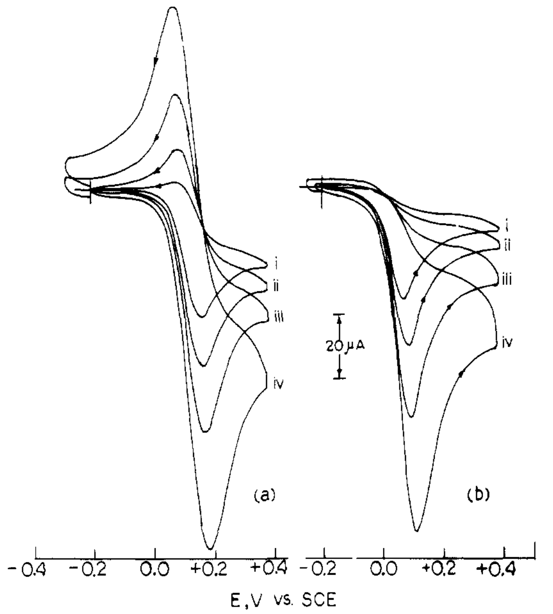


Figure 5. Cyclic voltammograms for ~1 × 10^{-4} M MoO(4-PhTSCsal)(bpy) in DMF showing the nature of the anodic wave (scan rates (i) 50, (ii) 100, (iii) 200, and (iv) 500 mV s^{-1}): (a) in 0.1 M TEAP; (b) in 0.1 M (TEA)Cl.

+0.16 V is observed (Figure 4a); reversal of the scan gives cathodic peaks near +0.10 and −1.60 V. An initial negative scan gives the reductive wave near −1.60 V; reversal of the scan produces a broad anodic wave around −1.55 V and the well-defined oxidative response near +0.16 V; a second cycle yields the same cathodic and anodic peaks. On multiple scan reversal, the waves retain the original shapes, indicating high reversibility of the electrode reactions. From these results it appears that the reduced species at −1.60 V is reoxidized around −1.55 V to the initial Mo(IV)–oxo complex and also the oxidized species around +0.16 V is reduced back to the parent complex at +0.10 V. The overall process may be represented by the Mo(V)–Mo(IV) and Mo(IV)–Mo(III) couples.

$$[\mathrm{Mo^{V}OL(N\text{-}N)}]^{+} + e^{-} \overset{(E_{1/2})_1}{\rightleftharpoons} [\mathrm{Mo^{IV}OL(N\text{-}N)}] \qquad (1)$$

$$[\mathrm{Mo^{IV}OL(N\text{-}N)}] + e^{-} \overset{(E_{1/2})_2}{\rightleftharpoons} [\mathrm{Mo^{III}OL(N\text{-}N)}]^{-} \qquad (2)$$

It should be noted here that the anodic process at +0.16 V becomes considerably more reversible as the scan rate increases (Figure 5), indicating the existence of a competing chemical reaction associated with the electrochemical oxidation.

When the electron-transfer behavior of the complexes **2c–f** is examined with (TEA)Cl as the supporting electrolyte instead of TEAP, quite different results are obtained. Surprisingly the cyclic voltammograms (Figure 4b) for these complexes in 0.1 M (TEA)Cl are identical with those obtained for **2a** and **2b** in 0.1 M (TEA)Cl (Figure 3b). This clearly indicates the involvement of Cl^- ion(s) during electrolysis of these complexes also. However, it is noted that the couple (1), which is a quasi-reversible metal-centered one-electron transfer comprising the Mo(V) and Mo(IV) oxidation states, becomes irreversible in the presence of (TEA)Cl (Figure 5).

Reactivity of the Complexes. Substrate Binding. The dioxomolybdenum(VI) complexes **1a** and **1b** have been synthesized and isolated from CH_3OH medium, and these compounds are found to be oligomeric[16] in the solid state. When they are dissolved in coordinating solvents such as DMF/DMSO, the oligomeric chain is broken and the solvent molecule is coordinated in the sixth coordination position. When MoO_2L and MoO_2L' are reacted with monodentate heterocyclic bases (B) such as γ-picoline and imidazole in methanol, the corresponding MoO_2LB and $MoO_2L'B$ compounds are obtained. Again, when these compounds are dissolved in coordinating solvents such as DMF/DMSO, the monodentate ligand B is readily replaced by the solvent molecule, as is evident from the color change of the solutions, electronic spectra, and electrochemical results. The Mo(IV)–oxo complexes MoOL (**2a**) and MoOL′ (**2b**) have been isolated from CH_3OH/CH_3CN solutions, but surprisingly enough, the isolated complexes do not contain any solvent molecules. **2a** and **2b** are found to react readily with 2,2′-bipyridyl/*o*-phenanthroline to produce the stable six-coordinated complexes MoOL(N-N) (**2c,d**) and MoOL′(N-N) (**2e,f**).

Table V. Magnetic, EPR,[a] and Electrochemical[b] Data for the Oxomolybdenum(V) Complexes

complex	μ_{eff}(300 K), μ_B	g_{iso}	A_{iso}, G	*E*, V (vs SCE) E_{pc}[c]	E_{pa}
3a	1.50	1.9495	49	−0.36, −0.85 (−0.70)	+1.07
3b	1.52	1.9713	46	−0.35, −0.835 (−0.70)	+0.93
3c	1.64	1.9498	49	−0.42, −0.85 (−0.75)	+1.02
3d	1.52	1.9720	46	−0.35, −0.80 (−0.72)	+0.93

[a] Spectra were recorded in dry CH_3CN at room temperature. [b] Solvent DMF; solute concentration ~10^{-4} M; working electrode platinum; reference electrode SCE. [c] Values in parentheses are coupled oxidation peaks observed with complete CVA cycle.

Oxo Transfer to Substrate. The propensity of the complexes MoO_2L and MoO_2L' to transfer an oxygen atom to the substrate has been examined in $CH_3OH/CH_3CN/DMF$ containing PPh_3. The parent complex of type **1** has a band at 400 nm due to a S(pπ) → Mo(dπ) LMCT transition. When the complex is reacted with PPh_3, this band is found to be shifted to lower energy (~455 nm) and a new band appears at 650 nm. The isolated complexes MoOL and MoOL′ also have the same spectral features. The oxo-transfer reaction may be represented as

$$\mathrm{Mo^{VI}O_2L + PPh_3 \xrightarrow{CH_3CN} Mo^{IV}OL + OPPh_3}$$

This oxo-transfer reaction may be visualized[38] as a simple bimolecular reaction that involves the interaction between one MoO_2L and one PPh_3 molecule in the activated complex, leading to the transfer of an oxygen atom by the donation of the lone pair of electrons of the phosphorus atom into the antibonding Mo═O π* orbital. This leads to the formation of the P—O bond and an Mo(IV)–oxo complex with a $4d^2_{xy}$ configuration. Hence, the reaction may be considered as a two-electron-redox/oxygen atom transfer process.

Oxo Transfer from Substrate. The oxygen atom transfer from the substrate (DMSO) to the systems MoOL (**2a**) and MoOL′ (**2b**) has been studied spectrophotometrically in DMF solution. The parent complex MoOL exhibits a low-energy band at 650 nm with a low ε value and an intense band at ~450 nm. When a drop of DMSO is added to the solution of **2a** and **2b**, the intensity of these bands is found to decrease slowly. The bands finally disappear within 10 min, and a new band, characteristic of the complexes of type **1**, makes its appearance at ~400 nm. This observation clearly indicates[4,5a] the transfer of an oxygen atom from DMSO to the MoO^{2+} core, leading to the formation of MoO_2^{2+} species and Me_2S. The reaction may be shown as

$$\mathrm{MoOL + DMSO \xrightarrow{DMF} MoO_2L + Me_2S}$$

B. Oxomolybdenum(V) Complexes (3a–d). All the complexes are moderately soluble in acetonitrile but highly soluble in DMF and DMSO. The compounds behave as nonelectrolytes in dry acetonitrile. All these compounds are unstable in solution in long contact with air and are highly sensitive toward the presence of water. Hence, all the operations have been carried out with extreme care in dry conditions under a dinitrogen atmosphere. Room-temperature magnetic moments of these compounds lie in the range 1.5–1.6 μ_B (Table V), which is quite close to the spin-only value for a d^1 system. Such values are also indicative of the fact that in **3a–d** the orbital angular momentum is effectively quenched[20] by the low symmetry of the ligand field surrounding the oxometal acceptor center.

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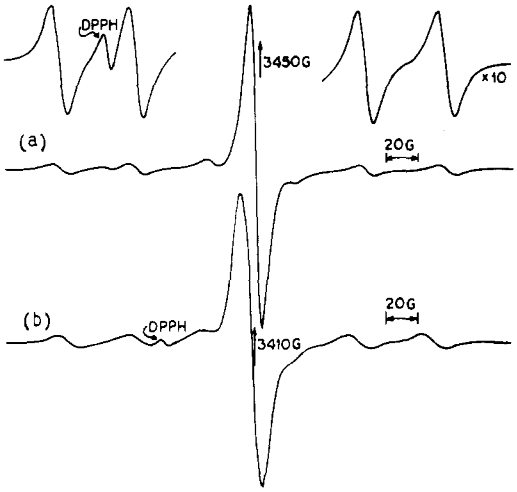

Figure 6. Solution EPR spectra recorded in CH_3CN at X-band frequency at room temperature: (a) $MoO(TSCsal)Cl_2$; (b) $MoO(TSCsal)Br_2$.

IR Spectra. The ligands TSCsal and 4-PhTSCsal are found to act in this case in a monoanionic tridentate manner, coordinating through the deprotonated phenolic oxygen, the imine nitrogen, and the thione sulfur atom in the relevant complexes, and this is further supported by the analytical and conductance data. All the complexes have been characterized by a strong sharp band in the 970–930-cm^{-1} region (Table I), representing the $\nu(Mo{=}O)_t$[20] mode. The presence of this band and the absence of any band corresponding to Mo–O–Mo bridge vibrations points to the monomeric nature of these Mo(V) compounds. This speculation gets further support from the observed one-electron magnetic moment of the complexes. In the far-infrared region, a medium-intensity band located around 380 cm^{-1} may be assigned to the $\nu(Mo{-}S)$[19,39] mode. The chloro complexes exhibit two medium-intensity bands in the 340–320-cm^{-1} region, probably arising[40] due to $\nu(Mo{-}Cl)$. On the other hand, the bromo compounds exhibit two bands in the region 270–230 cm^{-1}. The appearance of twin bands due to $\nu(Mo{-}X)$ is indicative of the presence of two nonequivalent halide ions in the coordination sphere. Hence, a distorted-octahedral geometry[4,40b] around the metal ion is likely for these complexes.

Electronic Spectra. An important feature of the electronic spectra of all these complexes in acetonitrile is the presence of one distinct absorption band (Table I) in the ligand field region (700–545 nm) arising out of the first crystal field transition[41-43] $^2B_2 \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{xz}, d_{yz}$), assuming the effective symmetry of C_{4v}. The second crystal field transition $^2B_2 \rightarrow {}^2B_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$) is obscured by other charge-transfer transitions. The bands observed below 300 nm are probably due to intraligand transitions. Between the two LMCT bands observed in the 450–300-nm region, the lower energy one could be associated with a ligand-to-metal charge transfer[19] originating from an electronic excitation from the HOMO of sulfur to the LUMO of molybdenum. The other band may be associated with a molybdenum–oxygen[44] charge transfer, which is characteristic of all oxomolybdenum species.

EPR Spectra. Powder EPR spectra of all these complexes, except **3a**, are characterized by broad spectral features. The solution EPR spectra of the complexes in dry acetonitrile are well resolved (Figure 6), and each spectrum consists of a strong central line due to the 75% of the molybdenum isotopes with $I = 0$ and six satellite lines arising from the hyperfine interaction of the unpaired electron with $^{95,97}Mo$ nuclei ($I = {}^5/_2$). The isotropic g and metal hyperfine coupling (A_{iso}) values are given in Table V. It is observed that the isotropic metal hyperfine coupling constant decreases from the chloro complex to the bromo analogue. The isotropic hyperfine interaction from the metal nucleus is supposed to arise from core polarization by the d electrons, and its sign is expected to be positive for ^{95}Mo, ^{97}Mo since the sign of the nuclear g value is negative. However, a decrease in A_{iso} for the metal ion indicates a decrease in d-orbital component(s) of the wave function for the unpaired electron and hence the consequent increase in covalent character. Thus, it may be concluded qualitatively that the covalency increases from coordinated chlorine to bromine in analogous complexes, which, of course, is expected on the basis of electronegativity. Similar results have been reported[45] previously for the series $MoOF_5^{2-}$ and $MoOCl_5^{2-}$. A_{iso} for the compounds **3a** and **3c** are the same. These two compounds differ in their ligand structures only in the replacement of an amine proton by a phenyl ring. This does not seem to affect the bonding at all. The isotropic g value increases drastically from a chloro complex to its bromo analogue. Although changes in covalency are expected to lead to changes in g anisotropy, the magnitude of shift in the g value from the chloro complex to its bromo analogue cannot be completely accounted for on the basis of covalency alone. Manoharan and Rogers[45] have explained similar effects on the basis of an increase in spin–orbit coupling of the ligand from chlorine to bromine. Our results are in accordance with their predictions.

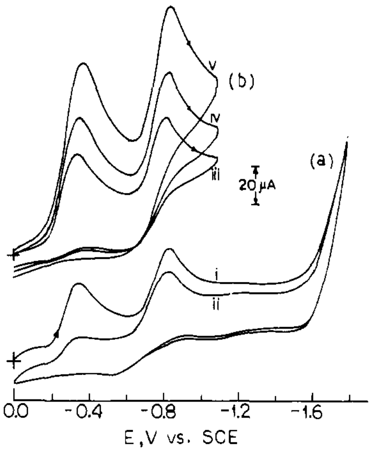

Figure 7. Cyclic voltammograms for $\sim 1 \times 10^{-4}$ M $MoO(TSCsal)Br_2$ in 0.1 M TEAP/DMF: (a) multiple scan reversal at a scan rate of 50 mV s^{-1}; (b) traces at scan rates of (iii) 50, (iv) 100, and (v) 200 mV s^{-1}.

Electrochemistry. The electrochemical behavior of the monomeric oxomolybdenum(V) complexes in DMF/0.1 M TEAP has been studied by cyclic voltammetry (CV) at a platinum working electrode, and the data in the potential range +1.1 to −2.0 V (vs SCE) are summarized in Table V. The complexes are found to exhibit a well-defined cyclic response in the potential range 0.0 to −1.8 V. The compounds display two successive cathodic responses near −0.40 and −0.85 V, respectively, possessing almost equal current heights (Figure 7). The second reduction wave at −0.85 V is found to be coupled to a weak and broad anodic peak around −0.7 V. No other anodic wave is observed within the potential range +0.5 V. A comparison of the current heights at E_{pc}'s with those of authentic one-electron reductions observed[6,35] in the cases of other monomeric Mo(V)–oxo complexes suggests that each of the reductions involves a metal-centered one-electron process. The cathodic peak near −0.40 V, obtained from an initial negative scan, is greatly reduced in intensity in the second cycle, which yields only the reductive response at −0.85 V (Figure 7a). This indicates that the species reduced at −0.85 V is reoxidized near −0.70 V, and this oxidized product is found to be reduced again at −0.85 V. If the potential is scanned in such a manner

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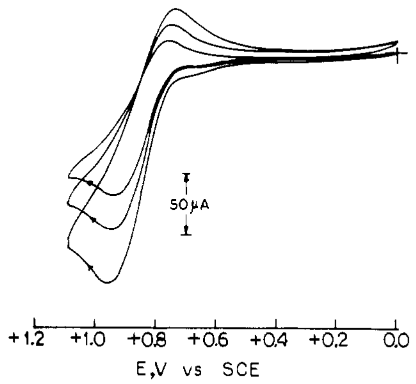

Figure 8. Cyclic voltammograms for ~1 × 10^{-4} M MoO(TSCsal)Br_2 in 0.1 M TEAP/DMF showing the oxidative response (scan rates of 50, 100, and 200 mV s^{-1}).

so as to cycle only the first response, it is observed that this reduction process is essentially irreversible. The small separation between the two reduction waves (~500 mV) indicates a postchemical path (electrochemical–chemical–electrochemical, ECE process) along with the electrode reactions. This is rationalized in terms of halide loss assisted by metal-centered reduction. The Mo(V) complex, when reduced near −0.40 V, readily loses a halide ion from the coordination sphere, resulting in the formation of a neutral Mo(IV) species. This electrogenerated Mo(IV) complex, MoO(LH)X, undergoes a facile reduction at −0.85 V probably followed by the further loss of the second halide ion to form a neutral Mo(III) species that, on scan reversal, is reoxidized to a halogenless Mo(IV) species near −0.70 V. Thus, the loss of the halide ion facilitates the second reduction, making the overall process irreversible. This can be represented as

$$[\mathrm{Mo^{V}O(LH)X_2}] \xrightarrow[-X^-]{+e^-} [\mathrm{Mo^{IV}O(LH)X}] \xrightarrow[-X^-]{+e^-} [\mathrm{Mo^{III}O(LH)}]$$

$$\mathrm{LH_2} = \mathrm{TSCsal};\ X = \mathrm{Cl, Br}$$

However, in stirred solution electrolysis occurs smoothly and both reduction waves are always observed (Figure 7b).

An anodic scan beginning from slightly more positive than the first reduction potential shows that the chloro compounds (**3a**,**c**) are irreversibly oxidized near +1.00 V. However, the oxidation process is quasi-reversible for both bromo compounds (**3b**,**d**) (Figure 8). In the latter case, the value of $i_{pa}/i_{pc} > 1$, suggesting that a postchemical process is in operation. These results indicate that the oxidized species, $\mathrm{Mo^{VI}O(LH)Br_2^+}$, is more stable than its chloro analogue. However, this result is in contrast to those reported[23] for other Mo(V)–oxo complexes, where no oxidation was observed even with rapid anodic scans extending to +1.00 V. It may be recalled here that the Mo(IV)/Mo(III) reduction potential (−1.00 V) of the Mo(IV)–oxo complexes (**2a**,**b**) is more cathodic than the Mo(IV)/Mo(III) reduction potential (−0.80 V) of the $\mathrm{Mo^{V}O(LH)X_2}$ complexes under study. This can be attributed to the fact that, LH being a monoanionic tridentate ligand, the generated Mo(III) species in the latter case becomes electrically neutral due to the loss of the halide ions, thus facilitating the reduction.

Concluding Remarks. In this work we have endeavored to obtain Mo(VI)–dioxo and Mo(IV)–oxo complexes containing coordination units resembling the binding site in the Mo cofactor of the oxo-transfer molybdoenzymes active in oxo-transfer reactions to and from the substrate. Oxo abstraction from Mo(VI)–dioxo complexes has been successfully employed here to get a number of Mo(IV)–oxo complexes. The synthesis of **2a**,**b** (70–80%) from the reaction of **1a**,**b** with PPh_3 in CH_3CN/MeOH is a good indication[5b] that these complexes are resistant to dimer formation. It should be mentioned here that μ-oxo species do not appear to be generated in detectable amounts or at all in the oxo-transfer reactions of many other complexes[46] containing dianionic tridentate Schiff base ligands devoid of bulky groups for steric shielding. Hence, extreme steric bulk[5b,34,37,46] is not always necessary to prevent Mo(V) dimer formation. The occurrence of quasi-reversible or nearly reversible Mo(IV,V) couples in the electrochemical results of the Mo(IV)–oxo complexes in 0.1 M TEAP is indicative of the stability of the oxidized Mo(V)–oxo species at the time scale used. Thus, monomeric oxomolybdenum complexes in all biologically relevant oxidation states of molybdenum are accessible with the ligands TSCsal and 4-PhTSCsal, which is an important criterion for modeling a molybdoenzyme.

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