Synthesis, Characterization, Electrochemistry and Oxo-transfer Kinetics of Oxomolybdenum-(VI), -(V) and -(IV) Complexes with ONS Donors

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cis-Dioxomolybdenum(VI) complexes of the type $[MoO_2L]$ [H_2L = *S*-benzyl 3-(2-hydroxyphenyl)methylenedithiocarbazate or its derivative having a 5-methyl substituent in the salicyl phenyl ring] are Mo=O···Mo bridged oligomers. In the presence of donors [D = Me_2CO, pyridine, dimethylformamide (dmf) or Me_2SO] they are converted into monomeric $[MoO_2L(D)]$. When a 5-Cl or 5-Br substituent occurs in the salicyl phenyl ring oligomers are not formed, but besides $[MoO_2L(D)]$ also $[MoO_2L(MeOH)]$ are obtained. All these complexes undergo oxo transfer to PPh_3 at room temperature, furnishing oxomolybdenum(IV) derivatives, [MoO(L)], and PPh_3O. The complexes [MoO(L)] in dmf accepts an oxygen atom from Me_2SO, affording $[MoO_2L(D)]$ and Me_2S. The ions $[MoOX_5]^{2-}$ (X = Cl or Br) react with the ligands H_2L furnishing thiolato-bridged dimers, $[Mo_2O_2X_2L_2]$, which show sub-normal magnetic moments and EPR spectra typical of an antiferromagnetic material. The MoO_2^{2+} complexes undergo irreversible electrochemical reduction furnishing oxomolybdenum(V) derivatives at potentials commensurate with the nature of substituent in the salicyl group of the ligand. The molybdenum-(V) and -(IV) complexes also show interesting electrochemical reductive as well as oxidative responses centred on the metal. The oxo transfer from $[MoO_2L]$ (unsubstituted salicyl ring) to PPh_3 occurs in a second-order process with rate constant 1.32×10^{-2} dm^3 mol^{-1} s^{-1} at 30 °C. The oxo transfer from Me_2SO to the MoO^{2+} core is much faster. The reaction between PPh_3 and Me_2SO furnishing PPh_3O and Me_2S becomes highly facile in the presence of $[MoO_2L]$ as catalyst.

Perhaps the most interesting aspect of dioxomolybdenum(VI) chemistry is the ability of suitably ligated MoO_2^{2+} to undergo reversible oxo-transfer reaction as described by equations (1) and (2). Since $[Mo^{IV}O(ligand)]$ type complexes are generally

$$[Mo^{VI}O_2(ligand)] + X \longrightarrow [Mo^{IV}O(ligand)] + XO \quad (1)$$

$$[Mo^{IV}O(ligand)] + YO\dagger \longrightarrow [Mo^{VI}O_2(ligand)] + Y \quad (2)$$

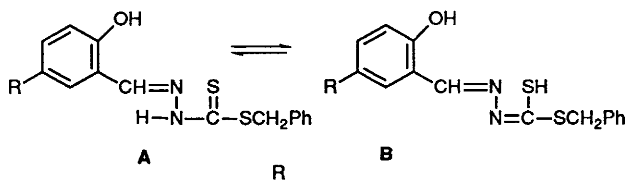
reconverted into $[Mo^{VI}O_2(ligand)]$ in aqueous aerobic media, the net effect caused by oxo-transfer molybdoenzymes,[2–5] which as oxidases or reductases catalyse the transfer or abstraction of an oxygen atom to or from substrate X or YO respectively, can be represented by equation (3). The forward reactions

$$X + H_2O \rightleftharpoons XO + 2H^+ + 2e^- \quad (3)$$

are exemplified in xanthine oxidase, sulfite oxidase and aldehyde oxidase.[2–4] Conversely, when molybdoenzymes act as reductases, *viz.* nitrate reductase,[4] sulfate reductase[4] and d-Biotin-d-(S-oxide) reductase[5,6] in the manner of equation (2) the net process identifiable is the back reaction in equilibrium (3).

In model studies the selection of the ligand is very important insofar as extended X-ray absorption fine structure (EXAFS) results[7–10] implicated sulfur and nitrogen or oxygen as ligand donor atoms to make up the co-ordination sphere of molybdenum. Earlier work,[11,12] including rate and activation parameter data, indicated that at least one sulfur atom is essential for the resulting complex to be suitable for model studies. However, very recently it has been shown that, albeit

† In the model compounds studied so far, except for a single case,[1] YO rather than XO is more appropriate in equation (2), since equation (1) as such often represents an irreversible chemical reaction.



	R
H_2L^1	H
H_2L^2	Me
H_2L^3	Cl
H_2L^4	Br

very slowly, the reaction also occurs with NNN functionalities generated by pyrazolylborate ligands.[13] The oxo-transfer activity of the model compounds generally decreases in the following order of ligand environment: $S_4 > N_2S_2 > N_2S >$ ONS > NNN.

Considering the EXAFS results[7–10] we thought it more appropriate to concentrate on ONS ligands; moreover, to avoid the formation of the biologically irrelevant μ-oxo-molybdenum(V) dimer during the course of the oxo-transfer reaction, the ligands were designed so as to possess some steric hindrance, so that dimerisation *via* $[Mo^V_2O_3(ONS)_2]$ type complex formation is inhibited.[1,14–16] The dianionic ONS Schiff-base ligands actually used are *S*-benzyl 3-(2-hydroxyphenyl)methylenedithiocarbazate and its derivatives, the undissociated forms of which are shown as the thione **A** and thiol **B**. Allied ligands were used by Purohit *et al.*[17] but their system did not contain any added S-containing thioether moiety, SCH_2Ph, which is herein supposed to induce steric crowding, since, at present, it is largely believed that the oxo-transfer reactions are inevitably accompanied by abiological μ-oxo dimer ($Mo_2O_3^{4+}$) formation unless such a possibility is excluded by steric encumbrance.[11,16,18,19]

The parent molybdenum(VI) complexes synthesized by us in the absence of any solvent donor (D) are represented by $[MoO_2L^1]$* **1a** and $[MoO_2L^2]$ **1b** while those obtained including donor molecules are $[MoO_2L^3(MeOH)]$ **1c**, $[MoO_2L^4(MeOH)]$ **1d**, as well as $[MoO_2L^1(D)]$ [D = Me_2CO **1e**, pyridine (py) **1f**, dimethylformamide (dmf) **1g**, or Me_2SO **1h**], $[MoO_2L^2(D)]$ (D = py **1i** or dmf **1j**), and $[MoO_2L^4(D)]$ [D = py **1k**, dmf **1l**, or Me_2SO **1m**]. After oxo-transfer, aided by PPh_3, the molybdenum(IV) complexes formed are $[MoO(L^1)]$ **2a** and [MoO(L)] [L = L^3 **2b**, L^4 **2c** or L^2 **2d**] from an acetonitrile or methanol reaction medium. In dmf, however, $[MoO(L^1)(dmf)]$ **2e** and [MoO(L)(dmf)] (L = L^3 **2f**, L^4 **2g** or L^2 **2h**) are isolable. The salts $[NH_4]_2[MoOX_5]$ (X = Cl or Br) on reaction with H_2L^1 or H_2L^4 afford dimeric oxomolybdenum(V) complexes, $[Mo_2O_2X_2L^1{}_2]$ (X = Cl **3a** or Br **3b**) and $[Mo_2O_2X_2L^4{}_2]$ (X = Cl **3c** or Br **3d**). Herein is also described a kinetic study of the oxo-transfer reaction (1), using the parent molybdenum(VI) complex **1a** as the model compound and PPh_3 as substrate, which shows that the reaction is unprecedentedly fast for an ONS ligand.

Experimental

Physical Measurements.—The IR spectra wre recorded using KBr or CsI discs on a Perkin-Elmer 597 IR spectrophotometer, ^1H NMR spectra using a Varian EM 390 (90 MHz) spectrometer and $SiMe_4$ as standard. X-Band ESR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at low temperatures. The spectra were calibrated with diphenylpicrylhydrazyl (dpph) (g = 2.0037). Electronic spectra were obtained using a Hitachi U-3400 UV/VIS-NIR spectrophotometer. Thermoanalyses were made on a Shimadzu thermoanalyser DT 30. Voltammetric measurements were done with a PAR model 370-4 electrochemistry system: model 174A polarographic analyser, model 175 universal programmer, model RE 0074 XY recorder, model 173 potentiostat, model 179 digital coulometer, and model 377A cell system. All experiments were made at 298 K under a dinitrogen atmosphere in a three-electrode configuration using a planar Beckman model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE). For coulometry a platinum wire-gauze working electrode was used. The potentials reported are uncorrected for the junction contribution. The magnetic susceptibilities were obtained by the Gouy method using $Hg[Co(NCS)_4]$ as a standard. The solution conductances were measured with a Systronics (India) model 304 digital conductivity meter. A Knauer (Berlin) vapour-pressure osmometer was used for molecular weight determination, calibrated with benzil solution in an appropriate solvent. Elemental analyses were performed using a Perkin-Elmer 240C elemental analyser and molybdenum was estimated by the gravimetric method.[20] All manipulations associated with the kinetic measurements were performed under a dinitrogen atmosphere. Solutions of the dioxomolybdenum(VI) complex (2×10^{-4} mol dm^{-3}) in dmf were employed. Pseudo-first-order conditions were maintained throughout by use of between 50- and 100-fold molar excesses of PPh_3 over the molybdenum concentration. The time dependence of the absorbance at 455 nm was recorded on a Philips Analytical SP8-150 UV/VIS spectrophotometer with a thermostatted (HAAKE F3) cell compartment. The observed rate constants were obtained from plots of $\ln(A_\infty - A_t)$ *vs.* time, where A_t and A_∞ are the absorbances at time t and infinity, respectively. These were all linear for more than 85% completion of the reaction. Data were extracted using a least-squares computer fitting program. Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained from an Eyring plot.

* As a class, these complexes will generally be represented as $[MoO_2(ONS)]$ or $[MoO_2(ONS)(D)]$ and [MoO(ONS)] or [MoO(ONS)(D)], for simplicity.

Materials.—Ammonium heptamolybdate (J. T. Baker, Phillipsburg, NJ), *p*-chlorophenol (AR BDH, UK), and *p*-cresol (S.D. Chemicals, India) were obtained commercially and used as such. The complex $[MoO_2(acac)_2]$ (acac = acetylacetonate) was synthesized as reported.[21] *S*-Benzyl dithiocarbazate[22] and $[NH_4]_2[MoOX_5]$[23] (X = Cl or Br) were prepared by the standard methods. 5-Bromosalicylaldehyde was obtained from Aldrich (USA) and the corresponding 5-methyl and 5-chloro derivatives were prepared in good yields by using the Duff reaction,[24] following the methods described in the literature. Triphenylphosphine (Sisco Research Laboratories, India) was twice recrystallized from ethanol-water. Dimethylformamide used for electrochemical and kinetics studies was dried by distillation *in vacuo* over P_2O_5 and then stored over Linde AW-500 molecular sieves. Dimethyl sulfoxide was distilled from CaH_2, degassed, and stored under dinitrogen.

Preparation of Ligands H_2L^1–H_2L^4.—The compounds were readily obtained by condensation of appropriate aldehydes (0.03 mol) with an ethanolic solution of *S*-benzyl dithiocarbazate (5.94 g, 0.03 mol). Yield: 85–90% (Found: C, 59.7; H, 4.6; N, 9.3. $C_{15}H_{14}N_2OS_2$ requires C, 59.6; H, 4.7; N, 9.3. Found: C, 60.6; H, 5.2; N, 8.7. $C_{16}H_{16}N_2OS_2$ requires C, 60.7; H, 5.1; N, 8.8. Found: C, 53.4; H, 3.9; N, 8.2. $C_{15}H_{13}ClN_2OS_2$ requires C, 53.5; H, 3.9; N, 8.3. Found: C, 47.4; H, 3.4; N, 7.4. $C_{15}H_{13}BrN_2OS_2$ requires C, 47.2; H, 3.4; N, 7.2%).

Preparation of the Complexes.—$[MoO_2L]$ (L = L^1 **1a** *or* L^2 **1b**). A solution of the appropriate ligand (2 mmol) in ethanol (*ca.* 50 cm^3) was filtered into an ethanol (30 cm^3) solution of $[MoO_2(acac)_2]$ (2 mmol) and the resulting solution heated under reflux. Subsequently the volume was reduced (to 50 cm^3) in a rotavaporator, when the crystalline brown product separated. It was filtered off, washed with cold ethanol and dried *in vacuo*. Yield: *ca.* 60%.

$[MoO_2L(MeOH)]$ (L = L^3 **1c** *or* L^4 **1d**). These complexes were prepared in the same manner as described for **1a**, using methanol instead of ethanol. Yield: 63–65%.

$[MoO_2L^1(Me_2CO)]$ **1e**. Compound **1a** (0.48 g) was dissolved in dry acetone (25 cm^3) and the solid product **1e** was precipitated by adding light petroleum (b.p. 40–60 °C). Yield: 65%.

$[MoO_2L^1(py)]$ **1f**. To a stirred solution of compound **1a** (0.43 g, 1 mmol) in ethanol (40 cm^3) was slowly added pyridine (0.08 g, 1 mmol). The reaction mixture was heated under reflux for 1.5 h. A yellow solution was obtained which on concentration yielded yellow microcrystals, which were filtered off, washed with cold ethanol and dried *in vacuo*. Yield: 0.28 g (55%).

Complexes **1g** and **1h**, **1i** and **1j**, and **1k**–**1m** were prepared from **1a**, **1b** and **1d**, respectively, as starting materials following the same method.

$[MoO(L^1)]$ **2a**. To a hot solution of complex **1a** (0.43 g, 1 mmol) in degassed acetonitrile (20 cm^3) was added with constant stirring triphenylphosphine (0.39 g, 1.5 mmol) dissolved in acetonitrile (15 cm^3), under dinitrogen. A dark brown solution was obtained which when refluxed on a steam-bath for about 10 min produced a brown compound. The product was filtered off while hot and washed with hot acetonitrile. Yield: 0.68 g (83%). The filtrate obtained after the separation of **2a** was evaporated to dryness and extracted with diethyl ether. The ether extract gave crystalline $OPPh_3$ on evaporation, in 85% yield, m.p. 157 °C. The IR spectrum of the product is superimposable with that of the authentic compound. Compound **2a** was also prepared directly from $[MoO_2(acac)_2]$ by refluxing first with H_2L^1 and then with PPh_3 in ethanol. Yield 64%.

Compounds **2b**–**2d** were prepared by a similar method to that described for **2a**. Yield: 75–80%.

Complexes **2e**–**2h**. The procedure applied for complex **2a** was followed using dmf instead of acetonitrile. Yield: 65–70%. These compounds were also prepared from respective [MoO(ONS)] by dissolving in dry dmf and precipitating by adding ether. Yield: *ca.* 68%.

Table 1 Analytical,[a] IR (cm^{-1})[b] and electronic spectral data (λ nm, ε/dm^3 mol^{-1} cm^{-1})[c] for the complexes

	Complex	Analysis (%) C	H	N	Mo	ν(Mo=O)[d]	Selected D vibrations	ν(C–O)	λ_{max}(ε)
1a	$[MoO_2L^1]$	42.2(42.1)	2.8(2.8)	6.6(6.5)	22.1(22.4)	943, 925, 916, 822[e]	—	1557m	417(1062)
1b	$[MoO_2L^2]$	43.6(43.4)	3.2(3.2)	6.4(6.3)	21.5(21.7)	940, 930, 900, 825[e]	—	1557m	425(1062)
1c	$[MoO_2L^3(MeOH)]$	38.8(38.8)	3.1(3.0)	5.7(5.6)	19.1(19.4)	930, 890	3350m (br),[f] 1015m	1555m	423(1312)
1d	$[MoO_2L^4(MeOH)]$	35.7(35.6)	2.8(2.8)	5.2(5.2)	17.7(17.8)	940, 890	3390m (br),[f] 1010m	1557s	425(875)
1e	$[MoO_2L^1(Me_2CO)]$	44.5(44.4)	3.7(3.7)	5.8(5.8)	19.6(19.7)	910, 885	1675s[g]	1555w	420(2187)
1f	$[MoO_2L^1(py)]$	47.6(47.3)	3.4(3.4)	8.3(8.3)	18.8(18.9)	934, 901	1455s, 1078s, 1050m	1560s	421(1250)
1g	$[MoO_2L^1(dmf)]$	43.3(43.1)	3.8(3.8)	8.4(8.4)	19.2(19.1)	935, 904	1650s,[h] 680m[i]	1557m	425(1128)
1h	$[MoO_2L^1(Me_2SO)]$	40.5(40.3)	3.5(3.6)	5.5(5.5)	19.1(18.9)	923, 895	1008s[j]	1560s	424(1120)
1i	$[MoO_2L^2(py)]$	48.7(48.4)	3.7(3.7)	8.0(8.1)	18.3(18.4)	927, 900	1455s, 1010m	1555m	427(1208)
1j	$[MoO_2L^2(dmf)]$	44.5(44.3)	4.1(4.1)	8.1(8.1)	18.5(18.6)	925, 895	1652s,[h] 682m[i]	1557s	421(1101)
1k	$[MoO_2L^4(py)]$	41.2(41.0)	2.7(2.7)	7.2(7.2)	16.5(16.3)	939, 902	1460s, 1045m, 1008m	1555s	437(817)
1l	$[MoO_2L^4(dmf)]$	37.3(37.2)	3.1(3.1)	7.2(7.2)	16.6(16.5)	938, 905	1652s,[h] 684m[i]	1555m	435(693)
1m	$[MoO_2L^4(Me_2SO)]$	34.9(35.0)	2.9(2.9)	4.8(4.8)	16.5(16.4)	925, 900	1010s[j]	1555m	432(897)
2a	$[MoO(L^1)]$	43.9(43.7)	2.8(2.9)	6.7(6.8)	23.2(23.3)	970	—	1555s	690(144), 455(4100)[k]
2b	$[MoO(L^3)]$	40.5(40.3)	2.5(2.5)	6.2(6.3)	21.4(21.5)	975	—	1555s	695(125), 468(4000)[k]
2c	$[MoO(L^4)]$	36.8(36.7)	2.2(2.3)	5.8(5.7)	19.7(19.5)	980	—	1557m	698(108), 465(3800)[k]
2d	$[MoO(L^2)]$	45.2(45.1)	3.3(3.3)	6.6(6.6)	22.7(22.5)	972	—	1556m	700(100), 460(3900)[k]
2e	$[MoO(L^1)(dmf)]$[l]	44.6(44.5)	4.0(3.9)	8.7(8.6)	19.9(19.8)	960	1650s,[h] 678m[i]	1550m	*m*
2f	$[MoO(L^3)(dmf)]$	41.8(41.6)	3.5(3.5)	8.2(8.1)	18.7(18.5)	965	1650s,[h] 675m[i]	1555m	*m*
2g	$[MoO(L^4)(dmf)]$	38.4(38.3)	3.1(3.2)	7.4(7.4)	17.2(17.0)	968	1655s,[h] 680m[i]	1556m	*m*
2h	$[MoO(L^2)(dmf)]$	45.8(45.7)	4.2(4.2)	8.5(8.4)	19.4(19.2)	958	1650s,[h] 670m[i]	1560m	*m*
3a	$[Mo_2O_2Cl_2L^1{}_2]$[l]	40.4(40.6)	2.7(2.7)	6.3(6.3)	21.5(21.4)	980, 973[n]	—	1557m	705(292), 466(9873)[k]
3b	$[Mo_2O_2Br_2L^1{}_2]$	36.8(36.6)	2.6(2.5)	5.7(5.7)	19.7(19.5)	978, 965[n]	—	1555m	685(316), 465(9993)[k]
3c	$[Mo_2O_2Cl_2L^4{}_2]$	34.8(34.5)	2.1(2.1)	5.3(5.3)	18.3(18.2)	976, 968[n]	—	1557m	698(165), 458(9858)[k]
3d	$[Mo_2O_2Br_2L^4{}_2]$	31.9(31.6)	1.9(1.9)	5.0(4.9)	16.9(16.8)	980, 970[n]	—	1558m	700(250), 467(9750)[k]

[a] Calculated values are shown in parentheses. [b] As KBr discs. [c] In acetonitrile; intraligand transitions are not listed. [d] All the absorptions are very strong. [e] Strong and broad band. [f] ν(C–O)(alkyl). [g] ν(C=O). [h] Amide band I. [i] δ(NCO). [j] ν(SO). [k] In dimethylformamide. [l] Molecular weight in Me_2CN–dmf: **2e**, 481(485); **3a**, 890(895). [m] Same as for complex **2a**, **2b**, **2c** and **2d**, respectively. [n] As CsI discs; ν(Mo–Cl) band for complexes **3a** and **3c** occurs at 340 and 335 cm^{-1} and 343 and 338 cm^{-1}, respectively.

Table 2 Proton NMR data in $CDCl_3$

Compound		CH=N	Aromatic H	SCH_2
H_2L^1	10.02(br)	8.02(s)	6.92–7.34(m)	4.48(s)
$[MoO_2L^1]$	—	8.68(s)	6.94–7.52(m)	4.45(s)

$[Mo_2O_2Cl_2L^1{}_2]$ **3a** Dinitrogen was passed through a clear solution of H_2L^1 (0.3 g, 1 mmol) in anhydrous ethanol (30 cm^3) for 20 min. To this, $[NH_4]_2[MoOCl_5]$ (0.3 g, 1 mmol) in dry ethanol (5 cm^3) was added dropwise while stirring magnetically. The resulting solution turned dark brown and was stirred for 2 h under dinitrogen. The dark brown precipitate which separated was filtered off, washed with dry ethanol and dried *in vacuo*. Yield: 0.35 g (58%).

Compounds **3b**–**3d** were prepared in the same manner, using appropriate starting materials. Yield: 55–60%.

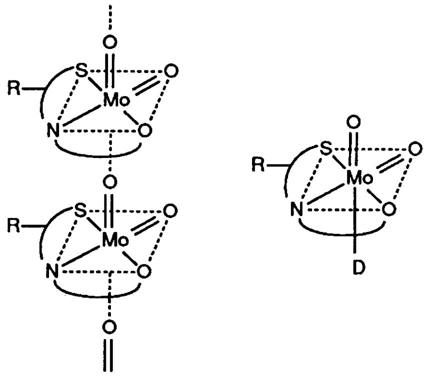
The analytical data for the isolated complexes are shown in Table 1.

Results and Discussion

(*a*) *Mode of Ligand Co-ordination: Tridentate Nature*.—The free ligands H_2L^1–H_2L^4 all exhibit a ν(C=S) vibration[25] in their IR spectra at *ca.* 1050 cm^{-1}, indicating that they exist in the thione form **A** in the solid state. On metal co-ordination 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) (*ca.* 3110 cm^{-1}) and ν(NH) (*ca.* 2975 cm^{-1}), as well as from the absence of any ν(SH) or ν(C=S), vibrations.[26] The ONS mode of metal co-ordination, *i.e.* through phenolic oxygen, azomethine nitrogen and thiol sulfur of **B** is ascertained from the blue shift (18–22 cm^{-1}) of ν(C–O) and the red shift (15–20 cm^{-1}) of the ν(C=N) vibrations of the parent ligands (*ca.* 1540 and *ca.* 1630 cm^{-1} respectively).[25,27] Moreover, comparison of the ^1H NMR spectrum of H_2L with that of its complex **1a** reveals that (*i*) the phenolic proton of the ligand disappears (Table 2), (*ii*) the azomethine proton signal is shifted downfield,[28] and (*iii*) the position of the SCH_2 proton resonance due to the *S*-benzyl group of H_2L^1, occurring at δ 4.48, virtually remains unaltered for complex **1a**. This supports the mode of co-ordination suggested from IR data, with added evidence that the sulfur atom in the SCH_2Ph group is not involved in co-ordination. Further support for this co-ordination mode is provided by the ν(Mo–O) and ν(Mo–S) vibrations at 550–600[29,30] and 340–345 cm^{-1},[31,32] respectively.

(*b*) *Complexes* $[MoO_2(ONS)]$, $[MoO_2(ONS)(D)]$, $[MoO(ONS)]$ *and* $[MoO(ONS)(D)]$.—The ligands H_2L^1 and H_2L^2 react with $[MoO_2(acac)_2]$ in ethanol or methanol producing apparently polymeric $[MoO_2(ONS)]$ type products, while H_2L^3 or H_2L^4 does not afford polymeric species but monomers with solvent donors, D, $[MoO_2L(MeOH)]$.

Complexes **1a** and **1b** display four strong ν(Mo=O) vibrations spanning the region 945–820 cm^{-1} (Table 1) whereas **1c** and **1d** exhibit only two such bands, one at 940 and the other at 890 cm^{-1} (Table 1). The appearance of four bands one of which is situated around 820 cm^{-1} is considered diagnostic[21] of a Mo $\cdots$ O→Mo moiety whereby the vacant sixth position of the molybdenum co-ordination sphere was considered to initiate axial polymerization leading to the $\cdots$ Mo $\cdots$ O→Mo $\cdots$ O $\cdots$ chain-like structure **C**.[33] Hence, we conclude that **1a** and **1b** have such a structure, and that **1c** and **1d** can be represented by **D**. The possibility of any polymerization *via* phenoxide oxygen as the bridging ligand[21] is ruled out from the fact that the ν(CO) vibration (*ca.* 1557 cm^{-1}) of polymeric $[MoO_2(ONS)]$ complexes **1a** and **1b** remains unaltered in $[MoO_2(ONS)(D)]$ **1c**–**1m**.



C R = H or Me **D** R = Cl or Br

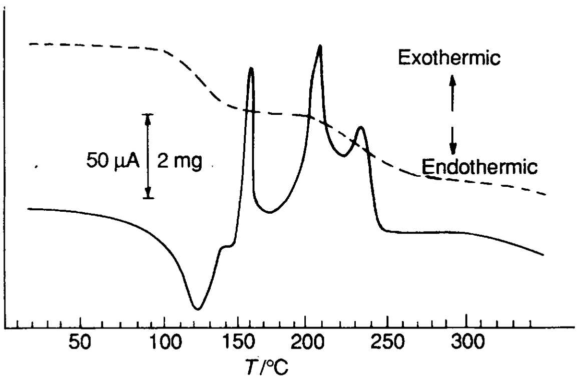


Fig. 1 TGA (– – –) and DTA (——) curves for [MoO(L^1)(dmf)]

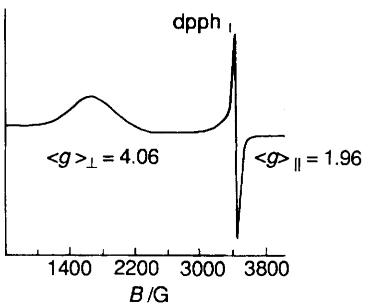


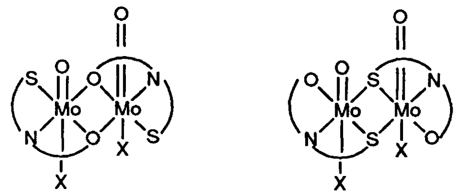
Fig. 2 X-Band EPR spectrum of $[Mo_2O_2Cl_2L^1{}_2]$ in frozen dmf–toluene, G = 10^{-4} T

The variation in reactivity of the L^{2-} ligands with the nature of the substituent R in the salicyl phenyl group is illuminating. In the cases where R = H and the electron-repelling Me group the electron density of the molybdenum centre is reasonably high, leading to a limited overlap between the filled $O_{p\pi}$ orbital of the oxide ligand and the empty $Mo_{d\pi}$ orbitals of the dioxomolybdenum(VI) moiety. This will help the oxide oxygen express its nucleophilicity towards the vacant sixth position of the second molybdenum centre, and so on. Conversely, when R is an electron-withdrawing substituent like Cl and Br the electron density on molybdenum will be too reduced to allow the above phenomenon. The discussion in sections (*a*) and (*b*) clearly indicates that in compounds **1a**–**1m** the ONS ligands span the three meridional positions. However, when **1a** and **1b** react with donor solvents whose nucleophilicity is higher than that of MeOH or EtOH, *viz.* Me_2CO, py, dmf and Me_2SO, $[MoO_2(ONS)(D)]$ type complexes, **1e**–**1j**, are formed whereby the IR band due to Mo⋯O→Mo at 820 cm^{-1} disappears (Table 1). These complexes also undergo ligand (D) substitution reaction of the type $[MoO_2(ONS)(D)] + D' \longrightarrow [MoO_2(ONS)(D')] + D$, where D′ are somewhat stronger ligands than D. {However, for the sake of simplicity, all the complexes as a class, as usual, will be represented by $[MoO_2(ONS)(D)]$}. The IR data (Table 1) suggest that all the D ligands (*viz.* Me_2CO, MeOH, dmf and Me_2SO) are O-co-ordinated to molybdenum. The existence of the D ligand in these complexes has been corroborated by thermoanalytical data. The respective D ligands can be lost endothermically (DTA), and TGA data confirm that the mass loss in each case is compatible with the loss of D ligands. From the decomposition temperatures in each case, a labile binding of D in the solid state can be inferred.

The oxomolybdenum(IV) species, [MoO(ONS)] **2a**–**2d** or [MoO(ONS)(dmf)] **2e**–**2h** are formed when $[MoO_2(ONS)]$ reacts with PPh_3 in methanol–acetonitrile or dmf solvents, respectively, whereby the $MoO_2{}^{2+}$ unit transfers one oxygen atom to PPh_3 converting it into PPh_3O. Obviously complexes **2a**–**2d** are polymeric, but afford only one band in the ν(Mo=O) region at *ca.* 975 cm^{-1} (Table 1) indicating oxo bridging is not occurring. The complexes are soluble only in dmf and Me_2SO whereby in the former case they are converted into the respective monomeric products **2e**–**2h**, and in the latter case reverse oxo transfer from the substrate (Me_2SO) to Mo^{IV}=O occurs, producing **1h** and **1m**. Complexes **2e**–**2h** also show a single ν(Mo=O) vibration at *ca.* 960 cm^{-1} very similar to that of $[MoO(S_2CNEt_2)_2]$.[34] All the complexes **2** are non-electrolytes in dmf and exhibit diamagnetism. Reported Mo^{IV}OL (L = tridentate ligand)[35,36] complexes are also diamagnetic or show feeble temperature-independent paramagnetism.[17] As is also apparent from the earlier work,[35] it is not at present possible to make any comment regarding the mode of polymerization in MoOL (here L = ONS). The IR data (Table 1) provide evidence that the phenoxide oxygen is not involved. To our knowledge complexes **2e**–**2h** constitute possibly the first report of mononuclear five-co-ordinate oxomolybdenum(IV) complexes containing ONS donor ligands. Besides molecular weight data, the mononuclearity and five-co-ordination are also supported by thermoanalytical data. The weight loss calculated from the TGA curve (Fig. 1) corresponds with the loss of one dmf and interestingly both TGA and DTA curves (Fig. 1) indicate that after the endothermic loss of the dmf there is a phase transition (note the exotherm at 150 °C which is not accompanied by any weight loss) which possibly indicates a structural change from a discrete five-co-ordinate to a polymeric entity. Assuming a meridional disposition of the ONS ligand, as in dioxomolybdenum(VI) complexes, a square-pyramidal geometry with a vacant co-ordination site *trans* to the Mo=O bond is a reasonable structure for **2e**–**2h**. This vacant site can then be utilized by the complexes for Me_2SO co-ordination and subsequent facile oxo transfer from the substrate to MoO^{2+}.

The electronic spectra of the molybdenum(VI) complexes **1a**–**1m** display a single low-energy absorption band (*ca.* 425 nm, Table 1) assignable to a $S(p_\pi) \rightarrow Mo(d_\pi)$ ligand to metal charge-transfer (l.m.c.t) transition.[31] The [MoO(ONS)] complexes **2a**–**2d** in degassed dmf solution are essentially the same as the dmf adducts **2e**–**2h** respectively (Table 1) and exhibit two absorption maxima above 400 nm, of which that at 695 nm (ε = 140 dm^3 mol^{-1} cm^{-1}) may represent one of the d–d transitions in the d^2 system; while earlier workers[17] obtained similar two-band spectra, others[34,37,38] obtained a single band in this region.

(*c*) *Complexes* $[Mo_2O_2X_2(ONS)_2]$.—The reaction of the above Schiff bases with $[NH_4]_2[MoOX_5]$ produces dark brown compounds which analysed as [MoOX(ONS)] **3a**–**3d** (see Experimental section). Molecular weight measurements in MeCN–dmf indicate that these apparently five-co-ordinate complexes are dimers. Further support for this is the subnormal magnetic moments of **3a**–**3d** (0.9–1.1) which arises out of direct or super-exchange of the electron spin between the two molybdenum centres. This is substantiated by their EPR spectra in frozen dmf–toluene where the signal due to the double quantum transition ($\Delta m_s = 2$) corresponding to $\langle g \rangle_\parallel = 4.06$ appears besides the prominent $\langle g \rangle_\parallel = 1.96$ line (Fig. 2).



E X = Cl or Br **F**

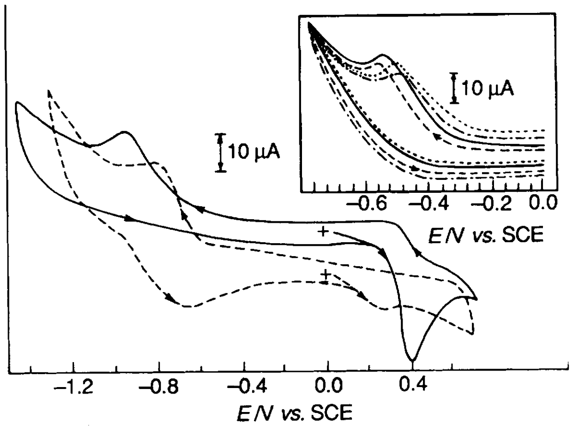


Fig. 3 Cyclic voltammograms for *ca.* 10^{-3} mol dm^{-3} [MoO(L^1)] in dmf (scan rate 50 mV s^{-1}): (*a*) in 0.1 mol dm^{-3} NEt_4ClO_4 (——) and (*b*) in 0.1 mol dm^{-3} NEt_4Cl (– – – –). Inset shows voltammograms of [MoO_2L] complexes [L = L^1 (——), L^2 (– – – –), L^3 (–·–·–), or L^4 (· · · ·)] at a scan rate of 50 mV s^{-1}

Table 3 Cyclic voltammetric[a] and kinetic data for molybdenum(VI) complexes

Complex	E_{pc}/V(n^b)	10^2k_1/dm^3 mol^{-1} s^{-1}	for **1a**
1a	−0.54(0.96);[c] −1.01	(20 °C)	0.602 ± 0.01
1b	−0.56	(25 °C)	0.89 ± 0.02
1c	−0.48	(30 °C)	1.32 ± 0.03
1d	−0.50	(35 °C)	1.87 ± 0.07
1f	−0.55(0.97)[c]		
1g	−0.62	$\Delta H^{\ddagger d}$/kJ mol^{-1}	54.6 ± 1.0
1h	−0.65		
1k	−0.52		
1l	−0.55	$\Delta S^{\ddagger d}$/J K^{-1} mol^{-1}	−102.2 ± 3.0
1m	−0.60		

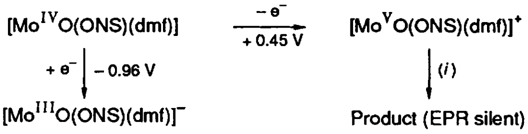
[a] Solvent MeCN, solute concentration *ca.* 10^{-3} mol dm^3, reference electrode SCE. [b] $n = Q/Q'$ where Q' is the calculated coulomb count for a one-electron transfer and Q is the observed value after exhaustive electrolysis of 10^{-3} mol dm^{-3} of solute. [c] Coulometry was done at −0.75 V. [d] Activation parameter pertaining to the kinetic studies involving complex **1a**.

However, no molybdenum or ligand hyperfine lines are exhibited. The IR spectra of the compounds do not show the ν(Mo–O–Mo) vibrations typical for the $Mo_2O_3^{4+}$ moiety.[39] Moreover, a split ν(Mo–Cl) vibration is observed in the IR spectra of **3a** and **3c** and both bands occur in the accepted region (*ca.* 340 cm^{-1}) for a terminal Mo–Cl vibration,[40] which rules out any possible chloride bridging. For the bromo complexes **3b** and **3d** no bands appear in this region, further evidence that for **3a** and **3c** the assignment of terminal ν(Mo–Cl) is authentic. On the other hand, the compounds are non-electrolytes. So their dimerization may involve ligand (ONS) bridging and a possible structure may be represented as **E** or **F**, insofar as the *syn* configuration of the chloride and oxo ligands [two ν(Mo=O) and ν(Mo–Cl) vibrations, see Table 1] are implicated from the IR data. The IR spectra of these compounds may be used to distinguish between the two possible structures **E** and **F**. It has been observed that the phenolic ν(C–O) band of mononuclear molybdenum(VI) complexes of the same ligand occurs at 1557 cm^{-1}. It is known[41] that this band is raised by 20–40 cm^{-1} when the oxygen atoms of the phenolic C–O groups are involved in bridging. The [$Mo_2O_2X_2(ONS)_2$] compounds actually display ν(C–O) at *ca.* 1558 cm^{-1} suggesting that the C–O oxygens are not involved in bridging.[25] Therefore, structure **E** is unlikely and the complexes should possess the thiolato-bridged dimeric structure **F**, as has been proposed for the nickel(II), platinum(II) and palladium(II) complexes.[42–44] This view has been further substantiated by the conspicuous presence of a weak band at 280 cm^{-1} [ν(Mo–S)(bridging)] for these complexes only. The electronic spectral data of the complexes are summarized in Table 1.

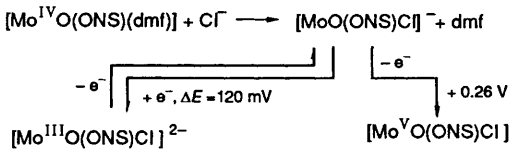
(*d*) *Electrochemistry*.—(*i*) *Molybdenum*(VI) *complexes*. All the dioxomolybdenum(VI) complexes isolated here, in accordance with other such complexes,[17,21,45] show an irreversible metal-centred voltammetric response (Fig. 3) in acetonitrile–0.1 mol dm^3 NEt_4ClO_4 at a platinum electrode in the potential range −0.48 to −0.65 V (*vs.* SCE), indicating that the presence of the sulfur donor in the ligand facilitates reduction of the molybdenum centre. Exhaustive electrolysis at −0.75 V of complexes **1a** and **1f** gives a coulomb consumption commensurate with a one-electron transfer at the metal centre, but the electroreduced solutions ($Mo^{VI} \xrightarrow{e^-} Mo^V$) are EPR silent, possibly due to chemical reaction, *e.g.* dimerisation of the generated oxomolybdenum(V). Interestingly, there is slight dependence of the redox potential on the substituents in the salicyl phenyl moiety of the ligand. The potential data (Table 3) suggest that the substituents helping to build up a greater electron density on the molybdenum centre are least easily reduced and *vice versa*. The very low negative potential for a $MoO_2^{2+} \longrightarrow MoO^{3+}$ system observed here, compared to analogous cases,[11,17,45] may also stem from the ligand donor strength and the extended π system of the metal–ligand ring which are able to weaken the Mo=O π bond in the MoO_2^{2+} unit.

(*ii*) *Molybdenum*(IV) *complexes*. Cyclic voltammetry of the isolated oxomolybdenum(IV) complexes has also been studied using a platinum working electrode and NEt_4ClO_4 or NEt_4Cl as supporting electrolyte. The electron-transfer behaviour of [MoO(ONS)(dmf)] in the presence of 0.1 mol dm^3 NEt_4ClO_4 shows (Fig. 3) an irreversible oxidative response at +0.42 V (*vs.* SCE) and only a feeble reductive response in the reverse sweep at +0.30 V. Constant-potential (+0.62 V) coulometry indicates that the oxidation involves a single electron transfer (n = 0.97), but the oxidized solution is EPR silent. When NEt_4Cl is used as the supporting electrolyte the oxidative response is found at +0.26 V and the reverse sweep does not show any growth of the reductive counterpart (Fig. 3). Here also constant-potential (+0.45 V) coulometry shows a one-electron change (n = 0.98). At the negative potentials a cathodic scan shows a reduction wave at −0.80 V and in the reverse sweep the anodic response is observed at −0.68 V (*vs.* SCE). In NEt_4ClO_4 (no chloride) medium the cathodic peak is shifted to −0.96 V, and the reverse sweep does not show an anodic counterpart as obtained in chloride medium. Thus, in the former (Cl^-) medium a quasi-reversible process (ΔE_p = 120 mV, E° = −0.74 V) occurs while in the latter (NEt_4ClO_4) there is an irreversible one. This difference in electrochemical behaviour can be attributed to the fact that Cl^- ions co-ordinate to the metal centre owing to the co-ordinatively unsaturated nature of the metal in [MoO(ONS)(dmf)]. The above observations are compatible with the electrochemical reactions as shown in Schemes 1 and 2. It may be mentioned that the electrochemical redox course in [MoO(NS_2)] [NS_2 = 2,6-bis(2-mercapto-2,2-diphenylethyl)pyridinate dianion][11] also differs depending on whether or not Cl^- is present in the reaction medium (compare Schemes 1 and 2 with 3 in ref. 11). In our case the chloride substitution is much faster (Scheme 2 as against 3) than in the [MoO(NS_2)].[11] system.

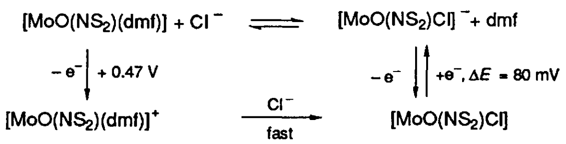
(*iii*) *Molybdenum*(V) *complexes*. Both the chloro complexes



Scheme 1 (*i*) Rapid dimerization



Scheme 2



Scheme 3

Table 4 Cyclic voltammetric data[a] for molybdenum(v) complexes

Complex	E_{pc}/V(n^b)	E_{pa}/V
3a	−0.90, −1.04, −1.48(3.84)[c]	+0.45
3c	−0.88, −1.24, −1.46(3.86)[c]	+0.47

[a] Solvent dmf, solute concentration *ca.* 10^{-3} mol dm^{-3}, reference electrode SCE. [b] For *n* see Table 3. [c] Coulometry was done at −1.66 V.

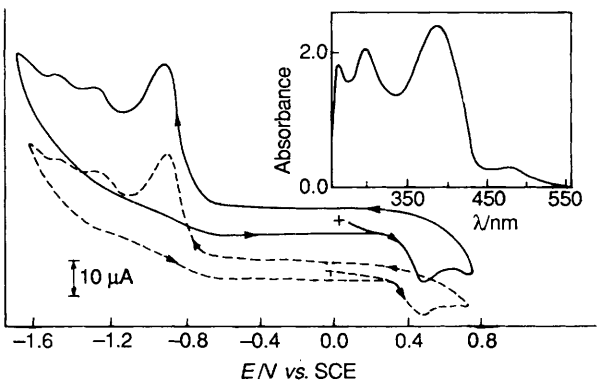
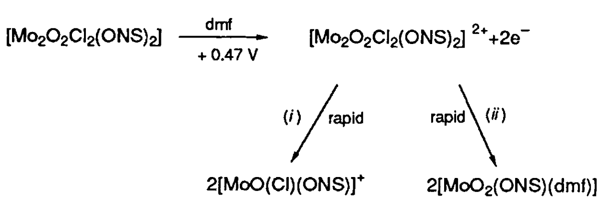


Fig. 4 Cyclic voltammograms for [$Mo_2O_2Cl_2L^4{}_2$] in dmf [scan rates: (*a*) 50 (– – – –), (*b*) 100 mV s^{-1} (——)]. The inset shows the electronic spectrum of the molybdenum(III) compound obtained by coulometric reduction of **3b** in dmf–0.1 mol dm^3 NEt_4ClO_4



Scheme 4 (*i*) Dissociation; (*ii*) hydrolysis due to traces of water or moisture. MoO^{4+} and MoO^+ species are extremely unstable towards hydrolysis by trace water absorption

[$Mo_2O_2Cl_2(ONS)_2$] show an irreversible metal-centred (ligand is electroinactive in this region) one-electron (per molybdenum, coulometry) oxidative response at +0.47 V (*vs.* SCE) (Table 4) as evidenced from their cyclic voltammograms (Fig. 4, in dmf). The electronic spectrum of the coulometrically oxidized solution almost traces the same curve as obtained for [MoO_2(ONS)(dmf)], indicating that the oxidative process can be described as shown in Scheme 4. Accordingly, the electrolytically oxidized solution is EPR silent.

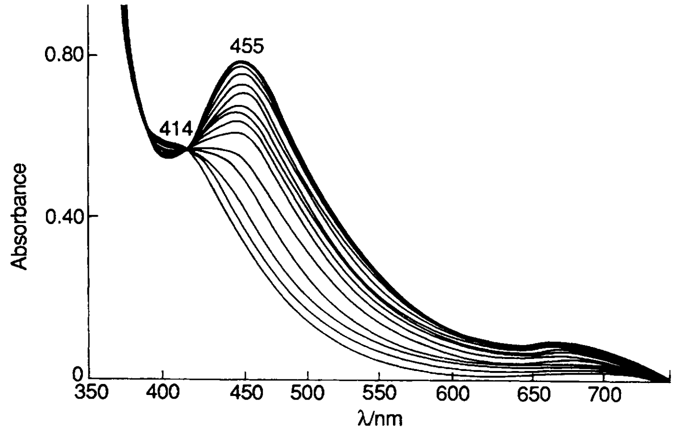


Fig. 5 Spectral changes observed during the reaction of [MoO_2L^1] with PPh_3 at 30 °C. Initial concentrations were 2×10^{-4} and 2×10^{-2} mol dm^{-3}, respectively

Besides the above oxidative responses, three other irreversible reductive responses at −0.88, −1.24 and −1.46 V (*vs.* SCE) are also exhibited by complexes **3a** and **3b**. The first peak (−0.88 V) draws more current (Fig. 4) than the other two and may involve a two-electron step, and the entire process may be described by equations (4)–(6). The total involvement of four electrons has

$$[Mo_2O_2Cl_2(ONS)_2] \xrightarrow{+2e^-} [Mo_2O_2Cl_2(ONS)_2]^{2-} \quad (4)$$

$$[Mo_2O_2Cl_2(ONS)_2]^{2-} \xrightarrow{+e^-} [Mo_2O_2Cl_2(ONS)_2]^{3-} \quad (5)$$

$$[Mo_2O_2Cl_2(ONS)_2]^{3-} \xrightarrow{+e^-} [Mo_2O_2Cl_2(ONS)_2]^{4-} \longrightarrow 2[MoOCl(ONS)]^{2-} \quad (6)$$

been corroborated by exhaustive electrolysis at a potential fixed at −1.65 V. The formulation of the end product as shown in equation (6), which contains Mo^{III}, is supported by the electronic spectrum which shows absorption maxima at 485 and 408 nm (Fig. 4), typical for octahedral oxomolybdenum(III)[36] and assignable to $^4A_{2g} \longrightarrow {}^4T_{2g}$ and $^4A_{2g} \longrightarrow {}^4T_{1g}$ transitions. The other ligand-field band due to the $^4A_{2g} \longrightarrow {}^4T_{1g}(p)$ transition is possibly obscured by the intra-ligand transitions (Fig. 4).

(*e*) *Kinetics: Oxo Transfer from* Mo^{VI} *to Substrate.*—The oxygen-atom transfer from [MoO_2L^1] to the substrate (PPh_3) has been studied spectrophotometrically in dmf solution. We have examined reaction (1), in particular equation (7), using

$$[MoO_2(L^1)(dmf)] + PPh_3 \xrightarrow{k_1} [MoO(L^1)(dmf)] + OPPh_3 \quad (7)$$

PPh_3 as the reducing agent in an effort to identify whether the modification of the ligand structure which gives rise to an easily reducible $MoO_2{}^{2+} \longrightarrow MoO^{3+}$ situation (see above) is also reflected in the rate of oxo-transfer reaction. Pseudo-first-order conditions (large excess of PPh_3 concentration) were used at 20, 25, 30 and 35 °C, monitoring the increase in absorbance at 455 nm. An isosbestic point was found at 414 nm (Fig. 5). The reaction is first order in the concentration of the molybdenum complex: plots of $\ln(A_\infty - A_t)$ *vs.* time are linear to nearly 85% completion of reaction. Plots of k_{obs} *vs.* [PPh_3] afford straight lines with nearly zero intercepts (Fig. 6) and give a second-order rate constant k_1 as shown in Table 3. As for previously reported oxo-transfer reactions from $MoO_2{}^{2+}$ complexes to PPh_3, the reaction follows a simple second-order rate law: $-d[Mo^{VI}O_2(ONS)]/dt = k_1[MoO_2(ONS)][PPh_3]$.

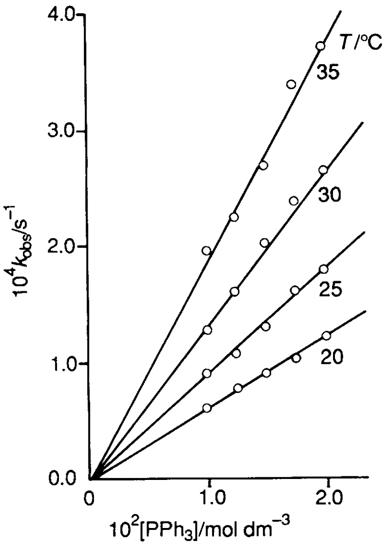


Fig. 6 Plots of k_{obs} *vs.* [PPh_3] for the reaction of [MoO_2L^1(dmf)] with PPh_3 at various temperatures

A comparison with the values of k_1 obtained and compiled by Topich and Lyon[12] shows that the present oxo-transfer reaction of [$MoO_2(L^1)$] with PPh_3 is *ca.* 10^2 times faster than that of other dioxomolybdenum(VI) complexes with ONS and even N_2S_2 donors towards $PEtPh_2$ or PPh_3 substrates, respectively.

(*f*) *Oxo Transfer from Substrate to* Mo^{IV}.—The reaction (2) involving oxygen-atom transfer from the substrate, Me_2SO, to the oxomolybdenum(IV) complexes **2a–2h** has been examined spectrophotometrically in dmf solution. On reaction with Me_2SO the intensity of both bands of these complexes progressively decreases accompanied by the growth of a new band at 425 nm which is complete within 5–10 min, when both the former bands have disappeared. The band at 425 nm is characteristic of the MoO_2^{2+} moiety in the [MoO_2(ONS)(D)] complexes isolated and characterized (see above). These observations clearly suggest[34,46] that an oxygen-atom transfer (8) occurs from Me_2SO* to the MoO^{2+} core.

$$[MoO(ONS)(dmf)] + 2\,Me_2SO \longrightarrow [MoO_2(ONS)(Me_2SO)] + Me_2S \qquad (8)$$

(*g*) *Homogeneous Catalytic Reduction of* Me_2SO *to* Me_2S *by* PPh_3 *using Complex* **1a** *as Catalyst.*—Reaction (9) which

$$PPh_3 + Me_2SO \longrightarrow OPPh_3 + Me_2S \qquad (9)$$

results on coupling reactions (7) and (8) does not reportedly occur even when the reactants are kept for 1 h at 190 °C.[47] However, we find that if [$MoO_2(L^1)$] **1a** is used as a catalyst, practically 100% conversion of Me_2S occurs at room temperature almost instantaneously. The concentration of Me_2S was quantified by precipitating [$(HgCl_2)_3(Me_2S)_2$][14,47] from the reaction medium.

Conclusion

Substituents in the salicyl phenyl ring of the H_2L^1 ligand modify the chemical reactivity of the dioxomolybdenum(VI) complexes to a greater extent than the electrochemical properties. The unprecedented high rate of oxo transfer from [MoO_2(ONS)] to the PPh_3 substrate is traced to the occurrence of an extended π system in the metal–ligand ring followed by a favourable neighbouring-group (SCH_2Ph) participation in preventing μ-oxo-molybdenum(V) dimer formation. Even $MoOX_5^{2-}$ on reaction with the said ligand do not form any $Mo_2O_3^{4+}$ but generate possibly a thiolato-bridged dimer, [$Mo_2O_2X_2(ONS)_2$].

* Actually present much in excess of the reaction stoichiometry, for the reaction to occur so fast.

Acknowledgements

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