The Coordination Chemistry of Molybdenum and Tungsten.
Part XVI. Oxomolybdenum(V) and Oxotungsten(V) Complexes Containing Neutral Monodentate and Anionic Bidentate Schiff Base Ligands

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Reaction of $MoCl_3(THF)_2$ (M = Mo, W) with a series of Schiff base ligands with phenolic, imine and various side chain donors yields complexes of type $[MOCl_3(ligand)_2]$ in which the ligand generally binds as a neutral monodentate imine donor. Electron spin resonance spectra suggest that these complexes have a cis-mer *structure. These complexes are not converted to the bidentate anionic ligand complexes $[MoOCl(L')_2]$ by refluxing in alcohols, but the latter may be prepared from $MoOCl_3(THF)_2$ and the lithium salt of the ligand. The g values for $[MoOCl_3(ligand)]$ (~1.934) significantly change in $[MoOCl(L')_2]$ (~1.945) [1].*

Introduction

The current interest in the structure and functions of molybdenum-containing enzymes [2] has led to considerable work on molybdenum complexes of O-, N- and/or S-donor ligands. We have recently chosen to concentrate on polydentate Schiff bases as ligands because a variety of donor atoms can be introduced into the ligands formed by condensation of substituted aldehydes and substituted amines. We have been particularly interested in high-valent molybdenum and tungsten complexes and have investigated molybdenum(VI) derivatives of bidentate, tridentate and tetradentate Schiff bases [8]. However, for aid in comparing models with metalloenzymes such as xanthine oxidase [4] it is almost essential to use molybdenum(V) derivatives, which provide e.p.r. active centers. Thus, we have earlier reported our studies on potentially tetradentate Schiff bases, H_2L, complexes of oxomolybdenum(V) of type $[MoOCl(L)]$ [5], containing dianionic tetradentate ligands, and $[MoCl_3(H_2L)]$ (M = Mo, W) [6], containing neutral bidentate ligands coordinating through the imine functions; in both of these investigations e.p.r. spectroscopy was found to be of great utility in structure assignment.

In this paper we report the complexes formed by the reaction of $MoCl_3(THF)_2$ (THF = tetrahydrofuran) (M = Mo, W) with a series of bidentate ligands, Fig. 1.

Results and Discussion

The reaction of $MoOCl_3(THF)_2$ or $WOCl_3(THF)_2$ with ligands of types 1.H–3.H yield $MOCl_3(ligand)_2$ complexes containing neutral Schiff base ligands (Table I). These complexes exhibit magnetic moments, μ_{eff} = 1.61–1.76 B.M., consistent with d^1 systems. The infrared spectra exhibit a strong band at 948–975 cm^{-1} consistent with terminal $\nu(M=O)$ and there are several poorly resolved bands in the 350–290 cm^{-1} range assignable to terminal $\nu(M-Cl)$. It is noticeable that $\nu(M=O)$ shifts to higher frequency as the R substitutent changes Et $\approx$ Bu^n < C_6H_{11} < o-ClC_6H_4 < o-MeC_6H_4, suggesting that the metal is becoming a better π-acceptor towards the oxygen in this order. Bands assigned to $\nu(CN)$ of the free ligands are listed in Table II, and it is noticeable that on complexation these bands move to higher energy by *ca.* 20 cm^{-1}, the shift being in general greater in the case of the tungsten complexes than in the molybdenum derivatives. The significance of shifts has been previously discussed by us [6] and others [7] and we conclude that shifts to higher energy accompany the coordination of Schiff base ligands as neutral species *via* the imine nitrogen. The free ligands also exhibit weak broad absorptions at *ca.* 2700 cm^{-1} assignable to hydrogen-bonded OH groups, and on coordination of the azomethine nitrogen this hydrogen-bond system is broken and $\nu(OH)$ then appears at ~3100 cm^{-1}. Some of the complexes crystallize as tetrahydrofuran solvates, and in almost

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TABLE I. Color and Analytical Results of the Complexes.

Complexes	Color	%C[a]	%H[a]	%N[a]	%Cl[a]	%W
$MoOCl_3(1a.H)_2$	dark orange	41.3(41.2)	4.3(4.3)	5.4(5.4)	20.8(20.6)	
$MoOCl_3(1b.H)_2$	gold	46.1(46.1)	5.5(5.2)	4.6(4.9)	19.4(18.6)	
$MoOCl_3(1c.H)_2$	yellow	50.3(50.0)	5.7(5.4)	4.3(4.5)	16.8(17.0)	
$MoOCl_3(1d.H)_2$	orange	51.5(52.4)	4.3(4.1)	3.8(4.4)	16.2(16.6)	
$MoOCl_3(1e.H)_2$	brown	46.1(45.8)	3.1(2.9)	4.0(4.1)	25.6(26.0)	
$MoOCl_3(1f.H)_2$	orange-brown	48.7(48.4)	3.7(3.4)	4.2(4.3)	16.8(16.5)	
$MoOCl_3(1f.H).THF$	mustard	39.8(40.5)	3.9(3.8)	2.9(2.8)	21.7(21.2)	
$MoOCl_3(1g.H)_2$	dark orange	39.5(39.4)	4.2(4.0)	4.8(5.1)	20.8(19.4)	
$MoOCl_3(1j.H)_2$	orange	42.0(41.6)	5.0(4.5)	4.3(4.8)	18.8(18.5)	
$MoOCl_3(1j.H)_2$ ½THF	gold	38.1(38.7)	3.3(2.8)	2.7(2.7)	21.4(21.4)	
$MoOCl_3(2a.H)$	orange-brown	35.0(34.6)	2.4(2.4)	6.4(6.7)	25.0(25.5)	
$MoOCl_3(3.H)$	green-brown	46.3(46.1)	3.3(3.2)	3.6(4.1)	14.9(15.7)	
$MoOCl_3(2b)$½THF	red-brown	36.5(38.8)	2.2(2.9)	6.3(6.0)	22.4(22.7)	
$WOCl_3(1a.H)_2$ ½THF	grey	38.3(37.5)	4.2(4.1)	4.5(4.4)	17.0(16.6)	29.3(28.8)
$WOCl_3(1c.H)_2$	grey	45.0(43.8)	5.2(5.0)	3.9(3.9)	15.0(14.9)	25.2(25.7)
$WOCl_3(1d.H)_2$	green	45.9(46.3)	3.5(3.5)	3.8(3.9)	14.5(14.6)	
$WOCl_3(1e.H)_2$	green	39.6(40.5)	2.7(2.6)	3.5(3.6)	22.6(22.3)	23.8(23.8)
$WOCl_3(1f.H)_2$½THF	green	44.2(43.8)	3.6(3.4)	3.6(3.6)	14.2(13.8)	24.3(24.8)
$WOCl_3(1h.H)_2$½THF	blue-grey	37.7(37.7)	4.4(4.3)	3.6(4.0)	15.0(15.2)	25.8(26.1)
$WOCl_3(1j.H)_2$THF	green	45.6(44.8)	3.9(3.5)	3.3(3.3)	11.7(12.3)	
$WOCl_3(1k.H)_2$½THF	green	30.8(31.0)	2.8(2.6)	5.2(5.2)	19.5(19.7)	34.8(34.1)
$WOCl_3(3.H)_2$	grey	40.2(40.8)	3.2(2.9)	3.1(3.6)	13.4(13.9)	24.2(24.0)
$WOCl_3(2b.H)$THF	blue-grey	32.3(32.2)	2.7(3.0)	5.3(4.7)	16.9(17.9)	29.9(31.0)

[a] Found (Calculated).

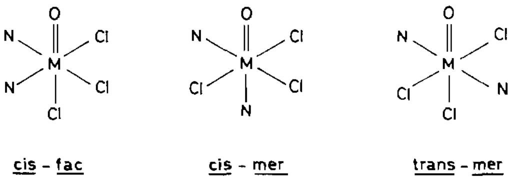
TABLE II. Infrared Spectra in the ν(CN) Region (cm^{-1}) of the $MOCl_3$(ligand)$_2$ Complexes.

Ligand	Free Ligand	Mo Complex	W Complex
1a.H	1632, 1582	1645, 1598	1655, 1602
1b.H	1640, 1585	1660, 1604	
1c.H	1630, 1583	1650, 1600	1655, 1604
1d.H	1620, 1600	1648, 1609	1645, 1605
1e.H	1612, 1590	1628, 1600	1640, 1608
1f.H	1635, 1595	1645, 1610	1645, 1610
1g.H	1655, 1590	1670, 1615	
1h.H	1625, 1595	1630, 1601	1640, 1605
1j.H	1618, 1595	1630, 1605	1630, 1605
1k.H	1612, 1590		1669, 1618

all of these cases the ν_{sym}(COC) and ν_{asym}(COC) vibrations of THF can be identified and occur at almost identical frequencies, 1070 and 910 cm^{-1}, as do these vibrations of the uncoordinated molecule, implying non-coordination of this solvent [8, 9].

The electronic spectra of the complexes are listed in Table III and show a number of ill-defined absorptions in the region, 13,000–24,000 cm^{-1}; the weak low-energy band in the 12,000 to 14,000 cm^{-1} region is assigned to $^2B_2 \rightarrow {}^2E$ in O_h symmetry. There are two intense absorptions at higher energy.

The possible structures for these complexes are:



The molybdenum complexes show adequate solubility in dichloromethane at room temperature and give isotropic esr spectra typical of molybdenum-(V) species (Table IV, Figs. 2, 3). These consist of a central line (^{96}Mo) flanked by six satellites (due to ^{95}Mo and ^{97}Mo hyperfine coupling, I = 5/2). However, with the molybdenum complexes of ligand 3.H, no resolvable superhyperfine coupling was observed. From the frozen solutions at 123 K anisotropic spectra were obtained. The isotropic g values cannot be used to distinguish the *cis- fac*, *cis- mer* and *trans-mer* structures; however the degree of anisotropy

TABLE III. Spectroscopic Data for the Complexes.

Complex	μ_{eff} (B.M.)[a]	ν(M=O) (cm^{-1})	ν(M–Cl) (cm^{-1})	$E_{max} \times 10^{-3}$ cm^{-1} [b]
$MoOCl_3(1a.H)_2$	1.69	950	340sh, 310, 305sh	13.6, 22.5
$MoOCl_3(1b.H)_2$	1.61	958	332sh, 315, 305sh	14.0, 22.5
$MoOCl_3(1c.H)_2$	1.76	959	325sh, 308, 295sh	14.3, 19.8sh, 23.3
$MoOCl_3(1d.H)_2$	1.70	970	332sh, 320, 305sh	13.6, 22.5
$MoOCl_3(1e.H)_2$	1.68	963	340, 325sh	13.2, 19.6sh, 23.1
$MoOCl_3(1f.H)_2$	1.61	948	338, 310, 300sh	13.4, 18.9sh, 22.5
$MoOCl_3(1f.H)THF$	1.56	990	340, 315, 302sh	13.2, 19.8sh, 22.8
$MoOCl_3(1g.H)_2$	1.61	960	345, 320br	14.3, 19.8sh, 23.0
$MoOCl_3(1h.H)_2$	1.50	978	335, 325, 300sh	13.2, 20.0sh, 23.3
$MoOCl_3(1j.H)½THF$	1.64	988	340, 320, 305sh	13.7, 20.0sh, 23.8
$MoOCl_3(2a.H)$	1.57	975	365, 335, 310sh	14.2, 18.2sh, 23.3
$MoOCl_3(3.H)_2$	1.50	965	330, 315sh, 305sh	14.5, 19.2sh, 23.3
$MoOCl_3(2b.H)½THF$	1.56	975	344, 329sh, 315sh	13.7, 19.25sh, 23.3
$WOCl_3(1a.H)_2½THF$	1.56	960	318sh, 308, 290	14.9, 16.9sh, 23.0
$WOCl_3(1c.H)_2$	1.58	960	315sh, 305, 293	12.7, 14.9, 18.7sh, 24.1
$WOCl_3(1d.H)_2$	1.78	974	318sh, 300	14.2, 16.9sh, 23.0
$WOCl_3(1e.H)_2$	1.76	955	325, 296	14.2, 16.9sh, 22.5
$WOCl_3(1e.H)_2½THF$	1.57	965	310sh, 300, 290sh	14.9, 23.0
$WOCl_3(1h.H)_2½THF$	1.61	965	325sh, 310, 300	18.3sh, 24.7
$WOCl_3(1j.H)_2THF$	1.70	972	330sh, 310, 300	14.1, 16.8sh, 23.3
$WOCl_3(1k.H)½THF$	1.60	972	325sh, 308sh, 300	14.1, 16.9sh, 24.1
$WOCl_3(3.H)_2$	1.78	975	330sh, 310, 303sh	14.1, 16.9sh, 23.3
$WOCl_3(2b.H)THF$	1.61	975	330sh, 315, 305sh	12.3, 15.0, 17.1sh, 22.0

[a] ±0.05 B.M. [b] Diffuse reflectance.

TABLE IV. Electron Spin Resonance Data for the Complexes.

Complexes	g_{iso}[a]	10^4 A_{iso} (cm^{-1})[a]	g_1[b]	g_2[b]	g_3[b]
$MoOCl_3(1a.H)_2$	1.945	46	1.945[c]	1.945[c]	1.945[c]
$MoOCl_3(1b.H)_2$	1.940	49			
$MoOCl_3(1c.H)_2$	1.937	50	1.937[c]	1.937[c]	1.937[c]
$MoOCl_3(1d.H)_2$	1.938	48	1.940[c]	1.940[c]	1.940[c]
$MoOCl_3(1e.H)_2$	1.941	51	1.972	1.936	1.918
$MoOCl_3(1f.H)_2$	1.947	50	1.963	1.940	1.940
$MoOCl_3(1f.H)(THF)$	1.943	46	1.954	1.934	1.934
$MoOCl_3(1g.H)_2$	1.941	50	1.952	1.936	1.936
$MoOCl_3(1h.H)_2$	1.940	47	1.940[c]	1.940[c]	1.940[c]
$MoOCl_3(1j.H)½THF$	1.939	49	1.962	1.938	1.919
$MoOCl_3(2a.H)$	1.941	49	1.941[c]	1.941[c]	1.941[c]
$MoOCl_3(4)$	1.941	49	1.951	1.937	1.920
$MoOCl_3(3.H)_2$	1.961	45[d]	1.983	1.951	1.951
$MoOCl_3(2b.H)½THF$	1.943	47	1.964	1.944	1.925
$WOCl_3(1a.H)_2½THF$	1.73		1.75	1.73	1.70
$WOCl_3(1c.H)_2$	1.72		1.75	1.72	1.69
$WOCl_3(1d.H)_2$	1.73		1.77	1.72	1.72

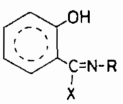
(continued overleaf)

TABLE IV. *(continued)*

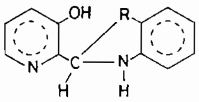
Complexes	g_{iso}^{a}	10^4 A_{iso} (cm^{-1})^a	g_1^{b}	g_2^{b}	g_3^{b}
$WOCl_3(1e.H)_2$	1.71		1.77	1.72	1.68
$WOCl_3(1f.H)_2$½THF	1.73		1.77	1.71	1.71
$WOCl_3(1h.H)_2$½THF	1.71		1.74	1.72	1.66
$WOCl_3(1j.H)$THF	1.72		1.76	1.72	1.68
$WOCl_3(1k.H)$½THF	1.72		1.76	1.72	1.69
$WOCl_3(3H)_2$	1.73	e	1.75	1.72	1.72
$WOCl_3(2b.H)_2$THF	1.76		1.79	1.75	1.75

^{a}In dichloromethane solution at 298 K. ^{b}As solid solutions in dichloromethane at 123 K. ^{c}Very broad. ^{d}s(1:2:3:3:2:1); (A, ^{14}N) = 2, >1 G. ^{e}s(1:2:3:3:2:1); (A, ^{14}) N = 10, >3 G; (A, ^{1}H) = 20, 10 G.

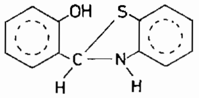
Fig. 1. Ligands used in this study.



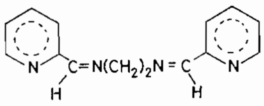
X	R	
X = H	R = CH_2CH_3	1a.H
X = H	R = CH_2CH_2OH	1.g.H
X = H	R = $(CH_2)_3CH_3$	1b.H
X = CH_3	R = CH_2CH_2OH	1h.H
X = H	R = o-C_6H_4OH	1.f.H
X = H	R = C_6H_{11}	1c.H
X = H	R = o-$C_6H_4CH_3$	1d.H
X = H	R = o-C_6H_4Cl	1e.H
X = H	R = C_5H_4N	1k.H
X = H	R = o-C_6H_4COOH	1j.H



(R=O) 2a.H
(R=S) 2b.H



3.H



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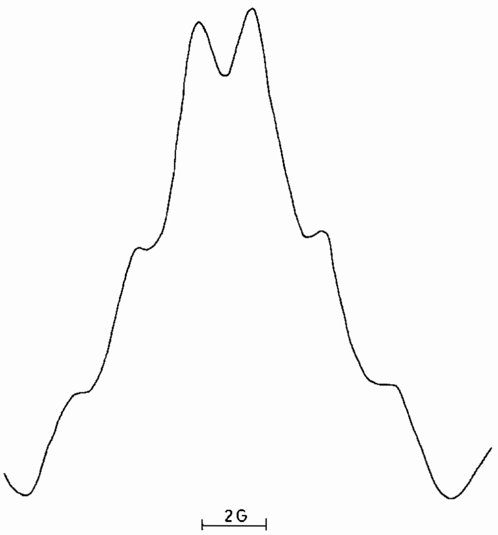


Fig. 2. Double derivative ESR spectrum of $MoOCl_3(3.H)_2$ in CH_2Cl_2 at 25 °C.

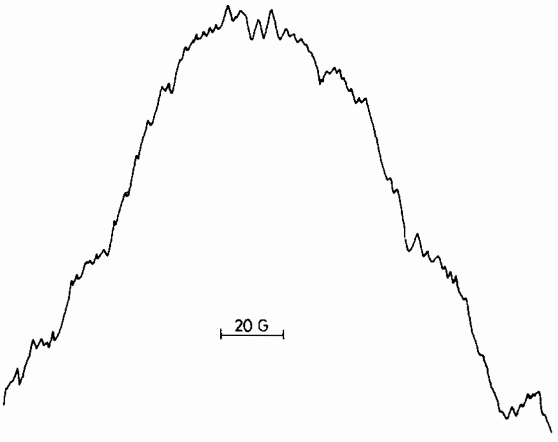


Fig. 3. Double derivative ESR spectrum of $WOCl_3$ $(3.H)_2$ in CH_2Cl_2 at 25 °C.

favors the less symmetrical *cis- mer* structure rather than the other two possibilities.

It has also been possible to isolate some 1:1 adducts of these Schiff base ligands with $MoOCl_3(THF)_2$. These complexes, $MoOCl_3$(ligand) (ligand = 1.f.H, 1j.H) are probably pentacoordinate. There is

TABLE V. Color and Analytical Results for Some $MoOCl(L)_2$ Complexes.

Complex	Color	Analytical Results Fd(calc)			
		C	H	N	Cl
$MoOCl_3(1b)_2$	dark wine	51.9(52.8)	5.9(5.6)	5.2(5.6)	8.0(7.1)
$MoOCl_3(1a)_2$	wine	47.8(48.7)	4.7(4.5)	5.7(6.3)	8.5(8.0)
$MoOCl_3(1d)_2$	brown	58.7(59.2)	4.4(4.2)	4.7(4.9)	7.0(6.3)
$MoOCl_3(1e)_2$	brown	51.3(50.7)	3.3(3.0)	3.9(4.6)	172(17.5)

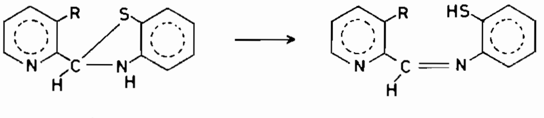
TABLE VI. Infrared and ESR Spectra of Some $MoOCl(L)_2$ Complexes.

Complex	Infrared Spectra (cm^{-1})	$g_{iso}^{e.s.r.}$	A_{iso} 10^4 cm^{-1}
$MoOCl_3(1b)_2$	1610, 1555, 940, 760, 305	1.945	
$MoOCl_3(1a)_2$	1605, 1600, 936, 755, 308	1.945	
$MoOCl_3(1d)_2$	1602, 1583, 932, 760, 312	1.945	
$MoOCl_3(1e)_2$	1608, 1585, 950, 760, 310	1.946	(A = 50)

ν(C=N) $\cong$ 1605 cm^{-1}, ν(C–C) $\cong$ 1595 cm^{-1}, ν(M=O) $\cong$ 940 cm^{-1}, ν(disubstituted benzene ring) $\cong$ 760 cm^{-1}, ν(M–Cl) $\cong$ 310 cm^{-1}.

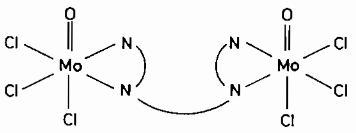
no evidence in the infrared spectra for either Mo–O–Mo or Mo–Cl–Mo bridging, but it is noticeable that the ν(M=O) absorption occur at *ca.* 1000 cm^{-1} (Table III). This shift to much higher energy as compared with the bis(ligand) complexes is consistent with pentacoordination, *cf.* ν(Mo=O) at 1008 cm^{-1} in $MoOCl_3(SPPh_3)$, which is known to be five-coordinate [10]. These are likely to be further examples of this coordination number of molybdenum(V) complexes. In contrast, however, it would seem that the tungsten complex $WOCl_3$ (1k.H) is hexacoordinate, as evidenced by the appearance of bands at 1600 cm^{-1} indicative of coordinated pyridine [11] and the fact that ν(W=O) occurs at relatively low energy (Table III). This appears to be the only complex of a type 1 ligand which gives evidence for the side chain (R) participation in coordination; the other side chain groups *e.g.* $-CO_2H$, or –OH do not appear to coordinate.

Ligands of type 2.H and 3.H exist in the thiazolyl form and show no evidence for ν(SH) or ν(C=N), but do exhibit ν(NH) and absorptions in the 970–910 cm^{-1} due to the C–S–C linkage. On coordination there is no evidence for a ligand rearrangement of type:



as no ν(C=N) band appears and the C–S–C linkage appears to be intact. This is surprising in view of our earlier results with such ligands [5]. Moreover, there is a further anomaly in the reactivity of ligands of type 2.H and 3.H. The latter complexes to both metal salts to yield $MoCl_3(3.H)_2$, but ligands of type 2.H give only the $MOCl_3$ (2.H) stoichiometry. The ESR spectra of $MOCl_3(3.H)_2$ are most useful in assigning structures to these complexes. The spectra of both complexes exhibit a 1:2:3:3:2:1 sextet, clearly indicating superhyperfine coupling to two inequivalent N–H groups, thus pointing strongly to the *cis-mer* structure involving only N-coordination, (Figs. 2, 3). The $MOCl_3(2b.H)$•nTHF complexes show no evidence for pyridine coordination, but the ν(M=O) frequencies are not high enough for pentacoordination to be assigned. Although there is not any evidence for THF coordination it is possible for an octahedral structure, in which uncoordinated solvent merely blocks a coordination position, to be present.

The molybdenum complex of ligand 2a.H, $MoOCl_3(2a.H)$, appears to be six-coordinate, and ligand 4 forms complexes with a molybdenum: ligand ratio of 2:1. It is most likely that this complex has a structure similar to



The $MoOCl_3(L.H)_2$ complexes are not converted to $MoOCl(L)_2$ complexes upon refluxing in n-butanol

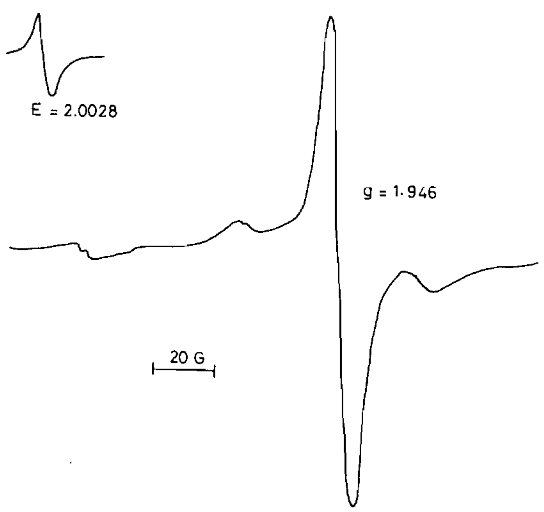


Fig. 4. ESR spectrum of $MoOCl(1e)_2$ in CH_2Cl_2 at 25 °C.

for two or more hours [5]. These latter complexes were isolated, however, when prepared from a Schiff base lithium salt and $MoOCl_3(THF)_2$ in ethanol, (Table V). The ν(Mo=O) vibrations are observed at approximately 940 cm^{-1}, lower than for the $MoOCl_3(L.H)_2$ species and this appears to be characteristic of bonding of the ligands as anions [6], (Table VI). A single ν(Mo–Cl) absorption was observed at 300–315 cm^{-1} and the ν(CN) absorption was shifted to lower frequency by ~20 cm^{-1}. These molybdenum complexes had adequate solubility in dichloromethane at room temperature to obtain ESR spectra, and give isotropic ESR spectra typical of Mo(V), but no resolvable superhyperfine coupling was observed. A significant change is observed in the g-value on going from the neutral to anionic ligand (1.934 → 1.945 respectively). A typical $MoOCl(L)_2$ ESR spectrum is shown in Fig. 4.

Experimental

Drying of Solvents

Tetrahydrofuran (THF)

THF (BDH reagent grade) was dried by refluxing with freshly extruded sodium wire and benzophenone (Aldrich Chemical Co.) under a dry dinitrogen atmosphere until a blue colour (sodium benzophenone ketyl) was attained, indicating that the solvent was dry. It was freshly distilled, using a take-off head, as required.

Toluene

Toluene (Fisons analar) was dried by refluxing with sodium and benzophenone (Aldrich Chemical Co.) under a dry dinitrogen atmosphere until the mixture attained a blue/green colour (sodium benzophenone ketyl) indicating that the solvent was dry. It was then distilled using a take-off head and stored over fresh, degassed 4A molecular sieves until required.

Dichloromethane

Dichloromethane (BDH analytical grade) was dried by distillation over P_2O_5, on to fresh, degassed 4A molecular sieves and used as required.

Ethanol

Ethanol (BDH reagent grade) was dried by initially storing over CaO for 72 hours. It was then decanted and refluxed over 5 g magnesium turnings and 0.1 g iodine, under a dry dinitrogen atmosphere and distilled as required.

Cyclohexane

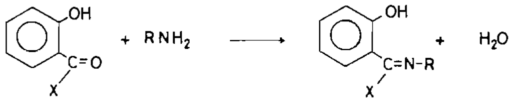
Cyclohexane (BDH reagent grade) was dried over freshly extruded sodium wire.

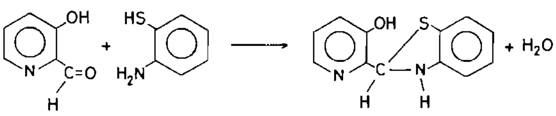
n-Pentane

n-Pentane (Fisons analar) was dried by storing over freshly degassed molecular sieves for a minimum period of one week.

Preparation of Schiff Base Ligands

The Schiff base ligands were prepared by the condensation reaction between the relevant amine or diamine and the relevant aldehyde. The reactions were generally carried out on a 0.1 molar scale, the product being recrystallised from ethanol and washed with n-pentane or diethyl ether. All reagents were purchased from the Aldrich Chemical Co. Some examples are shown below.





Preparation of $MOCl_3(THF)_2$ [8, 12]

To approx. 20 g (7.3 × 10^{-2} mol) molybdenum pentachloride (Climax Molybdenum Co.) or 25–30 g (6.3–7.6 × 10^{-2} mol) tungsten hexachloride (Research Inorganic Chemicals) in a dry flask under a dry dinitrogen atmosphere, approx. 130 cm^3 dry cyclohexane were added. The mixture was then stirred until the solid dissolved. 50 cm^3 freshly distilled THF were then added slowly by means of a pressure equalisation dropping funnel. A vigorous exothermic reaction was observed to occur and the mixture was allowed to cool under a dry dinitrogen atmosphere. After approx. one hour green crystals (M = Mo) or a blue solid (M = W) was deposited. The product was filtered using Schlenk apparatus and dried *in vacuo* after having been washed with cyclohexane (4 × 10 cm^3) and dry n-pentane (3 × 10 cm^3). The product was stored under a sealed dry dinitrogen atmosphere.

Preparation of $MOCl_3(HL)_2$ Complexes: (M = Mo, W; HL = neutral Schiff base ligand)

The complexes of general formula $MOCl_3(HL)_2$ were prepared by the reaction of stoichiometric quantities of the relevant Schiff base with $MOCl_3(THF)_2$.

To 50 cm^3 of a 1:1 mixture of dry dichloromethane and toluene 0.004 mol (0.002 for the diimine) of the relevant Schiff base were added and the mixture stirred until the ligand dissolved. 0.004 mol (M = Mo, 1.4 g; M = W, 1.7 g) of $MOCl_3(THF)_2$ were then added with vigorous stirring, under a dry dinitrogen atmosphere until the product was precipitated (usually after 30 min). The product was then filtered using Schlenk apparatus, washed with 1:1 dichloromethane/toluene (2 × 10 cm^3) and diethyl ether (1 × 10 cm^3) and dried *in vacuo*. The yield was generally in the order of 90%.

Preparation of $MoOCl(L)_2$ Complexes; (L = anionic Schiff base ligand)

Complexes of general formula $MoOCl(L^-)_2$ were prepared by the method reported by Weissenhorn [13] from $MoOCl_3(THF)_2$ and the anionic Schiff base ligand in the form of the lithium salt.

To 50 cm^3 of dry ethanol 0.004 mol of the lithium salt of the relevant Schiff base were added and the mixture stirred. 0.004 mol (1.4 g) of $MoOCl_3(THF)_2$ were then added and the mixture refluxed under a dry dinitrogen atmosphere for 2 hours. When the reaction was complete the mixture was allowed to cool, the product was then filtered using Schlenk apparatus, washed with dry n-pentane (2 × 10 cm^3) and dry diethyl ether (2 × 10 cm^3) and dried *in vacuo*. The yield was generally in the order of 85–90%.

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