The Chemistry of Molybdenum and Tungsten. Part 7.[1] Oxomolybdenum(V) and Oxotungsten(V) Complexes of Neutral Aromatic Schiff-base Ligands

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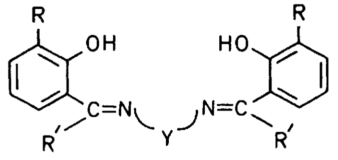
A series of oxomolybdenum(V) and oxotungsten(V) complexes of potentially quadridentate (N_2O_2 donor set) and quinquedentate (N_3O_2 donor set) Schiff-base ligands, $[MOCl_3(H_2L)]$ (M = Mo or W), has been prepared in which the ligands bind only *via* the imine nitrogens, acting as neutral N_2 donors in contrast to the usual binding of these ligands as dianionic N_2O_2 or N_3O_2 species. With small chelate backbones between the imine groups the resulting $[MOCl_3(H_2L)]$ complexes appear to be monomeric, and whilst i.r. spectra do not enable a choice to be made between *mer* and *fac* structures we have employed e.s.r. results, notably using a series of specially synthesised model complexes, to deduce that these complexes have a *mer* configuration. With long chelate backbones (six carbon atoms) between the imine groups it is suggested that the $[MOCl_3(H_2L)]$ complexes are dimeric and contain at least two isomeric forms. The molybdenum(V) complexes exhibit $g_{iso.}$ values in the range 1.934—1.945 and the tungsten(V) complexes in the range 1.72—1.80.

THE complexes of Schiff-base ligands of type (1) with many of the later transition metals have been studied in some detail,[2,3] the vast majority of the complexes containing the ligands in the dianionic form co-ordinated as quadridentate (N_2O_2) chelates. The reaction with early transition-metal ions have been less studied, although recent work has involved titanium-(III) and -(IV),[4] oxovanadium(IV),[5] dioxomolybdenum(VI),[6] oxomolybdenum(V),[1] oxotungsten(VI),[7] and molybdenum(IV).[8] Co-ordination of Schiff bases as neutral ligands is quite rare and only a few examples have been characterised. These include $[TiCl_3(thf)(1a)]$ (thf = tetrahydrofuran),[4] $[WO_2Cl_2(HL)_2]$ [HL = o-$C_6H_4(OH)CH{=}NR$],[9] $[FeCl_3(HL)_2]$,[10] and $SnCl_4(HL)_2$.[11] In our previous study[1] the reaction of $[MoOCl_3(thf)_2]$ with several ligands of type (1) (H_2L) in absolute ethanol was found to yield a mixture of $[MoOCl_3(H_2L)]$ and $[MoOCl_2(HL)]$ which were not separated, whilst $[MoOCl(L)]$ containing the dianionic quadridentate L were obtained using Li_2L, H_2L in the presence of NEt_3, or $(Me_3Si)_2L$.



	R	R'	Y		R	R'	Y
(1a)	H	H	$[CH_2]_2$	(1i)	MeO	H	$[CH_2]_3$
(1b)	H	H	$[CH_2]_3$	(1j)	MeO	H	o-C_6H_4
(1c)	H	H	$[CH_2]_6$	(1k)	H	Me	$[CH_2]_2$
(1d)	H	H	o-C_6H_4	(1l)	H	Me	$[CH_2]_3$
(1e)	H	H	o-C_6H_3Me-4	(1m)	H	Me	$CH(Me)CH_2$
(1f)	H	H	o-$C_6H_2Me_2$-4,5				
(1g)	H	H	$CH(Me)CH_2$	(2a)	H	H	$[CH_2]_2NH[CH_2]_2$
(1h)	MeO	H	$[CH_2]_2$	(2b)	H	Me	$[CH_2]_2NH[CH_2]_2$

Here we report the synthesis and some properties of a series of $[MOCl_3(H_2L)]$ [M = Mo or W; H_2L = ligand of type (1)]. In addition to providing a considerable number of examples of the neutral Schiff base acting as a bidentate ligand, these complexes undergo a wide range of metathetical reactions and reactions with base to form $[MOCl(L)]$ species, which will be discussed in a future publication. The current interest in the structure and functions of molybdenum-containing enzymes[12] has led to the study of a range of molybdenum complexes of *O*-, *N*-, and/or *S*-donors, and the complexes reported here and the range of reactions they undergo make them attractive systems for studying the effect of varying the environment of the metal on the spectroscopic (especially e.s.r.) properties.

RESULTS AND DISCUSSION

The reaction of Schiff bases of type (1) (H_2L) with $[MoOCl_3(thf)_2]$ in toluene–dichloromethane yields the microcrystalline yellow-brown $[MoOCl_3(H_2L)]$ (Table 1). These complexes constitute the largest group of metal derivatives of neutral Schiff bases yet prepared. Their ready isolation is predominantly due to their insolubility

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[5] K. S. Patel and J. C. Bailar, *J. Co-ordination Chem.*, 1973, **3**, 113.

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[8] A. Van den Bergen, K. S. Murray, and B. O. West, *Austral. J. Chem.*, 1975, **25**, 105.

[9] K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta*, 1974, **11**, 223.

[10] A. Van den Bergen, R. J. Cozens, and K. S. Murray, *J. Chem. Soc.* (*A*), 1970, 3060.

[11] A. Van den Bergen, K. S. Murray, M. J. O'Connor, N. Rehak, and B. O. West, *Austral. J. Chem.*, 1968, **21**, 1505.

[12] See, for example, F. L. Bowden in 'Techniques and Topics in Bioinorganic Chemistry,' ed. C. A. McAuliffe, Macmillan, London, 1975, p. 207; L. G. Ljungdahl, *Trends in Biochem. Sc.*, 1976, **1**, 63.

in this solvent mixture, and once isolated the complexes appear to be indefinitely stable in sealed tubes; after 3 months no hydrogen chloride was detectable. However, as previously reported,[1] in polar solvents such as ethanol partial conversion into [$MOCl_2(HL)$] and [MOCl(L)] occurs, and the [$MOCl_3(H_2L)$] are converted into [MOCl(L)] (M = Mo or W) by treatment with sodium methoxide.[13] The [$MoOCl_3(H_2L)$] complexes were occasionally, and the [$WOCl_3(H_2L)$] usually, obtained as tetrahydrofuran solvates (Table 1), but the complexity of the i.r. spectra of the Schiff-base ligands makes it difficult to determine from such spectra whether the

TABLE 1

Physical properties and analytical and spectroscopic data for the molybdenum and tungsten complexes

Complex	Colour	Analysis (%) [a]				$\mu_{eff.}$ [b]/ B.M.	$E_{max.}$ [c]/10^3 cm^{-1}	I.r. bands (cm^{-1})	
		C	H	N	Cl			(M=O)	(M–Cl)
[$MoOCl_3$(1a)]	Mustard-brown	40.9 (39.5)	3.9 (3.3)	5.0 (5.8)	20.0 (21.6)	1.63	13.3, 19.3 (sh), 24.2br	960	330, 315, 310 (sh)
[$MoOCl_3$(1a)]·thf	Mustard-brown	43.4 (43.0)	4.0 (4.4)	5.6 (5.0)	18.7 (19.1)	1.63	13.3, 19.3 (sh), 24.3br	960	330, 315, 310 (sh)
[MoOCl(1b)]·thf	Mustard	44.2 (44.0)	4.4 (4.5)	4.9 (4.8)	18.0 (18.6)	1.66	13.4, 19.6 (sh), 25.0	958	330, 311, 303 (sh)
[$MoOCl_3$(1c)]·thf	Mustard-yellow	46.3 (46.3)	4.7 (5.2)	4.6 (4.5)	17.1 (17.0)	1.64	13.5, 19.8 (sh), 24.0	958	330, 310
[$MoOCl_3$(1d)]	Orange-brown	43.2 (44.9)	3.0 (3.0)	4.8 (5.2)	21.7 (19.9)	1.60	13.0, 17.4 (sh), 24.0	967	320, 312, 300
[$MoOCl_3$(1e)]	Orange-brown	46.1 (45.9)	3.4 (3.3)	5.0 (5.1)	19.7 (19.4)	1.71	13.1, 17.2 (sh), 23.0	964	346 (sh), 321, 304
[$MoOCl_3$(1f)]	Orange-brown	45.9 (46.9)	3.6 (3.6)	4.8 (4.9)	18.6 (18.9)	1.72	13.1, 17.1 (sh), 23.2	972	338, 312, 300
[$MoOCl_3$(1h)]	Mustard-brown	38.5 (39.4)	3.7 (3.7)	4.5 (5.1)	17.9 (18.2)	1.64	14.1, 19.0 (sh), 25.0	945	355, 340, 310
[$MoOCl_3$(1i)]	Mustard-brown	41.5 (40.7)	4.2 (3.9)	4.6 (4.9)	18.4 (19.0)	1.69	14.2, 18.5 (sh), 22.2	948	350 (sh), 341, 310
[$MoOCl_3$(1j)]	Orange-brown	43.7 (44.4)	3.6 (3.5)	4.7 (4.7)	18.7 (17.9)	1.65	13.0, 18.6, 23.0	955	342 (sh), 325, 315
[MoOCl(1k)]	Mustard	42.1 (42.0)	4.2 (3.9)	4.9 (5.4)	20.5 (20.7)	1.70	13.5, 20.0 (sh), 24.4	960	327, 315, 290 (sh)
[$MoOCl_3$(1l)]	Mustard-yellow	44.4 (43.2)	4.5 (4.2)	4.9 (5.3)	19.4 (19.1)	1.67	13.5, 23.8	973	324, 305, 283
[$MoOCl_3$(1m)]	Mustard-yellow	43.0 (43.2)	4.4 (4.2)	4.9 (5.3)	19.4 (19.1)	1.63	13.2, 20.0 (sh), 25.0	960	324, 283
[$MoOCl_3$(2a)]·thf	Brown	44.3 (44.6)	4.7 (4.7)	7.7 (7.1)	17.3 (17.0)	1.62	13.7, 18.8 (sh), 26.0	940	320, 300 (sh)
[$MoOCl_3(PhCH{=}NCH_2CH_2N{=}CHPh)$]	Brown	42.5 (42.2)	3.7 (3.5)	5.8 (6.2)	23.2 (23.3)	1.48		960	350, 330, 315
[$MoOCl_3$(1g)]·0.25thf	Mustard-brown	41.5 (41.6)	3.9 (4.0)	5.9 (5.4)	19.5 (20.0)	1.59		970	345, 305
[$MoOCl_3$(2b)]	Brown	44.9 (45.1)	5.2 (5.0)	6.4 (7.1)	17.2 (18.1)	1.62		965	318, 302 (sh)
[$WOCl_3$(1a)]·thf	Turquoise	35.2 (36.5)	3.6 (3.4)	4.5 (4.6)	15.9 (16.4)	1.40	13.6, 16.5 (sh), 26.1	960	315, 302, 290
[$WOCl_3$(1b)]·thf	Blue	36.7 (38.4)	3.5 (3.9)	4.4 (4.3)	16.3 (16.1)	1.60	12.9, 17.3 (sh), 26.2	965	320, 305, 295
[$WOCl_3$(1c)]·0.5thf	Blue-green	35.6 (39.6)	4.0 (4.2)	3.7 (4.2)	15.7 (15.9)	1.53	12.2, 16.7 (sh), 25.6	963	320, 300, 295 (sh)
[$WOCl_3$(1d)]·thf	Blue	40.5 (41.3)	3.2 (3.4)	4.2 (4.0)	14.1 (15.3)	1.52	13.4, 16.7 (sh), 23.8, 25.6 (sh)	970	320, 303, 290 (sh)
[$WOCl_3$(1e)]·thf	Green	41.7 (42.4)	3.3 (3.6)	4.0 (3.9)	14.8 (15.0)	1.50	12.2, 15.4 (sh), 23.3, 25.4 (sh)	955	315, 300, 290 (sh)
[$WOCl_3$(1h)]·thf	Green	35.7 (37.3)	3.9 (3.8)	3.8 (3.9)	14.1 (15.0)	1.54	13.0, 17.1, 23.8, 25.4	945	320 (sh), 305
[$WOCl_3$(1i)]·thf	Blue-green	38.7 (38.3)	3.8 (4.1)	3.4 (3.9)	14.2 (14.8)	1.57	12.7, 16.5 (sh), 26.0	950	325, 305, 295 (sh)
[$WOCl_3$(1j)]·thf	Green	39.3 (38.9)	3.3 (3.7)	3.7 (4.1)	14.0 (14.1)	1.56	13.2, 16.7, 23.4	955	320, 300, 290 (sh)
[$WOCl_3$(1k)]	Blue	35.4 (35.9)	3.7 (3.3)	4.4 (4.7)	16.9 (17.7)	1.59	12.3, 16.9, 25.3	965	330, 303, 290
[$WOCl_3$(1h)]·thf	Blue	38.7 (39.7)	4.0 (4.3)	4.3 (4.1)	15.2 (15.8)	1.60	12.4 (sh), 16.7, 25.7	970	310, 305, 295 (sh)
[$WOCl_3$(2a)]·thf	Green	37.3 (38.0)	4.2 (4.4)	6.5 (6.1)	14.0 (15.7)	1.63	12.4 (sh), 16.3, 24.7	955	320, 300, 295 (sh)
[$WOCl_3$(1m)]·thf	Blue	39.7 (40.0)	4.1 (4.3)	4.1 (4.1)	14.8 (15.8)	1.59	12.7, 16.3, 24.6, 26.0	967	318, 310, 298 (sh)
[$WOCl_3$(2b)]	Blue-green	38.6 (39.1)	4.1 (3.9)	6.7 (6.5)	16.4 (16.5)	1.49	12.4, 15.6, 26.0	945	320, 300, 295 (sh)

[a] Calculated values are given in parentheses. [b] ±0.05 B.M.: [c] Diffuse reflectance.

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[13] W. Levason, C. A. McAuliffe, F. P. McCullough, and C. A. Rice, unpublished work.

thf is co-ordinated or merely in the lattice. In the cases where the ν_{sym}(COC) and ν_{asym}(COC) vibrations of the thf could be identified they were found to be very little shifted from the frequencies in the free ether, suggesting that the thf is unco-ordinated since co-ordination shifts these vibrations to lower frequencies.[14] In support of this conclusion several of the complexes were obtained in both solvated and unsolvated forms {one example, [$MoOCl_3$(1a)], is included in Table 1} and, apart from the i.r. spectral absorptions attributable to thf, the spectral and magnetic properties of the two forms are identical.

The [$MoCl_3(H_2L)$] complexes hydrolyse rapidly in air, give acidic solutions in polar solvents, and dissolve only very slightly in solvents such as thf or dichloromethane. This lack of solubility in any solvent in which reaction did not occur precluded solution measurements except for e.s.r. All the complexes have magnetic moments consistent with one unpaired electron per metal atom, the values lying in the ranges *ca.* 1.6—1.7 (Mo) and *ca.* 1.5—1.6 B.M. (W).* The reflectance spectra of the solids consist of a number of ill defined absorptions; a weak low-energy band at 12 000—14 000 cm^{-1} is tentatively assigned as $^2B_2 \rightarrow {}^2E$ in O_h symmetry. There is an intense absorption at *ca.* 20 000 cm^{-1} and an ill defined shoulder at lower energy.

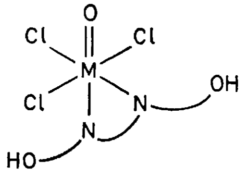
Infrared Spectra.—All the complexes exhibit one strong ν(M=O) vibration at 945—970 cm^{-1}, at 10—20 cm^{-1} to higher frequency than in the corresponding [MOCl(L)] complexes containing the dianionic form of the Schiff bases.[1,13] Several of these complexes also exhibit moderately strong ligand absorptions in the same region, but in no case did we observe more than one ν(M=O) vibration, suggesting that only one structural isomer is present. No absorptions appeared at lower frequency attributable to M–O–M bridges. The far-i.r. spectra also exhibit strong incompletely resolved absorptions at 280—350 cm^{-1} assignable to ν(M–Cl), but it is not possible to distinguish between a *mer* and *fac* arrangement of chlorines on the basis of these spectra.

There is much confusion in the literature about the assignment of the i.r. spectra of Schiff-base ligands and their metal complexes, due both to the complexity of the spectra and the extensive vibrational coupling present. Previous empirical assignments have attributed absorptions in the 'double-bond' region of the spectrum to various combinations of ν(CN), ν(CC), and ν(CO).[6,11,15] A recent study [16] of ^{15}N-labelled *N*-arylsalicylideneimines and their metal complexes assigned the three vibrations observed in the range 1 550—1 660 cm^{-1} to ν(CN), ν(CC), and ν(CN); however, all are extensively coupled. The higher-frequency ν(CN) vibration is particularly diagnostic of the mode of co-ordination of the ligands; when co-ordinated as anionic ligands through both O and N atoms, the ν(CN) vibration shifts to lower frequency by 20 cm^{-1},[6-9,15,16] whilst co-ordination as neutral species through the N atom only shifts this band to higher frequency.[4,15] The free ligands also exhibit weak broad absorptions at *ca.* 2 700 cm^{-1} assignable to hydrogen-bonded OH groups, and on co-ordination of the azomethine nitrogens only the hydrogen bonding is broken and a broad ν(OH) band appears in the spectra of the complexes at 3 050—3 100 cm^{-1}.[4,15] The [$MOCl_3(H_2L)$] complexes (Table 2) all show ν(CN) vibrations shifted to higher frequency by *ca.* 20 cm^{-1} and ν(OH) at *ca.* 3 050 cm^{-1} consistent with co-ordination through the azomethine nitrogens. In order to confirm this assignment we synthesised the Schiff base $PhCH{=}NCH_2CH_2N{=}CHPh$ and from it prepared [$MoOCl_3(PhCH{=}NCH_2CH_2N{=}CHPh)$]. This ligand can only co-ordinate through the nitrogen atoms, and as expected it exhibits a shift in ν(CN) to higher frequency on co-ordination. The very similar i.r. spectra of this complex and [$MOCl_3(H_2L)$] clearly point to the same mode of co-ordination of the ligands and rule out the possibility of co-ordination through the oxygen with the Schiff bases in the keto–amine tautomeric form.[9,17] Thus, we conclude that the [$MOCl_3(H_2L)$] complexes have either structures (I) or (II).

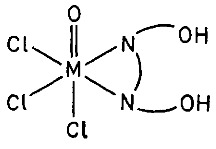
TABLE 2

Infrared spectra (cm^{-1}), ν(C=N) region

	Free ligand	Mo complex	W complex
(1a)	1 630, 1 575	1 650, 1 605	1 650, 1 605
(1b)	1 632, 1 575	1 655, 1 602	1 655, 1 602
(1d)	1 610, 1 560	1 635, 1 606	1 635, 1 606
(1c)	1 630, 1 578	1 655, 1 600	1 655, 1 600
(1e)	1 615, 1 560	1 622, 1 593	1 635, 1 606
(1f)	1 610, 1 560	1 625, 1 602	
(1h)	1 625, 1 576	1 655, 1 600	1 655, 1 600
(1i)	1 625, 1 580	1 658, 1 608	1 635, 1 608
(1j)	1 610, 1 575	1 630, 1 605	1 660, 1 605
(1k)	1 605, 1 575	1 630, 1 600	1 625, 1 600
(1l)	1 610, 1 570	1 625, 1 600	1 630, 1 600
(1m)	1 605, 1 757	1 635, 1 590	1 630, 1 600
$PhCH{=}NCH_2CH_2N{-}{=}CHPh$	1 645, 1 580	1 668, 1 595	
(2a)	1 630, 1 580	1 650, 1 605	1 650, 1 600
(2b)	1 610, 1 575		1 655, 1 602
(1g)	1 630, 1 582	1 680 (sh), 1 675 1 618, 1 608	



(I)



(II)

The distinction between these two structures on the basis of i.r. spectra is difficult, although the variations in ν(M=O) are more consistent with (I) and could be due to the different electronic properties of the *trans*-azomethine nitrogen. It is not likely that either of these structures obtains for the complexes of (1c) where the C_6 linkage

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* Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

[14] D. W. A. Fowles, D. A. Rice, and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3119.

[15] V. A. Kogan, O. A. Dripov, V. I. Minkin, and V. P. Sodolov, *Russ. J. Inorg. Chem.*, 1965, **10**, 45.

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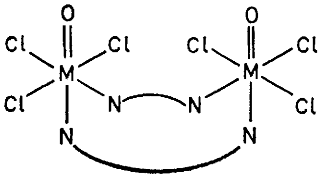
[17] L. Randaccio, *J. Organometallic Chem.*, 1973, **55**, C58.

between the nitrogen donors (and hence the unlikely formation of a necessarily nine-membered chelate ring) makes it more probable that the ligand functions as a bridging bidentate, as in (III) or (IV).

The ligands of type (2) which contain an extra potential donor in the secondary amino-nitrogen also formed [$MOCl_3(H_2L)$] complexes, the i.r. spectra of which exhibit similar shifts in the ν(CN) frequency on co-ordination as observed with type (1) ligands, consistent with co-ordination through the azomethine nitrogens as neutral ligands. In addition to ν(OH) frequencies at *ca.* 3 100 cm^{-1}, the i.r. spectra of the complexes also show broad absorptions at *ca.* 3 300 cm^{-1}, which we tentatively assign to ν(NH) [since such absorptions are not present in complexes of ligands of type (1)], and this is also evidence for the secondary amino-nitrogen being unco-ordinated.[18] On this evidence we tentatively propose a six-co-ordinate dimeric structure similar to that formed by (1c), *i.e.* (III) or (IV).


(III)

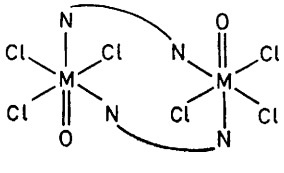

(IV)

TABLE 3

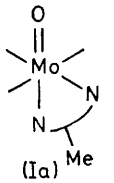
E.s.r. data for the complexes

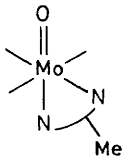
Ligand H_2L	[$MoOCl_3(H_2L)$] $g_{iso.}$ [a]	$10^4A_{iso.}$ [a]/cm^{-1}	g_1 [b]	g_2 [b]	g_3 [b]	[$WOCl_3(H_2L)$] $g_{iso.}$ [a]	g_1 [b]	g_2 [b]	g_3 [b]
(1a)	1.940	51	1.960	1.942	1.922	1.77	1.79	1.79	1.72
(1d)	1.936	47	1.961	1.937	1.918	1.79	1.82	1.80	1.76
(1b)	1.946	45	1.963	1.939	1.939	1.75	1.81	1.73	1.73
(1c)	1.945, 1.936 [c]	46	1.963	1.940	1.940	1.72	1.75	1.73	1.68
(1e)	1.942, 1.937 [c]	50	1.960	1.933	1.933	1.72	1.76	1.73	1.68
(1f)	1.937	44	1.953	1.942	1.930				
(1h)	1.945	48	1.961	1.944	1.925	1.80	1.84	1.82	1.74
(1i)						1.80	1.85	1.81	1.73
(1j)	1.940	49	1.955	1.940	1.913	1.79	1.82	1.80	1.76
(1k)	1.934	46	1.947	1.936	1.927	1.71	1.75	1.73	1.69
(1l)	1.935	50	1.936	1.936	1.936	1.72	1.75	1.73	1.68
(1m)	1.941, 1.935	53	1.959	1.934	1.934	1.71	1.75	1.71	1.67
$PhCH{=}NCH_2CH_2N{=}CHPh$	1.940	49	1.970	1.940	1.920				
(2a)	1.941		1.941	1.941	1.941				
(2b)	1.941		1.941	1.941	1.941			*d*	
(1g)	1.960, 1.944 [c]		1.945 [e]	1.945 [e]	1.945 [e]			*d*	

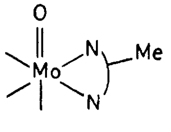
[a] In dichloromethane solution at 298 K. [b] As solid solutions in dichloromethane at 123 K. [c] Two approximately equal peaks at 298 K. [d] No signal observed. [e] Very broad.

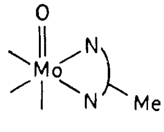
E.S.R. Spectra.—The molybdenum complexes showed adequate solubility in dichloromethane at room temperature and give isotropic e.s.r. spectra, typical of Mo^V, consisting of a central line (^{96}Mo) flanked by six satellites (due to ^{95}Mo and ^{97}Mo hyperfine coupling, $I = \frac{5}{2}$). No resolvable superhyperfine coupling was observed. From the frozen solutions at 123 K, anisotropic spectra were obtained. The e.s.r. parameters are summarised in Table 3.

The isotropic *g* values cannot be used to distinguish between structures (I) and (II). However, the degree of anisotropy of the frozen solutions favours the less-symmetrical structure (I) rather than (II). Complexes of type (1) ligands with symmetrical chelate backbones are expected to give one e.s.r. signal for each of the structures (I) and (II). The observation that there is only one signal is consistent with there being only one of the two possible isomers present. In the cases of complexes with type (1a) ligands with unsymmetrical backbones [(1e), (1g), or (1m)] two isomeric forms of both structures (I) and (II) are possible, *viz.* (Ia), (Ib), (IIa), and (IIb). Isomers (IIa) and (IIb) are related by a mirror plane of symmetry and are therefore not expected to be e.s.r. distinguishable. Only with the unsymmetrical type (1) ligands do complexes provide two e.s.r. signals. It can be argued that these are due to the presence of a mixture of structures (I) and (II). However, complexes of symmetrical ligands give only one signal. There is no apparent reason on steric or electronic grounds why the symmetrical ligands such as (1d) or (1f) should be present only as structure (I) or (II) while the unsymmetrical ligand (1e) should give a mixture of both (I) and (II). Therefore, on the basis of the e.s.r. evidence, we assign structure (I) to the com-


(Ia)


(Ib)


(IIa)


(IIb)

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[18] R. T. Conley, 'Infrared Spectroscopy,' 2nd edn., Allyn and Bacon, Boston, Massachusetts, 1970.

plexes of the symmetrical and unsymmetrical ligands. In the case of the unsymmetrical ligands we are seeing approximately equimolar quantities of (Ia) and (Ib).

The molybdenum complex of (1c) affords two overlapping signals, which is consistent with a mixture of ligand-bridging dimers such as (III) and (IV).

EXPERIMENTAL

Physical measurements * were made as described previously.[1] The Schiff-base ligands were prepared by condensation of the appropriate substituted benzaldehyde and diamine or triamine,[2] and were characterised by elemental analysis and i.r. and mass-spectral measurements. The complexes were prepared by the same general method from trichloro-oxobis(tetrahydrofuran)molybdenum(v) [19] or trichloro-oxobis(tetrahydrofuran)tungsten(v).[20] All the manipulations were conducted under a dry dinitrogen atmosphere using standard Schlenk-tube and dry-box techniques in predried solvents. The following preparation is typical.

Trichloro[NN'-ethylenebis(salicylideneimine)]oxomolybdenum(v).—A dichloromethane solution (100 cm^3) of (Ia) (5.0 mmol) was treated dropwise with vigorous stirring with a solution of [$MoOCl_3(thf)_2$] (5.0 mmol) in dichloromethane–toluene (1 : 1, 50 cm^3). After 1 h the solid was filtered off, washed with dichloromethane–toluene (1 : 1, 20 cm^3), and dried *in vacuo*, yield 95%. The product was stored in a sealed ampoule under dry dinitrogen to prevent hydrolysis.

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* In a number of cases the tungsten complexes failed to yield reproducible carbon analyses, a problem observed by other workers [A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652], and in these cases we relied on H, N, and Cl analyses and sought additional confirmation by spectroscopic methods.

[19] K. Feenan and G. W. A. Fowles, *Inorg. Chem.*, 1965, **4**, 310.
[20] G. W. A. Fowles and J. L. Frost, *J. Chem. Soc.* (*A*), 1967, 671.