

Formation of and Equilibria between some Five- and Six-co-ordinate Chloro-oxomolybdenum(v) Complexes in Dichloromethane

By P. Michael Boorman, C. David Garner, and Frank E. Mabbs,* The Chemistry Department, University of Manchester, Manchester M13 9PL

The equilibria $[\text{MoOCl}_3\text{L}_2] \rightleftharpoons [\text{MoOCl}_3\text{L}] + \text{L}$ in CH_2Cl_2 solution at 25 °C have been studied by e.s.r. spectroscopy. When $\text{L} = \text{Ph}_3\text{PO}$, $(\text{Me}_2\text{N})_3\text{PO}$, or thf , no $[\text{MoOCl}_3\text{L}]$ species have been detected, whereas when $\text{L} = \text{Ph}_3\text{PS}$, $(\text{Me}_2\text{N})_2\text{CS}$, or Me_2S , $[\text{MoOCl}_3\text{L}]$ predominates. The new complexes $[\text{MoOCl}_3\text{L}]$ [$\text{L} = \text{Ph}_3\text{PS}$, $(\text{Me}_2\text{N})_2\text{CS}$, Ph_3PSe , or Ph_3PO] and $[\text{MoOCl}_3\{\text{SC}(\text{NMe}_2)_2\}_2]$ have been isolated. Similarly the equilibria $[\text{MoOCl}_4]^- + \text{L}^{n-} \rightleftharpoons [\text{MoOCl}_4\text{L}]^{(n+)-}$ have been studied [$\text{L} = \text{Ph}_3\text{PO}$, $(\text{Me}_2\text{N})\text{PO}$, py , Et_3N , thf , H_2O , Ph_3PS , and $(\text{Me}_2\text{N})_2\text{CS}$, $n = 0$; $\text{L} = \text{Cl}^-$, $n = 1$]. When $\text{L} = (\text{Me}_2\text{N})_3\text{PO}$ only $[\text{MoOCl}_4\text{L}]^-$ has been detected. With the other neutral donors the order of ability to form $[\text{MoOCl}_4\text{L}]^-$ is $\text{py} > \text{Ph}_3\text{PO} \approx \text{H}_2\text{O} \gg \text{thf} \gg \text{Et}_3\text{N}$, whereas no six-co-ordinate species have been detected for $\text{L} = \text{Ph}_3\text{PS}$ or $(\text{Me}_2\text{N})_2\text{CS}$. With $\text{L} = \text{Cl}^-$ the degree of formation of $[\text{MoOCl}_5]^{2-}$ is low and dependent on both the nature of the cation and total molybdenum concentration. By comparison of the results in CH_2Cl_2 , it is concluded that the molybdenum(v) species formed on dissolving $[\text{Et}_3\text{N}]_2[\text{MoOCl}_5]$ or MoOCl_5 in concentrated aqueous HCl is $[\text{MoOCl}_4(\text{OH}_2)]^-$ and not $[\text{MoOCl}_5]^{2-}$ as is generally supposed.

STRUCTURAL studies¹ on a number of six-co-ordinate oxomolybdenum(v) complexes have shown that there is a significant lengthening of the molybdenum–ligand distance *trans* to the oxo-group compared with the corresponding distance when the ligand is in the *cis* position. This lengthening is interpreted as a *trans*-weakening effect caused by the oxo-group, which might be expected to facilitate the formation of five-co-ordinate species. However, there is only one instance in which it is established that a five-co-ordinate monomeric species exists in the solid state, *i.e.* $[\text{MoOCl}_3(\text{SPPPh}_3)]$.² A number of

suggest such five-co-ordinate species as intermediates in the reaction sequences. In view of the potential importance of co-ordinatively unsaturated species in both inorganic and biological redox systems, we report the results of e.s.r. and other studies of the equilibria between some five- and six-co-ordinate oxomolybdenum(v) species in dichloromethane solution.

EXPERIMENTAL

Preparation of Complexes.—*Trichloro-oxomolybdenum(v)*. This was prepared by converting resublimed MoCl_5 into

TABLE I
Analytical data (%) for complexes not previously reported

Complex	Found							Calc.						
	Mo	C	H	N	Cl	S	P	Mo	C	H	N	Cl	S	P
$[\text{MoOCl}_3(\text{SPPPh}_3)]$	18.6	41.6	3.0		21.2		6.0	18.8	42.2	2.9		20.9		6.1
$[\text{MoOCl}_3(\text{SePPh}_3)]$	17.4	36.9	2.9		20.6		5.3	17.2	38.6	2.7		19.1		5.6
$[\text{MoOCl}_3\{\text{SC}(\text{NMe}_2)_2\}_2]$	27.3	17.1	3.3	7.8	29.8	9.6		27.4	17.1	3.4	7.9	30.3	9.1	
$[\text{MoOCl}_3(\text{OPPh}_3)]$	19.1	43.3	3.3		22.1			19.4	43.5	3.0		21.5		
$[\text{MoOCl}_3\{\text{SC}(\text{NMe}_2)_2\}_2]$	20.0	25.3	4.8	11.3	22.2			19.9	24.9	5.0	11.6	22.1		
$[\text{Ph}_4\text{As}][\text{MoOCl}_4]$	15.1	45.6	3.3		23.5			15.1	45.2	3.1		22.3		
$[\text{Ph}_4\text{As}][\text{MoOCl}_4(\text{OH}_2)]$	14.9	43.6	3.2		22.0			14.7	44.0	3.4		21.7		
$[\text{Ph}_4\text{As}]_2[\text{MoOCl}_5] \cdot 2\text{CH}_2\text{Cl}_2$	7.9	48.8	3.4		25.8			7.8	48.9	3.6		26.1		

molybdenum(v) species are known which from their stoichiometry would appear to be five-co-ordinate and monomeric, $[\text{MoOCl}_3(\text{SR}_2)]$,³ $[\text{MoOCl}_4]^-$,⁴ $[\text{MoOBr}_4]^-$,⁴ and $[\text{MoO}(\text{CN})_4]^-$,⁵ although they have usually been considered to have six-co-ordinate polymeric structures in the solid state.⁶ However, it seems possible that in solutions of poorly co-ordinating solvents they may exist as discrete five-co-ordinate monomeric species. Kinetic studies of the substitution⁷ and redox⁸ reactions of complexes such as $[\text{MoOCl}_3\text{X}_2]^{n-}$ in dichloromethane

MoOCl_4 which was then treated with excess of chlorobenzene.⁹ The product was filtered off under dry nitrogen, washed rapidly with dry benzene followed by dry hexane, and finally pumped dry.

Monoadducts of trichloro-oxomolybdenum(v), $[\text{MoOCl}_3\text{L}]$ [$\text{L} = \text{Ph}_3\text{PS}$, Ph_3PSe , Ph_3PO , and $(\text{Me}_2\text{N})_2\text{CS}$]. These were prepared as described below for Ph_3PS . When $\text{L} = (\text{Me}_2\text{N})_3\text{PO}$ or Me_2S only solutions in dichloromethane were prepared. MoOCl_3 (2.2 g) and Ph_3PS (4.42 g) were dissolved in dry CH_2Cl_2 (*ca.* 25 cm³) and the solution filtered.

² P. M. Boorman, C. D. Garner, F. E. Mabbs, and T. J. King, *J.C.S. Chem. Comm.*, 1974, 663.

³ E. Feenan and G. W. A. Fowles, *Inorg. Chem.*, 1965, **4**, 310.

⁴ P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103 and refs. therein.

⁵ J. Selbin, *J. Chem. Educ.*, 1964, **41**, 86.

⁶ J. F. Allen and H. M. Neumann, *Inorg. Chem.*, 1964, **3**, 1612; R. A. Walton, *Progr. Inorg. Chem.*, 1972, **16**, 1.

⁷ C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J.C.S. Dalton*, 1975, 1175.

⁸ C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J.C.S. Dalton*, 1975, 1180.

⁹ R. Colton, I. B. Tomkins, and P. W. Wilson, *Austral. J. Chem.*, 1964, **17**, 496; R. Colton and I. B. Tomkins, *ibid.*, 1965, **18**, 447.

¹ A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Amer. Chem. Soc.*, 1964, **86**, 3024; F. A. Cotton and S. M. Moorhouse, *Inorg. Chem.*, 1966, **4**, 1377; J. G. Scane, *Acta Cryst.*, 1967, **23**, 85; J. R. Knox and C. K. Prout, *ibid.*, 1969, **B25**, 2281, 1857; R. M. Wing and K. P. Callahan, *Inorg. Chem.*, 1969, **8**, 2303; M. G. B. Drew and A. Kay, *J. Chem. Soc. (A)*, 1971, 1846, 1851; L. T. J. Delbaere and C. K. Prout, *Chem. Comm.*, 1971, 162; B. Spivak and Z. Dori, *J.C.S. Dalton*, 1973, 1173; L. Ricard, J. Estienne, P. Karagiannides, P. Toledano, J. Fischer, A. Mitschler, and R. Weiss, *J. Co-ordination Chem.*, in the press; L. O. Atovmyan, O. A. D'yachenko, and E. B. Lobkovskii, *Zhur. strukt. Khim.*, 1970, **11**, 469 and refs. therein.

The filtrate was stored overnight in a stoppered flask under nitrogen yielding dark green crystals (1.5 g) which were filtered off and sucked dry. Analytical data are given in Table 1. *Trichlorobis(tetramethylthiourea)oxomolybdenum(v)* was prepared as above using a 1:2 ratio of MoOCl_3 : $(\text{Me}_2\text{N})_2\text{CS}$.

TABLE 2

Conductance measurements in CH_2Cl_2 at 25 °C.
The conductance of CH_2Cl_2 is $2.6 \times 10^{-7} \text{ S}^{-1} \text{ cm}^{-1}$

Compound	Concentration mol l^{-1}	Conductance $\mu\text{S cm}^{-1}$	Molar conductance $(\lambda/S \text{ cm}^2 \text{ mol}^{-1})$
[Et ₄ N]Cl	1.00×10^{-2}	66.0	6.6
	1.00×10^{-3}	15.5	15.5
	1.00×10^{-4}	4.0	40.0
[Ph ₄ As]Cl	1.00×10^{-2}	358.0	35.8
	1.00×10^{-3}	58.7	58.7
	1.00×10^{-4}	8.9	89.3
[Ph ₄ As][MoOCl ₄]	5.00×10^{-3}	187.0	37.4
	1.00×10^{-3}	55.7	55.7
[Et ₄ N][MoOCl ₄]	5.00×10^{-3}	106.0	21.2
	1.00×10^{-3}	34.8	34.8
[MoOCl ₃ (SPPPh ₃)]	1.00×10^{-3}	3.2	3.2

Diadducts of trichloro-oxomolybdenum(v), $[\text{MoOCl}_3\text{L}_2]$
[L = tetrahydrofuran¹⁰ (thf), Ph₃PO, and $(\text{Me}_2\text{N})_3\text{PO}$ ¹¹].

TABLE 3

Room-temperature e.s.r. data for pure complexes dissolved in CH_2Cl_2 and $\nu(\text{MoO})$ stretching frequencies from Nujol-mull i.r. spectra

Dissolved complex (A)	$\nu(\text{MoO})/\text{cm}^{-1}$	g	Other species detected	
			(B)	g
[MoOCl ₃ (SPPPh ₃)]	1 008	1.957	[MoOCl ₄] ⁻	ca. 1.950
[MoOCl ₃ (SePPh ₃)]	990	1.959	b	a
[MoOCl ₃ {SC(NMe ₂) ₂ }]	1 000	1.959	b	
[MoOCl ₃ (OPPh ₃)]	1 000 ^c	1.944	[MoOCl ₄] ⁻	1.953
			[MoOCl ₃ (OPPh ₃) ₂]	1.937
			d	1.927
			b	≥50
[MoOCl ₃ {OP(NMe ₂) ₃ }] ^e		1.942	[MoOCl ₃ (SMc ₂) ₂]	ca. 1.957
[MoOCl ₃ (SMc ₂)] ^e		1.953	b	Trace
[Ph ₄ As][MoOCl ₄]	1 015	1.951	[MoOCl ₄] ⁻	1.951
[Ph ₄ As][MoOCl ₄ (OH ₂)]	985	ca. 1.945	[MoOCl ₄] ⁻	1.953
[Et ₄ N][MoOCl ₄ (OH ₂)]	992	ca. 1.947	[MoOCl ₄] ⁻	1.952
[Et ₄ N][MoOCl ₄ (OPPh ₃)]	973	1.943	[MoOCl ₄] ⁻	1.952
[Et ₄ N][MoOCl ₄ {OP(NMe ₂) ₃ }]	970	1.943	b	
[Ph ₄ As] ₂ [MoOCl ₄]	950	1.940	[MoOCl ₄] ⁻	1.952
[Et ₄ N] ₂ [MoOCl ₄]	950	1.940	[MoOCl ₄] ⁻	1.952
[MoOCl ₃ {SC(NMe ₂) ₂ } ₂]	952	ca. 1.954	[MoOCl ₃ {SC(NMe ₂) ₂ }]	1.959
[MoOCl ₃ (OPPh ₃) ₂]	974	1.935	d	1.928
[MoOCl ₃ {OP(NMe ₂) ₃ } ₂]	967	1.934	b	ca. 0.04
[MoOCl ₃ (thf) ₂]	985	1.942	b	ca. 30

^a Not estimated. ^b Not detected. ^c This refers to $[\text{MoOCl}_3(\text{OPPh}_3)]$ precipitated very rapidly from solution. When the complex was allowed to form slowly, this band was replaced by a broad one at ca. 800 cm^{-1} , which we take to indicate polymer formation. ^d Unknown. ^e These measurements refer to a 1:1 solution of MoOCl_3 and ligand in CH_2Cl_2 .

These were prepared by previously reported methods and were found to analyse satisfactorily.

Tetraethylammonium or tetraphenylarsonium tetrachloro-oxomolybdate(v). These were prepared by dissolving $[\text{MoOCl}_3(\text{SPPPh}_3)]$ in a minimum volume of dried CH_2Cl_2 and adding an equimolar quantity of dried $[\text{Et}_4\text{N}]\text{Cl}$ or $[\text{Ph}_4\text{As}]\text{Cl}$ and allowing the solution to crystallise under dry nitrogen.

Tetraethylammonium or tetraphenylarsonium pentachloro-oxomolybdate(v). These were prepared as for the corres-

ponding $[\text{MoOCl}_4]^-$ salts using a four-fold excess of the appropriate chloride salt.

Tetraethylammonium or tetraphenylarsonium aquatetrachloro-oxomolybdate(v). These were prepared as for the $[\text{MoOCl}_4]^-$ salts using undried reagents.

Tetraethylammonium salts of tetrachloro-oxo(triphenylphosphine oxide)molybdate(v) and tetrachloro-oxo[tris(dimethylamino)phosphine oxide]molybdate(v). These were prepared by published methods¹² and had satisfactory analyses.

Dichloromethane was dried over P_2O_5 , distilled on to CaH_2 , fractionally distilled, and finally stored over degassed 4A molecular sieves under dry nitrogen. All solutions for e.s.r. and conductance measurements were prepared in a dry-box under dry nitrogen.

Conductivity measurements were made with an Industrial Instruments Inc. model RC-18 conductance bridge using a platinum-electrode cell thermostatted at 25 ± 1 °C. The results are given in Table 2. E.s.r. measurements were made on CH_2Cl_2 solutions at Q-band frequencies as previously described.¹³ The results for solutions of pure complexes are given in Table 3 and those for various reaction mixtures in Table 4. Since the peak-to-peak widths of the first-derivative spectra were the same to within experimental error, the relative concentrations of the species were assumed to be proportional to the amplitudes of the spectra. I.r. spectra were recorded on Nujol mulls using a Perkin-Elmer

257 spectrophotometer calibrated with a polystyrene film. The main interest in these measurements was the frequency of the band attributable to the Mo-O stretching vibration and these data are given in Table 3.

RESULTS AND DISCUSSION

Equilibria involving oxomolybdenum(v) species in aqueous solution of type (I) have previously been studied¹⁴ by observing the change in e.s.r. spectra as the

¹³ C. D. Garner, P. Lambert, F. E. Mabbs, and J. K. Porter, *J.C.S. Dalton*, 1972, 320.

¹⁴ I. N. Marov, Yu. N. Dubrov, V. K. Belyaeva, A. N. Ermakov, and D. I. Ryabchikov, *Russ. J. Inorg. Chem.*, 1966, **11**, 1311; I. N. Marov, V. K. Belyaeva, Y. N. Dubrov, and A. N. Ermakov, *ibid.*, 1969, **14**, 2640; 1972, **17**, 2968, and refs. therein.

¹⁰ K. Feenan and G. W. A. Fowles, *Inorg. Chem.*, 1965, **4**, 310.

¹¹ S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, 1962, **1**, 122; C. M. French and J. H. Garside, *J. Chem. Soc.*, 1962, 2006.

¹² C. D. Garner, F. E. Mabbs, and V. I. Routledge, unpublished work.

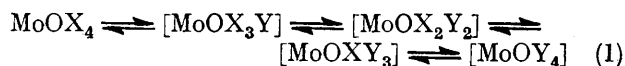
TABLE 4

Room-temperature e.s.r. data and relative concentrations for some reactions in CH₂Cl₂

Reaction A + B \rightleftharpoons C + D	[B] : [A]	[Mo] _T / mol l ⁻¹	g		Obs. ^a [C] : [A]
			A	C	
[MoOCl ₃ (SPPPh ₃) + MeCN \rightleftharpoons [MoOCl ₃ (NCMe) ₂] + Ph ₃ PS	2.4 6.0 10.0 20.0	0.00159 0.00159 0.00159 0.00159	1.957	1.944	0.21 (∞) 0.66 (∞) 1.41 (∞) 4.17 (∞)
[MoOCl ₃ (SPPPh ₃) + thf \rightleftharpoons [MoOCl ₃ (thf) ₂] + Ph ₃ PS	0.43 0.86 1.29 3.25 6.50 19.50	0.0020 0.0020 0.0020 0.0020 0.0020 0.0020	1.959	1.942	<0.01 (0.28) <0.01 (0.76) 0.04 (1.86) 1.02 (∞) <i>b</i> <i>b</i>
[MoOCl ₃ (OPPh ₃) + [Ph ₄ As]Cl \rightleftharpoons [Ph ₄ As][MoOCl ₄] + [MoOCl ₃ (OPPh ₃)]	0.5	0.0077		1.951 ^c	<i>c</i>
[MoOCl ₃ (OPPh ₃) + [Ph ₄ As]Cl \rightleftharpoons [MoOCl ₄] ⁻ + [MoOCl ₄ (OPPh ₃)] ⁻	1.0	0.0077		1.951 ^d	<i>d</i>
[Ph ₄ As][MoOCl ₄] + (Me ₂ N) ₃ PO \rightleftharpoons [MoOCl ₄ {OP(NMe ₂) ₃ }] ⁻ + [MoOCl ₃ {OP(NMe ₂) ₃ } ₂]	20.0	0.00256		1.943 ^e	<i>e</i>
[Ph ₄ As][MoOCl ₄] + Ph ₃ PO \rightleftharpoons [MoOCl ₄ (OPPh ₃)] ⁻ + [MoOCl ₃ (OPPh ₃) ₂]	40.0	0.00135		1.944 ^f	<i>f</i>
[Ph ₄ As][MoOCl ₄] + Ph ₃ PO \rightleftharpoons [Ph ₄ As][MoOCl ₄ (OPPh ₃)]	0.75 0.50 0.25 0.75 0.50 0.25	0.00295 0.00295 0.00295 0.00153 0.00153 0.00153	1.952	1.944	0.67 (3.0) 0.55 (1.0) 0.17 (0.33) 0.48 (3.0) 0.28 (1.0) 0.11 (0.33)
[Ph ₄ As][MoOCl ₄] + (Me ₂ N) ₃ PO \rightleftharpoons [Ph ₄ As][MoOCl ₄ {OP(NMe ₂) ₃ }]	0.75 0.50 0.25 0.75 0.50 0.25	0.00295 0.00295 0.00295 0.00153 0.00153 0.00153	1.952	1.944	3.04 (3.0) 1.01 (1.0) 0.37 (0.33) 3.03 (3.0) 1.16 (1.0) 0.31 (0.33)
[Ph ₄ As][MoOCl ₄] + py \rightleftharpoons [Ph ₄ As][MoOCl ₄ (py)]	0.33 0.65 1.30 4.55	0.020 0.020 0.020 0.020	1.950	1.944	0.37 (0.49) 1.83 (1.86) <i>b</i> <i>b</i>
[Ph ₄ As][MoOCl ₄] + Et ₃ N \rightleftharpoons [Ph ₄ As][MoOCl ₄ (NEt ₃)]	0.65 1.30 6.50	0.020 0.020 0.020	1.950	1.946	0.05 (1.86) 0.08 (∞) 0.21 (∞)
[Ph ₄ As][MoOCl ₄] + thf \rightleftharpoons [Ph ₄ As][MoOCl ₄ (thf)]	0.50 1.00 2.00 10.0 20.0	0.004 0.004 0.004 0.004 0.004	1.952	1.944	0.11 (1.0) 0.20 (∞) 0.33 (∞) 2.00 (∞) 5.87 (∞)
[Ph ₄ As][MoOCl ₄] + [Ph ₄ As]Cl \rightleftharpoons [Ph ₄ As] ₂ [MoOCl ₅]	2.0 5.0 15.0 3.78 3.78 3.78	0.0030 0.00153 0.00153 0.00268 0.00540 0.0268	1.951 1.953 1.953 1.952 1.952 1.952	1.941 1.941 1.943 1.940 1.940 1.940	0.07 (∞) 0.11 (∞) 0.31 (∞) 0.26 (∞) 0.47 (∞) 2.16 (∞)
[Ph ₄ As][MoOCl ₄] + {[Ph ₄ As]Cl + [Et ₄ N]Cl (1 : 1)} \rightleftharpoons [MoOCl ₅] ²⁻	2.0	0.0030	1.951	1.940	0.38 (∞)
[Ph ₄ As] ₂ [MoOCl ₅] \rightleftharpoons [MoOCl ₄] ⁻ + Cl ⁻		0.0226 0.0090 0.0023	1.942	1.953	4.1 9.2 <i>ca.</i> 98
[Ph ₄ As][MoOCl ₄ (OH ₂)] \rightleftharpoons [MoOCl ₄] ⁻ + H ₂ O		0.0170 0.0068 0.0017	<i>ca.</i> 1.946	1.952	<i>ca.</i> 0.5 <i>ca.</i> 4.4 <i>ca.</i> 13.0

^a Values in parentheses were calculated from the ratios of reactants assuming complete conversion. ^b Only species C was detected. ^{c-f} [C] : [D] = 0.99 (1.0), 0.13 (0), 0.33 (0), and 6.9 (0), respectively; for D, g = 1.937, 1.943, 1.934, and 1.936, respectively.

ratio [MoOX₄] : Y was changed (charges on the complexes have been omitted). Each of the species produced was formulated on the basis of changes in the e.s.r. spectra.



The general use of X-band frequencies often leads to

overlapping of the e.s.r. lines, particularly for the intermediate members of the series, making assignments more difficult. A further weakness in these previous studies was that very rarely were any attempts made to isolate and characterise the proposed complexes. In the present study we have used simpler systems in that usually only two e.s.r.-active components were present and because

we have worked at *Q*-band frequencies the e.s.r. lines were more clearly resolved. In addition key complexes in our systems have been isolated and characterised.

Formation of $[\text{MoOCl}_3\text{L}]$ Complexes and their Reactivity towards Neutral Donors.—The reaction between MoOCl_3 and the neutral donor ligands Ph_3PO , $(\text{Me}_2\text{N})_3\text{PO}$, Ph_3PS , Ph_3PSe , $(\text{Me}_2\text{N})_2\text{CS}$, and Me_2S in 1 : 1 molar ratios in CH_2Cl_2 produced the corresponding $[\text{MoOCl}_3\text{L}]$ complex in solution and all except the $(\text{Me}_2\text{N})_3\text{PO}$ and Me_2S complexes were isolated as pure solids. A single-crystal X-ray diffraction study² has shown that $[\text{MoOCl}_3(\text{SPPPh}_3)]$ consists of discrete five-co-ordinate monomers with essentially square-pyramidal geometry. Molecular-weight, conductivity, and e.s.r. data indicate that this

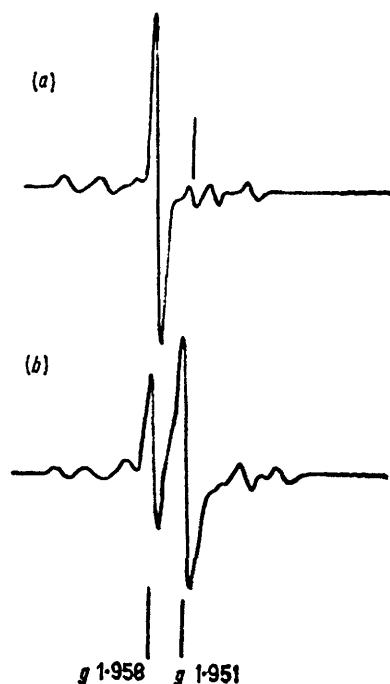


FIGURE 1 E.s.r. spectra in CH_2Cl_2 of (a) $[\text{MoOCl}_3(\text{SPPPh}_3)]$, (b) $[\text{MoOCl}_3(\text{SPPPh}_3)] + 0.6 [\text{Ph}_4\text{As}]\text{Cl}$

complex is also monomeric in CH_2Cl_2 solution. The solution e.s.r. spectra of all these $[\text{MoOCl}_3\text{L}]$ complexes are characteristic of monomeric molybdenum species and the solid-state Mo—O stretching frequencies at $\geq 990 \text{ cm}^{-1}$ (Table 3) suggest that the complexes are monomeric in both solid and solution.

These five-co-ordinate complexes are reactive towards many other donors (see below), $[\text{MoOCl}_3(\text{SPPPh}_3)]$ in particular reacting with loss of Ph_3PS . It was also observed that $[\text{MoOCl}_3(\text{SPPPh}_3)]$ reacted to a small extent with CH_2Cl_2 giving an extra e.s.r. signal with *g* corresponding to that of $[\text{MoOCl}_4]^-$ (see Figure 1 and later discussion). Addition of a large excess of the corresponding neutral donor ligand to the $[\text{MoOCl}_3\text{L}]$ complexes [$\text{L} = \text{Ph}_3\text{PO}$, $(\text{Me}_2\text{N})_3\text{PO}$, or $(\text{Me}_2\text{N})_2\text{CS}$] in CH_2Cl_2 enabled the $[\text{MoOCl}_3-$

$\text{L}_2]$ derivatives to be isolated, but this could not be achieved when $\text{L} = \text{Ph}_3\text{PS}$. Indeed $[\text{MoOCl}_3(\text{SPPPh}_3)_2]$ does not seem to exist in CH_2Cl_2 solution since the addition of a 20-fold excess of Ph_3PS to a solution of $[\text{MoOCl}_3(\text{SPPPh}_3)]$ produced no detectable change in the e.s.r. spectrum. In contrast to this, addition of excess of Me_2S to a solution of $[\text{MoOCl}_3(\text{SMe}_2)]$ resulted in an extra e.s.r. signal with *g* = 1.957 which we assign to $[\text{MoOCl}_3(\text{SMe}_2)_2]$, although we were unable to isolate this as a solid sample. The e.s.r. spectra of CH_2Cl_2 solutions of $[\text{MoOCl}_3(\text{SPPPh}_3)]$ containing up to a 20 : 1 molar ratio of MeCN showed that a methyl cyanide complex was formed, but in equilibrium with the original complex (see Table 4). The nature of the MeCN complex is not known for certain but it is assumed to be $[\text{MoOCl}_3(\text{NCMe})_2]$ since it had the same *g* as a solution of MoOCl_3 in MeCN, in which it is presumed that the complex is $[\text{MoOCl}_3(\text{NCMe})_2]$. However, the e.s.r. results show that MeCN does not easily replace Ph_3PS since nearly a 10 : 1 molar ratio of ligand was needed to produce approximately equal concentrations of $[\text{MoOCl}_3(\text{SPPPh}_3)]$ and $[\text{MoOCl}_3(\text{NCMe})_2]$. Similar observations were made with thf, although in this case only a *ca.* 3.3 : 1 molar ratio of ligand was needed to produce approximately equal concentrations of $[\text{MoOCl}_3(\text{SPPPh}_3)]$ and $[\text{MoOCl}_3(\text{thf})_2]$ (see Table 4).

The e.s.r. spectrum of $[\text{MoOCl}_3(\text{OPPh}_3)]$ dissolved in CH_2Cl_2 showed additional weak signals at *g* 1.953 and 1.937 attributable to $[\text{MoOCl}_4]^-$ and $[\text{MoOCl}_3(\text{OPPh}_3)_2]$, respectively, and also at *g* 1.927 due to an unknown species. This latter signal also appeared very weakly in CH_2Cl_2 solutions of $[\text{MoOCl}_3(\text{OPPh}_3)_2]$. We were able to generate e.s.r. signals at this *g* value in CH_2Cl_2 solutions of $[\text{MoOCl}_3(\text{OPPh}_3)_2]$ by addition of the known halide-abstracting agents $[\text{Et}_3\text{O}][\text{BF}_4]$, $\text{Na}[\text{BPh}_4]$, and $\text{CF}_3\text{SO}_3\text{F}$, and we therefore tentatively assign this *g* value to $[\text{MoOCl}_2(\text{OPPh}_3)_2]^+$ although we were unable to isolate this species from any of the extremely reactive solutions. The lower *g* value of 1.927 compared with that of 1.944 for $[\text{MoOCl}_3(\text{OPPh}_3)]$ is also compatible with this formulation since other workers¹⁵ have reported that the replacement of chloride by various oxygen donors leads to a decrease in *g*.

Properties of $[\text{MoOCl}_3\text{L}_2]$ Complexes in Solution.—The behaviour of the complexes $[\text{MoOCl}_3\text{L}_2]$ in CH_2Cl_2 solution depends on the nature of L. When $\text{L} = \text{Ph}_3\text{PO}$, $(\text{Me}_2\text{N})_3\text{PO}$, thf, or MeCN the e.s.r. spectra indicated that there is no measurable dissociation into $[\text{MoOCl}_3\text{L}]$. The geometry of $[\text{MoOCl}_3\{\text{OP}(\text{NMe}_2)_3\}_2]$ has been established in the solid state by a single-crystal X-ray study.¹⁶ The complex is a six-co-ordinate monomer with one $(\text{Me}_2\text{N})_3\text{PO}$ *trans* and the other *cis* to the Mo—O group. In CH_2Cl_2 solution, molecular-weight and conductivity measurements on $[\text{MoOCl}_3\{\text{OP}(\text{NMe}_2)_3\}_2]$ and $[\text{MoOCl}_3(\text{OPPh}_3)_2]$ ¹⁷ showed no detectable dissociation of these molecules,

¹⁵ I. N. Marov, Yu. N. Dubrov, V. K. Belyaeva, A. N. Ermakov, and D. I. Ryatchikov, *Russ. J. Inorg. Chem.*, 1968, **13**, 1107; D. I. Ryatchikov, I. N. Marov, Yu. N. Dubrov, V. K. Belyaeva, and A. N. Ermakov, *Doklady Akad. Nauk S.S.S.R.*, 1966, **166**, 623.

¹⁶ C. D. Garner, M. R. Hyde, P. Lambert, F. E. Mabbs, V. I. Routledge, and T. J. King, paper submitted at the Autumn Meeting of The Chemical Society, Leicester, 1974.

¹⁷ C. D. Garner, F. E. Mabbs, and V. I. Routledge, unpublished work.

thus supporting the e.s.r. data. This lack of dissociation is in sharp contrast to the sulphur donors studied where $[\text{MoOCl}_3(\text{SPPH}_3)_2]$ could not be formed even in solution, $[\text{MoOCl}_3(\text{SMe}_2)_2]$ is in equilibrium with the monoadduct in CH_2Cl_2 , and dissolution of $[\text{MoOCl}_3\{\text{SC}(\text{NMe}_2)_2\}_2]$ in CH_2Cl_2 gives a dominant species with g corresponding to $[\text{MoOCl}_3\{\text{SC}(\text{NMe}_2)_2\}]$ with only a weak incompletely resolved feature at $g \approx 1.954$ with *ca.* 0.04 times the intensity of the major absorption. This latter absorption is attributed to the diadduct. Attempts to increase the relative intensities of the e.s.r. signal for the diadduct by adding excess of ligand led to inconclusive results as we were unable to prevent precipitation of the bis complex in the e.s.r. tubes.

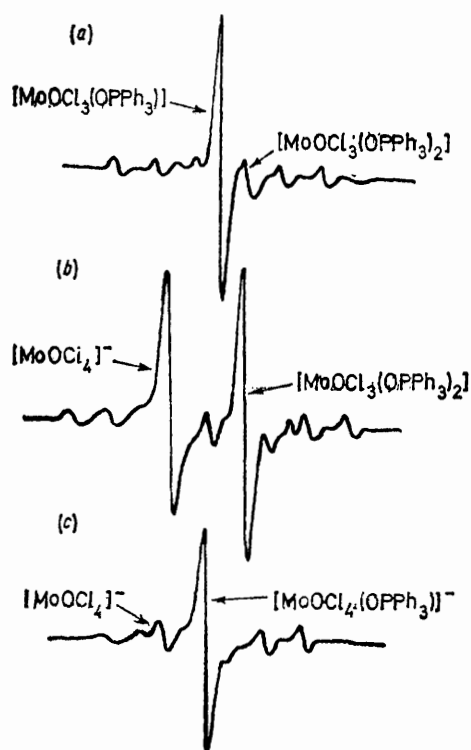
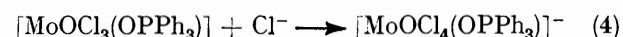
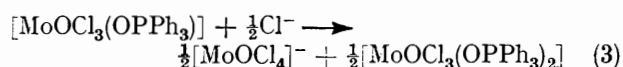
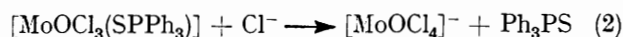


FIGURE 2 E.s.r. spectra in CH_2Cl_2 of (a) $[\text{MoOCl}_3(\text{OPPh}_3)]$ (0.008M), (b) $[\text{MoOCl}_3(\text{OPPh}_3)] + 0.5[\text{Ph}_4\text{As}]\text{Cl}$, (c) $[\text{MoOCl}_3(\text{OPPh}_3)] + 1.0[\text{Ph}_4\text{As}]\text{Cl}$

Reaction between $[\text{MoOCl}_3\text{L}]$ ($\text{L} = \text{Ph}_3\text{PS}$ or Ph_3PO) and Chloride.—Addition of $[\text{Ph}_4\text{As}]\text{Cl}$ or $[\text{Et}_4\text{N}]\text{Cl}$ to CH_2Cl_2 solutions of $[\text{MoOCl}_3(\text{SPPH}_3)]$ up to a molar ratio of 1 : 1 resulted in a new species with g 1.951, identical to that of a CH_2Cl_2 solution of $[\text{Ph}_4\text{As}][\text{MoOCl}_4]$ (see Figure 1), showing that Ph_3PS has been completely displaced by chloride. The g value for $[\text{MoOCl}_4]^-$ determined here is in excellent agreement with that reported for this species in $\text{MeCN}-\text{CHCl}_3$ solutions of phenothiazine tetrachloromolybdate(v).¹⁷ The value of 1015 cm^{-1} for $\nu(\text{MoO})$ in $[\text{Ph}_4\text{As}][\text{MoOCl}_4]$ is comparable with that found in $[\text{MoOCl}_3(\text{SPPH}_3)]$ and is very much higher than found for complexes of the type $[\text{MoOCl}_4\text{L}]^-$ and $[\text{MoOCl}_5]^{2-}$ where it is known that there is a ligand bound *trans* to the MoO group. On this basis we assign a monomeric five-co-ordinate structure to $[\text{MoOCl}_4]^-$ in

$[\text{Ph}_4\text{As}][\text{MoOCl}_4]$. The reaction between $[\text{MoOCl}_3(\text{OPPh}_3)]$ and chloride leads to a different overall result due to the increased co-ordinating ability of Ph_3PO compared with Ph_3PS (see Figure 2). The overall reactions occurring can be summarised by the following equations.



Reaction of $[\text{MoOCl}_4]^-$ with Neutral Donors.—The interaction of $[\text{MoOCl}_4]^-$ in CH_2Cl_2 solution with the neutral donors Ph_3PS , $(\text{Me}_2\text{N})_2\text{CS}$, Ph_3PO , $(\text{Me}_2\text{N})_3\text{PO}$, thf, pyridine (py), and Et_3N was investigated. E.s.r. spectra of solutions containing up to a 30-fold excess of Ph_3PS or $(\text{Me}_2\text{N})_2\text{CS}$ showed no interaction with Ph_3PS and only small traces [at the highest $(\text{Me}_2\text{N})_2\text{CS}$ ratios] of a species with a g value the same as that for $[\text{MoOCl}_3\{\text{SC}(\text{NMe}_2)_2\}]$. All the other ligands co-ordinate but to differing degrees. Up to 1 : 1 molar ratios all the added $(\text{Me}_2\text{N})_3\text{PO}$ co-ordinated to give an e.s.r. spectrum identical with that of the known anion $[\text{MoOCl}_4\{\text{OP}(\text{NMe}_2)_3\}]^-$, whereas the uptake of Ph_3PO was incomplete. Attempts to calculate the equilibrium constant for formation of $[\text{Ph}_4\text{As}][\text{MoOCl}_4(\text{OPPh}_3)]$ from $[\text{Ph}_4\text{As}][\text{MoOCl}_4]$ gave results which showed a steady increase as the ratio of ligand increased, the range of values being covered by $K = 500 \pm 200\text{ l mol}^{-1}$. The position of the equilibrium between $[\text{MoOCl}_4(\text{OPPh}_3)]^-$ and $[\text{MoOCl}_4]^-$ was dependent on the total concentration of $[\text{MoOCl}_4(\text{OPPh}_3)]^-$ originally dissolved (Figure 3). As this total concentration was increased the position of equilibrium shifted in favour of the six-co-ordinate $[\text{MoOCl}_4(\text{OPPh}_3)]^-$ species. Similar behaviour was also observed for the $[\text{MoOCl}_4(\text{OH}_2)]^-$ complex (Figure 4). This behaviour will be discussed in more detail when the behaviour of the $[\text{MoOCl}_5]^{2-}$ anion is considered.

The reaction with py showed that uptake of this ligand was very close to 100% at molar ratios up to 1 : 1. Addition of a four-fold excess of py did not result in formation of any other species and we therefore assume that the complex formed was $[\text{MoOCl}_4(\text{py})]^-$. In contrast to the ligands discussed above, co-ordination of both thf and Et_3N to form the complexes $[\text{MoOCl}_4\text{L}]^-$ was extremely poor (see Table 4) and the estimated equilibrium constants were 61 ± 14 and $3 \pm 1\text{ l mol}^{-1}$, respectively. The addition of a large excess of $(\text{Me}_2\text{N})_3\text{PO}$ or Ph_3PO to $[\text{MoOCl}_4]^-$ resulted in formation of significant amounts of the $[\text{MoOCl}_3\text{L}_2]$ complexes, with $(\text{Me}_2\text{N})_3\text{PO}$ displacing chloride more readily than did Ph_3PO (see Table 4).

Reaction between $[\text{MoOCl}_4]^-$ and Chloride.—It was qualitatively observed that dissolution of $[\text{Ph}_4\text{As}]_2[\text{MoOCl}_5]$ or $[\text{Et}_4\text{N}]_2[\text{MoOCl}_5]$ in CH_2Cl_2 resulted in e.s.r. spectra which showed more $[\text{MoOCl}_4]^-$ than $[\text{MoOCl}_5]^{2-}$, and that $[\text{Et}_4\text{N}]^+$ gave a higher proportion of $[\text{MoOCl}_5]^{2-}$ than did $[\text{Ph}_4\text{As}]^+$. The reaction between $[\text{Ph}_4\text{As}][\text{MoOCl}_4]$ and $[\text{Ph}_4\text{As}]\text{Cl}$ in CH_2Cl_2 was therefore studied quantitatively in some detail over a range of reactant ratios and total

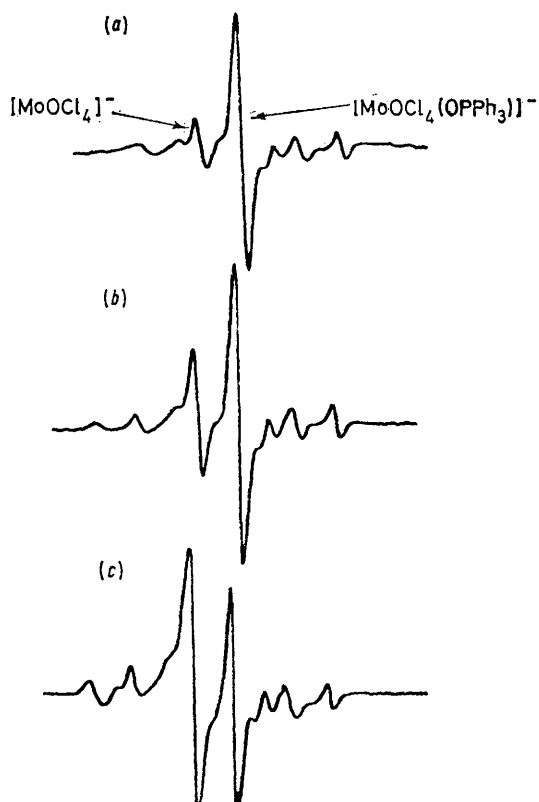


FIGURE 3 E.s.r. spectra of $[\text{Et}_4\text{N}][\text{MoOCl}_4(\text{OPPh}_3)]$ in CH_2Cl_2 (a) 0.0035, (b) 0.0012M, (c) 0.0004M

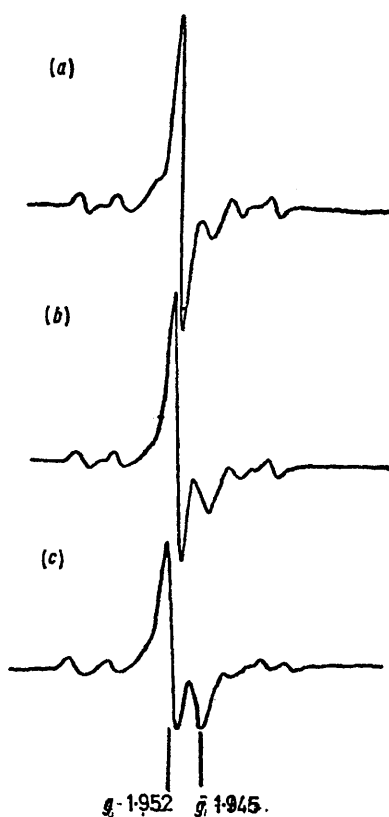


FIGURE 4 E.s.r. spectra of $[\text{Ph}_4\text{As}][\text{MoOCl}_4(\text{OH}_2)]$ in CH_2Cl_2 (a) 0.0017, (b) 0.0068, (c) 0.017M

molybdenum concentration. At molybdenum concentrations $\leq 5 \times 10^{-3}\text{M}$ the extent of formation of

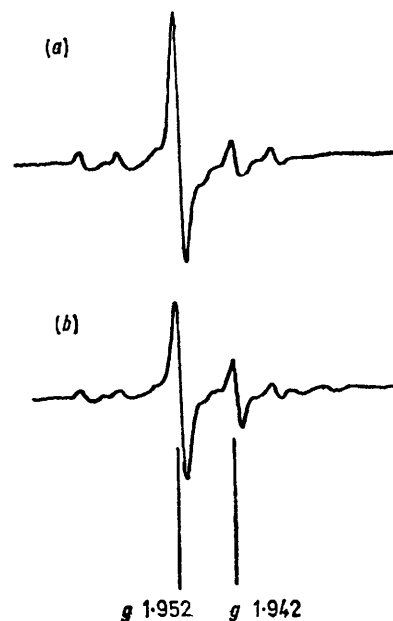


FIGURE 5 E.s.r. spectra of $[\text{Ph}_4\text{As}][\text{MoOCl}_4]$ (0.0015M) in CH_2Cl_2 with added $[\text{Ph}_4\text{As}]\text{Cl}$ in the Cl : Mo molar ratio (a) 5 : 1, (b) 15 : 1

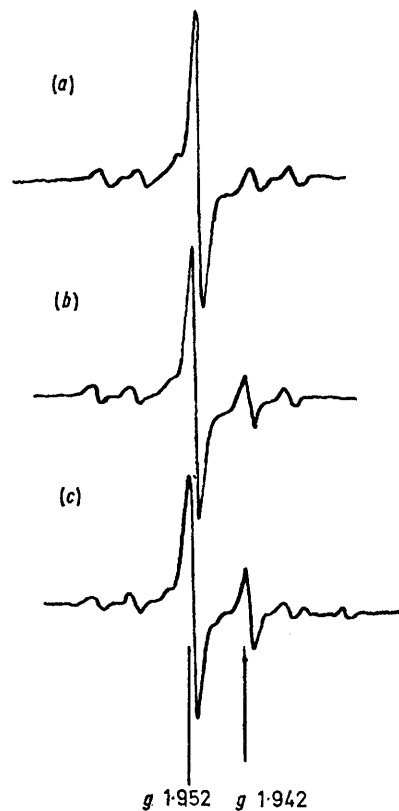


FIGURE 6 E.s.r. spectra of $[\text{Ph}_4\text{As}]_2[\text{MoOCl}_5]$ in CH_2Cl_2 (a) 0.0023, (b) 0.009, (c) 0.0023M

$[\text{MoOCl}_5]^{2-}$ was very low as shown by the relative ratios of the intensities of the e.s.r. signals (see Table 4 and Figures 5—7). In this concentration range the equi-

Equilibrium constant for formation of $[\text{Ph}_4\text{As}]_2[\text{MoOCl}_5]$ was found to be $20 \pm 8 \text{ l mol}^{-1}$. Two other important effects also emerged: (i) the extent of formation of

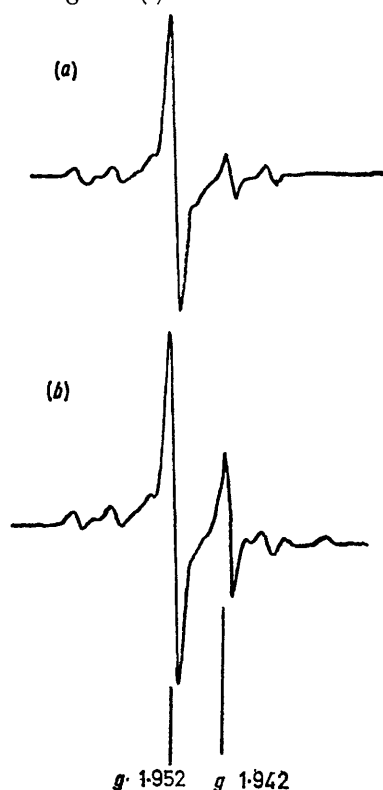


FIGURE 7 E.s.r. spectra of $[\text{Ph}_4\text{As}][\text{MoOCl}_4]$ (0.003M) in CH_2Cl_2 with chloride added as (a) $[\text{Ph}_4\text{As}]\text{Cl} : \text{Mo} = 2 : 1$, (b) $[\text{Ph}_4\text{As}]\text{Cl} + [\text{Et}_4\text{N}]\text{Cl}$ (both 1 mol) : $\text{Mo} = 1 : 1$

$[\text{MoOCl}_5]^{2-}$ was enhanced by increasing the overall concentrations of the reactants (see Table 4) or by increasing the concentrations of added $[\text{Ph}_4\text{As}]_2[\text{MoOCl}_5]$ (see Figure 6), *cf.* $[\text{MoOCl}_4(\text{OPPh}_3)]^-$ and $[\text{MoOCl}_4(\text{OH}_2)]^-$; (ii) at a given total-molybdenum concentration and ratio of reactants, replacing $[\text{Ph}_4\text{As}]^+$ by $[\text{Et}_4\text{N}]^+$ increased the concentration of $[\text{MoOCl}_5]^{2-}$ relative to $[\text{MoOCl}_4]^-$ (see Figure 7).

The second of these two observations cannot be explained in terms of the free-chloride-ion concentration. This will be less for $[\text{Et}_4\text{N}]\text{Cl}$ than for $[\text{Ph}_4\text{As}]\text{Cl}$ at an equivalent concentration since the conductivity data (Table 2) indicate that the former is the more strongly ion paired, yet it is this compound which enhances the formation of $[\text{MoOCl}_5]^{2-}$. The above observations suggest that a dominant effect in the formation of $[\text{MoOCl}_5]^{2-}$ in CH_2Cl_2 solution is the extent of its interaction with the cation, presumably through ion-pairing effects (the greater the ion pairing the greater the degree of formation of $[\text{MoOCl}_5]^{2-}$). This interpretation is supported by the conductivity data on $[\text{Ph}_4\text{As}][\text{MoOCl}_4]$ and $[\text{Et}_4\text{N}][\text{MoOCl}_4]$ (see Table 2). Although the charges on these latter anions are smaller, the degree of ion pairing of $[\text{MoOCl}_4]^-$ with $[\text{Et}_4\text{N}]^+$ is greater than it is with $[\text{Ph}_4\text{As}]^+$. It seems unlikely that this order is reversed for the more negatively charged $[\text{MoOCl}_5]^{2-}$ anion.

The present studies on oxomolybdenum(v) complexes in CH_2Cl_2 indicate that the position of equilibrium between five- and six-co-ordinate monomeric complexes depends on all or some of the following: (i) the nature of the ligands *cis* to the MoO group; (ii) the nature of the ligands *trans* to the MoO group; (iii) the total concentration of the molybdenum species; and (iv) ion-pairing effects. The results indicate that for anionic complexes the equilibrium shifts in favour of the five-co-ordinate species as the dilution is increased or as the ability of the cation to ion-pair is decreased. For the neutral complexes there is some tentative evidence that the presence of a sulphur donor may assist formation of a five-co-ordinate complex in solution. If the present findings are generally applicable it would seem that the occurrence of five-co-ordinate monomeric oxomolybdenum(v) centres in media of low dielectric constant should be widespread. Such centres may be important in the molybdenum-enzyme systems in providing a readily available site for the initial attack by a substrate.

Behaviour of $[\text{MoOCl}_5]^{2-}$ in Concentrated Aqueous HCl.—In view of the equilibria between $[\text{MoOCl}_4]^-$ and $[\text{MoOCl}_5]^{2-}$ observed in CH_2Cl_2 , we examined the e.s.r. spectra of $[\text{Et}_4\text{N}]_2[\text{MoOCl}_5]$ in concentrated HCl at a number of different concentrations. We found no change in

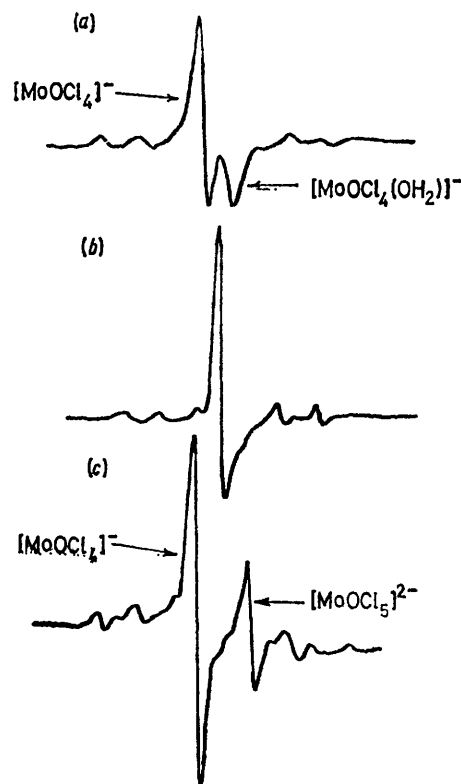


FIGURE 8 E.s.r. spectra of (a) $[\text{Ph}_4\text{As}][\text{MoOCl}_4(\text{OH}_2)]$ (0.017M) in CH_2Cl_2 , (b) $[\text{Et}_4\text{N}]_2[\text{MoOCl}_5]$ (0.003M) in concentrated aqueous HCl, (c) $[\text{Ph}_4\text{As}][\text{MoOCl}_4]$ (0.003M) and $[\text{Ph}_4\text{As}]\text{Cl} + [\text{Et}_4\text{N}]\text{Cl}$ (both 1 mol) : $\text{Mo} = 1 : 1$

the form of the spectrum between a saturated (*ca.* 0.08M) and a 0.008M solution. An example of a spectrum is shown in Figure 8 together with the spectrum of

$[\text{Ph}_4\text{As}][\text{MoOCl}_4(\text{OH}_2)]$ and ' $[\text{MoOCl}_5]^{2-}$ ' in CH_2Cl_2 solution for comparison. In contrast to the CH_2Cl_2 solutions, we detected only one species with certainty. However, assuming that changing the solvent does not change the g value for a given species, we assign the e.s.r. spectrum in our concentrated HCl solutions to $[\text{MoOCl}_4(\text{OH}_2)]^-$ and not to the $[\text{MoOCl}_5]^{2-}$ species originally dissolved. Solutions of MoOCl_3 (0.05—0.003M) in con-

centrated HCl gave identical results. This interpretation is in contrast to the generally held view that the major species in $[\text{HCl}] \geq 10\text{M}$ is $[\text{MoOCl}_5]^{2-}$.⁴

We thank the University of Calgary, Alberta, Canada for leave of absence (to P. M. B.).

[4j2254 Received, 1st November, 1974]
