Crystal and Molecular Structure, Electron Spin Resonance, and Electronic Spectrum of Tetraphenylarsonium Tetrachloro-oxomolybdenum(v)

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Crystals of the title compound are tetragonal, space group *P4/n*, with a = 12.766(7), c = 7.785(5) Å, Z = 2. The crystal structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to R 0.050 over 735 statistically significant reflections from diffractrometer measurements. The square-pyramidal $[MoOCl_4]^-$ anion has 4*mm* (C_{4v}) symmetry with Mo–O 1.610(10), Mo–Cl 2.333(3) Å, O–Mo–Cl 105.2(1)°. The $[AsPh_4]^+$ cation has crystallographic $\bar{4}$ (S_4) symmetry, with As–C 1.902(7) Å, and C–As–C angles of 105.3(3) and 111.6(3)°. The polarised single-crystal electronic spectra at room temperature and 5 K show that the first two bands at 15.4 and 22.5 kK are due to $b_2{}^*(4d_{xy}) \longrightarrow e^*(4d_{xz,yz}$, Mo–$O_{\pi^*})$ and e(Mo–O_π) $\longrightarrow a_1{}^*$(Mo–O_{σ^*}) excitation respectively. The single-crystal e.s.r. parameters ($g_\parallel$ 1.967 ± 0.002, $g_\perp$ 1.950 ± 0.002) and the Mo hyperfine parameters from solutions in CH_2Cl_2 and solid $[AsPh_4][NbOCl_4]$, ($\bar{A}$ 47.9×10^{-4} cm^{-1}, $A_\parallel$ 72.8×10^{-4} cm^{-1}), have been used in conjunction with the electronic spectrum to estimate the metal *d*-orbital contributions to the metal–ligand antibonding molecular orbitals.

BASED on a wide range of solution electron spin resonance and electronic absorption spectra measurements the electronic structures of monomeric MoO^{3+} chromophores have been the subject of much discussion.[1-10] However there are only a few reports of single-crystal *X*-ray

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structural studies[11-14] and no reports of single-crystal polarised electronic spectra or e.s.r. spectra on pure compounds of known structure. The only single-crystal e.s.r. work reported involves dilution studies of MoO^{3+} in the host lattices $K_2[SnF_6(H_2O)]$, $[NH_4]_2[GeF_6]$, $[NH_4]_2[SnCl_6]$, $K_2[SnCl_6]$, $[NH_4]_2[SnBr_6]$,[15] $[NH_4]_2[InCl_5]\cdot H_2O$, $[NH_4]_2[InBr_5]\cdot H_2O$ and $K_2[NbOF_5\cdot KHF_2]$.[4,6-16] In each of these cases it was assumed that the species incorporated was $MoOX_5^{2-}$. However, our recent studies[17] of the behaviour of $[MoOCl_4]^-$, $[MoOCl_4(H_2O)]^-$ and $[MoOCl_5]^{2-}$ in dichloromethane solution where $\bar{g}$ is 1.951, 1.947, and 1.940 respectively for these species, suggest that in the chloro-examples, either the species being studied was probably $[MoOCl_4(H_2O)]^-$ and not $[MoOCl_5]^{2-}$, or that the molecular geometry is sensitive to environment since the observed $\bar{g}$ were in the range 1.947—1.952. In view of this lack of single-crystal data we have undertaken a detailed study of a series of monomeric MoO^{3+} complexes, and now present our first report in this series.

EXPERIMENTAL

Preparation.—$[AsPh_4][MoOCl_4]$ was prepared as reported previously[17] and single crystals were grown from dried CH_2Cl_2 under dry dinitrogen. Microcrystalline samples of $[AsPh_4][(Nb,Mo)OCl_4]$ were prepared by dissolving various ratios of $NbCl_5$ and $MoCl_5$ in conc. HCl and adding the stoicheiometric quantity of $[AsPh_4]Cl$ dissolved in a minimum volume of EtOH. The resulting $[AsPh_4][(Nb,Mo)OCl_4(H_2O)]$ was dehydrated *in vacuo*.

Crystal Data.—$C_{29}H_{20}AsCl_4MoO$, $M = 637.1$, Tetragonal, $a = 12.766(7)$, $c = 7.785(5)$ Å, $U = 1\,268$ Å^3, D_m (flotation) $= 1.67$, $Z = 2$, $D_c = 1.668$, $F(000) = 630$. Cu-K_α radiation, $\lambda = 1.541\,8$ Å, μ(Cu-K_α) $= 100.4$ cm^{-1}. Space group $P4/n$ from Laue symmetry and systematic absences: $hk0$ when $h + k \neq 2n$.

Crystallographic Measurements.—For all these measurements crystals were sealed inside thin-walled glass capillaries under nitrogen to prevent decomposition. Preliminary unit-cell dimensions and space-group data were obtained from precession photographs taken with Mo-K_α radiation ($\lambda = 0.710\,7$ Å). A crystal of dimensions *ca.* $0.20 \times 0.20 \times 0.50$ mm was oriented to rotate with the c axis approximately parallel to the ϕ axis of an Enraf–Nonius CAD 3 diffractometer (Ni-filtered Cu-K_α radiation, take-off angle 3°) and accurate unit-cell dimensions were derived by least-squares treatment of the θ, χ, and ϕ angles for 40 high-order reflections widely separated in reciprocal space. Intensity data to θ 67° were then recorded by the $\theta-2\theta$ scanning procedure with scanwidths $(1.00 + 0.50\tan\theta)°$. Background measurements were taken at each end of the scan range for half the duration of the scan. The intensity of a strong reflection remeasured after each batch of 99 reflections showed no significant variation over the entire data-collection period. From these measurements 735 independent reflections for which $I > 2.0\sigma(I)$ [$\sigma^2(I) =$ scan count + total background count] were corrected for the usual Lorentz and polarization effects. Absorption corrections, established from the ϕ dependence of the intensity of the 004 reflection measured at χ 90°, were also applied to these data.

Structure Analysis.—With two formula units in the unit cell the molybdenum and arsenic atoms are constrained to lie on special positions of space group $P4/n$. The arsenic atom was placed at 0.25, 0.75, 0.00 [Wyckoff position (2*a*),[18] space-group origin at $\bar{1}$] and the variable z co-ordinate of the molybdenum atom [Wyckoff position 2(*c*)] was determined from the three-dimensional Patterson map. Positions for the chlorine, oxygen, and carbon atoms were established from a three-dimensional F_o Fourier synthesis phased by the arsenic and molybdenum atoms (R 0.38). Atomic positional and thermal parameters were then refined by full-matrix least-squares calculations to R 0.081. Calculated hydrogen-atom positions were confirmed to coincide with regions of positive electron density in a difference-Fourier synthesis and their fixed contributions were included in all further structure-factor calculations. Several further rounds of least-squares calculations brought the refinement to convergence at R 0.050. Final atomic positional parameters are in Table 1. Anisotropic thermal parameters and a list of observed and calculated structure amplitudes have been deposited in Supplementary Publication No. SUP 21952 (8 pp., 1 microfiche).*

TABLE 1

Fractional atomic co-ordinates * ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z
Mo	2 500	2 500	1 095(2)
As	7 500	2 500	0
O	2 500	2 500	−973(13)
Cl	1 590(2)	990(2)	1 883(3)
C(1)	7 388(6)	1 321(6)	1 482(9)
C(2)	6 608(7)	580(6)	1 223(11)
C(3)	6 496(8)	−229(7)	2 375(13)
C(4)	7 155(9)	−290(7)	3 783(12)
C(5)	7 919(9)	431(7)	4 044(11)
C(6)	8 033(7)	1 251(6)	2 894(11)
H(2)	609	62	235
H(3)	592	−80	222
H(4)	708	−91	466
H(5)	841	38	517
H(6)	863	184	307

* Hydrogen atom co-ordinates ($\times 10^3$) were not refined and an isotropic temperature factor U 0.063 Å^2 was assumed.

For all structure-factor calculations scattering factors for arsenic, molybdenum, carbon, chlorine, and oxygen were from ref. 19 and for hydrogen from ref. 20, with those of arsenic, chlorine, and molybdenum corrected for the real part of anomalous dispersion.[21] In the least-squares calculations $\Sigma w\Delta^2$ was minimised with weights w being

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

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assigned by the scheme $\sqrt{w} = 1$ for $|F_o| \leqslant 20.0$, $\sqrt{w} = 20.0/|F_o|$ for $|F_o| > 20.0$.

Electronic Spectral Measurements.—Absorption spectra (10—30 kK) * were recorded for CH_2Cl_2 solutions at room temperature and suitably thinned single crystals at room temperature and 5 K using equipment previously described.[22] The orientations of the crystals were such that the electric vector of the incident beam could be polarised parallel to and perpendicular to the crystallographic *c* axis. The data obtained are shown in Figure 1 and summarised in Table 2.

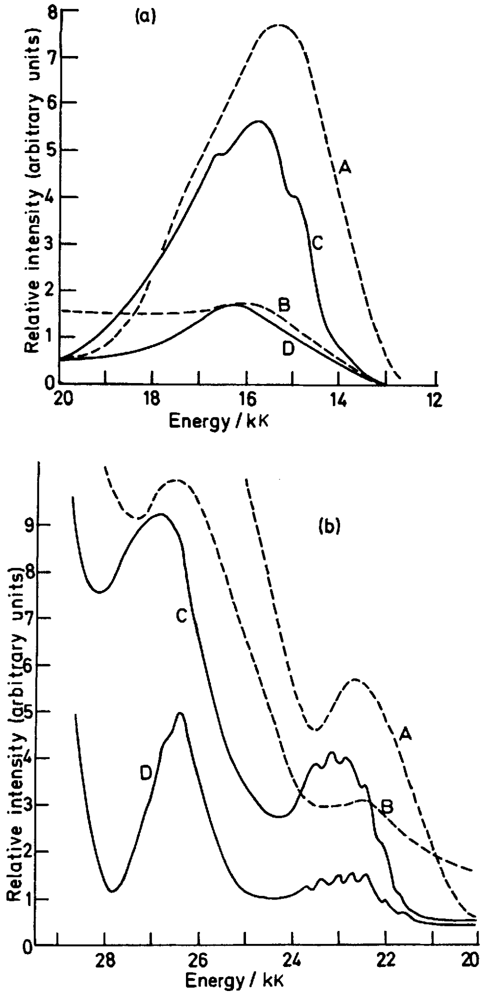

FIGURE 1 Polarised single-crystal electronic spectrum of $[AsPh_4][MoOCl_4]$: (a) 12—20 and (b) 20—29 kK; dashed line room temperature, full line 5 K. Curves A and C, *xy* polarisation; curves B and D, *z* polarisation

Electron Spin Resonance Spectra.—E.s.r. spectra were recorded at room temperature and *Q*-band frequencies as previously described [23] on single crystals mounted such that the magnetic field could be oriented in a plane perpendicular to the *c* axis and also in a plane containing the *c* axis. No molybdenum hyperfine structure was observed at any orientation in either of these planes. The results of these measurements on two different crystals gave $g_{\parallel}$ 1.967 ± 0.002 and $g_{\perp}$ 1.950 ± 0.002. Powder e.s.r. spectra were recorded on $[AsPh_4][(Nb,Mo)OCl_4]$ at room temperature and *ca*. 150 K. The observed *g* values were identical, within experimental error, to those obtained for the single crystals. So far we have only been able to determine $A_{\parallel}$ from the molybdenum hyperfine splitting in the powder spectra. The value of $A_{\perp}$ has been calculated from this and $\bar{A}$ found for $[AsPh_4][MoOCl_4]$ in CH_2Cl_2 solution. The values were $\bar{A}$ 47.9 × 10^{-4} cm^{-1} and $A_{\parallel}$ 72.8 × 10^{-4} cm^{-1}.

TABLE 2

Electronic spectral data for $[AsPh_4][MoOCl_4]$

Single crystal					
	Liq. helium temp.				
Room temp.	*z*	*xy*		CH_2Cl_2 soln.	*f*
15.4 ($xy \gg z$)	16.4w, vbr	14.99sh			
		15.82	$xy \gg z$	14.3	2.4×10^{-4}
		16.67sh			
	21.62w, sh				
	22.05	22.16sh			
	22.39	22.51sh			
22.5 ($xy > z$)	22.73	22.85	$xy > z$	22.6	9.7×10^{-5}
	23.07	23.18			
	23.43	23.52sh			
	23.77sh				
26.5 [a]	26.39			26.5	2.1×10^{-3}
	26.72sh				
		26.83br			
				31.3	6.9×10^{-1}

[a] Only seen in *z* pol., *xy* too intense.

DISCUSSION

Crystal and Molecular Structure.—The crystals containing discrete complex square-pyramidal $[MoOCl_4]^-$ anions with 4*mm* (C_{4v}) point symmetry and $[AsPh_4]^+$ cations with crystallographic $\bar{4}$ (S_4) point symmetry; the mutual relationship of a pair of ions is shown in Figure 2. Interatomic distances and angles are in Table 3.

The Mo–Cl distance [2.333(3) Å] is close to the mean (2.324 Å) at five-co-ordinate molybdenum(V) in $[MoOCl_3(SPPh_3)]$ [13] and, not unexpectedly, is slightly shorter than the corresponding distances in six-co-ordinate complexes, *e.g.* 2.359(2) Å in $[MoOCl_4(H_2O)]$,[24] and 2.350(8)—2.376(8) Å in $[MoOCl_4\{OP(OMe)_3\}]^{n-}$.[25]

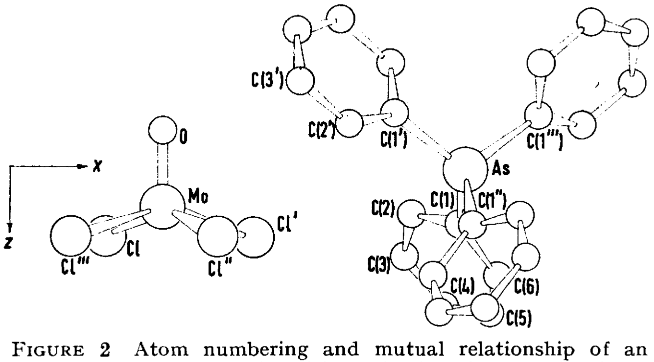

FIGURE 2 Atom numbering and mutual relationship of an anion and a cation, viewed in projection along the *b* axis

The Mo–O distance [1.610(10) Å] in the $[MoOCl_4]^-$ anion is significantly less than that [1.647(3) Å] in

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* 1kK = 10^3 cm^{-1}.

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$[MoOCl_3(SPPh_3)]$ [13] and the mean [1.679(2) Å] in di-μ-oxo-bis[(diethyldithiocarbamato)oxomolybdenum(V)],[26] and it is the shortest value yet found for such a bond at five-co-ordinate molybdenum. A comparably short Mo–O bond length [1.604(23) Å] has been reported at six-co-ordinate molybdenum in $[MoOCl_4\{OP(OMe)_2\}]^{n-}$,[25] but this is of lower precision and appears to be anomalous for the usual values range from 1.64 to 1.72 Å.[27] The striking similarity of the $[MoOCl_4]^-$ anion geometry to those encountered in $[RuNCl_4]^-$,[28] $[OsNCl_4]^-$,[29] and $[CrOCl_4]^-$ [30] (after allowance for the smaller chromium covalent radius) is evident from the dimensions presented in Table 4. In each of these anions the very short M–X distance may be rationalised by assuming $d_{x^2-y^2}sp^3$ hybridisation at the metal atom, thus leaving available two vacant d_{xz} and d_{yz} orbitals for strong π-bonding involving the *p* orbitals of the X ligands in addition to the σ bond along the C_4 axis, and this leads to the formation of multiple-order M–X bonds which would appear to correspond to triple bonds in these four ions.

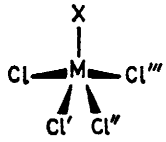
TABLE 3

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bond lengths			
Mo–Cl	2.333(3)	C(2)–C(3)	1.375(12)
Mo–O	1.610(10)	C(3)–C(4)	1.384(14)
As–C(1)	1.902(7)	C(4)–C(5)	1.356(14)
C(1)–C(2)	1.388(11)	C(5)–C(6)	1.385(12)
C(1)–C(6)	1.376(11)		
(*b*) Valency angles			
Cl–Mo–O	105.2(1)	As–C(1)–C(6)	119.4(6)
Cl–Mo–Cl′	86.0(1)	C(2)–C(1)–C(6)	120.1(7)
Cl–Mo–Cl″	149.5(1)	C(1)–C(2)–C(3)	119.4(8)
C(1)–As–C(1′)	111.6(3)	C(2)–C(3)–C(4)	119.7(9)
C(1)–As–C(1″)	105.3(3)	C(3)–C(4)–C(5)	121.2(9)
As–C(1)–C(2)	120.3(6)	C(4)–C(5)–C(6)	119.4(9)
C(1)–C(6)–C(5)	120.2(8)		

TABLE 4

Distances (Å) and angles (°) in $[MXCl_4]^-$ ions with square pyramidal (C_{4v}) symmetry



$[MXCl_4]^-$	M–X	M–Cl	Cl–M–Cl′	Cl–M–Cl″	X–M–Cl	X · · · Cl	Cl · · · Cl′	Δ [e]
$[RuNCl_4]^-$ [a]	1.570(7)	2.310(1)	86.37(5)	150.84(6)	104.58(4)	3.102(5)	3.161(3)	0.58
$[OsNCl_4]^-$ [b]	1.604(10)	2.310(2)	86.39(7)	150.94(7)	104.53(5)	3.125(7)	3.162(4)	0.58
$[CrOCl_4]^-$ [c]	1.519(12)	2.240(3)	86.4(1)	151.0(2)	104.5(1)	3.004(8)	3.066(4)	0.56
$[MoOCl_4]^-$ [d]	1.610(10)	2.333(3)	86.0(1)	149.5(1)	105.2(1)	3.164(8)	3.183(4)	0.61

[a] Ref. 28. [b] Ref. 29. [c] Ref. 30. [d] Present work. [e] Δ is the displacement (Å) of the metal atom from the basal plane through the halogen atoms.

The geometries of the $[AsPh_4]^+$ cations in the isomorphous crystals of each of the complexes listed in Table 4 show similar departures from tetrahedral valency angles around the arsenic atom, C(1)–As–C(1′) 105.3(3), C(1)–As–C(1″) 111.6(3)° in the $[MoOCl_4]^-$ salt, with corresponding values 104.9 (2) and 111.8(2)° in $[RuNCl_4]^-$, 105.1(2) and 111.7(2)°, in $[OsNCl_4]^-$, and 105.5(3) and 111.5(3)° in $[CrOCl_4]^-$. It has been suggested elsewhere [28,29] that this deformation occurs in the case of the N^{3-} ligand as a result of weak repulsion between this axial ligand and the adjacent phenyl rings. However, in terms of the sums of the van der Waals radii [31] there exists an equally short Cl · · · Ph interaction in each of these salts [O · · · C(3′) 3.35, Cl″ · · · C(2′) 3.60 Å in the present work] and so it would seem more appropriate to ascribe the deformation to the combined repulsive interaction of the axial N or O and basal Cl ligands with the phenyl rings. In addition to these valency-angle deformations, the As atom is significantly displaced (Δ 0.123 Å), in the present study, from the phenyl-ring least-squares plane (root-mean-square deviation 0.003 Å) in a direction which also minimizes these interactions. Other bond lengths and valency angles in the cation show no unusual features.

Electronic Spectrum.—The electronic spectrum of $[AsPh_4][MoOCl_4]$ dissolved in dry CH_2Cl_2 has absorption maxima at *ca.* 14.3, 22.6, 26.5, and 31.3kK. The oscillator strength *f* of the first band is *ca.* 2.5 times greater than that of the second band and thereafter *f* increases with increasing transition energy (see Table 2). The relative values of *f* for the first two bands are in the opposite sense to that observed for $[CrOCl_4]^-$.[32] The room-temperature polarised spectra show clearly that the two lowest-energy transitions are *xy* polarised. In the solid state the energy of the first transition is 1.1 kK greater than that observed in solution. This, coupled with the small difference in the *g* value observed in the solid state and solution, suggests that there may be some changes in the detailed geometry of the $[MoOCl_4]^-$ ion in these two phases. The general features of the room-

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temperature single-crystal spectra are reproduced at liquid helium temperatures, where some further splittings are observed on the first band in *xy* polarisation and considerable fine structure is resolved for the second band in both polarisations.

The sense of the polarisation of the first two electronic-spectral absorptions for the $[MoOCl_4]^-$ chromophore of C_{4v} symmetry show that they each arise from a transition of $E \rightleftharpoons B(A)$ in character. By analogy with $[CrOCl_4]^-$ and in agreement with previous assignments [1-10] this first band is attributed to the $b_2^*(4d_{xy}$ Mo–Cl$_{\pi^*})$ $\longrightarrow$ $e^*(4d_{xz,yz}$ Mo–O$_{\pi^*})$ excitation. The spatial degeneracy of the ^2E excited state occurs within the orbitals which are predominantly molybdenum 4*d* in character, and it would be expected that the orbital degeneracy would be raised by spin–orbit coupling effects at this metal centre. This would split the ^2E state into two new energy levels, Γ_6 and Γ_7, separated by approximately the value of the spin-orbit coupling constants, ξ, with Γ_6 lying lower than Γ_7. Reference to the selection rules, (Table 5), indicates that the higher-energy component should appear in *z* polarisation whereas both components may appear in *xy* polarisation. The spectral resolution obtained is insufficient to allow the assignment of the electronic origins, and the observed fine structure is best assigned to coupling with a vibrational mode of *ca.* 840 cm^{-1} in energy. This vibration is attributed to the Mo–O stretching mode of the first electronic excited state (in the ground state this mode has a frequency of 1 015 cm^{-1}).[17] Such a reduction in the frequency of this vibrational mode would be expected since the excitation $b_2^*(4d_{xy}$, Mo–Cl$_{\pi^*})$ $\longrightarrow$ $e^*(4d_{xz,yz}$, Mo–O$_{\pi^*})$ would weaken the Mo–O bonding interaction.

TABLE 5

Selection rules

C_{4v}	Transition	Polarisation	
		xy	*z*
$B_2(d_{xy})$	$\longrightarrow A_1(d_{z^2})$	F (E)	F (B_2)
	$\longrightarrow B_1(d_{x^2-y^2})$	F (E)	F
	$\longrightarrow E(d_{xz,yz})$	A (A_1, B_1, B_2)	F (E)
C_{4v}'			
$\Gamma_7(d_{xy})$	$\longrightarrow \Gamma_6$ $(E_{\frac{1}{2}})$	A (A_1, B_1, B_2, E)	F (B_1, B_2, E)
	$\longrightarrow \Gamma_7(E_{\frac{3}{2}})$	$A(A_1, B_1, B_2, E)$	A (A_1, E)

Symmetry of vibrational modes which keep or make the transitions allowed are in parentheses. Vibrational modes for $MOCl_4$ in C_{4v} correspond to $3A_1$, $+2B_1$, $+B_2 + 3E$ representations.

The assignment of the electronic transition responsible for the absorption at *ca.* 22.5 kK is less straightforward. There appear to be two principal possibilities, either the excitation $b_2^*(4d_{xy}$, Mo–Cl$_{\pi^*})$ $\longrightarrow$ $b_1^*(4d_{x^2-y^2}$, Mo–Cl$_{\sigma^*})$ suggested earlier [2] as the assignment for this band of pentachloro-oxomolybdenum(V), or the excitation $e(4d_{xz,yz}$, Mo–O$_{\pi})$ $\longrightarrow$ $a_1^*(4d_{z^2}$, Mo–O$_{\sigma^*})$ favoured [32] as the assignment for the corresponding transition of $[CrOCl_4]^-$. This latter interpretation is also preferred to the former in the case of $[MoOCl_4]^-$ for several reasons. The polarisation of this transition indicates that, given a $^2B_2$ ground-state, the transition is $^2B_2 \longrightarrow {}^2E$ in nature. The details of the fine structure (*vide infra*) resolved at liquid-helium temperatures suggest that the electronic origin in *xy* differs from that in *z* polarisation, again strongly implying that the excited state is spatially degenerate. The excitation $b_2^*(4d_{xy}$, Mo–Cl$_{\pi^*})$ $\longrightarrow$ $b_1^*(4d_{x^2-y^2}$, Mo–Cl$_{\sigma^*})$ is electronically forbidden whereas $e(4d_{xz,yz}$, Mo–O$_{\pi})$ $\longrightarrow$ $a_1^*(4d_{z^2}$, Mo–O$_{\sigma^*})$ is electronically allowed. Although it could be argued that the transition at *ca.* 22.5 kK arises due to the former excitation, allowed by coupling with a vibrational mode of *E* symmetry, the oscillator strength of this transition is of similar magnitude to that of the electronically allowed absorption at *ca.* 16 kK. Furthermore, no marked reduction in the intensity of the transition at 22.5 kK is observed * on cooling from room to liquid-helium temperatures, thus suggesting that the intensity of this absorption is not due solely to a relaxation of the selection rules by vibronic coupling. Finally, the invariance [33] in the energy of the band at *ca.* 22—23 kK with the nature of the ligands co-ordinated to the oxomolybdenum(V) centre clearly indicates that this transition cannot be due to $b_2^*(4d_{xy}$, Mo–Cl$_{\pi^*})$$\rightarrow$$b_1^*(4d_{x^2-y^2}$, Mo–Cl$_{\sigma^*})$ which represents 10*Dq* for the ligands *cis* to the oxo-group. In contrast the excitation $e(4d_{xz,yz}$, Mo–O$_{\pi})$$\rightarrow$$a_1^*(4d_{z^2}$, Mo–O$_{\sigma^*})$ is effectively confined within the oxomolybdenum(V) groups and its energy would not be expected to exhibit a marked dependence on the nature of the other ligands. The assignment of this transition in the lower C_4 point-symmetry {the $[MoOCl_4]^-$ ion is on a site of $C_4(4)$ symmetry in the crystal} does not resolve these difficulties, since the only change in the electronic selection rules is that the $4d_{xy}$$\rightarrow$$4d_{x^2-y^2}$ transition is now allowed in *z* polarisation. This prediction is not consistent with the observed polarisation of this band.

The details of the fine structure resolved at liquid-helium temperatures for the absorption at 22.5 kK call for some comment. Given a ^2E excited state, the orbital degeneracy of which arises from the configuration e^3, $(4d_{xz,yz}$, Mo–O$_{\pi})$,[3] there appear to be two possible interpretations of the data obtained.

(1) Spin-orbit coupling effects within the e^3 configuration, which is localised primarily on the oxygen atom, would result in the ^2E excited state being split into the states Γ_7 and Γ_6, with the former being the lower in energy. The selection rules for C_{4v}' (Table 5) indicate that only the transition from the $^2B_2$ (Γ_7) ground-state to the Γ_7 component of the ^2E excited state is allowed in *z* polarisation, whereas $\Gamma_7 \rightarrow \Gamma_6$ and Γ_7 are both allowed in *xy* polarisation. The maxima observed in *z* polarisation are *ca.* 120 cm^{-1} lower in energy than those observed in *xy* polarisation. Thus it could be argued that this energy difference represents the separation of the Γ_7 and Γ_6 components of the ^2E excited state, split by spin–orbit

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* Although the value of the $\varepsilon_{max.}$ at *ca.* 23 kK is reduced on cooling from room to liquid-helium temperatures (Figure 1), an analysis of the spectra suggests that it results mainly from a reduction in the extent to which the absorption at *ca.* 26.5 kK overlaps with this band.

[33] C. D. Garner, I. H. Hillier, F. E. Mabbs, and M. F. Guest, *Chem. Phys. Letters*, 1975, **32**, 224, and refs. therein.

coupling effects mainly at the oxygen atom, the spin–orbit coupling constant for an electron in an oxygen $2p$ orbital being estimated[34] as 151 cm^{-1}. Given this separation of the Γ_7 and Γ_6 levels, vibronic coupling effects could then result in the profile observed. The separation of the fine-structure maxima is *ca.* 340 cm^{-1} in both polarisations and, assuming that the same vibrational mode is responsible for this fine structure in both polarisations, likely vibrations include the ν(Mo–O) (A_1), ν(Mo–Cl) (A_1,E), or δ(O–Mo–Cl) (A_1) modes. Since the favoured assignment of the electronic transitions involves essentially $\text{Mo–O}_{\pi}\rightarrow\text{Mo–O}_{\pi^*}$, vibronic coupling with ν(Mo–O) might have been anticipated. Although the nature of this excitation would substantially weaken the Mo–O bonding interaction, the value of 340 cm^{-1} still appears to be rather low for ν(Mo–O) of this excited state.

(2) As suggested[32] for $[\text{CrOCl}_4]^-$, it is possible that a very low value of the spin–orbit coupling constant at the oxygen atom may require that the orbital degeneracy of the ^2E excited state be removed, at least partially, by coupling with a suitable mode. Symmetry requirements[35] dictate that this mode should have B_1 or B_2 symmetry and it is therefore possible that the fine structure results from vibronic coupling with the B_1 ν(Mo–Cl) stretching mode.

TABLE 6

Molecular orbital parameters for $[\text{MoOCl}_4]^-$

Formal charge on Mo	χ_{Mo} $(4d)$/ cm^{-1} [a]	$-P_{\text{Mo}}$/ 10^4 cm^{-1} [b]	%Cl $(3p_{\pi})$ assumed in e^*	Calc. % $4d$ character in [c]	
				b_2^*	e^*
+5	1 030	67.5	4	63	43
			0	63	58
+3	820	55.0	4	77	45
			0	77	58
+2	695	48.2	4	89	54
			0	89	66

[a] T. M. Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441. [b] $\chi\text{Cl}(3p)$ 587 cm^{-1} (ref. 34). [c] Estimated range of values from fitting process: $<\pm 0.5\%$ for b_2^* and $\pm 1.5\%$ for e^*.

The interpretation of the bands above *ca.*23 kK is ambiguous. The large reductions in their intensities on cooling from room to liquid-helium temperature suggests a significant vibronic contribution to their intensities, although their considerable intensities clearly indicate that they are at least in part electronically allowed. The low-temperature spectra show a mainly *z*-polarised band at *ca.* 26.4 kK along with a mainly *xy*-polarised band at *ca.* 26.8 kK. By comparison with $[\text{CrOCl}_4]^-$, the *z*-polarised band is tentatively assigned to one or more of the excitations $a_1(4d_{z^2}, \text{Mo–O}_{\sigma})\rightarrow a_1^*(4d_{z^2},\text{Mo–O}_{\sigma^*})$, $e(4d_{xz\,yz}, \text{Mo–O}_{\pi})\rightarrow e^*(4d_{xz,yz}, \text{Mo–O}_{\pi^*})$ and $b_1(4d_{x^2-y^2}, \text{Mo–Cl}_{\sigma})\rightarrow b_1^*(4d_{x^2-y^2}, \text{Mo–Cl}_{\sigma^*})$. The *xy*-polarised band likewise may contain one or more of the excitations $e(4d_{xz,yz}, \text{Mo–O}_{\pi})\rightarrow a_1^*(4d_{z^2}, \text{Mo–O}_{\sigma^*})$, $a_1(4d_{z^2}, \text{Mo–O}_{\sigma})\rightarrow e^*(4d_{xz,yz}, \text{Mo–O}_{\pi^*})$, $b_1(4d_{x^2-y^2}, \text{Mo–Cl}_{\sigma})\rightarrow e^*$-$(4d_{xz,yz}, \text{Mo–O}_{\pi^*})$. The band observed in solution at 31.3 kK, but which is too intense for single-crystal measurement, is probably best assigned to a chlorine-to-molybdenum charge-transfer transition on the basis of the high oscillator strength.

Similar to the situation discussed[32] for $[\text{CrOCl}_4]^-$, we have been unable to suggest the position of the b_2^*-$(4d_{xy}, \text{Mo–Cl}_{\pi^*}) \longrightarrow b_1^*(4d_{x^2-y^2}, \text{Mo–Cl}_{\sigma^*})$ excitation and, because of its expected low intensity, it may be obscured by the more intense bands at >26 kK.

Electron Spin Resonance Parameters.—Expressions relating the principal molecular e.s.r. parameters, the electronic transition energies, and the molecular orbital coefficients, assuming square-pyramidal geometry and neglecting metal-ligand overlap terms, have been given previously.[36] The difficulties inherent in this over-parameterised approach were also discussed. Because of the inability to locate the $b_2^*\rightarrow b_1^*$ transition we have used the experimental values of $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, and $A_{\perp}$ and the energy of the $b_2^*\rightarrow e^*$ transition to estimate the percentage $4d$ orbital contribution to the b_2^* and e^* molecular orbitals only. The resulting values are summarised in Table 6. The established pattern of the molecular orbital coefficients depending upon the formal charge assumed for the metal ion was found. In addition, the percentage $4d$ orbital character found in e^* depended on the amount of $\text{Cl}(3p_{\pi})$ character assumed for this orbital. Assuming that +2 is the appropriate formal charge in the molybdenum ion in this complex the estimated metal $4d$ character in b_2^* is very similar to that both estimated and calculated[36] for $[\text{CrOCl}_4]^-$. On the other hand, the metal $4d$ character in e^* is significantly smaller than that reported for $[\text{CrOCl}_4]^-$.

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[6/995 *Received, 25th May*, 1976]

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[34] A. Carrington and A. D. McLachlan, ‘Introduction to Magnetic Resonance,’ Harper and Row, London, 1967, p. 138.

[35] C. J. Ballhausen, ‘Introduction to Ligand-Field Theory,’ McGraw-Hill, New York, 1962, chaps. 6 and 8.

[36] C. D. Garner, I. H. Hillier, F. E. Mabbs, C. Taylor, and M. F. Guest, *J.C.S. Dalton*, 1976, 2258.