Single-crystal Molecular and Electronic Structure of Trichloro-oxo(triphenylphosphine sulphide)molybdenum(V)

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The crystal structure of the title compound has been determined by *X*-ray crystallographic methods. This compound crystallises in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell of dimensions a = 14.243(2), b = 14.353(2), and c = 10.021(1) Å. The crystals are composed of individual [$MoCl_3O(SPPh_3)$] molecules, each of which has an arrangement of the five ligand donor atoms about the central metal atom intermediate between that of a square-based pyramid, with the oxo-group at the axial position, and that of a trigonal bipyramid, with sulphur and chlorine atoms at the axial positions. Interatomic distances include Mo–O 1.647(3), Mo–S 2.460(1), Mo–Cl 2.324(20) Å (mean), and P–S 2.041(1) Å. The electronic spectral and e.s.r. characteristics of [$MoCl_3O(SPPh_3)$] are presented and the electronic structure of this molecule is discussed with reference to these data.

COMPLEXES containing an early transition-metal atom multiply bonded to an oxo-group have attracted considerable and sustained interest.[1-6] We have been concerned to improve the understanding of the electronic structures of such centres,[7-10] and to provide new kinetic,[11] structural, and spectroscopic [12-15] data particularly for mononuclear oxomolybdenum(V) centres. Here we report the single-crystal molecular structure and the electronic and e.s.r. spectral characteristics of [$MoCl_3O(SPPh_3)$], a complex which represents a rare example of an authenticated discrete, five-co-ordinate, oxomolybdenum(V) moiety. A preliminary account of this work has appeared.[12]

EXPERIMENTAL

The complex [$MoCl_3O(SPPh_3)$] was prepared, crystallised, and characterised as previously described.[12]

Structure Determination.—Well formed rhombohedral crystals of [$MoCl_3O(SPPh_3)$] were chosen and sealed into thin-walled glass capillaries. Oscillation and Weissenberg photographs showed that these crystals belonged to the orthorhombic space group $P2_12_12_1$ from systematic absences: $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$. A suitable crystal of dimensions *ca.* 0.2 × 0.2 × 0.3 mm was selected and mounted on a Hilger and Watts four-circle diffractometer and the lattice parameters refined as a = 14.243(2), b = 14.353(2), and c = 10.021(1) Å. The unit-cell volume of 2 049(1) Å^3 is consistent with that expected for $Z = 4$, $D_c = 1.66$ g cm^{-3}, the asymmetric unit having a formula (= molecular) weight of 512.7. The space-group requirements impose no symmetry restrictions on this molecular unit.

Reflections $0kl$—$19kl$ were measured using Mo-K_α radiation (λ 0.717 Å) and a graphite monochromator. 3 115 Reflections with $I > 3\sigma(I)$ in the range $0 < 2\theta < 55°$ were considered observed and used in the subsequent refinement. No account was taken of anomalous dispersion and no corrections were made for secondary extinction or absorption effects, μ(Mo-K_α) = 11.9 cm^{-1}; the maximum error introduced by the neglect of absorption effects is estimated to be *ca.* 16% in F. Data-reduction and crystallographic calculations were carried out on the Nottingham I.C.L. 1906A computer, using the Oxford University 'Crystals' programs. Atomic-scattering factors were used as published.[16] The metal-atom positions were located from a three-dimensional Patterson synthesis and subsequent Fourier syntheses clearly indicated the positions of all the other non-hydrogen atoms. These atomic positions and the atomic thermal parameters were refined using full-matrix least-squares procedures. A subsequent difference-Fourier synthesis revealed approximate positions for all the hydrogen atoms and these were included in the final least-squares refinement, together with their isotropic thermal parameters. This last refinement was accomplished with unit weighting for all the reflections and converged at a conventional R value of 0.047.

Observed and calculated structure amplitudes and thermal parameters are in Supplementary Publication No. SUP 22307 (35 pp.).*

Spectroscopic Studies.—The electronic-absorption spectrum was recorded on a Cary 14 spectrometer at room temperature for [$MoCl_3O(SPPh_3)$] dissolved in CH_2Cl_2 and mulled in Nujol in the range 10 000—35 000 cm^{-1}. It has

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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not yet been possible to grow single crystals of sufficient size for polarised single-crystal studies. E.s.r. spectra were recorded at room temperature using methods outlined previously[17] for the powdered material and for single crystals coated with silicone grease. The crystallographic directions of particular crystals were determined by *X*-ray oscillation and Weissenberg measurements, and the e.s.r. characteristics of the crystallographic *ab*, *ac*, and *bc* planes were then obtained. The principal molecular *g* values and their orientations with respect to the crystal axes were calculated from these data using the procedure of Schonland.[18]

RESULTS AND DISCUSSION

Crystal Structure.—The final atomic co-ordinates refined for [$MoCl_3O(SPPh_3)$] are presented in Table 1.

TABLE 1

Refined positional parameters for [$MoCl_3O(SPPh_3)$]

Atom	*x*	*y*	*z*
Mo	0.169 40(2)	0.233 17(2)	0.130 36(3)
Cl(1)	0.139 54(8)	0.312 58(8)	0.325 73(10)
Cl(2)	0.241 19(11)	0.260 13(15)	−0.074 45(11)
Cl(3)	0.034 11(8)	0.302 81(9)	0.042 57(13)
S(1)	0.336 32(6)	0.221 95(7)	0.191 48(8)
P(1)	0.352 28(6)	0.189 59(5)	0.388 54(8)
O(1)	0.136 8(3)	0.123 5(2)	0.143 9(4)
C(1)	0.456 1(2)	0.117 9(2)	0.393 7(3)
C(2)	0.537 3(3)	0.149 1(3)	0.329 1(5)
C(3)	0.617 2(3)	0.093 3(4)	0.330 6(5)
C(4)	0.617 2(2)	0.008 2(3)	0.395 1(5)
C(5)	0.537 7(4)	−0.022 0(3)	0.457 4(6)
C(6)	0.457 0(3)	0.032 0(3)	0.458 7(5)
C(7)	0.257 3(2)	0.123 6(2)	0.458 6(4)
C(8)	0.211 0(3)	0.152 6(3)	0.572 8(5)
C(9)	0.138 6(4)	0.099 1(4)	0.626 1(6)
C(10)	0.112 1(3)	0.017 1(4)	0.561 6(6)
C(11)	0.156 5(3)	−0.010 9(3)	0.448 8(6)
C(12)	0.229 4(3)	0.041 8(3)	0.394 9(5)
C(13)	0.373 4(2)	0.291 5(2)	0.488 3(4)
C(14)	0.356 6(3)	0.380 1(3)	0.439 2(5)
C(15)	0.372 1(4)	0.457 6(3)	0.520 9(6)
C(16)	0.402 6(4)	0.445 5(4)	0.649 4(6)
C(17)	0.419 3(4)	0.356 8(4)	0.698 4(5)
C(18)	0.405 8(3)	0.279 2(3)	0.618 3(4)

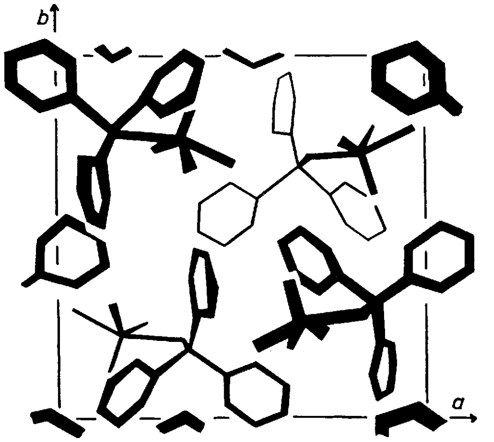

FIGURE 1 Crystal structure of [$MoCl_3O(SPPh_3)$]

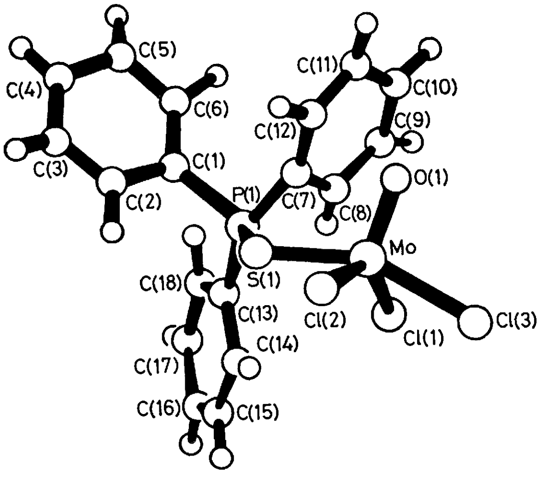

FIGURE 2 Molecular structure of [$MoCl_3O(SPPh_3)$]

The values obtained for the hydrogen atoms are not included as these involve relatively large errors. A representation of the crystal structure is shown in Figure 1. The structure comprises discrete molecular units orientated so that each Mo–O vector makes angles of 73.6, 17.0, and 85.3° with, and each Mo–S vector is inclined at 14.9, 86.2, and 75.6° to, the *a*, *b*, and *c* crystallographic axes, respectively. A diagram of the [$MoCl_3O(SPPh_3)$] molecule is presented in Figure 2, selected intramolecular dimensions are listed in Table 2, and details of certain intramolecular least-squares planes are given in Table 3. The complex exists as discrete five-co-ordinate molecules which have a geometry intermediate between that of a square-based pyramid, with O(1) at the apex, and a trigonal bipyramid, with S(1) and Cl(3) at the apical positions. The stereochemistry resembles that described[19] for the monomeric [$NbCl_3S(SPPh_3)$] complex. For the square-pyramidal geometry, the average displacement of the atoms S(1), Cl(1), Cl(2), and Cl(3) from their least-squares plane is ±0.17(1) Å; the Mo atom is 0.65 Å above this plane, with the Mo–O axis perpendicular (89.8°) to the plane. The average apical–Mo–basal and basal–Mo–basal interbond angles are 106.1(5.4) and 86.0(4.9)°, respectively. The trigonal bipyramidal geometry is a poorer description for this complex. Although the average equatorial–Mo–equatorial interbond angle is 120.0(16.0)° and the average apical–Mo–equatorial interbond angle of 91.5(8.4)° also approaches the ideal value, the individual values depart considerably from these mean values and the apical–Mo–apical angle is 156.4(4)°. Furthermore, the Mo atom is situated 0.05 Å from the equatorial [O(1),Cl(1),Cl(2)] plane, and the Mo–Cl(3) and Mo–S(1) vectors make angles of 79.8 and 76.1°, respectively, with this equatorial plane. The highest symmetry which the $MoCl_3OS$ unit can adopt is C_s and, although the atoms Mo, O(1), Cl(3), and S(1) *are* coplanar, to within ±0.07 Å, Cl(1) is 2.27 Å above this plane, whereas Cl(2) is 2.05 Å below it. Thus no symmetry relationships are strictly

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obtained within the co-ordination sphere about the metal atom in [$MoCl_3O(SPPh_3)$].

TABLE 2

Bond lengths (Å) and interbond angles (°) for [$MoCl_3O(SPPh_3)$]

(*a*) Co-ordination about Mo

Mo–O(1)	1.647(3)	O(1)–Mo–S(1)	100.9(1)
Mo–S(1)	2.460(1)	O(1)–Mo–Cl(1)	110.5(1)
Mo–Cl(1)	2.305(1)	O(1)–Mo–Cl(2)	110.9(1)
Mo–Cl(2)	2.325(1)	O(1)–Mo–Cl(3)	102.0(1)
Mo–Cl(3)	2.342(1)	S(1)–Mo–Cl(1)	89.95(4)
Average Mo–Cl	2.324(20)	S(1)–Mo–Cl(2)	78.80(4)
		S(1)–Mo–Cl(3)	156.41(4)
		Cl(1)–Mo–Cl(2)	138.46(6)
		Cl(1)–Mo–Cl(3)	87.49(4)
		Cl(2)–Mo–Cl(3)	87.67(5)

(*b*) Triphenylphosphine sulphide group

S(1)–P(1)	2.041(1)	Mo–S(1)–P(1)	111.31(4)
P(1)–C(1)	1.802(4)	S(1)–P(1)–C(1)	104.4(1)
P(1)–C(7)	1.794(4)	S(1)–P(1)–C(7)	114.5(1)
P(1)–C(13)	1.798(4)	S(1)–P(1)–C(13)	111.8(1)
Average P–C	1.798(4)	Average S–P–C	110.2(5.2)
C(1)–C(2)	1.399(5)	C(1)–P(1)–C(7)	107.8(2)
C(2)–C(3)	1.391(6)	C(1)–P(1)–C(13)	108.2(2)
C(3)–C(4)	1.382(7)	C(7)–P(1)–C(13)	109.8(2)
C(4)–C(5)	1.364(7)	Average C–P–C	108.6(1.1)
C(5)–C(6)	1.386(7)		
C(6)–C(1)	1.395(5)		
C(7)–C(8)	1.385(6)	C(6)–C(1)–C(2)	119.4(4)
C(8)–C(9)	1.392(7)	P(1)–C(1)–C(2)	118.9(3)
C(9)–C(10)	1.395(8)	P(1)–C(1)–C(6)	121.7(3)
C(10)–C(11)	1.357(8)	P(1)–C(7)–C(8)	121.6(3)
C(11)–C(12)	1.393(6)	P(1)–C(7)–C(12)	118.7(3)
C(12)–C(6)	1.395(5)	P(1)–C(13)–C(14)	121.4(3)
C(13)–C(14)	1.384(5)	P(1)–C(13)–C(18)	118.2(3)
C(14)–C(15)	1.398(6)	Average P–C–C	120.1(1.7)
C(15)–C(16)	1.370(8)		
C(16)–C(17)	1.386(8)		
C(17)–C(18)	1.386(7)		
C(18)–C(13)	1.393(6)	C(6)–C(1)–C(2)	119.4(4)
Average C–C	1.386(12)	C(1)–C(2)–C(3)	119.2(4)
		C(2)–C(3)–C(4)	120.9(4)
		C(3)–C(4)–C(5)	119.7(5)
		C(4)–C(5)–C(6)	121.0(5)
		C(5)–C(6)–C(1)	119.8(4)
		C(12)–C(7)–C(8)	119.7(4)
		C(7)–C(8)–C(9)	120.3(4)
		C(8)–C(9)–C(10)	119.3(5)
		C(9)–C(10)–C(11)	120.6(5)
		C(10)–C(11)–C(12)	120.7(4)
		C(11)–C(12)–C(7)	119.4(5)
		C(18)–C(13)–C(14)	120.4(4)
		C(13)–C(14)–C(15)	119.7(4)
		C(14)–C(15)–C(16)	120.0(4)
		C(15)–C(16)–C(17)	120.2(5)
		C(16)–C(17)–C(18)	120.7(5)
		C(17)–C(18)–C(13)	119.0(4)
		Average C–C–C	120.0(6)

The Mo–O bond length [1.647(3) Å] is short for such a separation and approaches that [1.61(1) Å] characterised [10] in [$AsPh_4$][$MoCl_4O$] and which currently represents the shortest known Mo–O bond length. The implication of strong and multiple-bonded interactions over these short Mo–O separations is supported by the relatively high values of their ν(Mo–O) stretching frequencies at 1 008 and 1 015 cm^{-1}, for [$MoCl_3O(SPPh_3)$] and [$MoCl_4O$]$^-$, respectively. In each case, this strong molybdenum–oxygen bonding appears to be related to the absence of any ligand *trans* to the oxo-group; for [$MoCl_3O(SPPh_3)$] there is no approach to this position closer than 4.5 Å. The Mo–Cl (mean) and Mo–S bond lengths of 2.324(20) and 2.460(1) Å, respectively, are similar to those identified in studies of related complexes.[13–15, 20, 21]

The dimensions of the co-ordinated PPh_3S molecule are very similar to those reported [22] for $2PPh_3S{\cdot}3I_2$. The length of the P–S bond in this latter compound [2.01(3) Å] is similar to that [2.041(1) Å] identified in the present study, and these values are slightly but sig-

TABLE 3

Equations [a] of some least-squares planes [b] and their dihedral angles for [$MoCl_3O(SPPh_3)$]

Plane (1): Cl(1), Cl(2), Cl(3), S(1)

$$-0.285X - 0.955Y + 0.081Z + 4.425 = 0$$

[Mo(1) 0.647, O(1) 2.294, Cl(1) −0.162, Cl(2) −0.181, Cl(3) 0.170, S(1) 0.172, P(1) 0.711]

Plane (2): Mo(1), O(1), Cl(3), S(1)

$$-0.268X + 0.214Y + 0.939Z - 1.228 = 0$$

[Mo(1) 0.069, O(1) −0.016, Cl(3) −0.027, S(1) −0.026, Cl(1) 2.266, Cl(2) −2.050, P(1) 1.669]

Plane (3): Mo(1), O(1), Cl(1), Cl(2)

$$-0.891X + 0.262Y - 0.371Z + 1.795 = 0$$

[Mo(1) 0.037, O(1) −0.012, Cl(1) −0.012, Cl(2) −0.012, Cl(3) 2.341, S(1) −2.351, P(1) −3.408]

Plane (4): O(1), Cl(1), Cl(2)

$$-0.891X + 0.262Y - 0.371Z + 1.806 = 0$$

[Mo(1) 0.049, Cl(3) 2.354, S(1) −2.339, P(1) −3.395]

Plane (5): Mo(1), Cl(1), Cl(3), S(1)

$$-0.338X - 0.898Y + 0.281Z + 3.782 = 0$$

[Mo(1) 0.328, Cl(1) −0.002, Cl(3) −0.167, S(1) −0.158, O(1) 1.937, Cl(2) −0.942, P(1) 0.737]

Plane (6): Mo(1), Cl(2), Cl(3), S(1)

$$-0.202X - 0.965Y - 0.164Z + 4.208 = 0$$

[Mo(1) 0.275, Cl(2) 0.032, Cl(3) −0.156, S(1) −0.151, O(1) 1.867, Cl(1) −1.061, P(1) −0.073]

Plane (7): C(1), C(2), C(3), C(4), C(5), C(6)

$$0.302X + 0.444Y + 0.844Z - 6.040 = 0$$

[Mo(1) −2.725, S(1) −1.562, P(1) −0.034]

Plane (8): C(7), C(8), C(9), C(10), C(11), C(12)

$$0.658X - 0.513Y + 0.552Z - 4.046 = 0$$

[Mo(1) −3.437, S(1) −1.453, P(1) 0.025]

Plane (9): C(13), C(14), C(15), C(16), C(17), C(18)

$$0.946X + 0.554Y - 0.319Z - 3.708 = 0$$

[Mo(1) −1.656, S(1) 0.389, P(1) −0.051]

Dihedral angles (°) between planes

Plane	1	2	3	4	5	6	7	8
2	92.98							
3	91.49	93.09						
4	91.49	93.09	0.00					
5	12.31	80.67	92.20	92.20				
6	14.89	107.87	90.67	90.67	27.20			
7	116.22	36.20	117.73	117.73	105.29	128.93		
8	69.70	76.54	157.65	157.65	66.82	74.25	64.13	
9	110.39	122.74	135.27	135.27	117.31	101.09	87.65	65.29

[a] These refer to the *a*, *b*, and *c* crystal axes, with *X*, *Y*, and *Z* in Å. [b] The perpendicular distances (Å) of certain atoms from a plane are given in square brackets.

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nificantly longer than those (*ca.* 1.89—1.97 Å) identified as typical for a terminal P^V–S bond length in compounds including $P(C_6H_{11})_3S$,[23] PEt_3S,[24] PMe_3S,[25] and PCl_3S.[26] This implied weakening of the P–S bonding on co-ordination is supported by the change in the ν(P–S) stretching band from 637 (free ligand)[27] to 575 cm^{-1} (complex). The latter value is slightly lower than for ν(P–S) bands reported[27–29] for other metal complexes of PPh_3S, but similar to those recorded[30] for $PPh_3S{\cdot}BX_3$ (X = Cl, Br, or I) adducts.

Electronic Structure.—The electronic-absorption spectrum of $[MoCl_3O(SPPh_3)]$ solutions in CH_2Cl_2 at room temperature consists of a band centred at 15 200 cm^{-1} (ε 21.7 dm^3 mol^{-1} cm^{-1}) and shoulders at 23 300 and 33 300 cm^{-1}, on the low-energy side of an extremely intense absorption. These features are also characteristic of $[MoCl_3O(SPPh_3)]$ in the solid state where absorption maxima at 14 900, 22 700, 27 000, 29 900, and 37 700 cm^{-1} are apparent. We have already discussed[14,15] the nature of the absorptions characteristic of monomeric oxomolybdenum(v) chromophores centred at 13 000—15 400 and 22 400—23 300 cm^{-1}. The favoured assignment[14] is that these arise due to the $^2B_2 \rightarrow {}^2E$ transitions b_2*(Mo $4d_{xy}$, Mo–L_{cis} π*)→ *e**(Mo $4d_{xy,yz}$; Mo–O π*) and *e*(O $2p_{x,y}$; Mo–O π)→ b_2*(Mo $4d_{xy}$; Mo–L_{cis} π*), respectively. Accordingly, we suggest that these assignments are appropriate to $[MoCl_3O(SPPh_3)]$ but emphasise that further studies are necessary to fully establish the nature of the absorption centred at *ca.* 23 000 cm^{-1} of these complexes. The intense absorptions extending into and through the u.v. spectral region are assigned to S→Mo and Cl→Mo charge-transfer transitions.

TABLE 4

Angular dependence of the *g*-value resonance * magnetic field (T) for $[MoCl_3O(SPPh_3)]$ at room temperature

Angle of rotation (°)	*ab* plane, *b* = 0	*bc* plane, *c* = 0	*ac* plane, *c* = 0 molecule 1	*ac* plane, *c* = 0 molecule 2
0	1.2645	1.2605	1.2604	1.2604
15	1 2637	1.2607	1.2577	1.2613
30	1.2616	1.2612	1.2566	1.2609
45	1.2591	1.2623	1.2548	1.2594
60	1.2566	1.2631	1.2536	1.2576
75	1.2549	1.2637	1.2532	1.2556
90	1.2544	1.2642	1.2541	1.2541
105	1.2552	1.2635	1.2560	1.2541
120	1.2570	1.2631	1.2580	1.2531
135	1.2595	1.2622	1.2597	1.2548
150	1.2617	1.2612	1.2609	1.2569
165	1.2636	1.2607	1.2611	1.2577
180	1.2645	1.2605	1.2604	1.2604

* ν = 34 815 MHz.

The e.s.r. data are summarised in Table 4 and the principal molecule *g* values[18] are in Table 5. The powder e.s.r. spectrum is presented in Figure 3 together with the values obtained for the principal molecule *g* values. The two alternative sets of molecule *g* values derived from the single-crystal e.s.r. study are identical in magnitude. Furthermore, the two sets of direction cosines are very similar in magnitude and the senses of the vectors obtained are related by the crystallographic $C_{21}(c)$ axis. There is no real distinction possible between these two sets of direction cosines and thus the orientations of the principal molecular *g* values are not uniquely defined. g_3 Subtends an angle of 6.4(0.7) *or* 34.4(0.5)° with the Mo–S intramolcular direction, and g_2 is inclined at 12.9(1.0) *or* 37.5(0.5)° to the normal to the Mo,O(1),-S(1),Cl(1) plane. However, for both sets g_1 makes an angle of 17.0(1.0)° with the Mo–O direction of each

TABLE 5

Molecular *g* values, reference directions, and their direction cosines *

Set		*g* Value	Direction cosines *a*	Direction cosines *b*	Direction cosines *c*
1	g_1	1.955	0.017 8	−0.999 8	−0.011 9
	g_2	1.959	−0.344 8	−0.017 3	0.938 5
	g_3	1.972	0.938 5	0.012 6	0.345 0
2	g_1	1.955	−0.017 4	0.999 8	−0.010 9
	g_2	1.959	0.331 3	0.016 1	0.943 4
	g_3	1.972	−0.943 4	−0.012 8	0.331 5
		Mo–O(1)	−0.282 0	−0.956 1	0.082 7
		Mo–S(1)	0.966 5	−0.065 5	0.249 0
Normal to Mo, O(1), S(1), Cl(1) plane			−0.267 6	0.214 1	0.939 4

* With respect to the crystal axes.

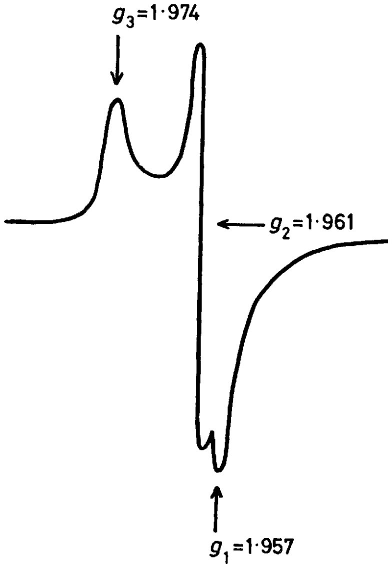

FIGURE 3 Powder e.s.r. spectrum of $[MoCl_3O(SPPh_3)]$

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molecule. In the simplest case, relating the principal molecular g value directions to the bond axes, g_1 is inclined at 17.1(1.3)° to Mo–O and at 86.2(0.9)° to Mo–S, g_3 makes angles of 6.4(0.7) and 103.7(0.8)° with Mo–S and Mo–O respectively, and g_2 subtends an angle of 12.9(1.0)° with the normal to the Mo,O(1),S(1),Cl(1) plane. The displacement of the directions of the principal molecular g values from the metal–ligand axes originates in the extensive d-orbital mixing allowed by the low-symmetry ligand field in this complex.

In contrast to the systems $[AsPh_4][MoCl_4O]$,[10] $[AsPh_4][MoCl_4O(OH_2)]$,[13] $[AsPh_4]_2[MoCl_5O]$,[15] $[AsPh_4][MoBr_4O(OH_2)]$,[15] and $[MoCl_3O\{P(NMe_2)_3O\}_2]$,[14] the largest g value of $[MoCl_3O(SPPh_3)]$ does not lie along or close to the Mo–O bond axis. This illustrates the caution which should be exercised when assigning g values, obtained from powder or frozen-glass spectra, to particular molecular directions. In the present case, although the g values deduced from the powder spectrum (Figure 3) are in good agreement with those obtained from the single-crystal study, a comparison with the single-crystal results for the other halogeno-complexes would have led us to place the largest g value along or close to the Mo–O direction. Such a misassignment could have serious consequences when attempting to relate e.s.r. parameters to the electronic structure of a particular molecule.

A detailed quantitative interpretation of the g values in terms of the electronic structure of $[MoCl_3O(SPPh_3)]$ is not possible, not only for the reasons discussed previously [9,10] for $[CrCl_4O]^-$ and $[MoCl_4O]^-$ but also because of the additional complications introduced by the low-symmetry ligand field.

For the following discussion it is assumed that the principal molecular g values *do* lie closest to the bond directions. The expressions [9] (see Appendix) for the principal molecular g values of square-pyramidal, $[MOX_4]$, d^1 complexes lead to the suggestion that at least three factors may contribute to the sense of the g-value anisotropy in the complex $[MoCl_3O(SPPh_3)]$: (*i*) the removal of the degeneracy of the metal $4d_{xz}$ and $4d_{yz}$ orbitals by the low-symmetry ligand field; (*ii*) the differences in the magnitude of the ligand spin–orbit coupling constants; and (*iii*) differences in metal–ligand covalency. With respect to (*i*), the anisotropy in the plane perpendicular to the oxo-group (g_2 *versus* g_3) could arise from a significant splitting of the $d_{xy} \rightarrow d_{xz},d_{yz}$ one-electron promotion energies. If the anisotropy observed for these g values is due entirely to this effect, then the ratio of these two transition energies should be 1.43 : 1. This ratio is in reasonable agreement with that obtained (*ca.* 1.50 : 1) for the two lowest transitions observed for $[MoCl_3O(SPPh_3)]$. However, since these spectral features are typical of those observed [7,14] for a range of other oxomolybdenum(V) complexes, the assignment of these features to a splitting of the $b_2^* \rightarrow e^*$ transition is not likely. (*ii*) The spin–orbit coupling constant [31] of sulphur (382 cm^{-1}) is significantly smaller than that of chlorine (586 cm^{-1}) and the sense of this difference would tend to make the g value closest to the Mo–S direction ($g_3 \sim g_y$) larger than the other g value ($g_2 \sim g_x$) in the plane perpendicular to the oxo-group. (*iii*) A similar prediction concerning the relative magnitudes of these two g values follows from metal–ligand covalency arguments. Thus, for relatively small amounts of covalency, as the ligand contributions to the metal–ligand antibonding orbitals increase, the terms in $(N')^2$ decrease numerically more than the terms in $\gamma\delta$, $\delta\omega$ . . ., *etc.* increase. In the present case, the experimental values of $g_x(\sim g_2)$ and $g_y(\sim g_3)$ imply that overall there is a greater degree of covalency in the π(donor) bonding associated with the ligands near to the y axis (Cl and $SPPh_3$) compared to those along the x axis. Such a view is consistent with the longer Mo–O distance in $[MoCl_3O(SPPh_3)]$, as compared to that [10] in $[MoCl_4O]^-$. It is, however, noted that g_1 for $[MoCl_3O(SPPh_3)]$, which approximately corresponds to $g_\parallel$ in a square-pyramidal complex, has a numerical value similar to that (1.967) of $g_\parallel$ for $[AsPh_4][MoCl_4O]$,[10] suggesting that the in-plane (σ) bonding effects of 3Cl and S are not very different from those of 4Cl atoms.

APPENDIX

The g-value expressions [9] for a square-pyrimidal, $[MOX_4]$, d^1 chromophore may be modified to be appropriate to the corresponding $[MoCl_3OS]$ moiety at the simplest level by recognising that: (*a*) different molecular-orbital (m.o.) coefficients are involved for Mo–Cl and Mo–S bonding, and (*b*) the degeneracy of the $e(d_{xz},d_{yz})$ level will be removed. To illustrate the arguments given in the text only $g_\perp(g_x \neq g_y)$ will be considered and, for simplification, the second-order term in these g-value expressions [11] is neglected.

The relevant antibonding m.o. expressions (A1)—(A3) may be written, whence we obtain (A4) and (A5). The

$$b_2^* = N_3'[d_{xy} - \delta(x_1 + y_2 + y_4) - \delta_5 x_5] \quad \text{(A1)}$$

$$e_1^* = N_4'[d_{xz} - \gamma(y_1 + x_4) - \gamma_3 x_3] \quad \text{(A2)}$$

$$e_2^* = N_5'[d_{yz} - \omega x_2 - \omega_5 x_5 - \omega_3 x_3] \quad \text{(A3)}$$

$$g_x = 2.0023 - [(N_3')^2(N_4')^2(4 + 8\gamma\delta)(\xi_{Mo} + 2\xi_{Cl}\delta\gamma)/2E(b_2^* \rightarrow e_1^*)] \quad \text{(A4)}$$

$$g_y = 2.0023 - [(N_3')(N_5')^2(4 + 4\delta\omega + 4\delta_5\omega_5)(\xi_{Mo} + \xi_{Cl}\delta\omega + \xi_S\delta_5\omega_5)/2E(b_2^* \rightarrow e_2^*)] \quad \text{(A5)}$$

S atom is in the 5 position, on the y axis, and ξ_{Mo}, ξ_{Cl}, and ξ_S represent the single-electron spin–orbit coupling constants for an electron in a molybdenum $4d$, chlorine $3p$, and sulphur $3p$ orbital, respectively.

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