Crystal and Molecular Structure and Electron Spin Resonance Spectrum of Trichloro-oxobis(triphenylphosphine oxide)molybdenum(V)

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Monoclinic crystals of the title complex belong to space group $P2_1/c$, and have unit-cell dimensions of a = 18.977(5), b = 16.860(5), c = 22.099(6) Å, β = 96.50(5), and Z = 8. The crystal structure has been solved by direct methods using 3 286 statistically significant reflections from diffractometer measurements. Atomic parameters have been refined by full-matrix least-squares calculations to R 0.067. One of the two crystallographically independent $[MoOCl_3(PPh_3O)_2]$ molecules in the asymmetric unit is disordered over two orientations. Bond lengths at the octahedrally co-ordinated molybdenum atom in the ordered complex molecule are: Mo–O 1.662(13), Mo–O(PPh_3O) 2.136(11) (*trans* to Mo–O), 2.065(10) (*trans* to Mo–Cl), and Mo–Cl 2.348(5)—2.386(5) Å. Single-crystal e.s.r. spectra at room temperature give the following molecular values: g_1 = 1.929 ± 0.002, g_2 = 1.935 ± 0.002, and g_3 = 1.950 ± 0.002. The orientations of these values are different to those found for $[MoOCl_3\{P(NMe_2)_3O\}_2]$ in that g_3 is closest to the Cl–Mo–Cl direction in $[MoOCl_3(PPh_3O)_2]$, whereas g_2 is closest to this direction in $[MoOCl_3\{P(NMe_2)_3O\}_2]$. The molecular g tensors for these two systems are compared qualitatively on the basis of the ligand-field strengths of the various ligands concerned.

As part of an integrated study of the molecular and electronic structures and reactivity of mononuclear molybdenum(V) complexes we have previously reported appropriate data for $[MoOCl_3\{P(NMe_2)_3O\}_2]$,[1-3] but only reactivity data for $[MoOCl_3(PPh_3O)_2]$.[1,4] Different kinetic parameters and equilibrium constants were found for corresponding substitution reactions involving these two complexes. In addition, two possible orientations for the molecular g values in $[MoOCl_3\{P(NMe_2)_3O\}_2]$ were reported. In order to provide additional information on the above properties we now report the single-crystal structure and e.s.r. properties of the chemically similar $[MoOCl_3(PPh_3O)_2]$ complex.

EXPERIMENTAL

Preparation.—The complex $[MoOCl_3(PPh_3O)_2]$ was prepared according to the method of Tyree and Horner,[5] and crystals were grown under dry dinitrogen from dry CH_2Cl_2 (Found: C, 55.8; H, 3.9; Cl, 13.8; Mo, 12.6; P, 8.1. Calc. for $C_{36}H_{30}Cl_3MoO_3P_2$: C, 55.8; H, 3.9; Cl, 13.7; Mo, 12.4; P, 8.1%).

Crystal Data.—$C_{36}H_{30}Cl_3MoO_3P_2$, M = 774.9, Monoclinic, a = 18.977(5), b = 16.860(5), c = 22.099(6) Å, β = 96.50(5)°, U = 7 025.2 Å^3, D_m (flotation) = 1.47 g cm^{-3}, Z = 8, D_c = 1.465 g cm^{-3}, $F(000)$ = 3 144, Cu-K_α radiation, λ = 1.541 8 Å, μ(Cu-K_α) = 64.2 cm^{-1}, space group $P2_1/$ (C^5_{2h}) uniquely from the systematic absences $h0l$ when $l \neq 2n$, and $0k0$ when $k \neq 2n$.

Crystallographic Measurements.—Preliminary unit-cell dimensions and space-group information were obtained from oscillation and Weissenberg photographs taken with Cu-K_α radiation, and from precession photographs taken with Mo-K_α radiation (λ 0.710 7 Å). For intensity measurements a crystal of dimensions *ca.* 0.20 × 0.30 × 0.40 mm was placed in a thin-walled glass capillary and orientated to rotate with its b axis parallel to the ϕ axis of an Enraf–Nonius CAD 3 diffractometer (Ni-filtered Cu-K_α radiation, 3° take-off angle). Refined unit-cell parameters were obtained by least-squares treatment of the θ, χ, and ϕ angles for 48 reflections widely separated in reciprocal space. All the unique data in the range $4 < \theta < 67°$ were measured by use of the θ—2θ scanning technique with scanwidths (1.20 + 0.50 tanθ)°. Background measurements were taken at each end of the scan for times equal to half the duration of the scan. Crystal and instrument stability were monitored throughout by remeasuring the intensity of a standard reflection after each batch of 99 measurements; no significant variation was noted. From a total of *ca.* 13 000 independent measurements only 3 286 for which $I > 2.0\ \sigma(I)$, where I = (scan count + total background count)$^{\frac{1}{2}}$, were corrected for the usual Lorentz and polarization effects and used in the structure analysis and refinement. Absorption corrections, established from the ϕ dependence of the intensity of the 080 reflection measured at χ 90°, were also applied to these data.

Structure Analysis.—Initial positions for the two crystallographically independent molybdenum atoms, derived from the three-dimensional Patterson map, were found to be related by an approximate centre of symmetry at $x = \frac{1}{4}$, $y = 0$, $z = \frac{3}{8}$, and in addition their y co-ordinates were $\pm\frac{1}{4}$. As a result of the pseudo-symmetry which was consequently introduced into the molybdenum-phased F_o Fourier map, it was not possible to derive co-ordinates for a satisfactory partial structure model. A partial structure was, however, obtained by application of MULTAN[6] to the highest 255 $|E|$ values, previously scaled to ensure that $\langle E^2 \rangle = 1$ for both the $l = 2n$ and $l = 2n + 1$ parity groups since reflections in the latter were systematically weak. In addition to confirming the positions of the molybdenum atoms, the E map calculated by use of that set of phase constants which produced the lowest residual and highest figure of merit yielded positions for five chlorine, three phosphorus, and four oxygen atoms. When structure factors were calculated for this group of atoms R was 0.42. Positions for the remaining non-hydrogen atoms were determined from two subsequent F_o Fourier syntheses.

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[1] P. M. Boorman, C. D. Garner, and F. E. Mabbs, *J.C.S. Dalton*, 1975, 1299.

[2] C. D. Garner, P. Lambert, F. E. Mabbs, and T. J. King, *J.C.S. Dalton*, 1977, 1191.

[3] C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J.C.S. Dalton*, 1977, 1198.

[4] C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J.C.S. Dalton*, 1975, 1175, 1180.

[5] S. Y. Tyree and S. M. Horner, *Inorg. Chem.*, 1962, **1**, 122.

[6] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) for the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z
Mo	4 123.6(7)	2 254.6(8)	3 274.7(6)
Cl(1)	3 223(3)	1 314(3)	2 959(2)
Cl(2)	4 119(3)	1 870(3)	4 295(2)
Cl(3)	4 872(3)	3 357(3)	3 573(2)
P(1)	2 751(2)	3 682(3)	3 523(2)
P(2)	4 007(2)	2 678(3)	1 755(2)
O(1)	3 259(6)	3 013(7)	3 424(5)
O(2)	3 948(5)	2 775(6)	2 425(5)
O(3)	4 794(7)	1 684(7)	3 118(6)
Mo′	9 479.2(8)	2 496.8(10)	1 054.2(7)
Cl′(1)	8 749(3)	1 413(3)	1 282(2)
ClO′(2)	10 132(5)	2 508(5)	1 938(4)
Cl′(3)	10 047(3)	3 690(3)	788(3)
P′(1)	8 263(3)	3 905(3)	1 571(2)
P′(2)	8 373(2)	2 460(3)	−363(2)
O′(1)	8 692(6)	3 220(7)	1 379(5)
O′(2)	8 800(6)	2 602(8)	235(4)
OCl′(3)	10 151(5)	1 770(6)	649(4)
C(A1)	3 138(9)	4 348(10)	4 089(8)
C(A2)	2 858(11)	5 114(13)	4 149(10)
C(A3)	3 177(13)	5 577(14)	4 631(11)
C(A4)	3 731(14)	5 305(15)	5 036(11)
C(A5)	3 958(12)	4 585(13)	4 986(10)
C(A6)	3 672(11)	4 073(12)	4 522(9)
C(B1)	1 956(9)	3 305(11)	3 747(8)
C(B2)	1 785(11)	2 512(13)	3 660(9)
C(B3)	1 168(14)	2 168(16)	3 861(12)
C(B4)	719(12)	2 687(14)	4 089(11)
C(B5)	867(12)	3 462(14)	4 198(10)
C(B6)	1 487(11)	3 780(12)	4 016(9)
C(C1)	2 526(10)	4 239(11)	2 836(9)
C(C2)	3 045(11)	4 591(13)	2 576(10)
C(C3)	2 913(12)	5 016(14)	2 006(10)
C(C4)	2 263(13)	4 977(14)	1 738(11)
C(C5)	1 728(14)	4 650(16)	1 974(12)
C(C6)	1 852(11)	4 203(12)	2 519(10)
C(D1)	3 180(7)	2 565(9)	1 341(6)
C(D2)	3 093(10)	2 300(13)	746(9)
C(D3)	2 418(11)	2 292(14)	374(10)
C(D4)	1 846(11)	2 459(13)	671(10)
C(D5)	1 894(11)	2 721(13)	1 247(9)
C(D6)	2 559(11)	2 738(13)	1 596(9)
C(E1)	4 445(9)	3 556(10)	1 522(8)
C(E2)	4 750(10)	4 066(11)	1 940(8)
C(E3)	5 094(12)	4 743(13)	1 745(10)
C(E4)	5 110(13)	4 896(14)	1 118(11)
C(E5)	4 822(12)	4 370(13)	722(10)
C(E6)	4 479(11)	3 671(12)	894(9)
C(F1)	4 512(9)	1 833(10)	1 601(8)
C(F2)	5 201(12)	1 911(13)	1 481(10)
C(F3)	5 582(14)	1 217(15)	1 368(12)
C(F4)	5 300(12)	495(13)	1 428(10)
C(F5)	4 617(11)	416(12)	1 573(9)
C(F6)	4 233(10)	1 101(11)	1 644(8)
C(A′1)	8 794(10)	4 514(11)	2 108(8)
C(A′2)	8 584(11)	5 290(12)	2 188(9)
C(A′3)	8 938(12)	5 746(14)	2 656(11)
C(A′4)	9 493(11)	5 415(13)	3 008(10)
C(A′5)	9 716(13)	4 707(14)	2 926(11)
C(A′6)	9 333(11)	4 223(13)	2 491(10)
C(B′1)	7 558(10)	3 520(11)	1 947(8)
C(B′2)	7 444(11)	2 740(13)	1 982(9)
C(B′3)	6 929(12)	2 395(14)	2 306(10)
C(B′4)	6 504(11)	2 895(13)	2 564(10)
C(B′5)	6 562(13)	3 659(15)	2 547(11)
C(B′6)	7 077(12)	4 000(14)	2 235(10)
C(C′1)	7 940(9)	4 510(10)	935(8)
C(C′2)	8 430(13)	4 857(15)	597(11)
C(C′3)	8 173(12)	5 314(14)	77(11)
C(C′4)	7 502(14)	5 481(16)	−31(12)
C(C′5)	7 018(14)	5 163(16)	262(12)
C(C′6)	7 243(12)	4 686(14)	803(10)
C(D′1)	7 473(8)	2 796(10)	−340(7)
C(D′2)	7 099(11)	3 075(12)	−843(10)
C(D′3)	6 367(13)	3 242(15)	−853(12)
C(D′4)	6 100(13)	3 147(15)	−306(12)
C(D′5)	6 469(13)	2 909(15)	216(11)
C(D′6)	7 195(10)	2 738(12)	202(9)
C(E′1)	8 771(9)	2 991(10)	−921(8)
C(E′2)	8 691(11)	2 703(13)	—1 565(9)
C(E′3)	9 029(11)	3 109(12)	−2 000(9)
C(E′4)	9 410(11)	3 744(13)	−1 793(10)
C(E′5)	9 479(11)	4 058(12)	−1 234(9)
C(E′6)	9 152(10)	3 657(11)	−796(9)
C(F′1)	8 320(11)	1 440(13)	−550(10)
C(F′2)	7 736(14)	1 141(16)	−918(12)
C(F′3)	7 733(15)	307(17)	—1 090(13)
C(F′4)	8 245(14)	−125(16)	−843(12)
C)F′5)	8 817(16)	122(18)	−536(13)
C(F′6)	8 863(13)	934(15)	−350(11)

The structure model was then refined to R 0.105 by several cycles of full-matrix least-squares calculations, at first with isotropic temperature factors for all the atoms, and later with anisotropic temperature factors for Mo, Cl, P, and O. During these refinement cycles the temperature factor for one of the chlorine atoms bonded to Mo′ became abnormally high while that for the terminal oxygen atom bonded to this same atom became correspondingly low. Moreover, evaluation of bond lengths showed that these two atoms were approximately equidistant from the molybdenum. It was therefore apparent that this chlorine and oxygen atom were disordered over these two sites with *ca.* 50% population in each and so an average scattering factor $(f_{\mathrm{Cl}} + f_{\mathrm{O}})/2$ was employed for each of these atoms in all the subsequent calculations. A difference map at R 0.105 showed no unusual features and served to confirm that most of the positions calculated for the hydrogen atoms coincided with regions of low positive electron density. Fixed hydrogen-atom contributions were included in subsequent rounds of least-squares refinement of the non-hydrogen-atom parameters which converged at R 0.067.

Final atomic positional parameters for the non-hydrogen atoms are in Table 1. Calculated hydrogen-atom positions and thermal parameters, observed and calculated structure amplitudes, inter-bond distances and angles, and least-square planes are available as Supplementary Publication No. SUP 22353 (34 pp.).* For all the structure-factor calculations, neutral-atom scattering factors for the non-hydrogen atoms were from ref. 7, with those of Mo, Cl, and P corrected for anomalous-dispersion effects; [8] for hydrogen that from ref. 9 was used. In the least-squares calculations $\Sigma w\Delta^2$ was minimized, with weights w assigned according to the scheme, $w^{\frac{1}{2}} = 1$ for $|F_o| < 169.0$ and $w^{\frac{1}{2}} = 169.0/|F_o|$ for $|F_o| > 169.0$, and this appeared satisfactory when $<w\Delta^2>$ was analyzed in ranges of $|F_o|$.

Spectra.—Room-temperature e.s.r. spectra were recorded as previously described [10] on single crystals of $[\mathrm{MoOCl_3(PPh_3O)_2}]$. These crystals were mounted such that the magnetic field could be orientated in the crystallographic *ab*, *bc**, and *ac** planes. Electronic-absorption spectra

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

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

were recorded as described previously[11] for [MoOCl$_3$(PPh$_3$O)$_2$] dissolved in CH$_2$Cl$_2$ at room temperature, and, using unpolarized incident radiation, on suitably thinned crystals at room temperature and 5 K.

RESULTS AND DISCUSSION

The asymmetric crystal unit comprises two discrete monomeric [MoOCl$_3$(PPh$_3$O)$_2$] complex molecules. One of these molecules is disordered over two orientations as a consequence of the large difference between the spatial demands of the bulky triphenylphosphine oxide ligands which contrast with those of the much smaller, more equal, oxygen and chlorine ligands. Molecules which have this type of ligand distribution and which are held together in the solid state by only weak intermolecular forces lend themselves well to structural disorder, *e.g.* in crystals of the non-isomorphous [WSCl$_3$(PPh$_3$O)$_2$] complex[12] the molecules are also disordered over two orientations which in this case are related by a crystallographic two-fold axis of space group *C*2/*c*. The geometries of the individual molecules and their atom-numbering schemes are shown in Figure 1; interatomic distances and angles at the Mo, O, and P atoms are listed in Table 2. The packing arrangement in the crystal is illustrated in Figure 2; all of the shorter intermolecular separations correspond to weak van der Waals type interactions.

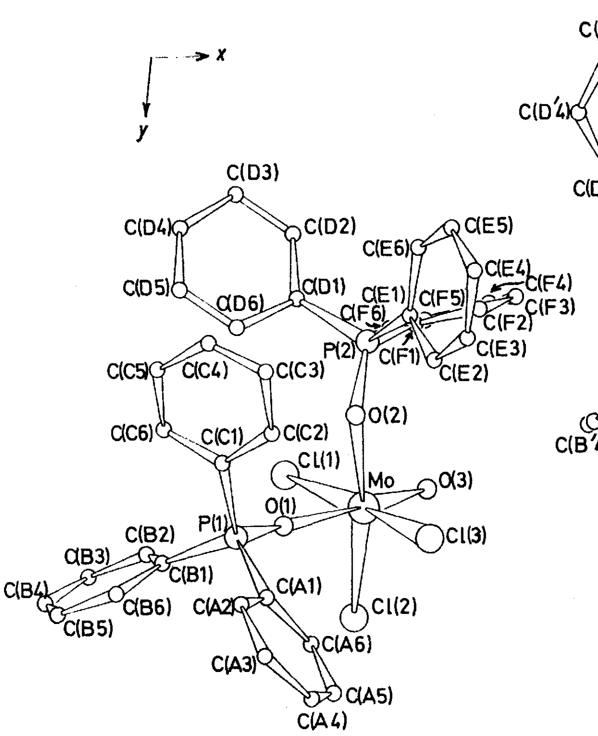

FIGURE 1 Atom-numbering scheme in the two crystallographically independent [MoOCl$_3$(PPh$_3$O)$_2$] molecules; ClO′ (2) and OCl′ (3) denote 50% site occupation by O and Cl in the disordered (primed) molecule

Since one of the molecules is disordered, the discussion of the bonding and molecular geometry will deal initially with the parameters derived for the ordered (unprimed) molecule, and the result of disordering on this geometry will be considered subsequently with regard to the corresponding parameters in the disordered (primed) molecule.

Ordered Molecule.—The molybdenum atom is in a distorted octahedral environment in which one of the mutually *cis* PPh$_3$O oxygen atoms lies *trans* to a multiply bonded oxygen atom. Distortions from regular octahedral geometry are controlled by ligand $\cdots$ ligand repulsions and the *trans* influence of the ligands.

The mean of the mutually *trans* Mo–Cl distances [2.383(5) Å] agrees very well with the means for similar bonds at six-co-ordinate molybdenum in other recent studies, *e.g.* 2.383(2) in [MoOCl$_3$\{P(NMe$_2$)$_3$O\}$_2$],[2] 2.372(6) in MoCl$_5$O,[2-13] 2.368(12) in [MoOCl$_4$\{OP(OMe)$_2$\}]$^{n-}$,[14] and 2.359(3) Å in [MoOCl$_4$(OH$_2$)]$^-$.[15] A slightly shorter distance [2.348(5) Å] occurs with the Mo–Cl bond which lies *trans* to the PPh$_3$O ligand. This bond length

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[11] D. L. McFadden, A. T. McPhail, C. D. Garner, and F. E. Mabbs, *J.C.S. Dalton*, 1975, 263.

[12] A. T. McPhail and K. D. Onan, unpublished work.

[13] D. L. McFadden and A. T. McPhail, unpublished work.

[14] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1975, 1984.

[15] C. D. Garner, L. H. Hill, F. E. Mabbs, D. L. McFadden, and A. T. McPhail, *J.C.S. Dalton*, 1977, 1202.

is similar to the corresponding one [2.353(2) Å] in [$MoOCl_3\{P(NMe_2)_3O\}_2$].[2]

The very short Mo–O multiple bond length [1.662(13) Å] does not differ significantly from the corresponding distances of 1.685(5) in [$MoOCl_3\{P(NMe_2)_3O\}_2$],[2] 1.672(15) in [$MoOCl_4(OH_2)$]$^-$,[15] 1.668(5) in [$MoO(OH_2)(CN)_4$]$^{2-}$,[16] and 1.677(5) and 1.686(13) Å in [Mo_6O_{19}]$^{2-}$.[17,18] This disparity between the two Mo–O distances, 2.136(11) *trans* to O(3) and 2.065(10) Å *trans* to Cl(2), reflects the greater *trans*-weakening influence of the multiply bonded oxygen atom. These dimensions are again very similar to those found in [$MoOCl_3\{P(NMe_2)_3O\}_2$].[2] Thus, overall, the bond lengths and angles in the first co-ordination sphere of the molybdenum show no significant differences from those in [$MoOCl_3\{P(NMe_2)_3O\}_2$].

TABLE 2

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

(*a*) Molybdenum co-ordination sphere

	Unprimed	Primed
Mo–Cl(1)	2.378(5)	2.382(6)
Mo–Cl(2) [a]	2.348(5)	2.191(8)
Mo–Cl(3)	2.386(5)	2.387(6)
Mo–O(1)	2.136(11)	2.115(12)
Mo–O(2)	2.065(10)	2.107(10)
Mo–O(3) [b]	1.662(13)	2.047(10)
Cl(1)–Mo–Cl(2) [a]	91.0(2)	95.9(3)
Cl(1)–Mo–Cl(3)	170.5(2)	171.3(2)
Cl(1)–Mo–O(1)	84.6(3)	85.4(3)
Cl(1)–Mo–O(2)	88.8(3)	86.1(4)
Cl(1)–Mo–O(3) [b]	95.4(4)	92.3(3)
Cl(2) [a]–Mo–Cl(3)	90.9(2)	89.3(3)
Cl(2) [a]–Mo–O(1)	86.0(3)	92.4(4)
Cl(2) [a]–Mo–O(2)	166.7(3)	173.6(4)
Cl(2) [a]–Mo–O(3) [b]	97.2(5)	94.5(3)
Cl(3)–Mo–O(1)	86.3(3)	87.4(3)
Cl(3)–Mo–O(2)	87.2(3)	88.1(4)
Cl(3)–Mo–O(3) [b]	93.6(4)	94.3(3)
O(1)–Mo–O(2)	80.7(4)	81.7(4)
O(1)–Mo–O(3) [b]	176.7(5)	172.9(4)
O(2)–Mo–O(3) [b]	96.1(5)	91.5(4)

(*b*) At the oxygen and phosphorus atoms

	Unprimed	Primed
P(1)–O(1)	1.515(12)	1.501(12)
P(1)–C(A1)	1.776(18)	1.791(19)
P(1)–C(B1)	1.759(18)	1.775(19)
P(1)–C(Cl)	1.795(19)	1.788(18)
P(2)–O(2)	1.506(12)	1.490(11)
P(2)–C(D1)	1.736(15)	1.805(16)
P(2)–C(E1)	1.801(18)	1.762(18)
P(2)–C(F1)	1.772(18)	1.771(22)
Mo–O(1)–P(1)	168.6(7)	164.9(8)
Mo–O(2)–P(2)	145.6(7)	165.3(8)
O(1)–P(1)–C(A1)	110.7(7)	110.3(8)
O(1)–P(1)–C(B1)	110.5(8)	108.2(8)
O(1)–P(1)–C(C1)	111.2(8)	111.5(8)
C(A1)–P(1)–C(B1)	109.2(8)	107.2(9)
C(A1)–P(1)–C(C1)	107.8(9)	108.1(8)
C(B1)–P(1)–C(C1)	107.3(9)	111.5(8)
O(2)–P(2)–C(D1)	111.5(7)	110.2(7)
O(2)–P(2)–C(E1)	106.3(7)	107.8(8)
O(2)–P(2)–C(F1)	112.2(7)	112.2(9)
C(D1)–P(2)–C(E1)	110.1(8)	110.1(8)
C(D1)–P(2)–C(F1)	106.7(8)	106.4(9)
C(E1)–P(2)–C(F1)	109.2(8)	110.1(9)

[a] ClO′ (2) in the primed molecule. [b] OCl′ (3) in the primed molecule.

In accord with conclusions derived from previous studies of six-co-ordinate complexes,[15,19] the valency angles subtended at the molybdenum atom appear to be determined principally by the effects of ligand · · · ligand repulsions. Thus, all the four angles between the multiply bonded oxygen atom O(3) and the *cis* PPh_3O oxygen atom O(2) and three chlorine atoms exceed 90°.

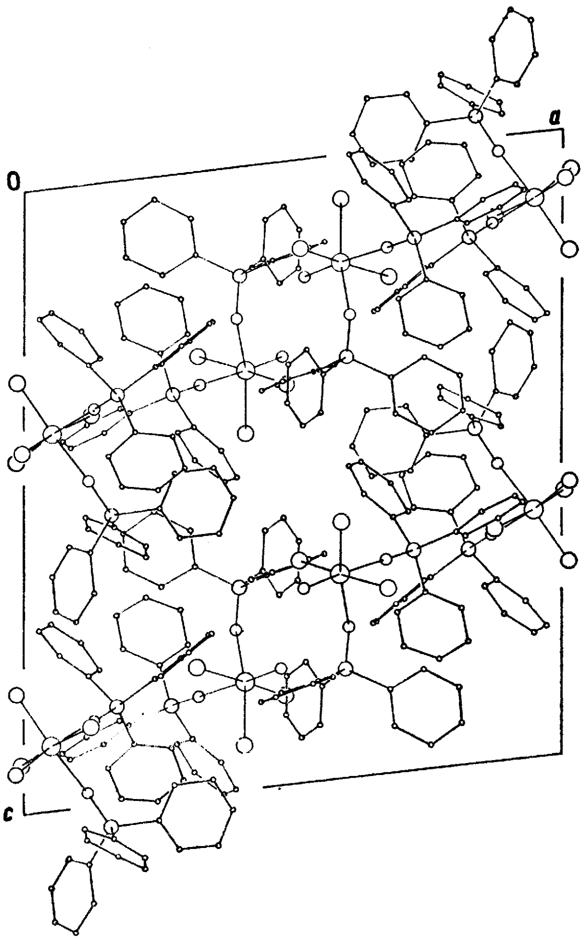

FIGURE 2 Packing of [$MoOCl_3(PPh_3O)_2$] molecules in the crystal, viewed in projection along the *b* axis

The net result of these departures from orthogonality is to nearly equalize all the *cis* ligand · · · ligand O · · · Cl (2.99—3.12 Å) and O · · · O (2.72 and 2.78 Å) distances.

Interbond distances and angles in the phenyl rings and equations of least-squares planes through several groups of atoms and displacements of selected atoms from these planes are deposited in SUP 22353. The PPh_3O ligands exhibit no unusual features. The mean C–C distance in the phenyl rings is 1.38 Å, the atoms in each ring are approximately coplanar, and typically small variations in out-of-plane phosphorus displacements (Δ 0.017—0.134 Å) occur. Individual P–C lengths vary from

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1.736(15) to 1.801(18) Å and lie close to those found in other complexes.[20,21] The equality in the P–O bond lengths [1.515(12) and 1.506(12) Å] indicates their insensitivity to the different Mo–O bond lengths. The mean of the two distances [1.511(12) Å] is in good agreement with those of 1.498(6) in $[MoOCl_3\{P(NMe_2)_3O\}_2]$,[2] 1.523(8) in $[W(CO)_5(OPh_2PCHPPh_3)]$,[22] and 1.492(4) Å in $[CuCl_2(PPh_3O)_2]$,[21] and, not unexpectedly, is slightly elongated over that of 1.46(1) Å in the free ligand [23] as a consequence of co-ordination.

The Mo–O–P angles [145.6(7) and 168.6(7)°] clearly differ by a highly significant amount. Although the corresponding Mo–O distances [2.065(10) and 2.136(11) Å] are also unequal owing to the different nature of their *trans* ligands (see above), the equality in the P–O distances militates against electronic factors being responsible for these valency-angle variations. In addition, when the results of the present study are considered together with those from other structural investigations on like complexes, no simple correlation between bond length and valency angle is noted, *e.g.* in $[MoOCl_4\{OP(OMe)_3\}]^{n-}$,[14] the Mo–O–P angle of 147.1(12)° is associated with a Mo–O bond length of 2.179(18) Å, while corresponding values in $[W(CO)_5(OPh_2PCHPPh_3)]$ [22] are 137.1(4)° and 2.200(7) Å. Accordingly, it may be concluded that the M–O–P angles in such systems are easily deformable. The value found in any particular complex in solutions of non-interacting solvents will therefore be governed by intramolecular ligand ··· ligand steric interactions but, in the solid state, crystal-packing forces may also contribute significantly to the observed values.

Disordered Molecule.—This molecule is disordered over two orientations which are related not by any space-group symmetry but by a pseudo-C_2 axis which passes through the midpoints of the O(1) ··· O(2) and O(3) ··· Cl(2) edges of the co-ordination octahedron. The effect of this C_2 symmetry operation is to leave unaltered the pair of mutually *trans* Mo–Cl distances and to equalize the observed *cis* Mo–O(PPh$_3$O) distances [2.107(10) and 2.115(12) Å]. In addition, the *cis* Mo–O(3) and Mo–Cl(2) distances [2.047(10) and 2.191(8) Å] tend towards the mean of these two bond lengths in the ordered molecule. Although the mean of the latter pair of distances in the disordered molecule (2.119 Å) lies close to the weighted (8 : 17) mean of the Mo–O(3) and Mo–Cl(2) distances in the ordered molecule (2.129 Å), the difference between the individual distances possibly indicates a small departure from exactly 50% occupation of each site by the oxygen and chlorine atoms, *e.g.* 60 : 40 and 40 : 60% site occupations by O and Cl would yield distances of 2.064 and 2.184 Å. Whereas the Mo–O–P angles in this disordered molecule are equal [164.9(8) and 165.3(8) Å] in accord with the pseudo-two-fold symmetry, they differ significantly from the mean (157.1°) of the two values in the ordered molecule. This difference may be a reflection of crystal-packing effects. The PPh$_3$O ligands again show no unusual features.

Electronic-absorption Spectrum.—The electronic-absorption spectrum (see Table 3) in CH$_2$Cl$_2$ solution is almost identical to that reported [2] for $[MoOCl_3\{P(NMe_2)_3O\}_2]$ and consists of two distinct bands of equal intensity at 13 280 and 22 220 cm^{-1}, followed by a more intense band at 33 670 cm^{-1} which has a distinct shoulder at 28 990 cm^{-1}. Since we did not observe any polarization in the spectrum of single crystals of $[MoOCl_3(PPh_3O)_2]$ we report only the results of a study using unpolarized incident radiation. At room temperature the crystal spectrum consisted of two bands centred on 13 400 and 22 300 cm^{-1} followed by an absorption which was too intense to record. This spectrum compares well with the above solution spectrum, and the band positions are close to those observed [2] for single crystals of $[MoOCl_3\{P(NMe_2)_3O\}_2]$ (13 000 and 22 500 cm^{-1}). On cooling to 5 K the first band showed partly resolved features at 12 300, 13 100, and 14 000 cm^{-1} similar to those observed [2] in the much better resolved spectrum of $[MoOCl_3\{P(NMe_2)_3O\}_2]$. Although these splittings are larger than in the latter complex, we attribute them to vibrational fine structure superimposed on the $d_{xy}{}^* \rightarrow d_{xz}{}^*, d_{yz}{}^*$ excitation due to the coupling with the ν(Mo–O) stretching mode in the excited state. The second band system in the present complex showed no resolution on cooling but merely shifted to 22 500 cm^{-1}. This behaviour is very similar to that observed for $[MoOCl_3\{P(NMe_2)_3O\}_2]$.

TABLE 3

Electronic-absorption spectra for $[MoOCl_3(PPh_3O)_2]$. Absorption maxima in 10^3 cm^{-1}

Single crystal		
Room temperature	5 K	CH$_2$Cl$_2$ solution at room temperature
13.44	12.3 (sh)	13.28 (20) *
	13.10	
	14.0 (sh)	
22.27	22.46	22.22 (20)
		28.99 (sh) (*ca.* 1 400)
		33.67 (4 400)

* Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses.

E.S.R. Spectrum.—In the *ab* crystallographic plane, e.s.r. signals due to two magnetically distinct molecules were observed but in the *bc** and *ac** planes there were signals from only one type of molecule, although in some orientations the signals were slightly asymmetric. The peak–peak widths of the derivative spectra were in the range 50—90 G.* These observations are contrary to

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* Throughout the paper; 1 G = 10^{-4} T.

[20] See, for example, M. Ul-Haque, C. N. Caughlan, F. A. Hart, and R. Van Nice, *Inorg. Chem.*, 1971, **10**, 115; G. Bombieri, U. Croatto, E. Forsellini, B. Zarli, and R. Graziani, *J.C.S. Dalton*, 1972, 560; D. L. Kepert, D. Taylor, and A. H. White, *ibid.*, 1973, 1658.

[21] J. A. Bertrand and A. R. Kalyanaraman, *Inorg. Chim. Acta*, 1971, **5**, 341.

[22] S. F. Goldberg and K. N. Raymond, *Inorg. Chem.*, 1973, **12**, 2923.

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expectations because two crystallographically independent molecules in a monoclinic unit cell should give rise to four e.s.r. signals in each of the *ab* and *bc** planes and two signals in the *ac** plane. Presumably, the orientations of the molecules in the unit cell are such that the e.s.r. signals from the two crystallographically independent molecules are not resolvable under the conditions of measurement. Cooling the samples to 150 K did not improve the resolution. The data for the *g* resonances are recorded in Table 4. These data were treated according to the method of Schonland[24] and the results are given in Table 5. A comparison of the direction cosines of the principal molecular *g* values with those of metal–ligand directions show that, as in the case of $[MoOCl_3\{P(NMe_2)_3O\}_2]$, the principal molecular *g* values do not coincide with any metal–ligand directions. However, in the present system we find that the largest principal molecular *g* value (g_3) lies closest to the Cl–Mo–Cl direction in both the ordered and disordered molecule, although the individual angles between g_3 and the Mo–Cl directions are not the same for each type of molecule (see Table 5). These orientations are in contrast to those in $[MoOCl_3\{P(NMe_2)_3O\}_2]$ where g_3 is closest to the terminal Mo–O direction and g_2 closest to Cl–Mo–Cl.

TABLE 4

E.s.r. data for single crystals of $[MoOCl_3(PPh_3O)_2]$ (ν = 35 000 MHz)

	10 *H*/T			
	ab plane, $a = 0$			
θ/°	Molecule 1	Molecule 2	*bc* * plane, $b = 0$	*ac* * plane, $c^* = 0$
0	12.884	12.884	12.885	12.954
15	12.860	12.908	12.894	12.939
30	12.841	12.928	12.906	12.919
45	12.833	12.935	12.920	12.899
60	12.840	12.930	12.939	12.885
75	12.862	12.911	12.948	12.880
90	12.885	12.885	12.953	12.885
105	12.910	12.857	12.950	12.900
120	12.930	12.841	12.939	12.920
135	12.936	12.833	12.925	12.939
150	12.930	12.839	12.909	12.954
165	12.913	12.858	12.897	12.959
180	12.884	12.884	12.855	12.954

In order to ensure that there is a real difference in the relative orientation of the molecular *g* values in these two systems, we have calculated the expected angular variation of the e.s.r. spectrum of the ordered molecule in the $[MoOCl_3(PPh_3O)_2]$ system by superimposing the principal molecular *g* values and their associated directions found for $[MoOCl_3\{P(NMe_2)_3O\}_2]$ on to this molecule. This was done by defining molecular *x*, *y*, *z* axes in the following manner. In the ordered $[MoOCl_3(PPh_3O)_2]$ molecule the *z* axis was taken parallel to Mo–O(3), the *x* axis perpendicular to *z* and in the Mo–O(3)–Cl(3) plane, and *y* perpendicular to the Mo–O(3)–Cl(3) plane. The corresponding directions in $[MoOCl_3\{P(NMe_2)_3O\}_2]$ are *z* parallel to Mo–O(1), *x* perpendicular to *z* and in the Mo–O(1)–Cl(2) plane, and *y* perpendicular to the Mo–O(1)–Cl(2) plane. The calculated angular variations of the e.s.r. spectra, using each alternative set of $[MoOCl_3\{P(NMe_2)_3O\}_2]$ *g* values, are incompatible with those observed. A plot of one of the sets of calculated and experimental data is shown in Figure 3.

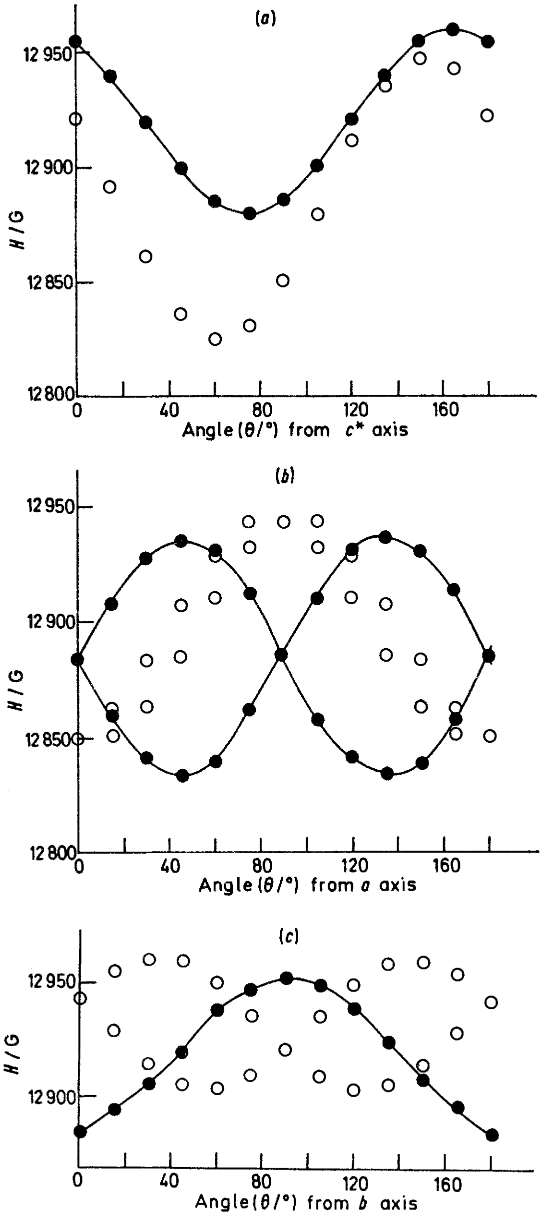

FIGURE 3 Calculated angular variation of the e.s.r. spectrum of the ordered $[MoOCl_3(PPh_3O)_2]$ molecule using the principal molecular *g* values and directions (alternative 1 in ref. 2) from $[MoOCl_3\{P(NMe_2)_3O\}_2]$: (○) calculated, (●) experimental; in the (*a*) *ac**, (*b*) *ab*, and (*c*) *bc** planes

Thus it appears that there is a real difference in the magnitudes and orientations of the molecular *g* values in these two systems despite their almost identical molecular structures.

To facilitate the comparison between $[MoOCl_3(PPh_3O)_2]$ and $[MoOCl_3\{P(NMe_2)_3O\}_2]$ the molecular *g*

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[24] D. S. Schonland, *Proc. Phys. Soc.*, 1959, **73**, 788.

tensors have been calculated with reference to the above molecular *x*, *y*, *z* axes. These tensors are:

$[MoOCl_3(PPh_3O)_2]$

Alternative 1

$$\begin{array}{cc} & \begin{array}{ccc} x & y & z \end{array} \\ \begin{array}{c} x \\ y \\ z \end{array} & \begin{pmatrix} 1.946 & 0.0018 & 0.0026 \\ 0.0018 & 1.932 & -0.0024 \\ 0.0026 & -0.0024 & 1.933 \end{pmatrix} \end{array}$$

Alternative 2

$$\begin{array}{cc} & \begin{array}{ccc} x & y & z \end{array} \\ \begin{array}{c} x \\ y \\ z \end{array} & \begin{pmatrix} 1.944 & 0.0051 & 0.0029 \\ 0.0051 & 1.931 & 0.0026 \\ 0.0029 & 0.0026 & 1.935 \end{pmatrix} \end{array}$$

$[MoOCl_3\{P(NMe_2)_3O\}_2]$

Alternative 1

$$\begin{array}{cc} & \begin{array}{ccc} x & y & z \end{array} \\ \begin{array}{c} x \\ y \\ z \end{array} & \begin{pmatrix} 1.935 & 0.0040 & 0.0071 \\ 0.0040 & 1.932 & 0.0083 \\ 0.0071 & 0.0083 & 1.943 \end{pmatrix} \end{array}$$

Alternative 2

$$\begin{array}{cc} & \begin{array}{ccc} x & y & z \end{array} \\ \begin{array}{c} x \\ y \\ z \end{array} & \begin{pmatrix} 1.934 & 0.0001 & 0.0080 \\ 0.0001 & 1.935 & 0.0089 \\ 0.0080 & 0.0089 & 1.944 \end{pmatrix} \end{array}$$

These tensors clearly show that, as far as the e.s.r. properties are concerned, there is no effective symmetry associated with either of these molecules. The non-zero off-diagonal elements have their origins in the intermixing of the metal *d* orbitals caused by the low-symmetry ligand field, and the subsequent mixing of excited states into the ground state by spin–orbit coupling. The forms of the tensors suggest that all the five metal *d* orbitals intermix to some extent. Thus the number of mixing parameters and the uncertainty of the assignment of the electronic-absorption spectra [2] make anything other than a qualitative interpretation of the e.s.r. data unrealistic at the present time.

TABLE 5

Magnitudes and direction cosines of principal molecular *g* values for $[MoOCl_3(PPh_3O)_2]$ at room temperature

		Alternative 1			Alternative 2		
		direction cosines with respect to			direction cosines with respect to		
	g value	*a*	*b*	*c* *	*a*	*b*	*c* *
g_1	1.929 ± 0.002	−0.3745	0.2060	0.9041	0.3956	−0.2603	0.8807
g_2	1.935 ± 0.002	0.6242	−0.6650	0.4101	0.6092	−0.6433	−0.4638
g_3	1.950 ± 0.002	0.6856	0.7179	0.1205	0.6873	0.7200	−0.0959

Angles between the principal molecular *g* values and selected metal–ligand directions in the ordered $[MoOCl_3(PPh_3O)_2]$ molecule

Molecular direction	g_1	g_2	g_3	g_1	g_2	g_3
Mo–Cl(1)	81.7	84.0	10.3	69.2	98.4	22.6
Mo–Cl(3)	101.4	86.9	168.2	105.2	73.5	157.3
Mo–Cl(2)	148.0	120.3	80.7	150.2	64.3	68.5
Mo–O(2)	45.0	46.4	98.9	21.7	96.3	110.6
Mo–O(1)	123.8	34.3	84.8	70.6	20.7	9.6
Mo–O(3)	53.0	142.4	95.7	106.2	161.6	98.3

The diagonal tensor elements for the two systems may be compared at a qualitative level if we assume that any metal *d*-orbital mixing makes only a small contribution to these terms. On this basis the smaller value of g_{zz} in $[MoOCl_3(PPh_3O)_2]$, compared with that in $[MoOCl_3\{P(NMe_2)_3O\}_2]$, is consistent with an overall weaker ligand-field strength perpendicular to the terminal Mo–O direction in this molecule. Support for this interpretation is provided by electronic-absorption spectral measurements on the vanadyl pentane-2,4-dionate system,[25] and kinetic [3,4] and equilibrium studies [1] which have previously been interpreted in terms of a higher donor strength for $P(NMe_2)_3O$ compared with PPh_3O. The magnitudes of g_{xx} and g_{yy}, which would be expected to be controlled primarily by the multiply bonded terminal Mo–O group,[26] would, in the absence of any other effects, be expected to be the same in both $[MoOCl_3\{P(NMe_2)_3O\}_2]$ and $[MoOCl_3(PPh_3O)_2]$, since they have almost identical Mo–O bond lengths. However, different anisotropies in g_{xx} and g_{yy} are observed in these two systems, and they are compatible with the relative ligand-field strengths $Cl^- \approx P(NMe_2)_3O < PPh_3O$. Although the above arguments provide a reasonably consistent qualitative rationalization of the e.s.r. data for $[MoOCl_3(PPh_3O)_2]$ and $[MoOCl_3\{P(NMe_2)_3O\}_2]$, the close similarity of the electronic-absorption spectra of these two systems does not confirm them. This may be because the necessary energy separation between the d_{xz}* and d_{yz}* orbitals, in the two systems, are obscured by the lack of resolution in the electronic spectra.

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