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X-Ray Crystal-structure Analysis and Magnetic and Spectral Properties of Tetrachlorotris[dichloro(methyl)phosphine]molybdenum(IV)–Carbon Disulphide (3/1)

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The title complex (1) is one product of the reaction between $MoCl_5$, $PMeCl_2$, and Bu^tCl. It can also be prepared by direct reaction between $MoCl_5$ and the phosphine. Crystals of (1) are trigonal, with unit-cell dimensions $a = b = 9.760(2)$, $c = 71.167(16)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $Z = 12$, and space group $R\bar{3}c$. The structure has been determined from *X*-ray diffractometer data by Patterson and Fourier syntheses, and refined by full-matrix least-squares calculations to *R* 0.061 for 726 observed reflections (3σ). The Mo and Cl(1) atoms lie on three-fold special positions and a CS_2 solvent molecule straddles a six-fold site, but with-two thirds occupancy. The Mo atom is seven-co-ordinate having capped-octahedral stereochemistry. Three Cl atoms occupy an uncapped face whilst the fourth caps a face occupied by the three P atoms. The magnetic properties of (1) are consistent with a strong-field, high delocalisation of the metal *d* electrons, and a low-symmetry ligand-field component. The Mo–Cl bond-stretching frequencies and a spin-forbidden electronic transition have been identified.

REACTIONS [1-4] between a metal halide, phosphorus(III) chloride [or dichloro(methyl)phosphine], and t-butyl chloride have led to complexes containing a cation (either $[PBu^tCl_3]^+$ or $[MePBu^tCl_2]^+$) and an anion containing the metal atom and halide only. For the reaction system $MoCl_5 + PMeCl_2 + Bu^tCl$ (solvent CS_2) at least two products are formed, one of which is the title complex, $[MoCl_4(PMeCl_2)_3]\cdot 0.33CS_2$.

EXPERIMENTAL

Preparation.—The crystals for the *X*-ray study were prepared as follows. A two-fold molar excess of dichloro(methyl)phosphine (2.60 g) was added to a solution of molybdenum(V) chloride (1.0 g) in carbon disulphide (100 cm³) in an argon atmosphere. The solvent was freshly distilled, dried (P_4O_{10}), and degassed. The solution immediately became dark green and large, dark green, hexagonal prisms formed over several hours. These were filtered off and dried under argon (Found: Cl, 57.5; Mo, 15.6; P, 15.1. $C_3H_9Cl_{10}MoP_3\cdot 0.33CS_2$ requires Cl, 57.75; Mo, 15.6; P, 15.1%).

The physical methods used were the same as those reported earlier.[3]

X-*Ray Crystal-structure Analysis*.—A crystal fragment of size *ca.* 0.5 × 0.5 × 0.4 mm sealed in a Lindeman glass tube was used for *X*-ray studies. A choice of space groups and preliminary unit-cell dimensions were determined from Weissenberg and precession photographs. Accurate unit-cell parameters were obtained from least-squares refinement of the 2θ values of 12 general reflections measured on a General Electric XRD-6 diffractometer.

Crystal data. $C_3H_9Cl_{10}MoP_3\cdot 0.33CS_2$, $M = 613.88$, Trigonal, $a = b = 9.760(2)$, $c = 71.167(16)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $U = 5\,870.4$ Å³, D_m (by flotation) 2.07 g cm⁻³, $Z = 12$, $D_c = 2.083$ g cm⁻³, $F(000) = 3\,560$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu(\text{Mo-}K_\alpha) = 22.64$ cm⁻¹, space groups $R3c$ (no. 161, C^6_{3v}) or $R\bar{3}c$ (no. 167, D^6_{3d}) from systematic absences $hkil$ for $-h + k + l \neq 3n$, $hh\bar{2}hl$ for $l \neq 3n$, and $h\bar{h}0l$ for $h + l \neq 3n$, $l \neq 2n$.

Data collection. The crystal was mounted with a^* parallel to the ϕ axis of a Datex automatic General Electric XRD-6 diffractometer. Of 1 544 independent reflections measured ($2\theta < 55°$), 726 with intensities $>3\sigma$ above background were considered observed and used for the structure determination. Zirconium-filtered Mo-K_α radiation was used and the θ—2θ scan method employed. The scan rate was 2° min⁻¹. The intensity of a standard reflection was monitored every 30 reflections and diminished by 5% during the course of data collection; this was used to scale the data to a common level. No absorption correction was made ($\mu R \simeq 0.5$).

Structure solution and refinement. Statistical treatment

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[1] J. I. Bullock, F. W. Parrett, and N. J. Taylor, *J.C.S. Dalton*, 1972, 1843.

[2] J. I. Bullock, F. W. Parrett, and N. J. Taylor, *J.C.S. Dalton*, 1973, 522.

[3] J. I. Bullock, F. W. Parrett, and N. J. Taylor, *Canad. J. Chem.*, 1974, **52**, 2880.

[4] J. I. Bullock, F. W. Parrett, and N. J. Taylor, *Inorg. Chem.*, 1976, **15**, 2003.

of the $|E|$ values suggested the centrosymmetric space group $R\bar{3}c$ to be correct and its choice was supported throughout the structure determination. With 12 molecules in the unit cell, the molybdenum atoms must lie on the three-fold special positions $0,0,\pm z$; $0,0,\frac{1}{2}\pm z$ or both general positions $0,0,0$; $0,0,\frac{1}{2}$ and $0,0,\frac{1}{4}$; $0,0,\frac{3}{4}$, the latter being unlikely from a consideration of the co-ordination characteristics of molybdenum and the amount of material in the cell. From a Patterson synthesis the molybdenum and one chlorine atom were placed, both in three-fold positions. A subsequent Fourier synthesis using these atoms suffered from false symmetry but, taken together with the Patterson map, all the remaining non-hydrogen atoms were located. Full-matrix least-squares refinement with all the atoms isotropic yielded R 0.132. A difference-Fourier synthesis indicated the presence of residual electron density on the c axis in the region of $z = 0.25$ and this was assigned to CS_2 with the carbon atom on the general position $0,0,\frac{1}{4}$. The magnitude of the peaks indicated partial occupancy and a value of two-thirds gave satisfactory results during subsequent refinement of the CS_2 parameters. Another cycle of isotropic refinement of all the atoms with a weighting scheme of the form $w = 1.0$ for $|F_o| < F^*$ and $w^{\frac{1}{2}} = F^*/|F_o|$ for $|F_o| \geqslant F^*$ with $F^* = 35.0$ gave R 0.097. Refinement was continued using anisotropic thermal parameters to yield, after three cycles, R 0.061. In the last cycle F^* was increased to 40.0 and no parameter shift was $>0.03\sigma$. A final difference Fourier did not resolve any hydrogen-atom positions; there was no residual electron density >0.65 e Å^{-3} other than in the vicinity of the heavy atom. The final positional parameters are given in Table 1. Structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22319 (9 pp.).*

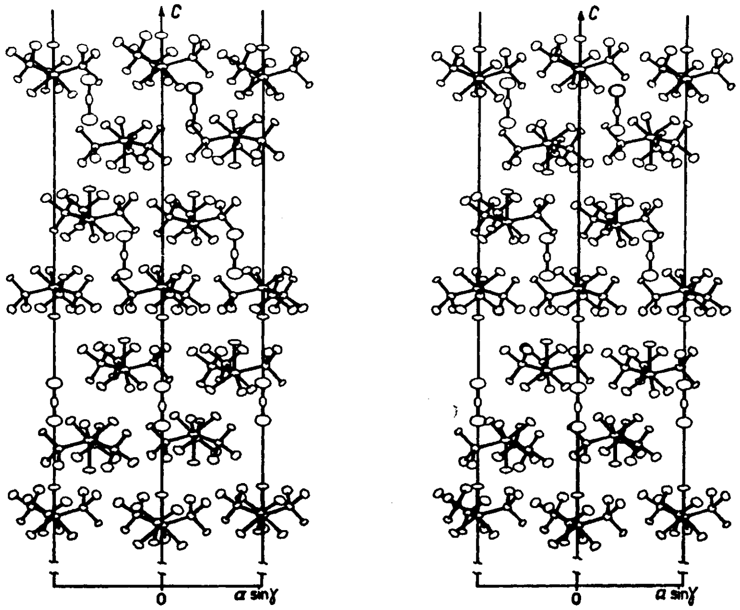

FIGURE 1 Stereoscopic packing diagram viewed perpendicularly to the (110) plane

TABLE 1

Atomic positions (fractional, × 10^4)

Atom	x	y	z
Mo	0	0	1 200.3(2)
Cl(1)	0	0	1 531.1(6)
Cl(2)	2 443(4)	4 017(4)	1 450.0(5)
Cl(3)	−1 178(5)	2 794(5)	1 435.0(5)
Cl(4)	2 195(4)	1 746(4)	1 005.5(4)
P	532(4)	2 772(4)	1 282.9(4)
C(1)	934(14)	4 251(12)	1 096(1)
C(2)	0	0	2 500
S	0	0	2 284(2)

RESULTS AND DISCUSSION

The Preparative Method.—In the reaction systems[3,4] $WCl_6 + PCl_3$ (or $PMeCl_2$) + Bu^{t}Cl and $ReCl_5 + PCl_3$ + Bu^{t}Cl, reduction of the metal halide occurred to give the complexes [PBu^{t}Cl$_3$][WCl$_6$], [PMeBu^{t}Cl$_2$][WCl$_6$], and [PBu^{t}Cl$_3$]$_2$[Re$_3$Cl$_9$][ReCl$_6$]. The analogous system $MoCl_5 + PMeCl_2$ + Bu^{t}Cl (solvent CS_2) precipitated a partially characterised brown powder which may contain a polymeric molybdenum(IV) anion (empirical formula, $C_5H_{12}Cl_6MoP$). On standing, the filtrate gave dark green crystals which did not contain the [PMeBu^{t}Cl$_2$]$^+$ cation.

Molydenum(V) chloride and $PMeCl_2$ (solvent CS_2) reacted to give a dark green crystalline material (see Experimental section) which had analytical and spectroscopic properties identical to those of the green crystals obtained in the presence of Bu^{t}Cl. It was of interest therefore to characterise the complex by *X*-ray crystal-structure analysis and magnetic and spectroscopic studies.

The X-*Ray Crystal-structure Analysis.*—The unit-cell contents (Figure 1) comprise discrete molecules of [MoCl$_4$(PMeCl$_2$)$_3$] (1) with no non-hydrogen intermolecular contacts at distances less or near to the sum of the van der Waals radii, and molecules of CS_2 well separated both from each other and molecules of (1).

Figure 2 shows that Mo^{IV} in (1) is seven-co-ordinate

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

with the capped-octahedral geometry. The face occupied by three phosphorus atoms is capped by Cl(1) whilst Cl(4), Cl(4′), and Cl(4″) occupy the non-capped face. Bond lengths and angles are shown in Tables 2 and 3. This is the usual arrangement[5,6] for such a polyhedron although the unit-cell symmetry ($R\bar{3}c$) is much higher than any observed hitherto for this geometry. Closely related structures are those of $[MoBr_4(PMe_2Ph)_3]$ (2)[5] and $[MoCl_4(PMe_2Ph)_3]\cdot EtOH$ (3).[6]

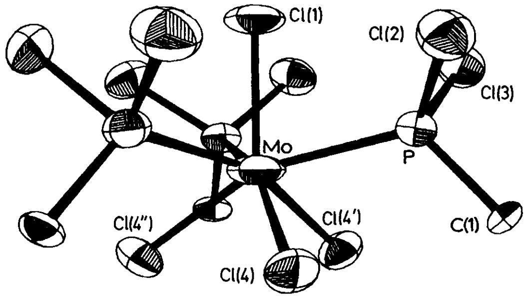

FIGURE 2 Perspective view of the molecule (CS_2 omitted) with all the atoms represented by 50% probability ellipsoids. Cl(4′) is at $\bar{y}, x - y, z$; Cl(4″) is at $y - x, \bar{x}, z$

TABLE 2

Bond distances (Å) and angles (°)

Mo–Cl(1)	2.354(4)	P–Cl(3)	2.000(5)
Mo–Cl(4)	2.401(3)	P–C(1)	1.857(9)
Mo–P	2.555(3)	C(2)–S	1.527(12)
P–Cl(2)	2.025(5)		
Cl(1)–Mo–Cl(4)	125.3(1)	Mo–P–Cl(2)	114.1(2)
Cl(1)–Mo–P	76.7(1)	Mo–P–Cl(3)	114.0(2)
Cl(4)–Mo–Cl(4′)	90.0(1)	Mo–P–C(1)	120.6(3)
Cl(4)–Mo–P	75.2(1)	Cl(2)–P–C(1)	100.5(4)
Cl(4′)–Mo–P	74.1(1)	Cl(3)–P–C(1)	103.5(4)
Cl(4″)–Mo–P	158.0(1)	Cl(2)–P–Cl(3)	101.5(2)
		P–Mo–P	114.8(2)

TABLE 3

Intramolecular contacts (Å)

Cl(1) ··· Cl(2)	3.470(4)	Cl(3) ··· C(1)	3.029(11)
Cl(1) ··· Cl(3)	3.517(4)	P ··· Cl(4)	3.026(5)
Cl(2) ··· Cl(3)	3.117(6)	P ··· Cl(4′)	2.990(5)
Cl(2) ··· C(1)	2.987(10)	Cl(4) ··· Cl(4′)	3.395(6)
P ··· P	4.307(5)	P ··· Cl(1)	3.050(4)

TABLE 4

Comparative bond lengths (Å) for seven-co-ordinate Mo^{IV}

	Mo–X(1)	Mo–X(4)	Mo–P	Ref.
(1) $[MoCl_4(PMeCl_2)_3]\cdot 0.33CS_2$	2.354	2.401	2.555	*a*
(2) $[MoBr_4(PMe_2Ph)_3]$	2.425	2.560	2.580	5
(3) $[MoCl_4(PMe_3Ph)_2]\cdot EtOH$	2.399	2.448[b]	2.577[b]	6

[a] This work. [b] Mean of three different distances.

The bond lengths in (1)—(3) are compared in Table 4. The bond lengths from Mo to Cl(4), Cl(4′), and Cl(4″) are equal in (1) as are the Mo–P bond lengths; the same relations were found for (2) but not for (3). In addition, the bond angles in (1) and (2) indicate less marked distortion toward the alternative, capped-trigonal-prismatic, stereochemistry than in (3). As is usual, Mo–Cl(1) is shorter in (1) than the Mo–Cl(4) bond lengths on the uncapped face.

There is no other crystal structure of a molybdenum complex containing the ligand $PMeCl_2$ so that comparisons between the structure of (1) and other molybdenum(V) complexes will be limited particularly since the structural differences between the closely related (2) and (3) are not well understood. However, any structural differences between (1), (2), and (3) cannot be explained by unusual variations in the P–C and P–Cl bond lengths in (1) since in[7] $[ReCl_3(PMeCl_2)_3]$ these average 1.835 and 2.022 Å, respectively (compare Table 3).

All molybdenum–ligand bonds in (1) are significantly shorter than the corresponding bonds in (3) although the shortening to P is much less than to either Cl(1) or Cl(4). For the Mo–X (X = Cl or Br) bonds in the uncapped face there is excellent agreement between (1) and (2) if we allow 0.15 Å for the difference in radii between Cl and Br. Such agreement is not found for the capping halide atoms, for the shortening in Mo–Cl(1) is much less than 0.15 Å. The Mo–P bond lengths show little variation in the three complexes so that these differences cannot be used to explain the changes in the Mo–X(1) bond lengths.

In the six-co-ordinate complexes *cis-mer*-$[MoCl_2O(PR_2Ph)_2]$ (R = Me or Et),[8] Mo–Cl (*trans* to P) are 2.464 (R = Me) and 2.479 Å (R = Et) with Mo–P (*trans* to Cl) 2.500 (R = Me) and 2.521 Å (R = Et) so that a shorter Mo–P bond was accompanied by a shorter Mo–Cl bond. However, in the seven-co-ordinate complexes Mo–Cl(4) are shorter and Mo–P longer than the bond lengths quoted above.[8] We can offer no reasoned argument for these differences.

There is an interesting difference between (1) and (2). For (2) the capped position is more sterically crowded than the occupied positions in the uncapped face containing three bromine atoms. This is *not* the case for (1). For (1), P ··· Cl(4), P ··· Cl(4′), and P ··· Cl(1) are 3.026, 2.990, and 3.050 Å respectively whilst for (2), P ··· Br(4), P ··· Br(4′), and P ··· Br(1) are 3.22, 3.18, and 3.04 Å respectively so that the capping position may not be at a steric disadvantage in chloro-complexes, unlike the case with the larger bromide or iodide. Greater stereochemical variation in seven-co-ordinate chloro-complexes may be predicted but the short Mo–X(1) bond lengths remain to be explained and present the greater stereo-chemical problem.

Magnetic-susceptibility Measurements.[9]—Molybdenum(IV) has the $4d^2$ configuration and would have the

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[5] M. G. B. Drew, J. D. Wilkins, and A. P. Wolters, *J.C.S. Chem. Comm.*, 1972, 1278.

[6] L. M. Muir, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 59.

[7] N. J. Taylor, unpublished work.

[8] J. Chatt, L. M. Muir, and K. W. Muir, *Chem. Comm.*, 1971, 655.

[9] B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc.* (*A*), 1966, 1411.

$^3T_{1g}$ ground term in cubic symmetry and a high spin–orbit coupling constant. These conditions would normally mean that the experimental effective magnetic moments should be considerably less than the spin-only value and be markedly temperature dependent.

However, the effective magnetic moment of $[MoCl_4(PMeCl_2)_3]\cdot 0.33CS_2$ varied little with temperature (90—340 K) and was close to the d^2 spin-only value (2.83 B.M.).* This unusual behaviour can be correlated with that expected for a complex under the influence of a low-symmetry ligand-field component which would lift the orbital degeneracy of the T term derived from cubic symmetry only if three conditions are met. First, the $^3T_{1g}$ ground term should approach the strong-field limit. Secondly, the orbital-reduction factor is small, *i.e.* high delocalisation of the $t_{2g}{}^2$ electrons is present. Thirdly, the low-symmetry ligand-field component would need to be such that, in the nomenclature used in ref. 9, the parameter $\nu = \Delta/\lambda$ is large. Here, Δ is the splitting of the T orbital wavefunction by the low-symmetry ligand-field component and λ is the spin–orbit coupling constant of the term. The second and third effects both quench orbital angular momentum by destroying the degeneracy of the t_{2g} orbital set.

The first criterion is supported by the high oxidation state of the Mo atom, the second by the short molybdenum–ligand bond lengths mentioned earlier, and the third by the pseudo-trigonal distortion revealed by the crystallographic study. It would be of interest to measure the magnetic moments of the other[6] monocapped octahedral molydenum(IV) complex which has longer molybdenum-ligand bond lengths in order to determine the relative importance of electron delocalisation and a low-symmetry ligand-field component on the magnetic behaviour. The magnetic moments should decrease sharply for all the molybdenum(IV) at complexes at temperatures lower than those used in the present study.

The Diffuse-reflectance Electronic Spectrum.[10]—Although the magnetic evidence indicated that the effect of spin–orbit coupling is reduced, the coupling constant for the $4d^2$ configuration would still be much higher than that expected for most first-row transition metals. This, combined with the strong-field configuration, allowed us to observe a low-frequency spin-forbidden transition in the electronic spectrum (Figure 3) at 9 600 cm^{-1} which had shoulders to high wavenumbers which may be caused by the low symmetry. The spectrum in Figure 3 was recorded near to liquid-nitrogen temperature. Transitions from the $^3T_{1g}$ ground state to $^1T_{2g}$, ^1E_g, and $^1A_{1g}$ are likely (using the cubic-field terms).

There are insufficient data to allow reliable assignments of the spin-allowed transitions which are contained in the broad high-energy envelope; the $^3T_{1g}\rightarrow{}^3T_{2g}(F)$ or $^3T_{1g}\rightarrow{}^3T_{1g}(P)$ transitions would be expected to have the lowest energies.

The Far-i.r. Absorption Spectrum (*Table* 5).—The assignments of vibrational modes associated with $PMeCl_2$ are derived from those quoted by Griffiths and Corbridge.[11] There was evidence for an absorption band assignable to a fundamental vibration[12] of CS_2; i.r. ν_3 at 1 533 cm^{-1} for (1).

TABLE 5

Infrared spectrum (cm^{-1}) of (1)

Wavenumber	Assignment	Ref.
720s	ν(P–C)	11
520s	ν_{asym}(P–Cl)	11
500s	ν_{sym}(P–Cl)	11
368ms	ν[Mo–Cl(1)]	
362s	+	
296vs	ν[Mo–Cl(4)]	
289s	δ_{sym}(C–P–Cl)	11
265m	ν(Mo–P)?	
238m	δ_{asym}(C–P–Cl)	11
187ms	δ(Cl–Mo–Cl)	11

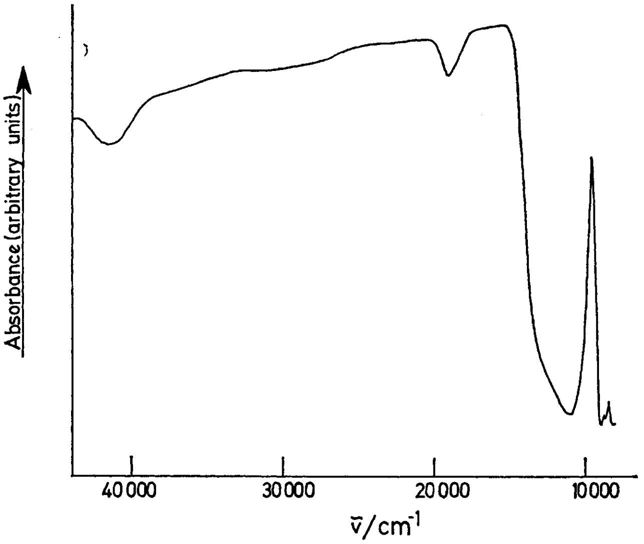

FIGURE 3 Low-temperature diffuse-reflectance spectrum of (1)

For six-co-ordinate phosphine complexes of Mo^{IV}, $[MoCl_4L_2]$, Butcher and Chatt report[13] ν(Mo–Cl) between 325 and 348 cm^{-1} whilst values for[13,14] $[MoCl_2O(PR_nPh_{3-n})_3]$ (R = alkyl, n = 1 or 2) and $[MoCl_4L^1{}_2]$ (L^1 = nitrogen base) lie between 243 and 341 cm^{-1}. In (1), ν[Mo–Cl(4)] is unlikely to be much lower in frequency than ν(Mo–Cl) in $[MoCl_2O(PR_nPh_{3-n})_3]$ (325—348 cm^{-1}) in view of the crystallographic evidence, and ν[Mo–Cl(1)]

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

T/K	$\mu_{eff.}$/B.M.	
340	2.77	$\theta = 33°$
300	2.71	
90	2.50	

[10] For d^2 correlation diagram see, A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968, p. 98.

[11] (*a*) J. E. Griffiths, *Spectrochim. Acta*, 1965, **21**, 1135; (*b*) D. E. C. Corbridge, *Topics Phosphorus Chem.*, 1969, **6**, 235.

[12] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley–Interscience, New York, 1970, p. 83.

[13] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652.

[14] W. M. Carmichael and D. A. Edwards, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1181.

may well be much higher since Mo–Cl(1) is much the shortest Mo–Cl bond length.

The only remaining absorption is a band of medium intensity at 265 cm^{-1} and this may be Mo–P, although this assignment is doubtful in view of the dearth of reliable literature values.

[8/182 *Received, 3rd February*, 1978]