Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

D–H$\cdots A$	Position of acceptor atom	$D\cdots A$	H$\cdots A$	$\angle D$–H$\cdots A$
O(1)–H(101)$\cdots$Cl$^-$	$\bar{x}+1, \bar{y}+1, \bar{z}+1$	3·177 (6)	2·44 (9)	159 (9)
O(1)–H(102)$\cdots$O(2)	$x+1, y, z$	2·859 (12)	1·88 (9)	171 (8)
O(2)–H(3)$\cdots$Cl$^-$	x,y,z	3·113 (5)	2·10 (7)	177 (5)
N(2)–H(2)$\cdots$Cl$^-$	$x+1, y, z$	3·060 (6)	2·15 (5)	174 (5)

hydrogen-bond distances (Table 3) are similar to those found in cyproheptadine hydrochloride (Birknes, 1977). The N(2)$\cdots$Cl$^-$ distance of 3·060(6) Å is comparable with the 3·088 Å found by Datta Gupta & Saha (1970) in the structure of piperidine hydrochloride. The large thermal parameters associated with the ethanol atoms and the high σ values for the bond lengths and valence angles indicate that the ethanol molecule is not rigidly fixed in its cavity. The crystal packing of the unit cell is shown in Fig. 2. The H atoms on the methyl end of the ethanol did not show up in the difference map and they are omitted from Fig. 2.

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{(η-Cyclohexadiene)(η-cyclopentadiene)[1,2-bis(diphenylphosphino)ethane]-molybdenum(V)} Hexafluorophosphate, Sulphur Dioxide

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Abstract. $\{(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_8)Mo[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]\}PF_6,SO_2$, $M_r = 848{\cdot}6$, monoclinic, $P2_1/c$, $a = 10{\cdot}880\ (7)$, $b = 15{\cdot}205\ (8)$, $c = 22{\cdot}36\ (1)$ Å, $\beta = 97{\cdot}5\ (1)°$, $V = 3666{\cdot}8$ Å^3, $D_c = 1{\cdot}54$ g cm^{-3}, $Z = 4$. Patterson and Fourier methods were used to determine the structure from four-circle diffractometer intensity measurements. The final R was 0·061. The geometry of the cation is similar to that in bent bis(cyclopentadienyls). The SO_2 molecules occupy holes in the structure.

Introduction. Crystals were provided by Dr J. Segal and Dr M. L. H. Green (Segal, Green, Daran & Prout, 1976). The compounds are sensitive to air, and were mounted under dry nitrogen in glass capillaries.

The crystal system was determined from precession photographs (Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å). Systematic extinctions $h0l$, $l = 2n+1$, $0k0$, $k = 2n+1$ indicated space group $P2_1/c$. A crystal (0·3 × 0·3 × 0·3 mm) was set up on a Hilger & Watts PDP8-controlled four-circle diffractometer and cell dimensions and orientation matrix were obtained by a least-squares fit to the setting angles of 17 reflexions.

The intensities of each independent reflexion with $\sin\theta/\lambda < 0{\cdot}59$ were measured by an $\omega/2\theta$ scan with ordinate analysis (Watson, Shotton, Cox & Muirhead, 1970). Mo $K\alpha$ radiation from a graphite monochromator was used. 3513 independent reflexions with $I > 4\sigma$, where σ is the standard deviation based on simple counting statistics, were used in subsequent calculations. Reflexions for which the apparent centre was more than 0·2° from the predicted position were given an absolute weight of 0·01. The measurements were corrected for Lorentz and polarization effects but not for absorption or extinction.

The Mo atom was located from a Patterson function. P, F and C atoms were found from a heavy-atom phased F_o synthesis. The trial structure was refined by full-matrix least squares with isotropic temperature factors, leading to $R = 0{\cdot}27$. A difference synthesis showed three large remaining peaks which could be attributed to a SO_2 solvent molecule. When these three atoms were included, R dropped to 0·12. A diagonal approximation to the full matrix, based on one block for each atom, was used in the last cycles including anisotropic temperature factors. H atoms were found from difference syntheses, but their coordinates were not refined. With the weighting scheme $w = 1/\Sigma_{r=1}^{n} A_r T_r^*(X)$ with n coefficients, A_r, for the Chebychev polynomial $T_r^*(X)$ where X is $F_o/F_o(\max)$ (Rollett, 1965) ($n = 3$ and A_r 18·4, 23·7, 7·9) convergence was reached at R 0·061 and R_w 0·076. The scattering factors and corrections for the real part of the anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1962). All calculations were performed on the Oxford University ICL 1906A computer with the Oxford *CRYSTALS* package (Carruthers, 1976).

Final atomic parameters are given in Table 1; Tables 2 and 3 show bond lengths and angles involving non-hydrogen atoms with estimated standard deviations calculated from the terms of the variance–covariance matrix.†

Table 1. *Fractional coordinates*

	x	*y*	*z*
Mo	0·25702 (7)	0·14646 (5)	0·19847 (3)
P(1)	0·0639 (2)	0·0566 (1)	0·1878 (1)
P(2)	0·1812 (2)	0·1612 (1)	0·0885 (1)
P(3)	0·2995 (3)	0·8147 (2)	0·3871 (1)
F(1)	0·394 (1)	0·8373 (7)	0·3444 (6)
F(2)	0·398 (1)	0·829 (1)	0·4380 (5)
F(3)	0·2089 (8)	0·7851 (9)	0·4320 (5)
F(4)	0·326 (2)	0·7195 (7)	0·3795 (9)
F(5)	0·269 (1)	0·9089 (7)	0·3884 (9)
F(6)	0·191 (1)	0·8030 (9)	0·3378 (5)
C(1)	0·0435 (8)	0·6109 (6)	0·3716 (4)
C(2)	0·0171 (8)	0·1218 (6)	0·0715 (4)
C(3)	0·0290 (8)	0·5443 (5)	0·2497 (4)
C(4)	0·0297 (8)	0·0090 (6)	0·3042 (4)
C(5)	0·0389 (9)	0·4917 (6)	0·1486 (4)
C(6)	0·162 (1)	0·5122 (7)	0·1541 (5)
C(7)	0·2182 (8)	0·5479 (7)	0·2062 (5)
C(8)	0·1557 (8)	0·5651 (6)	0·2551 (4)
C(9)	0·0671 (8)	0·9412 (6)	0·1643 (4)
C(10)	0·1478 (9)	0·8824 (6)	0·1974 (4)
C(11)	0·149 (1)	0·7932 (7)	0·1824 (5)
C(12)	0·067 (1)	0·7623 (7)	0·1355 (5)
C(13)	−0·017 (1)	0·8188 (7)	0·1028 (5)
C(14)	0·0163 (9)	0·4083 (6)	0·3826 (4)
C(15)	0·1847 (8)	0·2700 (6)	0·0538 (4)
C(16)	0·0781 (9)	0·3139 (6)	0·0257 (4)
C(17)	0·089 (1)	0·3931 (7)	−0·0028 (5)
C(18)	0·205 (1)	0·0688 (7)	0·4961 (5)
C(19)	0·309 (1)	0·3904 (7)	0·0261 (5)
C(20)	0·2988 (9)	0·3118 (7)	0·0544 (5)
C(21)	0·2557 (7)	0·0925 (6)	0·0348 (4)
C(22)	0·2394 (9)	0·0008 (6)	0·0384 (4)
C(23)	0·2861 (9)	0·9459 (7)	−0·0029 (5)
C(24)	0·3498 (9)	0·5193 (8)	0·4517 (5)
C(25)	0·3688 (9)	0·4297 (8)	0·4494 (4)
C(26)	0·3190 (8)	0·3738 (6)	0·4902 (4)
C(27)	0·4771 (8)	0·1561 (7)	0·2142 (5)
C(28)	0·4375 (9)	0·1051 (7)	0·1629 (5)
C(29)	0·3751 (8)	0·0277 (7)	0·1810 (4)
C(30)	0·3739 (9)	0·0360 (7)	0·2444 (5)
C(31)	0·4329 (8)	0·1138 (7)	0·2633 (4)
C(32)	0·2888 (8)	0·2971 (6)	0·2045 (5)
C(33)	0·345 (1)	0·3240 (7)	0·2671 (5)
C(34)	0·290 (1)	0·2716 (8)	0·3165 (5)
C(35)	0·1996 (9)	0·2019 (6)	0·2882 (4)
C(36)	0·1137 (9)	0·2304 (6)	0·2404 (4)
C(37)	0·1565 (9)	0·2823 (6)	0·1961 (4)
S(1)	0·3515 (6)	0·6907 (6)	0·0672 (2)
O(1)	0·419 (2)	0·618 (1)	0·0825 (8)
O(2)	0·417 (2)	0·761 (2)'	0·086 (1)

Table 2. *Interatomic distances* (Å)

Mo(1)–P(1)	2·492 (2)	Mo(1)–C(27)	2·38 (1)
Mo(1)–P(2)	2·500 (2)	Mo(1)–C(28)	2·30 (1)
P(1)–C(1)	1·845 (9)	Mo(1)–C(29)	2·28 (1)
P(1)–C(3)	1·838 (8)	Mo(1)–C(30)	2·27 (1)
P(1)–C(9)	1·834 (9)	Mo(1)–C(31)	2·30 (1)
P(2)–C(2)	1·875 (9)	C(27)–C(28)	1·41 (2)
P(2)–C(15)	1·829 (9)	C(27)–C(31)	1·41 (2)
P(2)–C(21)	1·856 (9)	C(28)–C(29)	1·44 (1)
C(1)–C(2)	1·52 (1)	C(29)–C(30)	1·42 (1)
C(3)–C(4)	1·40 (1)	C(30)–C(31)	1·39 (2)
C(3)–C(8)	1·40 (1)		
C(4)–C(5)	1·40 (1)	Mo(1)–C(32)	2·32 (1)
C(5)–C(6)	1·37 (2)	Mo(1)–C(35)	2·34 (1)
C(6)–C(7)	1·36 (2)	Mo(1)–C(36)	2·31 (1)
C(7)–C(8)	1·39 (1)	Mo(1)–C(37)	2·34 (1)
C(9)–C(10)	1·40 (1)	C(32)–C(37)	1·44 (1)
C(9)–C(14)	1·39 (1)	C(37)–C(36)	1·39 (1)
C(10)–C(11)	1·40 (1)	C(35)–C(36)	1·39 (1)
C(11)–C(12)	1·36 (2)	C(32)–C(33)	1·51 (2)
C(12)–C(13)	1·39 (2)	C(33)–C(34)	1·55 (2)
C(13)–C(14)	1·40 (1)	C(34)–C(35)	1·52 (1)
C(15)–C(16)	1·41 (1)		
C(15)–C(20)	1·39 (1)	S(1)–O(1)	1·35 (2)
C(16)–C(17)	1·38 (1)	S(1)–O(2)	1·33 (2)
C(17)–C(18)	1·40 (2)		
C(18)–C(19)	1·38 (2)	P(3)–F(1)	1·53 (1)
C(19)–C(20)	1·36 (1)	P(3)–F(2)	1·47 (1)
C(21)–C(22)	1·41 (1)	P(3)–F(3)	1·56 (1)
C(21)–C(26)	1·38 (1)	P(3)–F(4)	1·49 (1)
C(22)–C(23)	1·39 (1)	P(3)–F(5)	1·47 (1)
C(23)–C(24)	1·41 (2)	P(3)–F(6)	1·52 (1)
C(24)–C(25)	1·38 (2)		
C(25)–C(26)	1·41 (1)		
Mean C–C(Ph)	1·39 (2)		

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32567 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Interbond angles* (°)

P(1)–Mo(1)–P(2)	77·8 (1)	C(27)–C(28)–C(29)	109·1 (9)
Mo(1)–P(1)–C(1)	105·7 (3)	C(28)–C(29)–C(30)	105·8 (9)
Mo(1)–P(1)–C(3)	121·6 (3)	C(29)–C(30)–C(31)	108·4 (9)
Mo(1)–P(1)–C(9)	120·3 (3)	C(30)–C(31)–C(27)	110·1 (9)
C(1)–P(1)–C(3)	103·5 (5)	C(31)–C(27)–C(28)	106·5 (9)
C(1)–P(1)–C(9)	104·9 (4)	Mean C–C–C(C_5H_5)	108 (1)
C(3)–P(1)–C(2)	98·8 (4)		
		C(32)–C(33)–C(34)	112·1 (8)
Mo(1)–P(2)–C(2)	110·7 (3)	C(33)–C(34)–C(35)	110·5 (8)
Mo(1)–P(2)–C(15)	118·4 (3)	C(34)–C(35)–C(36)	115·6 (9)
Mo(1)–P(2)–C(21)	118·0 (3)	C(35)–C(36)–C(37)	117·9 (9)
C(2)–P(2)–C(15)	106·0 (4)	C(36)–C(37)–C(32)	114·5 (9)
C(2)–P(2)–C(21)	100·0 (4)	C(37)–C(32)–C(33)	116·0 (9)
C(15)–P(2)–C(21)	101·6 (4)		
C(3)–C(4)–C(5)	119·7 (8)	F(1)–P(3)–F(2)	88·2 (7)
C(4)–C(5)–C(6)	120·3 (9)	F(1)–P(3)–F(3)	175·5 (7)
C(5)–C(6)–C(7)	119·5 (8)	F(1)–P(3)–F(4)	82·5 (6)
C(6)–C(7)–C(8)	122·9 (8)	F(1)–P(3)–F(5)	88·1 (8)
C(7)–C(8)–C(3)	117·9 (9)	F(1)–P(3)–F(6)	95·5 (8)
C(8)–C(3)–C(4)	119·6 (8)	F(2)–P(3)–F(3)	90·2 (6)
C(9)–C(10)–C(11)	121·2 (9)	F(2)–P(3)–F(4)	95 (1)
C(10)–C(11)–C(12)	120·0 (9)	F(2)–P(3)–F(5)	89 (1)
C(11)–C(12)–C(13)	120·5 (9)	F(2)–P(3)–F(6)	176 (1)
C(12)–C(13)–C(14)	119·8 (9)	F(3)–P(3)–F(4)	86·5 (7)
C(13)–C(14)–C(9)	120·6 (9)	F(3)–P(3)–F(5)	96·0 (9)
C(14)–C(9)–C(10)	118·3 (8)	F(3)–P(3)–F(6)	86·4 (7)
C(15)–C(16)–C(17)	120·4 (9)	F(4)–P(3)–F(5)	175 (1)
C(16)–C(17)–C(18)	120·3 (9)	F(4)–P(3)–F(6)	87 (1)
C(17)–C(18)–C(19)	119·2 (9)	F(5)–P(3)–F(6)	88·5 (9)
C(18)–C(19)–C(20)	121 (1)		
C(19)–C(20)–C(15)	121 (1)		
C(20)–C(15)–C(16)	117·9 (8)	O(1)–S(1)–O(2)	109 (1)
C(21)–C(22)–C(23)	119·8 (9)		
C(22)–C(23)–C(24)	121 (1)		
C(23)–C(24)–C(25)	119·2 (9)		
C(24)–C(25)–C(26)	120·1 (9)		
C(25)–C(26)–C(21)	121·0 (9)		
C(26)–C(21)–C(22)	119·1 (8)		
Mean C–C–C(Ph)	120·1 (9)		

Discussion. The unit cell contains four of the cations shown in Fig. 1, four anions, and four molecules of SO_2 of crystallization. The Mo coordination is similar to that found in the bent bis(η-cyclopentadienyls) $(\eta\text{-}C_5H_5)_2MX_2$ (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974).

The C_6H_8 group is folded along the direction defined by C(32) and C(35); the planes containing both these atoms and C(33), C(34) and C(36), C(37) respectively make an angle of 135·5°. This C_6H_8 group is bonded to the Mo atom through the plane containing C(32), C(35), C(36), C(37); the mean distance between these atoms and Mo is 2·33 Å; in this plane the C–C distances are 1·44 (1), 1·39 (1) and 1·39 (1) Å. The length of the normal to this plane at the Mo atom is 1·91 Å. The fold is such that C(33) and C(34) are pointed away from the Mo atom.

In the cyclopentadienyl ring the average bond length is 1·41 Å and within one e.s.d. of that found by Prout *et al.* (1974); the average bond angle is 108°. The Mo–C distances lie in the range 2·27–2·38 Å and the normal to the ring at the Mo atom is 1·97 Å.

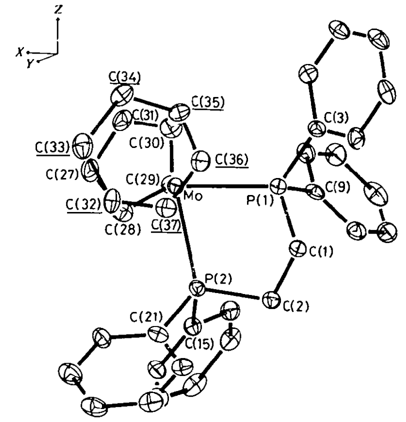

Fig. 1. The cation $\{(\eta\text{-}C_6H_8)(\eta\text{-}C_5H_5)Mo[(C_6H_5)_2P(CH_2)_2\text{-}P(C_6H_5)_2]\}$ in projection on the plane defined by the Mo and both the P atoms.

The line of intersection of the P(1)–Mo–P(2) plane and the plane defined by both normals to the C_5H_5 ring and the C_4 system [C(32), C(35), C(36), C(37)] roughly bisects the angle formed by these normals, making angles of 57·7 and 62·6°. These values are smaller than that found by Prout *et al.* (1974). The steric effect caused by the relatively bulky substituents on the P atoms could explain the decrease.

The P atoms lie in a plane that makes an angle of 93·5° with the plane formed by the normals defined above. The Mo—P distances of 2·500 and 2·492 Å may be compared with other Mo—P distances of 2·550 and 2·526 Å in $(\eta\text{-}C_5H_5)_2MoP_2H_2$ (Cannillo, Coda, Prout & Daran, 1977) and 2·435 and 2·498 Å in $[(C_6H_5)_2(PCH_2)_2(C_6H_5)_2Mo(\eta\text{-}C_5H_5)CoCl]$ (Cross & Fenn, 1970). C(1) and C(2) are both on the same side of the Mo, P(1), P(2) plane (0·973 and 0·408 Å). The bond distances and angles in the diphenylphosphine ligand are essentially the same as those reported by Churchill & O'Brien (1969).

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Un Niobate de Thallium de Type 'Bronze Hexagonal' Excédentaire en Cations

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Abstract. $TlNb_{3+x}O_{9-y}$, orthorhombic, $C222_1$, a = 7·551 (4), b = 13·005 (6), c = 7·734 (4) Å, Z = 4. R = 0·069 for 535 observed reflexions. A structural study shows an excess of cations at the usually empty trigonal sites and probably a deficiency of anions. The formula suggested for this compound is $TlNb_{3\cdot175}(O_{8\cdot25}F_{0\cdot375})$.

Introduction. Lors de la récente description d'un composé du système Tl_2O–Nb_2O_5 de composition 4:11, il était mentionné que la synthèse de cette phase rhomboédrique s'accompagnait toujours de celle d'une phase de type 'bronze hexagonal' (Gasperin, 1977). Or ce type structural bien connu, qui correspond à des oxydes de formule AB_3O_9 (A, de grand rayon ionique pouvant être lacunaire), pose un problème d'équilibre de charges lorsqu'il s'applique aux cations Tl^+ et Nb^{5+}: leur présence conduit à envisager soit un excès de cations, soit un défaut d'anions, soit encore un assemblage d'octaèdres légèrement différent. C'est pour choisir entre ces trois hypothèses que nous avons entrepris la structure d'un monocristal dont nous ignorions la composition exacte.

Le cristal retenu est un petit prisme incolore légèrement opaque allongé selon **c** (200 μm). Les diagrammes de Weissenberg et de précession révèlent une maille hexagonale de symétrie $6/m$ avec a = 7,55, c = 3,865 × 2 Å et une extinction pour $00l \neq 2n$. Toutefois, un réglage précis laisse apparaître un léger écart à la symétrie hexagonale et fait attribuer au cristal soit une maille monoclinique $P2_1$ ou $P2_1/m$ avec a = 7,551, b = 7,519, c = 7,734 Å, γ = 120,30° et Z = 2, soit une maille orthorhombique $C222_1$ avec a = 7,551, b = 13,005, c = 7,734 Å et Z = 4. Toutes les hypothèses qui suivent ont été envisagées dans ces trois groupes mais nous ne mentionnerons plus que le groupe $C222_1$ qui a donné les meilleurs résultats. Les mesures d'intensité ont été faites avec la radiation Mo $K\alpha$ d'un diffractomètre Philips PW 1100 muni d'un monochromateur au graphite, par la méthode d'intégration $\omega/2\theta$. Le quart de l'espace réciproque ayant été exploré, seuls les plus intenses des plans équivalents ont été retenus et, en raison des faibles dimensions du cristal, aucune autre correction d'absorption n'a été appliquée bien que le coefficient d'absorption linéaire calculé pour la formule '$TlNb_3O_9$' soit voisin de 250