X-RAY CRYSTALLOGRAPHIC STUDIES OF FOUR ORGANO-METALLIC COMPOUNDS

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INTRODUCTION

Four organometallic compounds were studied to determine unambiguously their molecular structure. The results of these X-ray crystallographic studies are reported in this thesis along with a few computer programmes which were developed as the need arose.

The crystal structure of dichloro bis(tri-pentafluorophenylphosphine)platinum(II) was determined and refined by full matrix least squares to an R factor of 0.114. The molecular structure of this compound was already known but the exact conformation of the pentafluorophenyl groups was not and it was desired to know the exact relationships of the fluorine atoms with respect to each other.

For the next compound studied, (diphenylphosphinodithioato) bis(triethylphosphine)palladium II diphenylphosphinodithioate, the interest lay in determining the molecular structure, with especial interest in the nature of the co-ordination around the palladium atom. This structure was determined and refined by full matrix least squares to an R factor of 0.126 using data recorded on film and scanned by an automatic film scanner. The molecule was shown to be ionic and contain a four-co-ordinated palladium atom. During the course of this work an empirical estimate was made of the accuracy of the data as recorded, scanned and processed.

The crystal and molecular structure of tetraphenylarsonium tetrachlorobis(triphenylphosphine)-rhodate(III) was then determined. Though the molecular structure as postulated on the basis of other chemical evidence was not in doubt it was thought worth confirming the molecular structure by X-ray analysis and determining the position of the acetone of crystallisation relative to the molecule.

The structure was refined by full matrix least squares to an R factor of 0.137 using a constrained refinement programme to refine only six positional and orientational parameters for each of the ten phenyl groups.

The final crystal studied and molecular structure determined was that of tri-μ-monochloromonothiocarbonyltetrakis(triphenylphosphine)diruthenium(II). The structure and precise chemical analysis of this compound had not been previously determined and was of considerable interest in connection with interpreting reaction mechanisms involving ruthenium complexes. In the finally determined structure the molecule was shown to contain two ruthenium atoms linked by a triple bridge of chlorine atoms with a terminal chlorine atom and a terminal thiocarbonyl group. This structure was refined to an R factor of 0.115 using the least squares constrained refinement programme mentioned above to refine the twelve phenyl groups in the molecule.

Work done on using a computer to index oscillation photographs is reported at the end of this thesis. Though this work was finished only in part and was not used in any structure determination it was felt that the work accomplished was worth recording briefly to help with any future attempts to index oscillation photographs.

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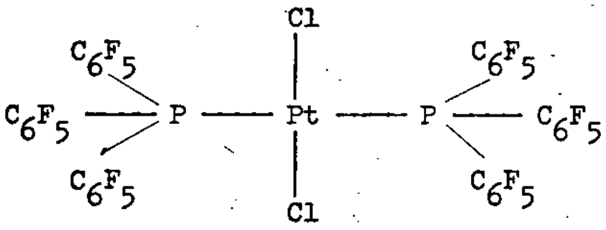
PART I

The Crystal Structure of Dichloro bis(tri-pentafluorophenylphosphine)platinum(II)

INTRODUCTION

The X-ray structure determination of Dichloro bis(tri-pentafluorophenylphosphine)platinum(II) was undertaken at the request of Dr. D. Nichols, of the Chemistry Department, Edinburgh University. Being interested in the interpretation of nuclear magnetic resonance spectrographs of this compound, he wished to know the positions of the fluorine atoms relative to each other in the molecule. It was hoped that the conformation of the pentafluorophenyl groups in the crystalline state would give some indication of the preferred conformation of these groups in solution.



An attempt was firstly made to solve the structure in two dimensions, trying to determine the projection of the structure on the [001] and on the [100] planes. Both these projected structures were refined to an R factor of 0.25. A three dimensional structure determination was then successfully undertaken, being refined to a final R factor of 0.114.

EXPERIMENTAL AND RESULTS

Summary of Crystal Data.

Dichloro bis(tri-pentafluorophenylphosphine)platinum(II), $C_{36}F_{30}P_2Cl_2Pt$, D_m=2.1 g/cm^3 (by flotation), D_c=2.25 g/cm^3, z=1, M=1330, yellow triclinic crystals, space group $P\bar{1}$, a=9.51(1)Å, b=11.90(10)Å, c=11.45(1)Å, α=123(1)°, β=67(1)°, γ=83(1)°, V=990Å^3.

Determination of Cell Dimensions

A crystal was mounted about the [c] axis and X-ray diffraction pictures taken, using a five-inch diameter camera designed by Dr. C.A. Beevers. From an oscillation photograph the [c] cell dimension was found to be 11.41Å. From the corresponding zero layer Weissenberg photograph the following reciprocal cell dimensions were calculated:

$a^* = 0.1789(1)$ r.l.u.
$b^* = 0.1556(1)$ r.l.u.
$\gamma^* = 96.8(2)^\circ$

Similarly, photographs taken with the crystal mounted about the [a] axis gave the following dimensions:

$a = 9.51$Å
$b^* = 0.1556(1)$ r.l.u.
$c^* = 0.1739(1)$ r.l.u.
$\alpha^* = 57.0(2)^\circ$

The β^* angle was calculated using information from an upper layer normal beam Weissenberg photograph taken with the crystal mounted about the [c] axis. The film co-ordinates of six spots with indices ranging from $(\bar{2}0\bar{1})$ to $(\bar{7}0\bar{1})$ were measured. The distances in reciprocal space of the corresponding reciprocal lattice points from the axis of rotation of the crystal were then calculated using the following formula[1]:

$$\xi^2 = 2-\zeta^2-\sqrt{1-\zeta^2}\,(\cos(X.360/2\pi R_F))$$

where R_F is the film radius and X is the distance of the spot from the centre line of the film.

From figure 1 it can be seen that

$$OX^2 = \xi^2+\zeta^2$$

and $$\cos\beta^* = \frac{(ha^*)^2 + c^{*2} - OX^2}{2.(ha^*)^2.c^{*2}}$$

$$\therefore \cos\beta^* = \frac{(ha^*)^2 + c^{*2} - \xi^2 - \zeta^2}{2.(ha^*)^2.c^{*2}}$$

Using formulae[2] connecting the reciprocal and real lattices the following self consistent set of cell dimensions were calculated.

$a = 9.51(2)$Å $b = 11.90(10)$Å $c = 11.41(2)$Å

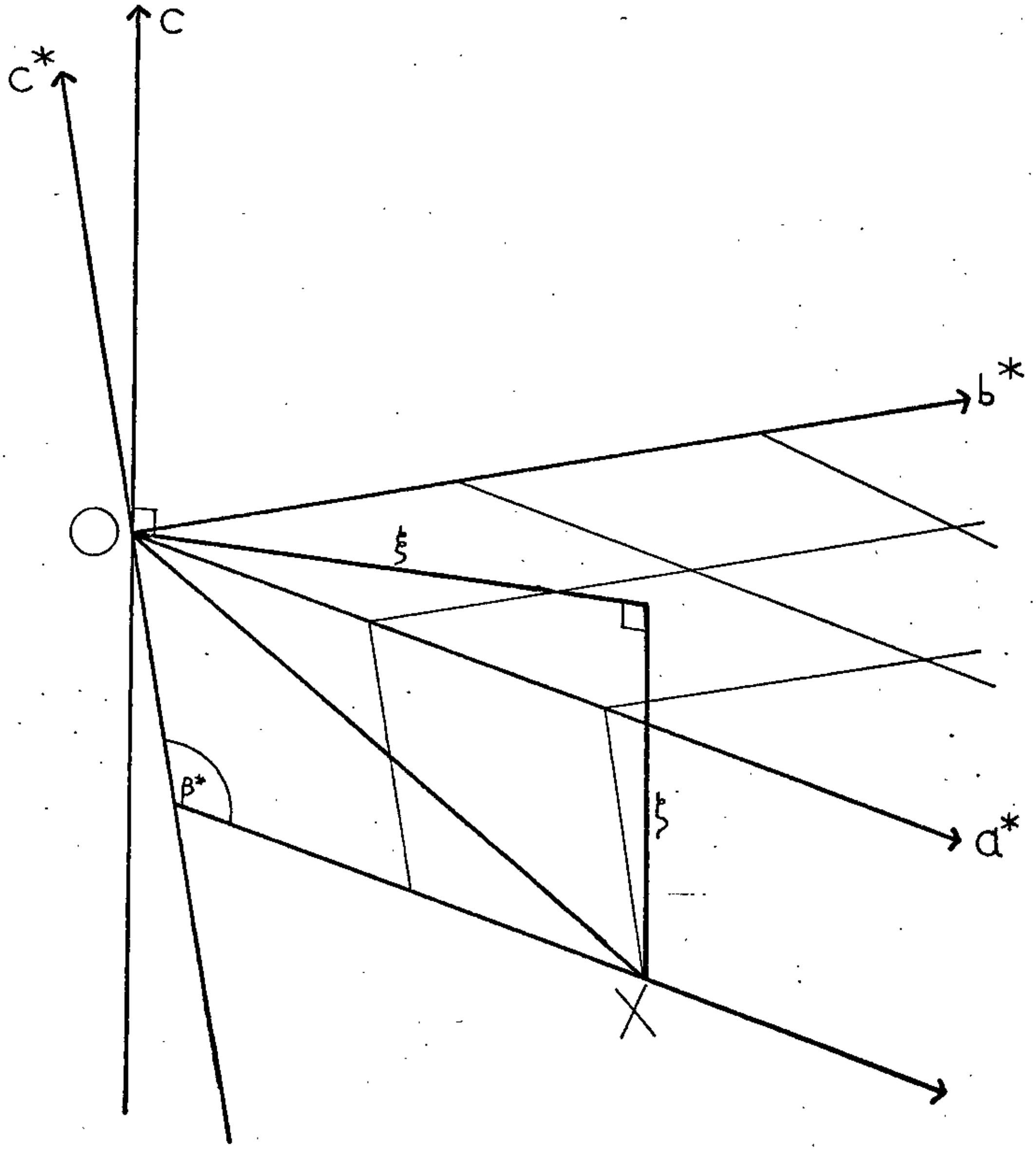
$\alpha = 123(1)^\circ$ $\beta = 67(1)^\circ$ $\gamma = 83(1)^\circ$

$a^* = 0.1789(1)$ r.l.u. $b^* = 0.1556(1)$ r.l.u. $c^* = 0.1739(1)$ r.l.u.

$\alpha^* = 57.0(2)^\circ$ $\beta^* = 113(1)^\circ$ $\gamma^* = 96.8(2)^\circ$

Figure 1

The reciprocal lattice of a triclinic cell.



The formulae used were:

to determine α $\quad \cos\alpha = (\cos\beta^{*}\cos\gamma^{*} - \cos\alpha^{*})/\sin\beta^{*}\sin\gamma^{*}$

" " β $\quad \sin\beta = 1/(aa^{*}\sin\gamma^{*})$

" " γ $\quad \cos\gamma = (\cos\alpha^{*}\cos\beta^{*} - \cos\gamma^{*})/\sin\alpha^{*}\sin\beta^{*}$

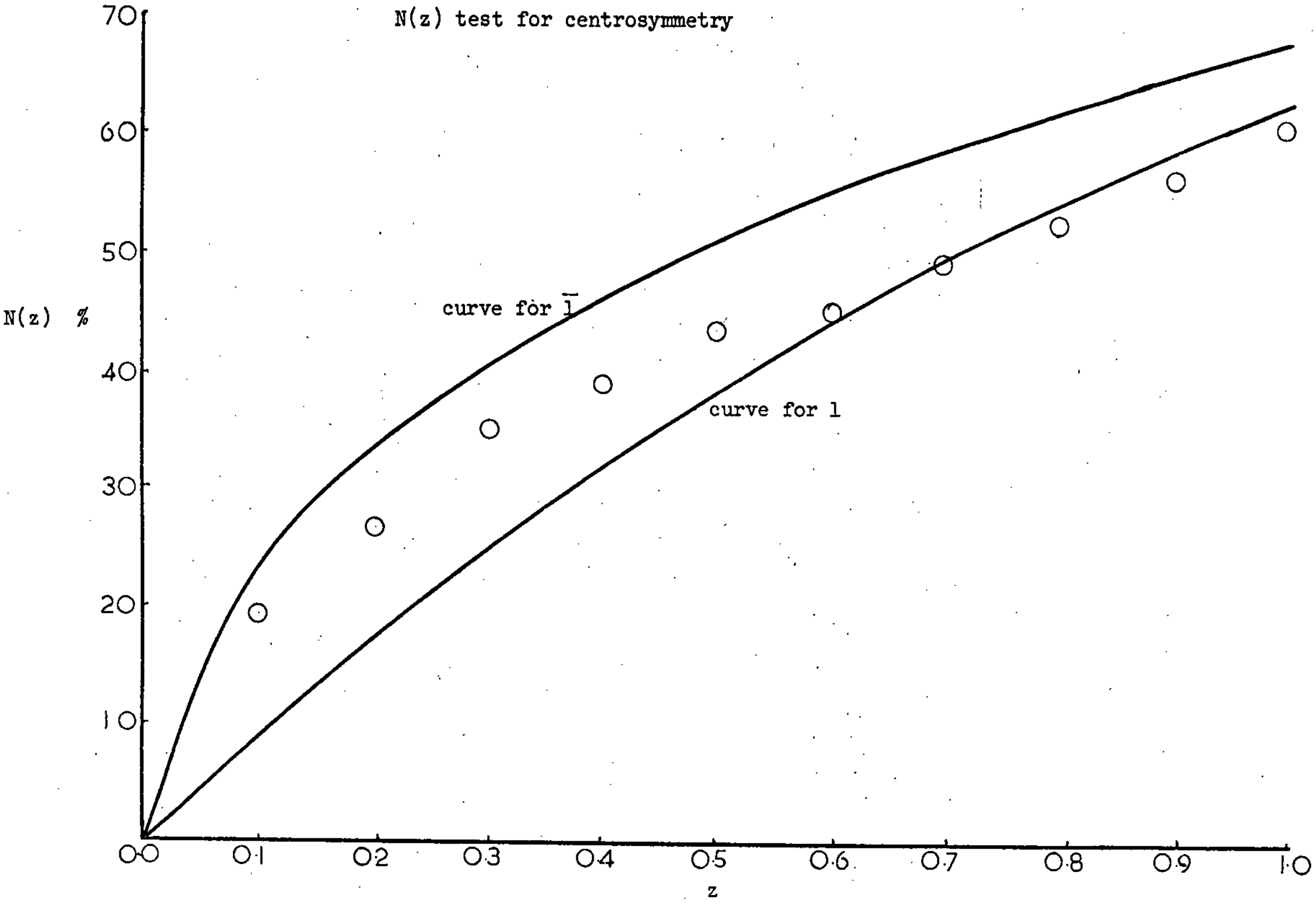
" " b $\quad b = 1/(b^{*}\sin\alpha\,\sin\gamma^{*})$

Projection on to the [001] plane

With the crystal mounted about the [c] axis, two zero level Weissenberg photographs were taken, with the exposure time for the first photograph ten times that for the second. Visually comparing one film with the other enabled the intensities of 220 reflections to be estimated. The N(z) test[3] for a centre of symmetry was applied to this data but the result was inconclusive due to the effect of the heavy atom in the crystal[4] (figure 2). The intensities were corrected for Lorentz and polarisation factors.

A temperature sharpened Patterson map gave the positions of the chlorine and phosphorus atoms. As there was only one molecule per unit cell, determined by density measurements, and as it was assumed the cell was centrosymmetric the platinum atom was deduced to be situated on a centre of symmetry which was also chosen to be the origin of the unit cell. By Fourier methods the rest of the atoms were found. This structure was finally refined by full matrix least squares to an R factor of 0.25. The positional and thermal parameters of this projection are shown in table 1.

Figure 2



N(z) test for centrosymmetry
70
60
50
40
30
20
10
N(z) %
curve for $\bar{1}$
curve for 1
0·0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
z

TABLE 1

Fractional co-ordinates of the atoms projected on to the [001] plane.

	x	y		x	y
Pt	0	0	F(11)	-0.250	-0.000
Cl	0.215	0.125	F(12)	-0.430	-0.180
P	0.040	-0.040	F(13)	-0.400	-0.440
C(11)	-0.100	-0.170	F(14)	0.150	0.505
C(12)	-0.225	-0.115	F(15)	-0.035	0.325
C(13)	-0.310	-0.230	F(21)	-0.320	0.170
C(14)	-0.290	-0.350	F(22)	0.430	0.320
C(15)	-0.180	-0.380	F(23)	0.425	0.380
C(16)	-0.085	-0.290	F(24)	0.345	-0.275
C(21)	0.195	-0.135	F(25)	0.100	-0.125
C(22)	-0.327	0.195	F(31)	0.200	0.135
C(23)	-0.455	0.270	F(32)	-0.150	-0.360
C(24)	-0.460	0.302	F(33)	0.080	0.500
C(25)	0.340	-0.250	F(34)	0.300	-0.400
C(26)	0.200	-0.165	F(35)	-0.235	0.140
C(31)	0.000	0.125			
C(32)	0.080	0.190			
C(33)	0.075	0.300			
C(34)	0.060	-0.390			
C(35)	0.175	-0.315			
C(36)	-0.140	0.200			

Projection on to the [100] plane

With the crystal mounted about the [a] axis a zero layer Weissenberg photograph was taken using a film pack containing three films. From these films 275 reflections were visually estimated and then corrected for Lorentz and polarisation factors. A temperature-sharpened Patterson function was calculated which gave the positions of the chlorine and phosphorus atoms, the position of the platinum atom on the origin being already determined. Fourier methods enabled the rest of the projected structure to be determined, knowing one of the co-ordinates of each atom from the previous projected structure. The projected structure was refined by full matrix least squares to a final R-factor of 0.25. The positional and thermal parameters for this projection are shown in table 2.

TABLE 2

Fractional co-ordinates of the atoms projected on to the [100] plane.

	y	z		y	z
Pt	0	0	F(11)	0.000	0.450
Cl	0.130	0.032	F(12)	-0.190	0.465
P	-0.040	0.160	F(13)	-0.435	0.230
C(11)	-0.166	0.185	F(14)	0.510	0.030
C(12)	-0.125	0.330	F(15)	0.325	0.060
C(13)	-0.220	0.340	F(21)	0.170	0.145
C(14)	-0.350	0.215	F(22)	0.320	0.230
C(15)	-0.375	0.095	F(23)	0.385	0.040
C(16)	-0.290	0.075	F(24)	-0.285	0.235
C(21)	-0.125	0.100	F(25)	-0.125	0.320
C(22)	0.200	0.040	F(31)	0.125	0.310
C(23)	0.270	0.100	F(32)	-0.370	0.460
C(24)	0.310	0.005	F(33)	0.485	0.355
C(25)	-0.255	0.135	F(34)	-0.375	0.420
C(26)	-0.160	0.200	F(35)	0.125	0.350
C(31)	0.125	0.325			
C(32)	0.180	0.375			
C(33)	0.320	0.505			
C(34)	-0.375	0.440			
C(35)	-0.325	0.475			
C(36)	0.190	0.366			

Three Dimensional Structure Determination

A crystal was mounted about the [a] axis and intensities collected on film by the equi-inclination Weissenberg technique up to an h of 4. 1713 intensities were visually estimated and corrected for Lorentz and polarisation factors. A temperature-sharpened Patterson function was calculated from which the positional parameters of all the atoms in the structure were found. These parameters were in approximate agreement with those found from the two projected structures. The observed structure factors (F_o) were weighted by assigning a standard deviation (σ) to each observed structure factor according to the following scheme:

$$\sigma = (F_o/170)\text{x}17 \qquad \text{if} \qquad |F_o|>170$$

$$\sigma = (170/F_o)\text{x}17 \qquad \text{if} \qquad 1\leqslant|F_o|\leqslant170$$

$$\sigma = 170\text{x}17 \qquad \text{if} \qquad |F_o|<1$$

A full matrix least squares refinement was carried out on the layer scale factors and the positional and isotropic thermal parameters of all the atoms, refining the structure to an R factor of 0.134. The temperature factors of the platinum, and chlorine atoms were then allowed to vary anisotropically bringing the R factor down to its final value of 0.114. A difference Fourier synthesis, calculated using the final refined set of parameters, showed no significant features.

The fractional co-ordinates and thermal parameters of each atom are shown in table 3. A projection of the structure is shown in figure 3 which also shows the labelling of all the atoms and the thermal ellipsoids of the heavy atoms. Interatomic distances and angles are shown in table 4.

Figure 3

Projection of the molecule without showing the fluorine atoms of the pentafluorophenyl groups

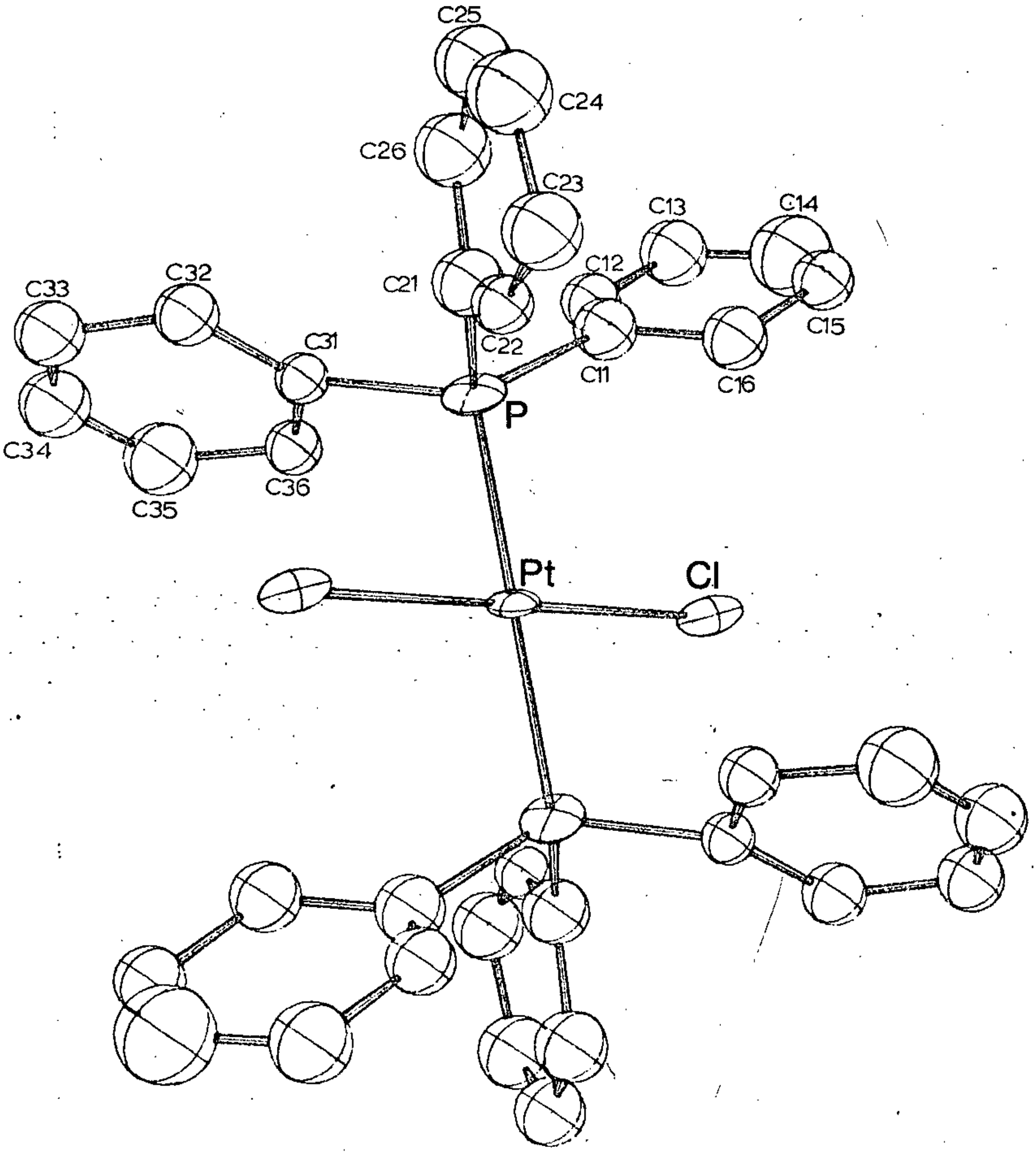


TABLE 3

Fractional co-ordinates and thermal parameters of the atoms in the finally determined structure.

	x	y	z	B
Pt	0	0	0	
Cl	0.2005(12)	0.1301(8)	0.0317(10)	
P	0.0338(13)	-0.0468(7)	0.1536(10)	3.4
C(11)	-0.1080(44)	-0.1587(30)	0.2005(37)	3.6
C(12)	-0.2252(44)	-0.1258(29)	0.3210(35)	3.3
C(13)	-0.3150(49)	-0.2093(34)	0.3527(41)	4.5
C(14)	-0.2940(58)	-0.3357(44)	0.2292(51)	6.8
C(15)	-0.1772(45)	-0.3807(30)	0.0996(36)	3.5
C(16)	-0.0972(45)	-0.2860(31)	0.0753(37)	3.8
C(21)	0.2178(46)	-0.1321(31)	0.0981(38)	3.8
C(22)	0.3463(43)	-0.1898(28)	-0.0424(34)	2.7
C(23)	0.4497(51)	-0.2757(35)	-0.1023(42)	4.5
C(24)	0.4742(54)	-0.3001(37)	-0.0037(45)	5.2
C(25)	0.3498(51)	-0.2479(34)	0.1453(41)	4.3
C(26)	0.2366(50)	-0.1692(35)	0.1904(41)	4.5
C(31)	0.0109(44)	0.1152(27)	0.3236(31)	2.3
C(32)	0.1103(49)	0.1690(32)	0.3841(36)	3.3
C(33)	0.0890(52)	0.3081(33)	0.4972(38)	3.7
C(34)	-0.0506(55)	0.3781(36)	0.5571(40)	4.1
C(35)	-0.1638(59)	0.3368(40)	0.5197(44)	4.9
C(36)	-0.1350(47)	0.1941(29)	0.3935(33)	2.8

	x	y	z	B
F(11)	-0.2571(25)	-0.0024(18)	0.4567(22)	5.0
F(12)	-0.4424(30)	-0.1769(22)	0.4841(26)	6.9
F(13)	-0.3945(33)	-0.4340(26)	0.2398(29)	8.8
F(14)	-0.1503(32)	-0.5069(24)	-0.0275(27)	7.4
F(15)	0.0352(23)	-0.3300(15)	-0.0597(18)	3.2
F(21)	0.3174(26)	-0.1780(19)	-0.1494(22)	5.2
F(22)	0.5769(28)	-0.3166(20)	-0.2290(24)	5.7
F(23)	0.6013(28)	-0.3775(20)	-0.0438(22)	5.2
F(24)	0.3751(27)	-0.2769(19)	0.2369(23)	5.5
F(25)	0.1156(26)	-0.1280(17)	0.3237(21)	4.6
F(31)	0.2532(28)	0.1051(18)	0.3242(21)	4.6
F(32)	0.1962(33)	0.3598(24)	-0.5493(27)	7.4
F(33)	-0.0667(29)	-0.5136(23)	-0.6726(26)	7.2
F(34)	-0.2957(36)	0.4074(27)	-0.5673(30)	8.8
F(35)	-0.2518(29)	0.1465(20)	0.3437(23)	5.3

Anisotropic thermal parameters

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Pt	0.0404(25)	0.0270(6)	0.0365(8)	-0.0053(7)	-0.0252(9)	0.0195(6)
Cl	0.0595(100)	0.0531(47)	0.0589(53)	-0.0309(50)	-0.0474(51)	0.0430(43)

TABLE 4

Intramolecular distances (Å) and angles (°) with standard deviations in parenthesis.

Pt-Cl	2.298(29)	Cl-Pt-P	87.3(4)
Pt-P	2.210(16)		
P-C(11)	1.925(46)	C(11)-P-Pt	116.1(16)
P-C(21)	1.796(51)	C(21)-P-Pt	118.2(15)
P-C(31)	1.795(49)	C(31)-P-Pt	104.3(16)
		C(11)-P-C(21)	101.5(20)
		C(11)-P-C(31)	109.3(15)
		C(21)-P-C(31)	107.1(19)
C(11)-C(12)	1.28(5)	F(11)-C(12)	1.38(5)
C(12)-C(13)	1.35(6)	F(12)-C(13)	1.41(5)
C(13)-C(14)	1.35(6)	F(13)-C(14)	1.45(6)
C(14)-C(15)	1.32(6)	F(14)-C(15)	1.36(5)
C(15)-C(16)	1.38(6)	F(15)-C(16)	1.43(5)
C(16)-C(11)	1.38(5)		
C(21)-C(22)	1.43(5)	F(21)-C(22)	1.40(6)
C(22)-C(23)	1.18(6)	F(22)-C(23)	1.36(5)
C(23)-C(24)	1.38(9)	F(23)-C(24)	1.35(6)
C(24)-C(25)	1.48(6)	F(24)-C(25)	1.35(7)
C(25)-C(26)	1.24(7)	F(25)-C(26)	1.37(5)
C(26)-C(21)	1.40(8)		
C(31)-C(32)	1.26(6)	F(31)-C(32)	1.34(5)
C(32)-C(33)	1.41(5)	F(32)-C(33)	1.27(6)
C(33)-C(34)	1.34(7)	F(33)-C(34)	1.40(5)
C(34)-C(35)	1.23(8)	F(34)-C(35)	1.32(7)
C(35)-C(36)	1.48(5)	F(35)-C(36)	1.33(5)
C(36)-C(31)	1.42(6)		

Interatomic distances of less than 3.5 Å involving fluorine atoms closest to the heavy atoms. F(11) is bonded to C(12), F(12) to C(13), F(13) to C(14), etc.

Pt-F(21)	2.64	Cl(2)-F(15)	2.85
Pt-F(35)	2.89	Cl(2)-F(35)	3.47
Cl(1)-F(21)	2.81	F(11)-F(25)	3.02
		F(11)-F(35)	2.70

Table 5

Observed and Calculated Structure Factors for $PtCl_2(P(C_6F_5)_3)_2$

Columns are: l, |F|obs., |F|calc

l	|F|obs.	|F|calc
0,0,L		
1	828	989
2	1131	1154
3	828	809
4	698	712
5	439	426
6	815	676
7	253	262
8	148	199
9	148	234
0,1,L		
0	1081	1022
1	1050	911
2	439	364
3	389	361
4	389	259
5	358	377
6	389	437
7	327	348
-1	358	421
-2	439	448
-3	982	988
-4	717	737
-5	463	415
-6	1131	1160
-7	439	521
-8	414	436
-9	253	266
-10	148	188
0,2,L		
0	148	97
1	327	319
2	1112	1005
3	327	408
4	463	449
5	253	271
6	414	423
7	358	418
-1	698	785
-3	1180	1231
-4	414	440
-5	698	715
-6	599	594
-7	655	643
-8	290	270
-9	358	373
-10	148	219
-11	204	221
0,3,L		
0	327	343
1	871	752
2	1050	893
4	389	348
5	290	267
7	204	222
8	204	226
-1	414	527
-2	877	970
-3	463	449
-4	1408	1528
-5	463	473
-6	204	286
-7	507	587
-8	327	361
-9	327	309
-10	253	205
-11	253	244
-12	148	188
0,4,L		
0	148	74
1	729	657
2	507	458
3	327	296
4	290	276
6	148	197
7	204	253
8	253	315
-1	667	713
-2	358	369
-3	148	48
-4	568	648
-5	865	967
-6	358	456
-7	568	527
-8	327	338
-10	253	255
-11	253	293
-12	204	238
-13	148	161
0,5,L		
0	327	358
1	507	492
2	865	776
3	148	222
4	253	275
5	290	317
6	148	237
7	253	247
8	148	244
-1	204	65
-2	482	533
-3	204	179
-4	148	104
-5	717	773
-7	568	511
-11	358	389
-12	148	174
-13	148	148
0,6,L		
0	1013	952
1	667	520
2	525	549
3	389	396
4	290	293
5	204	207
6	148	151
7	148	151
-1	389	340
-2	865	878
-3	327	309
-4	853	866
-5	698	716
-6	785	774
-8	290	297
-10	253	207
-11	290	240
0,7,L		
0	618	605
1	358	377
2	439	366
3	148	280
4	204	257
-1	544	515
-2	290	323
-3	667	706
-4	655	660
-5	439	518
-6	327	407
-8	290	308
-9	327	367
-10	358	319
-11	204	208
0,8,L		
0	587	449
1	482	440
2	358	405
3	358	364
-1	290	257
-2	525	462
-3	1001	887
-4	482	503
-5	253	277
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  3    219    244
  4    219    225
  5    191    164
  6    154    122
  7    154    166
 -1    219    293
 -2    312    341
 -3    312    237
 -4    350    338
 -5    410    474
 -7    364    395
 -8    219    227
 -9    191    184
-10    154    147
-11    154    163

      3,8,L

  1    219    214
  2    312    350
  3    294    239
  4    270    226
  5    154    182
  6    154    160
 -1    219    183
 -2    154     94
 -3    219    252
 -4    312    401
 -5    331    331
 -6    219    237
 -7    331    347
 -8    154    179
 -9    154    147
-10    154    189
-11    112    151

      3,9,L

  0    382    354
  1    382    305
  2    382    389
  3    294    295
  4    247    232
  5    112    144
 -1    294    257
 -2    219    204
 -3    294    254
 -4    294    309
 -5    294    273
 -6    112    142
 -7    112     83
-10    112    166
-11    112    171

      3,10,L

  0    294    333
  1    270    276
  2    294    310
  3    270    306
  4    112    189
 -1    219    239
 -2    312    286

 -3    382    400
 -4    294    351
 -5    294    341
 -6    270    314
-10    112    133
-11    112    117

      3,11,L

  0    247    277
  1    247    235
  2    191    195
 -1    270    219
 -2    270    288
 -3    410    430
 -4    443    399
 -5    410    405
 -6    270    283
 -7    112    200
 -8    154    200
 -9    154    248
-10    154    194

      3,12,L

  0    219    222
  1    154    198
 -1    154    205
 -2    191    265
 -3    312    348
 -4    312    298
 -5    191    257
 -6    191    194
 -7    191    189
 -8    191    234
 -9    191    279
-10    154    210

      3,13,L

 -1    112    159
 -2    219    237
 -3    219    291
 -4    219    254
 -5    191    245
 -6    154    181
 -7    191    206
 -8    154    216
 -9    154    234

      3,14,L

 -7    112    164

      3,-1,L

  0    625    675
  1    429    555
  2    862    896
  3    154    147
  4    839    892
  5    634    679
  6    662    692
  7    583    595
  8    396    382
 -1    592    614
 -2    247    367
 -3    112     38
 -4    154    109
 -5    191    165
 -6    247    284
 -7    154    121
 -8    112    234

      3,-2,L

  0    364    445
  1    396    394
  2    429    465
  3    979    801
  4    191    158
  5    410    410
  6    410    397
  7    154    186
  8    191    268
  9    247    261
 -1    154    119
 -2    681    720
 -3    429    485
 -4    294    254
 -5    294    319
 -6    191    194
 -7    247    207
 -8    191    201

      3,-3,L

  0    704    702
  1    769    862
  2    154    201

  3    779    783
  4   1566   1597
  5    364    291
 -1    643    678
 -2    671    694
 -3    382    393
 -5    382    433
 -6    112    122
 -7    191    180
 -8    154    185

      3,-4,L

  0    270    344
  1    312    333
  2    112    150
  3    830    813
  4   1063    917
  5    573    569
  6    704    623
 -1    583    554
 -2    625    675
 -3    270    245
 -4    191    170
 -5    112    140
 -6    112    123
 -7    112    149

      3,-5,L

  0    517    486
  1    396    414
  2    517    536
  3    410    458
  4    825    811
  5    741    705
  6   1156    902
  7    625    532
 -1    573    629
 -2    723    662
 -3    550    577
 -4    294    312
 -5    154    131

      3,-6,L

  0    191    248
  1    410    412
  2    946    872
  3    937    877
  4    643    605
  5    923    849
  6    928    813
  7    527    472
 -1    643    614
 -2    112    142
 -3    350    365
 -4    191    218
 -5    112     46

      3,-7,L

  0    382    350
  1    112     88
  2    564    578
  3    690    561
  4    653    659
  5    937    780
  6    643    643
  7    550    524
  8    848    683
 -1    112    133
 -2    112     60
 -3    112    157
 -4    219    200

      3,-8,L

  0    247    250
  2    466    452
  3    270    317
  4    350    390
  5    247    275
  6    541    496
  7    112     38
  8    583    437
  9    443    428
 -1    154    161
 -2    154    172
 -3    294    239
 -4    154    162

      3,-9,L

  0    112    182
  1    350    328
  2    219    228
  3    695    582
  4    466    397
  5    364    326

  6    331    314
  8    331    339
  9    494    412
 -1    219    192
 -2    247    227
 -3    191    199

      3,-10,L

  0    112    135
  1    154    206
  2    219    203
  3    270    307
  4    443    452
  5    112    172
  6    112    110
  7    191    234
  8    312    323
  9    466    382
 -2    154    191

      3,-11,L

  0    112    137
  1    331    324
  2    382    321
  3    270    269
  4    527    461
  6    219    216
  7    350    304
  8    312    271
  9    247    225
 -1    112    127

      3,-12,L

  1    219    270
  2    294    288
  3    294    262
  4    154    261
  5    219    231
  6    154    208
  7    592    496
  8    429    343
  9    294    284

      3,-13,L

  2    154    228
  3    191    185
  4    219    224
  5    247    250
  6    331    307
  7    364    375
  8    364    388
  9    331    339

      3,-14,L

  5    154    211
  6    191    248
  8    312    368

      4,0,L

  0    601    585
  1    457    395
  2    780   1109
  3    621    580
  4    789    682
  5    685    693
  6   1266   1153
  7    611    635
  8    288    322
  9    457    468
 10    164    239
 11    233    286
 12    164    235
 -1    407    436
 -2    288    229
 -3    422    391
 -6    164    144
 -7    288    210

      4,1,L

  0   1365   1469
  1    422    673
  2    586    656
  3    864    800
  4    437    506
  5    665    625
  6    561    618
  7    482    455
  8    333    308
  9    164    263
 11    119    189
 -1   1003    880
 -2    655    679
 -3    164    166

 -4    725    550
 -5    333    168
 -6    387    320
 -7    372    316

      4,2,L

  0    789    862
  2    735    795
  3    372    438
  4    353    324
  5    536    532
  6    640    599
  7    233    237
  8    457    377
  9    164    125
 -1    839    884
 -2    482    296
 -3    119    131
 -4    611    493
 -5    263    192
 -6    561    456
 -7    511    410
 -8    263    187
 -9    119     61

      4,3,L

  0   1038   1041
  1    536    570
  2    735    823
  3    333    337
  4    333    317
  5    536    597
  6    288    312
  7    353    306
 -1    685    621
 -2    760    721
 -3    497    464
 -4    472    356
 -5    437    339
 -6    407    262
 -7    472    383
 -8    288    205

      4,4,L

  0    263    239
  1    387    404
  2    119    181
  3    119    164
  5    372    341
  6    119    138
  7    288    267
  8    119    156
  9    119    117
 -1    561    562
 -2    511    504
 -3    551    433
 -4    497    464
 -5    601    506
 -6    526    409
 -7    353    282
 -8    313    241
 -9    164    108

      4,5,L

  0    119    166
  1    164    258
  4    422    385
  6    233    242
  8    164    238
 -1    288    209
 -2    263    294
 -4    288    227
 -5    789    651
 -6    333    356
 -7    204    144
 -8    204    236
 -9    164    120

      4,6,L

  0    561    556
  1    854    788
  2    655    543
  3    164    214
  4    288    278
  5    119    209
  6    263    262
  7    233    304
  8    164    199
 -2    233    256
 -3    119     56
 -4    313    199
 -5    164    124
 -6    233    131
 -7    233    141
```

4,6,L

-9	164	102

4,7,L

0	387	404
1	586	595
2	457	417
3	422	341
4	119	198
5	119	173
6	119	223
7	164	220
-1	233	228
-2	407	378
-3	288	267
-4	313	297
-5	407	370
-6	407	342
-7	233	187

4,8,L

0	472	459
1	164	170
2	422	356
3	333	352
4	204	229
5	164	175
6	164	203
-2	233	269
-3	288	258
-4	387	298
-5	333	291
-6	313	292
-7	164	132
-8	164	59

4,9,L

0	472	465
1	407	352
2	437	402
3	333	361
4	204	204
5	164	164
-1	313	312
-2	422	337
-3	422	386
-4	422	370
-5	313	252
-6	333	321
-7	263	187
-8	233	147
-9	119	131
-10	119	144

4,10,L

0	288	257
1	263	266
2	263	267
3	263	225
4	119	147
-1	372	279
-2	233	167
-3	422	430
-4	422	437
-5	407	354
-6	313	313
-7	288	264
-9	204	176
-10	164	167

4,11,L

0	164	146
1	119	157
2	204	203
-1	164	163
-2	233	209
-3	288	246
-4	422	400
-5	313	312
-6	288	254
-7	204	189
-9	233	203
-10	164	202

4,12,L

0	119	117
1	119	147
-2	204	205
-3	204	191
-4	333	312
-5	204	207
-6	119	169
-7	204	122
-8	119	136
-9	204	155

4,13,L

-2	164	191
-3	204	194
-4	204	184
-5	164	184
-6	119	68
-7	119	126
-8	164	169

4,-1,L

0	611	608
1	655	744
3	640	718
4	869	800
5	482	506
6	665	613
7	407	471
8	288	313
9	333	409
10	472	458
11	263	307
12	263	341
-1	263	231
-2	437	408
-3	387	385
-6	288	281

4,-2,L

0	725	743
1	119	26
2	204	15
3	204	253
4	611	567
5	640	605
7	665	599
8	164	224
9	372	389
10	422	418
11	372	386
12	263	293
-1	353	384
-2	621	582
-3	263	265
-5	204	208

4,-3,L

0	233	255
1	422	500
2	233	79
3	119	67
4	924	877
5	705	695
6	611	577
7	551	537
9	164	160
10	387	351
11	372	326
-1	437	382
-2	695	652
-3	472	401
-4	164	115
-5	204	221

4,-4,L

0	353	294
1	333	294
2	511	452
3	422	444
4	814	694
5	631	585
6	407	369
7	472	441
8	263	339
10	387	331
11	204	330
-1	422	343
-2	705	670
-4	288	242

4,-5,L

0	437	441
1	313	342
2	725	717
3	204	290
4	854	835
5	333	312
6	407	404
8	288	310
9	551	432
10	233	251
-1	387	325
-2	372	422
-3	333	263
-4	263	251
-5	119	128

4,-6,L

0	164	195
1	263	288
2	437	562
3	482	622
4	576	555
5	789	749
6	457	378
-1	372	355
-2	119	130
-3	313	282
-4	288	228

4,-7,L

0	333	315
2	621	711
3	665	786
4	497	507
5	804	762
6	611	567
-1	233	267
-2	333	258
-3	233	240
-4	119	169

4,-8,L

0	164	258
2	288	429
3	333	430
4	437	479
5	472	529
6	422	423
-1	164	204
-2	119	203
-3	204	214

4,-9,L

0	204	231
1	313	329
2	233	276
3	482	522
4	372	414
5	333	367
6	233	304
7	164	306
-1	119	130
-2	164	147

4,-10,L

1	164	185
2	288	260
3	233	289
4	387	360
6	313	399
7	536	519
-1	119	65

4,-11,L

1	119	165
2	119	219
3	204	201
4	204	277
6	119	261
7	333	338

4,-12,L

1	119	205
2	233	235
3	119	206
4	204	207
5	164	200

4,-13,L

3	164	187
4	204	212
5	119	209
6	119	188

References

1. M.J. Buerger, "X-ray Crystallography", John Wiley and Sons, Inc., (1942), 144.

2. Ibid., 360.

3. H. Lipson and W. Cochran, "The Determination of Crystal Structures", 'The Crystalline State', Vol. II, ed. Bragg, G. Bell and Sons Ltd., (1966), 50.

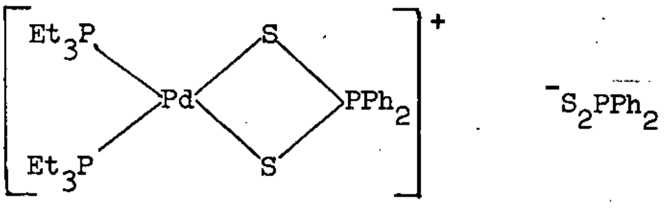
4. Ibid., 57.

PART II

The Crystal and Molecular Structure of (Diphenylphosphinodithioato)bis(triethylphosphine)palladium(II) Diphenylphosphinodithioate.

INTRODUCTION

In a paper[1] published in 1970, Dr. T.A. Stephenson, now at Edinburgh University, reported the isolation of pale yellow crystals when an excess of triethylphosphine was added to bis(diphenylphosphinodithioato)palladium(II). Chemical analysis showed the compound to have the empirical formula $C_{36}H_{50}P_4PdS_4$. A six-co-ordinated palladium complex containing two $Ph_2PS_2^-$ groups and two PEt_3 groups was tentatively suggested as the structure of this compound basing this suggestion on the evidence of the infrared spectrum of the compound. An X-ray analysis of this compound was therefore undertaken to establish unambiguously its molecular structure. During the course of the preliminary two dimensional X-ray analysis, conductivity measurements[2] were made on a sample of the material which suggested the compound was ionic in nature. Consequently the following formula was suggested, containing a four-co-ordinated palladium atom



This was confirmed by the single crystal X-ray structure analysis reported in this thesis.

EXPERIMENTAL

Summary of Crystal Data

(Diphenylphosphinodithioato)bis(triethylphosphine)palladium(II) Diphenylphosphinodithioate, $C_{36}H_{50}P_4S_4Pd$, M=841.3, yellow monoclinic crystals, space group C 2/c, a=33.63(4)Å, b=8.71(2)Å, c=32.30(5)Å, β=121.4(1)°, U=8080(50)$Å^3$, D_m=1.3 g/cm^3 (by flotation), D_c=1.55 g/cm^3, z=8, Cu-K_α radiation, λ=1.5418Å, μ=79.9 cm^{-1}, $t_{opt.}$=0.025 cm.

Determination of Cell Dimensions and Space Groups

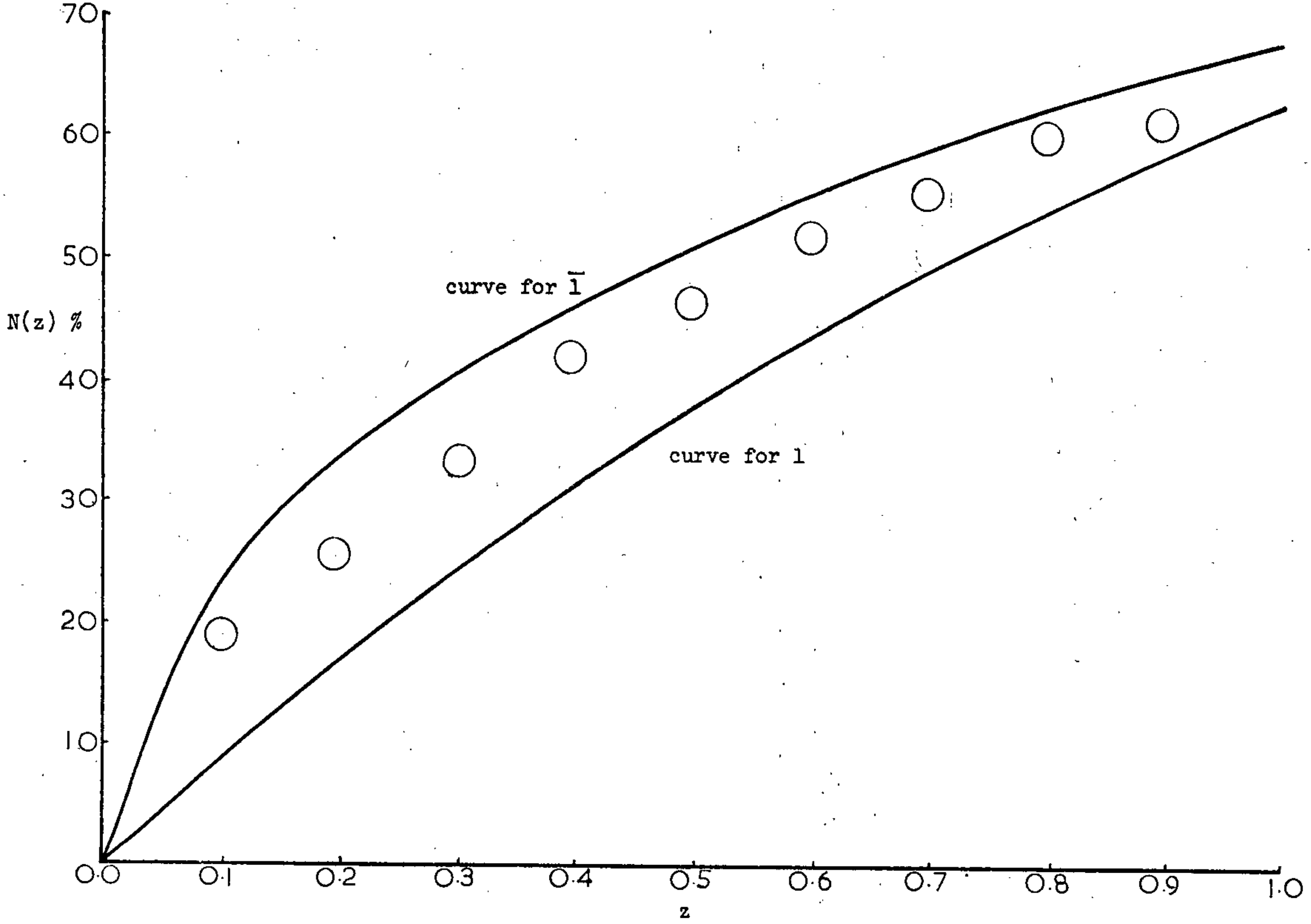
The material supplied, consisting of very thin needle like crystals, could not be recrystallised as the compound decomposed in solution. One crystal was found which had a maximum dimension perpendicular to the needle axis less than the optimum thickness for the material, but which was large enough to be used in single crystal diffraction studies. This crystal was mounted about its needle axis and an oscillation photograph taken from which was calculated the [b] cell dimension. A zero level Weissenberg photograph was then taken from which [a], [c] and [β] cell dimensions were obtained.

a=33.63(6)Å	b=8.71(2)Å	c=32.30(5)Å
	β=121.4(1)°	
a^*=0.0536(1) r.l.u.	b^*=0.1770(4)r.l.u.	c^*=0.0558(1) r.l.u.
	β^*=58.6(1)°	

The conditions for reflection were found to be hkl: h+k=2n, hol: l=2n,(h=2n), oko: (k=2n), indicating that the space group is Cc(number 9) or C 2/c (number 15)[3]. The N(z) test for centrosymmetry

Figure 1

N(z) test for centrosymmetry



indicated the presence of a centre of symmetry in the crystal and so the structure determination proceeded on the assumption that the correct space group was C 2/c (Figure 1).

Chemical Analysis

The results of the chemical analysis[1] of a sample of the material were found to be C,51.1%; H,6.2%; P,14.8%; S,13.8%. The structure determined, $C_{36}H_{50}P_4S_4Pd$, requires the composition C,51.4%; H,6.0%; P,14.7%; S,15.2%.

Two Dimensional Structure Analysis. - Projection down the [b] axis

A very thin knife like crystal was mounted along its longest axis and a zero layer Weissenberg photograph taken. 208 intensities were visually estimated and corrected for Lorentz and Polarisation factors. The symmetry of the projected structure conformed to that of plane group p2 where a'=a/2 and c'=c/2.

A sharpened Patterson map was calculated. Around the origin of this map were situated peaks of the correct weight, distance from the origin, and orientation with respect to the origin to be interpreted as a square planar arrangement of sulphur and phosphorus atoms around a central palladium atom. The longest non-origin peaks were considered as possible representations of vectors between symmetry related palladium atoms. Several structure factor calculations were carried out phased on two sulphur and two phosphorus atoms co-ordinated to a palladium atom situated in turn at positions in the unit cell consistent with the observed large peaks in the Patterson map. The calculation with the lowest R factor was considered to indicate the true position of the palladium atom. All attempts failed however to find by Fourier methods two other atoms co-ordinated to the palladium atom to make a six-co-ordinated species.

It was at this stage that conductivity measurements indicated that the compound was ionic containing a four-co-ordinated palladium atom and a dithioate ion. The two sulphur atoms and the phosphorus atom of the dithioate ion were now found by Fourier methods as were all the carbon atoms except two, the positions of which remained undetermined by the two dimensional structure analysis. This structure was then refined by least squares to an R factor of 0.19.

The positional parameters of this structure are shown in table 2 and refer to the projected cell which is bound by the axis a'=a/2 and c'=c/2. In comparing the co-ordinates of the two dimensional structure with those of the finally determined structure it must be noted that the origin of the two dimensional structure is co-incident with the point $(0,0,\frac{1}{4})$ in the three dimensional cell.

TABLE 2

Fractional Co-ordinates Determined by the Two Dimensional Structure Analysis

	x	z
Pd	.439	.140
S(1)	.277	.064
S(2)	.380	$.\overline{023}$
S(3)	.366	.499
S(4)	.220	$.\overline{459}$
P(1)	.251	$.\overline{051}$
P(2)	$.\overline{414}$	.193
P(3)	.466	.298
P(4)	.229	.456

Ethyl groups bonded to P(2)

$.\overline{225}$	.275
$.\overline{385}$	.110
$.\overline{480}$	.025
$.\overline{305}$	.275
$.\overline{380}$	.270

Ethyl groups bonded to P(3)

.265	.235
.375	.275
.465	.355
.440	.275
$.\overline{455}$	.490
$.\overline{433}$	.390

2.6.

Phenyl groups bonded to P(1)

x	z
.185	$\overline{.050}$
.020	$\overline{.140}$
.055	$\overline{.070}$
.085	$\overline{.155}$
.150	.025
.210	.020
.195	$\overline{.225}$
.080	$\overline{.350}$
.150	$\overline{.310}$
.075	$\overline{.255}$
.172	$\overline{.160}$

Phenyl groups bonded to P(4)

.200	.455
.153	.430
.147	.450
.055	.405
.010	.410
.060	.430
.090	.155
.110	.145
.180	.245
.225	.330
.175	.320
.135	.255

THREE DIMENSIONAL STRUCTURE DETERMINATION

Data Collection

1696 reflections were recorded on film (Kodak Industrex D) by the equi-inclination Weissenberg technique, using film packs each of which contained three films. The data was collected up the [b] axis to a k of seven corresponding to an equi-inclination angle (μ) of 38.8°.

1594 intensities having indices ranging from hol to h61 were measured on the SAAB Automatic Film Scanner Mark II, whilst the remaining 102 reflections from the seventh layer were visually estimated. The structure determination was begun using the 1243 reflections with k values ranging from 0 to 5, the sixth layer intensities being added before the refinement of the phenyl rings and the seventh layer intensities added during the final stages of refinement. The intensities were corrected for Lorentz and polarisation factors.

Accuracy of Data

The raw measurements of light transmission from the scanner were processed by three programmes, 'Findspots', 'Filmfit' and 'Packscal', as described in Appendix A. There are two possible sources of error in this process. Firstly the relationship between the intensity of a reflected X-ray beam and the optical density of the corresponding spot on a film is linear only within certain limits of intensity. This error may be counteracted by accepting for the final data set only spots with intensities less than the chosen threshhold level of 500. If a spot on the weaker film of a film pack is more intense than this then the intensity of this spot will be calculated only from the weaker films of the pack. Secondly errors will arise as described in Appendix A due to the effect of the processing of the scanner light transmission values at the edges of spots. These errors can only be approximately corrected by the modification factor described in Appendix A, and new errors may be introduced by this modification factor. Figure 3 shows the profile of several spots of different sizes and shape and how they may be wrongly corrected.

The various errors which would arise in the total process were investigated by constructing graphs where film factors were plotted against integrated intensity for two films from a tri-film pack of a second layer Weissenberg photograph. These film factors should be the same for all spots if the optical density of a spot is proportional to the intensity of the reflected X-ray beam. From these graphs (figures 4 and 5) the following conclusions were drawn. Intensity values refer to the intensity of the spot on the weaker film.

a) Intensity values less than 200 are unreliable.

b) Intensity values in the range 200 to 500 are the most reliable.

c) Intensity values greater than 500 are increasingly unreliable.

The falling film factor (see figure 4) of these spots is probably due to the reflected beam being of such intensity that it causes saturation of the sensitive emulsion on the strongest film only.

d) Contracted spots tend to have lower film factors than expanded spots. This may be due to the saturation effect mentioned above

Figure 3

Profiles of spots of different shapes showing parts of spots (hatched areas) which are not recorded by film scanner.

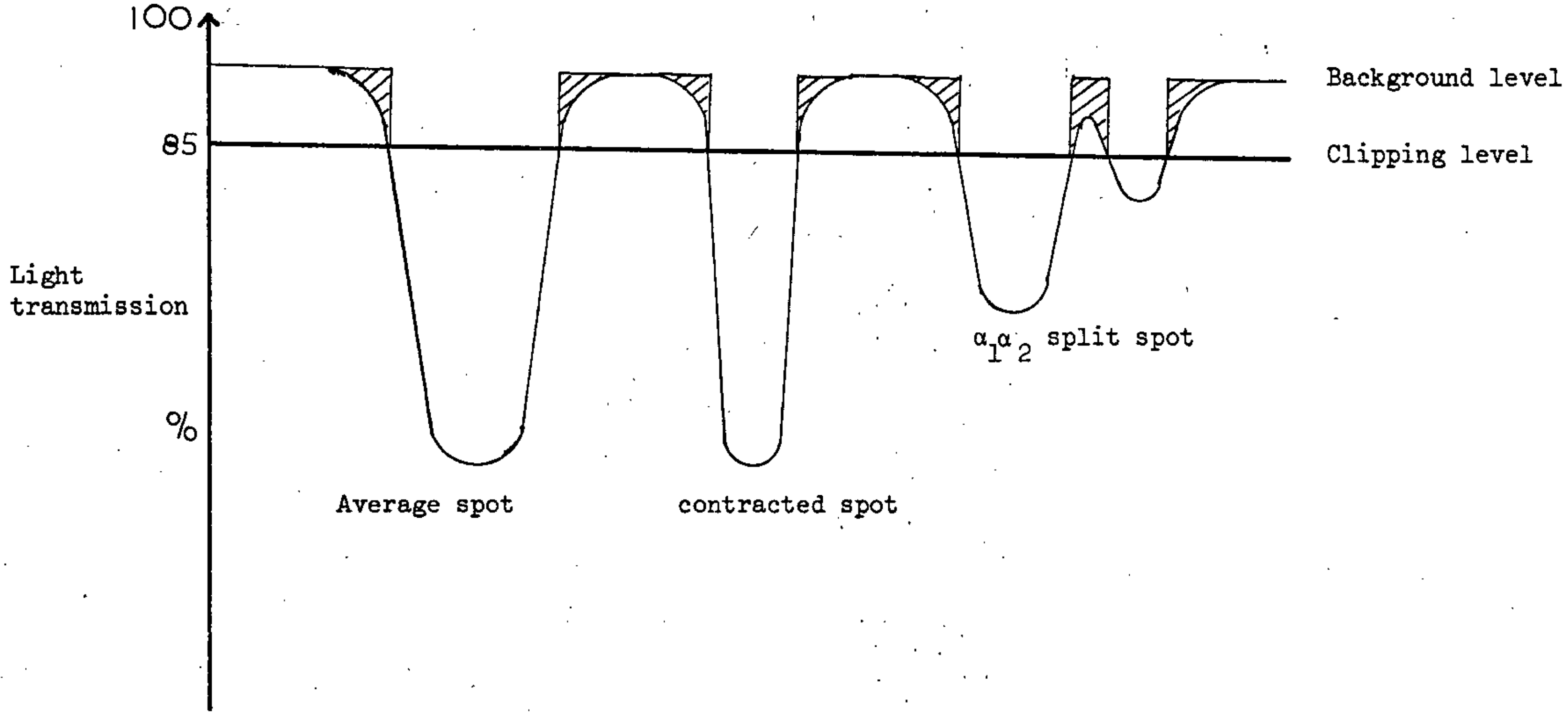


Figure 4

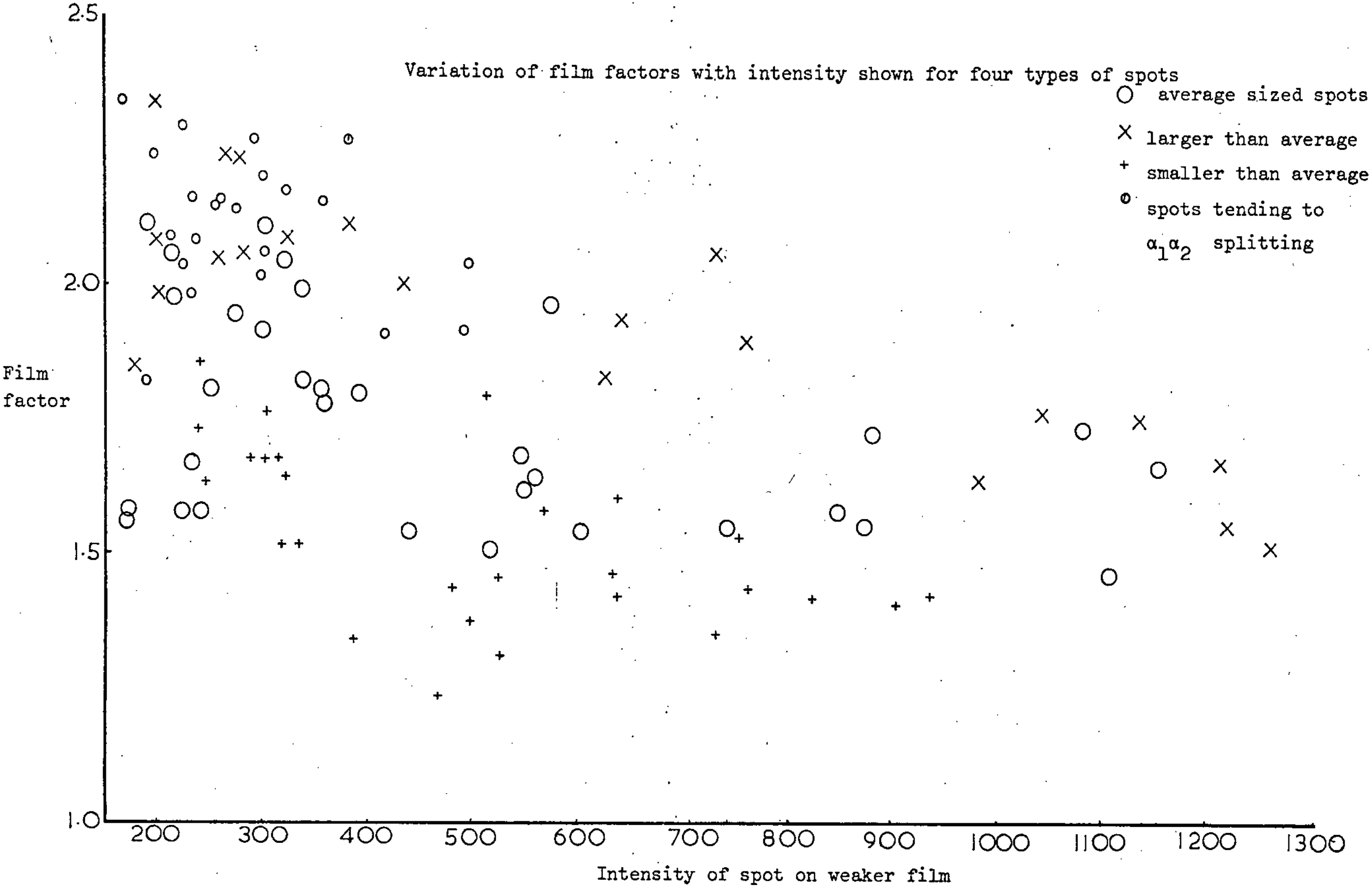
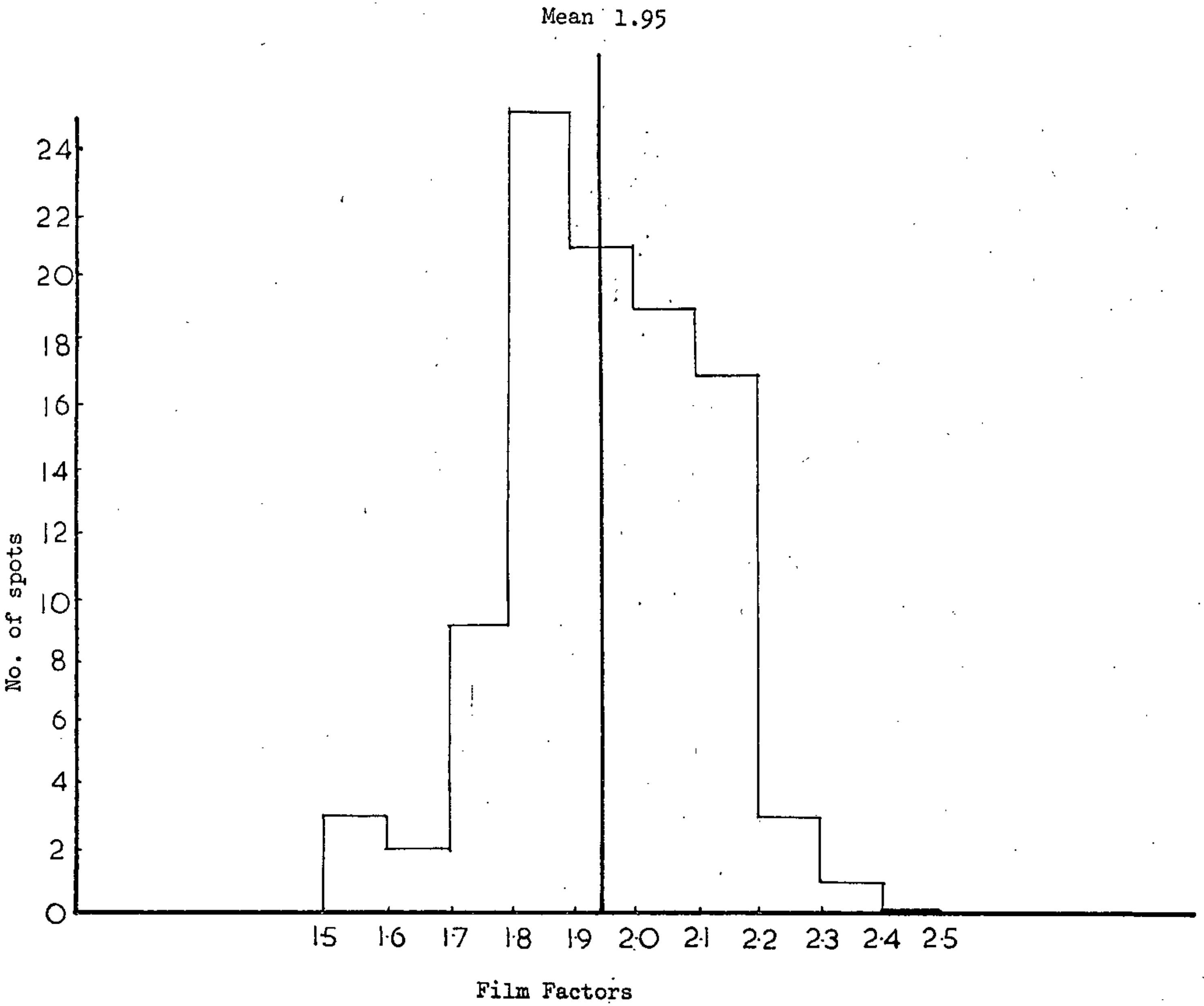

Variation of film factors with intensity shown for four types of spots
○ average sized spots
× larger than average
+ smaller than average
⊙ spots tending to $\alpha_1\alpha_2$ splitting
Film factor
2.5
2.0
1.5
1.0
200
300
400
500
600
700
800
900
1000
1100
1200
1300
Intensity of spot on weaker film

Figure 5

Spread of film factors for one pair of films



becoming noticeable at lower intensity values.

e) Spots with a tendency to $\alpha_1\alpha_2$ splitting have higher film factors. This may be due to the loss of the α_2 contribution to the integrated intensity of the spot on the weaker film only (see figure 3).

f) 91% of the spots on the second layer Weissenberg photograph have film factors which lie within ±12.8% of the overall mean film factor of 1.95.

Using these and similar graphs for all the Weissenberg photographs film factors were calculated and a scheme devised as shown below to compile a list of intensities for the structure determination.

If $I<200$ intensities were taken only from the strongest film in the film pack.

If $200\leqslant I\leqslant 500$ intensities from the different films in a film pack were placed on the same scale and then averaged.

If $I>500$ intensities were taken only from the weakest film of the film pack and scaled up to the same scale as the other intensities.

Interpretation of Patterson Function

An unsharpened Patterson map was calculated from which the position of the palladium atom was deduced. The largest non origin peak in the Patterson map was situated at $u=0.435$, $v=0.092$, $w=0.638$. This was interpreted as a peak of the type $2x$, $2y$, $2z$ representing the vector between a palladium atom at x,y,z and another palladium atom related to it by a centre of symmetry. Harker peaks should then occur with co-ordinates $u=2x$, $v=0$, $w=\frac{1}{2}+2z$; and $u=0$, $v=2y$, $w=\frac{1}{2}$.

The co-ordinates of the palladium atom were therefore x=0.218, y=0.046, z=0.319. These co-ordinates are consistent with the x and z co-ordinates found from the two dimensional structure analysis.

Determination of Structure

A difference Fourier synthesis phased on the palladium atom situated at the position 0.218, 0.046, 0.319 enabled the sulphur and phosphorus atoms co-ordinated to the palladium atom to be found. The rest of the atoms in the structure were found from successive difference Fourier maps giving a structure with an R factor of 0.27. The layer scale factors and the positional and isotropic thermal parameters of palladium, phosphorus and sulphur atoms were then refined by full matrix least squares, bringing the R factor down to 0.18.

The positions of the phenyl ring carbon atoms, found from difference Fourier maps, were modified to make them part of an idealised phenyl ring which was co-planar with the best plane through the original six carbon atoms. A full matrix least squares refinement was then carried out on the whole structure constraining the phenyl rings to move as complete idealised phenyl rings. In one cycle the shape of the phenyl ring was allowed to vary. Lastly the thermal parameters of the palladium and sulphur atoms were allowed to vary anisotropically, bringing the R factor to its final value of 0.126.

RESULTS

The molecular structure of this compound has been unambiguously determined, its ionic nature confirmed and the palladium atom shown clearly to be four-co-ordinated. The shortest interatomic distance between the palladium atom and either of the sulphur atoms of the dithioate ion is 6.15 Å, whilst, the phosphorus atom is never closer to the palladium atom than 7.2 Å. There is therefore no ambiguity about the co-ordination number of the palladium atom. Very slight deviation from a square planar arrangement of the ligands around the palladium atom may be interpreted in terms of steric interactions between the two bulky tri-ethylphosphine groups. Figure 6 shows the co-ordination around the palladium atom and its anisotropic vibration.

Figure 6.

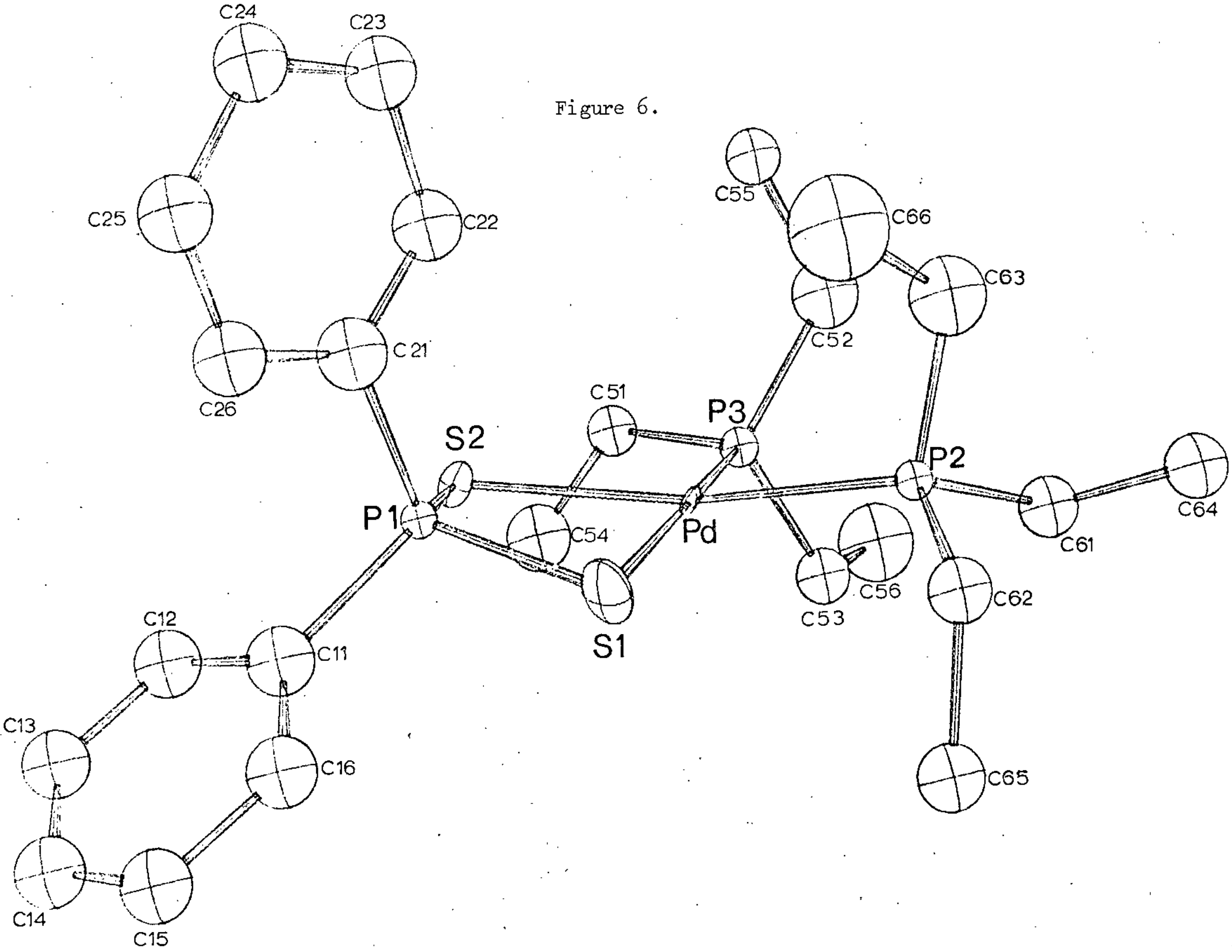

C24
C23
C25
C22
C55
C66
C63
C21
C26
C52
C51
P3
S2
P2
C64
P1
C54
Pd
C61
C56
C53
C62
S1
C12
C11
C13
C16
C65
C14
C15

Table 3

The R factor as a function of the layer index and the magnitude of $|F_o|$

k	$\Sigma\|F_o\|$	$\|\Sigma F_c\|$	$\Sigma\|\Delta\|$	No	R
0	47364	47533	5727	191	0.121
1	53727	53409	6801	266	0.127
2	61485	60561	7934	339	0.129
3	31382	33256	4034	161	0.129
4	34960	35844	3913	199	0.112
5	35403	35818	3844	224	0.109
6	29683	29979	3662	187	0.123
7	18870	18970	3376	129	0.179
overall	312830	315330	39288	1696	0.126
$0 \leq \|F_o\| < 100$	23742	25762	6145	276	0.259
$100 \leq \|F_o\| < 150$	53428	50368	7796	352	0.146
$150 \leq \|F_o\| < 200$	64020	62521	8004	357	0.125
$200 \leq \|F_o\| < 250$	44865	44787	4703	222	0.105
$250 \leq \|F_o\| < 300$	29261	29709	2911	136	0.099
$300 \leq \|F_o\| < 350$	24032	24149	1975	102	0.082
$350 \leq \|F_o\| < 800$	62565	65735	6061	224	0.097

Table 4

Fractional co-ordinates of atoms and thermal parameters (Å^2).

With standard deviations in parenthesis.

	x	y	z	U
Pd	0.2183(1)	0.0414(3)	0.3195(1)	
S(1)	0.1387(4)	-0.0503(15)	0.2831(4)	
S(2)	0.1894(4)	0.1273(12)	0.2379(4)	
S(3)	0.1790(5)	0.0468(24)	0.5001(5)	
S(4)	0.1056(5)	-0.1739(12)	0.5154(5)	
P(1)	0.1275(4)	0.0742(11)	0.2261(4)	0.013(3)
P(2)	0.2316(4)	-0.0042(10)	0.3965(4)	0.015(3)
P(3)	0.2935(4)	0.1130(12)	0.3453(4)	0.018(3)
P(4)	0.1157(4)	-0.0146(11)	0.4776(4)	0.016(3)
		Ethyl carbon atoms		
C(51)	0.2996	0.1835	0.2985	0.030
C(52)	0.3183	0.2663	0.3912	0.054
C(53)	0.3322	-0.0490	0.3671	0.036
C(54)	0.3015	0.0878	0.2601	0.053
C(55)	0.2859	0.4279	0.3739	0.033
C(56)	0.3867	-0.0142	0.3951	0.076
C(61)	0.2893	-0.0565	0.4460	0.036
C(62)	0.1921	-0.1361	0.3972	0.033
C(63)	0.2224	0.1680	0.4197	0.056
C(64)	0.2942	-0.0579	0.4972	0.039
C(65)	0.1968	-0.3200	0.3813	0.041
C(66)	0.1709	0.2405	0.3843	0.092

Table 4 contd.

Phenyl carbon atoms.

C(11)	0.0945	-0.0360	0.1706	0.042
C(12)	0.0970	-0.0026	0.1291	0.042
C(13)	0.0694	-0.0805	0.0857	0.042
C(14)	0.0388	-0.1934	0.0834	0.042
C(15)	0.0337	-0.2341	0.1214	0.042
C(16)	0.0623	-0.1541	0.1674	0.042
C(21)	0.0911	0.2371	0.2188	0.042
C(22)	0.1146	0.3516	0.2517	0.042
C(23)	0.0885	0.4887	0.2487	0.042
C(24)	0.0392	0.4971	0.2113	0.042
C(25)	0.0181	0.3721	0.1791	0.042
C(26)	0.0438	0.2427	0.1827	0.042

	x	y	z	U
C(31)	0.0900	-0.0745	0.4145	0.042
C(32)	0.0706	0.0310	0.3755	0.042
C(33)	0.0522	-0.0182	0.3280	0.042
C(34)	0.0529	-0.1747	0.3190	0.042
C(35)	0.0707	-0.2856	0.3541	0.042
C(36)	0.0903	-0.2370	0.4043	0.042
C(41)	0.0781	0.1512	0.4693	0.042
C(42)	0.0347	0.1248	0.4619	0.042
C(43)	0.0068	0.2574	0.4583	0.042
C(44)	0.0261	0.4101	0.4626	0.042
C(45)	0.0714	0.4250	0.4702	0.042
C(46)	0.0974	0.2967	0.4736	0.042

Anisotropic thermal parameters

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	0.009(2)	0.006(1)	0.006(2)	-0.002(2)	0.002(1)	0.003(2)
S(1)	0.031(8)	0.035(6)	0.021(7)	-0.021(7)	0.007(6)	-0.005(7)
S(2)	0.018(7)	0.018(5)	0.015(7)	0.002(5)	0.008(6)	0.006(5)
S(3)	0.018(8)	0.139(13)	0.028(9)	-0.034(11)	0.004(7)	-0.036(11)
S(4)	0.051(10)	0.015(6)	0.046(9)	0.009(6)	0.031(8)	0.007(5)

Table 5

Intramolecular distances (Å) and angles (°) with standard deviations in parenthesis

Pd-S(1)	2.429(13)	S(1)-Pd-S(2)	81.9(4)
Pd-S(2)	2.405(13)	P(2)-Pd-P(3)	95.6(5)
Pd-P(2)	2.320(15)	P(2)-Pd-S(1)	90.6(5)
Pd-P(3)	2.300(14)	P(3)-Pd-S(2)	93.0(5)
S(1)-P(1)	1.996(18)	Pd-S(1)-P(1)	84.2(6)
S(2)-P(1)	1.966(20)	Pd-S(2)-P(1)	85.4(7)
		S(1)-P(1)-S(2)	106.1(6)
		C(11)-P(1)-C(21)	105.2(5)
P(4)-S(3)	1.932(20)	S(3)-P(4)-S(4)	117.9(8)
P(4)-S(4)	1.990(20)	C(31)-P(4)-C(41)	99.9(4)
P(2)-C(61)	1.817(10)	C(61)-P(2)-C(62)	106.9(5)
P(2)-C(62)	1.765(13)	C(61)-P(2)-C(63)	100.4(5)
P(2)-C(63)	1.775(12)	C(62)-P(2)-C(63)	104.3(8)
P(3)-C(51)	1.739(16)	C(61)-P(2)-Pd	120.5(8)
P(3)-C(52)	1.841(11)	C(62)-P(2)-Pd	113.6(5)
P(3)-C(53)	1.795(11)	C(63)-P(2)-Pd	109.3(5)
P(1)-C(11)	1.816(10)	C(51)-P(3)-C(52)	103.6(6)
P(1)-C(21)	1.808(11)	C(51)-P(3)-C(53)	103.3(8)
P(4)-C(31)	1.826(12)	C(52)-P(3)-C(53)	108.8(5)
P(4)-C(41)	1.844(12)	C(51)-P(3)-Pd	112.7(5)
		C(52)-P(3)-Pd	116.0(8)
		C(53)-P(3)-Pd	111.4(5)

Table 6

Observed and Calculated Structure Factors for $PdS_4P_4C_{36}H_{50}$

Columns are: l, |F|obs., |F|calc.

l	|F|obs.	|F|calc.
0,0,L		
4	785	1430
6	2789	3150
8	2424	1611
10	2884	2711
12	2226	2148
14	3267	3688
20	2424	2262
22	2155	2147
2,0,L		
-18	1695	1115
-16	2910	2583
-14	2214	2137
-12	4875	5560
-8	2414	2159
-6	1942	1825
-4	817	171
4	2742	2600
6	734	243
10	2866	2665
12	948	756
16	2119	1958
18	2113	1652
22	2333	2569
24	2161	2121
4,0,L		
-28	2161	2556
-24	2533	2645
-20	1969	1227
-18	1975	1850
-16	1955	1701
-14	3828	4410
-12	3851	4572
-10	3723	3796
-6	906	1781
-4	6079	7554
0	531	382
2	1936	2139
4	2076	1915
6	2161	1919
8	2558	2445
10	2915	3089
12	1969	1848
14	2419	2047
16	2789	2862
22	2365	2300
24	2294	2403
6,0,L		
-26	3674	4101
-20	3188	2982
-16	3376	3614
-14	3123	3242
-12	4681	5532
-10	2045	2056
-8	698	604
-6	974	1207
-4	2202	2800
-2	2214	2345
0	2548	3258
2	1166	1225
6	1133	638
8	2095	2141
10	2839	2773
12	2321	2166
16	2197	1811
18	2825	2984
24	2349	3029
8,0,L		
-26	3428	3932
-20	3510	3990
-18	2811	2738
-16	3451	3756
-12	2408	2491
-10	3027	3375
-8	2282	2007
-6	1819	1474
-4	1841	1031
-2	2811	3422
0	2980	3206
2	2349	2330
4	2857	3006
6	1013	1218
10	3252	3364
12	4610	5058
18	2197	2002
10,0,L		
-30	2248	2362
-26	2039	1756
-24	2487	2144
-20	2039	1735
-18	2558	2501
-16	3119	3119
-14	1922	1980
-10	2327	2137
-8	2288	1889
-6	1688	1161
-4	3027	3757
0	4445	5265
2	2548	2243
6	3119	3140
8	1942	1430
10	2603	2267
12	3730	3955
12,0,L		
-30	3115	3666
-24	3023	3169
-20	2033	1700
-18	2305	1875
-16	2327	2208
-14	2007	2054
-8	1868	1742
-6	974	926
-4	3868	4750
-2	5313	6874
0	3564	4656
4	2700	2612
6	2807	2686
8	2919	2623
12	1895	1567
14,0,L		
-30	2288	2274
-16	2305	2103
-14	2811	2691
-10	988	605
-8	2993	3133
-6	877	661
-4	2365	2228
-2	4065	5361
0	1748	1371
2	1740	1494
4	2568	2310
6	2113	2032
8	4125	4448
16,0,L		
-28	2333	2360
-20	1868	1423
-16	2793	2853
-14	3086	3294
-10	2202	2217
-8	3828	4205
-6	2751	2957
-4	2387	2165
0	2014	1729
4	2173	2241
6	2113	1756
8	2440	2559
18,0,L		
-26	2327	2428
-20	3499	3752
-14	2834	2496
-12	2026	1922
-8	3184	3432
-6	3825	5021
-4	2466	2488
0	1755	1583
2	1936	1377
6	2045	1868
20,0,L		
-26	1962	674
-22	2137	1821
-20	3360	3721
-18	3888	3941
-14	1982	1647
-12	1805	1170
-6	2414	2260
-4	2387	1993
0	1969	1927
4	2001	1745
10	2137	1819
22,0,L		
-28	2149	1730
-22	2661	2639
-20	2360	2091
-18	4062	4608
-12	2932	2965
2	2020	1916
4	2101	1815
10	2558	2863
24,0,L		
-32	2588	2939
-30	2070	2007
-18	2101	1658
-10	1895	2016
-4	2179	2264
-2	2070	1867
4	2392	2442
26,0,L		
-32	2007	2103
-26	2248	2397
-22	2915	2778
-16	2185	1998
-8	2191	1891
-4	2563	2306
-2	2666	2555
4	2533	2421
6	2288	2720
28,0,L		
-10	2045	1595
-8	2548	2625
-6	2288	2078
30,0,L		
-10	2282	2027
-8	2398	2434
-6	2414	2636
32,0,L		
-22	2214	2237
-20	2310	2637
34,0,L		
-20	2528	2967
1,1,L		
-24	1877	2154
-20	1838	1531
-12	2752	2745
-11	2462	2272
-10	3623	4347
-8	797	722
-7	2658	2981
-5	2428	2817
4	2064	2072
5	2433	3048
6	2399	2542
7	1600	1187
9	3260	3722
10	1514	1401
12	3440	3990
13	1804	1358
16	1871	1389
20	1844	1832
26	2137	2629
3,1,L		
-24	2312	2382
-17	1675	1374
-16	2487	2376
-14	1438	1224
-13	2029	1679
-12	1431	1148
-10	4417	5652
-8	1501	1280
-7	1593	1293
-6	429	493
-5	2113	2619
1	286	474
2	1866	1974
3	1619	1353
4	809	732
5	1473	1103
6	2078	1746
7	757	760
8	686	600
11	1898	1791
12	2118	2092
16	1758	1376
18	1914	1955
20	2156	2337
22	2024	2179
5,1,L		
-22	1681	1318
-21	2044	1913
-20	1681	1160
-19	1770	1199
-18	1723	1282
-16	4218	5449
-15	2474	2360
-14	3062	3450
-13	797	685
-11	2967	2883
-10	3039	3708
-9	1998	1643
-8	730	909
-6	894	883
-4	1534	1628
-3	554	397
-2	3025	3889
-1	834	1175
0	286	4
1	1508	1390
4	2285	2508
6	715	671
7	1631	1290
8	1580	1313
9	1770	1454
12	3039	3039
14	2536	2760
22	2019	2507
7,1,L		
-28	1893	2276
-22	1844	1823
-20	1554	1188
-17	2039	1663
-16	3193	3667
-15	1042	745
-14	4525	5404
-10	2184	2226
-9	2294	2251
-8	2253	2079
-7	757	456
-6	2103	2126
-5	2003	1924
-4	5269	6398
-3	2054	2478
-2	797	1032
-1	2715	3109
0	2603	2947
1	1051	1067
2	730	683
4	2360	2118
5	905	977
6	1866	1848
7	981	1124
8	2767	2964
9	894	641
10	1936	1556
12	3059	3033
14	3086	3138
16	2303	2213
22	1909	2320
9,1,L		
-30	1860	1947
-28	2161	2125
-26	2098	1818
-24	2611	2508
-22	1936	1844
-20	3577	3916
-17	1002	775
-14	2804	2913
-13	1930	1664
-12	970	949
-8	1431	1128
-7	1514	1230
-6	1675	1541
-5	784	1116
-4	656	694
-3	1473	1173
-2	1705	1493
-1	1860	1753
0	2599	3178
1	894	955
2	1487	1254
3	905	834
4	822	611
5	2083	1932
6	2003	1849
7	1693	1232
8	2584	2544
10	2627	2570
14	2312	2264
11,1,L		
-28	2069	2110
-26	2226	2339
-24	1787	1394
-22	1930	1837
-20	2381	2630
-15	1644	1256
-14	2161	2187
-13	822	665
-12	1663	1867
-10	2137	1974
-8	859	859
-6	2285	2281
-5	607	904
-4	2137	2289
-3	2342	2306
-2	2069	1679
0	2722	3142
2	3592	4488
3	1051	1040
5	1051	1009
8	3347	3900
9	2437	2429
10	2737	2690
12	2059	1745
14	2019	2374
13,1,L		
-28	2039	2232
-24	1770	1533
-18	2523	2301
-14	1978	1557
-13	1687	1263
-12	1988	1867
-10	834	588
-6	2088	2007
-5	1567	1412
-4	4670	6066
-3	2407	2529
-2	834	836
0	1431	1188
2	3434	3763
6	1669	1393
8	3049	3024
10	2453	2603
15,1,L		
-28	1866	1707
-19	2029	1842
-18	2113	2119
-16	1741	1480
-15	2184	1737
-14	938	919
-12	2013	1870
-10	2024	1894
-9	1764	1288
-7	991	1021
-6	3257	3396
-5	2478	2157
-4	3473	4253
-3	1042	879
-2	3589	4043
1	1804	1546
4	1832	1722
10	1941	2321
17,1,L		
-18	3089	2898
-17	1459	949
-16	2925	3024
-15	1606	1240
-14	1002	820
-12	2734	2643
-10	1951	1810
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19,1,L		
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-14	1898	1771
-12	2619	2724
-11	2127	1863
-10	1613	1398
-8	3648	3903
-6	2615	2282
-2	2240	1875
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6	1752	1884
12	1887	2217
21,1,L		
-30	2240	2636
-24	2342	2132
-22	1866	1520
-20	2078	2071
-18	1821	1474
-16	2034	1978
-12	1548	1399
-11	1930	1699
-10	1770	1715
-8	1920	1471
-6	1951	1737
-3	1593	1090
6	2756	1794
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23,1,L		
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-28	1877	1488
-26	1925	1725
-24	1810	1471
-22	3138	3543
-20	1998	1808
-18	1735	1306
-16	2351	2375
-10	1860	1618
-6	1920	1912
-2	1951	1783
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2	1962	1292
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25,1,L		
-28	2271	2302
-23	1816	1377
-22	2207	1994
-20	1810	1420
-18	1741	1524
-16	2156	2211
-6	2544	2570
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27,1,L		
-26	1936	2000
-6	3052	2930
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29,1,L		
-12	1893	1655
-6	2170	2503
31,1,L		
-18	2373	2747
-12	2013	2263
-10	2560	2665
33,1,L		
-10	1946	2351
35,1,L		
-22	2137	2696
0,2,L		
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6	1971	2349
7	1309	1031
8	569	733
9	1460	1261
10	1532	1456
11	734	815
12	1523	1281
13	1235	1040
14	1726	1513
16	1272	985
18	1413	1095
20	1730	1523
22	1974	1980
2,2,L		
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-21	1483	1115
-18	1671	1602
-16	2197	1955
-15	2267	2239
-14	1803	1551
-13	2374	3754
-12	3090	3625
-11	3017	3635
-10	1298	1176
-9	1190	940
-8	1359	960
-6	4139	5314

2,2,L

-5	1455	1002
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-3	788	960
-2	284	188
2	569	753
3	1642	1492
4	1179	718
5	2129	2462
7	2483	2924
8	2154	2115
9	2691	2723
10	1723	1553
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14	2293	2404
16	1283	1157
17	1319	1029
22	2258	2418
24	1562	1718

4,2,L

-27	1487	1605
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-23	1940	1951
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-13	2380	2344
-12	2906	3088
-11	2589	3245
-10	1474	1041
-9	1161	781
-8	2058	2188
-7	1298	742
-6	2515	2842
-5	813	1811
-4	2938	3703
-3	1514	2043
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2	1201	1270
3	1324	1065
4	1536	988
6	557	485
7	1880	1586
8	1418	1107
9	1384	1094
10	2903	2857
11	1613	1273
14	1991	1816
16	2363	2416
17	1464	1154
20	1501	1249
24	1523	1616

6,2,L

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-25	1974	1908
-23	1905	1593
-20	2453	2496
-19	1887	1737
-18	1898	1555
-17	1267	1154
-16	2216	2331
-14	3660	4066
-12	2320	2408
-10	2968	3314
-9	1184	1096
-8	821	1036
-7	1746	1907
-6	1505	1432
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1	2191	2093
2	2746	3282
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12	1991	1949
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14	1821	1728
16	2669	2931
17	1422	1115
18	1854	1734
23	1754	2001

8,2,L

-26	2331	2352
-25	1642	1378
-20	1742	1565
-19	2182	1911
-18	2276	2207
-17	2045	1995
-16	2743	2677
-14	687	775
-13	1776	1607
-12	1742	1682
-9	603	391
-8	581	512
-7	1854	1868
-6	545	507
-5	1374	1047
-4	3301	3511
-3	2970	3308
-2	845	323
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0	1844	1377
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2	2405	2502
4	1464	1367
6	2615	2525
7	770	758
9	2061	1842
10	2074	1960
11	1359	1243
12	3332	3443
13	1510	1223
18	1545	1446
23	1427	1537
24	1679	2286

10,2,L

-31	1446	1581
-26	1926	2033
-24	1814	1756
-21	1277	945
-19	1523	1156
-18	2299	2375
-17	1761	1695
-16	2592	2786
-14	1738	1528
-12	1784	1702
-11	1474	1260
-9	1487	1372
-8	1991	2026
-7	603	181
-6	1384	1007
-5	581	688
-4	1167	946
-3	2317	2594
-2	2305	3176
-1	2231	2177
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2	2573	2548
4	2176	2121
6	2439	2219
7	1695	1347
9	1844	1704
10	1891	1547
11	1926	1732
12	2873	3907
13	1908	1770

12,2,L

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-20	1549	1112
-19	2015	1511
-16	2018	1728
-15	1364	1153
-13	1562	1305
-12	1926	1957
-10	1862	1902
-9	770	684
-8	1319	1096
-7	697	945
-6	1840	1487
-4	2866	3218
-3	1314	1031
-2	3127	3409
-1	3094	3370
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1	1207	792
2	1288	975
4	1256	987
5	1460	1184
6	1592	1359
8	2015	1871
10	1288	916
11	1541	1127
14	1580	1404
16	1646	1833

14,2,L

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-24	1554	1516
-20	1873	1799
-19	1496	1336
-17	1339	1109
-16	2806	3031
-15	2555	2417
-14	2273	2272
-13	2025	1845
-11	1880	1552
-10	1478	1583
-8	744	501
-6	829	895
-3	1651	1671
-2	2818	2765
-1	1912	1673
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2	1757	1439
3	1862	1737
4	1626	1333
5	2635	2930
7	1638	1509
8	2758	2751

16,2,L

-28	1862	2124
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-13	2811	2828
-12	805	621
-11	762	928
-9	1334	1213
-8	3159	3540
-7	2141	1940
-6	2145	1951
-5	1862	1633
-4	3028	3042
-2	2676	2673
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2	1427	1162
3	1836	1427
5	1784	1635
7	2225	2220
8	1562	1561
12	1483	1498

18,2,L

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-16	1651	1247
-15	1201	897
-14	2663	2490
-13	1765	1462
-11	1761	1566
-9	2314	2246
-8	1422	1243
-7	2736	2928
-6	2993	2979
-5	1304	891
-4	2689	2800
0	2055	1984
14	1501	1777

20,2,L

-22	1469	1269
-21	2374	2405
-20	1984	1852
-19	2110	2030
-18	2835	2499
-17	2028	2073
-14	1251	956
-12	2433	2275
-9	1699	1521
-8	1840	1316
-7	2141	1852
-6	2428	2624
-3	1277	1030
0	2461	2607
3	1638	1725
4	1510	1690
8	1821	1815
10	1703	1973

22,2,L

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-19	1773	1558
-18	2917	3036
-15	1324	1023
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-12	2145	2433
-11	1309	1258
-10	1626	1237
-8	1364	1147
-4	1398	1389
-1	1446	1154
2	1663	1913
10	1799	2217

24,2,L

-28	1505	1722
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-24	1687	1774
-18	1464	1266
-16	1344	1468
-10	1384	1545
-4	2733	3105
-2	1527	1149
-1	1441	1292
5	2068	1458
10	1432	2182

26,2,L

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-8	1483	1323
-4	1626	1436
-3	2270	1223
-2	2276	2449

28,2,L

-32	1324	2017
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-16	1750	1793
-8	2064	2221
-7	1597	1457

30,2,L

-30	1667	2026
-21	1667	1942
-16	1719	1921
-9	1609	1770
-8	1451	1444
-6	2025	2260

32,2,L

-21	1715	1894
-20	1562	1725
-16	1527	1759
-6	1441	1742

34,2,L

-20	1469	1984

1,3,L

-18	2043	1958
-16	1974	1618
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-11	2773	2877
-9	2320	2228
-7	1287	1576
-5	1339	1740
-4	455	675
-3	1099	1863
-2	2378	3325
-1	415	1492
2	1352	1876
3	1390	2025
4	1866	1848
5	1099	1417
6	2236	2436
7	2371	2226
9	3312	3579
11	2560	2673
12	2312	2197

3,3,L

-16	2704	2727
-15	2150	1955
-12	1067	1198
-10	2966	3353
-9	1930	1580
-6	2150	2149
-5	1189	1941
-4	1175	1716
-2	929	1515
-1	788	1051
0	2051	2491
1	525	712
3	1034	1165
4	1099	1411
5	1130	1307
6	1273	1478
8	1948	1686
16	2580	2475

5,3,L

-16	2371	2353
-15	2742	2842
-13	1099	1155
-10	3096	3560
-9	1939	1619
-8	910	1178
-7	965	1148
-6	3102	3692
-5	1273	1804
-3	2421	3042
-2	1067	1863
-1	2305	3086
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2	851	1010
3	2076	1923
4	1912	1839
5	1326	1489
6	2109	1958
7	2678	2972
8	2017	1824
9	2000	1570
12	2221	2103
13	2009	1660

7,3,L

-17	1876	1568
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-12	2229	2423
-11	1160	1176
-9	1083	1021
-8	2364	2551
-7	1965	2198
-6	1017	1167
-5	871	1279
-4	3217	3896
-3	1921	1924
-2	1083	1680
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1	1034	1277
4	2158	1905
5	1130	845
6	2798	2963
7	2356	2259
12	2761	2725

9,3,L

-20	2320	2440
-15	1965	1842
-14	2942	3310
-8	910	1123
-8	1402	1123
-7	1160	1512
-6	1145	1567
-5	1912	1920
-4	983	1248
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2	1034	1535
3	2748	3037
8	2034	1989

11,3,L

-21	2142	1711
-18	2685	2603
-14	1377	1593
-13	1857	1744
-12	2639	3030
-10	1099	1279
-7	983	1242
-6	1992	2071
-4	983	711
-3	1983	2047
-2	1313	1635
-1	1051	1214
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2	2244	1949
3	2068	1757
6	1912	1651
7	2174	2032
9	2221	2270

13,3,L

-19	2101	2067
-18	2026	2114
-14	2580	2381
-13	2736	2932
-12	1204	1512
-11	2034	1963
-9	2349	2151
-5	1083	1254
-4	3000	3176
-3	2652	2856
0	1866	1583
2	2320	2168
3	2197	2020
5	1983	1680
7	2613	2515
9	2457	2519

15,3,L

-15	1974	1741
-14	3152	3711
-12	1885	1707
-10	2134	2138
-5	1232	1553
-4	2567	2363
-3	2930	3136

17,3,L

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-15	2672	2781
-12	2859	3096
-11	1326	1487
-8	2134	2283
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-2	2659	2696
3	2567	2612

19,3,L

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-12	1957	1794
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-9	2093	2275
-8	2498	2572
-2	2755	2917

21,3,L

-29	2320	2567
-23	2290	2113
-16	2182	2140
-11	2076	2246
-9	2085	1929
-7	2174	2362
-4	2221	2130
-2	2205	2169
-1	2197	1974

23,3,L

-23	2342	2227

0,4,L

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6	836	1191
7	1434	1325
8	772	720
9	2002	1851
10	2728	2721
11	1732	1658
12	983	752
13	1647	1718
14	1469	1401
15	2545	2560
21	1976	1948

2,4,L

-21	2078	2163
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-13	2860	3157
-11	2750	2980
-10	2412	2186
-8	759	918
-7	731	816
-6	1762	1957
-5	1684	1767
-4	918	1250
-3	1034	1361
-2	848	1684
-1	321	497
0	517	240
1	2083	2527
7	3550	4237
8	2043	2024
9	1875	1766
10	1853	1397
11	2058	1880
13	1448	1174

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      2,4,L

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      4,4,L

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-19   1814   1739
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-14   1014    859
-13   2589   2492
-11    962   1145
-10    872    889
 -8    824    974
 -7   1897   1922
 -6    555    973
 -5   2017   2784
 -4   1945   2166
 -3    497    751
 -2    824    744
  1   2425   2939
  2   1929   2114
  3    745    907
  4   1476   1406
  6   1004   1073
  7   2403   2653
  9   2092   2100
 11   2122   2000
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 16   1924   2098
 17   1918   2063

      6,4,L

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-23   1720   1533
-19   1577   1452
-17   1981   2187
-16   1825   1695
-15   1004   1180
-14   1024   1168
-11    918   1152
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 -7   1907   2105
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  2   2663   2856
  3   2973   3373
  4   1842   1894
  5   1945   1883
  6    860    564
 10   1997   2118
 16   1738   1591
 17   1842   1767

      8,4,L

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-17   1791   2113
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-12   2028   2001
-11   2184   2301
-10    895   1016
 -9    836    982
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 -5   1997   2401
 -3   1584   1740
 -2   2131   2292
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  0   1584   1512
  1   1720   1883
  2   1939   1934
  3   2165   2140
  4    918   1204
  5   2698   2745
 12   1647   1371

      10,4,L

-25   1773   1659
-20   1647   1208
-19   1830   1758
-15   1375    995
-14    836   1090
-13   2028   2124
-12   2589   2715
-11   1768   1661
-10    785    945
 -9   2892   3355
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 -7    785   1181
 -4    972   1371

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  2   2360   2478
  5   1603   1401
  6   1732   1458
  9   1907   1707
 11   1955   2244
 13   1738   1814

      12,4,L

-20   1891   1961
-19   1955   1244
-17   1063   1532
-16   2017   1915
-15   1571   1287
-12   1073   1305
-10   2487   2488
 -9   2846   2878
 -6   1955   2309
 -5   1497   1378
 -4    993   1233
 -3   2330   2647
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  8   1696   1760
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 13   1913   2344

      14,4,L

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-16   1762   2023
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-13   2795   2824
-12   1802   1763
-10   1497   1209
 -7   2412   2472
 -3   1635   1646
 -2   1678   1466
 -1   2017   1758
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  7   2078   2088
  8   1714   1478

      16,4,L

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  2   2321   2335
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  7   1714   1607
  9   1738   1856

      18,4,L

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-13   1462   1407
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 -7   1961   2058
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      20,4,L

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  3   2063   2314

      22,4,L

-13   1934   2035
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 -3   1934   2115

      24,4,L

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 -4   1750   1937

      26,4,L

-17   1738   1930

      28,4,L

-15   1814   2427

      1,5,L

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-11   2414   2340
 -9   2139   1859
 -8   1617   1318
 -7   1214   1224
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  1    577    614
  2   1643   1739
  3   1898   1371
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  5   2186   2161
  6   2172   2258
  7    545    314
  8   1459   1423
  9    626    639
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 12   1299   1314
 13   1164   1174
 16   1248    922
 17   2664   2841
 19   2411   2131
 21   1446   1551

      3,5,L

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-19   1317   1100
-17   1479   1666
-15   2361   2471
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-10    816    685
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 -6   1621   1531
 -5    393     49
 -3   2040   2176
 -1   1511   1554
  2   1422   1458
  3   2493   2863
  5   3238   3632
  6   1117    826
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-15   1383   1297
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 -9   2952   3006
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  0   1975   1998
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  2   1281   1220
  3   1841   1783
  7   1096    938
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 15   1841   2238

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-19   1841   2095
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 -8   1159    976
 -7   1811   1719
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      29,5,L

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 -7   1733   1499
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 -4    532    814
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  3   1595   1533
  5   1641   1200
  6   1388   1149
  7   2785   2853
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 13   1570   1417
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-10   1160   1158
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  1   2986   3240
  2   2155   2215
  3   1900   2006
  4   1195   1255
  5   1343   1172
  6   1383    984
  7   2590   2223
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 17   1962   2229
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  1   2922   3181
  3   3015   2952
  5   2378   1910
  6   1694   1538
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 15   1292   1264
 17   1578   1792

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 17   1244   1730

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 -9   3172   3970
 -8   1373   1207
 -7    964    786
```

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13	1223	1304

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-11	1809	1777
-9	3363	3163
-7	1578	1534
-3	1412	1293
-1	1472	1385
2	1725	1550
5	1633	1448
11	1363	1395
13	1864	2297
15	1318	1701

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-17	1363	1681
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-9	1701	1600
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-4	1318	1153
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5	1709	1584
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7	2003	2284
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9	1363	1806

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-4	1694	1077
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-15	1348	1789

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5	2551	1877
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11	2131	1901
13	1131	1386
17	1093	1359
18	1260	1464
19	1518	1918

	3,7,L	
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3	1093	1024
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7	2022	1963
11	2053	2116
13	1750	1984

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2	593	216
3	777	644
4	813	858
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7	2433	2089
9	1013	770
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13	1180	1266

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1	2259	2396
3	1006	912
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13	1266	1640

	9,7,L	
7	1137	1248

	11,7,L	
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2	992	1128
3	1243	1944

	13,7,L	
1	1452	1624

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3	1408	1724
5	1266	1723
11	1326	2264

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3	1546	1893

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-1	2262	2226
-2	1433	1404
-3	1634	1538

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-5	1718	1523
-6	1481	1340
-7	2218	2010
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-9	2150	1863
-13	970	682
-14	821	565
-15	1027	954

	9,7,L	
-1	1541	1669
-2	956	1035
-5	2323	1877
-6	813	706
-7	3013	2982
-8	1186	1071
-9	1806	1595
-12	1817	374

	11,7,L	
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-11	1821	1943
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-15	1466	1741
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-19	1186	1500
-20	1413	1606
-21	1546	1966

	13,7,L	
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-7	956	804
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-11	1714	1750
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-13	2199	2357
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-21	1413	1802

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-25	1564	2450

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-23	1372	1744
-25	1378	1838
-3	1523	1739

	19,7,L	
-1	1266	1772
-3	1413	1975

	21,7,L	
-1	2231	2850

	23,7,L	
-1	1315	1700

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Part III

The Crystal and Molecular Structure of Tetraphenylarsonium Tetrachlorobis(triphenylphosphine)-rhodate (III)

INTRODUCTION

In a series of studies of rhodium(III) complexes of tertiary monophosphines and arsines[1] Dr. T.A. Stephenson prepared the compound tetraphenylarsonium tetrachlorobis(triphenylphosphine)-rhodate(III). X-ray powder photographs of this compound when compared with the corresponding ruthenium compound indicated that both compounds were isomorphous. This, along with evidence from infrared spectra, indicated a molecular structure for the compound which has been confirmed by the X-ray structure determination reported in this thesis.

EXPERIMENTAL

Summary of Crystal Data

$C_{60}H_{50}P_2Cl_4AsRh$, M=1152.7, dark red crystals, monoclinic space group $P2_1/c$, a=26.13(1)Å, b=14.89(1)Å, c=18.25(2)Å, β=129.5(1)°, U=5547Å^3, D_m=1.41 g/cm^3 (by flotation), D_c=1.41 g/cm^3 (neglecting solvent of crystallisation), z=4, Cu-K_α radiation, λ=1.5418Å, μ=57.84 cm^{-1}, $t_{opt.}$=0.035 cm.

Determination of Cell Dimensions and Space Group

A crystal was mounted about the [a] axis and an oscillation photograph taken from which the [a] cell dimension was calculated. The [b^*] and [c^*] reciprocal cell dimensions were calculated from the corresponding zero layer Weissenberg photograph. Another crystal was mounted about the [b] axis and an oscillation photograph and a zero layer Weissenberg photograph taken. From these were calculated values for [b], [a^*], [c^*] and [β^*]. The following self consistent set of real and reciprocal cell dimensions were then calculated.

a=26.13(2)Å	b=14.89(2)Å	c=18.24(2)Å
	β=129.5(1)°	
a^*=0.0761(1)	b^*=0.1033(1)	c^*=0.1093(3)
	β^*=50.5(1)°	

The conditions[2] for reflection were found to be hkl : no condition, hol : l=2n, oko : k=2n, which uniquely determines the space group to be $P2_1/c$ (No. 14).

Data Collection

3403 reflections were recorded on film by the equi-inclination Weissenberg technique, using film packs each of which contained three films. The data was collected up the [b] axis to a k of 9 corresponding to an equi-inclination angle (μ) of 27.8°. These intensities were visually estimated by comparison with an intensity strip made using the same crystal as was used for the data collection. The intensities were corrected for Lorentz and polarisation factors using the programme described in appendix B.

Interpretation of Patterson Map

The co-ordinates of the equivalent positions[2] for an atom in a general position in the space group $P2_1/c$ are: x,y,z; $\bar{x},\bar{y},\bar{z}$; $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$; $x,\frac{1}{2}-y,\frac{1}{2}+z$. In a Patterson map there will therefore be peaks with co-ordinates u,v,w which represent vectors between atoms in any two of these equivalent positions such that $u=2x$, $v=2y$, $w=2z$; or $u=2x$, $v=\frac{1}{2}$, $w=\frac{1}{2}+2z$; or $u=0$, $v=\frac{1}{2}+2y$, $w=\frac{1}{2}$.

The largest non-origin peaks in the Patterson map are found at $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,0$; and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. It is assumed that these peaks represent vectors between rhodium atoms. The peak in the Patterson map at $\frac{1}{2}00$

is the only one of the three large peaks which could represent vectors between centrosymmetrically related rhodium atoms, i.e. have co-ordinates $2x,2y,2z$. Interpreting the other large peaks to be of the type $2x,2y,2z$ would give rise to peaks in the Patterson map which are not observed. The sets of positions numbered I and II below are therefore the only sets of general positions which would be consistent with the Patterson map. However the Patterson map could also be interpreted on the basis of rhodium atoms situated at a pair of special positions, i.e. on a symmetry element. It is found that the positions III and IV below are the only ones consistent with the Patterson map.

I			II			III			IV		
$\frac{1}{4}$	0	$\frac{1}{2}$	$\frac{1}{4}$	0	0	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	0
$\frac{3}{4}$	$\frac{1}{2}$	0	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$\frac{3}{4}$	0	$\frac{1}{2}$	$\frac{3}{4}$	0	0	0	0	$\frac{1}{2}$	0	0	0
$\frac{1}{4}$	$\frac{1}{2}$	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	$\frac{1}{2}$

Evidence from structure factor and Fourier calculations suggested that the rhodium atoms lay in positions as in III above. Peaks were now found in the Patterson map which represented vectors between two arsenic atoms in symmetry related positions and vectors between rhodium atoms and chlorine or phosphorus atoms. From these were deduced several possible sets of co-ordinates for the arsenic, chlorine and phosphorus atoms, assuming the rhodium atoms to be in the set of positions numbered III above. All the different combinations of these possible sets of positions were checked to see if they gave rise to vectors between arsenic atoms and chlorine or phosphorus atoms which were consistent with the Patterson map. Only a few possible positions for chlorine and phosphorus atoms emerged and these were confirmed as correct by a structure factor calculation.

Structure Determination

A Fourier map was calculated phased on a partial structure which included the rhodium, arsenic, chlorine and phosphorus atoms situated at positions deduced from the Patterson map. From this map were discovered the positions of some of the carbon atoms. The positions of the rest of the carbon atoms of the ten phenyl rings were gradually discovered from successive Fourier maps.

The six carbon atom positions of each phenyl ring were then replaced by an idealised phenyl ring which was described by six parameters, three positional and three orientational. The whole structure was then refined by full matrix least squares constraining the carbon-atoms to move so as to retain the idealised shape of each phenyl ring. This refined the structure to an R-factor of 0.21. A difference Fourier map of the structure at this stage of refinement enabled the presence of acetone of crystallisation to be detected and the parameters of its constituent atoms determined. Full matrix least squares refinement was then resumed, constraining the movement of the phenyl ring carbon atoms as before and allowing the thermal parameters of the rhodium, arsenic, and chlorine atoms to vary anisotropically leading to a final R factor of 0.137

RESULTS AND DISCUSSION

The molecular structure of tetraphenylarsonium tetrachlorobis (triphenylphosphine)- rhodate (III) has been confirmed by this X-ray structure analysis to consist of an ionic rhodate complex and a tetraphenyl arsonium ion with an acetone molecule situated in a clathrate position in the crystal. As the rhodium atoms are situated on centres of symmetry in the crystal whilst the arsenic atom is in a completely general position in the unit cell there exists two different centrosymmetric rhodate ions for each pair of identical ions. From table 1, which shows the positional and thermal parameters of all the atoms in one asymmetric unit, it can be seen that the chlorine atoms bonded to the rhodium atom Rh2 have much higher temperature factors than those belonging to the chlorine atoms bonded to Rh1. This feature may be explained in terms of possible disorder in the crystal, a theory which is strengthened by evidence from a final difference Fourier map shich showed small positive peaks in the plane of the chlorine atoms around the atom Rh2 and mid way between pairs of adjacent chlorine atoms. Apart from this minor difference the two rhodate ions have essentially the same molecular structure, both having octahedral configurations with trans phosphine groups. The arsonium ion has the usual tetrahedral configuration.

The anisotropic thermal parameters shown in table 1 are u's referred to orthogonalised cell axis. Attempts were made to produce a refined structure on the X-ray 72 set of programmes which would have given a more usual presentation of the anisotropic thermal parameters and given standard deviations for all the refined parameters and hence for the bond distances and angles. These attempts failed,due mainly to computing difficulties at the last moment which were outwith the control of the author. For this reason also there is no list of structure factors published in this thesis for this particular structure determination but attempts are continuing to produce this structure factor list.

Finally table 2 shows the interatomic distances and angles for this structure. Carbon to carbon bond distances are not shown for the phenyl ring as these were constrained during the least squares refinement to be 1.39Å. It was assumed that the shape of the phenyl rings was a regular hexagon.

Table 1

Fractional coordinates of atom and thermal parameters ($\AA^2$)

	x	y	z	u
Rh(1)	0.0	0.0	0.5	
Cl(11)	0.0204	0.0499	0.6392	
Cl(12)	0.0844	0.0908	0.5299	
P(1)	0.0699	0.8728	0.5831	0.028
C(111)	0.1525	-0.1154	0.6188	0.061
C(112)	0.2100	-0.1308	0.7108	0.061
C(113)	0.2710	-0.1197	0.7333	0.061
C(114)	0.2746	-0.0932	0.6638	0.061
C(115)	0.2171	-0.0778	0.5718	0.061
C(116)	0.1560	-0.0889	0.5493	0.061
C(121)	0.0800	-0.1502	0.6897	0.061
C(122)	0.0418	-0.2168	0.6868	0.061
C(123)	0.4780	-0.2345	0.7666	0.061
C(124)	0.0921	-0.1857	0.8493	0.061
C(125)	0.1303	-0.1191	0.8522	0.061
C(126)	0.1243	-0.1014	0.7724	0.061
C(131)	0.0442	-0.2378	-0.4775	0.061
C(132)	-0.0162	-0.2518	-0.5667	0.061
C(133)	-0.0327	-0.3366	-0.6075	0.061
C(134)	0.0112	-0.4074	-0.5591	0.061

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	x	y	z	u
C(135)	0.0717	-0.3934	-0.4699	0.061
C(136)	0.0882	-0.3087	-0.4291	0.061
Rh(2)	0.05	0.0	0.5	
Cl(21)	0.4241	0.0850	0.4954	
Cl(22)	0.4675	0.0599	0.3604	
P(2)	0.4162	0.8898	0.4142	0.038
C(211)	0.3447	-0.0837	0.2916	0.061
C(212)	0.3130	-0.1500	0.2223	0.061
C(213)	0.2562	-0.1294	0.1313	0.061
C(214)	0.2312	-0.0427	0.1095	0.061
C(215)	0.2629	0.0235	0.1788	0.061
C(216)	0.3197	0.0030	0.2699	0.061
C(221)	0.4456	-0.2149	0.3998	0.061
C(222)	0.4692	-0.2157	0.3500	0.061
C(223)	0.4888	-0.2960	0.3360	0.061
C(224)	0.4848	-0.3755	0.3717	0.061
C(225)	0.4612	-0.3748	0.4214	0.061
C(226)	0.4416	-0.2945	0.4355	0.061
C(231)	0.3045	-0.2131	0.5179	0.061
C(232)	0.3721	-0.1989	0.5833	0.061
C(232)	0.4057	-0.1665	0.5534	0.061
C(234)	0.3717	-0.1482	0.4580	0.061
C(235)	0.3040	-0.1624	0.3926	0.061
C(236)	0.2704	-0.1948	0.4225	0.061

	x	y	z	u
As	0.2353	0.2194	0.4445	
C(311)	0.1881	0.1151	0.3752	0.061
C(312)	0.1357	0.0852	0.3697	0.061
C(313)	0.1013	0.0085	0.3181	0.061
C(314)	0.1193	-0.0383	0.2719	0.061
C(315)	0.1717	-0.0084	0.2774	0.061
C(316)	0.2061	0.0683	0.3291	0.061
C(321)	0.1791	0.2884	0.4558	0.061
C(322)	0.1766	0.2641	0.5268	0.061
C(323)	0.1335	0.3076	0.5345	0.061
C(324)	0.0928	0.3754	0.4712	0.061
C(325)	0.0953	0.3998	0.4002	0.061
C(326)	0.1384	0.3563	0.3924	0.061
C(331)	0.3111	0.1868	0.5669	0.061
C(332)	0.3412	0.2473	0.6416	0.061
C(333)	0.3985	0.2232	0.7307	0.061
C(334)	0.4258	0.1387	0.7451	0.061
C(335)	0.3957	0.0782	0.6704	0.061
C(336)	0.3383	0.1022	0.5812	0.061
C(341)	0.2625	0.2793	0.3829	0.061
C(342)	0.3292	0.2820	0.4267	0.061
C(343)	0.3502	0.3250	0.3826	0.061
C(344)	0.3044	0.3653	0.2947	0.061
C(345)	0.2377	0.3627	0.2510	0.061
C(346)	0.2168	0.3197	0.2951	0.061

	x	y	z	u
O	0.4155	0.5556	0.5418	0.15
C(O1)	0.3674	0.5373	0.5515	0.13
C(O2)	0.3929	0.5082	0.6443	0.14
C(O3)	0.3024	0.5314	0.4690	0.14

Anisotropic temperature factors

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	0.0352	0.0241	0.0238	-0.0016	-0.0078	-0.0002
Rh(2)	0.0428	0.0371	0.0285	0.0057	-0.0048	0.0015
As	0.0430	0.0345	0.0427	-0.0027	-0.0127	0.0011
Cl(11)	0.0563	0.0438	0.0294	0.0073	-0.0022	-0.0061
Cl(12)	0.0450	0.0470	0.0479	-0.0020	-0.0179	0.0007
Cl(21)	0.0737	0.1004	0.2979	0.0441	-0.0687	-0.1155
Cl(22)	0.2482	0.2885	0.0370	-0.2089	-0.0421	0.0415

Table 2.

Intramolecular distances (Å) and angles (°).

Rh(1) - Cl(11)	2.364	Cl(11) - Rh(1) - Cl(12)	91.9
Rh(1) - Cl(12)	2.347	Cl(11) - Rh(1) - P(1)	90.5
Rh(1) - P(1)	2.394	Cl(12) - Rh(1) - P(1)	94.6
Rh(2) - Cl(21)	2.319	Cl(21) - Rh(2) - Cl(22)	92.5
Rh(2) - Cl(22)	2.297	Cl(21) - Rh(2) - P(2)	86.5
Rh(2) - P(2)	2.370	Cl(22) - Rh(2) - P(2)	90.1
As - C(311)	1.888	C(311) - As - C(321)	107.0
As - C(321)	1.915	C(311) - As - C(331)	109.4
As - C(331)	1.883	C(311) - As - C(341)	108.9
As - C(341)	1.898	C(321) - As - C(331)	108.4
		C(321) - As - C(341)	114.7
		C(331) - As - C(341)	108.3
P(1) - C(111)	1.834	C(111) - P(1) - C(121)	107.6
P(1) - C(121)	1.825	C(111) - P(1) - C(131)	101.3
P(1) - C(131)	1.858	C(121) - P(1) - C(131)	102.8
		C(111) - P(1) - Rh(1)	114.0
		C(121) - P(1) - Rh(1)	111.0
		C(131) - P(1) - Rh(1)	118.9

P(2) - C(211)	1.833	C(211) - P(2) - C(221)	101.9
P(2) - C(221)	1.834	C(211) - P(2) - C(231)	98.9
P(2) - C(231)	1.876	C(221) - P(2) - C(231)	103.7
		C(211) - P(2) - Rh(2)	117.3
		C(221) - P(2) - Rh(2)	112.8
		C(231) - P(2) - Rh(2)	119.7

O - C(01)	1.41	O - C(01) - C(02)	115
C(02) - C(01)	1.44	O - C(01) - C(03)	117
C(03) - C(01)	1.39	C(02) - C(01) - C(03)	126

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PART IV

The Crystal and Molecular Structure of
Tri-μ-chloromonochloromonothiocarbonyltetrakis(triphenylphosphine) diruthenium (II)

INTRODUCTION

From a series of reactions[1] of ruthenium (II) compounds, carried out by Dr. T.A. Stephenson, red crystals were isolated. On initial chemical analysis these crystals were thought to be composed of a compound with empirical formula $C_{37}H_{30}P_2Cl_2SRu$. An X-ray structure determination of these crystals was undertaken to try to establish unambiguously the molecular structure of this compound. During the course of the X-ray work further, more accurate, chemical analysis showed that the compound had an empirical formula $C_{73}H_{60}Cl_4SP_4Ru_2$. This concurred with the earlier results of the X-ray determination which demonstrated the presence in the crystal of a triple bridged di-ruthenium molecule. The final determined structure showed these bridging atoms to be chlorine with an interatomic distance between the ruthenium atoms of 3.35 Å.

EXPERIMENTAL

Summary of Crystal Data.

Tri-μ-chloromonochloromonothiocarbonyltetrakis(triphenylphosphine) diruthenium (II), $C_{73}H_{60}Cl_4SP_4Ru_2$, M=1473, dark red orthorhombic crystals, a=21.53 Å, b=23.43 Å, c=14.20 Å, V =7154 $Å^3$, D_m=1.41 g/cm^3 (by flotation), D_c=1.35 g/cm^3 (neglecting any solvent of crystallisation), z=4, Cu-K_α radiation, λ=1.5418, μ=63 cm^{-1}, optimum thickness[2]=0.322 cm, the maximum dimension of the crystal used was less than 0.02 cm.

Method of Crystallisation.

Recrystallisation of the material supplied, which was polycrystalline, had to be carried out under an atmosphere of nitrogen. The compound whilst in solution decomposed in the presence of oxygen to give a very dark solution. Two methods of recrystallisation were tried, viz. a) the solvent dilution method and b) the liquid diffusion method[3]. In each case acetone (Density: 0.792 g/cm^3) was used as a non-solvent and methyl chloride (Density: 0.991 g/cm^3) and benzene (Density: 0.879 g/cm^3) were each used as solvents. The first method gave polycrystalline masses and no crystal could be found suitable for single crystal diffraction studies. But with the second method when the material was dissolved in methyl chloride and a layer of acetone carefully introduced above the solution small crystals were formed at the interface between the two liquids. From these crystals one was found which was suitable for use with single crystal X-ray diffraction methods.

Determination of Cell Dimensions and Space Group

The [b] and [c] cell dimensions were obtained from Weissenberg photographs of the zero and first layers respectively, with the crystal mounted about the [a] axis. The [a] cell dimension was obtained from the corresponding oscillation photograph.

$a = 21.53\ (2)$ Å $\quad b = 23.63\ (3)$ Å $\quad c = 14.24\ (4)$ Å

$\alpha = \beta = \gamma = 90^{\circ}$

$a^{*} = 0.0716\ (2)$ r.l.u. $b^{*} = 0.0660\ (1)$ r.l.u. $c^{*} = 0.1083\ (3)$ r.l.u.

The conditions for observed reflections were found to be okl : k+l = 2n, hol : no conditions, hko : h = 2n, indicating that the space group[4] is Pnma (No. 62) or $Pn2_1a$ (alternative setting of $Pna2_1$, No. 33). The results of the statistical tests for centrosymmetry were considered unreliable because of the influence of the heavy atoms in the crystal[5].

Data Collection

The intensities were collected on film by the equi-inclination Weissenberg technique using a Philips X-ray generator, a Philips fine focus tube, and a Unicam camera. The intensity of reflections fell off rapidly with increasing θ so that only a few reflections were recorded on film with a sin θ/λ value greater than 0.40. Data was collected up the [a] axis for layers okl to 15 kl.

From the Weissenberg photographs 1258 reflections were visually estimated using an intensity strip made with the same crystal as was used when taking the Weissenberg photographs. No reflection was measured for which sin θ/λ was greater than 0.40. The intensity data was corrected for Lorentz and polarisation factors and intensity statistics used to calculate an initial set of relative scale factors.

Structure Analysis

An attempt was firstly made to solve the structure in the centric space group Pnma. An unsharpened three dimensional Patterson function was calculated from which the positions of the ruthenium atoms were discovered, and these positions then used to calculate a difference Fourier synthesis. From this was gleaned the information that the molecule contained two ruthenium atoms, each having octahedral co-ordination where the two octahedra share a common face coplanar with the mirror plane and defined by three bridging atoms. As the chemical analysis results at this stage showed a percentage composition of sulphur consistent with one sulphur atom per molecule the smallest bridging peak was taken to be sulphur and the other two chlorine, while the largest terminal peak was taken to be chlorine and the other two phosphorus. Least squares refinement of this partial structure converged at an R factor of 0.30.

The contour lines of a difference Fourier map phased on this partial structure were drawn on clear acetate sheets which were stacked on top of each other to give a three dimensional representation of the Fourier map. A two way mirror was arranged above the sheets and a light shone through the sheets to give an image of the Fourier map in which a scale model of a phosphine group could be freely moved.

This partial structure proved to be unsatisfactory in several ways. The temperature factors of some of the atoms, particularly the terminal chlorine atom and one of the phosphorus atoms, varied unrealistically and a thorough investigation of the Fourier map phased on this partial structure failed to give any satisfactory positions for the phenyl rings. Comparing this partial structure, the co-ordinates of which are shown in table 1, with the finally determined structure shows that the chlorine atoms were in positions which corresponded to those occupied by a phosphorus atom and the thiocarbonyl group, whilst a pair of phosphorus atoms related by the pseudo mirror plane were in positions which corresponded to those occupied by the terminal chlorine atom and a phosphorus atom.

An attempt was then made to find a structure which would satisfy the less rigid symmetry of the space group $Pn2_1a$. A difference Fourier map was calculated, phased on the partial structure determined above but omitting one of the ruthenium atoms. Following this a partial structure was postulated containing all the heavy atoms and five phenyl rings. The positional and thermal parameters of the heavy atoms were then refined by least squares, keeping constant the y parameter of each ruthenium atom in turn on alternate cycles.

By a series of Fourier maps the positions of the rest of the phenyl rings were determined. These Fourier maps also suggested that the thiocarbonyl group was not a bridging group and so the sulphur atom was placed in a terminal position, as in figure 1(a), and one of the terminal chlorine atoms moved to the vacant bridging position.

A full matrix least squares refinement of the whole structure was carried out, constraining the carbon atoms to move as complete idealised phenyl rings. On one cycle of least squares the shape of the ring was allowed to vary.

A difference Fourier map calculated at this stage, when the R-factor was 0.12, confirmed the absence of any extramolecular material in the crystal and indicated the presence or partial presence of a carbon atom in two places, between the sulphur atom and its nearest ruthenium atom and between the terminal chlorine atom and its nearest ruthenium atom. Adding to this the evidence that the chlorine and sulphur atoms both had high temperature factors and the interatomic distances Cl(4)...... Ru(2) of 2.68 Å was longer than expected for a terminal chlorine atom bonded to ruthenium and the interatomic distance S(1)...... Ru(1) of 3.05 Å was shorter than expected, it was thought that a certain amount of disorder must be present in the crystal. Two different molecular structures were therefore refined which differed only in the relative positions in the molecule of the terminal chlorine atom and the thiocarbonyl group (figures 1(a) and 1(b)). During these least squares refinements the parameters of the phenyl rings were kept constant and the thermal parameters of the ruthenium atoms allowed to vary anisotropically. In both cases the refinement converged at an R factor of 0.115. Interatomic distances and angles were calculated in each case.

Figure 1 (a)

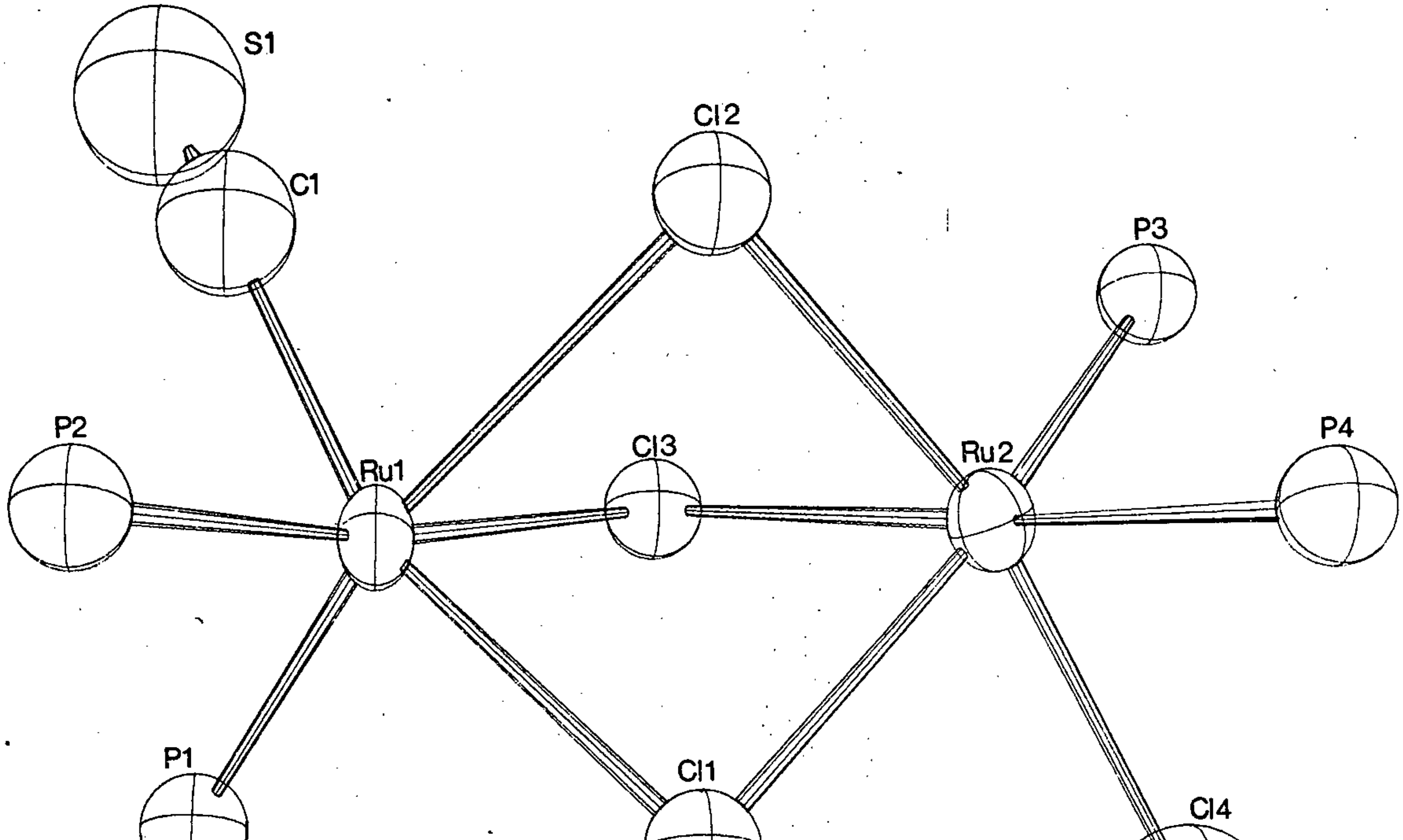
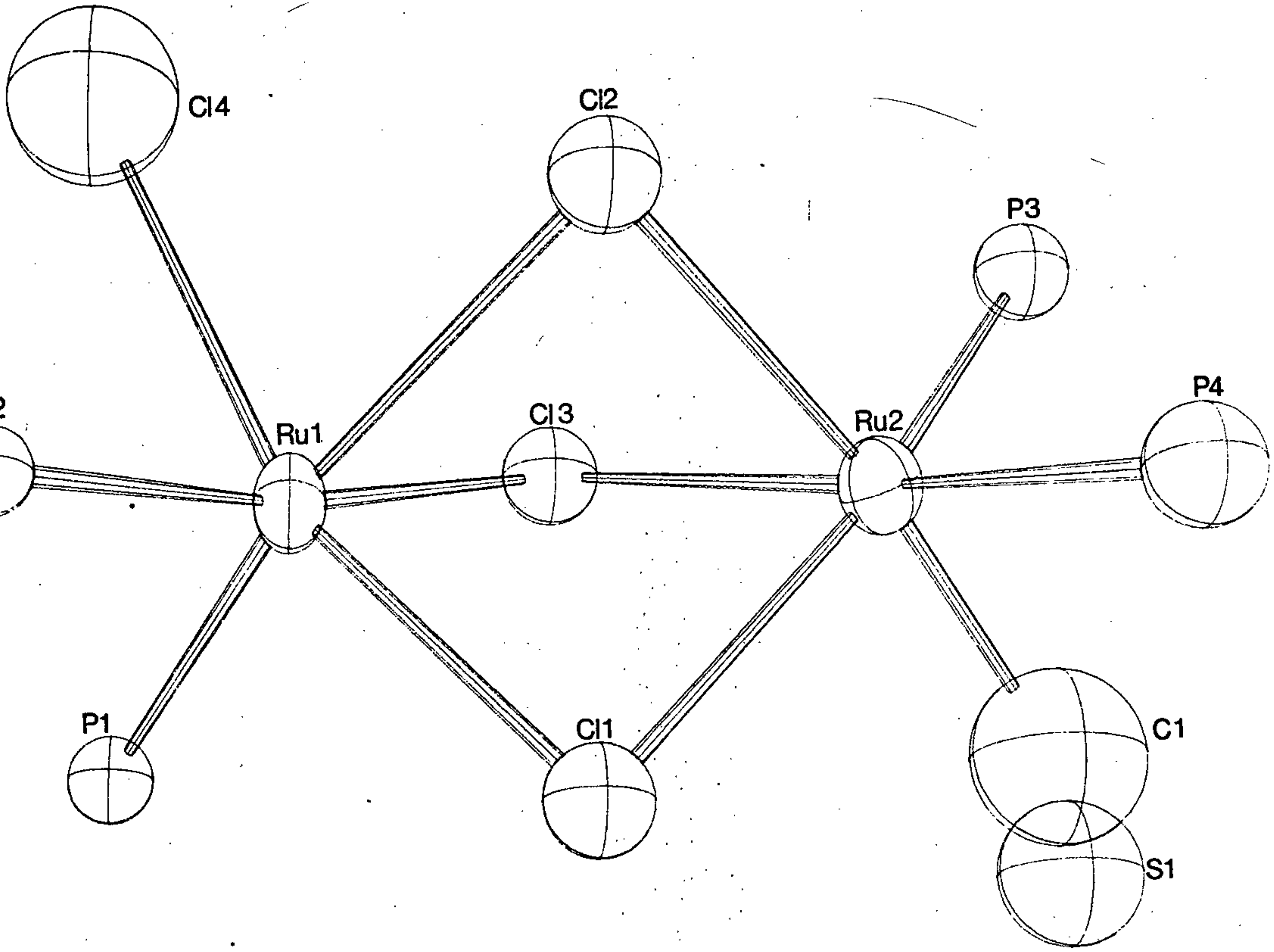


Figure 1 (b)



RESULTS AND DISCUSSION

An analysis of the agreement between the observed and calculated structure factors is shown in table 2. The positional and thermal parameters of all the atoms are shown in table 3. Co-ordination around the ruthenium atoms is shown in figure 1 and a projection of the molecule in two halves is shown in figure 2 which also shows the labelling of the atoms. The observed and calculated structure factors are shown in table 5.

The structure determination confirms the chemical analysis of the crystals and determines the basic structure of the molecule. An ambiguity exists with regard to the relative positions of the chlorine atom and the thiocarbonyl group. Both possible structures, shown in figure 1, are chemically sensible. In both structures the Ru...... Cl(4) bond length determined is much longer than would be expected if there was no disorder in the crystal. In similar molecules, of which the structure has been determined by X-ray diffraction methods, values for a ruthenium to terminal chlorine bond length have been reported of 2.395 Å in $Ru_2Cl_4(EtPhP)_5$[6] and 2.349 Å in $Ru_2Cl_5(BuP)_4$[7].

The ruthenium to sulphur distances are shorter than expected in both structures. These abnormal interatomic distances and the high isotropic temperature factors of Cl(4) and S(1) may be explained by disorder in the crystal with the two molecules shown in figure 1 crystallising together in random relative proportion. The bond lengths involving disordered atoms obtained from the refinement of the molecule as in figure 1(a) were much better than those obtained from the refinement of the alternative structure as in figure 1(b) and so it is suggested that the former molecular structure predominates in the crystal. A table of interatomic distances is drawn up in table 4.

All the bond lengths and angles between atoms co-ordinated to ruthenium except for Cl(4), S(1) and C(1) were statistically identical for both models and therefore only one list of these distances and angles is shown in table 4. Also, as the phenyl carbon atoms were constrained to refine as complete phenyl rings, all the phenyl groups will have the same size and shape and an indication of this is shown for one of the rings in table 4.

Figure 2.

Projection of the complete molecule in two halves, viewed from the mid point between the ruthenium atoms looking towards each ruthenium in turn.

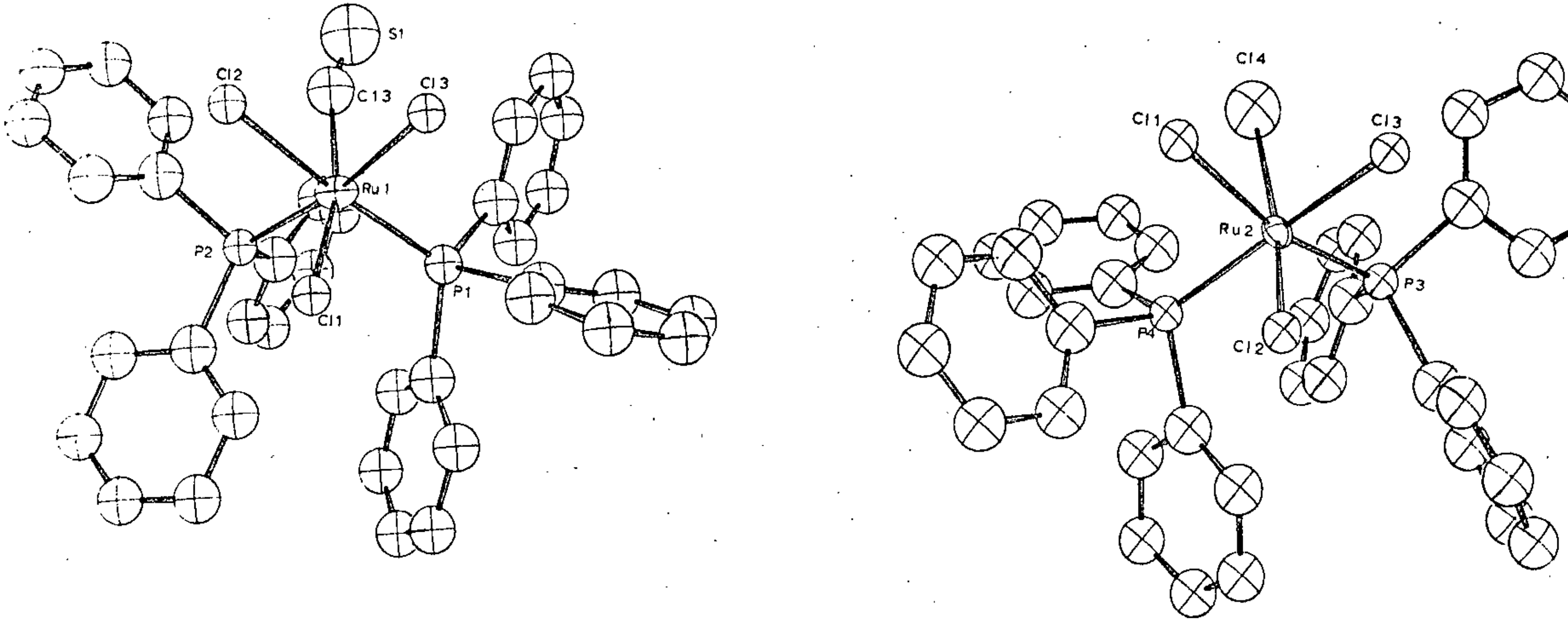


Table 1

Fractional co-ordinates and thermal parameters ($\AA^2$) of atoms determined in the centrosymmetric space group.

		x	y	z	u
Ru	Ru(1)	0.0897	0.3217	0.2169	0.032
	Ru(2)				
Cl	Cl(1)	0.0075	0.25	0.2218	0.043
Cl	Cl(2)	0.1430	0.25	0.3158	0.014
S	Cl(3)	0.1257	0.25	0.0927	0.030
Cl	S(1)	0.1956	0.375	0.1809	0.097
	P(3)				
P	P(1)	0.0239	0.3653	0.0991	0.082
	P(4)				
P	P(2)	0.0660	0.3791	0.3451	0.043
	P(4)				

Table 2

The R factor as a function of the layer index and the magnitude of $|F_o|$.

h	$\Sigma\|F_o\|$	$\|\Sigma F_c\|$	$\Sigma\|\Delta\|$	No	R
0	9088	8972	816	63	0.090
1	11781	11528	1255	115	0.107
2	12229	12252	1137	129	0.093
3	11649	11006	1546	100	0.133
4	11850	11894	1068	113	0.090
5	11049	10663	1257	108	0.114
6	11249	11120	1112	125	0.099
7	9399	8964	992	97	0.106
8	7801	7896	1002	78	0.128
9	6516	5988	1014	72	0.156
10	6923	6772	764	75	0.110
11	4016	3666	712	48	0.177
12	4949	4789	710	53	0.143
13	2727	2650	370	31	0.136
14	2703	2572	477	31	0.176
15	1454	1459	185	20	0.127
Overall	125360	122170	14414	1258	0.115
$10 \leqslant \|F_o\| \leqslant 50$	6313	6668	209	161	0.240
$50 < \|F_o\| \leqslant 75$	20935	19657	3398	332	0.162
$75 < \|F_o\| \leqslant 100$	21975	20356	3079	251	0.140
$100 < \|F_o\| \leqslant 125$	22138	21464	2260	198	0.102
$125 < \|F_o\| \leqslant 150$	18494	18336	1627	136	0.088
$150 < \|F_o\| \leqslant 500$	35520	35702	2538	179	0.071

Table 3

Fractional co-ordinates of atoms and thermal parameters (Å^2) with standard deviations in parenthesis

Parameters for Structure as in Fig. 1 (a)

	x	y	z	u
Ru(1)	0.0870(3)	0.3181(5)	0.2090(4)	
Ru(2)	0.0933(3)	0.1751(5)	0.2190(4)	
Cl(1)	0.0057(6)	0.2468(11)	0.2389(11)	0.037(5)
Cl(2)	0.1441(7)	0.2477(12)	0.3187(10)	0.037(5)
Cl(3)	0.1251(6)	0.2440(11)	0.0987(11)	0.036(5)
Cl(4)	0.0157(12)	0.1134(12)	0.1096(18)	0.089(10)
P(1)	0.0335(10)	0.3607(10)	0.0907(15)	0.041(7)
P(2)	0.0612(10)	0.3815(10)	0.3325(15)	0.035(8)
P(3)	0.1727(10)	0.1215(10)	0.1648(15)	0.034(7)
P(4)	0.0631(10)	0.1277(10)	0.3555(15)	0.031(7)
S(1)	0.2158(15)	0.3733(13)	0.1835(20)	0.106(11)
C(1)	0.1700(44)	0.3549(40)	0.2104(60)	0.064(34)

Anisotropic temperature factors for Ru(1) and Ru(2)

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ru(1)	0.029(6)	0.018(4)	0.054(6)	-0.000(4)	0.000(4)	0.001(4)
Ru(2)	0.031(5)	0.027(4)	0.023(5)	-0.002(4)	0.001(4)	0.007(5)

Parameters for Structure as in Fig. 1(b)

	x	y	z	u
Ru(1)	0.0872(3)	0.3204(5)	0.2089(4)	
Ru(2)	0.0930(3)	0.1772(5)	0.2190(4)	
Cl(1)	0.0058(6)	0.2478(11)	0.2388(11)	0.038(5)
Cl(2)	0.1438(7)	0.2497(12)	0.3187(11)	0.037(5)
Cl(3)	0.1251(7)	0.2457(11)	0.0986(11)	0.036(5)
Cl(4)	0.2096(13)	0.3730(13)	0.1870(19)	0.114(11)
P(1)	0.339(10)	0.3617(10)	0.0903(15)	0.028(7)
P(2)	0.0615(9)	0.3831(9)	0.3327(14)	0.020(7)
P(3)	0.1710(10)	0.1244(10)	0.1669(15)	0.034(7)
P(4)	0.0641(10)	0.1293(11)	0.3570(16)	0.037(8)
S(1)	0.0118(14)	0.1125(13)	0.1006(23)	0.078(11)
C(1)	0.0340(30)	0.1250(30)	0.159 (50)	0.105(19)

Anisotropic Temperature Factors for Ru(1) and Ru(2)

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ru(1)	0.031(6)	0.020(4)	0.056(6)	-0.001(4)	-0.000(4)	0.000(4)
Ru(2)	0.035(5)	0.028(4)	0.026(5)	-0.003(4)	0.002(4)	0.010(5)

Parameters for Carbon Atoms in Phenyl Rings

$u = 0.062$

	x	y	z
C(111)	-0.048	0.395	0.114
C(112)	-0.102	0.362	0.091
C(113)	-0.161	0.385	0.126
C(114)	-0.162	0.436	0.169
C(115)	-0.112	0.471	0.187
C(116)	-0.052	0.448	0.158
C(121)	0.084	0.413	0.021
C(122)	0.059	0.468	-0.002
C(123)	0.103	0.503	-0.050
C(124)	0.159	0.488	-0.075
C(125)	0.183	0.434	-0.061
C(126)	0.142	0.395	-0.009
C(131)	+0.005	0.308	-0.018
C(132)	-0.008	0.249	-0.001
C(133)	-0.036	0.218	-0.079
C(134)	-0.044	0.244	-0.163
C(135)	-0.028	0.300	-0.184
C(136)	-0.002	0.333	-0.106
C(211)	0.060	0.458	0.301
C(212)	0.109	0.480	0.242
C(213)	0.106	0.541	0.222
C(214)	0.063	0.574	0.265
C(215)	0.017	0.555	0.326
C(216)	0.017	0.494	0.344

	x	y	z
C(221)	0.120	0.377	0.423
C(222)	0.115	0.336	0.498
C(223)	0.162	0.341	0.572
C(224)	0.209	0.378	0.562
C(225)	0.219	0.415	0.488
C(226)	0.170	0.414	0.415
C(231)	-0.013	0.374	0.395
C(232)	-0.012	0.385	0.493
C(233)	-0.072	0.385	0.540
C(234)	-0.123	0.370	0.491
C(235)	-0.126	0.355	0.397
C(236)	-0.066	0.358	0.347
C(311)	0.187	0.126	0.034
C(312)	0.145	0.132	-0.043
C(313)	0.172	0.129	-0.137
C(314)	0.233	0.117	-0.147
C(315)	0.274	0.106	-0.075
C(316)	0.249	0.112	0.020
C(321)	0.300	0.099	0.234
C(322)	0.253	0.141	0.219
C(323)	0.272	0.201	0.235
C(324)	0.330	0.212	0.268
C(325)	0.375	0.172	0.289
C(326)	0.358	0.113	0.270

	x	y	z
C(331)	0.162	0.044	0.178
C(332)	0.183	0.016	0.261
C(333)	0.169	-0.045	0.267
C(334)	0.141	-0.071	0.184
C(335)	0.124	-0.047	0.110
C(336)	0.135	0.015	0.103
C(411)	0.020	0.168	0.445
C(412)	0.055	0.188	0.523
C(413)	0.021	0.223	0.592
C(414)	-0.039	0.237	0.574
C(415)	-0.073	0.223	0.495
C(416)	-0.041	0.185	0.428
C(421)	0.128	0.095	0.430
C(422)	0.186	0.123	0.448
C(423)	0.227	0.093	0.514
C(424)	0.207	0.045	0.558
C(425)	0.150	0.020	0.549
C(426)	0.109	0.047	0.479
C(431)	0.011	0.062	0.354
C(432)	-0.035	0.057	0.427
C(433)	-0.082	0.012	0.412
C(434)	-0.077	-0.023	0.338
C(435)	-0.031	-0.022	0.270
C(436)	-0.015	0.024	0.279

Table 4

Intramolecular distances (Å) and angles (°) with standard deviations in parenthesis

Distances and angles involving atoms co-ordinated to ruthenium

Ru(1)-Ru(2)	3.35(2)	Cl(1)-Ru(1)-Cl(2)	78.5(7)
Ru(1)-Cl(1)	2.46(2)	Cl(1)-Ru(1)-Cl(3)	82.5(7)
Ru(1)-Cl(2)	2.58(2)	Cl(2)-Ru(1)-Cl(3)	77.1(7)
Ru(1)-Cl(3)	2.48(2)	Cl(1)-Ru(2)-Cl(2)	79.1(7)
Ru(2)-Cl(1)	2.54(2)	Cl(1)-Ru(2)-Cl(3)	81.3(7)
Ru(2)-Cl(2)	2.47(2)	Cl(2)-Ru(2)-Cl(3)	79.8(7)
Ru(2)-Cl(3)	2.45(2)	Ru(1)-Cl(1)-Ru(2)	84.3(5)
Ru(1)-P(1)	2.27(2)	Ru(1)-Cl(2)-Ru(2)	83.3(6)
Ru(1)-P(2)	2.36(2)	Ru(1)-Cl(3)-Ru(2)	85.8(6)
Ru(2)-P(3)	2.26(2)		
Ru(2)-P(4)	2.33(2)		

Cl(1)-Ru(1)-P(1)	93.7(7)	Cl(1)-Ru(2)-P(4)	90.9(7)
Cl(1)-Ru(1)-P(2)	97.5(7)	Cl(2)-Ru(2)-P(3)	104.0(8)
Cl(2)-Ru(1)-P(2)	93.7(7)	Cl(2)-Ru(2)-P(4)	88.5(7)
Cl(3)-Ru(1)-P(1)	90.4(7)	Cl(3)-Ru(2)-P(3)	85.2(8)
P(1)-Ru(1)-P(2)	98.9(9)	P(3)-Ru(2)-P(4)	103.4(9)

Distances and angles involving disordered atoms

as in figure 1(a)		as in figure 1(b)	
Ru(2)-Cl(4)	2.70(3)	Ru(1)-Cl(4)	2.93(3)
Ru(1)-C(1)	1.98(10)	Ru(2)-C(1)	1.94(6)
Ru(1)-S(1)	3.08(3)	Ru(2)-S(1)	2.86(3)
C(1)-S(1)	1.14(10)	C(1)-S(1)	1.02(7)
Ru(1)-C(1)-S(1)	160(7)	Ru(2)-C(1)-S(1)	149(5)
Cl(2)-Ru(1)-C(1)	80.9(27)	Cl(1)-Ru(2)-C(1)	88.7(19)
Cl(3)-Ru(1)-C(1)	90.7(27)	Cl(3)-Ru(2)-C(1)	106.8(19)
P(1)-Ru(1)-C(1)	105.9(27)	P(3)-Ru(2)-C(1)	89.8(19)
P(2)-Ru(1)-C(1)	86.2(27)	P(4)-Ru(2)-C(1)	83.8(20)
Cl(1)-Ru(2)-Cl(4)	87.6(7)	Cl(2)-Ru(2)-Cl(4)	84.8(7)
Cl(3)-Ru(2)-Cl(4)	97.1(7)	Cl(3)-Ru(2)-Cl(4)	86.2(7)
P(3)-Ru(2)-Cl(4)	88.6(9)	P(1)-Ru(2)-Cl(4)	101.5(8)
P(4)-Ru(2)-Cl(4)	93.0(8)	P(2)-Ru(2)-Cl(4)	91.7(8)

Average values

Ru-μCl	2.49	Ru-μCl-Ru	84.4
Ru-P	2.30	μCl-Ru-μCl	80.7

Distances and angles in phosphine groups

P(1)-C(111)	1.95	P(3)-C(311)	1.89
P(1)-C(121)	1.90	P(3)-C(321)	1.93
P(1)-C(131)	2.08	P(3)-C(331)	1.86
P(2)-C(211)	1.83	P(4)-C(411)	1.82
P(2)-C(211)	1.82	P(4)-C(421)	1.92
P(2)-C(231)	1.83	P(4)-C(431)	1.93
C(111)-P(1)-C(121)	110	C(311)-P(3)-C(321)	104
C(111)-P(1)-C(131)	96	C(311)-P(3)-C(331)	99
C(121)-P(1)-C(131)	99	C(321)-P(3)-C(331)	107
C(111)-P(1)-Ru(1)	120	C(311)-P(3)-Ru(2)	116
C(121)-P(1)-Ru(1)	112	C(321)-P(3)-Ru(2)	114
C(131)-P(1)-Ru(1)	116	C(331)-P(3)-Ru(2)	115
C(211)-P(2)-C(221)	105	C(411)-P(4)-C(421)	101
C(211)-P(2)-C(231)	105	C(411)-P(4)-C(431)	97
C(221)-P(2)-C(231)	103	C(421)-P(4)-C(431)	96
C(211)-P(2)-Ru(1)	115	C(411)-P(4)-Ru(2)	118
C(221)-P(2)-Ru(1)	108	C(421)-P(4)-Ru(2)	117
C(231)-P(2)-Ru(1)	120	C(431)-P(4)-Ru(2)	123

Distances and angles in the phenyl rings

C(XX1)-C(XX2)	1.43	C(XX1)-C(XX2)-C(XX3)	116
C(XX2)-C(XX3)	1.47	C(XX2)-C(XX3)-C(XX4)	120
C(XX3)-C(XX4)	1.35	C(XX3)-C(XX4)-C(XX5)	127
C(XX4)-C(XX5)	1.38	C(XX4)-C(XX5)-C(XX6)	115
C(XX5)-C(XX6)	1.47	C(XX5)-C(XX6)-C(XX1)	120
C(XX6)-C(XX1)	1.39	C(XX6)-C(XX1)-C(XX2)	123

Table 5

Observed and Calculated Structure Factors for $Ru_2Cl_4SP_4C_{73}H_{60}$

Columns are: k, |F|obs., |F|calc.

	0,K,0	
2	1430	999
4	2867	3488
6	1437	1584
8	2830	2737
10	1034	936
14	3317	3290
16	3037	3121
18	520	407
	0,K,1	
3	1928	812
5	3344	3143
7	563	421
9	564	907
11	740	538
13	2033	2064
15	2683	2771
17	1422	1414
	0,K,2	
0	2476	2534
2	1868	1837
4	1519	1325
6	2524	2428
8	1965	2001
10	713	662
12	894	1110
14	2083	2090
16	1269	1374
	0,K,3	
1	2252	2390
3	2670	2779
5	556	454
7	2709	2689
9	1403	1277
11	782	534
13	1889	1978
15	1064	1160
17	515	540
	0,K,4	
0	1562	1780
2	1259	1163
4	1279	1308
6	1321	1381
8	2618	2692
10	871	925
12	1603	1491
14	1554	1499
	0,K,5	
1	1406	1385
3	1521	1701
7	1257	1337
9	1183	1069
11	961	951
13	1401	1428
15	503	341
	0,K,6	
2	981	1019
4	952	1004
6	1260	1305
8	704	712
10	437	364
12	1330	1400
14	713	452
	0,K,7	
1	659	750
3	776	608
5	698	611
	0,K,8	
2	728	661
	0,K,9	
1	788	919
3	799	863
	0,K,10	
0	917	1018
	1,K,1	
1	994	817
2	1036	941
3	865	863
4	200	263
5	1236	1131
6	2217	2046
7	793	472
8	494	371
9	611	580
10	952	761
12	638	491
	1,K,2	
0	775	999
1	971	890
2	728	793
3	497	320
4	934	964
5	327	386
6	1704	1582
7	676	535
8	591	511
9	833	746
10	529	405
13	886	900
15	618	640
16	457	303
	1,K,3	
0	2134	2065
1	1878	1717
2	1774	1740
3	1145	1054
4	1045	965
5	1808	1756
6	1516	1294
7	1245	1074
8	1814	1748
9	736	469
10	921	606
12	670	773
13	575	462
14	1129	1213
15	446	386
16	465	459
	1,K,4	
0	1096	1223
1	1012	1038
3	1187	972
4	1785	1662
5	1437	1279
6	1240	1235
7	2926	2944
8	876	859
9	1669	1695
10	817	740
13	1031	1084
14	440	335
15	794	800
	1,K,5	
0	1374	1184
1	1151	1072
2	1458	1322
3	729	818
5	2072	2019
6	1993	1848
8	2188	2407
9	828	820
10	773	613
11	696	442
12	1030	1104
14	1116	1098
15	668	632
16	845	549
	1,K,6	
0	1363	1344
1	1643	1647
2	564	609
4	1169	1290
5	1385	1468
6	1183	1289
7	1642	1916
8	1009	944
9	968	845
11	425	487
13	1022	1083
14	473	620
15	844	583
	1,K,7	
0	1917	2177
1	1009	1008
2	1393	1447
3	515	450
4	741	800
5	378	513
6	1549	1767
7	1193	1107
8	819	789
9	422	664
11	449	556
12	802	638
13	675	804
14	849	834
	1,K,8	
0	1237	1363
1	2074	2534
2	966	885
3	797	636
5	1162	1210
6	838	769
7	606	556
8	760	601
11	473	489
12	686	679
	1,K,9	
0	2215	2385
1	955	1046
2	1135	1182
4	437	467
6	712	795
7	458	584
	1,K,10	
0	727	676
1	1030	1243
3	465	723
	1,K,11	
0	490	436
	2,K,0	
3	508	421
4	1534	1706
5	2005	2228
6	2006	1781
7	1648	1206
8	891	800
9	814	658
10	1183	1019
11	1206	1247
12	1392	1261
13	2329	2505
14	1397	1272
15	2150	2192
16	1062	995
17	1310	1336
	2,K,1	
3	373	565
4	558	589
5	922	836
6	978	978
7	789	735
8	1042	1057
9	427	148
10	571	572
11	550	397
12	1099	1171
13	895	921
14	2122	2332
15	1161	1253
16	1719	1759
	2,K,2	
0	696	758
1	1400	1586
2	794	573
3	2087	2085
4	999	924
5	1778	1942
6	1286	1081
7	1595	1661
8	731	743
9	576	543
11	459	341
12	970	1033
13	1535	1546
14	1031	1081
15	1383	1531
16	590	487
17	614	592
	2,K,3	
0	2433	2509
1	742	813
2	987	966
3	2702	2753
4	469	338
5	871	898
6	2921	2998
7	1028	915
8	2037	2023
9	673	747
10	662	538
11	1025	1088
12	841	896
13	1322	1373
14	1006	953
15	665	651
16	490	657
	2,K,4	
0	531	452
1	1239	1289
2	1089	1074
4	1453	1570
5	1028	1067
6	317	309
7	2643	2507
8	1105	958
9	1272	1325
10	431	392
11	572	644
12	1122	1041
13	1087	1174
14	1136	1020
	2,K,5	
1	526	415
2	576	461
3	1217	1041
4	559	471
5	817	740
6	881	710
7	623	657
8	1324	1489
9	478	429
10	676	724
11	902	960
12	701	703
13	800	752
14	480	630
15	498	620
	2,K,6	
0	634	551
1	538	533
2	768	870
3	780	761
4	252	302
5	517	509
6	461	367
7	777	772
8	569	568
9	551	446
10	306	405
11	709	803
12	615	632
13	482	527
15	513	715
	2,K,7	
1	753	848
2	502	570
4	1034	1167
6	457	380
7	663	781
9	629	705
10	325	388
12	488	528
	2,K,8	
0	584	585
1	925	897
3	786	610
6	442	507
7	553	439
8	731	838
	2,K,9	
0	1054	1051
2	905	1052
3	510	431
5	467	535
7	592	725
9	355	429
	2,K,10	
1	687	825
2	345	231
	3,K,1	
0	656	664
1	720	755
2	1123	1185
3	1032	1050
4	1510	1632
5	1025	665
7	772	534
8	912	680
10	738	252
11	907	568
12	832	674
	3,K,2	
0	862	1028
1	750	836
2	1276	1343
3	992	955
4	1132	1158
5	823	726
6	1404	1245
7	954	915
8	1494	1583
9	712	556
10	874	653
12	1469	1321
14	665	685
15	698	417
16	729	569
	3,K,3	
0	2001	2331
1	1218	1554
2	1289	1460
3	1672	2195
4	1138	1088
5	1276	1441
6	723	677
7	2268	2550
9	1665	1696
11	1355	1153
12	1009	803
13	1403	1353
	3,K,4	
0	986	680
1	1169	1104
3	1551	1766
4	952	863
5	1245	1315
6	1863	2035
8	1885	2095
10	954	657
11	1119	949
12	1284	1258
13	950	787
14	1515	1244
	3,K,5	
0	990	882
1	1128	1061
2	1143	1005
3	550	330
4	2095	2470
5	1399	1417
6	1048	1022
7	1634	1919
9	2021	2145
10	713	589
11	743	525
12	1096	955
13	1397	1303
15	1063	756
	3,K,6	
0	1326	1195
2	1377	1333
3	748	525
4	540	441
5	904	885
6	1833	1928
7	1177	877
8	2168	2294
10	1069	684
11	784	683
12	1285	1041
14	1505	1262
	3,K,7	
1	1892	2045
3	672	460
4	1081	931
5	1305	1411
6	619	456
7	1641	1642
8	925	882
9	953	626
13	1386	1137
	3,K,8	
0	2953	2750
2	1029	1006
3	735	692
4	527	497
6	1338	1352
7	683	670
8	989	694
	3,K,9	
1	1845	1844
4	806	689
5	1000	819
7	1033	686
	3,K,10	
0	1338	1227
2	737	709
4	747	603
6	1060	914
	4,K,0	
1	1461	1664
2	1318	1128
3	1937	1931
4	1067	1139
5	2018	2013
6	2325	2073
7	2577	2752
8	1514	1373
9	1646	1671
10	502	419
11	452	386
12	1321	1425
13	1433	1463
14	1351	1322
15	1279	1213
16	525	543
	4,K,1	
1	2488	2269
2	2201	2053
3	1466	1225
4	1336	1122
5	883	827
6	1370	1368
7	1627	1597
8	1604	1760
9	878	894
10	856	697
11	575	409
12	964	879
13	1643	1618
14	1315	1380
15	873	1036
16	913	963
17	388	500
	4,K,2	
0	1349	1580
1	2496	2648
2	1351	1439
3	922	850
4	1111	997
5	740	855
6	1331	1385
7	1619	1453
8	1833	2005
9	1224	1175
10	707	536
11	509	441
12	659	590
13	1310	1313
14	1193	1275
15	1250	1113
16	753	692
	4,K,3	
0	1413	1266
1	649	491

4,K,3

2	1495	1565
3	1668	1649
5	2250	2209
6	1125	1023
7	2109	2203
8	1981	2032
9	1364	1313
10	912	969
11	569	537
12	1012	1038
14	1114	1232

4,K,4

0	660	863
1	1328	1276
2	371	455
3	794	1005
4	1498	1543
6	1673	1723
7	1793	1805
8	1345	1383
9	815	840
10	605	694
11	449	414
12	332	285
13	1253	1139
15	706	723

4,K,5

0	1165	1115
2	593	581
3	605	553
4	254	172
5	490	746
6	768	709
7	893	962
8	975	927
9	969	1000
10	320	373
12	695	649
14	750	548

4,K,6

1	654	837
2	382	487
3	613	734
5	287	504
6	418	507
8	631	519
10	678	734
13	532	399

4,K,7

1	418	491
2	942	1099
5	626	746

4,K,8

0	724	833
1	562	562
2	326	393
3	571	561
6	599	655

4,K,9

2	663	749
3	714	693
5	633	460
6	643	787
8	666	760

4,K,10

0	656	832
1	379	529
2	659	700

5,K,1

1	668	323
2	560	371
3	1235	1140
4	1198	1078
6	579	472
7	629	560
8	1400	1143
9	558	415
10	405	372
11	527	618
12	1147	1011
13	278	242
14	414	533

5,K,2

0	879	745
1	784	749
2	972	1077
3	1659	1475
5	242	110
6	759	550
7	1876	1939
8	669	636
9	1390	1231
10	536	524
11	1046	895
12	268	521
13	1622	1484

5,K,3

0	1240	824
1	695	432
2	1014	908
3	977	796
4	1478	1348
5	648	458
6	1882	1685
7	364	295
8	2228	2344
9	882	858
11	1202	1100
12	1294	1214
13	355	656
14	1175	1025

5,K,4

1	1231	1197
2	1754	1814
3	233	398
4	1591	1466
5	1456	1476
6	715	436
7	2202	2221
8	237	282
9	1472	1195
12	1461	1384
13	1305	1320
14	1209	1004
15	459	636

5,K,5

0	1452	1570
1	945	842
2	362	464
3	1262	1412
4	1051	1037
5	506	528
6	2225	2291
7	422	431
8	2061	1997
10	1233	960
11	1075	1051
12	1159	941
14	1207	1150

5,K,6

0	1525	1549
1	1403	1683
2	902	969
3	579	504
4	242	206
5	1624	1666
6	624	631
7	2154	2140
9	1409	1503
12	313	451
13	1373	1300
14	578	679

5,K,7

0	2114	2739
1	1443	1460
2	1408	1452
3	368	553
5	1145	891
6	2086	1894
8	1368	1214
10	309	334
12	567	544

5,K,8

0	1044	1193
1	1677	1663
4	1077	1070
5	1275	1163
6	894	790
7	1552	1342
11	334	289

5,K,9

0	1545	1588
1	679	578
2	807	589
3	615	625
4	822	819
5	770	833
6	958	957
7	325	317
8	738	951

5,K,10

0	326	326
1	1031	1116
4	331	532
5	1058	1106

6,K,0

1	1164	1352
2	1247	921
3	3128	2932
4	1384	1259
5	1687	1636
6	3165	3064
7	562	431
8	2821	2793
9	1086	1052
10	1675	1612
11	1526	1372
12	951	921
13	1629	1619
14	1393	1443
15	508	430
16	459	469

6,K,1

0	73	16
1	2090	2081
2	649	625
3	318	291
4	1366	1581
5	2489	2545
6	253	77
7	3732	3498
8	1322	1253
9	1829	1817
10	338	153
12	1202	1061
13	1428	1279
14	770	778
15	1021	1028

6,K,2

0	1394	1661
1	425	374
2	1381	1405
3	644	634
4	1643	1584
5	571	502
6	2711	2838
7	843	675
8	1976	2151
9	960	797
10	916	796
11	820	736
12	894	829
13	333	256
14	1210	1252
16	711	757

6,K,3

0	257	393
1	1364	1336
2	599	487
3	1221	1190
4	934	981
5	1713	1948
6	1284	1223
7	1801	1719
8	322	415
9	1586	1648
10	208	271
11	310	403
13	870	849
14	437	485
15	1052	1232
16	473	472

6,K,4

0	1581	1800
1	525	374
2	773	705
3	871	806
4	933	1024
5	1387	1420
6	1394	1265
7	377	394
8	1596	1703
9	208	230
10	654	602
11	456	360
12	414	534
13	557	576
14	636	759

6,K,5

0	858	771
1	422	551
2	428	259
3	564	645
4	777	485
5	423	301
6	339	433
7	1576	1398
8	367	383
9	662	639
10	608	627
12	498	481
13	578	692
14	536	350

6,K,6

0	429	443
1	545	496
2	753	818
3	1045	967
4	202	118
6	476	362
7	380	296
8	1015	929
9	470	415
11	712	565
12	260	264
13	269	338

6,K,7

0	601	663
3	869	1004
4	382	498
7	529	326
11	265	188
12	471	500

6,K,8

1	404	537
2	778	771
3	335	439
4	339	389
5	422	608

6,K,9

1	565	602
2	440	526
3	626	487
5	262	231
6	459	484
8	274	452

6,K,10

0	764	743
1	541	566
3	273	413
4	275	231

7,K,1

0	1199	1173
1	592	520
2	822	748
3	1237	1112
4	479	305
5	842	581
6	754	768
7	518	343
8	966	870
9	732	513
10	551	497
11	676	429
13	1067	832

7,K,2

0	588	609
1	1379	1395
2	714	483
3	562	520
4	1141	1116
7	1146	1283
8	1154	1152
9	1065	1027
11	846	571
12	1152	1112
13	766	743
14	984	794

7,K,3

0	594	726
1	1220	1373
2	1332	1425
3	647	624
4	903	889
5	442	359
6	663	608
7	994	1073
8	1052	1033
9	908	762
12	1185	1134
13	1110	1079
14	710	843
15	603	564

7,K,4

0	1859	1855
1	784	741
2	714	444
3	1559	1620
4	762	713
5	562	200
6	1610	1797
7	974	1218
8	1209	1197
9	830	671
10	710	497
11	910	847
13	1403	1267
14	842	616

7,K,5

0	1535	1508
1	1379	1373
2	806	788
4	598	601
5	1234	1423
6	1011	1239
7	1242	1254
9	951	741
12	991	790
14	1372	1224

7,K,6

0	1254	1232
1	1938	1866
2	1004	916
4	570	625
5	1066	1075
6	1202	1151
7	876	556
8	1169	1176
9	662	421
11	578	400
12	597	578
13	871	817

7,K,7

0	1200	1285
1	1203	1178
2	989	905
3	708	736
4	719	809
5	898	799
6	1186	1154
7	1333	1417
8	790	767
9	703	764

7,K,8

0	1312	1137
1	929	608
2	1079	1048
5	1253	1237
6	988	865
7	1164	1020
8	840	1069

7,K,9

1	1005	1022
3	719	702
4	838	923
6	1216	1205

7,K,10

0	1072	1271

8,K,0

2	1171	1051
3	293	353
4	1973	1732
5	1048	1115
6	1157	976
7	2482	2412
8	1095	805
9	3123	2639
10	1015	973
11	495	592
12	1079	1304
13	1234	1440
15	1247	1571

8,K,1

2	1638	1174
3	1801	1592
4	856	1144
6	2490	2377
7	604	863
8	2722	2425
9	623	914
10	813	970
11	1195	1037
12	833	988
13	679	733
14	1395	1474

8,K,2

0	922	746
1	1742	1932
2	578	716
3	254	239
4	1536	1585
5	2017	2077
6	455	456
7	1953	2206
8	602	452
9	1200	1243
10	481	497
11	360	452
13	890	1085
14	510	389
15	868	1038

8,K,3

0	1940	1975
1	384	271
2	1121	987
3	1042	873
4	873	732
6	1959	1860
7	670	477
8	868	969
10	499	447
12	675	627
14	736	938

8,K,4

0	364	300
1	1382	1465
2	264	145
3	332	405
4	563	648
5	1016	1136
7	1016	990
8	1038	1047
9	611	632

8,K,5

0	1372	1486
1	996	920
2	987	902
3	607	746
6	666	795
7	489	682
8	441	581

```
      8,K,6

 1    464    561
 3   1212   1176
 4    485    536
 6    443    323
 7    456    345
 8   1154   1114

      8,K,7

 2    728    718
 4    529    657

      8,K,8

 0    557    690
 2    561    557

      9,K,1

 0    298    209
 2   1025   1027
 3    748    733
 4    690    605
 5    542    368
 7   1018    898
 9   1285    899
14   1191    412

      9,K,2

 0    367    275
 1    866    929
 2    398    299
 3    607    635
 4    465    325
 6    885    814
 7    582    569
 8   2014   1009
10    700    374
14    696    930

      9,K,3

 0   1047   1321
 1   1296   1604
 2    545    534
 3    698    580
 4    736    823
 5    550    626
 6    583    344
 7   1008    943
 9    689    658
10    726    711
11    881    436

      9,K,4

 0   2413   2573
 1   1112   1135
 2   1217   1226
 3    646    480
 4    670    406
 5   1104   1123
 6   1033   1103
 7    541    449
 8    981    826
 9    839    764
13    993    769

      9,K,5

 0    603    573
 1   2449   2480
 2    709    577
 3    626    597
 4    525    462
 5   1063    916
 6    971    811
 7   1163    970
11   1173    645

      9,K,6

 0   2165   2193
 1    780    646
 2   1245   1419
 4    706    586
 6   1214   1216
 7    625    595
 8    790    845
 9    815    573

      9,K,7

 0   1049    968
 1   1214   1270
 5   1108   1002
 7   1339   1446
 9    995   1081
10    721    413

      9,K,8

 0    808    504
 1    809    683
 2    664    620
 3    670    863
 4    678    383
 6   1399   1235

      9,K,9

 0    869    670
 1    710    557
 2    873    997

      10,K,0

 1    683    932
 2    993    934
 3    812    623
 4    831    707
 5   1555   1627
 6   1816   1792
 7   2195   2031
 8   1633   1768
 9   1100   1052
10    605    447
11    641    884
12   1311   1245
14   1287   1333

      10,K,1

 0    972    834
 1   1117   1413
 2    562    512
 3    916    874
 4   1282   1219
 5    664    681
 6   1592   1603
 7   1516   1627
 8   1517   1223
 9    907   1036
10    747    752
11    559    496
13   1336   1606
14    914    938

      10,K,2

 0   1402   1344
 1   1256   1452
 2   1022   1099
 3    470    472
 4    589    290
 5   1405   1152
 6   1589   1560
 9    722    706
12    979    983
13    627    671
14   1067   1257

      10,K,3

 0   1826   1968
 1   1281   1438
 2    423    479
 3    382    302
 5    696    532
 7   1233   1160
 8    967    774
 9    753    802
12    710    684

      10,K,4

 0   1776   1941
 1    676    598
 2    942    948
 5    662    502
 6    565    568
 7    512    480
 8    536    506
 9    457    271
11    498    442
12    635    613
13    659    627

      10,K,5

 0    467    355
 1   1507   1413
 2    475    347
 8    931    798

      10,K,6

 0   1274   1129
 1    522    509
 2    608    559
 3    436    267
 4    445    497
 7    834    671
 9    886    954

      10,K,7

 0    660    765
 4    484    481
 1    573    445
 7    630    439

      10,K,8

 5    646    470
 6    536    620

      11,K,1

 1    408    288
 2    919    627
 4    757    543
 5    594    344
 6    531    533
 7    814    624
 8    875    479
 9    661    340

      11,K,2

 0    930   1283
 1    910   1111
 2    651    523
 3    628    539
 4    962    778
 5    901    795
 6    970    782
 7    734    525
 8   1108    997
 9    679    442
13    717    427

      11,K,3

 0   1100   1186
 1    750    706
 2   1145   1188
 3    722    508
 4    465    547
 5    804    621
10    526    301
12    575    480

      11,K,4

 1   1678   2172
 5    623    472
 7    833    757
10    548    362
11    571    558

      11,K,5

 1    624    565
 2   1413   1487
 5    590    597
 6    996    913
 8    655    734

      11,K,6

 0    599    569
 1   1699   1745
 3    615    674
 4    627    457
 5    740    647
 7   1352   1211

      11,K,7

 0   1313   1395
 2    855    853
 6   1151   1105

      11,K,8

 1   1162    766
 3    720    665

      12,K,0

 1    933    803
 2    866    912
 3    807    805
 5    966    719
 6   1805   1876
 7   1419   1147
 8   1651   1329
 9    817    900
10   1228   1233
12    787    658

      12,K,1

 0    896    965
 1   1281   1722
 2    824    852
 3    560    557
 5    993    729
 6   1411   1232
 7   1315   1367
 8   1093   1036
 9    825    914
11    533    763
12    791    643

      12,K,2

 0   1694   2126
 1    689    634
 2   1032   1219
 3    454    551
 5    651    440
 6   1279   1061
 7   1146    992
 8   1130    950
 9    692    642

      12,K,3

 0    831    581
 1   1609   1870
 2    433    548
 3    904    910
 5    711    660
 6    868    670
 7   1026    964
 8    684    737

      12,K,4

 0   1509   1422
 1    797    812
 2   1148   1353
 4    611    561
 5    779    380
 6    813    428
 7    600    569

      12,K,5

 0   1269   1104
 1    637    586
 2    456    742
 3    657    598
 5    491    426
 6    507    458

      12,K,6

 1    999   1056
 4    637    434

      13,K,1

 1    632    652
 3    846    768
 5    917    631
 8    822    664

      13,K,2

 0   1137   1206
 2    900    823
 4    909   1076
 6    746    727
 7    921    734
 9   1037    802

      13,K,3

 1   1417   1558
 3    556    557
 5    757    820
 6    462    493
 7    844    574
 8    629    652

      13,K,4

 0   1791   1869
 1    520    621
 2   1059    983
 3    544    755
 6    996    877
 7    520    597
 8    664    572

      13,K,5

 0    954    975
 1   1354   1538
 2    969    835
 3    494    649
 6    930    539

      13,K,6

 0   1293   1226
 1    749    896
 2    924    970

      14,K,0

 2    568    765
 4    330    507
 5   1013   1247
 6    814    862
 7   1875   1771
 8    822    618
 9   1073   1044

      14,K,1

 1    394    498
 2    934    943
 3    746    742
 4    687    530
 5    760    613
 6   1686   1485

      14,K,2

 1   1202   1601
 2    560    573
 3    604    470
 6    618    541
 7   1475   1162
 9    740    452

      14,K,3

 0   1448   1793
 1    644    578
 2    765   1023
 6    810    852
 8    634    439

      14,K,4

 1   1139   1027
 3    636    438

      14,K,5

 0    835    745
 2    693    574
 4    722    615
 5    909    597

      14,K,6

 0    921    783

      15,K,1

 0    679    717
 3    567    474
 4    833    773
 5    775    539
 6    345    449

      15,K,2

 0    610    722
 1    862    925
 2    539    517
 3    649    683
 4    543    692
 5   1014    956
 6    888    666

      15,K,3

 0   1468   1578
 1    619    653
 4    696    765
 5    637    604

      15,K,4

 0    616    868
 1   1011    855
 2    727    792
 3    457    513
```

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APPENDIX A

DATA COLLECTION ON THE SAAB AUTOMATIC FILM SCANNER MARK II.

The film was trimmed and fitted on to a cylindrical drum which rotated on a screw thread. As the drum rotated and moved along the axis of the screw a light shone through the film on to a light sensitive cell which recorded the intensity of light transmission in blocks 60μ in length along each track which measured 90μ in width. The film was thus divided by the scanner into a grid with one intensity measurement for each grid space and X and Y co-ordinates assigned to each measurement corresponding to the number of block along the track and the number of the track respectively. The film was mounted in the scanner such that the X axis of the film was co-directional with the camera axis.

Because of the storage limitations of the Digital Equipment Corporation PDP8 computer, which was linked to the scanner, all the transmitted light intensity values for one complete film could not be kept for processing. The film was therefore processed as it was scanned so as to retain on magnetic tape only the information necessary to determine an integrated intensity value for each spot. To achieve this reduction in information stored on tape a "clipping level" was chosen which was a fraction of the background transmission value (0.85 in the case of the films scanned for the structure determination reported in Part II of this thesis). The background level was calculated for each track and was taken to be equal to the average transmission value for that track. All transmission values which were above this "clipping level" were ignored by the computer as were all isolated transmission values below the "clipping level".

The following information was recorded on tape:

1) a track marker,
2) the track number or Y co-ordinate,
3) the clipping level (TCLIP),
4) the X co-ordinate at the beginning of a feature,
5) the transmission values (T) for that feature, followed by the X co-ordinate of any other feature on that track with their corresponding transmission values. A sample of this data is shown below.

Y	TCLIP	X	T	T	T	......
703	895					
704	895					
		1249	794			
		1423	749	503	820	
705	896					
706	894					
		1236	809	876		
		1242	871	859	884	854
		1251	887			
707	896					

Processing the Data

The light transmission measurements (T) received from the scanner were converted into values of one hundred times the optical density (D) by a programme called 'Findspots' written by Dr. M.M. Harding and using the equation: $D=100*\log_{10}(B/T)$ where B is the background transmission level. This programme also added together optical values for contiguous grid points so as to give integrated intensity values for each spot on the film, associating with this intensity a serial number and several labels which gave information on the size and shape of the spot.

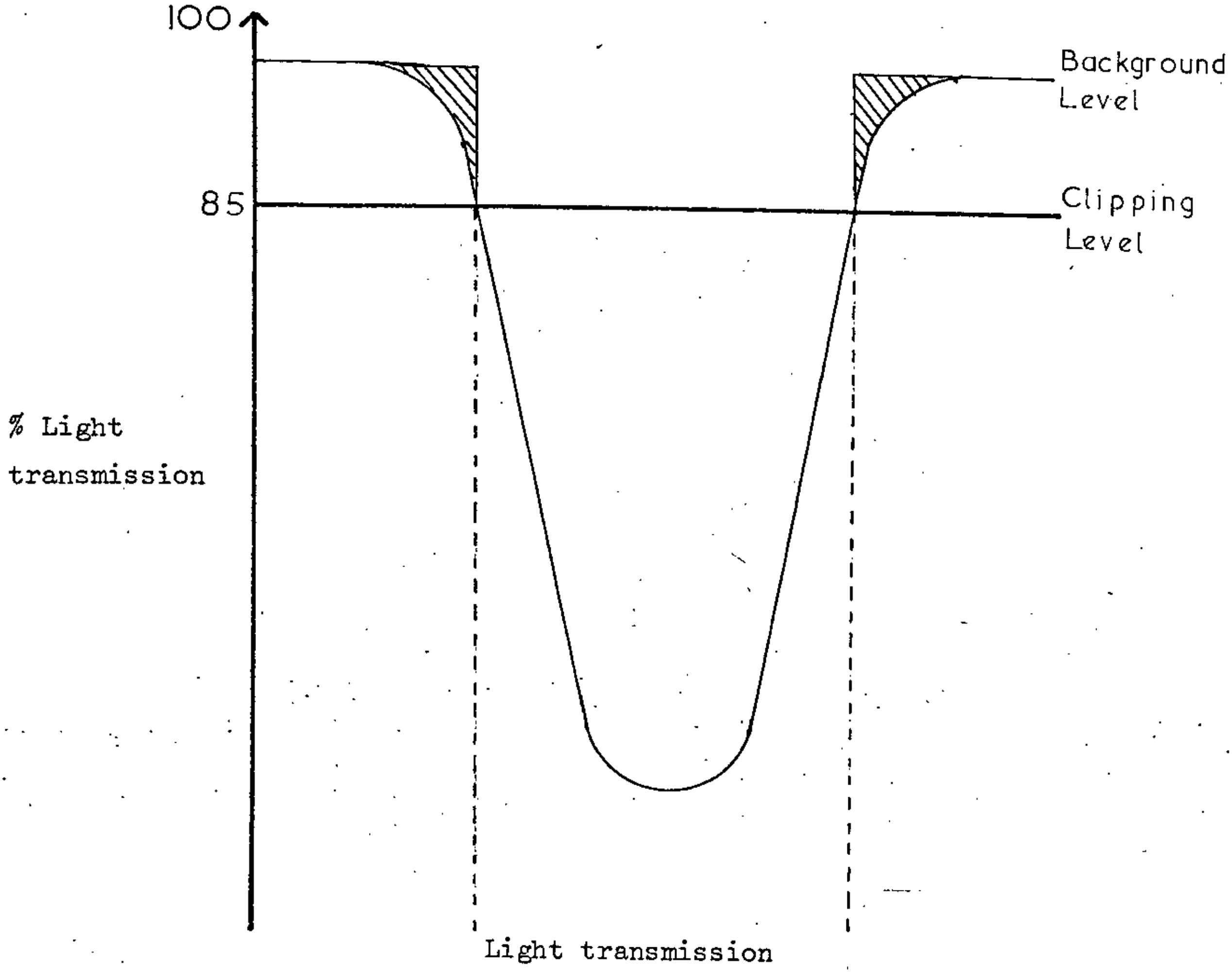
The output from the 'Findspots' programme was processed by two programmes 'Filmfit' and 'Packscal', both written by Dr. R.O. Gould. These programmes assigned Miller indices to each spot and averaged the separate measurements of symmetry related spots and spots with identical Miller indices. Finally corrections were made for Lorentz and polarisation factors.

Sources of Error

Figure 1 represents the variation of light intensity of transmission across a film showing which transmission values from the scanner will be recorded by the computer for later processing. It can be seen that all clear areas of film are ignored and only areas of high optical density retained. However, at the edge of each spot there exists an area, shaded in figure 1, where the optical density has tailed off to a value too low to give rise to a reading from the scanner which would be retained for processing. Ignoring this peripheral area of the spot would give rise to

Figure 1

Profile of spot showing which values of light transmission through a spot are not recorded by the scanner.



values within this frame only kept for processing appreciable errors in the final integrated intensity values for some spots. A correction factor was therefore applied to the final integrated intensity as follows. An average spot size, measured in number of grid points, was chosen for a film and any spot which was composed of fewer than average grid points was assigned an optical density equal to $\frac{1}{2}\log_{10}({}^{B}/_{TCLIP})$ for every grid point less than the average. This correction factor is obviously only approximate and may even introduce errors with spots of compact shape.

APPENDIX B

PROGRAMME TO APPLY SCALE FACTORS TO INTENSITY MEASUREMENTS AND CORRECT FOR LORENTZ AND POLARISATION FACTORS

This programme was specifically written for the data from the crystals of Tetraphenylarsonium Bis(triphenylphosphine)tetrachlororhodate, using FORTRAN IV G as computing language. The general scheme of the programme is described below.

Read from cards the reciprocal cell dimensions, $a^*, b^*, c^*, \cos\beta^*$

Read from cards the layer scale factors, FS(M).

Read from cards the Miller indices of spots and their measured intensities in groups of ten.

Calculate for each spot the value of $\sin^2\theta$(S) and the Lorentz and polarisation factor (LP) according to the following equations:

$$\sin^2\theta = S = \tfrac{1}{4}[(ha^*)^2 + (kb^*)^2 + (lc^*)^2 + 2hla^*c^*].$$

$$LP = [1 - 2\sin^2\theta + 2\sin^4\theta] / \sqrt{\sin^2\theta - \sin^4\theta - (kb^*)^2.(1 - \sin^2\theta)/4}$$

Print out a message for any spot where the calculated value of $\sin^2\theta$ is greater than or equal to one.

Apply the layer scale factors and Lorentz and polarisation factors to each intensity, printing out the results and at the sametime storing them in a one dimensional array in the form:

100 k l h F^2 h F^2 h F^2 ......

Punch the contents of this array on to cards in a format suitable for use with the Fourier programmes which were used for this structure determination.

A transcript of the programme as it was used is shown below.

```
        INTEGER H(10),IA(10000)
        REAL F(10),LP,FS(10)
20      FORMAT (2I4,10(I3,F4.1))
21      FORMAT (3I5,4F10.4)
22      FORMAT (4F10.2)
23      FORMAT ( ' ERROR IN PLANES ', 3I5,2F10.4)
24      FORMAT (18I4)
25      FORMAT (10F5.4)
        J=1
        LS=-100
        KS=100
        READ (5,22) AS,BS,CS,CBS
        READ (5,25)(FS(M),M=1,10)
        M=0
        READ (5,20,END=8) K,L,(H(I),F(I),I=1,10)
        DO 6 I=1,10
        IF(F(I).LT.0.5) GO TO 7
        S=0.25*((AS*H(I))**2+(BS*K)**2+(CS*L)**2+2*H(I)*L*CS*AS*CBS)
        IF(S-1)4,5,5
 5      WRITE (6,23)H(I),K,L,S,F(I)
        GO TO 6
 4      LP=(1-2*S+2*S*S)/(SQRT(S-S*S-((K*BS)**2)*(1-S)/4))
        IF(K-KS)30,31,30
30      M=M+1
31      SC=1/FS(M)
        FCOR=(3*SC*F(I))/LP
        WRITE (6,21)H(I),K,L,S,LP,F(I),FCOR
```

```
      IF(L-LS)10,11,10
10    IA(J)=100
      IA(J+1)=K
      IA(J+2)=L
      J=J+3
      LS=L
      KS=K
11    IA(J)=H(I)
      IA(J+1)=FCOR+0.5
      J=J+2
 6    CONTINUE
      GO TO 7
 8    J=J-1
      WRITE (7,24)(IA(I),I=1,J)
      STOP
      END
```

APPENDIX C

PROGRAMME FOR CALCULATING INTERATOMIC DISTANCES AND ANGLES

This programme was specifically written to determine the interatomic distances and angles in the molecular structure of Bis(tri-pentafluorophenylphosphine)dichloroplatinum(II). The programme language used was FORTRAN IV. The general scheme of the programme is described below.

Read from cards the cell dimensions, A,B,C, $\cos\alpha$,$\cos\beta$,$\cos\gamma$.

Read from cards the fractional co-ordinates of atoms and their estimated standard deviations, x,y,z,sigx,sigy,sigz.

For a pair of atoms calculate the bond length, BL, between them and its standard deviation, SIGBL, according to the following equations

$$\mathrm{BL} = \sqrt{\begin{aligned}\Big(&((x_2-x_1)a^*)^2 + ((y_2-y_1)b^*)^2 + ((z_2-z_1)c^*)^2 \\ &+2A^*B^*\cos\gamma(x_2-x_1)(y_2-y_1) \\ &+2A^*C^*\cos\beta(x_2-x_1)(z_2-z_1) \\ &+2B^*C^*\cos\alpha(y_2-y_1)(z_2-z_1)\Big)\end{aligned}}$$

$$\mathrm{SIGBL} = \sqrt{\begin{aligned}\Big[&(\mathrm{sigx}_2^2+\mathrm{sigx}_1^2)\Big([(x_2-x_1)A+(y_2-y_1)B\cos\gamma+(z_2-z_1)C\cos\beta]\ /\mathrm{BL}\Big)^2 \\ &+(\mathrm{sigy}_2^2+\mathrm{sigy}_1^2)\Big((y_2-y_1)B+(x_2-x_1)A\cos\gamma+(z_2-z_1)C\cos\alpha\ /\mathrm{BL}\Big)^2 \\ &+(\mathrm{sigz}_2^2+\mathrm{sigz}_1^2)\Big((z_2-z_1)C+(x_2-x_1)A\cos\beta+(y_2-y_1)B\cos\alpha\ /\mathrm{BL}\Big)^2\Big]\end{aligned}}$$

Print out the results

Choose three atoms, A,B,C, in which at least two of the interatomic distances are less than 2.5Å.

Calculate the angle, θ, between the two 'bond lengths' from the first atom chosen to the two other atoms, i.e. the angle between AB and AC, and its standard deviation, SIGθ, according to the formulae shown below.

$$\theta = \cos^{-1}\left((AB^2+AC^2-BC^2)/2AB*AC\right)$$

$$SIG\theta = sigx_1^2/AB^2+sigx_2^2*BC^2/AB^2*AC^2+sigx_3^2/AC^2$$

Print out the results.

A transcript of the programme as used is shown below.

```
          REAL AX(13),AY(13),AZ(13),SIGX(13),SIGY(13),SIGZ(13),
         #DX(13,13),DY(13,13),DZ(13,13),BL(13,13),SIGBL(13,13)
   20     FORMAT(6F12.5)
   21     FORMAT(2I5,5F10.5)
   22     FORMAT(3I5,5F10.5)
   25     FORMAT('1','AB=BL(I,M),AC=BL(I,K),BC=BL(J,K)')
          READ(5,20)A,B,C,CSA,CSB,CSG
          DO 1 I=1,13
          READ(5,20)AX(I),AY(I),AZ(I),SIGX(I),SIGY(I),SIGZ(I)
    1     CONTINUE
          DO 2 I=1,13
          DO 2 K=1,13
          IF((I-K).EQ.0)GO TO 2
          DX(I,K)=AX(I)-AX(K)
          DY(I,K)=AY(I)-AY(K)
          DZ(I,K)=AZ(I)-AZ(K)
          BL(I,K)=SQRT((DX(I,K)*A)**2+(DY(I,K)*B)**2+(DZ(I,K)*C)**2+
         #2*A*B*DX(I,K)*DY(I,K)*CSG+2*A*C*DX(I,K)*DZ(I,K)*CSB+
         #2*B*C*DY(I,K)*DZ(I,K)*CSA)
          SIGBL(I,K)=SQRT((SIGX(I)**2+SIGX(K)**2)*(((DX(I,K)*A+DY(I,K)*B*CSG
         #+DZ(I,K)*C*CSB)/BL(I,K))**2)+
         #(SIGY(I)**2+SIGY(K)**2)*(((DY(I,K)*B+DX(I,K)*A*CSG+
         #DZ(I,K)*C*CSA)/BL(I,K))**2)+
         #(SIGZ(I)**2+SIGZ(K)**2)*(((DZ(I,K)*C+DX(I,K)*A*CSB+
         #DY(I,K)*B*CSA)/BL(I,K))**2))
          WRITE(6,21)I,K,DX(I,K),DY(I,K),DZ(I,K),BL(I,K),SIGBL(I,K)
   2      CONTINUE
          PRINT 25
          DO 3 I=1,13
```

```
         DO 3 M=1,13
         IF((I-M).EQ.0)GO TO 4
         J=M
         IF(BL(I,M)-2.5)11,4,4
 11      AB=BL(I,M)
         GO TO 10
  4      CONTINUE
 10      CONTINUE
         DO 3 K=1,13
         IF((I-K).EQ.0)GO TO 3
         IF((J-K).EQ.0)GO TO 3
         IF(BL(J,K)-2.5)13,14,14
 14      IF(BL(I,K)-2.5)13,3,3
 13      AC=BL(I,K)
         BC=BL(J,K)
         THETA=ARCOS((AB*AB+AC*AC-BC*BC)/(2*AB*AC))
         SIGTH=SQRT(SIGX(M)**2/AB*AB+(SIGX(I)**2)*BC**2/
        #(AB**2)*(AC**2)+SIGX(K)**2/AC**2)
         WRITE(6,22)I,J,K,AB,AC,BC,THETA,SIGTH
  3      CONTINUE
         STOP
         END
```

It will be noted that the standard deviations calculated for the bond lengths and angles do not take into account the errors in the cell dimensions but are based only on the standard deviations of the atom parameters. For a crystal structure determination such as that described in Part I of this thesis this simplification would render the calculated standard deviations meaningless. Thus the results obtained with this programme were eventually superseded by other results using the X-ray 72 system of programmes.

APPENDIX D

PARTIAL DEVELOPMENT OF PROGRAMME FOR INDEXING OSCILLATION PHOTOGRAPHS

In order to improve the quality of the results from the determination of the crystal structure of Tetraphenylarsonium Bis(triphenylphosphine) tetrachlororhodate a crystal was mounted about the [a] axis and a series of oscillation photographs taken. These photographs were to be scanned, the data processed by Findspots (see Appendix A) and the spots indexed by a programme, the partial development of which is recorded below. As the results of the crystal structure determination as reported in Part III of this thesis were adequate for the purpose for which the determination was undertaken and as unavoidable delays were experienced before the films could be scanned the development of the programme was abandoned.

The programme was divided into two parts. The first programme calculated by linear least squares the film diameter and the centre point on the equatorial layer line which was used as the origin to which the co-ordinates of each spot on the film were referred. The second part of the programme assigned Miller indices to each spot and printed out a list of these indexed reflections corrected for Lorentz and polarisation factors. The successful application of these programmes to the indexing of an oscillation photograph of an orthorhombic crystal is described below.

1. Calculation of the Film Radius and the Origin

In this part of the programme the film radius was calculated using the known indices and film co-ordinates of a number, n, of spots on the zero layer line of the oscillation photograph found by comparison of the oscillation photograph with a zero level Weissenberg photograph which was indexed by inspection. The co-ordinates as measured by the scanner were referred to an arbitrary origin determined only by the way the film was placed in the scanner. It was therefore necessary to calculate the position of the centre point on the equatorial layer line in terms of the scanner co-ordinate, y, so that it could be used as the standard origin of the film and all measured co-ordinates from the scanner could be altered in part two of the programme to refer the spots to this origin. The following equations were used to determine the film radius, R, and the position of the origin, Y_o.

$$R = \frac{\sum_{i=1}^{n} y_i \cdot x_i - (\sum_{i=1}^{n} y_i) \cdot (\sum_{i=1}^{n} x_i)/n}{(\sum_{i=1}^{n} x_i)^2/n - \sum_{i=1}^{n} x_i^2}$$

$$Y_o = (\sum_{i=1}^{n} y_i + R.\sum_{i=1}^{n} x_i)/n$$

where $x_i = \cos^{-1}\left(\frac{2-\xi_i^2}{2}\right)$, where ξ_i is the co-ordinate of the point in reciprocal space which corresponds to the i^{th} spot on the film.

Proof of the Formulae used to Calculate the Film Radius (R) and the Origin of the Film (Y_o).

For spots on the zero layer of an oscillation photograph[1]

$$\frac{-y_i + Y_o}{R} = \cos^{-1}\left(\frac{2 - \xi_i^2}{2}\right)$$

Let $\cos^{-1}\left(\frac{2 - \xi_i^{\,2}}{2}\right) = x_i$

then $y_i = -R.x_i + Y_o$

Since a linear relationship exists between R and Y_o the method of linear least squares may be used to solve for R and Y_o given a number of observations y_i and x_i. A solution will therefore be found by minimising the function P where

$$P = \sum_i (y_i + R.x_i - Y_o)^2.$$

$$\frac{dP}{dR} = \sum_i 2(x_i)(y_i + R.x_i - Y_o)$$

$$= 2\sum_i x_i y_i + 2R\sum_i x_i^{\,2} - 2Y_o \sum_i x_i$$

$$\frac{dP}{dY_o} = \sum_i 2(-1)(y_i + R.x_i - Y_o)$$

$$= -2\sum_i y_i - 2R\sum_i x_i + 2Y_o.\sum_i 1$$

The function P will have minima with respect to R and Y_o when $\frac{dP}{dR} = 0$ and when $\frac{dP}{dY_o} = 0$

$$\frac{dP}{dR} = 2\sum_i x_i y_i + 2R.\sum_i x_i^{\,2} - 2Y_o.\sum_i x_i = 0$$

$$\therefore -R\sum_i x_i^{\,2} + Y_o.\sum_i x_i = \sum_i x_i y_i \qquad (1)$$

$$\frac{dP}{dY_o} = -2\sum_i y_i - 2R.\sum_i x_i + 2Y_o.n = 0$$

$$\therefore -R.\sum_i x_i + Y_o.n = \sum_i y_i \qquad (2)$$

Multiply equation (1) by n and equation (2) by $\sum_i x_i$

$$-n.R.\sum_i x_i^2 + n.Y_o.\sum_i x_i = n.\sum_i x_i y_i \qquad (3)$$

$$-R.(\sum_i x_i)^2 + Y_o.n.\sum_i x_i = (\sum_i y_i).(\sum_i x_i) \qquad (4)$$

Subtract equation (4) from equation (3)

$$R(\sum_i x_i)^2 - n.R.\sum_i x_i^2 = n.\sum_i x_i y_i - (\sum_i y_i).(\sum_i x_i)$$

$$\therefore R = \frac{n.\sum_i x_i y_i - (\sum_i y_i).(\sum_i x_i)}{(\sum_i x_i)^2 - n.\sum_i x_i^2}$$

$$= \frac{\sum_i y_i x_i - (\sum_i y_i).(\sum_i x_i)/n}{(\sum_i x_i)^2/n - \sum_i x_i^2}$$

From equation (2)

$$Y_o = (\sum_i y_i + R.\sum_i x_i)/n$$

Transcript of the Programme as used.

```
        INTEGER  IK(10),IL(10)
        REAL  YS(10),X(10)
12      FORMAT (2F 15.5)
10      FORMAT (2I5,F10.5)
15      FORMAT (4F10.5)
        READ (5,15) BS,CS,CBS,O
        N=0
        SYS=0
        SX=0
        SXX=0
        SXSY=0
        DO 1 I=1,10
        READ (5,10,END=2)IK(I),IL(I),YS(I)
        N=N+1
        SYS=SYS+YS(I)
        X(I)=ARCOS((2-(IK(I)*BS)**2-(IL(I)*CS)**2
      #-2*IK(I)*IL(I)*BS*CS*CBS)/2)
        IF((O-YS(I)).LT.0.0)X(I)=-X(I)
        SX=SX+X(I)
        SXX=SXX+X(I)**2
        SYSX=SYSX+YS(I)*X(I)
1       CONTINUE
2       R=(SYSX-SX*SYS/N)/(SX*SX/N-SXX)
        OY=(SYS+R*SX)/N
13      FORMAT(2F15.5)
        WRITE(6,13)(YS(I),X(I),I=1,10)
14      FORMAT(4F15.5)
```

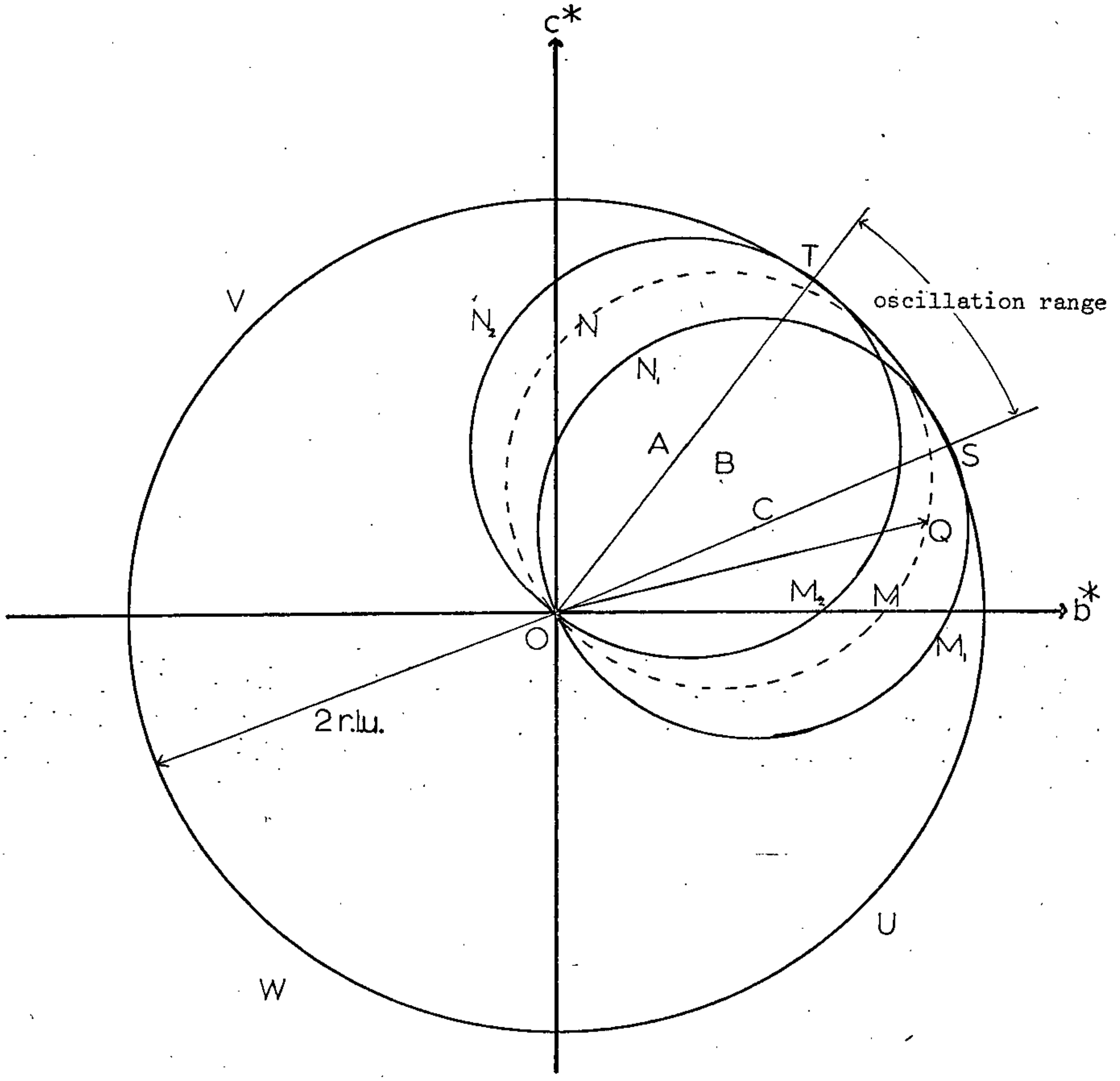
```
      WRITE(6,14)SYS,SX,SXX,SYSX
      WRITE(6,11)
11    FORMAT('      R        OY')
      WRITE(6,12)R,OY
      STOP
      END
```

2. Indexing observed reflections

Figure 1 represents a plane of the reciprocal lattice with UVW representing a cross section of the limiting sphere and with OM_1N_1, OM_2N_2 and OMN representing a cross section of the sphere of reflection, in the same plane, shown at different positions in its range of oscillation. The centres of these circles are at A,B, and C respectively. It is usually found convenient to think in this way of reflections being produced when a reciprocal lattice point passes through the surface of the sphere of reflection as it oscillates relative to the reciprocal lattice. If OM_1N_1 and OM_2N_2 represent the circle of reflection at either extreme of its oscillation range then AOC will represent the oscillation angle and the two lunes OM_1SM_2 and ON_1TN_2 will enclose all points on this plane of the reciprocal lattice for which a reflection may occur.

In indexing an oscillation photograph, therefore, it is necessary to know the range of oscillation of the crystal and the position of this range relative to the reciprocal lattice. The range of oscillation is fixed at the time the photographs are taken. It's position relative to the reciprocal lattice may be found by indexing the equatorial layer line by comparison with a zero level Weissenberg photograph and marking the observed reflections on a grid of the reciprocal lattice base. Two circles to represent the circle of reflection at either extreme of the oscillation range are drawn such that the lunes formed enclose the marked reciprocal lattice points (figure 2a). The co-ordinates of the centres of these circles measured in reciprocal lattice units can then be determined and the process repeated for every other oscillation range used. An accurate knowledge of the relationships between the different oscillation ranges

Figure 1



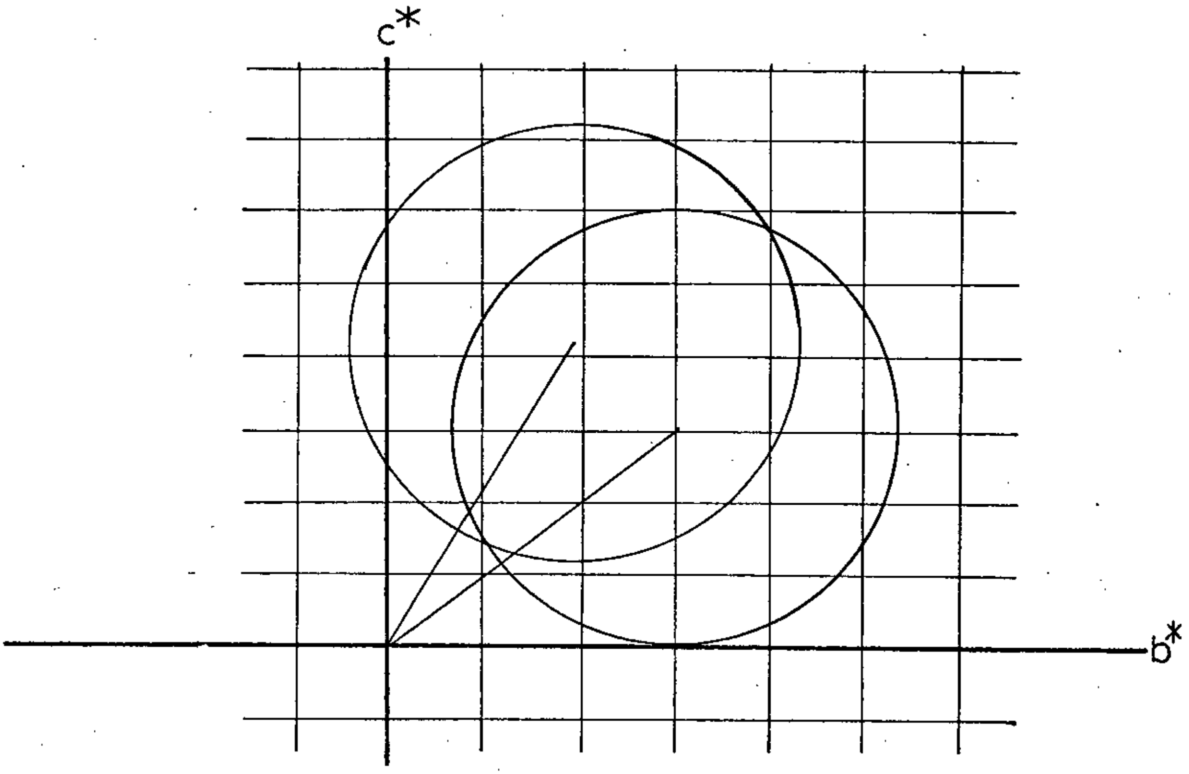


Figure 2(b) Upper Layer

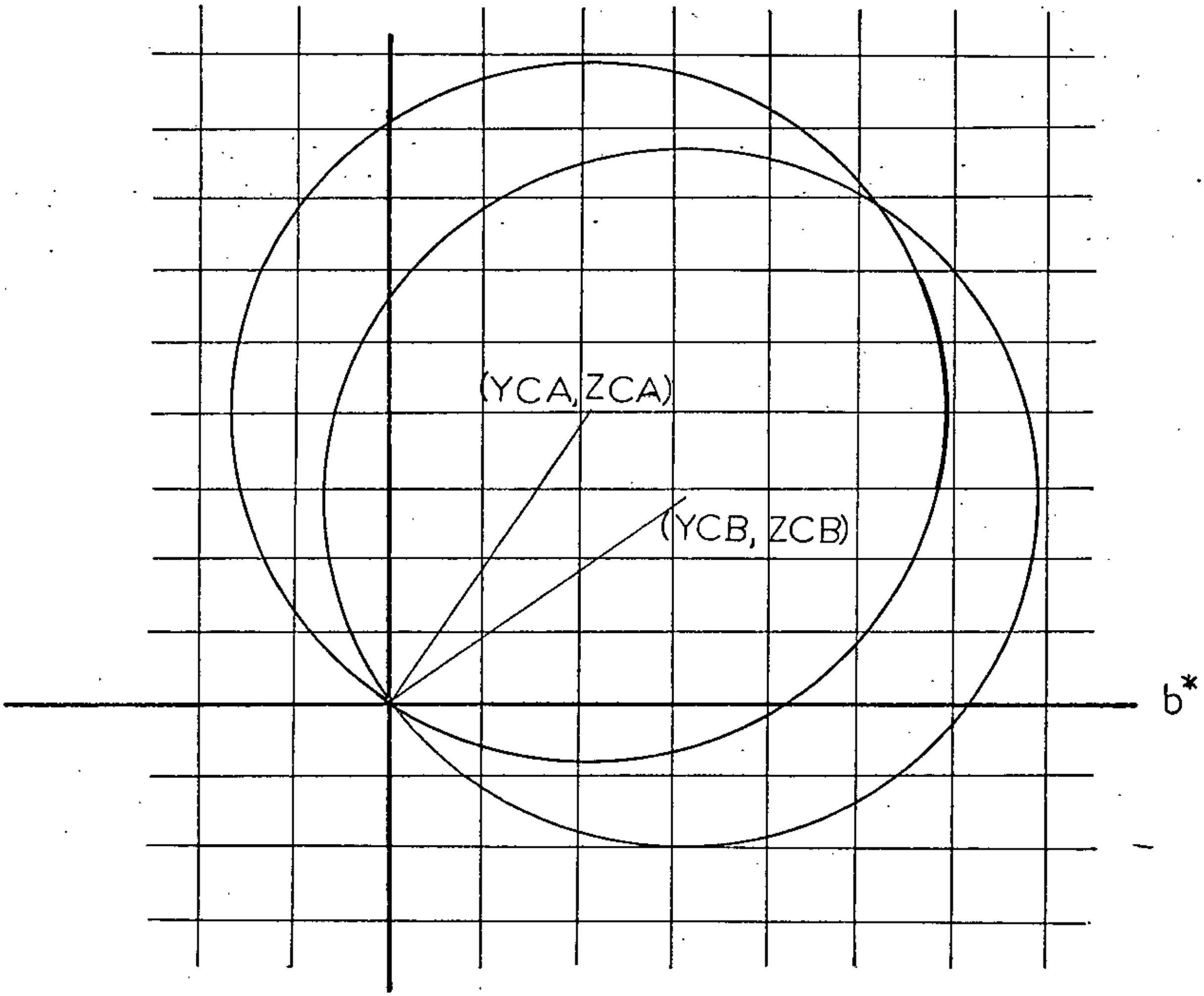


Figure 2(a) Zero Layer

can be used to improve the accuracy with which the centres of the various circles of reflection are determined.

The programme used to index an oscillation photograph of an orthorhombic crystal is described below. Though this version of the programme is limited to indexing a particular oscillation photograph of a crystal oscillating about the [a] axis, minor alterations to the programme would make it of more general application. The co-ordinates of the centre point of the equatorial layer line are built into the programme itself so that the only information which requires to be read from cards are the reciprocal cell constants, the co-ordinates of the centres of the circle of reflection at both extremes of its oscillation range, the film radius and the co-ordinates of the spots to be indexed as measured by the scanner (see Appendix A).

The film co-ordinates of each spot were first converted to a new set of co-ordinates referred to the origin of the film calculated in Part 1 of this programme and these co-ordinates then used to calculate for each spot and store in parallel arrays, the observed reciprocal space co-ordinate ξ_m, the number of the layer line on which the spot occurs (NL), and the film co-ordinate of the spot (XM) measured parallel to the layer lines, using the following equations:

$$\xi_m = \sqrt{2 - \zeta^2 - 2\sqrt{1 - \zeta^2} \cdot \cos\left(\frac{2X}{D}\right)}$$

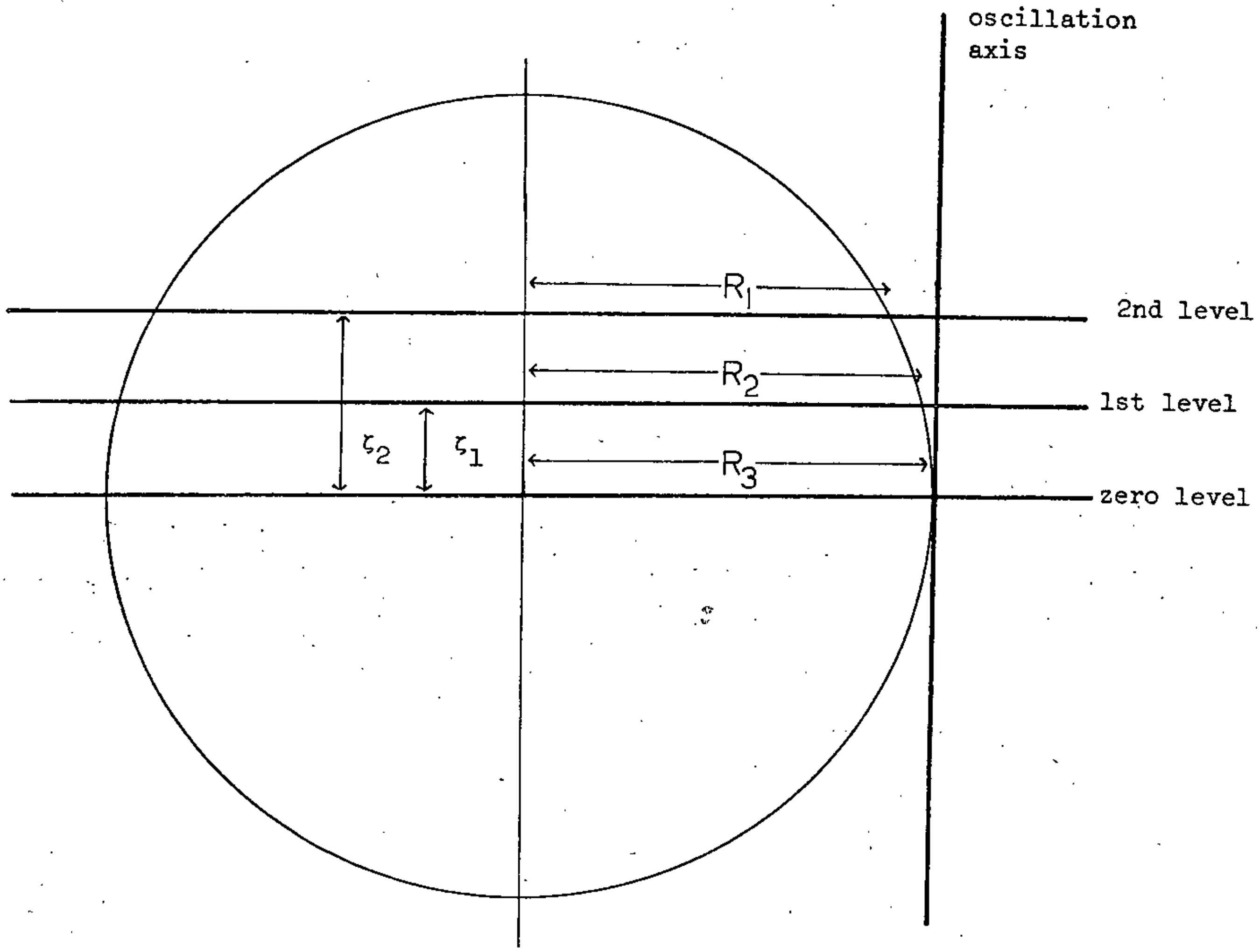
$$NL = \frac{y_m}{\sqrt{R^2 + {y_m}^2} * a^*}$$

where x_m and y_m are the film co-ordinates parallel to and perpendicular to the layer lines respectively.

The next section in the programme takes the reciprocal lattice layer by layer and determines which reciprocal lattice points on each layer could give rise to a reflection. As each layer is considered the radius of the appropriate circle of reflection is calculated. Figure 3 shows a section of the sphere of reflection in the plane which contains the oscillation axis and the centres of the circles of reflection for the different levels of the reciprocal lattice. R_0, R_1 and R_2 are the radii of these circles of reflection. Since the radius of the sphere of reflection is 1 r.l.u. then by Pythagoras $R_n = 1 - \xi_n^2$. The limits of a rectangular grid of reciprocal lattice points are then calculated such that it encloses the two lunes swept out by the circle of reflection as it oscillates relative to the reciprocal lattice (figure 2). Each point in this rectangular grid is tested to see if it lies inside one of the two lunes by calculating TESTA and TESTB. TESTA is the difference between the square of the radius of the circle of reflection and the square of the distance of the reciprocal lattice point from the centre of the circle of reflection at one extreme of its oscillation range. TESTB is similarly calculated using the centre of the circle of reflection at the other extreme of its oscillation range and the sign of the product TESTA times TESTB determined. A negative product indicates the reciprocal lattice point lies inside one of the lunes and so for this point the reciprocal lattice co-ordinate ξ_c, and the calculated film co-ordinate (XC) are calculated and stored in parallel arrays along with the appropriate indices, using the following formulae:

$$\xi_c = (kb^*)^2 + (lc^*)^2$$

Figure 3



Vertical section through the sphere of reflection showing how the radius of the circles of reflection are calculated for upper layers.

$$XC = R^* \cos^{-1}\left(\frac{2 - \xi^2 - \xi^2}{2\sqrt{1-\xi^2}}\right)$$

The appropriate Lorentz and polarisation factor is also calculated using the formula

$$Lp = \sqrt{S - S^2 - \zeta^2/4}$$

$$\text{where} \quad s = \sin^2\theta = (\zeta^2 + \xi^2)/4$$

Finally the two sets of parallel arrays containing the measured values of the film co-ordinates and the calculated values are compared and whenever calculated and measured co-ordinates agree within chosen limits the following information is printed out, h,k,l,Lp,ξ_c,ξ_m,XC,XM. A transcript of the programme as successfully used is shown below.

```
      INTEGER NL(1000), NLC(1000)
      REAL AX(6),AY(6),XIM(1000),XIC(3000),XC(1000),X(1000),LP(1000)
20    FORMAT(8F9.6)
26    FORMAT(4F12.6)
21    FORMAT(12F6.3)
24    FORMAT(4I5)
22    FORMAT(3I5,5F10.6)
      J=0
      READ(5,20)AS,BS,CS,YCA,ZCA,YCB,ZCB,R
      WRITE(6,51)
51    FORMAT('1       ASTAR       BSTAR       CSTAR       FILMRAD')
      WRITE(6,26)AS,BS,CS,R
      Z=AS
1     READ(5,21,END=8)(AX(I),AY(I),I=1,6)
      DO 2 K=1,6
      AX(K)=AX(K)-126.9
      AY(K)=AY(K)-41.9
      J=J+1
      IF(AX(K).EQ.0.0) GO TO 8
      ZM=AY(K)/SQRT(R**2+AY(K)**2)
      IF(AY(K).LT.0.0) GO TO 18
      NL(J)=(ZM/Z)+0.5
      GO TO 19
18    NL(J)=(ZM/Z)-0.5
19    XIM(J)=SQRT(2-(NL(J)*Z)**2-2*(SQRT(1-NL(J)*Z)**2))*cos(AX(K)/R))
      IF(AX(K).LT.0.0)XIM(J)=-XIM(J)
      X(J)=AX(K)
2     CONTINUE
      GO TO 1
```

```
8      MAXJ=J-1
       MAXNL=NL(1)
       DO 9 M=1,MAXJ
       IF(MAXNL.LT.NL(M)) MAXNL=NL(M)
       MAXI=2*MAXNL+1
9      CONTINUE
       DO 40 I=1,MAXI
       N=1
       RN=SQRT(1-((MAXNL-I+1)*Z)**2)
       DIF=SQRT((YCA-YCB)**2+(ZCA-ZCB)**2)+RN
       LKL=((YCA-(YCA-YCB)/2)-DIF)/BS-2
       LKU=((YCA-(YCA-YCB)/2)+DIF)/BS-2
       LLR=((ZCA-(ZCA-ZCB)/2)+DIF)/CS+2
       LLL=((ZCA-(ZCA-ZCB)/2)-DIF)/CS-2
       WRITE(6,53)
53     FORMAT('1     LKU      LKL      LLR      LLL')
       WRITE(6,24)LKU,LKL,LLR,LLL
       L=LLL
       K=LKL
       TESTA=(K*BS-YCA)**2+(L*CS-ZCA)**2-RN**2
       TESTB=(K*BS-YCB)**2+(L*CS-ZCB)**2-RN**2
       IF(TESTA*TESTB)10,10,11
11     GO TO 7
10     XIC(N)=K
       XIC(N+1)=L
       NLC(N+2)=MAXNL-I+1
       XIC(N+2)=SQRT((K*BS)**2+(L*CS)**2)
       IF(XIC(N+2).GT.2*RN) GO TO 7
```

```
      IF(TESTB.GT.0.0)XIC(N+2)=-XIC(N+2)
      XC(N+2)=R*ARCOS((2-(NLC(N+2)*Z)**2-XIC(N+2)**2)/
      (2*SQRT(1-(NCL(N+2)*Z)**2)))
      IF(TESTB.GT.0.0)XC(N+2)=-XC(N+2)
      S=((Z*NLC(N+2))**2+XIC(N+2)**2)/4
      LP(N+2)=SQRT(S-S**2-(Z*NLC(N+2))**2/4)
      N=N+3
7     L=L+1
      IF(L-LLR)4,4,5
5     K=K+1
      L=LLL
      IF(K-LKU)4,4,6
6     N=N-3
      WRITE(6,55)
55    FORMAT('-'/'0      H      K      L      XIC      XIM      XC      X')
      DO 30 J=3,N,3
      DO 30 M=1,MAXJ
      IF(NL (M).NE.(MAXNL-I+1)) GO TO 30
      IF(XIM(M)*XIC(J).LT.0.0)  GO TO 30
      IF(XC(J)-X(M)-0.5)33,33,30
33    IF(ABS(XC(J)-X(M)).GT.0.15) GO TO 30
      L=MAXNL-I+1
      INK=XIC(J-2)
      INL=XIC(J-1)
      WRITE(6,22)L,INK,INL,XIC(J),XIM(M),XC(J),X(M),LP(J)
30    CONTINUE
40    CONTINUE
      STOP
      END
```

Comments and Experimental Details

The main drawback in using oscillation photographs for collecting data for a structure determination is the time consuming task of indexing the reflections plus the fact that a number of spots with different indices will overlap on the film. These difficulties are usually overcome by using moving film methods of collecting data which enable indexing to be carried out by inspection and eliminate the overlap of different spots. However with modern computers the calculations required for indexing oscillation photographs are no longer prohibitive and short oscillation ranges can reduce the loss of reflections due to overlap of different spots.

The advantages of oscillation photographs lie in the speed with which the reflections may be recorded on film and the economy of film with which this is accomplished. In some cases, especially with unstable crystals, the time factor would prohibit the use of moving film techniques and oscillation photographs would then become a necessity, whilst the economy of film becomes a useful characteristic when it comes to scanning the films either manually or using an automatic film scanner. Having many more reflections per film reduces the number of films to be scanned whilst the arrangement of spots in parallel straight lines makes oscillation photographs ideal for use with a microdensitometer.

At the computing stage, however, there are a few more difficulties to be overcome. Slight errors in cell angles will cause complicated errors in the calculated film co-ordinates and these become serious with upper layer spots when the crystal being used is triclinic or monoclinic mounted about a non-unique axis. In these cases a fully automatic programme for indexing reflections will have to compare not only the absolute values of the observed and calculated spot positions but also the observed and calculated pattern of spots on each layer line.

These difficulties suggest that data collection on oscillation photographs would be most useful when a microdensitometer is available to measure the films. In this event a programme which calculated theoretical spot positions and if possible depicted graphically these theoretically possible spots for each film would enable the observed pattern of spots and spot positions measured on the microdensitometer to be visually compared with the calculated pattern, thus building up fairly quickly a list of indexed reflections, allowing spurious information on the film such as white radiation streaks to be easily noticed and rejected and allowing other difficulties with overlapping spots and with $\alpha_1\alpha_2$ doublets at the edge of the film to be easily overcome.

Other practical difficulties crop up at the stage of taking the oscillation photographs. These are mostly concerned with the uneven background scatter on the film which causes large background density near the centre of the film. This may be greatly reduced by the use of an efficient back stop to catch the main X-ray beam. If this backstop is constructed such that it casts a shadow down the centre of the film it will have the added advantage of eliminating odd shaped spots which occur on upper layers near to or on the centre line of the film. It is also necessary to take great care in developing the films and the careful choice of film can also be helpful. It was found in the course of these studies that Kodak Industri~~es~~al D was a film which gave the cleanest, most even background density, being in this respect superior to the faster film, Ilford Industrial G, and vastly superior to the fastest film used, Kodirex.

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