134. *The Crystal Structure of Phosphorus Pentachloride.*

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Independent determinations of the crystal structure made from the same photographic data are in good agreement and provide a justification for the use of visually estimated intensities. The tetragonal unit cell contains tetrahedral PCl_4^+ and octahedral PCl_6^- groups.

THERE is proof from electron-diffraction experiments that in the vapour state the molecules of several phosphorus pentahalides have the configuration of a trigonal bipyramid, and the same configuration is found for a number of other molecules of similar formula (Braune and Pinnow, *Z. physikal. Chem.*, 1937, *B*, **35**, 239; Rouault, *Compt. rend.*, 1938, **207**, 620; Moureu, Magat, and Wetroff, *ibid.*, 1937, **205**, 276; Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836; Ewens and Lister, *Trans. Faraday Soc.*, 1939, **35**, 681; Skinner and Sutton, *ibid.*, 1940, **36**, 668). However, the appreciable electrical conductivity of its solutions (Holroyd, Chadwick, and Mitchell, J., 1925, **127**, 2492) and other observations (Moureu, Magat, and Wetroff, *loc. cit.*, p. 545) suggest that phosphorus pentachloride may be able to exist in an ionised form. The physical properties of the solid lend support to this idea, and a comparison of the Raman spectra in various states shows

that the bipyramidal form of molecules does not persist in the solid (Moureu, Magat, and Wetroff, *loc. cit.*). An *X*-ray investigation has therefore been made in order to determine the structure adopted by the substance in the crystal.

Phosphorus pentachloride crystals are very rapidly decomposed in air owing to the presence of moisture and, for *X*-ray work, must be protected in some way, although Nordenskiold (Groth, " Chemische Kristallographie," I, p. 231), presumably working in a very cold and dry climate, was able to make rough goniometric measurements. Crystals were made in Cambridge by distilling the substance in a vacuum into a small Lindemann glass tube, and Weissenberg photographs of these provided sufficient data for a preliminary determination of the structure. However, the probability of growing good single crystals in this way is small and this method was later abandoned. In Oxford, it was found that single crystals obtained from nitrobenzene solution could be coated with a warm mixture of medicinal paraffin and vaselin which on cooling formed a thin, more or less

FIG. 1.
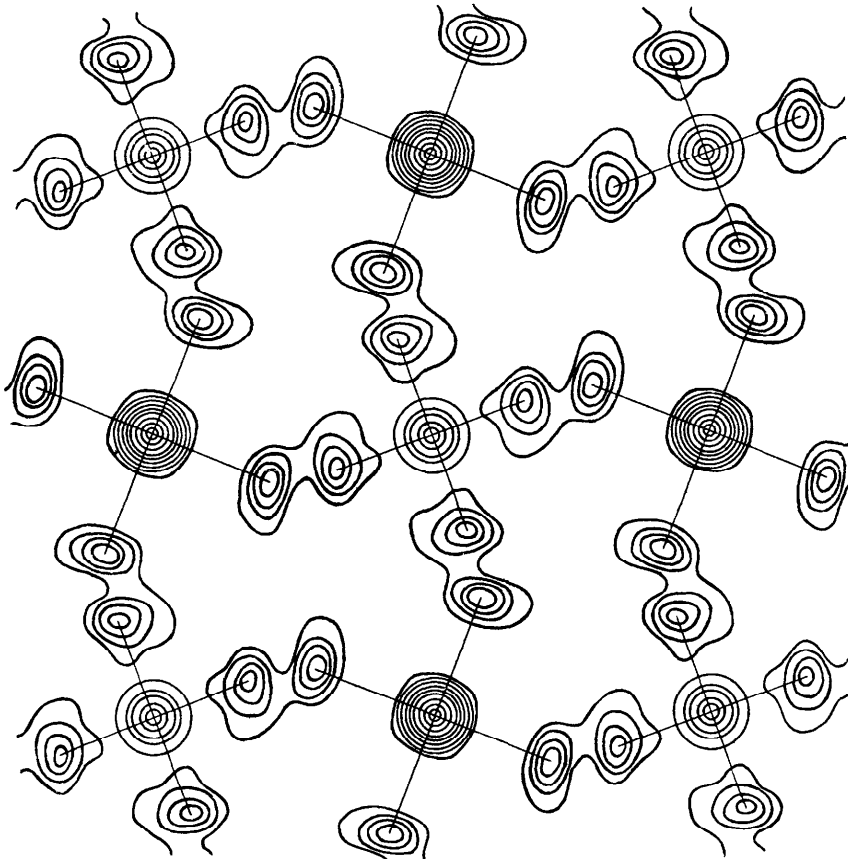
Fourier synthesis on (001). *Contours at arbitrary equal intervals. The highest peak shows overlapping of* P *and* 2Cl *in* PCl$_6$ *group.*

solid coating capable, in favourable cases, of preserving the crystal for a few days. Although this experiment failed nine times out of ten, for various reasons, it has the advantage that suitable single crystals may be selected by optical examination.

Oscillation photographs obtained from crystals so protected enabled the preliminary structure to be found and were suitable for further detailed work. When it was discovered at this stage that independent investigations in Oxford and Cambridge were taking place, it was decided to complete the experimental work in Oxford and the *X*-ray films were sent after measurement to Cambridge. The structure was then worked out entirely independently in the two laboratories and provides a useful check on the accuracy of the methods employed.

Two series of overlapping 15° oscillation photographs about the [001] and [100] axes were taken with copper radiation. The unit cell dimensions are $a = 9.22$, $c = 7.44$ a. The density is 2·12 g./c.c., and there are thus four molecules per unit cell. The space-group is shown to be $P4/n$ by the absence of $hk0$ when $h + k$ is odd and the observation that hkl and $\bar{h}kl$ are in general of unequal intensity. Confirmation of the absence of vertical planes of symmetry is provided by the appearance of etch pits on (001) in the form of inverted square pyramids with edges not quite parallel to the edges of the plate.

Among the more likely arrangements of atoms for a compound of empirical formula AX$_5$ are the following :

(a) Discrete molecules AX_5; (b) $[AX_4][AX_6]$; (c) rings or chains formed by AX_6 octahedra sharing two opposite corners; (d) $[AX_4]X$, the AX_4 complex consisting either of discrete tetrahedra or of an extended grouping of AX_6 octahedra sharing four X atoms. Preliminary analysis ruled out all of these possibilities except (b), which implies that there are two crystallographically different kinds of phosphorus atom. For convenience, the origin is taken at the centre of symmetry at $\frac{1}{4}\frac{1}{4}0$ as given in the " Internationale Tabellen zur Bestimmung von Kristallstrukturen." The atomic positions are found to be 2P in (a) $\frac{1}{4}\frac{1}{4}0, \frac{3}{4}\frac{3}{4}0$; 2P and two different sets of 2Cl in (c) $\frac{1}{4}\frac{1}{4}z, \frac{3}{4}\frac{3}{4}\bar{z}$ with their proper values of z; two different sets of 8Cl in general positions (g) $xyz, \bar{x}\bar{y}\bar{z}$, etc. This structure contains tetrahedral PCl_4^+ and octahedral PCl_6^- groups, and, by systematic trial, approximate values for all the parameters were found. Signs of F_{hk0} and F_{h0l} were then computed, and the Fourier series for electron density projected on (001) and (010) were evaluated. By successive approximations the final projections, Figs. 1 and 2, were obtained. The independent estimates of parameters given in Table I

FIG. 2.
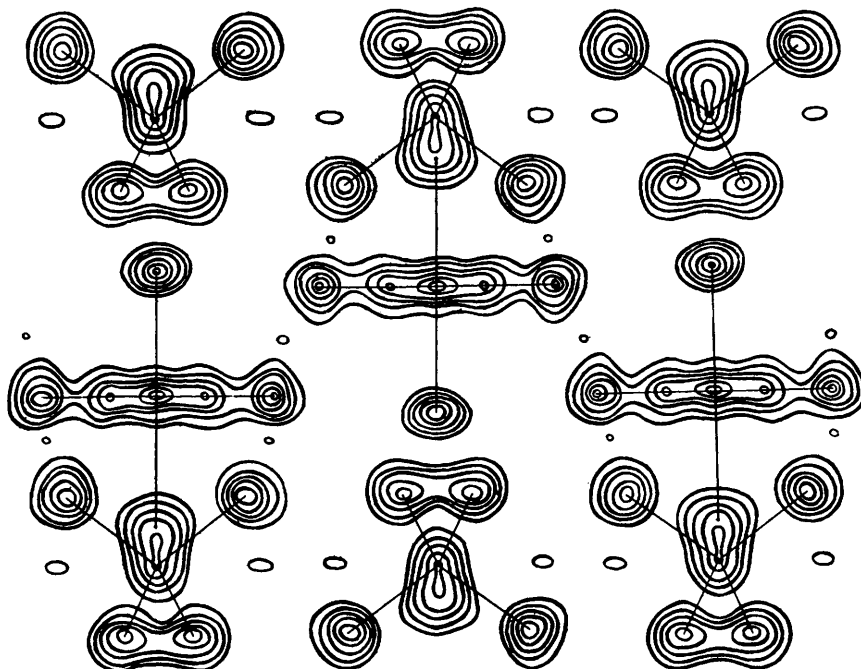
Fourier synthesis on (100). *Tetrahedral* PCl_4 *and octahedral* PCl_6 *groups shown by ruled lines.*

show very good agreement. As far as we are aware this is the first case in which two entirely independent determinations of a structure have been made from the same photographic data, and it provides an important justification of the use of visually estimated intensities. It must, of course, be remembered that the close agreement of the two sets of parameters does not indicate the possible error in these figures, since any inaccuracies in the experimental data, due, e.g., to absorption of the X-rays in the crystal, affect both determinations.

Table II gives calculated F values and two sets of observed F values derived from the independently estimated intensities. The more important interatomic distances are collected in Table III.

TABLE I.

Estimated parameters.

				Oxford.	Camb.					Oxford.	Camb.
2P$_I$	$\frac{1}{4}\frac{1}{4}0$	$\frac{3}{4}\frac{3}{4}0$				2Cl$_I$	$\frac{1}{4}\frac{1}{4}z_2$	$\frac{3}{4}\frac{3}{4}\bar{z}_2$	z_2	-0.09_5	-0.10
2P$_{II}$	$\frac{1}{4}\frac{1}{4}z_1$	$\frac{3}{4}\frac{3}{4}\bar{z}_1$	z_1	-0.38 ·	-0.38	2Cl$_{II}$	$\frac{1}{4}\frac{1}{4}z_3$	$\frac{3}{4}\frac{3}{4}\bar{z}_3$	z_3	0.34	0.34
8Cl$_{III}$	xyz etc.		x	0.31	0.30_5	8Cl$_{IV}$	$x'y'z'$ etc.		x'	0.334	0.337
			y	0.084	0.083				y'	-0.046	-0.045
			z	0.15	0.15				z'	-0.38	-0.38

The PCl_4 and PCl_6 ions are arranged in a structure which is essentially of the cæsium chloride type, but distorted, since these ions are not spherical. Each complex has eight neighbours of the opposite charge. The structure bears some resemblance to that of tetramethylammonium iodide (Wyckoff, *Z. Krist.*, 1928, **67**, 91), but belongs to a lower symmetry class of the tetragonal system; when the negative as well as the positive ions are complex, a more convenient packing is obtained if the vertical planes of symmetry are absent.

The small difference in the phosphorus–chlorine distances in the PCl_6 group may be real but is not significant

TABLE II.

Calculated and observed values of F_{hk0} and F_{h0l}.

F_{hk0} ($hk0$ in order of increasing sin θ).

hk0.	Observed. Oxf.	Camb.	Calc.	hk0.	Observed. Oxf.	Camb.	Calc.	hk0.	Observed. Oxf.	Camb.	Calc.	hk0.	Observed. Oxf.	Camb.	Calc.
110	18	18	26	530	17	22	−38	800	18	20	−21	770	20	—	50
200	72	60	−87	350	25	22	−55	820	14	20	−30	860	15	—	−38
220	10	10	21	600	46	52	−43	280	34	34	−60	680	20	—	−26
310	33	32	48	620	88	92	140	660	14	<20	8	1000	22	36	−40
130	76	76	−76	260	27	28	40	750	21	28	−53	950	14	—	16
400	60	56	58	550	24	28	−17	570	24	—	−9	970	18	—	−27
330	60	54	68	710	12	18	−20	840	12	<20	10	790	9	—	7
420	50	58	−69	170	25	<20	22	480	29	40	50	880	10	—	36
240	44	42	−60	640	20	28	−27	910	28	44	60	1020	24	—	32
510	14	<20	−9	460	23	28	−55	190	31	44	44	1040	16	—	−30
150	50	58	60	730	14	20	32	930	0	—	7	4100	43	—	−43
440	20	28	42	370	25	<20	−10	390	24	—	−24	1060	6	—	15

F_{h0l} ($h0l$ in order of increasing sin θ)

h0l.	Oxf.	Camb.	Calc.	h0l.	Oxf.	Camb.	Calc.	h0l.	Oxf.	Camb.	Calc.	h0l.	Oxf.	Camb.	Calc.
001	0	0	−7	104	20	14	−11	701	0	0	7	007	0	0	−14
101	30	34	−38	501	43	20	−43	702	84	84	100	107	56	80	57
201	39	40	−32	204	18	26	15	405	0	0	6	506	0	0	4
002	7	<10	−12	403	44	52	57	006	58	28	60	901	0	0	−7
102	43	44	55	502	19	22	−16	106	46	42	−53	207	0	<20	4
202	10	6	−15	304	21	28	27	206	18	32	−19	902	24	—	17
301	90	72	−66	601	20	26	−24	604	0	0	7	307	20	54	−14
003	15	20	26	503	30	44	−32	505	0	0	11	705	0	—	0
103	62	54	−70	005	69	52	59	801	0	0	11	606	17	—	−18
302	15	16	−2	404	0	0	−7	306	17	<20	13	407	39	—	−32
401	0	0	0	602	17	<20	−16	802	0	0	0	903	15	—	−25
203	20	26	−33	205	18	24	−19	406	0	0	3	008	60	56	70
402	24	36	15	305	54	58	63	704	17	—	−24	507	27	25	23
303	0	0	−11	603	0	0	7	605	0	—	10				
004	180	144	−160	504	30	40	28	803	17	—	32				

TABLE III.

Interatomic distances, A.

	Oxford.	Camb.		
P_I–Cl_{III} in PCl_4	1·97	1·98	Cl_{III}–Cl_{IV}	3·45, 3·6, 3·6, and 3·9
P_{II}–Cl_I in PCl_6	2·08	2·08	Cl_{II}–Cl_{III}	3·43
P_{II}–Cl_{II} in PCl_6	2·08	2·08	Cl_I–Cl_{III}	3·6
P_{II}–Cl_{IV} in PCl_6	2·04	2·05	Cl_{IV}–Cl_{IV}	3·64

Bond angles in PCl_4 tetrahedron : 111° and 119°.

as it is of the same order of magnitude as the possible error. The structure does, however, permit a comparison of the phosphorus–chlorine bond length for two different states of co-ordination of the phosphorus atom in one and the same compound. The decrease in phosphorus–chlorine distance from 2·06 (average) in PCl_6 to 1·98 A. in PCl_4 may be accounted for as follows. The change in covalent radius for a sequence of atoms, in a short period of the periodic table, which use the same orbitals in bond formation is due to the increase of effective nuclear charge in the sequence; it has been shown (Pauling and Sherman, *Z. Krist.*, 1932, **81**, 1) that unit positive charge on an atom of atomic number Z should lead to a decrease of covalent radius of about $\frac{2}{3}$ of the difference between the covalent radii for the atoms of atomic numbers Z and $Z + 1$, owing to the change in screening effect. An opposite effect occurs when the atom has a negative charge. If, in the present case, it is possible to neglect the difference in co-ordination number and the fact that different orbitals are used, a similar argument shows that the difference in bond lengths in PCl_4 and PCl_6 should equal two-thirds of the difference between the single bond radii for silicon and sulphur, the horizontal neighbours of phosphorus in the periodic table, *i.e.*, $\frac{2}{3}$ (1·17 − 1·04) = 0·087 A. ; this agrees with the observed difference. Apart from this difference, the P–Cl distance in PCl_4 is itself short by about 0·08 A. of the length 2·05 A. calculated for P–Cl from the sum of the normal tetrahedral covalent radii derived from methyl compounds, with a correction for the charge as above. Similar shortenings are observed for many halogen compounds (see, *e.g.*, Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 393).

FIG. 3.
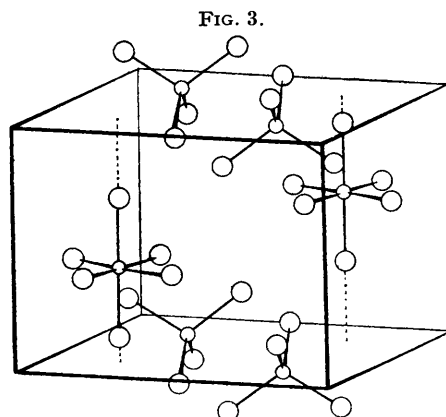
General view of unit cell. (Small circles— phosphorus ; large circles—chlorine.)

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