the structural principle of quinhydrone-type complexes, that is, the formation of molecular chains by the hydrogen bond, parallel overlapping of the carbon rings of donor and acceptor, and the C···O attraction.

The numerical calculations were performed on the *FACOM* 270–30 computer of this Institute, and on the *HITAC* 5020E computer of the Computer Centre of the University of Tokyo, with a universal crystallographic computation program system, *UNICS* (Sakurai, 1967). The authors express their sincere thanks to Dr T. Ito for his assistance during the preliminary stage of data collection, and to Miss Kobayashi for her aid in the computation.

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The Crystal Structure of $POCl_3$

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The crystal structure of $POCl_3$ has been determined. Unit-cell dimensions are $a=9{\cdot}185\pm0{\cdot}003$, $b=9{\cdot}326\pm0{\cdot}002$, $c=5{\cdot}749\pm0{\cdot}001$ Å. The space group is $Pn2_1a$. Average P–Cl distance is 1·98 Å and the P–O distance is 1·46 Å. The molecules form infinite chains by means of an intermolecular Cl–O bond of length 3·05 Å.

Vibrational spectra of solid $POCl_3$ indicate intermolecular bonding (Smitskamp, Olie & Gerding, 1968; Olie & Mijlhoff, 1969) as for $POBr_3$. To obtain more information about this bonding we attempted the determination of the crystal structure.

Experimental

Cylindrically shaped single crystals of diameter 0·05 cm were grown in thin-walled glass capillaries by repeated melting and crystallization. Zero level Weissenberg photographs (Cu radiation) about [100] and [001] were superposed with Al powder lines for calibration. Carefully measured glancing angles corresponding to $0kl$ and $hk0$ reflexions were used to determine the unit-cell dimensions by a least-squares procedure (Table 1).

Table 1. *Crystal data of* $POCl_3$

Cell dimensions:	$a=9{\cdot}185\pm0{\cdot}003$ Å $b=9{\cdot}326\pm0{\cdot}002$ $c=5{\cdot}749\pm0{\cdot}001$
Space group	$Pn2_1a$
Number of molecules per cell	$Z=4$
Calculated density	2·07 g.cm^{-3}
Absorption coefficient	$\mu=180{\cdot}4$ cm^{-1}

The listed errors correspond to three times the standard deviations. Systematically absent reflexions ($0kl$ for $h+k=2n+1$, $hk0$ for $h=2n+1$, $00l$ for $l=2n+1$) indicate as possible space groups: *Pnma* (No. 62) and $Pn2_1a$ (No. 33). The following non-integrated equi-inclination Weissenberg photographs (multiple-film technique) were made at about −100°C with Cu $K\alpha$ radiation: about [001] levels, $l=0$ to 4; about [100] levels, $h=0$, 1, 2. The reflexions were practically all slit-shaped; their intensities were scanned with a recording densitometer and the areas of the peaks were measured with a 'Kurvenauswerter' (a curve digitizing system, Atlas KA101). Thus it was not necessary to correct for α_1–α_2 splitting. The integrated intensities were corrected for absorption ($\mu R=4{\cdot}51$) and reduced to structure-factor moduli after accounting for Lorentz and polarization factors.

Several reflexions occurring on more than one film were used to put the structure factors on a common relative scale.

Structure determination and refinement

The cell dimensions of $POBr_3$ and $POCl_3$ are very similar, their axial ratios being nearly equal. A survey of the Patterson map showed that at least the chlorine atoms in $POCl_3$ are situated at nearly the same positions as the bromine atoms in $POBr_3$. We have chosen the space group $Pn2_1a$ (No. 33) as the basis of our re-

Table 2. *Atomic coordinates and standard deviations (in fractions of cell edges) of the asymmetric unit* $POCl_3$

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Cl(1)	0·3469	0·0005	0·0876	0·0005	0·1623	0·0010
Cl(2)	0·4824	0·0004	0·2500	0·0005	0·5871	0·0007
Cl(3)	0·3592	0·0006	0·4234	0·0005	0·1714	0·0010
P	0·3171	0·0003	0·2534	0·0011	0·3698	0·0006
O	0·1765	0·0010	0·2708	0·0013	0·4832	0·0019

Table 3. *Vibrational parameters and standard deviations* (10^{-4} Å^{-2}) *of the asymmetric unit* $POCl_3$

	U_{11}	σ	U_{22}	σ	U_{33}	σ	$2U_{12}$	σ	$2U_{23}$	σ	$2U_{31}$	σ
Cl(1)	266	21	265	22	246	25	217	10	−174	8	75	25
Cl(2)	276	18	519	26	207	5	6	4	148	15	−196	12
Cl(3)	410	16	224	25	214	41	279	86	267	88	202	60
P	155	17	172	6	95	11	69	17	26	2	91	5
O	214	49	106	34	287	28	−142	23	−18	1	282	35

Table 4. *Bond distances* (Å) *and angles* (°) *and their standard deviations in* $POCl_3$

		$\sigma(l)$
P–Cl(1)	1·972	0·010
P–Cl(2)	1·966	0·005
P–Cl(3)	1·990	0·010
P–O	1·456	0·010
O···Cl*	3·053	0·011

		$\sigma(\alpha)$
Cl(1)–P——Cl(2)	105·3	0·4
Cl(1)–P——Cl(3)	104·5	0·3
Cl(1)–P——O	103·1	0·4
Cl(2)–P——O	118·8	0·6
Cl(3)–P——O	109·9	0·7
P——Cl(2)–O*	164·6	0·3

* Intermolecular Cl(2)–O distance.

finement. If the wrong space group is used in refining the structure, no problem arises because the final structure will contain the mirror plane, necessary for space group *Pnma*.

The positions of three chlorine atoms were located from the Patterson map. The phases of the structure factors determined by the chlorine atoms were used in a Fourier synthesis which resulted in the location of the phosphorus atom. A second Fourier synthesis gave the position of the oxygen atom.

Next we used a least-squares program (Geise, Romers & Rutten, 1966; Rutten-Keulemans, 1966) for refining the parameters, with atomic scattering factors as listed in *International Tables for X-ray Crystallography* (1962) for neutral chlorine, phosphorus and oxygen.

The model converged smoothly to an R value of 0·075 (observed reflexions only) with individual anisotropic vibrational parameters. The positional parameters are listed in Table 2 and the vibrational parameters in Table 3.

The vibrational parameters are defined by the temperature factor as:

$$\exp\left[-2\pi^2(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}l^2c^{*2}+2u_{12}hka^*b^*+2u_{13}hla^*c^*+2u_{23}klb^*c^*)\right].$$

Several reflexions probably affected by extinction are left out. A list of observed and calculated structure factors is available on request.

Discussion

Inspection of Table 4 shows that $POCl_3$ molecules are linked by intermolecular halogen–oxygen bridges to infinite chains in the x direction just like the $POBr_3$ molecules. The intermolecular Cl(2)–O distance in the chain (3·05 Å) is significantly shorter than the expected van der Waals separation (3·20 Å). The molecules in the chain are related by the a-glide plane.

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