

Table 5. Unit-cell dimensions and space groups of the isostructural salts

Salt	<i>a</i>	<i>b</i>	<i>c</i>	Space group
$\text{NaK}_5\text{Cl}_2(\text{S}_2\text{O}_6)_2$	8.562	8.562	11.529	<i>P4/mnc</i>
Reoriented	12.107	12.107	11.529	<i>C4/mcn</i>
$\text{NaK}_2\text{ClS}_2\text{O}_6$	12.118	12.118	5.522	<i>P4/n</i>
$(\text{NH}_4)_3\text{ClS}_2\text{O}_6$	12.64	12.48	6.08	<i>Pbam</i>

wishes to thank the University of Saskatchewan for the award of a teaching assistantship during the tenure of which much of the work was done.

References

- ALVAREZ, SOTUCA, & VERDIER (1966). *An. Real Soc. esp. Fis. Quim.* **62A**, 285.
- BARNES, W. H. & WEHDLING, A. V. (1938). *Z. Kristallogr.* **99**, 153.
- BHUIYA, A. K. & STANLEY, E. (1963). *Acta Cryst.* **16**, 981.
- BUCKLEY, H. E. (1951). *Crystal Growth*. London: Chapman & Hall.
- COCHRAN, W. (1951). *Acta Cryst.* **4**, 408.
- FOCK, A. & KLUS, K. (1888). *Ber. dtsh. chem. Ges.* **246**, 179.
- FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412.
- GARCIA-BLANCO, S., GOMIS, V. & ABBAD, M. (1953). *An. Soc. esp. Fis. Quim.* **A3-4**, 114.
- MARTINEZ, S., GARCIA-BLANCO, S. & RIVOIR, L. (1956). *Acta Cryst.* **9**, 145.
- STANLEY, E. (1953). *Acta Cryst.* **6**, 187.
- STANLEY, E. (1956). *Acta Cryst.* **9**, 897.
- STANLEY, E. (1964). *Acta Cryst.* **17**, 1028.
- STANLEY, E. (1965). *Acta Cryst.* **19**, 1055.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.

Acta Cryst. (1969). **B25**, 974

The Crystal Structure of POBr_3 and Intermolecular Bonding

By K. OLIE

Laboratory for Inorganic Chemistry, University of Amsterdam, The Netherlands

AND F. C. MIJLHOFF

Laboratory for Organic Chemistry, University of Leiden, The Netherlands

(Received 5 June 1968)

Crystals of POBr_3 are orthorhombic, space group $Pn2_1a$. The unit cell with dimensions $a=9.467$, $b=9.938$, $c=6.192$ Å contains four molecules. The structure was determined by vector analysis and refined by the least-squares method from photometered $\text{Cu K}\alpha$ data. The average P-Br distance is 2.14 Å, the P-O distance is 1.44 Å. The molecules form infinite chains by means of intermolecular Br-O bonds with a length of 3.08 Å.

Introduction

Raman spectra of solid POBr_3 and POCl_3 show an extra vibration line in the vicinity of the P-O stretching frequency (Smitskamp, Olie & Gerding, 1968). Since this vibration is non-degenerate in the free molecule the apparent splitting cannot be explained by the assumption of lower site symmetry in the crystal. In order to check our suspicion that strong intermolecular interactions might exist we started the present crystal structure determination.

Experimental

The crystals of POBr_3 are colourless and rapidly attacked by atmospheric moisture. Nearly spherical crystals with a diameter of 0.02 cm were selected and inserted into thin walled glass capillaries with the directions

defined as [100], $[0\bar{1}1]$ and [001] parallel to the capillary axis. Zero-level Weissenberg photographs (Cu radiation) about [100] and $[0\bar{1}1]$ were superposed with Al powder lines for calibration purposes. Carefully measured glancing angles corresponding to *Okl* and *hkk* reflexions were used to determine the unit-cell dimensions by a least-squares procedure (Table 1). The listed errors correspond to three times the standard deviations.

Table 1. Crystal data of POBr_3

Cell dimensions:	$a=9.467 \pm 0.006$
	$b=9.938 \pm 0.006$
	$c=6.192 \pm 0.003$
Space group:	$Pn2_1a$
Number of molecules per cell:	$Z=4$
Calculated density:	3.27 g.cm^{-3}
Absorption coefficient:	$\mu=307 \text{ cm}^{-1}$

Systematically absent reflexions ($0kl$ for $k+l=2n+1$, $hk0$ for $h=2n+1$, $00l$ for $l=2n+1$) indicate as possible space groups $Pnma$ (No. 62) and $Pn2_1a$ (No. 33). The choice in favour of the latter is discussed in the next section.

The following set of non-integrated equi-inclination Weissenberg photographs (multiple film technique) was made at room temperature with copper radiation:

about $[100]$ levels $h=0$ to 6
about $[001]$ levels $l=1, 2, 3$.

All reflexion intensities were measured with a densitometer, corrected for absorption assuming a spherical shape ($\mu R=3.07$) and reduced to structure factor moduli after multiplication with Lorentz and polarization factors. Reflexions with large glancing angles were corrected for $\alpha_1-\alpha_2$ splitting. Several reflexions occurring twice on different films were used to put the structure factors on a common relative scale.

Structure determination and refinement

In the two possible space groups the number of molecules per cell must be a multiple of four. With $Z=4$

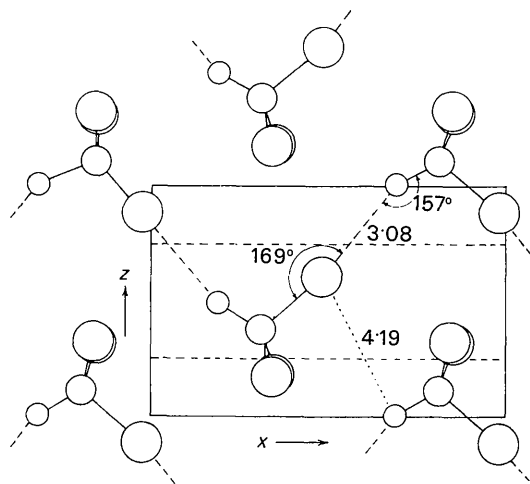


Fig. 1. Projection of the unit cell onto the (001) plane.

one calculates the plausible density value of 3.27 g.cm^{-3} . In space group $Pnma$ the special position $x, \frac{1}{4}, z$ on the mirror plane, $4(c)$, has a multiplicity of four and consequently one of the bromine atoms, one phosphorus atom and one oxygen atom must be placed in this plane, the other two bromine atoms being situated in general position $8(d)$. In space group $Pn2_1a$ the general position has a multiplicity of four and the molecule may have any orientation.

(a) Interpretation in space group $Pnma$

The three-dimensional Patterson map was interpreted on the assumption that the space group was $Pnma$. It was possible to obtain an approximate solution with one bromine atom in the mirror plane at $y=\frac{1}{4}$ and a pair of bromine atoms at x, y, z and $x, \frac{1}{2}-y, z$, related by reflexion with respect to that plane, the three forming an equilateral triangle with edges of about 3.4 \AA . The signs of the structure factors determined by the bromine positions were used in a Fourier synthesis, which resulted in the location of the phosphorus and oxygen atoms. The estimated P-O and P-Br separations compared favourably with those found earlier from gas diffraction work of the same molecule (Secrist & Brockway, 1944). We used a least-squares program written by Rutten (Geise, Romers & Rutten, 1966; Rutten-Keulemans, 1966) for refining the parameters, with atomic scattering factors listed in *International Tables for X-ray Crystallography* (1962) for neutral Br, P and O. Refinement, however, proved to be disastrous as we tried to introduce individual isotropic temperature factors. The program insisted on the assignment of a high negative B value to the oxygen atom. The discrepancy index R did not drop below 36%. A two-dimensional refinement of a projection along $[001]$ resulted in $R=24\%$ for the $hk0$ reflexions. Several other models were tried, in which the mutual separation of the bromine atoms was kept at 3.4 \AA . None of the models, however, refined adequately.

(b) Interpretation in space group $Pn2_1a$

The relative success of the interpretation of the Patterson function suggested that the solution was ap-

Table 2. Atomic coordinates and standard deviations (in fractions of cell edges) of the asymmetric unit POBr_3

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Br(1)	0.3419	0.0004	0.0855	0.0004	0.1741	0.0007
Br(2)	0.4796	0.0003	0.2500	0.0000	0.6105	0.0005
Br(3)	0.3503	0.0005	0.4272	0.0003	0.1825	0.0005
P	0.3105	0.0006	0.2540	0.0012	0.3814	0.0009
O	0.1773	0.0017	0.2567	0.0047	0.4942	0.0033

Table 3. Vibration parameters and standard deviations (10^{-4} \AA^{-2}) of the asymmetric unit POBr_3

	U_{11}	σ	U_{22}	σ	U_{33}	σ	$2U_{12}$	σ	$2U_{23}$	σ	$2U_{13}$	σ
Br(1)	883	26	479	16	777	24	-220	36	-429	32	-12	43
Br(2)	727	18	814	18	571	13	-7	95	139	77	-426	29
Br(3)	1040	29	374	14	590	16	9	33	230	27	394	37
P	338	26	366	25	401	26	-95	14	421	10	75	52
O	391	10	1081	17	537	93	728	44	117	54	325	19

Table 4. Bond distances (Å) and bond angles (°) and their standard deviations in POBr₃

Bond	Distance	$\sigma(l)$	Angle	α	$\sigma(\alpha)$
P-Br(1)	2.131	0.011	Br(1)-P-Br(2)	106.3	0.4
P-Br(2)	2.140	0.006	Br(1)-P-Br(3)	105.1	0.3
P-Br(3)	2.150	0.011	Br(2)-P-Br(3)	105.3	0.4
P-O	1.442	0.018	Br(1)-P-O	115.4	1.7
O---Br*	3.08	0.019	Br(2)-P-O	109.5	0.8
			Br(3)-P-O	114.6	1.8
			P-Br(2)-O*	168.7	0.4

* Intermolecular Br(2)-O distance.

proximately correct, but that the choice of the space group might be wrong. If the mirror plane were absent it should be possible to tilt the molecular P-O-Br(2) plane slightly out of the plane $y = \frac{1}{2}$. Close inspection of the electron density and Patterson maps revealed a slightly ellipsoidal shape for the peaks, which supported this supposition.

Starting with the first model as obtained in the previous section, the x and y parameters of the structure in projection along [001] were now refined assuming the space group $Pn2_1a$. With an overall B value of 3.29 Å² we arrived at an R value of 18.4%. Next a three-dimensional refinement was carried out, starting with the z parameters found previously in the centric refinement. The model converged smoothly to an R value of 11.3% (observed reflexions only) with individual anisotropic vibration parameters. Although parameter shifts were smaller than the standard deviations after 10 cycles, convergence was rather slow and it took 30 cycles to get shifts that tended to oscillate.

The positional parameters are listed in Table 2, the vibration parameters in Table 3.

The vibration parameters are defined by the temperature factor as:

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

It should be noted that only the random errors in the measured intensities are reflected in the standard deviations. A list of observed and calculated structure factors is available on request.

Discussion of the structure

Inspection of Table 4 and Figs. 1 and 2 shows that the POBr₃ molecules are linked by intermolecular Br---O bridges to make infinite chains. The molecules in the chains are related by the a -glide plane.

The deviations of the P-Br distances and the Br-P-Br angles from their average values (2.14 Å and 105.6°) do not exceed one standard deviation of the respective differences (0.017 Å and 0.7°) and, therefore, cannot be regarded as significant. The intermolecular Br(2)---O distance in the chain (3.08 Å) is significantly shorter than the expected van der Waals separation (3.35 Å), all other Br---O separations being larger than 3.40 Å. The Br(2)-P-O angle is smaller than the angles Br(1)-P-O and Br(3)-P-O, significance level 0.1%.

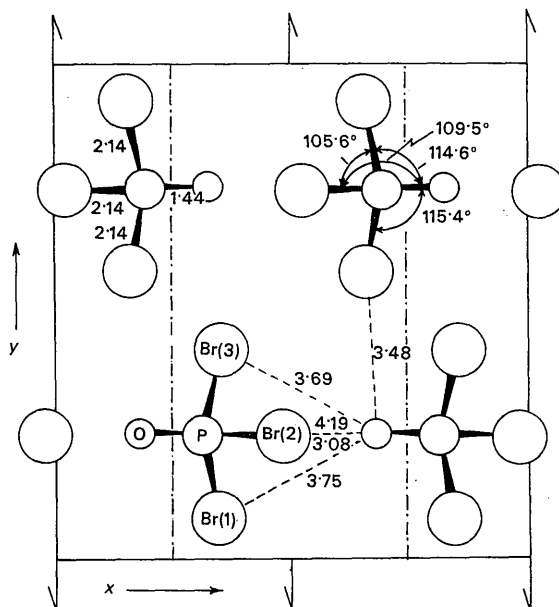


Fig. 2. Projection of one layer of the POBr₃ molecules onto the (010) plane. The next layer is obtained by the glide plane operation n .

These features indicate intermolecular bonding and a distortion from the C_{3v} symmetry of the free molecule.

Charge transfer bonds between neighbouring oxygen and bromine containing molecules have been observed in many cases. In particular, Hassel and collaborators have described a number of them. The POBr₃ molecule resembles oxalyl bromide (Groth & Hassel, 1962), and in this compound also one molecule functions simultaneously as donor and acceptor. The bonding, however, must be weaker, since the Br---O separation (3.27 Å) is larger. About the same bond angle (C-Br---O, 169°) was found. Groth & Hassel state that increasing electronegativity of the atom to which the halogen atom is directly bound favours the intermolecular bonding. Our results prove that electronegativity is not the only factor involved, since the electronegativity of phosphorus is even less than that of carbon.

Comparison of the vibrational spectra of POCl₃ in the liquid and solid state indicates that intermolecular bonding is also present in POCl₃ crystals.

We wish to thank Professor H. Gerding for his interest and support during this investigation, Mr A. Kreuger for taking the photographs and Dr C. Romers for his help and advice in preparing this article.

References

GEISE, H. J., ROMERS, C. & RUTTEN, E. W. M. (1966). *Acta Cryst.* **20**, 249.

GROTH, P. & HASSEL, O. (1962). *Acta Chem. Scand.* **16**, 2311.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

RUTTEN-KEULEMANS, E. W. M. (1966), *Acta Cryst.* **21**, A293.

SECRET, J. H. & BROCKWAY, L. O. (1944). *J. Amer. Chem. Soc.* **66**, 1941.

SMITSKAMP, C. C., OLIE, K. & GERDING, H. (1968). *Z. anorg. allg. Chem.* **359**, (5-6), 318.

Acta Cryst. (1969). **B25**, 977

Least-squares Weighting Schemes for Diffractometer-Collected Data. III. Optimization Process

BY R. C. G. KILLEAN

Department of Physics, University of St. Andrews, St. Andrews, Scotland

(Received 1 April 1968 and in revised form 25 July 1968)

The optimization equations of Shoemaker and Hamilton are critically discussed. The equation due to Hamilton is shown to be invalid as an optimizing equation and experimental limits to the use of the Shoemaker equation are discussed.

Recently Shoemaker (1968) has derived equations for the optimization of counting times in computer-controlled X-ray and neutron single-crystal diffractometry and shown that by making certain simplifying assumptions his derivation leads to the equation presented by Hamilton (1967) that the counting time for the j th structure factor, $|F_j|$, is given by

$$t_j \propto (\text{Lp})^{-1} \left| \frac{\partial |F_j|^2}{\partial \xi_i} \right| \frac{1}{|F_j|^3}, \quad (1)$$

where (Lp) is defined in the usual way and not as the reciprocal, as given by Hamilton.

The total time for the complete diffractometer experiment is

$$T = \varphi + \sum_i t_j \quad (2)$$

where φ is the total time required for setting the circles of the diffractometer. It is claimed that the use of (1) leads to a minimizing of the variances of the ξ_i . The importance of this claim is such that it requires careful investigation.

Let I_j be the integrated peak counts. Then

$$|F_j|^2 = \frac{KI_j}{\text{Lp } t_j}$$

and, following Hamilton, assuming a negligible background count

$$\sigma_1\{|F_j|\} = \frac{|F_j|}{2I_j^{1/2}}$$

where $\sigma_1\{|F_j|\}$ is due to counting statistics alone.

Hamilton also assumes that

$$\sigma_2\{|F_j|\} = C|F_j|$$

is the remaining contribution to the variance of a structure factor. This assumption has been shown to be a good approximation in practice (Grant, Killean & Lawrence, 1969). Consequently the weight of a structure factor is

$$\begin{aligned} \omega_j &= \frac{1}{\sigma_1^2\{|F_j|\} + \sigma_2^2\{|F_j|\}} \\ &= \frac{1}{\left\{ \frac{F_j}{2I_j^{1/2}} \right\}^2 + C^2|F_j|^2} \\ \omega_j &= \frac{1}{|F_j|^2} \cdot \frac{4I_j}{1 + 4C^2I_j}. \end{aligned} \quad (3)$$

Minimizing the variance of ξ_i subject to the linear constraint of equation (2) leads to (1) provided the approximation

$$4C^2I_j \gg 1 \quad (4)$$

is made. Under this condition equation (3) reduces to

$$\omega_j = \frac{1}{C^2|F_j|^2} = \frac{1}{\sigma_2^2\{|F_j|\}}$$

and no optimization of counting time with respect to minimizing the variance of ξ_i exists. If inequality (4) is true then the variance of the structure factor is only