

Crystal and Molecular Structure of a Metastable Modification of Phosphorus Pentachloride

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High resolution powder X-ray diffraction using synchrotron radiation has established the formulation $[\text{PCl}_4^+]_2[\text{PCl}_6^-][\text{Cl}^-]$ for a metastable form of PCl_5 with significant interaction between the PCl_4^+ and Cl^- ions.

The structures of crystalline phosphorous pentachloride ($\text{PCl}_4^+\text{PCl}_6^-$) and phosphorus pentabromide ($\text{PBr}_4^+\text{Br}^-$) were established by X-ray diffraction over 50 years ago.¹⁻⁴ However, there is a further well-documented⁵ metastable

modification of phosphorus pentachloride which, on standing at room temperature, slowly reverts to the normal $\text{PCl}_4^+\text{PCl}_6^-$ form. Detailed spectroscopic investigations⁶ of this metastable form have suggested a single chloride-containing structure

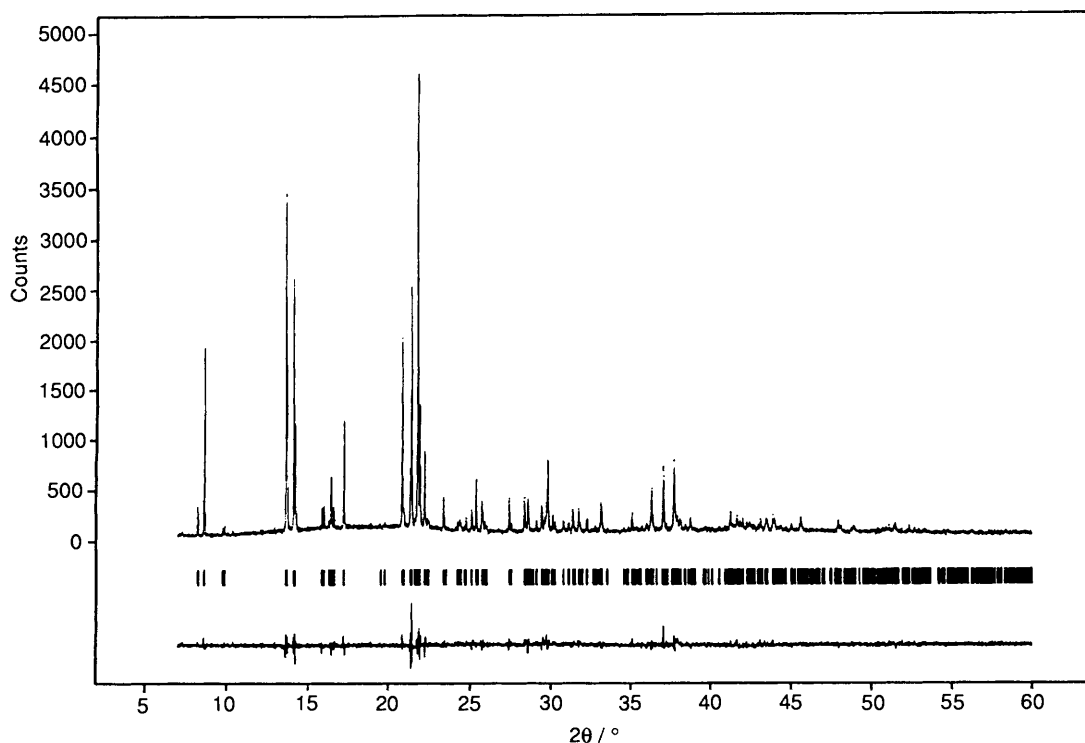


Fig. 1 Observed (dots), calculated (full curve) and difference (observed - calculated) profiles for metastable PCl_5 refined from high resolution powder diffraction data using synchrotron radiation. The 2θ positions of the peaks contributing to the diffraction profile are indicated by the vertical tick marks.

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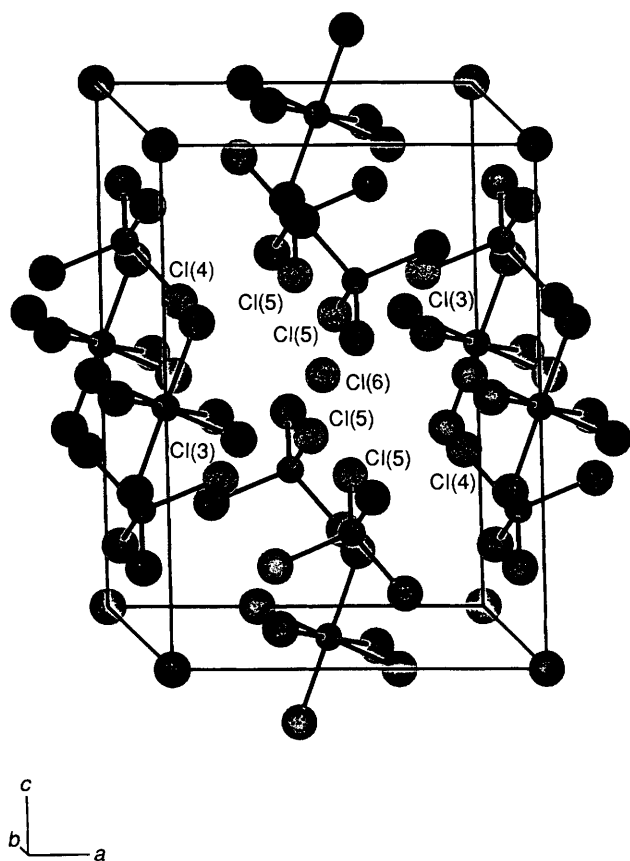


Fig. 2 A view of the structure of metastable PCl_5 . The PCl_4^+ unit is a regular tetrahedron, whereas the octahedral PCl_6^- has a small compression along the axial direction (see Table). These groups are arranged as in the antifluorite structure, with the extra Cl^- ion at the centre of the cavity surrounded by eight cations. The labelled atoms shown are those that are nearest to the Cl^- ion [Cl(6)] situated at the body centre of the unit cell. The distances are given in the second part of the Table. Interatomic distance (\AA) and angles ($^\circ$) for metastable PCl_5 .

$2 \times \text{P}(1)-\text{Cl}(1)$	2.114(8)	$1 \times \text{P}(2)-\text{Cl}(3)$	1.94(1)
$4 \times \text{P}(1)-\text{Cl}(2)$	2.143(6)	$1 \times \text{P}(2)-\text{Cl}(4)$	1.94(1)
$1 \times \text{Cl}(1)-\text{P}(1)-\text{Cl}(1)$	180	$2 \times \text{P}(2)-\text{Cl}(5)$	1.94(1)
$4 \times \text{Cl}(1)-\text{P}(1)-\text{Cl}(2)$	90.0(2)	$1 \times \text{Cl}(3)-\text{P}(2)-\text{Cl}(4)$	109.5(7)
$4 \times \text{Cl}(1)-\text{P}(1)-\text{Cl}(2)$	90.0(2)	$2 \times \text{Cl}(3)-\text{P}(2)-\text{Cl}(5)$	109.3(4)
$2 \times \text{Cl}(2)-\text{P}(1)-\text{Cl}(2)$	180	$2 \times \text{Cl}(4)-\text{P}(2)-\text{Cl}(5)$	109.6(4)
$2 \times \text{Cl}(2)-\text{P}(1)-\text{Cl}(2)$	89.2(2)	$1 \times \text{Cl}(5)-\text{P}(2)-\text{Cl}(5)$	109.6(6)
$2 \times \text{Cl}(2)-\text{P}(1)-\text{Cl}(2)$	90.8(2)		
$4 \times \text{Cl}(6) \cdots \text{Cl}(5)$	3.268(7)	$2 \times \text{Cl}(6) \cdots \text{Cl}(3)$	3.36(1)
$2 \times \text{Cl}(6) \cdots \text{Cl}(4)$	3.800(9)	$4 \times \text{Cl}(6) \cdots \text{Cl}(2)$	4.051(6)
$2 \times \text{Cl}(6) \cdots \text{Cl}(1)$	4.281(9)		

$[\text{PCl}_4^+]_2[\text{PCl}_6^-][\text{Cl}^-]$. Attempts to confirm this formulation and to determine the details of the structure have been frustrated by the inability to grow single crystals suitable for X-ray diffraction.

We now report the determination of the structure of this modification confirming the presence of a single chloride ion, using high resolution powder X-ray diffraction. The sample was prepared by dissolution of solid phosphorus pentachloride in anhydrous liquid hydrogen chloride at *ca.* -90°C , followed by evaporation of the solvent as the solution was slowly warmed to room temperature. The Raman spectrum was identical to that of other samples prepared by a variety of routes⁶ and showed no evidence for the presence of $\text{PCl}_4^+\text{PCl}_6^-$.

Powder X-ray diffraction data were obtained on station 9.1 at Daresbury. The lattice parameters (below) suggest that the

structure[‡] may be related to a body-centred tetragonal or face-centred cubic arrangement. With $Z = 6$ (from the density) and spectroscopic evidence⁶ for a formulation based on $[\text{PCl}_4^+]_2[\text{PCl}_6^-][\text{Cl}^-]$, a simple arrangement of octahedra and tetrahedra based on the antifluorite structure can be envisaged with the single Cl^- ions lying in the cavity surrounded by eight cations. The structure is shown in Fig. 2 together with important interatomic distances.

Earlier inferences of the single Cl^- ion in the structure of the metastable form were based mainly on spectroscopic measurements. The 20 cm^{-1} low frequency shifts of the symmetric and antisymmetric PCl_4^+ stretching modes on passing from the normal to the metastable form were interpreted as arising from a significant interaction between the Cl atoms of the PCl_4^+ ion and the single Cl^- ions, causing a slight lengthening of the PCl bonds with a consequent reduction in stretching force constant. These qualitative predictions have been confirmed by the present work in which a small increase in the PCl bond lengths from 1.90 \AA for the PCl_4^+ bonds in the normal form¹⁰ to 1.94 \AA in the metastable form is found. Each of the single Cl^- ions is surrounded by eight Cl atoms (from different PCl_4^+ ions) of which six are at distances significantly less than the van der Waals separations (3.6 \AA). It is of interest to note that the calculated density of the metastable form (2.252 g cm^{-3}) is greater by *ca.* 3% than that of the normal form, 2.187 g cm^{-3} calculated from the lattice parameters in ref. 10.

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[‡] Crystal data for metastable phosphorus(v) chloride: PCl_5 , $M = 208.24$, monoclinic, space group $I2/m$ (No. 12) $a = 8.7981(2)$, $b = 8.4765(2)$, $c = 12.3683(4)\text{ \AA}$, $\beta = 92.751(2)^\circ$, $V = 921.3(1)\text{ \AA}^3$, $Z = 6$, $D_c = 2.252\text{ g cm}^{-3}$. The sample was spun in a 0.3 mm diameter glass capillary tube, whilst powder diffraction data were collected with $\lambda = 1.0448(1)\text{ \AA}$ on station 9.1 at the Synchrotron Radiation Source, Daresbury, between 5 and 60° counting for 3 s per 0.01° step. Indexing was achieved from the positions of 20 low-angle peaks using the program FZON⁷ (with $M_{20} = 136$). The lack of systematic absences other than those required by the body-centred lattice suggested the space groups $I2/m$, Im or $I2$. A structure was devised from noting a possible relation to a body-centred tetragonal or face-centred cubic arrangement, and assuming the chemical formula of $\text{PCl}_6(\text{PCl}_4)_2\text{Cl}$ indicated by the spectroscopic studies. The structure was refined by the Rietveld method⁸ using the program PROFIL⁹ to constrain the thermal parameters to simulate rigid-body translations of the molecular ions. Librations of the groups are small and were set to zero. Final R factors, $R_{wp} = 13.3\%$, $R_{exp} = 7.2\%$, $R_1 = 7.3\%$. The observed and calculated profiles are shown in Fig. 1. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Inorganic Chemical Structure Database (Bonn). See Notice to Authors, Issue No. 1.