# Single-crystal and High-resolution X-Ray Diffraction Studies and Raman Spectrum of a Phosphorus(V) Chloride Complex containing a Single Bromide Ion, $P_3Cl_{14}Br$†

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The solid-state structure of the compound of empirical formula $P_3Cl_{14}Br$, has been investigated by single-crystal and high-resolution powder diffraction techniques. The results of the structural study are correlated with the Raman spectra of $P_3Cl_{14}Br$ and metastable $PCl_5$. Refinement in tetragonal space group $I4$, with $a = 8.739(2)$, $c = 12.320(1)$ Å, $Z = 2$ and $R = 0.058$ yielded a structure composed of two $PCl_4^+$ tetrahedra of $C_s$ symmetry, one $PCl_6^-$ octahedron of $C_{4v}$ symmetry, and one $Br^-$. Rietveld refinement of powder data was carried out in $I4$ and $I4/m$. The Raman spectrum of the *same* crystal used for single crystal X-ray analysis was found to be strikingly similar to that of metastable $PCl_5$ with vibrational degeneracies lifted. Metastable $PCl_5$ and $P_3Cl_{14}Br$ are structurally very similar.

There are few well defined compounds containing a chlorobromophosphonium(V) species and virtually no X-ray structural data are available. Lewis acid salts (*e.g.* $BCl_4^-$) of the $PCl_nBr_{4-n}^+$ ($1 \leqslant n \leqslant 3$) cations have been characterized by vibrational spectroscopy[1,2] and solid-state $^{31}P$ NMR spectroscopy.[3,4] Both $PBr_4^+Cl^-$[5] and $PBr_4^+Cl_3^-$[6] are ionic structures not involving mixed halogen cations. Some less well defined species, often involving polybromides[7–9] or solvates of tetrachloromethane[10] may also involve mixed cations although there have been problems of preparative reproducibility with some of these. There appear to be no well established examples of six-co-ordinate chlorobromophosphate anions apart from a claim that a compound of apparent stoichiometry $P_2Cl_9Br$ was actually $PCl_4^+PCl_5Br^-$.[11] Attempts to prepare salts of the type $NR_4^+PCl_5Br^-$ (R = H, alkyl or aryl) have been unsuccessful.[12,13] In an investigation of $P_2Cl_9Br$ by Raman and solid-state $^{31}P$ NMR spectroscopy, no evidence was found for $PCl_5Br^-$ ion and it was concluded that a more complicated structure probably existed involving multiple ions: $PCl_4^+$, $PCl_3Br^+$, $PCl_6^-$ and $Br^-$ ions.[14]

The crystal structures of phosphorus pentachloride ($PCl_4^+$ $PCl_6^-$) and phosphorus pentabromide ($PBr_4^+$ $Br^-$) were first established by X-ray diffraction in the early 1940s[15–18] and subsequently refined.[19,20] A metastable form of $PCl_5$ ($[PCl_4]^+{}_2$-$PCl_6^-Cl^-$) has been known for over 35 years,[21] but structural details from high-resolution powder X-ray diffraction studies have only recently been published.[22]

In 1956 Popov *et al.*[21] isolated a mixed halide from reaction of $PCl_3$ and $Br_2$ for which elemental analysis indicated a composition $PCl_{4.67}Br_{0.33}$ (*i.e.* $P_3Cl_{14}Br$). X-Ray powder data were interpreted in terms of a face-centred cubic unit cell with $a = 12.38$ Å and $Z = 4$. This was tentatively formulated as $[PCl_4]^+{}_2PCl_6^-Br^-$ but inference of structural details was not possible. A similar formulation was subsequently proposed for the metastable modification of $PCl_5$ from various spectroscopic methods[23] and recently confirmed by Rietveld refinement of high-resolution powder X-ray diffraction.[22] During tensimetric titration of the pyrazine•$PCl_5$ adduct[24,25] with HBr, HCl was recovered in an amount equivalent to excess HBr added. Systematic addition of HBr to $PCl_5$ in mole ratios in the range HBr : $PCl_5$ 0.25–5.00 yielded several products, one of which had the composition $P_3Cl_{14}Br$, identical to Popov's compound. During the course of an independent X-ray diffraction study (single crystal, Dayton) on this compound and a reinvestigation of '$P_2Cl_9Br$' (at Royal Holloway) it became clear on the basis of both powder diffraction and Raman spectra that one and the same compound was involved. This raises doubts about the elemental analysis[11,14] and spectral interpretation[14] of the previous work on '$P_2Cl_9Br$'. In this paper we report the solid-state structure of $P_3Cl_{14}Br$ using single-crystal and Rietveld refinement methods, together with a discussion of the analytical discrepancies and a reinterpretation of the Raman spectrum of '$P_2Cl_9Br$'.

## Experimental

*Synthesis.*—All manipulations of $P_3Cl_{14}Br$ were carried out in dry nitrogen-filled glove boxes. Method (*a*) was employed at the University of Dayton, and Method (*b*) at Royal Holloway. Raman spectra and powder X-ray diffraction patterns were identical for the two products.

*Method* (*a*). Using a standard high-vacuum line, HBr (3.15 mmol) was condensed into a reaction vessel containing $PCl_5$ (9.46 mmol) (HBr : $PCl_5$ = 0.333 : 1) in dichloromethane. A yellow solid remained after the removal of HCl and dichloromethane (Found: Br, 11.70; Cl, 74.00; P, 13.30. Calc. for $BrCl_{14}P_3$: Br, 11.85; Cl, 74.25; P, 13.90%) (Galbraith Laboratories, Knoxville, TN). Potentiometric titration conducted at Dayton for Cl (74.35%) was consistent with the Galbraith analysis.

*Method* (*b*). This method was first described by Kolditz and Feltz[11] for the preparation of $P_2Cl_9Br$. Phosphorus trichloride (0.06 mol) was suspended in $AsCl_3$ (8 cm$^3$) at 0 °C and $Br_2$ (0.031 mol) was added dropwise with stirring. The yellow precipitate was filtered off, washed with benzene and dried under vacuum.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

*Crystal Growth and Single-crystal X-Ray Analysis.*—A small amount of powdered $P_3Cl_{14}Br$ was introduced into a 0.5 mm glass capillary tube and flame-sealed under nitrogen. The end of the tube, containing the powder, was immersed in a 70 °C oil-bath for 1 day. A suitable single crystal of volume 0.0359 mm$^3$ grew by sublimation and was used for both single-crystal X-ray analysis and Raman spectroscopy.

An Enraf-Nonius CAD-4 diffractometer, utilizing a graphite monochromator and Mo-Kα radiation, was employed for X-ray data collection. Lattice parameters were obtained from 25 reflections in the range $20 < 2\theta < 34°$. General and systematic absences were characteristic of a body-centred tetragonal cell. Lorentz-polarization and numerical absorption corrections were applied. The structure was solved by direct methods in space group *I*4/*mmm* using the pseudotetragonal unit cell $a = 8.725(1)$, $c = 12.357(1)$ Å. The set with the best figure of merit gave an *E*-map which revealed the ions $PCl_4^+$, $PCl_6^-$ and $Br^-$. However, equivalent reflections could not be properly averaged, and the structure could not be refined in this cell. The Miller indices were transformed according to the matrix $\{0, -1, 1; -1, 0, 0; 1, 3, 1\}$ yielding the tetragonal cell given in Table 1. Attempts at refinement in *I*4/*m* and $I\bar{4}$ were not successful. These later two space groups were also rejected from further consideration due to a failure of the observed intensities data consistently to obey the space group condition $F(hhl) = F(-hhl)$. Space group *I*4 was eventually identified as the correct choice after a full-matrix anisotropic least-squares refinement was performed, based on *F*. Details are presented in Table 1.

All calculations were performed with a VAX 11/730 computer using SDPVAX[26] and ORTEP.[27]

Additional material available from the Fachinformationszentrum Karlsruhe comprises thermal parameters.

*High-resolution Powder X-Ray Diffraction.*—A high-resolution powder X-ray diffraction pattern was obtained on Station 9.1 at the Synchrotron Radiation Source, Daresbury. A specimen sealed in a 0.5 mm diameter capillary was spun at approximately 2 Hz whilst data were collected at a wavelength of 1.035 11(9) Å counting for 2 s per 0.01° step. The pattern showed a series of peaks reminiscent of a face-centred-cubic structure, but with small peak splittings indicating a lower-symmetry body-centred tetragonal cell. There were no systematic absences other than those required for the body-centred lattice.

**Table 1** Crystal data and experimental parameters

| | |
|---|---|
| Formula | $BrCl_{14}P_3$ |
| *M* | 669.17 |
| Space group | *I*4 (no. 79) |
| *Z* | 2 |
| *a*/Å | 8.739(2) |
| *c*/Å | 12.320(1) |
| *U*/Å$^3$ | 940.9 |
| *F*(000) | 636 |
| $D_c$/g cm$^{-3}$ | 2.36 |
| μ(Mo-Kα)/cm$^{-1}$ | 44.0 |
| Scan width/° | 0.6 + 0.340 tan θ |
| Scan rate/° min$^{-1}$ | 0–7 |
| Scan mode | θ–2θ |
| $2\theta_{max}$/° | 62 |
| *T*/°C | 22 |
| Index range | *h*, ±12; *k*, ±12; *l*, ±17 |
| No. data collected | 11 928 |
| No. independent reflections | 770 |
| No. reflections $I > 2\sigma(I)$ | 524 |
| No. variables refined | 44 |
| Linear decay correction factor range | 0.995–1.000 on *I* |
| $R^a$ | 0.058 |
| $R'^b$ | 0.060 |
| Max. shift/error | 0.04 |
| Max., min. electron density on difference map/e Å$^{-3}$ | 0.37, −0.41 |

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/\sigma(F)^2$.

A structure was derived in space group *I*4/*mmm* by arranging the two octahedral $PCl_6^-$ and four $PCl_4^+$ groups per unit cell (indicated by spectroscopy) in a manner analogous to the antifluorite structure, with $Br^-$ ion placed at the origin surrounded by eight cations. The structure was refined by the Rietveld method[28] using the program PROFIL[29] in various subgroups of *I*4/*mmm*. The most satisfactory model was obtained in space group *I*4/*m*, where the octahedral and tetrahedral groups are rotated about the *z* direction from their fixed orientations required by symmetry in *I*4/*mmm*. All atoms were refined with anisotropic thermal parameters, which were constrained to simulate rigid-body translational and librational motion for the $PCl_6^-$ and $PCl_4^+$ groups. Final *R*-factors were $R_{wp} = 0.071$, $R_I = 0.047$ and $R_{exp} = 0.026$, with lattice parameters of $a = 8.747\ 23(5)$ and $c = 12.3281(2)$ Å. Refinements were also carried out in space groups $I\bar{4}$ and *I*4, but were not stable, presumably due to an unfavourable data/refined-parameter ratio.

*Raman Spectroscopy.*—The Raman spectrum of the *same* crystal used for single-crystal X-ray data collection was recorded at Dayton on a Spex 1488, 0.22 m double spectrometer, utilizing a Spectra Physics 2020 argon ion laser operating at 488 nm. The crystal was spun in the laser beam to avoid orientational effects. A Raman spectrum of the powder prepared at Royal Holloway was recorded using a Coderg PHO spectrometer with excitation from a Coherent Radiation argon-ion laser at 514.5 nm.

The spectra from the two sources were essentially identical.

## Discussion

*Stoichiometry of* $P_3Cl_4Br$.—A comparison between the calculated elemental compositions (%) for $P_2Cl_9Br$ and $P_3Cl_{14}Br$ points to the difficulty in distinguishing between these two empirical formulas based solely on their elemental compositions. As shown below, whereas the phosphorus and total halogen analyses are consistent with either assignment, the best determinant of stoichiometry is obtained from the *individual* Cl and Br values.

| | P | Cl | Br | Total (Cl + Br) |
|---|---|---|---|---|
| $P_3Cl_{14}Br$ | 13.89 | 74.17 | 11.94 | 86.11 |
| $P_2Cl_9Br$ | 13.44 | 69.22 | 17.34 | 86.56 |

It is likely that the reported individual Cl and Br values[11,14] were in error and that this was carried forward since identification of products of subsequent syntheses relied on Raman spectra which were always identical.

*Single-crystal X-Ray Analysis.*—The unit cell contains four $PCl_4^+$, two $PCl_6^-$ and two $Br^-$ ions. Fig. 1 shows a stereoview

**Table 2** Fractional atomic coordinates

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Br | 0.0000 | 0.0000 | 0.0000 |
| P(1) | 0.5000 | 0.0000 | 0.2498(6) |
| P(2) | 0.5000 | 0.5000 | 0.0031(8) |
| Cl(1) | 0.5428(3) | 0.1784(3) | 0.3403(2) |
| Cl(2) | 0.3233(3) | 0.0313(4) | 0.1581(2) |
| Cl(3) | 0.2850(2) | 0.3857(3) | −0.0069(5) |
| Cl(4) | 0.5000 | 0.5000 | 0.1703(5) |
| Cl(5) | 0.5000 | 0.5000 | −0.1737(6) |

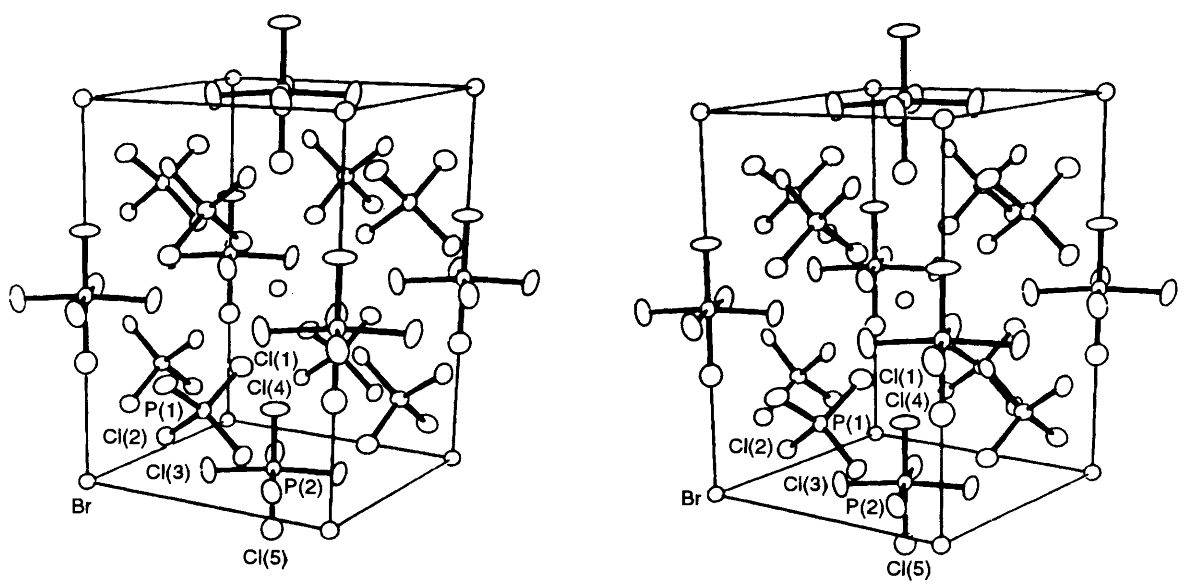

**Fig. 1** Stereoscopic view of the unit cell of $[PCl_4^+]_2PCl_6^-Br^-$, $Z = 2$. The shortest van der Waals separation (3.442 Å) is between $Br^-$ and Cl(2)

**Table 3** Bond distances (Å) and angles (°)

| $PCl_4^+$ | | $PCl_6^-$ | |
|---|---|---|---|
| P(1)–Cl(1) | 1.953(5) | P(2)–Cl(3) | 2.131(2) |
| P(1)–Cl(2) | 1.933(5) | P(2)–Cl(4) | 2.059(12) |
| | | P(2)–Cl(5) | 2.178(12) |
| Cl(1)–P(1)–Cl(1′) | 110.3(3) | Cl(3)–P(2)–Cl(3′) | 173.4(3) |
| Cl(2)–P(1)–Cl(2′) | 108.5(3) | Cl(3)–P(2)–Cl(4) | 93.3(3) |
| Cl(1)–P(1)–Cl(2) | 112.0(1) | Cl(3)–P(2)–Cl(5) | 86.7(3) |
| Cl(1)–P(1)–Cl(2′) | 107.1(1) | Cl(3)–P(2)–Cl(3″) | 89.8(3) |
| | | Cl(4)–P(2)–Cl(5) | 180.0 |

Symmetry transformations used to generate primed atoms: $1 - x, -y, z$ for $PCl_4^+$; $1 - x, 1 - y, z$ for Cl(3′) and $1 - y, x, z$ for Cl(3″) in $PCl_6^-$.

of the unit cell with anisotropic thermal ellipsoids. Table 2 contains the fractional atomic coordinates and the bond lengths and angles are given in Table 3.

The $PCl_4^+$ ion, which lies on a $4_2$ screw axis, is distorted from tetrahedral symmetry and belongs to point group $C_s$. Bond lengths differ by 0.020 Å and are considered equivalent to within 3σ. The bond angles, on the other hand, are not equivalent. Four of the six angles are unique while the remaining two have symmetry equivalents. Angles range from 107.1(1) to 112.0(1)°.

The $PCl_6^-$ ion, also distorted from ideal octahedral symmetry, has three significantly different P–Cl bond lengths—two axial and one equatorial. Atoms Cl(4), P(2) and C(5) lie on a four-fold crystallographic axis. The P(2) atom is displaced by 0.123 Å out of the equatorial plane. The *trans* Cl(3′)–P–Cl(3) angle is 173.4(3)°. The two axial P–Cl distances of 2.178(12) and 2.059(12) Å differ by more than 3σ, thus the point symmetry of the anion is $C_{4v}$.

*Powder Diffraction Analysis.*—Rietveld refinement of $P_3Cl_{14}Br$, although stable in *I4/m*, was not stable in *I4*, the correct space group of the material, because the powder pattern lacks sufficient information to fit the additional parameters required. This lack of data stems from the fact that the intensities of the individual Bragg reflections that are superimposed in a peak cannot be measured independently. The structure derived from the powder diffraction measurements is nevertheless compatible with that determined from the single-crystal analysis.

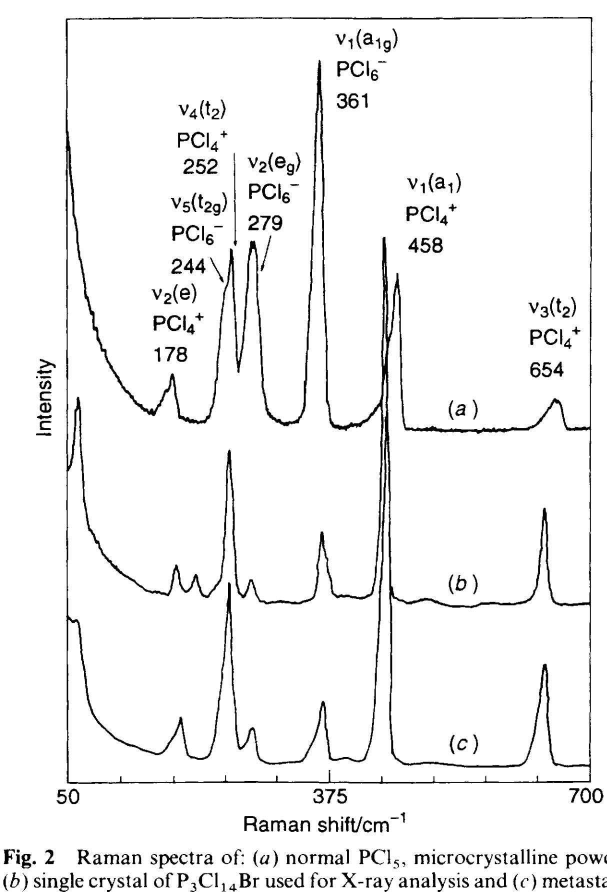

**Fig. 2** Raman spectra of: (*a*) normal $PCl_5$, microcrystalline powder; (*b*) single crystal of $P_3Cl_{14}Br$ used for X-ray analysis and (*c*) metastable $PCl_5$ (microcrystalline powder)

*Raman Spectra.*—Vibrational band assignments for the $PCl_4^+$ and $PCl_6^-$ ions in solid $PCl_5$ are well established.[30,31] In Fig. 2 the Raman spectra for $[PCl_4]^+{}_2PCl_6^-Cl^-$ and $[PCl_4]^+{}_2PCl_6^-Br^-$ are compared with that of $PCl_4^+PCl_6^-$, hereafter referred to as metastable $PCl_5$, $P_3Cl_{14}Br$ and normal $PCl_5$ respectively. There is a virtually identical enhancement of the intensities of the $PCl_4^+$ bands relative to the $PCl_6^-$ bands in both metastable $PCl_5$ and $P_3Cl_{14}Br$ compared to normal $PCl_5$. This must reflect, at least in part, the 2:1 ratio of $PCl_4^+$ to $PCl_6^-$ in metastable $PCl_5$ and $P_3Cl_{14}Br$, consistent with the crystallographic results. The wavenumber shift to lower values

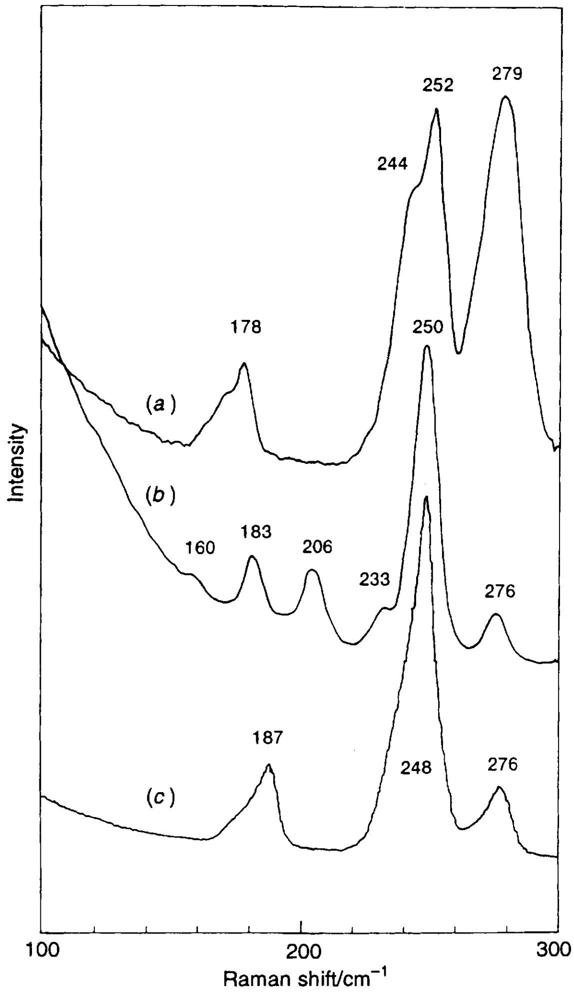

**Fig. 3** Raman spectra (100–300 cm$^{-1}$) as in Fig. 2 with expanded scale

(*ca.* 20 cm$^{-1}$) in the symmetric ($a_1$) and antisymmetric (e) stretching modes on passing from normal $PCl_5$ to either metastable $PCl_5$ or $P_3Cl_{14}Br$ is also virtually identical and almost certainly arises from non-bonded interactions between $PCl_4^+$ and the single $Cl^-$ or $Br^-$ ions respectively.[23] However, the spectrum of $P_3Cl_{14}Br$ in the 100–300 cm$^{-1}$ region (Fig. 3) has several low-intensity bands not seen in either normal or metastable $PCl_5$. In the previous work[22] on '$P_2Cl_9Br$' these bands were interpreted as arising from $PCl_3Br^+$ ion, the Raman bands of which[9] showed a reasonable correspondence with the additional bands. We now believe that these bands represent the splitting of degenerate modes of the ions due to the distortions from idealized symmetry evidenced by the crystal structure of $P_3Cl_{14}Br$.

The $PCl_4^+$ ion in normal $PCl_5$ has a unique P–Cl bond length of 1.90(1) Å and two Cl–P–Cl bond angles of 109.8(6) and 108.8(6)°.[5] The standard deviations for these angles make them equivalent to within 3σ. Therefore $PCl_4^+$ is tetrahedral in normal $PCl_5$. As discussed above, $PCl_4^+$ in $P_3Cl_{14}Br$ has point symmetry $C_s$.

Distortions from octahedral symmetry for $PCl_6^-$ are also greater for $P_3Cl_{14}Br$ compared to normal $PCl_5$, which is characterized by axial bond lengths of 2.13(1) and 2.16(1) Å, and 2.11(1) Å for the equatorial P–Cl length.[5] The $Cl_{ax}$–P–$Cl_{eq}$ angle is 90.6(6)°, and to within 3σ, $PCl_6^-$ is an octahedron. The $PCl_6^-$ ion in $P_3Cl_{14}Br$ belongs to point group $C_{4v}$.

In summary we believe these distortions remove the degeneracy of the Raman modes giving rise to the extra bands and baseline anomalies illustrated in Fig. 3.

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