A SPECTROSCOPIC INVESTIGATION OF SOME MIXED HALIDE COMPOUNDS OF PHOSPHORUS (V) AND ANTIMONY (V).

A thesis submitted by
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ABSTRACT

The fundamental vibrational frequencies of the mixed chlorobromophosphonium ions, PCl_3Br^+, $PCl_2Br_2^+$ and PBr_3Cl^+, have been assigned from solid-state Raman and infrared (PCl_3Br^+ only) measurements. The Raman spectra of the following have been compared:-

(i) PBr_4^+ Br^- and PBr_4^+ BBr_4^-

(ii) Normal PCl_5 (PCl_4^+ PCl_6^-) and "metastable" PCl_5 (containing Cl^- ions).

(iii) PCl_3Br^+ BCl_4^-, PCl_3 Br^+ PF_6^- and P_2Cl_9Br (containing PCl_3Br^+ and Br^- ions).

(iv) Compounds shown by solid-state ^{31}P n.m.r. Spectroscopy to contain the PCl_3Br^+, $PCl_2Br_2^+$ and PBr_3Cl^+ ions.

From the above, two sets of fundamental vibrational frequencies may be assigned to the tetrahalogenophosphonium ions, $PCl_nBr_{4-n}^+$ ($n = 0 - 4$), depending upon whether they are in the presence of:-

(a) A polyatomic anion only (eg. BCl_4^-), or

(b) Single halide ions(Cl^-, Br^-)

The addition of excess chlorine to PCl_2F yields initially a green liquid, probably molecular PCl_4F, and some white solid, probably PCl_4^+ $PCl_4F_2^-$. On standing at room temperature for 3-4 days, the whole solidified to give a compound of stoichiometry PCl_4F, which it is suggested (from Raman and infrared spectra and fluoride analyses) may be formulated as containing PCl_4^+, F^- and $PCl_4F_2^-$ ions. Raman and infrared spectra indicate a trans (D_{4h}) structure

for the octahedral $PCl_4F_2^-$ ion.

Comparison of X-Ray data for P_2Cl_9Br and the compound of stoichiometry $PCl_{4.66}Br_{0.33}$ indicate a unit cell for P_2Cl_9Br, comprising 6 PCl_4^+, 2 PCl_3Br^+, 4 PCl_6^- and 4 Br^- ions. Solid-state Raman and ^{31}P n.m.r. spectra strongly support the above formulation for P_2Cl_9Br. Solid-state Raman spectra of PCl_3Br_6 and $P\ SbCl_7Br_3$ do not confirm the expected formulations, $PCl_3Br^+Br^-(Br_2)_2$ and $PBr_3Cl^+\ SbCl_6^-$.

The two compounds Et_4NSbBr_6 and Bu_4NSbBr_6 (Bu = C_4H_9) may be formulated, according to Raman and infrared data, as $Et_4N^+\ SbBr_6^-$ and $Bu_4N^+\ SbBr_6^-$ respectively. The existence of $Et_4N^+\ SbCl_5Br^-$ as a discrete chemical compound and not a 5:1 mixture of $Et_4N^+\ SbCl_6^-$ and $Et_4N^+\ SbBr_6^-$ has been demonstrated by:-

(i) Raman spectroscopy,
(ii) X-Ray powder photography, and
(iii) Differential scanning calorimetry.

Raman and ^{31}P n.m.r. spectra of $PSbCl_9Br$ indicate the formulation $PCl_4^+\ SbCl_5Br^-$.

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Dedication

To my late Father,

my Mother and

my Wife, Barbara.

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THE HALIDES OF PHOSPHORUS (V)

SECTION 1

1.1. Introduction

The chemistry of the phosphorus halides has been reviewed extensively in recent years (1 - 7). The possibility of both ionic and molecular modifications (4) for almost all of the known pentahalides is of particular interest.

1.1.1. Phosphorus Pentachloride (PCl_5)and Phosphorus Pentabromide (PBr_5)

In the gas phase, phosphorus pentachloride exists as a trigonal bipyramidal molecule in equilibrium with chlorine and phosphorus trichloride (8). There is also evidence from mass spectrometry for some association, as P_2Cl_{10} units, in the gas phase (9). The gas phase trigonal bipyramidal structure of phosphorus pentachloride has been established by electron diffraction studies (10, 11, 12) and confirmed by infrared (13) and Raman (8) spectroscopy. Raman spectra also indicate a similar structure for molten phosphorus pentachloride (14, 15).

In the solid-state, however, phosphorus pentachloride exists as a pale yellow crystalline compound which has been shown by X-ray studies of material recrystallised from nitrobenzene to be of the form $PCl_4^+ PCl_6^-$ (16, 17). This has been confirmed by infrared and Raman spectroscopy (18, 19, 20, 95); ^{31}P nuclear magnetic resonance spectra indicate two peaks, corresponding to PCl_4^+ and PCl_6^- (21, 22, 23).

X-ray powder diagrams for phosphorus pentachloride purified by recrystallisation from carbon tetrachloride (24) and by sublimation (25), however, differ from the X-ray powder diagram for a sample of normal phosphorus pentachloride recrystallised from nitrobenzene. Moreover, when normal phosphorus pentachloride is sublimed using an "open" vacuum (that is, when the sublimation apparatus is left open to the pump) a metastable form of phosphorus pentachloride is obtained. The Raman spectrum (26) of this metastable form differs greatly from that of the original, the four bands assignable to the PCl_4^+ cation being more intense relative to the three assigned to the PCl_6^- anion. When heated to 120°C. for 200 seconds, the metastable form has been shown by Raman spectroscopy to revert to the normal form (27).

Phosphorus pentachloride reacts with a number of inorganic chlorides, in particular boron trichloride (28 - 37) and antimony pentachloride (37, 38, 39), to form complexes based on the PCl_4^+ cation. These complexes have been reviewed extensively (6, 7, 40, 41, 42). Their ionic nature has been suggested from vibrational spectroscopic studies.

Phosphorus pentabromide, although known for some time (43), has received little attention. Unlike the pentachloride, there is no evidence to support the existence of molecular phosphorus pentabromide (44) in the gas phase in which it is fully dissociated. In the solid phase, phosphorus pentabromide has been shown by X-ray studies to be of the form $PBr_4^+ Br^-$ (45, 46, 47). This has been confirmed by Raman spectroscopy (48, 49). Very few addition compounds of phosphorus pentabromide with inorganic bromides have been reported (6) though $PBr_5 . BBr_3$ (50, 51) is known.

1.1.2. The Mixed Halides of Phosphorus (V)

Of the mixed halides of phosphorus (V) the chlorofluorides have been investigated most thoroughly (4, 52). Of particular interest is the work of Holmes and co-workers (53, 54, 55, 56, 57). All the members of the series $PCl_n F_{5-n}$ (where n = 1, 2, 3 or 4) have been prepared in molecular form and have been shown by electron diffraction (58, PCl_2F_3), ^{19}F nuclear magnetic resonance spectroscopy (59, PCl_3F_2, PCl_2F_3; 60, PCl_2F_3; 61, $PCl F_4$) and vibrational spectroscopy (62, 63) to have trigonal bipyramidal structures with, where possible, fluorine atoms occupying axial positions. Apart from monochlorotetrafluorophosphorane, ($PCl F_4$), where evidence is lacking, the chlorofluorophosphoranes transform on standing at room temperature to their solid ionic modifications, all of which are based on the PCl_4^+ cation.

^{31}P n.m.r. spectra of the ionic form of PCl_2F_3 indicate the presence of two species, PCl_4^+ and PF_6^-. Infrared and Raman spectra confirm these conclusions (64). An X-Ray powder pattern for $PCl_4^+ PF_6^-$ prepared by direct fluorination of phosphorus pentachloride with arsenic trifluoride in arsenic trichloride (65) was identical to that for a sample prepared from molecular PCl_2F_3 (62). ^{31}P n.m.r. spectra of the ionic form of PCl_3F_2 indicate the formulation $PCl_4^+ PCl_2F_4^-$ (66).

On the basis of molecular weight determinations in glacial acetic acid, it was originally proposed that the ionic form of tetrachlorofluorophosphorane, PCl_4F, was $PCl_4^+ F^-$ (67). More recent unpublished measurements, however, in acetonitrile (5) indicate the presence of the $PCl_4F_2^-$ anion (68). The $PCl_4F_2^-$ anion has also been reported as the caesium salt (69). A recent infrared investigation of the ionic form of PCl_4F indicated reaction with glacial acetic acid and the alternative formulation $PCl_4^+ PCl_4F_2^-$ (70).

A compound of stoichiometry P_2Cl_9F has been prepared and the structure $PCl_4^+ PCl_5F^-$ inferred from qualitative electrolysis in acetonitrile solution (71) and mass spectrometry (9). Evidence from infrared and ^{19}F n.m.r. spectroscopy for the mixed chlorofluorophosphonium ion, PCl_3F^+, in $PCl_3F^+ SbCl_6^-$ has been reported (72).

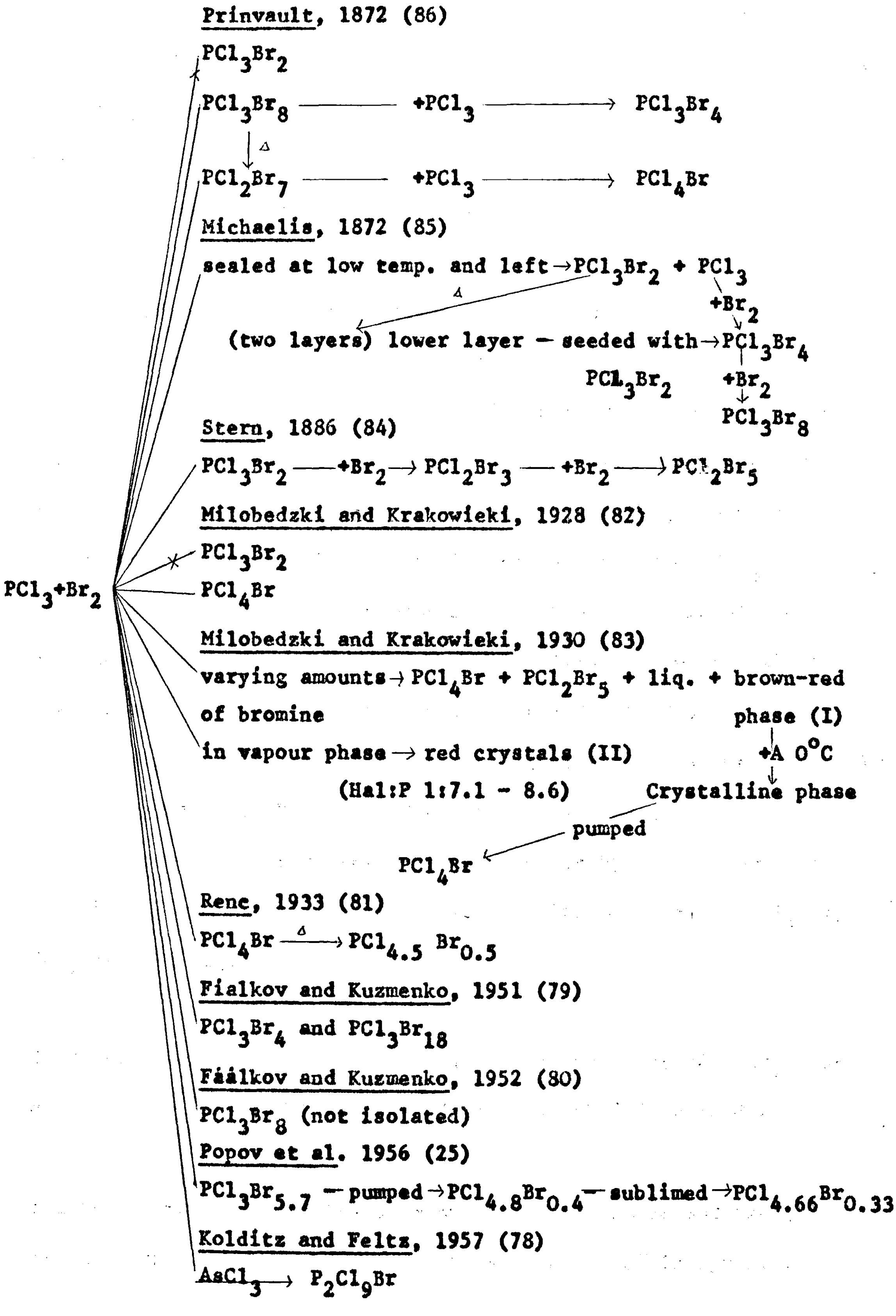
The bromofluorides of phosphorus (V) have not been investigated in any great detail. Dibromo trifluorophosphorane, PBr_2F_3, (73) has been shown to exist in molecular form as a trigonal bipyramid both by ^{19}F n.m.r. (60) and infrared and Raman (63) spectroscopy. The ionic form has been prepared by direct fluorination of phosphorus pentabromide (74) and the structure, $PBr_4^+ PF_6^-$, indicated by ^{31}P n.m.r. (23) and Raman (75) spectroscopy. Tetrabromofluorophosphorane, PBr_4F, has been prepared and the ionic form postulated as $PBr_4^+ F^-$ (76) though this is in doubt (6). Little is known of tribromo difluorophosphorane, PBr_3F_2 (77), and evidence from ^{31}P n.m.r. and infrared spectroscopy (61) for the molecular form only of bromotetrafluorophosphorane $PBrF_4$, has been reported. As yet no chlorobromo fluorides of phosphorus (V), in either ionic or molecular form, have been reported.

The chlorobromides of phosphorus (V) hase been investigated for over 100 years. Few conclusions can be drawn from the earlier literature and only two compounds of certain consistution, $PCl_{4.5}Br_{0.5}$ and $PCl_{4.66}Br_{0.33}$, have been reported.

$PCl_{4.5}Br_{0.5}$, or P_2Cl_9Br, a yellow crystalline compound was prepared by the reaction of phosphorus trichloride and bromine in arsenic trichloride (78). Fluorination in arsenic trichloride with arsenic trifluoride yielded the product $PCl_4^+ PF_6^-$ from which the formulation $PCl_4^+ PCl_5Br^-$, was inferred. Fluorination of phosphorus pentachloride, $PCl_4^+ PCl_6^-$, in a similar manner, also gives $PCl_4^+ PF_6^-$. Direct reaction of phosphorus trichloride and bromine (25) initially yielded an unstable aggregate, $PCl_3Br_{5.7}$, which on pumping gave a yellow solid, $PCl_{4.8}Br_{0.4}$. Sublimation of $PCl_{4.8}Br_{0.4}$ at 50°C. gave the compound $PCl_{4.66}Br_{0.33}$. An X-Ray powder diagram of $PCl_{4.66}Br_{0.33}$ showed it to be a unique single phase, all the lines of the diagram arising from a face-centered cubic unit cell. A structure determination based on powder data alone obtained fair agreement for an arrangement of 8 PCl_4^+ ions, 4 PCl_6^- ions and 4 Br^- ions in the unit cell.

The phosphorus trichloride-bromine system has been investigated by a number of workers and their results are summarised in Table 1. In general, the reaction is said to produce either some or all the compounds of general formula: PCl_4Br; $PCl_3(Br_2)_n$; and $PCl_2Br(Br_2)_n$ (where $n = 1$ to 10). Some Russian workers (79, 80)

TABLE 1. The Phosphorus Trichloride-Bromine System



PCl_3+Br_2

Prinvault, 1872 (86)

PCl_3Br_2

PCl_3Br_8 ——— $+PCl_3$ ———→ PCl_3Br_4

$\downarrow \Delta$

PCl_2Br_7 ——— $+PCl_3$ ———→ PCl_4Br

Michaelis, 1872 (85)

sealed at low temp. and left → PCl_3Br_2 + PCl_3

Δ

$+Br_2$

(two layers) lower layer — seeded with → PCl_3Br_4

PCl_3Br_2 $+Br_2$

PCl_3Br_8

Stern, 1886 (84)

PCl_3Br_2 —— $+Br_2$ → PCl_2Br_3 —— $+Br_2$ ——→ PCl_2Br_5

Milobedzki and Krakowieki, 1928 (82)

PCl_3Br_2

PCl_4Br

Milobedzki and Krakowieki, 1930 (83)

varying amounts → PCl_4Br + PCl_2Br_5 + liq. + brown-red

of bromine phase (I)

in vapour phase → red crystals (II) $+A$ 0°C

(Hal:P 1:7.1 - 8.6) Crystalline phase

pumped

PCl_4Br

Rene, 1933 (81)

$PCl_4Br \xrightarrow{\Delta} PCl_{4.5}Br_{0.5}$

Fialkov and Kuzmenko, 1951 (79)

PCl_3Br_4 and PCl_3Br_{18}

Fialkov and Kuzmenko, 1952 (80)

PCl_3Br_8 (not isolated)

Popov et al. 1956 (25)

$PCl_3Br_{5.7}$ — pumped → $PCl_{4.8}Br_{0.4}$ — sublimed → $PCl_{4.66}Br_{0.33}$

Kolditz and Feltz, 1957 (78)

$AsCl_3$ → P_2Cl_9Br

claim to have isolated the compounds $PCl_3\,Br_4$ and $PCl_3\,Br_{18}$ and to have detected a further compound, $PCl_3\,Br_8$, by viscosity measurements. Attempts, however, to repeat their preparation of $PCl_3\,Br_4$ failed (25). Renc (81) claimed to have prepared the yellow crystalline compound, $PCl_4\,Br$, which on heating to 135°C. gave $PCl_{4.5}\,Br_{0.5}$. Milobedzki and Krakowieki (82) also claim to have prepared $PCl_4\,Br$.

Mixtures of phosphorus trichloride and bromine in the ratio 1 : 0.0833 to 20 are said to yield four phases at 25°C. : a yellow crystalline phase of limited composition PCl_4Br; a red crystalline phase of limited composition PCl_2Br_5; a clear red liquid of varying composition from $PCl_{2.952}\,Br_{0.154}$ to $PCl_{2.795}\,Br_{0.461}$; and finally a brown-red phase (I) also of varying composition from $PCl_{3.439}\,Br_{4.677}$ to $PCl_3\,Br_{20}$ (83). In the vapour phase, phosphorus trichloride and bromine react to give a "ruby-like" crystalline compound (II) in which the halogen : phosphorus ratio varies from 7.1 to 8.6 : 1. The brown-red phase (I) mentioned previously, crystallises out completely on seeding with the "ruby-like" material (II) and cooling to 0°C. These crystals from the brown-red phase yield $PCl_4\,Br$ on pumping. Materials I and II were suggested to be solid mixtures of $PCl_4\,Br$, $PCl_2\,Br_5$ and Br_2.

Stern (84) and Michaelis (85) claim to have prepared $PCl_3\,Br_2$, but contemporary (86) and later work (82) leave this in some doubt.

The mutual reactions of the tri- and penta-chlorides and bromides of phosphorus have also been investigated as possible synthetic routes to the chloro-bromides of phosphorus (V). The phosphorus pentachloride–pentabromide reaction has been investigated by a number of workers (82, 87, 88, 89, 90). In general, the products are similar to those produced by direct reaction of phosphorus trichloride and bromine. It has been claimed that PBr_4Cl is produced from (i) the reaction of phosphorus pentachloride with excess phosphorus tribromide (81) and (ii) the reaction of excess phosphorus pentabromide with phosphorus trichloride (90).

The compound of stoichiometry $PBCl_7Br$ has been prepared by the reaction of phosphorus trichloride, bromine and boron trichloride in anhydrous liquid hydrogen chloride at -96°C. (91). A formulation of $PCl_3Br^+ \ BCl_4^-$ was inferred from the infrared spectrum. The reaction of antimony pentachloride with phosphorus tribromide (in a 2 : 1 mole ratio) gave a compound of formula $PSbCl_7Br_3$, which was formulated as $PBr_3Cl^+ \ SbCl_6^-$ (72). This compound, however, was unstable and could not therefore be satisfactorily characterised.

1.2. Results and Discussion

1.2.1. The Tetrabromophosphonium (PBr_4^+) and the Tetrachlorophosphonium (PCl_4^+) Cations

1.2.1.i. The Tetrabromophosphonium Cation (PBr_4^+)

The solid-state Raman spectra of phosphorus pentabromide ($PBr_4^+\ Br^-$) and the compound of stoichiometry $PBBr_8$ are presented in Figure 1. Solid-state Raman data for these two compounds, together with solid-state Raman data for the compound of stoichiometry $Et_4N\ BBr_4$, is presented in Table 2.

Comparison of the solid-state Raman spectrum of tetraethylammonium bromide ($Et_4N^+\ Br^-$), with bands at 426 and 682 cm^{-1}, with that for the compound of stoichiometry $Et_4N\ BBr_4$ strongly indicates the presence of the Et_4N^+ cation in this compound. Further, the presence of bands in the solid-state Raman spectra of the compounds of stoichiometry $Et_4N\ BBr_4$ and $PBBr_8$ at ~119, 170 and 245 cm^{-1} previously assigned to the BBr_4^- ion (92), strongly suggests the formulation of these compounds as $Et_4N^+\ BBr_4^-$ and $PBr_4^+\ BBr_4^-$ respectively. The four remaining bands in the solid-state Raman spectrum of $PBr_4^+\ BBr_4^-$ can now be assigned to the tetrahedral PBr_4^+ cation. They are at 104, 149, 252 and 499 cm^{-1}.

The four bands assigned to the PBr_4^+ ion in $PBr_4^+\ BBr_4^-$ differ, in both position and intensity, from the four bands assigned to

FIGURE 1. The Solid-State Raman Spectra of Phosphorus Pentabromide $PBr_4^+Br^-$ and the Compound of Stoichiometry $PBBr_8$.

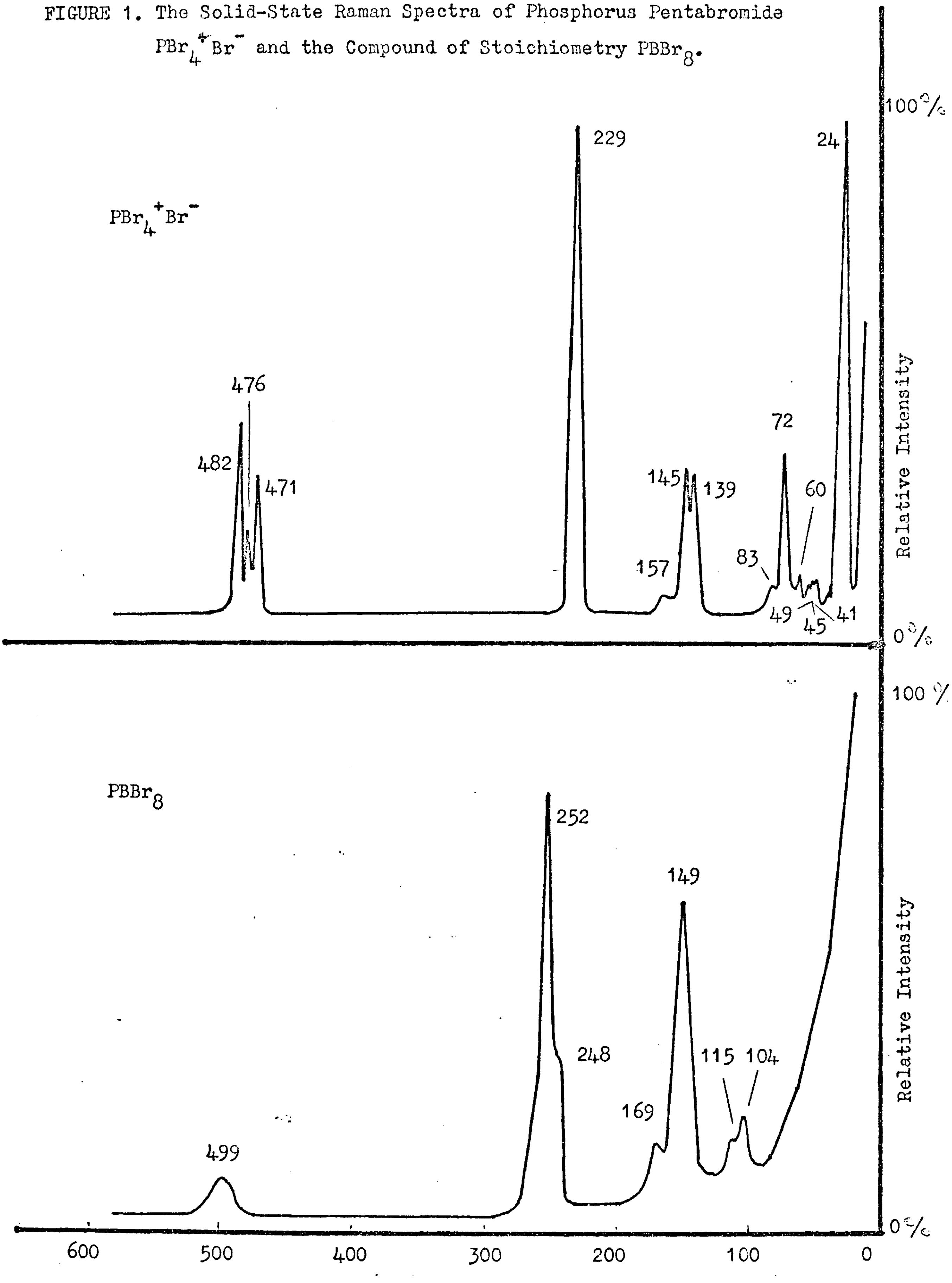


TABLE 2. Comparison of the Solid-State Raman Spectra of Phosphorus Pentabromide ($PBr_4^+ Br^-$) and the Compounds of Stoichiometry $PBBr_8$ and Et_4NBBr_4

PBr_4^+ cm^{-1}	Br^-	$PBBr_8$ cm^{-1}	$Et_4N\ BBr_4$ cm^{-1}	Assignment
24	(10)			lattice modes [a]
41	(1.5)			
45	(1)			
49	(1)			
60	(1.5)			
72	(3.5)	104 (2)		ν_2 (e) PBr_4^+
83	(1)			
		115 (1.5)	119 (6)	ν_2 (e) BBr_4^- [b]
139	(3)	149 (6)		ν_4 (t_2) PBr_4^+
145	(3)			
157	(1)			
		169 (1.5)	170 (5)	ν_4 (t_2) BBr_4^- [b]
		248sh.(3)	245 (10)	ν_1 (a_1) BBr_4^- [b]
229	(10)	252 (10)		ν_1 (a_1) PBr_4^+
			420 (2.5)	Et_4N^+
471	(3)	499 (1)		ν_3 (t_2) PBr_4^+
476	(2)			
482	(4)			
			678 (2.5)	Et_4N^+

Figures in parentheses are relative intensities on scale 0 - 10.

sh. - shoulder, a - reference 49, b - reference 92.

the cation in $PBr_4^+ Br^-$ (48, 49). The totally symmetric (a_1) band at 229 cm^{-1} in PBr_5 is shifted upwards by ~20 cm^{-1} to 252 cm^{-1} in $PBr_4^+ BBr_4^-$. A similar pattern is observed for the doubly degenerate (e) band at ~72 cm^{-1} and one of the remaining two, triply degenerate (t_2), bands at ~476 cm^{-1} in $PBr_4^+ Br^-$. The other triply degenerate (t_2) band at ~145 cm^{-1} in PBr_5 changes very little in position, but becomes more intense relative to the very strong a_1 band. The doubly degenerate band at ~72 cm^{-1} and the triply degenerate band at ~476 cm^{-1} in PBr_5 become less intense relative to the a_1 band. A similar pattern relative to $PBr_4^+ Br^-$ has been observed for the compounds tetrabromophosphonium hexabromotantalate ($PBr_4^+ TaBr_6^-$, 94) and tetrabromophosphonium hexafluorophosphate ($PBr_4^+ PF_6^-$, 93).

Thus there appears to be two sets of fundamental vibrational frequencies for the PBr_4^+ ion, depending upon whether the ion is in the presence of (i) a Br^- ion or (ii) a polyatomic anion (e.g. BBr_4^-, $Ta Br_6^-$, PF_6^- etc.).

1.2.1.ii. Phosphorus Pentachloride and the Tetrachlorophosphonium Cation (PCl_4^+)

The solid-state Raman spectrum of phosphorus pentachloride (PCl_4^+ PCl_6^-) has been recorded previously and results are summarised below:

The Solid-State Raman Spectrum of Phosphorus Pentachloride (PCl_4^+ PCl_6^-)

Reference	PCl_4^+				PCl_6^-		
	ν_1 (a_1)	$\nu_2(e)$	$\nu_3(t_2)$	$\nu_4(t_2)$	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_5(t_{2g})$
18 (1955)	451	173	627	244	358	285	244
19 (1963)	458	171	658	251	360	281	150
20 (1969)	460	182-179	642	255-252	354	273-264	243-240

The results of Livingston and Ozin (20) do not agree well with the previously published data. The band at 150 cm^{-1}, assigned by Carlson to the triply degenerate ν_5 (t_{2g}) band of PCl_6^-, has since been shown to be spurious (95) and there is some confusion concerning the triply degenerate ν_3 (t_2) band for PCl_4^+.

Correct assignment of the Raman spectrum of PCl_5 (PCl_4^+ PCl_6^-) is most important in the present work. Consequently, all the bands in the solid-state Raman spectrum of PCl_5 have been assigned by comparison with solid-state Raman data for Et_4N^+ PCl_6^-, PCl_4^+ BCl_4^-, and Me_4N^+ BCl_4^- (Table 3). Previous work (18, 19, 20) was used as a guideline in the assignment of bands. These

TABLE 3. Comparison of the Solid-State Raman Spectrum of Phosphorus Pentachloride ($PCl_4^+ PCl_6^-$), $Et_4N^+ PCl_6^-$, $PCl_4^+ BCl_4^-$, and $Me_4N^+ BCl_4^-$.

PCl_4^+ PCl_6^- cm^{-1}	Et_4N^+ PCl_6^- cm^{-1}	PCl_4^+ BCl_4^{-a} cm^{-1}	Me_4N^+ BCl_4^- cm^{-1}	Assignment
177 (2)		180 (3)		$\nu_2(e)$ PCl_4^+
		194 (3)	193 (10)	$\nu_2(e)$ BCl_4^{-6}
241 sh.(2)	241 (1)			$\nu_5(t_2)PCl_6^{-c}$
250 (6)		253 (7)		$\nu_4(t_2)PCl_4^+$
278 (4.5)	280 (2.5)			$\nu_2(e_g)PCl_6^{-c}$
		281 (1)	277 (7)	$\nu_4(t_2)BCl_4^{-6}$
359 (10)	360 (10)			$\nu_1(a_{1g})PCl_6^{-c}$
		409 (1)	408 (10)	$\nu_1(a_1)BCl_4^{-b}$
456 (4.5)		460 (10)		$\nu_1(a_1)PCl_4^+$
			459 (3)	Me_4N^+
656 (0.5)		656 (0.5)		$\nu_3(t_2)PCl_4^+$
			757 (10)	Me_4N^+

Figures in parentheses are relative intensities on scale 0 - 10.

a - reference 37. (for PCl_4^+ assignments).

b - reference 92.

c - reference 95.

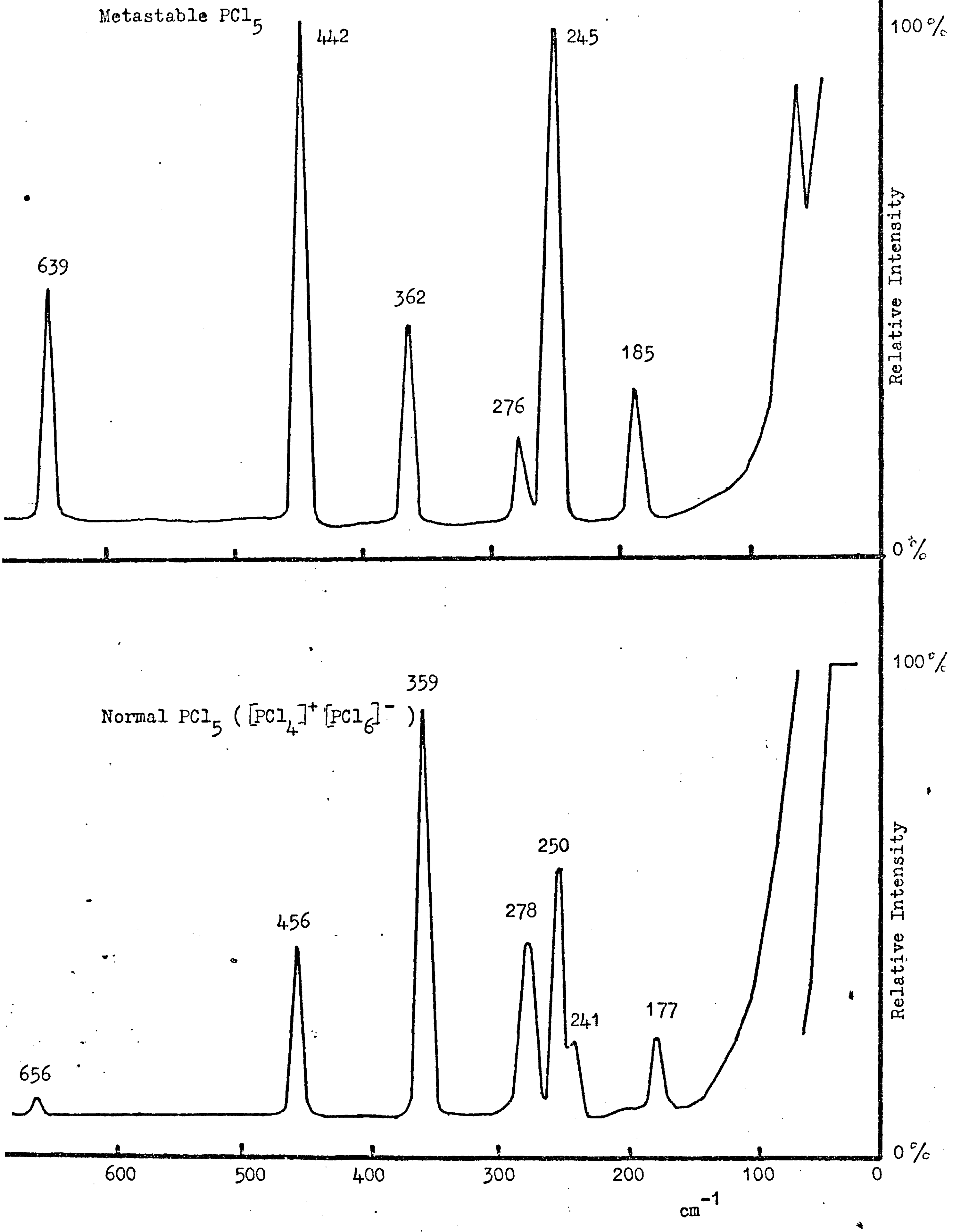
assignments are summarised below:

Assignment of the Solid-State Raman Spectrum of Phosphorus Pentachloride ($PCl_4^+ PCl_6^-$)

PCl_4^+				PCl_6^-		
ν_1 (a_1)	ν_2 (e)	ν_3 (t_2)	ν_4 (t_2)	ν_1 (a_{1g})	ν_2 (e_g)	ν_5 (t_{2g})
456	177	656	250	359	278	241

When phosphorus pentachloride is sublimed under open vacuum conditions (Section 1.1.1.), a metastable form of phosphorus pentachloride is produced (26, 27). The solid-state Raman spectrum of the metastable form differs from that of the normal form as shown in Figure 2 and Table 4.

FIGURE 2. The Solid-State Raman Spectra of Normal and Metastable Phosphorus Pentachloride.



Metastable PCl$_5$

Normal PCl$_5$ ($[PCl_4]^+[PCl_6]^-$)

TABLE 4. Comparison of the Solid-State Raman Spectrum of Normal and Metastable Phosphorus Pentachloride

Normal PCl_5 cm^{-1}	Metastable PCl_5 cm^{-1}	Assignment
177 (2)	185 (1.5)	ν_2 (e) PCl_4^+
241 sh. (2)		ν_5 (t_{2g}) PCl_6^-
250 (6)	245 (5.5)	ν_4 (t_2) PCl_4^+
278 (4.5)	276 (1)	ν_2 (e_g) PCl_6^-
359 (10)	362 (3)	ν_1 (a_{1g}) PCl_6^-
456 (4.5)	442 (10)	ν_1 (a_1) PCl_4^+
656 (0.5)	639 (2)	ν_3 (t_2) PCl_4^+

Figures in parentheses are relative intensities on scale 0 - 10.

sh. - shoulder.

A metastable form is also produced by the reaction of phosphorus pentachloride and bromine in dichloromethane. From Raman spectra it is clear that the metastable form reverts to the normal form on heating. The solid-state Raman spectrum of a sample of metastable PCl_5, prepared in dichloromethane, indicated partial conversion to the normal form on heating at 130°C. for two hours.

The bands at 276 and 362 cm^{-1} in the Raman spectrum of metastable PCl_5 indicate the presence of the PCl_6^- anion. The intensities of these two bands relative to the PCl_4^+ bands are considerably less for the metastable form. In normal PCl_5 there is a 1 : 1 ratio of $PCl_4^+ : PCl_6^-$. The Raman evidence thus suggests that there are fewer PCl_6^- ions than PCl_4^+ ions in the metastable form. If this is correct, then in order to preserve (i) electroneutrality and (ii) the observed stoichiometry, it seems probable that the metastable form contains some Cl^- ions in the crystal lattice. Thus a formulation containing PCl_4^+, PCl_6^- and Cl^- ions, is suggested for metastable PCl_5.

The differences (frequencies and intensities) between the PCl_4^+ bands in the solid-state Raman spectra of normal and metastable PCl_5 are summarised below and can clearly be seen in Figure 2.

The Fundamental Vibrational Frequencies of the PCl_4^+ Cation in Normal and Metastable PCl_5 (cm^{-1})

	ν_1 (a_1)	ν_2 (e)	ν_3 (t_2)	ν_4 (t_2)
Normal	456 (10)	177 (4.5)	656 (1)	250 (15.5)
Metastable	442 (10)	185 (1.5)	639 (2)	245 (5.5)

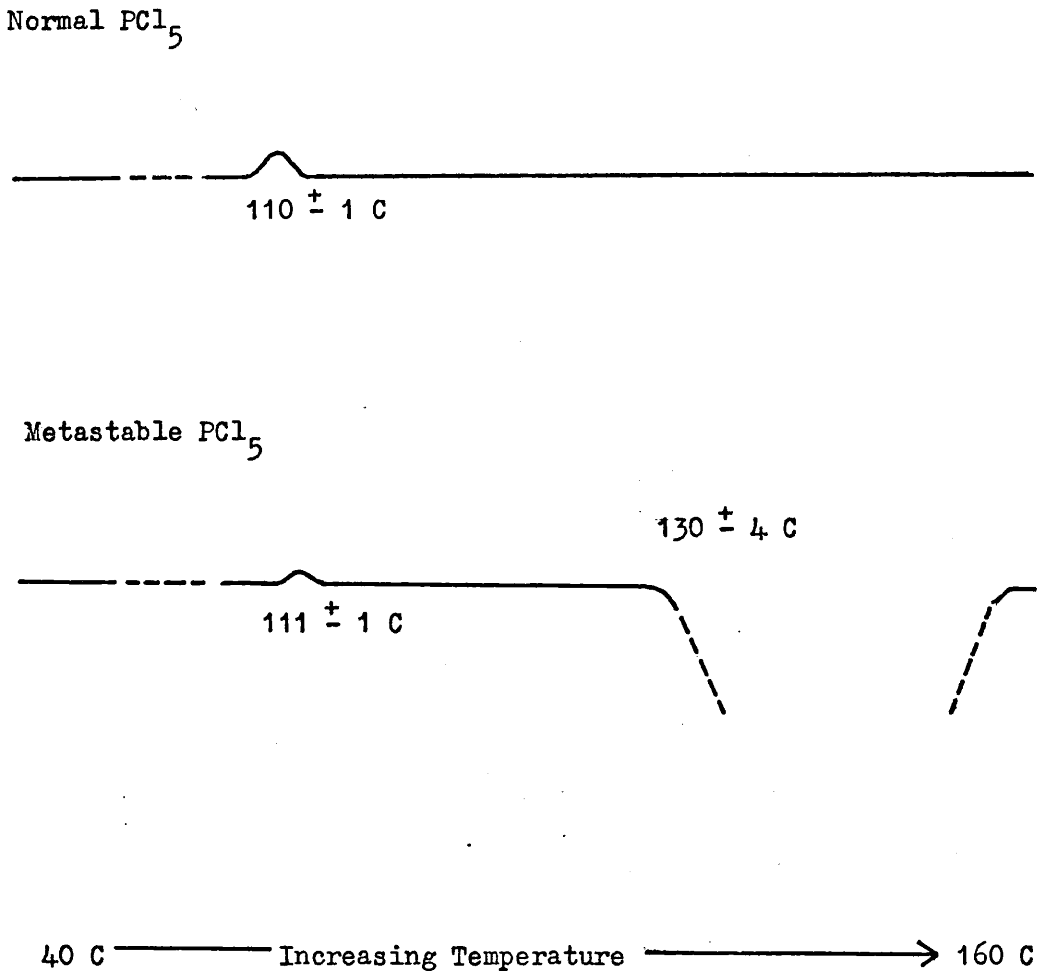
The two stretching frequencies at 456 and 656 cm^{-1} for PCl_4^+ in normal PCl_5 decrease by ~20 cm^{-1} in the metastable form. Further, the intensities of the bands at 177 and 250 cm^{-1} for PCl_4^+ in normal PCl_5 decrease for the metastable form.

A similar pattern of shifts for the two stretching frequencies is observed for the PBr_4^+ cation (Section 1.2.1.i.). The PBr_4^+ bands at 252 and 499 cm^{-1} in $PBr_4^+ BBr_4^-$ decrease by ~20 cm^{-1} in $PBr_4^+ Br^-$. Thus it appears that two sets of fundamental frequencies occur for the PCl_4^+ and PBr_4^+ ions depending upon whether they are in the presence of (i) a polyatomic anion only (e.g. BBr_4^-, PCl_6^-, BCl_4^-) or (ii) a single halide ion (e.g. Cl^-, Br^-).

Differential Scanning Calorimetry-

The results of a differential scanning calorimetric investigation of normal and metastable PCl_5 gave results diagrammatically illustrated in Figure 3. Results for four separate runs for normal PCl_5 indicate only one transition, at 110 ± 1°C. (383 ± 1°K), in the range 40 - 165°C. The transition is endothermic and results

FIGURE 3. Differential Scanning Calorimetry: Thermograms for Normal and Metastable PCl_5.



are summarised below:

Differential Scanning Calorimetric Results for Normal Phosphorus Pentachloride ($PCl_4^+ PCl_6^-$)

Sample(mg)	Transition Temperature (^oK)	Enthalpy of Transition (kJ mole^{-1}) ΔH_T	Entropy of Transition (J mole^{-1}) ($^oK^{-1}$) ΔS_T	$^{n_2}/_{n_1}$
A 19.18	383 ± 1	1.84±0.04	4.80±0.12	1.7 ± 0.1
B 19.37	383 ± 1	1.80±0.08	4.70±0.22	1.8 ± 0.0
B re-run	383 ± 1	1.96±0.08	5.12±0.22	1.9 ± 0.0
C 15.27	383 ± 1	1.80±0.29	4.70±0.77	1.8 ± 0.1
C re-run	383 ± 1	1.50±0.13	3.92±0.35	1.6 ± 0.1
D 6.30	384 ± 1	1.71±0.21	4.45±0.56	1.7 ± 0.1

The magnitude of the entropy change, ΔS_T, deserves comment. An endoentropic solid ⇆ solid transition has associated with it an increase in disorder (96). For such transitions an approximate value for the entropy change, ΔS_T, is given by the equation

$$\Delta S_T = R \ln {}^{n_2}/_{n_1}$$

where n_1 is the number of states of disorder statistically occupied in the initial phase and n_2 is the number of states of disorder statistically occupied in the final phase. For normal PCl_5, the ratio n_2/n_1 is approximately equal to two for the crystal transition at 110°C. (383°K). That is to say, either one of the ions in normal

PCl_5 (PCl_4^+ and PCl_6^-), occupies twice the number of orientations in the crystal above 110°C. as below. A detailed knowledge of the crystal structure of normal PCl_5, above and below 110°C, would be required to determine which ion can occupy the new set of orientations and what the nature of these orientations is (97).

Results for metastable PCl_5 for four runs and four re-runs in the region 40°C- 120°C and six runs and six re-runs in the region 120°C - 160°C, indicate two transitions, an endotherm at 111 ± 2°C. (384 ± 2°K) and an exotherm at 130 ± 4°C. (403 ± 4°K). The endotherm is invariably smaller than that for normal PCl_5 in the same region. Neither the endotherm nor the exotherm are reproducible and on re-running after covering the range 100°C - 160°C, the magnitude of the endotherm increases slightly, whereas the magnitude of the exotherm decreases or disappears.

Raman spectra indicate partial conversion only of metastable PCl_5 to normal PCl_5 after heating at 130°C. for two hours as none of the above runs for metastable PCl_5 were over two hours, this may account for the irreproducibility of the results.

1.2.1.iii. The Ionic Form of the Compound of Stoichiometry PCl_4F

Two alternative formulations, $PCl_4^+F^-$ and PCl_4^+ $PCl_4F_2^-$, have been proposed for the ionic form of the compound of stoichiometry PCl_4F. The formulation $PCl_4^+F^-$ (I) was originally suggested on the basis of molecular weight determinations in glacial acetic acid (67) but from more recent infrared investigations a formulation PCl_4^+ $PCl_4F_2^-$ (II) was proposed (70). In formulation I the PCl_4^+ cation is in the presence of a single halide ion (F^-) and in II a polyatomic anion ($PCl_4F_2^-$). In principle it should be possible to distinguish between the two by means of solid-state Raman spectroscopy on the basis of the conclusions above (Section 1.2.1.ii.).

PCl_4F was prepared by the addition of excess chlorine to dichlorofluorophosphine (PCl_2F) at ca. -78°C. At this stage, the reaction vessel contained in a small amount of white solid (Initial Product) and a large amount of pale green liquid, probably molecular PCl_4F (53). On standing at room temperature for 3-4 days, the whole solidified to give a white crystalline compound (Final Product). A total elemental analysis indicated the stoichiometry PCl_4F.

Final Product

The solid-state Raman and infrared spectra of the final product (of stoichiometry PCl_4F) from the reaction of excess Cl_2 and PCl_2F, are presented in Figures 4 and 5, and compared in Table 5.

The four bands at 190, 248, 442 and 639 cm^{-1} in the solid-state Raman spectrum are characteristic of the PCl_4^+ ion in the presence

FIGURE 4. The Solid-State Raman Spectrum of the Compound of Stoichiometry PCl_4F.

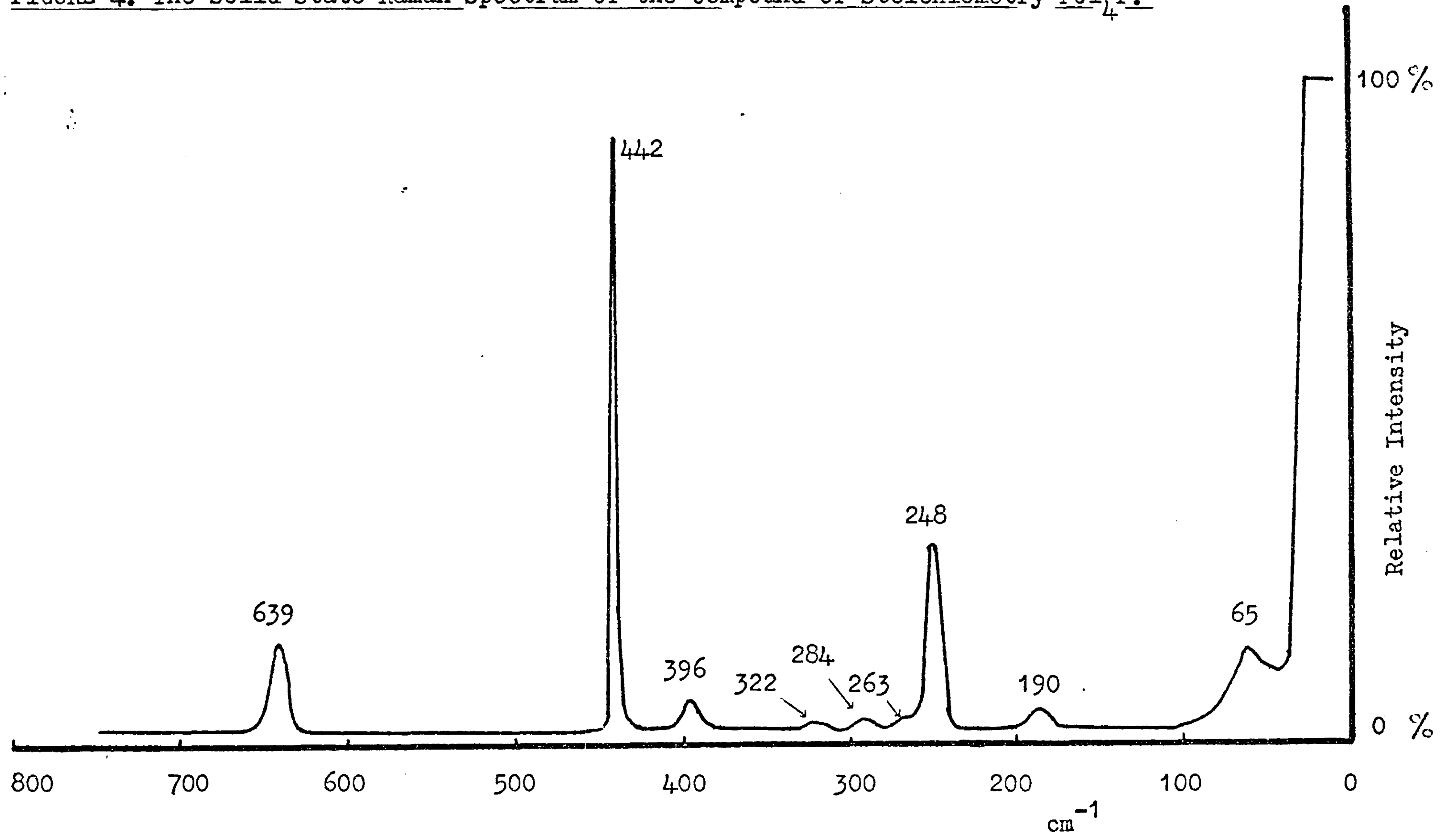


FIGURE 5. The Solid-State Infrared Spectrum of the Compound of Stoichiometry PCl_4F.

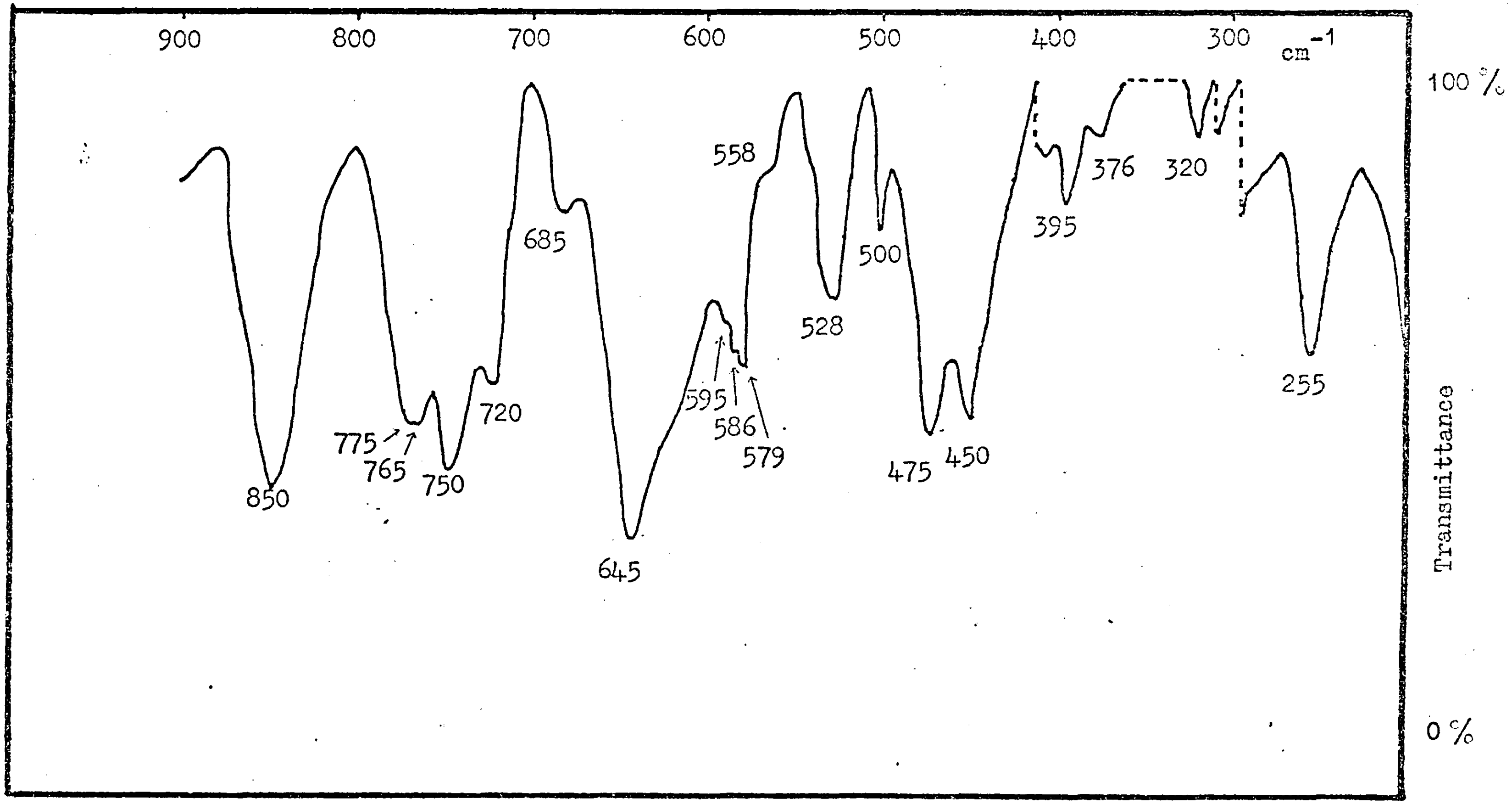


TABLE 5. Comparison of the Solid-State Raman and Infrared Spectra of the Compound of Stoichiometry PCl_4F.

Raman cm^{-1}	Infrared[a] cm^{-1}	Assignment
65 (2)		lattice mode
190 (0.5)		ν_2 (e) PCl_4^+
248 (3.5)	255 m	ν_4 (t_2) PCl_4^+
263 (0)		
284 (0)		
322 (0)	320 w	
	376 w	
396 (0.5)	395 w	
442 (10)		ν_1 (a_1) PCl_4^+
	450 m	ν_3 (t_{1u}) PCl_6^-[b]
	475 m	
	528 m/w	
	558 vw	ν_4 (t_{1u}) PF_6^-[b]
	579 m/w	
	586 m/w	
	595 m/w	
639 (2)	645 s	ν_3 (t_2) PCl_4^+
	685 w	
	720 m	Nujol
	750 m	
	765 m	
	775 m	
	850 s	ν_3 (t_{1u}) PF_6^-[b]

Figures in parentheses are relative intensities on the scale 0-10
a. range 200 - 1000 cm^{-1} m - medium, w - weak, m/w - medium to weak, vw - very weak, s - strong, b. reference 6 and references cited therein.

of a single halide ion. Thus, of the two alternatives proposed, the Raman spectroscopic evidence favours the $PCl_4^+F^-$ formulation, since for this only four bands would be expected.

There are, however, a number of weaker bands in the Raman spectrum at 263, 284, 322 and 396 cm^{-1}. Further, as fluorine-containing species (e.g. $PCl_4F_2^-$) are expected to be weaker scatterers (relative to the PCl_4^+ ion) it would be unlikely that P-F stretching bands would be observed in the Raman. Fluoride analyses of the hydrolysate, although variable were always low for the formulation $PCl_4^+F^-$ and indicated that not all the fluorine in PCl_4F was present as fluoride.

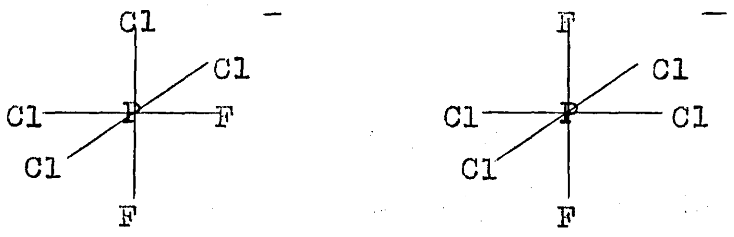
Examination of the solid-state infrared spectrum shows it to be more complex than that expected for the simple $PCl_4^+F^-$ formulation. The PCl_4^+ ion is indicated by bands at 255 and 645 cm^{-1}. The band at 450 cm^{-1} indicates the presence of the PCl_6^- anion and the two bands at 558 and 850 cm^{-1} suggest the presence of the PF_6^- anion. The presence of these ions (PCl_6^- and PF_6^-) as impurities is indicated by comparison of the infrared spectrum of PCl_4F with those of PCl_4^+ PCl_6^- and PCl_4^+ PF_6^-. The PF_6^- and PCl_6^- bands in the infrared spectrum of PCl_4F are less intense relative to the PCl_4^+ bands. The infrared spectrum is similar to that obtained by Walther (70) from which the formulation PCl_4^+ $PCl_4F_2^-$ was inferred. The presence of bands in the P-F stretching region at 750, 765 and 775 cm^{-1} and in the octahedral P-Cl stretching region at 475, 500 and 528 cm^{-1} strongly suggests the presence of a complex species containing P-F and

P-Cl bands. In view of the elemental analytical evidence for the stoichiometry PCl_4F and the presence of the PCl_4^+ ion, the most probable form of the above complex species is $PCl_4F_2^-$.

Thus Raman spectroscopy indicates the PCl_4^+ ion in the presence of a fluoride ion and infrared spectroscopy suggests the presence of the $PCl_4F_2^-$ anion. Further, analysis indicates some fluoride present in PCl_4F though not enough for the formulation $PCl_4^+F^-$. An intermediate formulation containing PCl_4^+, F^- and $PCl_4F_2^-$ satisfies the above evidence and may be a possibility. A similar formulation was proposed for metastable PCl_5 (Section 1.2.1.ii.) which was thought to contain PCl_4^+, Cl^- and PCl_6^- ions.

There are two alternative structures for the octahedral $PCl_4F_2^-$ anion, as indicated in Figure 6.

FIGURE 6. Alternative Structures for the $PCl_4F_2^-$ anion.



cis trans

Walther (70) proposed a cis structure for the $PCl_4F_2^-$ anion on the basis of the number of bands in the infrared spectrum of ionic PCl_4F. The number of bands expected for a cis (C_{2v}) structure is

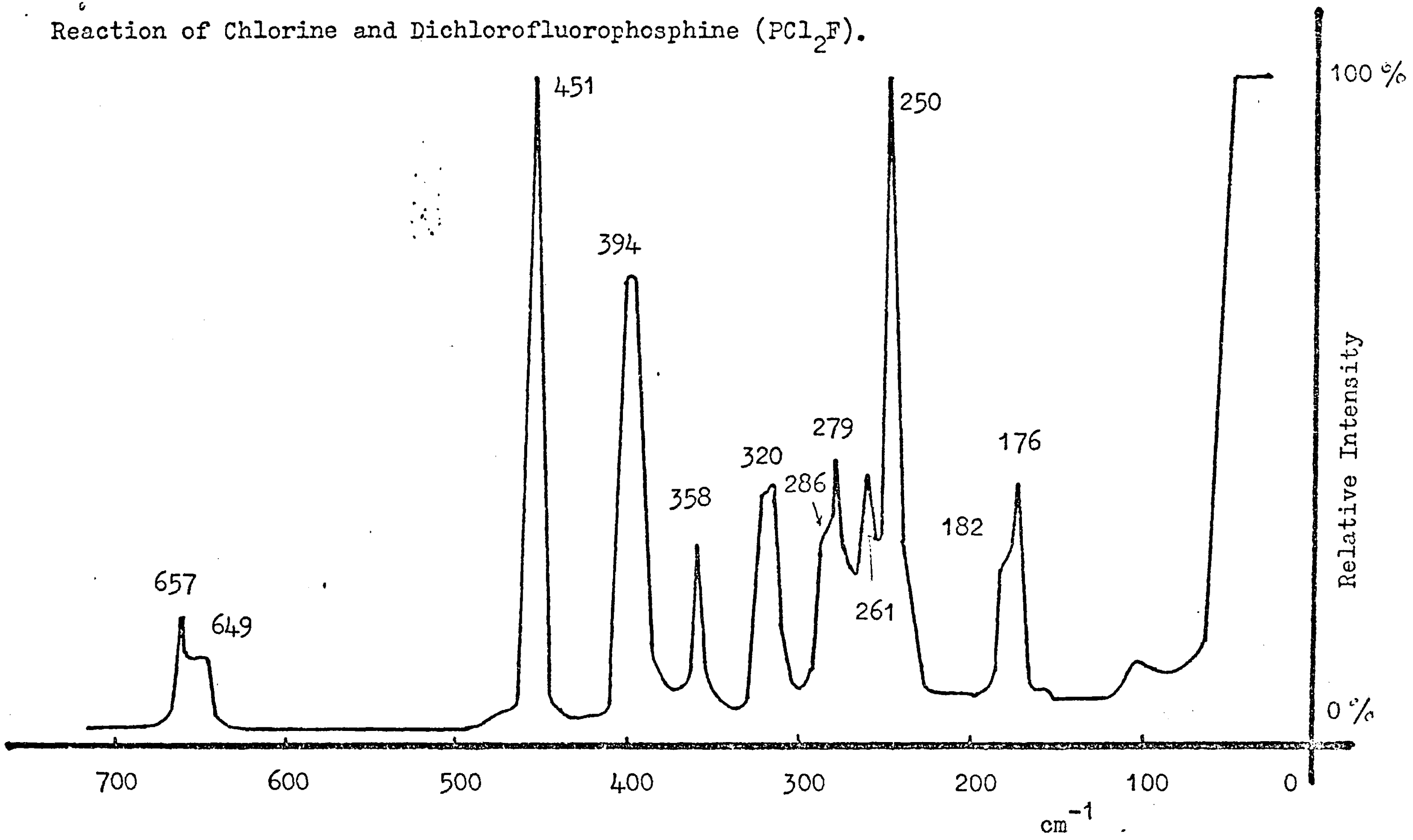
13 (Appendix B). However, the number of coincident Raman and infrared bands for the cis and trans (D_{4h}) structures are 13 and 0, respectively (Appendix B). The small number of coincident Raman and infrared bands (Table 5), assignable to the $PCl_4F_2^-$ ion, does not agree with Walther's results and strongly favours a trans structure for the $PCl_4F_2^-$ ion.

Initial Product

The solid-state Raman spectrum of the initial product of the reaction of excess chlorine and PCl_2F is presented in Figure 7. Elemental analysis indicated a slightly high chlorine content for the stoichiometry PCl_4F and may explain the presence of the PCl_6^- band at 358 cm^{-1}. The bands at 176, 250, 451 and 657 cm^{-1} are characteristic of the PCl_4^+ ion in the presence of a polyatomic anion only. The bands at 261, 279, 320 and 394 cm^{-1} are present in the Raman spectrum of the final product (above) and have been assigned to the $PCl_4F_2^-$ ion. Thus the above evidence favours the formulation PCl_4^+ $PCl_4F_2^-$ where the PCl_4^+ ion is in the presence of the $PCl_4F_2^-$ anion only.

Comparison of the Raman spectra of the initial and final products shows a decrease in intensity of the $PCl_4F_2^-$ bands relative to the PCl_4^+ bands for the final product. The above evidence is consistent with the conclusions concerning the formulations of the initial and final products. For a formulation containing PCl_4^+, F^- and $PCl_4F_2^-$ ions, for the final product, there are fewer $PCl_4F_2^-$ ions relative to PCl_4^+ ions than for a formulation PCl_4^+ $PCl_4F_2^-$, proposed for the initial product.

FIGURE 7. The Solid-State Raman Spectrum of the Initial Product of the Reaction of Chlorine and Dichlorofluorophosphine (PCl_2F).



On standing at room temperature for 3-4 days or heating at 130°C. for 24 hours, Raman spectra indicate that the initial product reverts to the final product.

Thus the conclusions to date concerning the ionic form of the compound of stoichiometry PCl_4F may be summarised as follows:

(1) PCl_2F reacts initially with excess chlorine to form a small amount of white solid, probably PCl_4^+ $PCl_4F_2^-$, and a large amount of pale green liquid, probably molecular PCl_4F.

(2) On standing at room temperature for 3-4 days, the white solid, probably PCl_4^+ $PCl_4F_2^-$, and the pale green liquid transform to a white solid containing PCl_4^+,F^- and $PCl_4F_2^-$ ions in the crystal lattice.

(3) The most probable structure for the octahedral $PCl_4F_2^-$ ion is a trans structure with fluorine atoms occupying axial positions.

1.2.2. The Trichlorobromophosphonium Ion (PCl_3Br^+)

1.2.2.i. The Compounds of Stoichiometry $PBCl_7Br$ and $P_2Cl_3BrF_6$

The compound of stoichiometry $PBCl_7Br$ was prepared by the addition, in order, of boron trichloride, phosphorus trichloride, and bromine to liquid anhydrous hydrogen chloride at ca. -96°C. On warming to room temperature, the solvent evaporated, leaving a white solid. Elemental analysis indicated a P:Cl:Br ratio of 1:7:1, and the stoichiometry $PBCl_7Br$. The solid-state Raman spectrum of the above compound is presented in Figure 8.

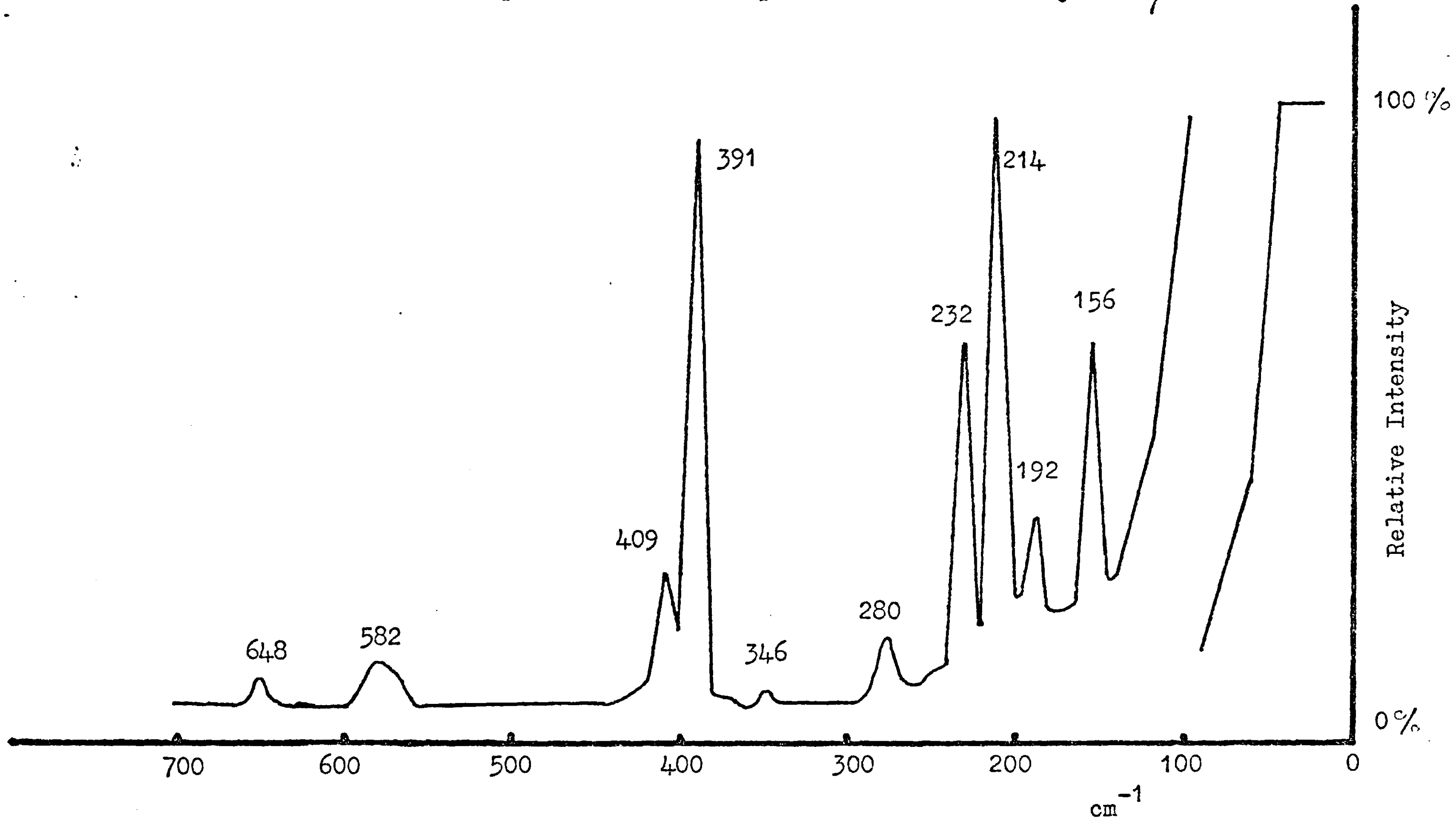
The presence of the BCl_4^- ion in $PBCl_7Br$ is strongly indicated by (i) the bands at 192, 280 and 409 cm^{-1} in the Raman spectrum (92) (ii) comparison with the solid-state Raman spectrum of $Me_4N^+ BCl_4^-$ and (iii) ^{11}B n.m.r. spectroscopy. A value of $+11.7 \pm 0.5$ p.p.m. for the ^{11}B n.m.r. shift (measured relative to $B(OMe)_3$ used as an external standard) agrees well with values for $Me_4N^+ BCl_4^-$ ($+12.1 \pm 1$ p.p.m.) and $(C_6H_5)_3C^+ BCl_4^-$ ($+ 12.9 \pm 1$ p.p.m.) (99). The evidence above strongly suggests the formulation $PCl_3Br^+ BCl_4^-$ for the compound of stoichiometry $PBCl_7Br$.

The close correspondence between the fundamental vibrational frequencies of the PCl_4^+ ion and the isoelectronic $SiCl_4$ (98) provides a convenient starting point for the assignment of the frequencies of the PCl_3Br^+ ion.

	ν_1 (a_1)	ν_2 (e)	ν_3 (t_2)	ν_4 (t_2)
PCl_4^+	456	177	656	250
$SiCl_4^+$	424	150	610	221

The reduction from the T_d (PCl_4^+, $SiCl_4$) to the C_{3v} (PCl_3Br^+, $SiCl_3Br$) point group results in the splitting of the two t_2

FIGURE 8. The Solid-State Raman Spectrum of the Compound of Stoichiometry $PBCl_7Br$.



modes into a_1 and e modes.

$$\begin{tikzcd}
T_d & a_1 \arrow[d] & e \arrow[d] & & t_2 \arrow[dl] \arrow[dr] & & & t_2 \arrow[dl] \arrow[dr] & \\
C_{3v} & \mathrm{al} & e & a_1 & & e & a_1 & & e
\end{tikzcd}$$

The six fundamental vibrational frequencies for the PCl_3Br^+ ion are all active in both the Raman and in the infrared. In the absence of Raman polarisation data the assignments have been made by analogy with the isoelectronic $SiCl_3Br$ (98) as follows:

	ν_1 (a_1)	ν_2 (a_1)	ν_3 (a_1)	ν_4 (e)	ν_5 (e)	ν_6(e)
PCl_3Br^+	582	391	214	648	232	156
$SiCl_3Br$	545	368	191	610	205	135

Assignment of the solid-state Raman and infrared spectra of trichlorobromophosphonium tetrachloroborate (PCl_3Br^+ BCl_4^-) is presented in Table 6.

Solid-state ^{31}P n.m.r. spectroscopy (99) gave a value of -48 ± 1 p.p.m. (measured relative to 85% H_3PO_4) for the ^{31}P chemical shift of the PCl_3Br^+ ion in PCl_3Br^+ BCl_4^-. This corresponds well with the value predicted for PCl_3Br^+ by interpolation between the ^{31}P chemical shifts for PCl_4^+ in PCl_5 (-88.3 ± 0.5 p.p.m.) and for PBr_4^+ in PBr_5^+ ($+ 104 \pm 1$ p.p.m.) (104).

In order to confirm the assignment of the fundamental vibrational frequencies of the PCl_3Br^+ ion an alternative source of the ion,

TABLE 6. Assignment of the Solid-State Raman and Infrared Spectra of $PCl_3Br^+ BCl_4^-$.

Raman cm^{-1}	Infrared cm^{-1}	Partial Assignment
156 (5)	155[a]	ν_6 (e) $PCl_3 Br^+$
192 (2.5)		ν_2 (e) BCl_4^- [b]
214 (10)	213 m	ν_3 $(a_1)PCl_3Br^+$
232 (6)	231 m	ν_5 (e) PCl_3Br^+
280 (1)	275 vw	ν_4 $(t_2)BCl_4^-$ [b]
346 (0.5)		impurity
391 (10)	390 m	ν_2 $(a_1)PCl_3Br^+$
409 (2.5)		ν_1 $(a_1)BCl_4^-$ [b]
	493 m	
	520 m	
582 (1)	574 s	ν_1 $(a_1)PCl_3Br^+$
648 (0.5)	634 s	ν_4 (e) PCl_3Br^+
	663 vs. br.	ν_3 $(t_2)BCl_4^-$ [b]

Figures in parentheses are relative intensities on scale 0-10.

a. recorded using a Grubb-Parsons Cube Interferometer

m - medium, vw - very weak, s - strong, vs - very strong, br - broad, b. reference 92.

trichlorobromophosphonium hexafluorophosphate ($PCl_3Br^+ PF_6^-$), was investigated (100). $PCl_3Br^+ PF_6^-$ was prepared by the addition of phosphorus trichloride, bromine and phosphorus pentafluoride to liquid anhydrous hydrogen chloride at ca. -96°C. Evaporation of the solvent left a white solid. A total elemental analysis indicated the stoichiometry $P_2Cl_3BrF_6$. The solid-state Raman spectrum of $PCl_3Br^+PF_6^-$ is presented in Figure 9. Assignment of the solid-state Raman and infrared (above 200 cm^{-1}) spectra of $PCl_3Br^+ PF_6^-$ is presented in Table 7.

The presence of the PF_6^- ion in $PCl_3Br^+ PF_6^-$ is indicated by (i) bands in the Raman spectrum at 472 and 743 cm^{-1} and in the infrared spectrum at 552 and 834 cm^{-1} (6) (ii) comparison with the solid-state Raman and infrared spectrum of $Et_4N^+ PF_6^-$ and (iii) solid-state ^{31}P n.m.r. spectroscopy. A ^{31}P chemical shift (99) of + 142.7 ± 1 p.p.m. (measured relative to 85% H_3PO_4) agrees well with that for PF_6^- in $PCl_4^+ PF_6^-$ (+ 140 p.p.m.) (23). The presence of PCl_4^+, as an impurity, is indicated by bands, weak relative to the PCl_3Br^+ bands, at 180, 254 and 462 cm^{-1} in the Raman. Further impurity bands at 200, 208, 309, and 353 cm^{-1} result from the mixed chlorobromophosphonium ions, $PCl_2Br_2^+$ and PBr_3Cl^+ (Section 1.2.3.).

The bands assigned to the fundamental vibrational frequencies of the PCl_3Br^+ ion in $PCl_3Br^+ PF_6^-$ (Table 7) agree well in both position and intensity, in the Raman and the infrared, with those assigned to the PCl_3Br^+ ion in $PCl_3Br^+ BCl_4^-$. Thus the original assignment is confirmed.

FIGURE 9. The Solid-State Raman Spectrum of Trichlorobromophosphonium Hexafluorophosphate ($PCl_3Br^+PF_6^-$).

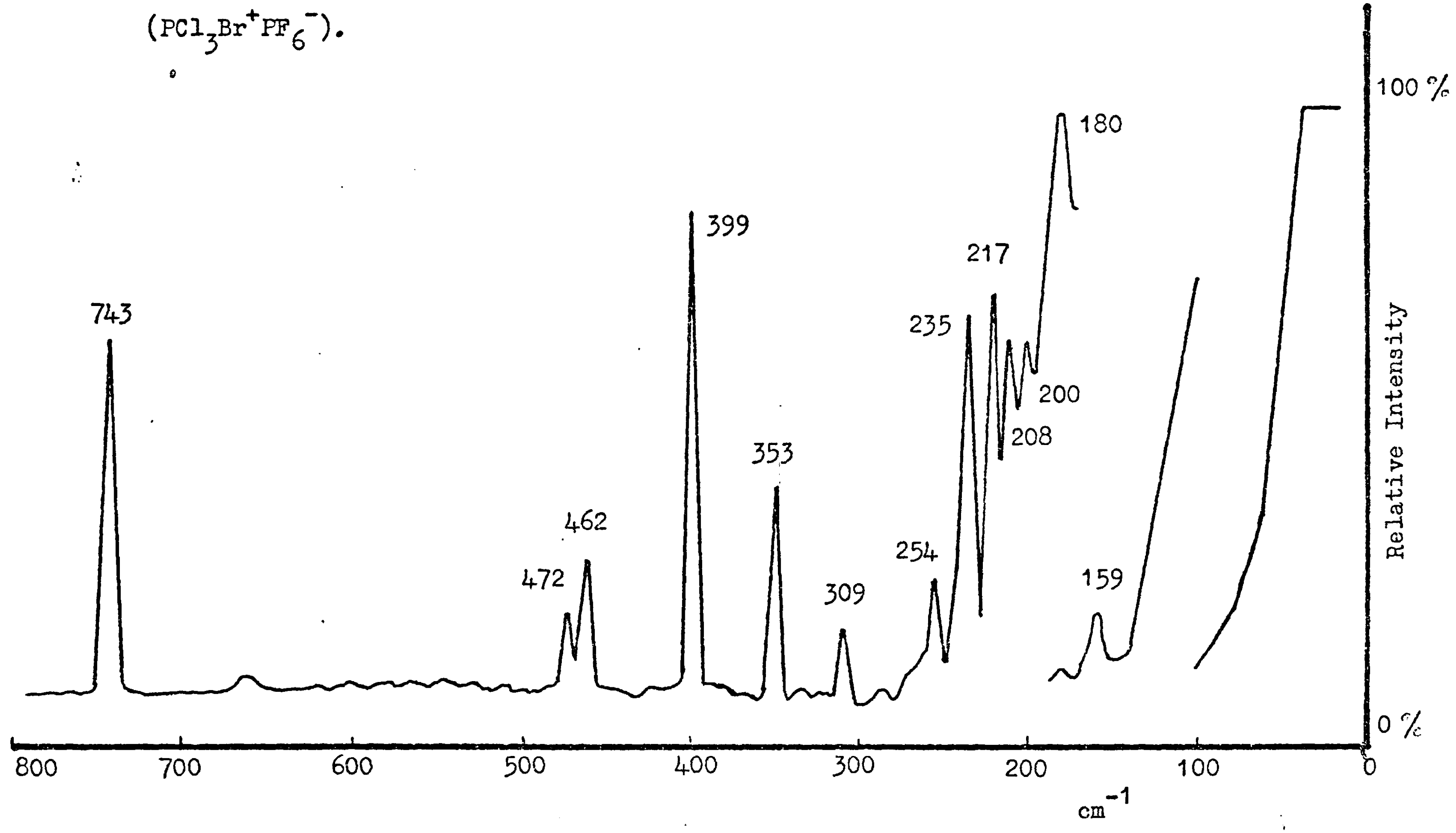


TABLE 7. Assignment of the Solid-State Raman and Infrared (above 200 cm^{-1}) Spectra of Trichlorobromophosphonium Hexafluorophosphate ($PCl_3Br^+ PF_6^-$).

Raman[a] cm^{-1}	Infrared cm^{-1}	Assignment
159	n.i.	ν_6 (e) PCl_3Br^+
180		PCl_4^+ impurity
200		impurity
208		impurity
217	216 m	ν_3 (a_1) PCl_3Br^+
235	233 m	ν_5 (e) PCl_3Br^+
254	253 w	PCl_4^+ impurity
309		impurity
353	352 w	impurity
399	397 m	ν_2 (a_1) PCl_3Br^+
462		PCl_4^+ impurity
	490 m	
472		ν_5 (t_{2g}) PF_6^- [b]
	525 m	
	552 s	ν_4 (t_{1u}) PF_6^- [b]
	558 m	ν_1 (a_1) PCl_3Br^+
	647 m	ν_4 (e) PCl_3Br^+
743		ν_1 (a_{1g}) PF_6^- [b]
	834 vs	ν_3 (t_{1u}) PF_6^- [b]

a. Raman intensities (Figure 9) are difficult to interpret as the spectrum is still coming off the exciting line at 250 cm^{-1}. n.i. - not investigated, m - medium, w - weak, s - strong, v.s. - very strong b. Reference 6.

1.2.2.ii. The Compound of Stoichiometry P_2Cl_9Br.

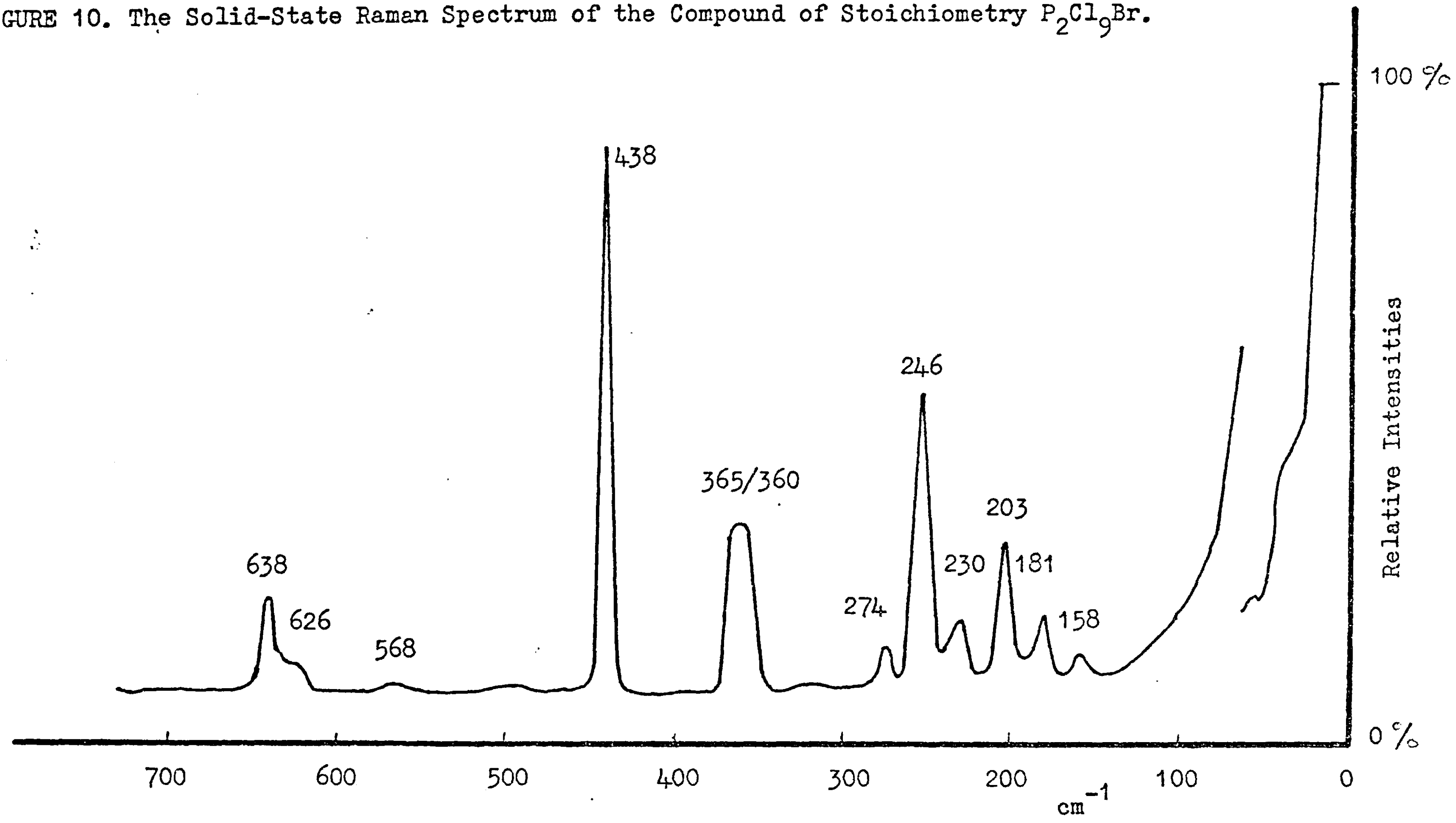
The compound of stoichiometry P_2Cl_9Br, prepared by the reaction of phosphorus trichloride and bromine in arsenic trichloride, was originally proposed to have one of the alternative formulations:

$$PCl_3Br^+\ PCl_6^- \qquad\qquad PCl_4^+\ PCl_5Br^-$$
$$\text{(I)} \qquad\qquad\qquad\qquad \text{(II)}$$

The original investigation (78), using partial fluorination of the complex with AsF_3 in $AsCl_3$, indicated formulation II. During the present work, efforts to prepare a compound containing the PCl_5Br^- ion (e.g. $Et_4N\ Br$ + PCl_5 in CH_2Cl_2), in order to confirm the formulation II by Raman and infrared spectroscopy, were unsuccessful. The solid-state Raman spectrum of P_2Cl_9Br is presented in Figure 10.

The bands at 181, 246, 438 and 638 cm^{-1} in the Raman spectrum of P_2Cl_9Br are characteristic of the PCl_4^+ ion in the presence of a single halide ion. Apart from these, the presence of the PCl_6^- ion is also indicated, by bands at 360 and 274 cm^{-1}. Solid-state ^{31}P n.m.r. spectroscopy confirms the presence of both these ions and in addition the PCl_3Br^+ ion (99). The remaining unassigned bands in the Raman spectrum at 158, 203, 230, 568, and 626 may be assigned to the PCl_3Br^+ ion. The strong a_1 band at 391 cm^{-1} in the Raman spectrum of $PCl_3Br^+\ BCl_4^-$ (Section 1.2.2.i.) does not appear to be present in the Raman spectrum of P_2Cl_9Br. Resolution, however, of the broad band at 360 cm^{-1} indicates two bands, one at 360 cm^{-1} (PCl_6^-) and the other at 365 cm^{-1} assignable to the PCl_3Br^+ ion. Thus Raman and ^{31}P n.m.r. spectroscopy strongly suggest the presence of the PCl_4^+, PCl_3Br^+ and PCl_6^- ions, together with single halide

FIGURE 10. The Solid-State Raman Spectrum of the Compound of Stoichiometry P_2Cl_9Br.



ions, in P_2Cl_9Br. Thus a simple formulation such as I or II appears to be impossible. Assignment of the solid-state Raman and infrared spectra of P_2Cl_9Br is presented in Table 8.

An X-Ray powder photograph (103) for P_2Cl_9Br confirms that a unique single phase is present and not a mixture of different crystalline components. All the lines on the diagram can be interpreted as arising from a face-centred cubic cell with a = 12.32 ± 0.05 Å. Previously a compound which gave an elemental analysis corresponding to $PCl_{4.66}Br_{0.33}$ (25) was investigated by X-Ray powder photography. $PCl_{4.66}Br_{0.33}$ also has face-centred cubic geometry (with a = 12.38 Å) and thus appears to be similar to P_2Cl_9Br. From powder data alone, the unit cell for $PCl_{4.66}Br_{0.33}$ was proposed to comprise of 8 PCl_4^+, 4 PCl_6^- and 4 Br^- ions.

By analogy with $PCl_{4.66}Br_{0.33}$, it is suggested that P_2Cl_9Br might be formulated as 6 PCl_4^+, 2 PCl_3Br^+, 4 PCl_6^-, and 4 Br^- ions. Such a formulation satisfies the P_2Cl_9Br stoichiometry and qualitatively accounts for the relative intensities of the bands for the different species from both Raman and ^{31}P n.m.r. spectra.

Comparison of the Raman spectrum of P_2Cl_9Br with that of $PCl_3Br^+ BCl_4^-$ (Section 1.2.2.i.) indicates some shifts in the bands assigned to the PCl_3Br^+ ion. The PCl_3Br^+ bands at 214, 391, 582 and 648 cm^{-1} in the Raman spectrum of $PCl_3Br^+ BCl_4^-$ are shifted down to 203, 365, 568 and 638 cm^{-1} in P_2Cl_9Br. The evidence thus suggests that there are two sets of fundamental vibrational frequencies for the PCl_3Br^+ ion (presented below) depending on the

TABLE 8. Assignment of the Solid-State Raman and Infrared (above 200 cm^{-1}) Spectra of the Compound of Stoichiometry P_2Cl_9Br.

Raman cm^{-1}	Infrared cm^{-1}	Assignment
158 (1)	n.i.	ν_5 (e) PCl_3Br^+
181 (2)		ν_2 (e) PCl_4^+
203 (3)		ν_3 (a_1) PCl_3Br^+
230 (2)	228 w	ν_5 (e) PCl_3Br^+
246 (6)	250 m	ν_4 (t_2) PCl_4^+
274 (1)		ν_2 (e_g) PCl_6^-
	288 w	
365/360 (3)		ν_1 (a_{1g}) PCl_6^- and ν_2(a_1) PCl_3Br^+
438 (10)		ν_1 (a_1) PCl_4^+
	450 vs	ν_3 (t_{1u}) PCl_6^- [a]
	494 w	
568 (0.5)	565 w	ν_1 (a_1) PCl_3Br^+
	579 m	
	587 m	
626 (0.5)	625 m	ν_4 (e) PCl_3Br^+
638 (2)	643 vs	ν_3 (t_2) PCl_4^+

Figures in parentheses are relative intensities on scale 0-10.

a. reference 6 and references cited therein. n.i. not investigated.

w - weak, m - medium, vs - very strong.

presence of either (i) a polyatomic anion (BCl_4^-, PF_6^-) or (ii) a single halide ion (Br^-).

The Fundamental Vibrational Frequencies of the Trichlorobromophosphonium Ion (PCl_3Br^+)

In the presence of	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(a_1)$	$\nu_4(e)$	$\nu_4(e)$	$\nu_4(e)$
i) A polyatomic anion (BCl_4^-)	582	391	214	648	232	156
ii) A single halide ion (Br^1)	568	365	203	626	230	158

Thus we have two sets of fundamental vibrational frequencies for the three phosphonium ions, PBr_4^+, PCl_4^+ and PCl_3Br^+.

1.2.3. The Dichlorodibromophosphonium and the Chlorotribromophosphonium Ions ($PCl_2Br_2^+$ and PBr_3Cl^+).

The following four reactions were investigated in attempts to prepare pure compounds containing either of the two ions $PCl_2Br_2^+$ and PBr_3Cl^+ : (Appendix C).

(1) $PCl_3 + Br_2 + BCl_3$ in CH_2Cl_2

(2) $PCl_3 + Br_2 + BCl_3$ in liquid HCl.

(3) $PCl_3 + Br_2 + BBr_3$ in CH_2Cl_2.

(4) $PCl_3 + Br_2 + BBr_3$ in liquid HCl.

Under certain conditions reaction (2) yields $PCl_3Br^+ BCl_4^-$ (Section 3.1.1.). Mostly, however, the solid- state Raman spectra of the products of such reactions were too complex to be explained in terms of simple formulations (e.g. $PCl_2Br_2^+ BCl_4^-$ etc.).

The solid-state Raman spectrum of the product (A) of an unsuccessful $PCl_3Br^+ BCl_4^-$ preparation is presented in Figure 11 and Table 9. Elemental analyses for (A) indicated a high bromine content and a low chlorine content for the formulation $PCl_3Br^+ BCl_4^-$.

A number of bands in the Raman spectrum can be assigned to the PCl_4^+, PBr_4^+, PCl_3Br^+ and BCl_4^- ions. The PCl_4^+ and PBr_4^+ bands are weak relative to the bands for PCl_3Br^+. It should be noted that those bands assigned to the phosphonium ions are characteristic of these ions in the presence of polyatomic anions only.

FIGURE 11. The Solid-State Raman Spectrum of the Product (A) of an Unsuccessful Preparation of $PCl_3Br^+BCl_4^-$.

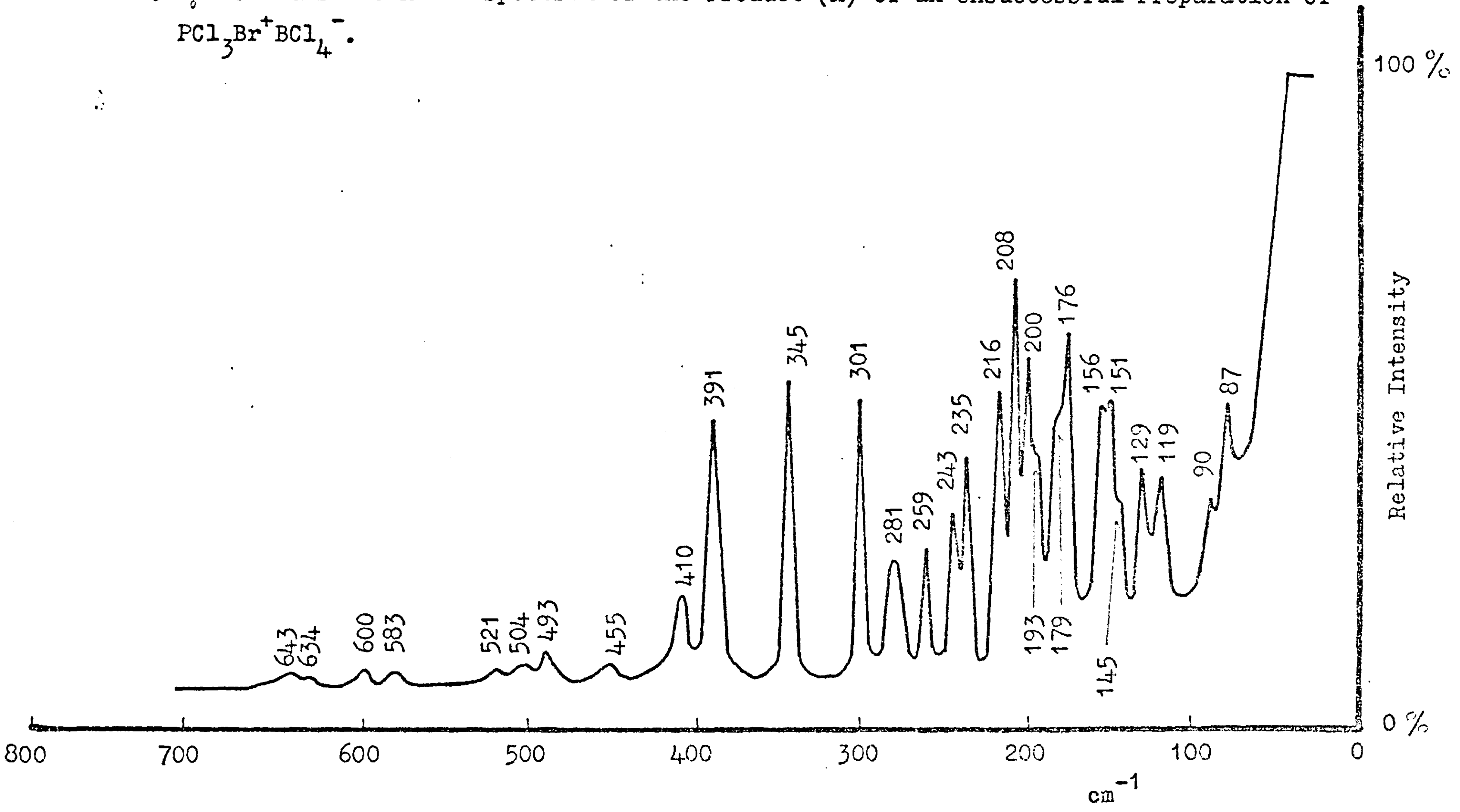


TABLE 9. The Solid-State Raman Spectrum of the Product (A) of an Unsuccessful Preparation of $PCl_3Br^+ BCl_4^-$

cm^{-1}			Partial Assignment
81	(7)		
90	(5)		
119	(6)		
129	(6)		
145	(6)	sh.	
151	(7)		
156	(7)		ν_5 (e) PCl_3Br^+
176	(9)		
179	(7)	sh.	
193	(6)	sh.	ν_2 (e) BCl_4^{-} [a]
200	(8)		
208	(10)		
216	(7)		ν_3 (a_1) PCl_3Br^+
235	(6)		ν_5 (e) PCl_3Br^+
242	(5)		ν_1 (a_1) PBr_4^+
259	(4)		ν_4 (t_2) PCl_4^+
281	(4)		ν_4 (t_2) BCl_4^{-} [a]
301	(7)		
345	(7)		
391	(6)		ν_2 (a_1) PCl_3Br^+
410	(3)		ν_1 (a_1) BCl_4^{-} [a]
455	(1)		ν_1 (a_1) PCl_4^+
493	(2)		ν_3 (t_2) PBr_4^+
504	(1)		
521	(1)		
583	(1)		ν_1 (a_1) PCl_3Br^+
600	(1)		
634	(1)		
643	(1)		ν_4 (e) PCl_3Br^+

Figures in parentheses are relative intensities on scale 0 - 10.

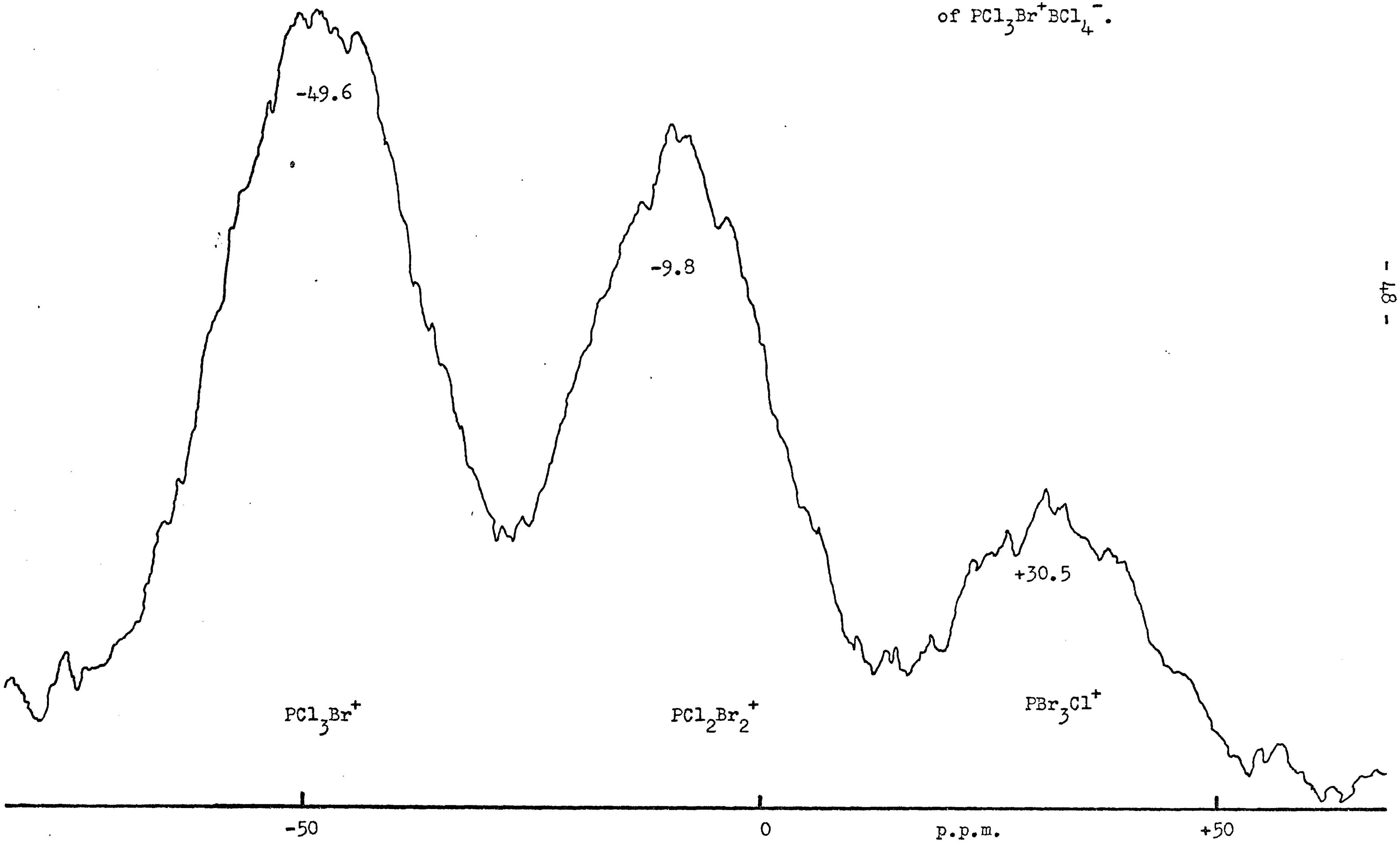
sh. - shoulder.

a. reference 92.

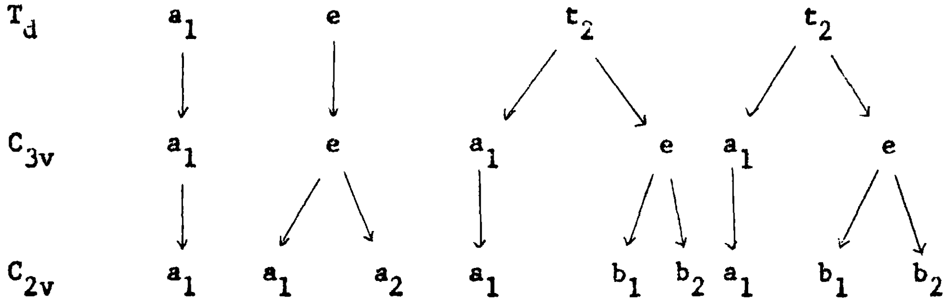
The ^{31}P n.m.r. spectrum of A, presented in Figure 12, indicates three ^{31}P n.m.r. chemical shifts at -49.6, -9.8 and +30.5 p.p.m. (relative to 85% H_3PO_4) (99). The ^{31}P n.m.r. shift at -49.6 p.p.m. has previously been assigned to the PCl_3Br^+ ion in $PCl_3Br^+\ BCl_4^-$ (Section 1.2.2.i.). The ^{31}P shifts at -9.8 and + 30.5 p.p.m. correspond closely with values predicted for the $PCl_2Br_2^+$ and PBr_3Cl^+ ions, respectively, by interpolation between the ^{31}P chemical shifts for PCl_4^+ in PCl_5 (-88.3 ± 0.5 p.p.m.) and PBr_4^+ in PBr_5 (+ 104 ± 1 p.p.m.)(104). Thus solid-state Raman and ^{31}P n.m.r. spectra indicate the presence, mainly, of the following ions in A: PCl_3Br^+; $PCl_2Br_2^+$; PBr_3Cl^+; and BCl_4^-. The number of Raman bands expected for the $PCl_2Br_2^+$ (9) and the PBr_3Cl^+ (6) ions (Appendix A) corresponds well with the number of unassigned bands in the Raman spectrum of A (16).

A number of preparations yielded solids whose Raman spectra were similar to the Raman spectrum of A with respect to frequency. The intensity of the Raman bands, however, varied from compound to compound. A study of the Raman spectra of these compounds indicated that the bands do not vary independently with respect to intensity but can be grouped together according to whether they increase or decrease relative to one another. In this way the unassigned bands in the Raman spectrum of A can be divided into two groups at (i) 129, 145, 179, 200, 208, 345, 521, 600 and 634 cm^{-1} and at (ii) 119, 151, 176, 301 and 504 cm^{-1}. These two groups of bands can thus be assigned to the $PCl_2Br_2^+$ and the PBr_3Cl^+ ions, respectively. Assignment of these vibrational frequencies to the fundamental modes of the $PCl_2Br_2^+$ and PBr_3Cl^+ ions (in the presence

FIGURE 12. The Solid-State ^{31}P N.M.R. Spectrum of the Product (A) of an Unsuccessful Preparation of $PCl_3Br^+BCl_4^-$.



of a polyatomic anion only) was then carried out by analogy with the isoelectronic $SiCl_2Br_2$ and $SiBr_3Cl$ (Section 1.2.1.i., 98). Reduction from the T_d (PCl_4^+, PBr_4^+, $SiCl_4$, $SiBr_4$) to the C_{3v} (PCl_3Br^+, PBr_3Cl^+, $SiCl_3Br$, $SiBr_3Cl$) and finally to the C_{2v} ($PCl_2Br_2^+$, $SiCl_2Br_2$) point groups results in the following pattern of splittings (101).



All of the fundamental vibrational frequencies for the $PCl_2Br_2^+$ and the PBr_3Cl^+ ions are active in the Raman and most (except for the a_2 mode of $PCl_2Br_2^+$) are active in the infrared (Appendix A).

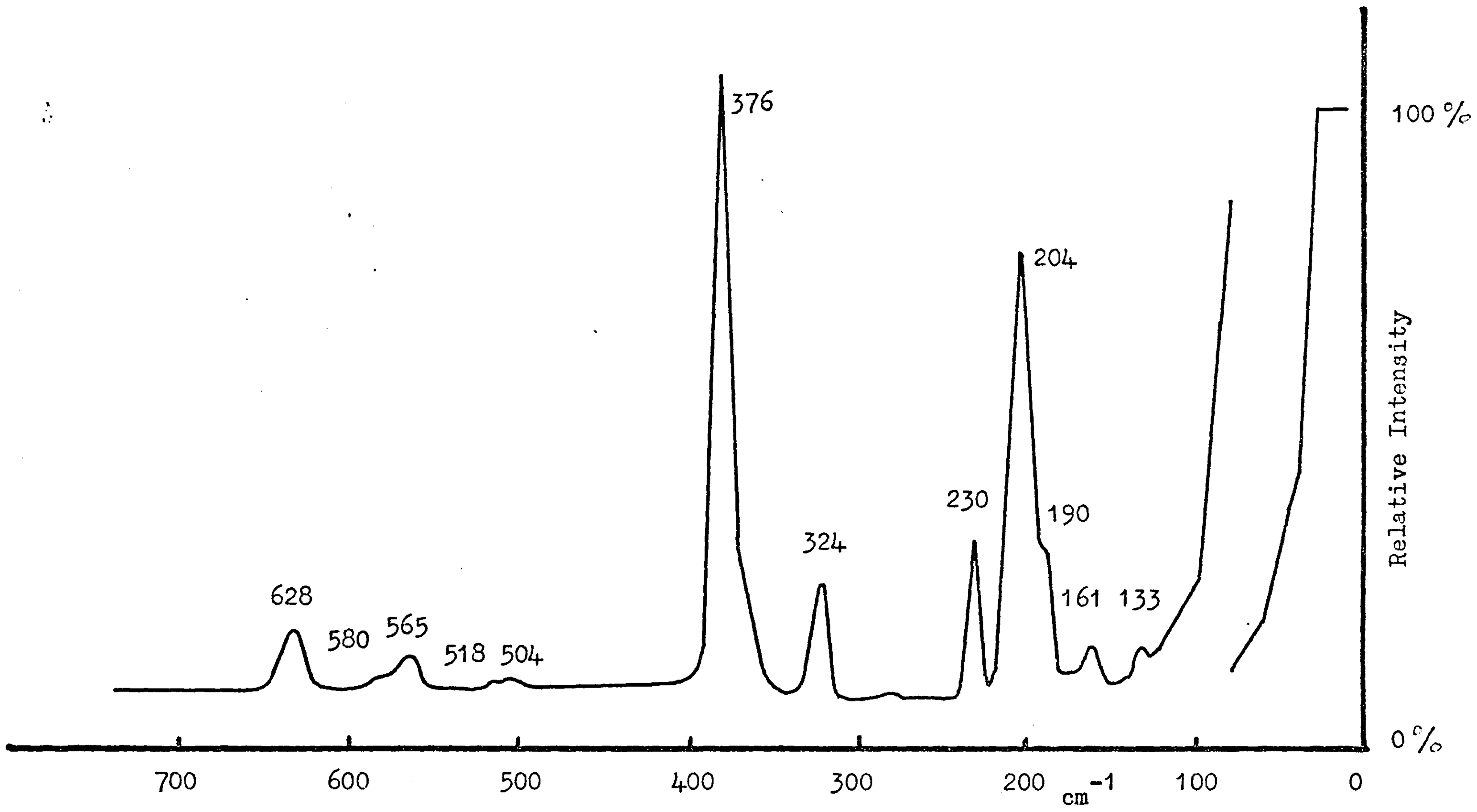
In Table 10, the $PCl_2Br_2^+$ and PBr_3Cl^+ ions (in the presence of a polyatomic anion only) are listed and compared with the isoelectronic $SiCl_2Br_2$ and $SiBr_3Cl$ species. Assignments for the PCl_4^+ ion (in PCl_4^+ PCl_6^-), the PCl_3Br^+ ion (in PCl_3Br^+ BCl_4^-) and the PBr_4^+ ion (in PBr_4^+ BBr_4^-) are also incldded.

The solid-state Raman spectrum of the product (B) from the addition, in order, of boron trichloride, phosphorus trichloride and bromine to dichloromethane is presented in Figure 13. The simplicity of the Raman spectrum suggested a pure compound.

TABLE 10. Assignment and Comparison of the Fundamental Vibrational Frequencies of the $PCl_2Br_2^+$ and PBr_3Cl^+ ions in the Presence of a Polyatomic Anion Only (Cm^{-1})

	a_1	e		t_2			t_2		
PCl_4^+	456	177		656			250		
($SiCl_4$)	(424)	(150)		(610)			(221)		
	↓	↓		↙	↘		↙	↘	
	a_1	e		a_1	e		a_1	e	
PCl_3Br^+	391	156		582	648		214	232	
($SiCl_3Br$)	(368)	(135)		(545)	(610)		(191)	(205)	
	↓	↙	↘	↓	↙	↘	↓	↙	↘
	a_1	a_1	a_2	a_1	b_1	b_2	a_1	b_1	b_2
$PCl_2Br_2^+$	345	129	145	600	521	634	200	179	208
($SiCl_2Br_2$)	(326)	(111)	(122)	(563)	(508)	(605)	(182)	(174)	(191)
	↓	↘	↙	↓	↘	↙	↓	↘	↙
	a_1	e		a_1	e		a_1	e	
PBr_3Cl^+	301	119		-	504		151	176	
($SiBr_3Cl$)	(288)	(101)		(579)	(498)		(159)	(173)	
	↓	↓		↘	↙		↘	↙	
	a_1	e		t_2			t_2		
PBr_4^+	252	104		499			149		
($SiBr_4$)	(249)	(90)		(487)			(137)		

FIGURE 13. The Solid-State Raman Spectrum of the Product (B) from the Addition of Boron Trichloride, Phosphorus Trichloride and Bromine to Dichloromethane.



Total elemental analysis, however, did not indicate a simple stoichiometry but a P:Cl:Br:B ratio of 1.7:7.9:3.0:1.0. ^{31}P n.m.r. spectroscopy showed one ^{31}P chemical shift at −41.8 p.p.m.(relative to 80% H_3PO_4) (99) indicating the PCl_3Br^+ ion.

Comparison of the bands (positions and intensities) assigned to the PCl_3Br^+ ion in the Raman spectrum of P_2Cl_9Br (Section 1.2.2.ii.) with a number of bands in the Raman spectrum of B strongly supports the presence of the PCl_3Br^+ ion in B.

Vibrational Frequencies of the PCl_3Br^+ Ion (cm^{-1})

	ν_1 (a_1)	$\nu_2(a_1)$	$\nu_3(a_1)$	$\nu_4(e)$	$\nu_4(e)$	$\nu_4(e)$
in P_2Cl_9Br	568	365	203	626	230	158
in B	565	376	204	628	230	161

There is strong evidence for the presence of single halide ions in P_2Cl_9Br (Section 1.2.2.ii.). The close correspondence between the bands assigned to the PCl_3Br^+ ion in the Raman spectra of P_2Cl_9Br and B thus indicates the presence of single halide ions in B. Elemental analysis for B indicates a phosphorus to boron ratio of 1.7 : 1.0. For formulations containing polyatomic anions only (i.e.) equal amounts of tetrahalophosphonium and tetrahaloborate ions; e.g. PCl_3Br^+, $PCl_2Br_2^+$ and 2 BCl_4^- etc.), the ratio would be 1:1.

The solid-state infrared spectrum of B (above 200 cm^{-1}) showed bands at 204, 231 and 368 cm^{-1} indicative of the PCl_3Br^+ ion. The bands, however, at 565 and 628 cm^{-1} (in the Raman) expected in the infrared for the PCl_3Br^+ ion are obscured by a very broad and intense band covering the 500-700 cm^{-1} region. The BCl_4^- anion has a very broad infrared band in the 500-700 cm^{-1} region. ^{11}B n.m.r. spectroscopy indicates one ^{11}B chemical shift at + 14.7 p.p.m. (measured relative to $B(OMe)_3$)close to the ^{11}B chemical shift for $Me_4N^+BCl_4^-$ (+12.1 ± 1 p.p.m.) (99).

The solid-state Raman spectrum of the product (C) of a reaction similar to that for B is presented in Figure 14 and Table 11. Elemental analysis indicates a Cl:Br:B ratio of 7.3: 2.9: 1.0 (calculating phosphorus by difference the P:Cl:Br:B ratio would be 1.7: 7.3: 2.9: 1.0). A number of weak bands in the Raman spectrum can be assigned to the PCl_4^+, PBr_4^+, PCl_3Br^+ (both in the presence of halide and polyatomic anions) and BCl_4^- ions. The bands at 160, 200, 230, 373, 567 and 629 cm^{-1} have been assigned, above,to the PCl_3Br^+ ion in the presence of a single halide ion. The band at 200 cm^{-1}, however, is too intense relative to the other PCl_3Br^+ bands to be accounted for entirely by this ion.

In the present work, the solid-state Raman spectra of a large number of compounds, prepared by reactions (1), (2), (3) and (4), were found to be similar to that of C with respect to the position of bands. The intensities of the Raman bands, however, varied from compound to compound. Solid-state ^{31}P n.m.r. spectra of a

FIGURE 14. The Solid-State Raman Spectrum of the Product (C) from the Reaction of Phosphorus Trichloride, Bromine and Boron Trichloride in Dichloromethane.

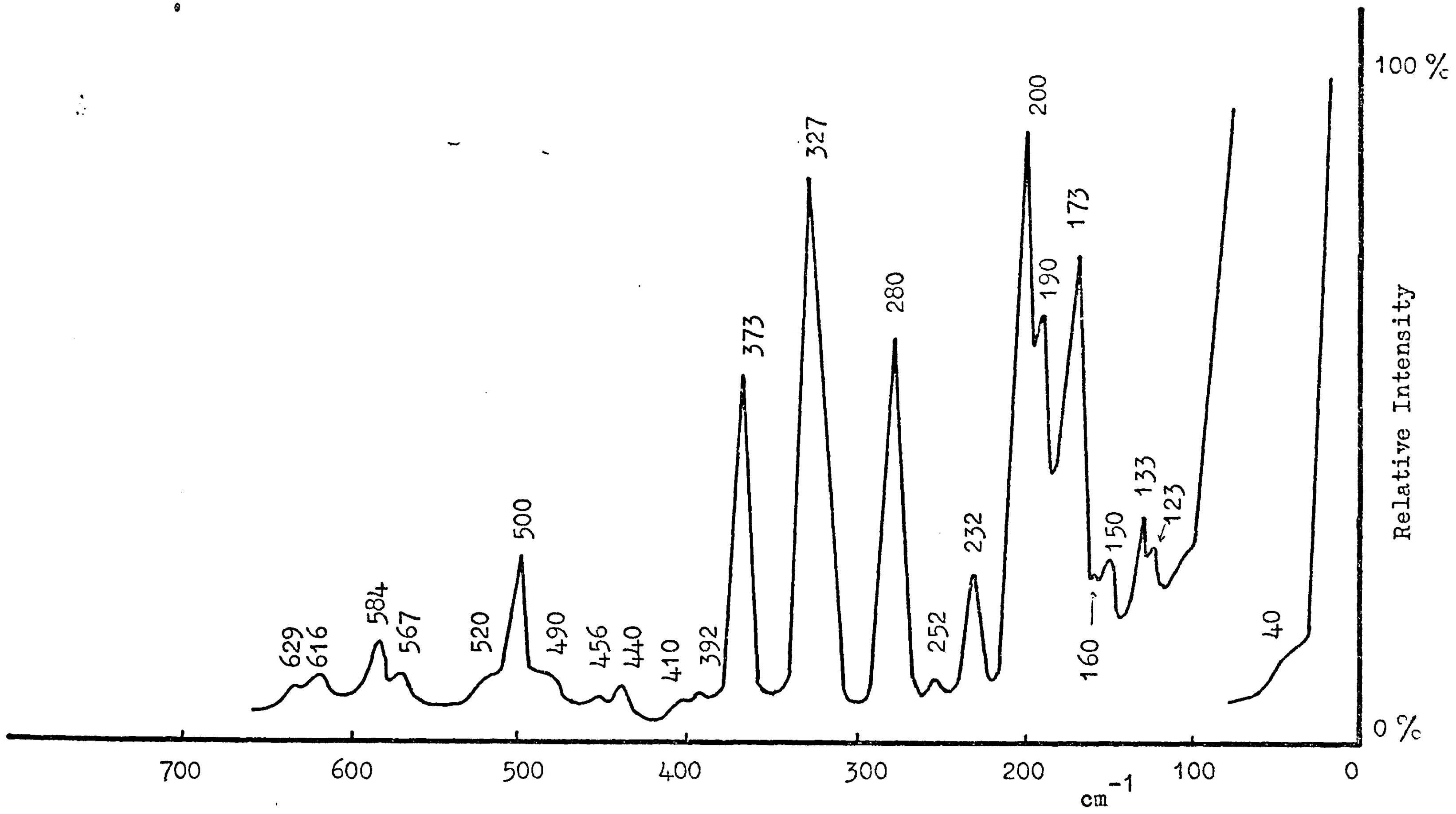


TABLE 11. The Solid-State Raman Spectrum of the Product (C) From the Reaction of Phosphorus Trichloride, Bromine and Boron Trichloride in Dichloromethane

cm^{-1}	Partial Assignment
40	
123 (3)	
133 (4)	
150 (3.5)	
160 (3)	$\nu_6(e)$ PCl_3Br^+
173 (9)	
190 (8)	
200 (10)	$\nu_3(a_1)$ PCl_3Br^+
232 (3.5)	$\nu_5(e)$ PCl_3Br^+
252 (1)	$\nu_4(t_2)$ PCl_4^+
280 (7.5)	
327 (10)	
373 (7)	$\nu_2(a_1)$ PCl_3Br^+
392 (0.5)	$\nu_2(a_1)$ PCl_3Br^+ (polyatomic anion)
410 (0.0)	$\nu_1(a_1)$ BCl_4^-
440 (0.5)	$\nu_1(a_1)$ PCl_4^+
456 (0.0)	$\nu_1(a_1)$ PCl_4^+ (polyatomic anion)
490 (0.5)	$\nu_3(t_2)$ PBr_4^+ (polyatomic anion)
500 (3)	
520 (0.5)	
567 (0.3)	$\nu_1(a_1)$ PCl_3Br^+
584 (1.5)	
616 (1)	
629 (0.5)	$\nu_4(e)$ PCl_3Br^+

Figures in parentheses are relative intensities on scale 0-10. Unless otherwise stated, assignments for phosphonium ions are in the presence of single halide ions.

number of these compounds indicated the presence of all three chlorobromophosphonium ions. The ^{31}P n.m.r. spectrum of a compound whose Raman spectrum is similar to C, is presented in Figure 15.

Thus solid-state Raman and ^{31}P n.m.r.spectra indicate the presence of the PCl_3Br^+, $PCl_2Br_2^+$ and PBr_3Cl^+ ions, together with single halide ions, in C. A study of the Raman spectra of the compounds referred to above indicated that the intensities of the bands do not vary independently but can be grouped together according to whether they increase or decrease relative to one another. In the same way, as for compound A, it was possible to divide the unassigned bands in the Raman spectrum of C into two groups at (i) 133, 150, 173, 190, 200, 327, 520, 584 and 616 cm^{-1} and (ii) 123, 150,173, 280, 500, and 584 cm^{-1}. These two groups of bands are assignable, on the basis of position and intensity, to the $PCl_2Br_2^+$ and PBr_3Cl^+ ions, respectively.

The $PCl_2Br_2^+$ and PBr_3Cl^+ ions, in the presence of single halide ions, are assigned in Table 12 by analogy with the isoelectronic $SiCl_2Br_2$ and $SiBr_3Cl$ (98) and compared with assignments for the PCl_4^+ ion (in metastable PCl_5), the PCl_3Br^+ ion (in B) and the PBr_4^+ ion (in $PBr_4^+ Br^-$).

Thus it appears that the $PCl_2Br_2^+$ and PBr_3Cl^+ ions, together with the PCl_4^+, PBr_3Cl^+ and PBr_4^+ ions, may be assigned two sets of fundamental vibrational frequencies depending upon the presence of either (i) polyatomic anions only (e.g. BCl_4^-, BBr_4^- etc) or (ii) single halide ions (Cl^- or Br^-).

FIGURE 15. The Solid-State ^{31}P N.M.R. Spectrum of a Compound whose Raman Spectrum is similar to that of C.

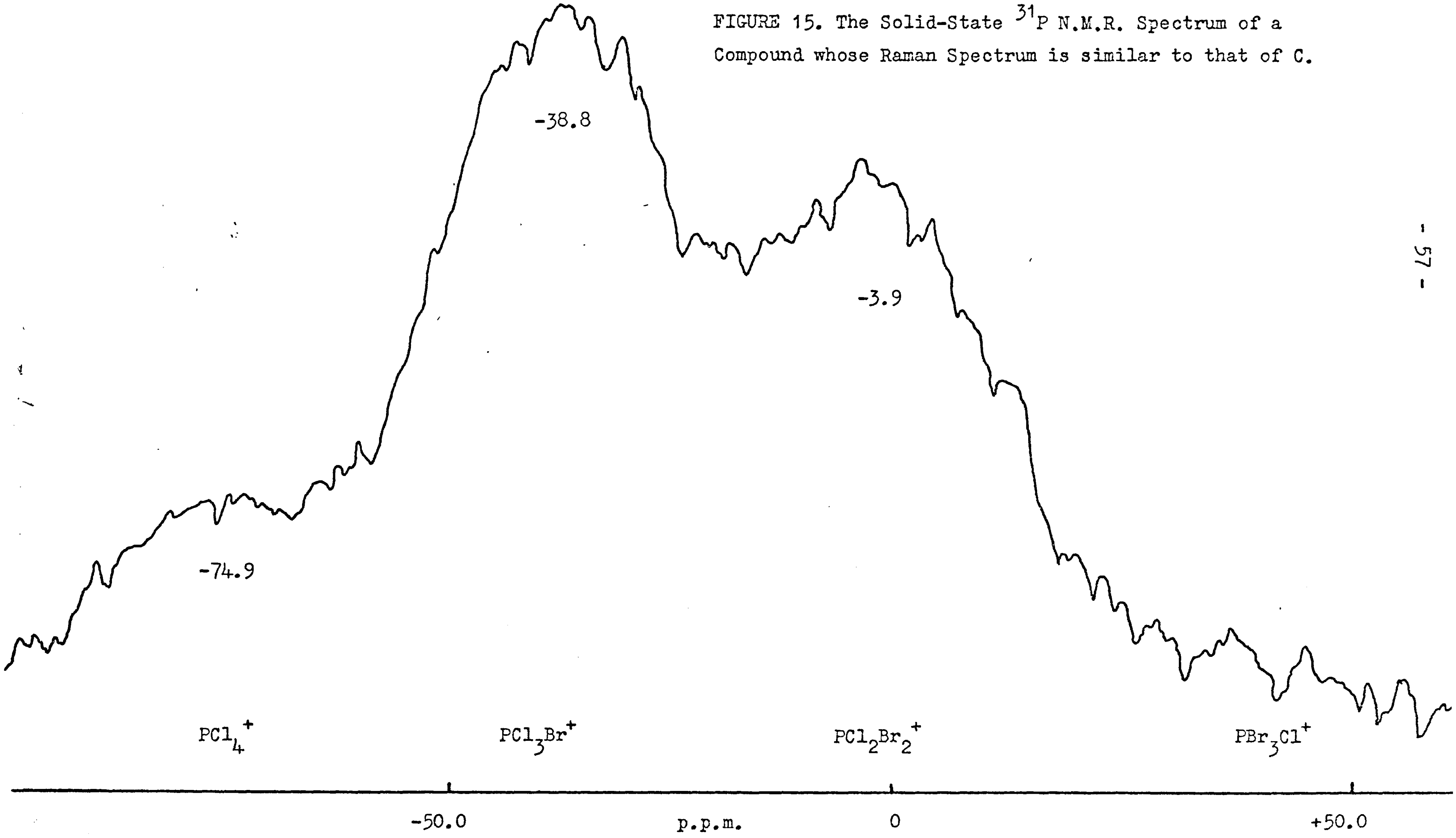


TABLE 12. Assignment and Comparison of the Fundamental Vibrational Frequencies of the $PCl_2Br_2^+$ and PBr_3Cl^+ ions in the Presence of Single Halide Ions (cm^{-1})

	a_1	e		t_2			t_2		
PCl_4^+	442	185		639			245		
($SiCl_4$)	(424)	(150)		(610)			(221)		
	↓	↓		↙	↘		↙	↘	
	a_1	e		a_1	e		a_1	e	
PCl_3Br^+	376	161		565	628		204	230	
($SiCl_3Br$)	(368)	(135)		(545)	(610)		(191)	(205)	
	↓	↙	↘	↓	↙	↘	↓	↙	↘
	a_1	a_1	a_2	a_1	b_1	b_2	a_1	b_1	b_2
$PCl_2Br_2^+$	327	133	150	584	520	616	190	173	200
($SiCl_2Br_2$)	(326)	(111)	(122)	(563)	(508)	(605)	(182)	(174)	(191)
	↓	↘	↙	↓	↘	↙	↓	↘	↙
	a_1	e		a_1	e		a_1	e	
PBr_3Cl^+	280	123		584	500		150	173	
($SiBr_3Cl$)	(288)	(101)		(579)	(498)		(159)	(173)	
	↓	↓		↘	↙		↘	↙	
	a_1	e		t_2			t_2		
PBr_4^+	229	72		~476			~145		
($SiBr_4$)	(249)	(90)		(487)			(137)		

1.2.4. Other Compounds

1.2.4.i. The Compound "PCl_3Br_4"

It has been suggested (5) that compounds of the general formula $PCl_3\ (Br_2)_n$ (n = 1 - 10) may be formulated as $PCl_3Br^+\ Br^-(Br_2)_{n-1}$. In an attempt to prepare a compound containing the PCl_3Br^+ ion, the compound of stoichiometry PCl_3Br_4 was investigated. Preparation was attempted by the method of Fialkov and Kuzmenko (79), i.e. the direct addition of bromine to phosphorus trichloride. The solid product was sublimed at room temperature, yielding a red crystalline sublimate and a yellow residue.

Neutral hydrolysis of the red crystalline sublimate indicated the release of free bromine. As a consequence, the hydrolysate was tested for chloride, bromide and free bromine with the following results:

% Phosphorus	% Chloride	% Bromide	% Free Bromine	% Total Bromine
5.3	17.1	26.2	50.4	76.6

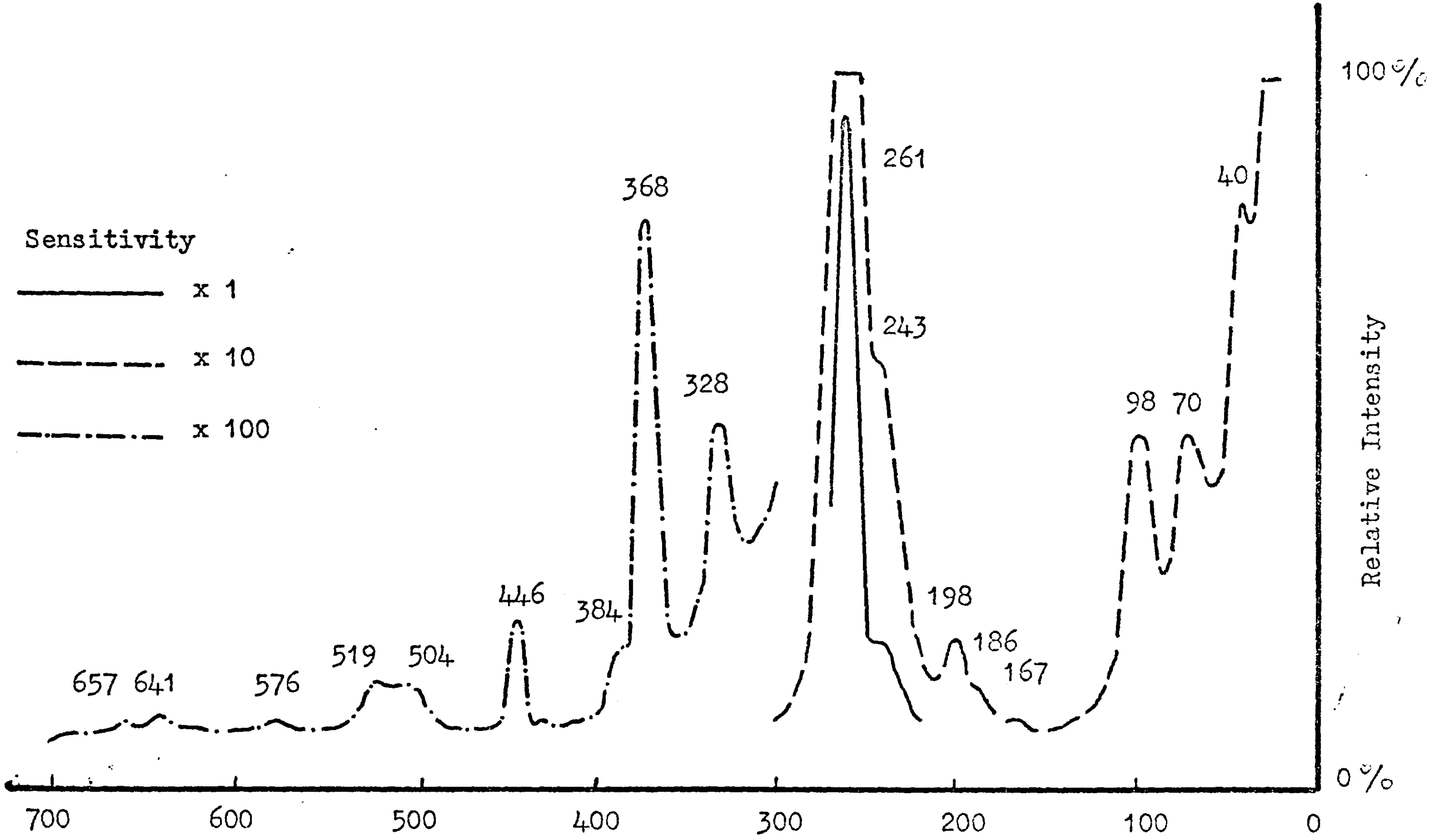
These results do not correspond to the expected analysis figures for PCl_3Br_4 (calc. for PCl_3Br_4 : P, 6.8; Cl, 23.2; Br, 70.0%). The above figures indicate the stoichiometry PCl_3Br_6. Further, the Cl^-: Br^- ratio is exactly 3:2 and the (free) bromine to bromide ratio is 1:1, indicating a formulation $PCl_3Br^+\ Br^-\ (Br_2)_2$.

The solid-state Raman spectra of the compound of stoichiometry PCl_3Br_6, presented in Figure 16, does not indicate the $PCl_3Br^+Br^-\ (Br_2)_2$ formulation. Bands in the Raman at 167, 198, 368, 576 and 641 cm^{-1} are assignable to the PCl_3Br^+ ion. There are, however, bands at (i) 186, 328 and 519 cm^{-1} and at (ii) 446, and 657, assignable to the $PCl_2Br_2^+$ and PCl_4^+ ions, respectively. The very intense band at 261 cm^{-1} is probably assignable to the polybromide ion. It was not, possible, however, to prepare a compound containing the Br_5^- ion (i.e. Br^- $(Br_2)_2$) in order to confirm its presence in PCl_3Br_6 by comparison of Raman spectra.

The solid-state Raman spectra of a number of preparations of PCl_3Br_6, by direct reaction of Br_2 and PCl_3, were identical to the original presented above. Further, preparation of PCl_3Br_6 by addition of bromine to phosphorus trichloride (in a 2:1 mole ratio) in liquid anhydrous hydrogen chloride at ca. -96°C. yielded a compound whose solid-state Raman spectrum was also identical to that of the original PCl_3Br_6 (Figure 16).

The solid-state Raman spectrum of yellow residue, from the sublimation of the solid product of the addition of Br_2 to PCl_3, identified it as P_2Cl_9Br (Section 1.2.2.ii.). Total halogen analysis confirmed this.

FIGURE 16. The Solid-State Raman Spectrum of the Compound of Stoichiometry PCl_3Br_6.



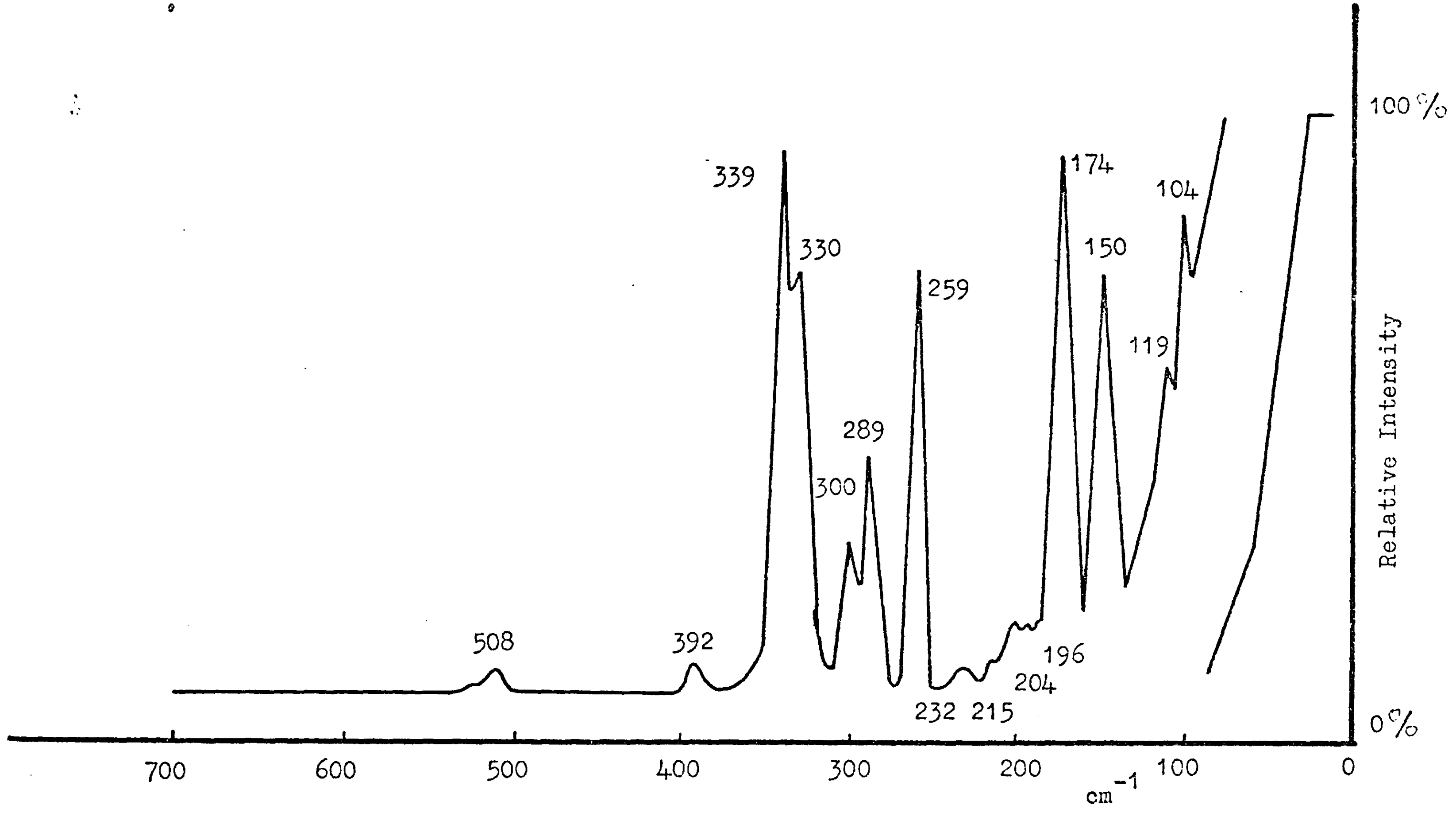
1.2.4.ii. The Compound of Stoichiometry $PSbCl_7Br_3$

It was proposed (72) that the addition of phosphorus tribromide to antimony pentachloride (in a 1:2 mole ratio) yielded the compound of stoichiometry $PSbCl_7Br_3$. A possible formulation for $PSbCl_7Br_3$ is $PBr_3Cl^+SbCl_6^-$. The above preparation was investigated as a possible source of the PBr_3Cl^+ ion.

Total elemental analysis of the product from the addition of PBr_3 to $SbCl_5$ in dichloromethane indicated the stoichiometry $PSbCl_7Br_3$. The solid-state Raman spectrum is presented in Figure 17. The presence of the $SbCl_6^-$ anion is indicated by bands at 174, 289, and 330/339 cm^{-1} (6). The band at 174 cm^{-1}, however, is too intense to be accounted for entirely by this ion. Bands at 119, 150, 174, 300 and 508 cm^{-1} indicate the presence of the PBr_3Cl^+ ion; however, the PBr_3Cl^+ ion does not entirely explain the intensities of the bands at 150 and 174 cm^{-1}. A number of weak bands indicate the presence of the PCl_3Br^+ ion (215, 232 and 392 cm^{-1}) and the $PCl_2Br_2^+$ ion (196 and 204 cm^{-1}). The intense band at 259 cm^{-1}, together with the bands at 104, 150, and 508 cm^{-1}, are characteristic of the PBr_4^+ ion in the presence of a polyatomic anion only.

The Raman spectra of a number of preparations of $PSbCl_7Br_3$ were identical to that above. Thus, solid-state Raman spectroscopy does not indicate the formulation $PBr_3Cl^+ SbCl_6^-$ for the compound of stoichiometry $PSbCl_7Br_3$.

FIGURE 17. The Solid-State Raman Spectrum of the Compound of Stoichiometry $PSbCl_7Br_3$.



SECTION 2 - THE HALIDES OF ANTIMONY(V)

2.1. Introduction

A number of reviews concerning the chemistry of the halides of antimony (3, 4, 5, 6, 106) have been published recently. For the purposes of Section 2, the term "halide" refers to chloride and bromide only. In this section, the chlorobromoantimonate anions, $Sb^{V}Cl_nBr_{6-n}^-$ (n = 0 to 6) will be discussed.

The hexachloroantimonate ion, $SbCl_6^-$, has been identified in a number of complexes; e.g. $PCl_4^+ SbCl_6^-$, $Et_4N^+ SbCl_6^-$, $CH_3CO^+ SbCl_6^-$ etc.(6). In contrast, until recently the hexabromoantimonate ion, $SbBr_6^-$, was thought to exist only as a polybromide ion of tripositive antimony (i.e. $Sb^{III}Br_4^- Br_2$, 107, 108) and chlorobromoantimonates were not thought to exist at all (5, 106).

Recently, (109) the compound prepared by the addition of tetraethylammonium bromide, bromine and antimony tribromide in concentrated hydrobromic acid was shown, by X-ray studies, to be of the form $Et_4N^+ SbBr_6^-$. Infrared and Raman spectroscopy confirm this (110). The preparation and vibrational spectra of the compounds $CH_3CO^+ SbCl_5Br^-$ (111), $Et_4N^+ SbCl_5Br^-$, $Et_4N^+ SbCl_3Br_3^-$, and $Et_4N^+ SbClBr_5^-$ (110) have also been reported recently.

2.2. RESULTS AND DISCUSSION

2.2.1. The Hexabromoantimonate Ion ($SbBr_6^-$)

The addition of Et_4N Br to $SbBr_3$ and bromine in dichloromethane gave a deep red solid. Elemental analysis for bromine was consistent with the stoichiometry Et_4N $SbBr_6$. The solid-state Raman spectrum is presented in Figure 18 and the solid-state Raman and infrared frequencies are listed in Table 13.

The proposed formulation Et_4N^+ $SbBr_4^-$, Br_2 (107, 108) is not indicated by comparison with solid-state Raman data for Bu_4N^+ $SbBr_4^-$ (Bu = C_4H_9, 112). The simplicity of the Raman and infrared spectra and the absence of coincident bands strongly indicates an octahedral $SbBr_6^-$ ion and hence the formulation Et_4N^+ $SbBr_6^-$; results agree well with those of Adams and Downs (110).

A similar preparation using Bu_4NBr yielded a deep red solid. Elemental analysis for bromine was consistent with Bu_4N Sb Br_6. Three Raman bands (at 195, 169 and 157 cm^{-1}) suggest the presence of an octahedral Sb Br_6^- ion.

FIGURE 18. The Solid-State Raman Spectrum of the Compound of Stoichiometry Et_4NSbBr_6.

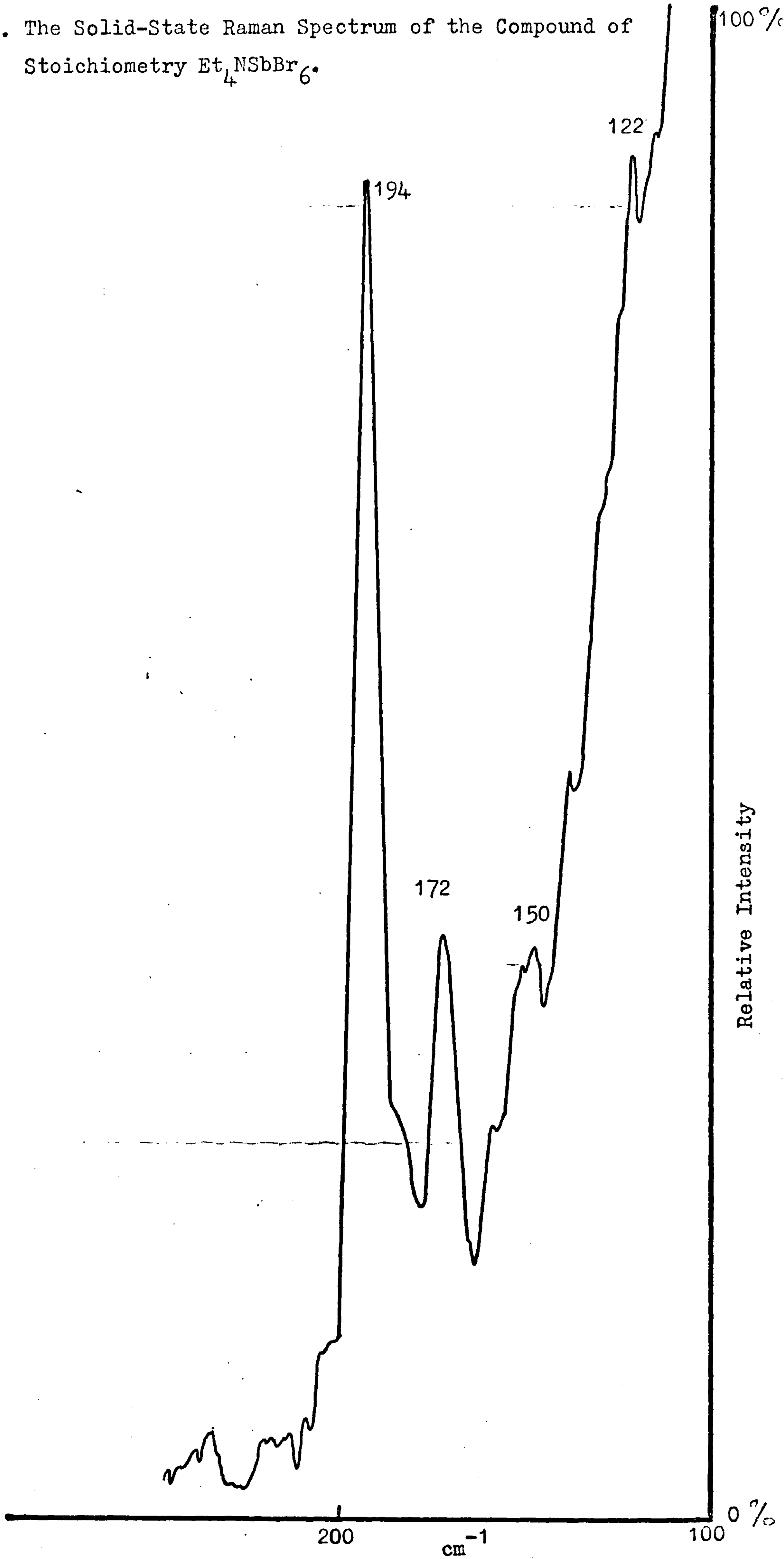


TABLE 13. The Solid-State Raman and Infrared Spectrum of Et_4N^+ $SbBr_6^-$ (cm^{-1})

Raman	Infrared	Assignment[b]
	118[a]	ν_4 (t_{1u}) $SbBr_6^-$
122 w		ν_5 (t_{2g}) $SbBr_6^-$
150 w		
172 m		ν_2 (e_g) $SbBr_6^-$
	177 s	
	180 s	
194 s		ν_1 (a_{1g}) $SbBr_6^-$
	224 s)) 235 s)	ν_3 (t_{1u}) $SbBr_6^-$

w - weak, m - medium, s - strong.

a - determined by interferometric methods

b - reference 110.

2.2.2. The Pentachlorobromoantimonate Ion ($SbCl_5Br^-$)

2.2.2.i. The Compound of Stoichiometry $Et_4N\ SbCl_5Br$

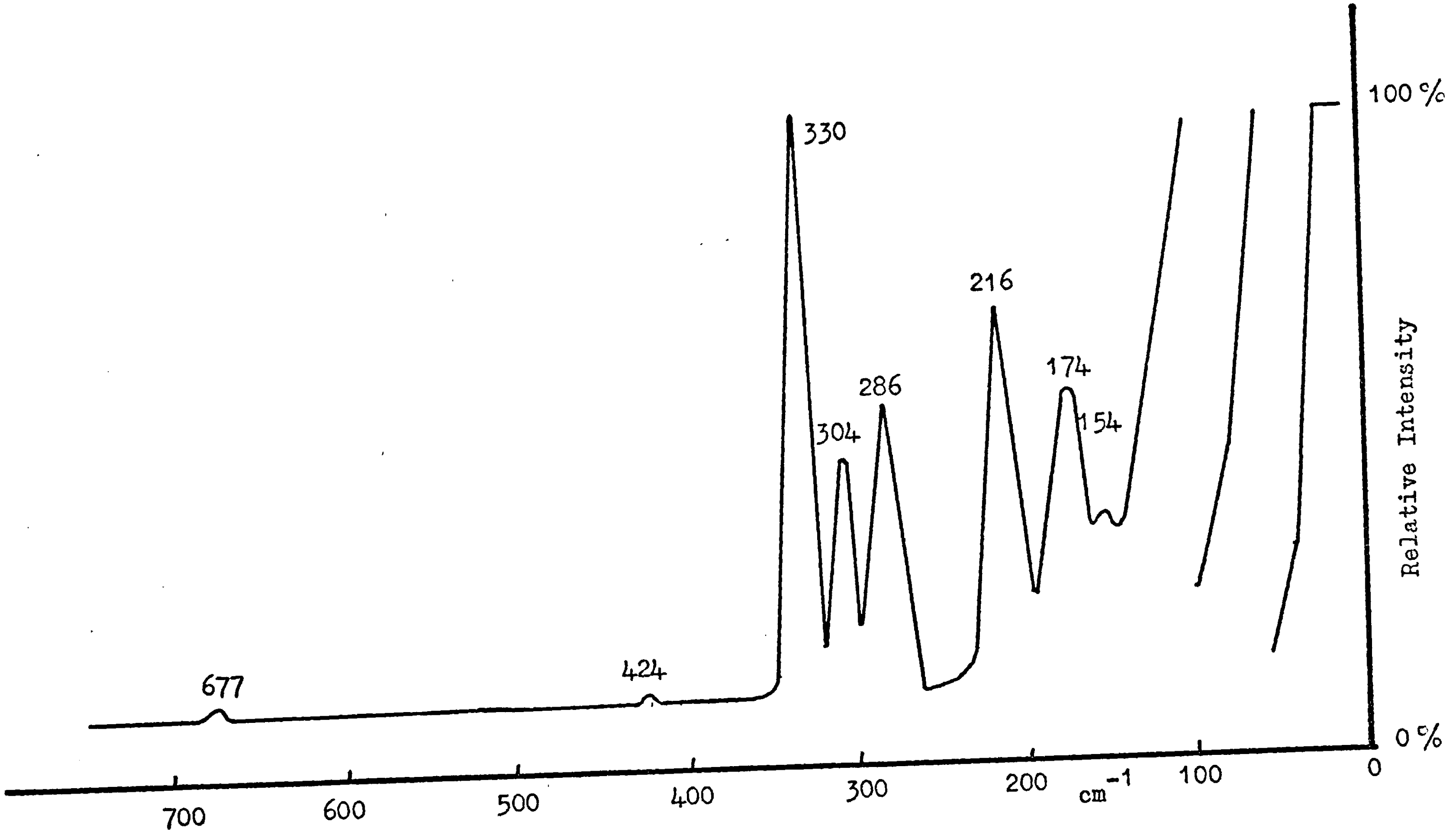
The addition of $Et_4N\ Br$ to $SbCl_5$ in dichloromethane yielded a yellow solid (A). Elemental analyses for antimony, chlorine and bromine were consistent with the stoichiometry $Et_4N\ SbCl_5Br$. The solid-state Raman spectrum is presented in Figure 19. Comparison with the Raman spectrum of $Et_4N^+Br^-$ (with bands at 426 and 682 cm^{-1}) indicates the presence of the Et_4N^+ ion and the formulation $Et_4N^+\ SbCl_5Br^-$.

Chlorobromoantimonates (e.g. $SbCl_5Br^-$), however, were thought not to exist (5, 106). Under conditions when the complex, $Et_4N^+\ SbCl_5Br^-$, should be produced (e.g. as above) a study of the X-Ray diagrams indicated a 5:1 mixture of $Et_4N^+SbCl_6^-$ and $Et_4N^+\ SbBr_6^-$.

Evidence, however, to support the existence of $Et_4N^+\ SbCl_5Br^-$ as a discrete chemical compound and not a 5:1 mixture of $Et_4N^+\ SbCl_6^-$ and $Et_4N^+\ SbBr_6^-$ has been obtained from (i) Raman spectroscopy, (ii) X-Ray powder photography and (iii) differential scanning calorimetry.

$Et_4N^+\ SbCl_6^-$ (white solid) and $Et_4N^+\ SbBr_6$ (deep red solid) were mixed lightly (in a 5:1 mole ratio) to give a pinkish solid (B) which was compared with the compound of stoichiometry $Et_4N\ SbCl_5Br$ (A). The absence of a band at 194 cm^{-1} in the Raman spectrum of A, assigned to the $SbBr_6^-$ ion (Section 2.2.1.) and clearly present in the Raman spectrum of B, did not support the formulation of $Et_4N\ SbCl_5Br$ as a 5:1 mixture of $Et_4N^+SbCl_6^-$ and $Et_4N^+\ SbBr_6^-$. Further, a number of bands (at 154, 216, and 304 cm^{-1}) in the Raman spectrum of A were not present in that of B. Comparison

FIGURE 19. The Solid-State Raman Spectrum of the Compound of Stoichiometry Et_4NSbCl_5Br (A).



of the X-Ray powder photographs for A and B also did not indicate that $Et_4N\ SbCl_5Br$ was a 5:1 mixture of $Et_4N^+SbCl_6^-$ and $Et_4N^+SbCl_6^-$.

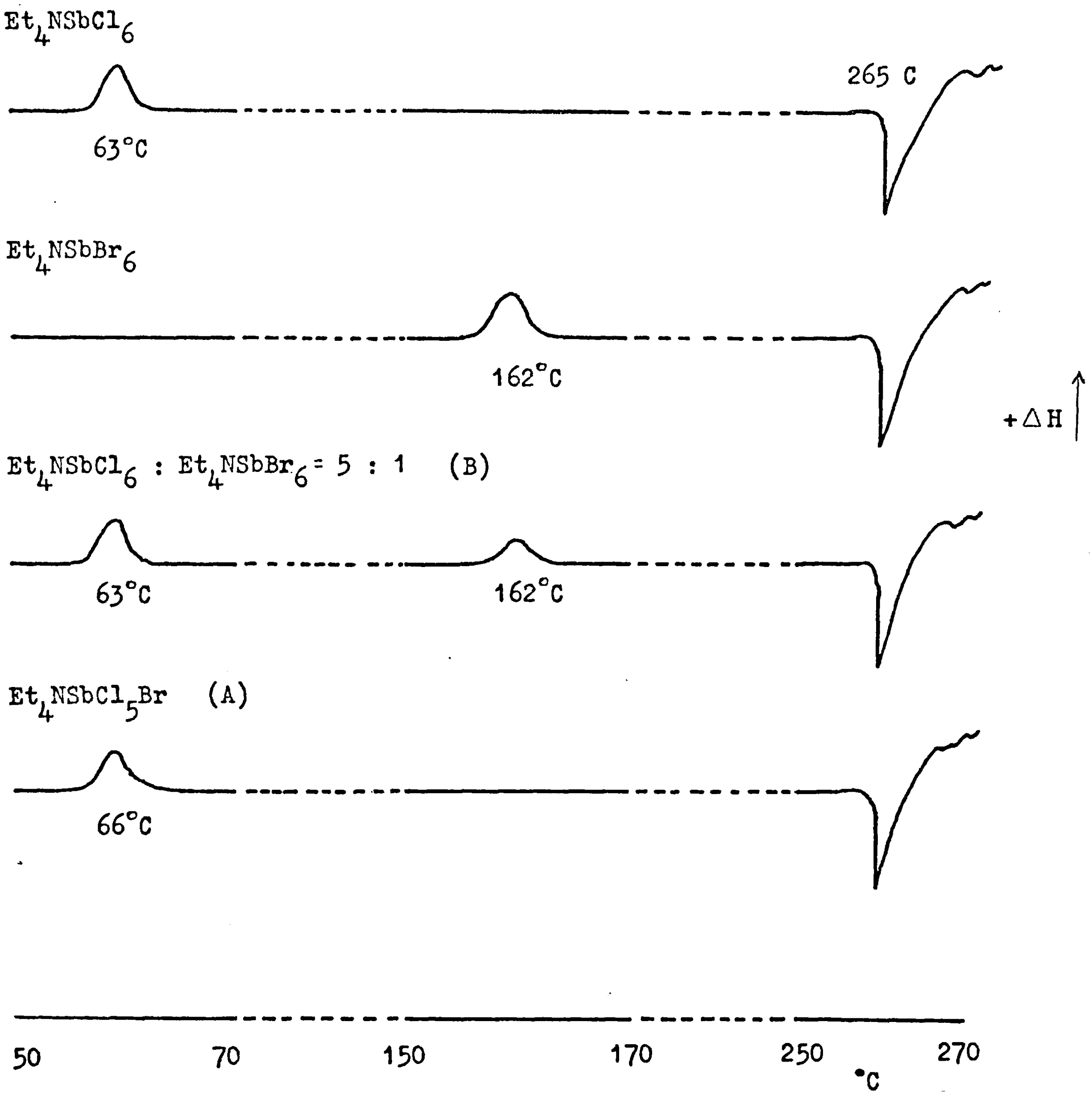
Differential scanning calorimetric results for $Et_4N\ SbCl_6$, $Et_4N\ SbBr_6$, B and A are represented diagrammatically in Figure 20. Results for $Et_4N\ SbCl_6$, $Et_4N\ SbBr_6$ and $Et_4N\ SbCl_5Br$ are detailed below:

Compound	Transition Temperature (°K)	Enthalpy of Transition kJ mole^{-1}
$Et_4N\ SbCl_6$	336° ± 1° (63° ± 1°C.)	18.0 ± 0.4
$Et_4N\ SbBr_6$	435° ± 1° (162° ± 1°C.)	30.1 ± 0.4
$Et_4N\ SbCl_5Br$	339° ± 1° (66° ± 1°C)	18.4 ± 0.4

The thermograms of $Et_4N\ SbCl_6$ and $Et_4N\ SbBr_6$ both indicate only one endothermic transition at 63°C. and 162°C., respectively. It is reasonable to assume that on first running the 5:1 mixture (B) the low temperature peak at 63°C. can be attributed to $Et_4N\ SbCl_6$ and the high temperature peak at 162°C. to $Et_4N\ SbBr_6$. Comparison of the thermogram of A. (with only one endothermic transition at 66°C.) with that of B does not support the 5:1 mixture formulation.

Re-running the 5:1 mixture (B) indicated only one endothermic transition, in the d.s.c. thermogram, at ~65°C. Further, the solid-state Raman spectrum of a sample of B heated to 120°C. for two hours was not the same as that of an unheated sample. The

FIGURE 20. Differential Scanning Calorimetry.



Raman spectrum of the heated sample, with bands at 171, 220, 292, 308 and 334 cm^{-1}, was identical to that for $Et_4N\ SbCl_5Br$. A distinct colour change from the pink colour of the 5:1 mixture to yellow, the colour of $Et_4N\ SbCl_5Br$, accompanied heating. Thus evidence suggests that a 5:1 mixture of $Et_4N^+SbCl_6^-$ and $Et_4N^+\ SbBr_6^-$ reacts in the solid-state to give $Et_4N\ SbCl_5Br$.

Reaction, in the solid-state, to produce $Et_4N\ SbCl_5Br$ is also indicated by Raman spectroscopy when $Et_4N^+SbCl_6^-$ and $Et_4N^+\ SbBr_6^-$ (in a 5:1 mole ratio) are mixed either by grinding or in a ball-mill. Thus observations on a 5:1 mixture prepared in this way would have similar results to those for a sample of $Et_4N\ SbCl_5Br$. This may provide a possible explanation of Kolditz' X-Ray results (5,106). The X-Ray powder diagram for a sample of $Et_4N\ SbCl_5Br$, prepared as above, would be identical to that for a 5:1 mixture of $Et_4N^+\ SbCl_6^-$ and $Et_4N^+\ SbBr_6^-$ mixed thoroughly (e.g. in a ball-mill.).

It was possible to resolve a number of bands in the solid-state Raman spectrum of $Et_4N^+\ SbCl_5Br^-$(113) and results are presented, and compared with those of Goetz et al (111) and Adams and Downs (110), in Table 14. Results agree well with those expected for an octahedral ion of C_{4v} symmetry. All eleven fundamental vibrational frequencies for an octahedral $SbCl_5Br^-$ ion are Raman active. Four Sb-Cl stretching frequencies, one Sb-Br stretching frequency and six deformation frequencies are expected in the Raman (Appendix B).

TABLE 14. The Solid-State Raman Spectrum of $Et_4N^+ SbCl_5Br^- (cm^{-1})$

This Work	Goetz et al[a]	Adams and Downs[b]	Assignment[b]
		73 w	Deformation and possible lattice modes
		80 w	
		85 w	
114 w	110 w	108 mw	
146 w	142 v.s.		
159 w		156 m	
171	170 sh.		
176 m		178 mw.sh.	
184	186 v.s.		
210 m.sh.	210 sh.		Sb-Br stretching
		215 v.s.	
220 s			
	230 s		
289 s	290 s	284 m	Sb-Cl stretching
308 s	310 m	304 v.s.	
320 w			
333 v.s.	334 v.s.	331 s	
		340 sh.	

w - weak, m - medium, sh - shoulder, s - strong, v.s. - very strong, m.w. - medium weak

a - reference 111 (June 1970), b - reference 110 (August 1971)

This work (May 1971).

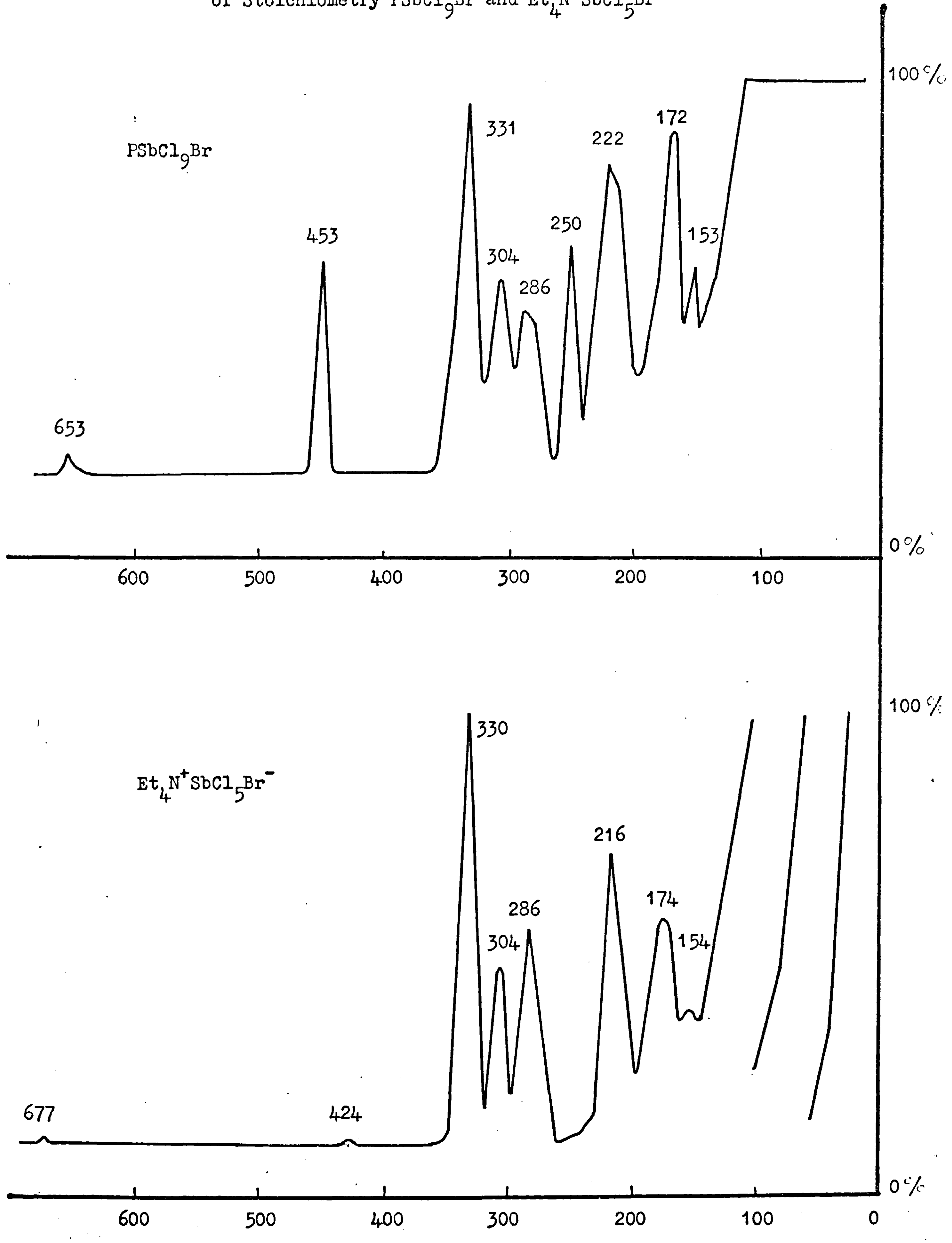
2.2.2.ii. The Compound of Stoichiometry $PSbCl_9Br$

The addition of PCl_3, Br_2 and BCl_3 in liquid HCl at ca.-96°C. yields, under certain conditions, the compound PCl_3Br^+ BCl_4^- (Section 1.2.2.i.). In an attempt to prepare the alternative source of the PCl_3Br^+ ion, PCl_3Br^+ $SbCl_6^-$, $SbCl_5$ and not BCl_3 was added.

Antimony pentachloride ($SbCl_5$) was added to Br_2 and PCl_3 in liquid HCl at ca.-96°C. On warming to room temperature the excess solvent evaporated leaving a yellow solid. Total elemental analysis indicated the expected stoichiometry, $PSbCl_9Br$.

The absence of bands at 214, 232, 391 and 582 cm^{-1}, (assigned to the PCl_3Br^+ ion in $PCl_3Br^+BCl_4^-$) in the solid-state Raman spectrum did not indicate the formulation PCl_3Br^+ $SbCl_6^-$. Comparison, however, with the solid-state Raman spectrum of Et_4N^+ $SbCl_5Br^-$, Figure 21, indicates the presence of the $SbCl_5Br^-$ ion and the formulation PCl_4^+ $SbCl_5$ Br^-. The bands at 250, 453 and 653 cm^{-1} in the Raman spectrum of $PSbCl_9Br$ agree well in both position and intensity with bands expected for the PCl_4^+ ion (e.g. by comparison with the Raman spectrum of PCl_4^+ PCl_6^-, Figure 2). ^{31}P n.m.r. spectroscopy shows one ^{31}P chemical shift at -80.0 ± 1 p.p.m. (relative to 85% H_3 PO_4) (99) indicative of the PCl_4^+ ion. Thus solid-state Raman and ^{31}P n.m.r. spectroscopy strongly suggest the formulation PCl_4^+ $SbCl_5Br^-$ for the compound of stoichiometry $PSbCl_9Br$.

FIGURE 21. Comparison of the Solid-State Raman Spectra of the Compound of Stoichiometry $PSbCl_9Br$ and $Et_4N^+SbCl_5Br^-$



2.2.3. Other Antimony Compounds

The compounds of stoichiometry $Et_4N\ SbCl_4Br_2$, $Et_4N\ SbCl_3Br_3$ and $Et_4N\ SbBr_5Cl$ were prepared for the following general reaction:

$$Sb\ X_3 + Br_2 + Et_4N\ Y \text{ in } CH_2Cl_2\ (X,\ Y = Br_1Cl)$$

Elemental analysis for chlorine and bromine indicated the above stoichiometries. The solid-state Raman spectra are presented below:

$Et_4N\ SbCl_4Br_2$ (cm^{-1})	$Et_4N\ SbCl_3Br_3$ (cm^{-1})	$Et_4N\ SbBr_5Cl$ (cm^{-1})
156 w	137 w	139 w
172 m	172 m	172 w
180 m	182 m	184 m
	195 m	194 s
	208 m.sh.	208 m.
218 v.s.	219 v.s.	
287 m	286 m	
305 m	304 m	
332 s	331 m	

All of the above bands, except for that at ∿195 cm^{-1} are present in the Raman spectrum of $Et_4N^+\ SbCl_5Br^-$. The band at ∿195 cm^{-1} has been assigned previously to the $SbBr_6^-$ anion. Thus Raman evidence indicates that these three compounds are mixtures of $Et_4N^+SbCl_5Br^-$ and $Et_4N^+\ SbBr_6^-$.

Adams and Downs (110), however, suggested the formulations $Et_4N^+ SbCl_3Br_3^-$ and $Et_4N^+ SbBr_5Cl^-$ for $Et_4N SbCl_3Br_3$ and $Et_4N SbBr_5Cl$, in the solid-state and in solution, from a study of both the Raman and the infrared spectra. Solid-state Raman data for $Et_4N SbCl_3Br_3$ and $Et_4N SbBr_5Cl$ presented above agrees well with that of Adams and Downs.

SECTION 3 - EXPERIMENTAL

3.1. SYNTHESIS

3.1.1. Materials

Reagents of the best available commercial grade were used, generally without further purification. Dichloromethane (May and Baker Laboratory Reagent) was dried over $CaCl_2$ and fractionally distilled according to the method of Mathews (115).

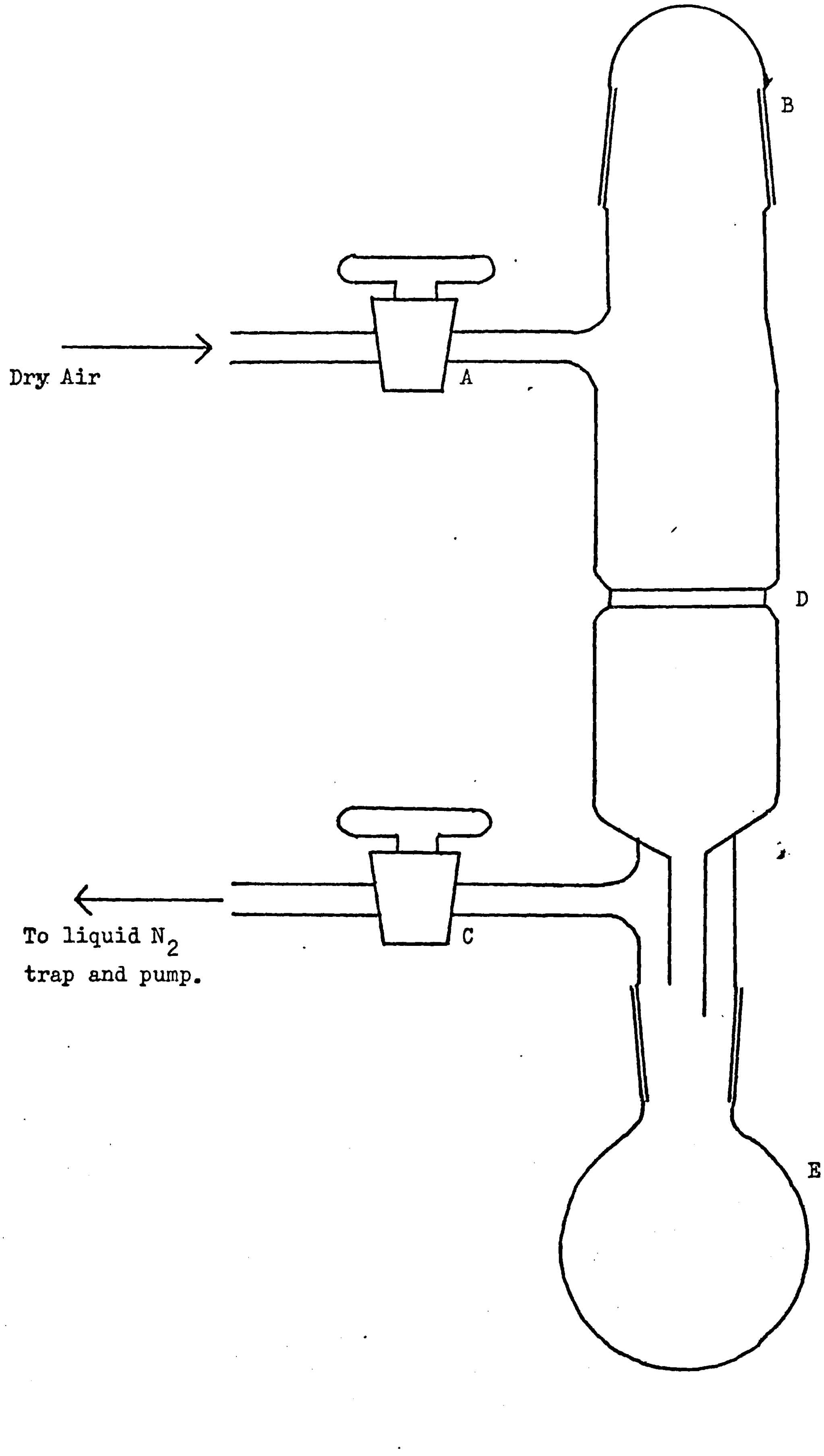
3.1.2. Apparatus and Procedure

3.1.2.i. Reactions in Dichloromethane (CH_2Cl_2)

Reactions were carried out by the addition, with stirring, of CH_2Cl_2 solutions of reactants under anhydrous conditions. The resultant precipitate was filtered and dried using the apparatus described in Figure 22.

Before use, the filtration apparatus was thoroughly dried in an oven at 130°C. and left to cool under vacuum. Dry air was introduced through the stopcock, A, and the CH_2Cl_2 solution and the precipitate were quickly poured into the top, B, of the apparatus. With stopcock A closed, the apparatus was evacuated through stopcock C. When all the filtrate had been pulled through the glass sinter, D, stopcock C to the pump was closed and dry air was introduced through stopcock A. The flask, E, was then replaced by an empty flask to prevent CH_2Cl_2 being pulled over under vacuum into the liquid N_2 trap. The precipitate was then dried under vacuum.

FIGURE 22. Filtration Apparatus for Reactions in Dichloromethane.



3.1.2.ii. Reactions in Liquid Hydrogen Chloride

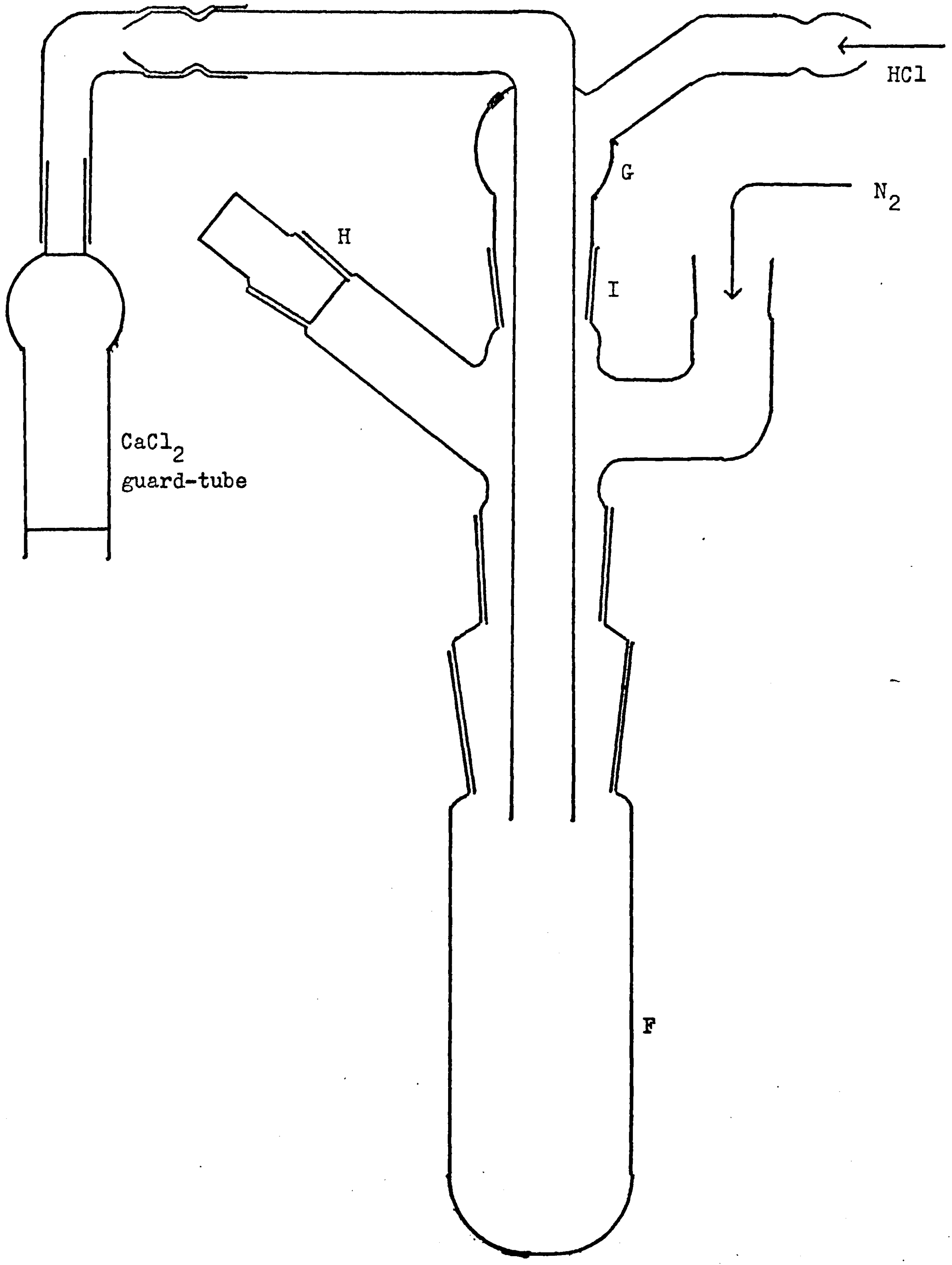
Hydrogen chloride gas was generated by the addition of concentrated hydrochloric acid to concentrated sulphuric acid. Concentrated hydrochloric acid (~ 150 ml.) in a pressure-equalising dropping funnel was added slowly, with stirring, to concentrated sulphuric acid (~ 300 ml.) in a 3-necked flask. The HCl gas evolved was then passed through two traps; the first containing concentrated sulphuric acid to remove water; and the second, an empty splash trap, to remove traces of sulphuric acid carried over.

The reaction vessel (Figure 23) was dried thoroughly in an oven at 130°C. and cooled by flushing with dry nitrogen. HCl gas was then condensed into the reaction flask, F, at ca. -196°C. The reaction vessel, was then flushed vigorously with dry nitrogen while the trap head, G, was replaced by a $CaCl_2$ guard tube. The flow-rate of dry nitrogen was then adjusted to give a very slight excess pressure within the reaction vessel.

The HCl was liquefied using a toluene slush bath (ca.-96°C.). It was found advisable to use a wide-necked dewar for the slush bath to facilitate stirring and removal of any toluene which solidifies initially on the outer walls of the reaction flask.

Solid reactants were introduced into the reaction flask before HCl was condensed in. BCl_3 and $B Br_3$, from ampoules, were added to the liquid HCl through the side neck, H, of the multiple adaptor. Other liquids were added from weight pipettes through the central neck, I, of the multiple adaptor when the stopper in the side

FIGURE 23. Reaction Vessel for Reactions in Liquid Hydrogen Chloride.



neck, H, had been replaced by a $CaCl_2$ guard tube.

When all the reactants had been added, excess solvent was evaporated by allowing the reaction vessel to warm to room temperature. Solid residues were then pumped for ca. 30 minutes.

3.1.3. Preparations

3.1.3.i. $PB\ Br_8$

PBr_5 (14.02 g., 0.033 mol.) in CH_2Cl_2 ($\sim$50 ml.) was added to $B\ Br_3$ (8.34 g., 0.033 mol.) also in CH_2Cl_2 ($\sim$50 ml.). The resultant yellow precipitate was filtered and dried under vacuum. (Found : Br, 93.0; Calc for $PB\ Br_8$; Br, 94.0%).

3.1.3.ii. $Et_4N\ B\ Br_4$

$Et_4N\ B\ Br_4$ was peepared according to the method of Waddington and White (51). Hydrogen bromide was used as solvent and the procedure was similar to that for hydrogen chloride preparations.

$Et_4N\ Br$ (5.19 g; 0.025 mol.) was weighed into a reaction vessel and hydrogen bromide (Matheson lecture bottle) was condensed in at ca. -196°C. The HBr was liquefied using a slush bath at ca.-84°C. (ethyl acetate) and $B\ Br_3$ (6.20 g; 0.025 mol.) added. Evaporation of the solvent left a white solid (Found: Br, 69.3; Calc. for $Et_4N\ B\ Br_4$: Br, 69.4%).

3.1.3.iii. $Et_4N^+ PCl_6^-$

In an early attempt to prepare $Et_4N^+ PCl_5Br^-$, a CH_2Cl_2 solution of Et_4N Br was added to PCl_5 also in CH_2Cl_2. A white precipitate was formed. Total halogen analysis (expressed as mg. sample/ 1 ml. 0.1N $ClgNO_3$), indicated the stoichiometry $Et_4N\ PCl_6$ (Found: 6.22; Calc for $Et_4N\ PCl_6$: 6.23; Calc for $Et_4N\ PCl_5Br$: 6.97 mg.ml.$^{-1}$). All the bands in the solid state Raman spectrum can be explained by the formulation $Et_4N^+ PCl_6^-$.

3.1.3.iv. $PCl_4^+ BCl_4^-$

PCl_5 (10.60 g, 0.051 mol.) was dissolved, with stirring in CH_2Cl_2. To this BCl_3 (6.97 g., 0.060 mol.) in CH_2Cl_2 was added. The white precipitate, which formed immediately, was filtered and dried under vacuum. (Found: P, 9.5; B, 3.4; Cl, 86.9; Calc. for $P\ B\ Cl_8$; P, 9.5; B, 3.3; Cl, 87.2%).

3.1.3.v. $Me_4N^+ BCl_4^-$

$Me_4N\ BCl_4$ was prepared according to the method of Waddington and Klanberg (114). Me_4N Cl was dried under vacuum at 40°C. and a weighed amount (4.20 g., 0.038 mol.) placed in the reaction vessel. HCl was condensed in and liquefied. BCl_3 (4.50 g., 0.038 mol.) was added and the excess solvent evaporated. A white solid remained and was pumped for ca. 30 minutes. (Found: Cl, 62.3; Calc. for $Me_4N\ BCl_4$; Cl, 62.5%).

3.1.3.vi. Metastable PCl_5

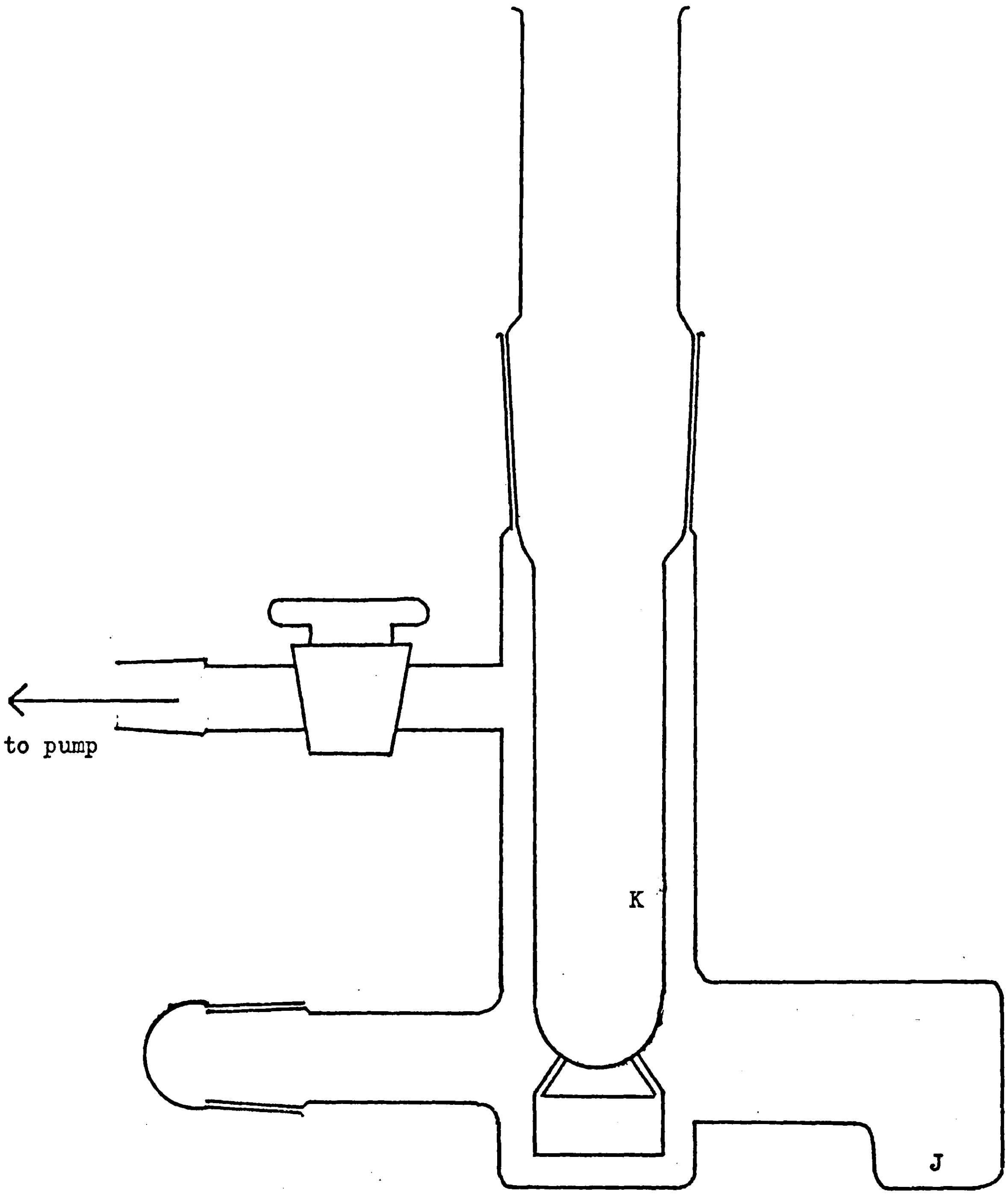
The sublimation apparatus for the production of the metastable PCl_5 is detailed in Figure 24. Normal PCl_5 was crushed, placed in the apparatus at J, and sublimed at room temperature onto the cold finger, K, (at ca. -78°C). Of the four attempts to prepare metastable PCl_5 by sublimation, only one was successful.

Preparation of metastable PCl_5 by the addition of Br_2 to PCl_5 in CH_2Cl_2 was found to be more successful and more convenient for the preparation of large amounts Br_2(3.0 g., 0.019 mol.) in CH_2Cl_2 was added to a CH_2Cl_2 solution of PCl_5 (4.2 g., 0.020 mol.). A white solid was precipitated out and was filtered and dried under vacuum (Found: Cl, 84.2; Calc.for PCl_5: Cl, 85.1%).

3.1.3.vii. PCl_4F

Initially, PCl_2F was prepared according to the method of Booth and Bozarth (116). PCl_3 (87.9 g., 0.640 mol.) and $SbCl_5$ ($\sim$1 ml. catalyst) were refluxed at 40°C. and 240 m.m. pressure. SbF_3(178.8 g., 0.705 mol.) was added over a period of three hours and the gaseous products (PF_3, $PClF_2$, PCl_2F and some PCl_3) collected in a trap at ca. -196°C. Purification was by low temperature vacuum fractionation. PCl_2F and PCl_3 were retained by a -125°C. trap (methylcyclohexane) and PCl_3 was retained by a trap at -96°C. (tolvene).

FIGURE 24. Sublimation Apparatus for the Preparation of Metastable PCl_5.



Excess chlorine (as indicated by a green coloration) was added to PCl_2F at ca. -78°C. A white solid (Initial Product) and a large amount of green liquid resulted. The white solid was isolated by pumping off the green liquid into a further trap at ca.-196°C. (Found: Cl, 77.9; Calc for PCl_4F, 74.0%).

The green liquid was left at room temperature for 3 days and yielded a white solid (Final Product). (Found: P,16.0; Cl, 74.0; F, 9.7; Calc for PCl_4F; P, 16.1; Cl, 74.0; F,9.9%). Fluoride analyses on the hydrolysate indicated 3.8%, 4.2% and 3.0% F^- (Calc for $PCl_4^+ F^-$: 9.9%).

3.1.3.viii. $PCl_3Br^+BCl_4^-$

BCl_3, (3.70 g., 0.032 mol.), PCl_3 (3.89 g., 0.028 mol.) and Br_2 (4.00 g., 0.025 mol.), in that order, were added to liquid HCl at ca.-96°C. Evaporation of the solvent yielded a white solid. (Found: P, 8.2; Cl, 65.1; Br, 20.9; Calc for $PBCl_7Br$; P, 8.4; Cl, 67.1- Br, 21.6%, P:Cl:Br = 1.0:7.0:1.0).

3.1.3.ix. $PCl_3Br^+PF_6^-$

HCl, PCl_3 (2.37 g., 0.017 mol.) and Br_2 (2.50 g., 0.016 mol.) were distilled under vacuum into a reaction vessel fitted with a teflon stopcock at -196°C. They were liquefied to give a clear solution using a -96°C. slush bath. PF_5 was then distilled in under vacuum at -196°C.

PF_5 was produced from p - chlorobenzene-diazonium hexafluorophosphate (Phosfluorogen A, Ozark-Mahoning Company). Phosfluorogen A (~12 g) was dried by heating to 80°C. and pumping. It was then heated to 150°C. in an oil bath under vacuum and decomposed to give nitrogen, p - chlorofluorobenzene and PF_5. p - ClC_6H_4F and PF_5 were trapped at -196°C. and then fractionally distilled through a -78°C. trap, which retained the p - Cl C_6H_4F.

The teflon stopcock on the reaction vessel was then closed and the contents of the vessel liquefied using a -96°C. slush bath. The reaction vessel was detached from the vacuum line, fitted with a $CaCl_2$ guard tube and with the stopcock open was allowed to warm to room temperature. The excess solvent evaporated leaving a white solid which was pumped for ca. 30 minutes. (Found: P, 16.5; Cl, 28.5; Br, 23.2; F, 30.3; Calc for $P_2Cl_3Br F_6$; P, 17.1; Cl, 29.4; Br, 22.1; F, 31.4%).

3.1.3.x. $Et_4N^+ PF_6^-$

Excess PF_5, generated from phosfluorogen A, was distilled into a reaction vessel, fitted with a teflon stopcock, containing HCl and Et_4N Br at -196°C. With the stopcock closed, the whole was liquefied using a -96°C. slush bath. After detaching the reaction vessel from the vacuum line and fitting a $CaCl_2$ guard tube, the stopcock was opened and the solvent allowed to evaporate. All the bands in the Raman spectrum are consistent with the formulation $Et_4N^+ PF_6^-$.

3.1.3.xi. P_2Cl_9Br

Br_2 (19.20 g., 0.120 mol.) was added to PCl_3 (33.00 g., 0.240 mol.) in $AsCl_3$ (30 ml.) according to the method of Kolditz and Feltz (74). The yellow precipitate resulting was filtered and dried under vacuum (Found: Cl, 69.6; Br, 17.3; Calc for P_2Cl_9Br; Cl, 69.2; Br, 17.3%).

3.1.3.xii. The Product (A) of an Unsuccessful $PCl_3Br^+BCl_4^-$ Preparation

PCl_3 (6.76 g., 0.049 mol.), Br_2 (7.47 g., 0.047 mol.) and BCl_3 (6.50 g., 0.055 mol.), in that order, were added to liquid HCl at -96°C. A white residue was left on evaporation of the solvent. (Found: Cl, 54.2; Br, 35.6%).

3.1.3.xiii. The Product (B) from the Addition of Boron Trichloride, Phosphorus Trichloride and Bromine in Dichloromethane

A CH_2Cl_2 solution of Br_2 (5.47 g., 0.034 mol.) was added to a CH_2Cl_2 solution of BCl_3 (7.67 g., 0.065 mol.) and PCl_3 (7.35 mol., 0.054 mol.). The white precipitate was filtered and dried under vacuum. (Found: P, 8.9; Cl, 47.7; Br, 41.6; B, 1.8%, P:Cl:Br:B = 1.7:7.9:3.0:1.0).

3.1.3.xiv. The Product (C) of a Reaction Similar to that for B (3.1.3.xiii).

In this preparation, similar to that above, BCl_3(3.91 g., 0.033 mol.) was added to PCl_3 (4.60 g., 0.034 mol.) and Br_2 (5.23 g., 0.033 mol.) all in CH_2Cl_2. The resultant pale yellow precipitate was filtered and dried under vacuum. (Found: Cl, 46.5; Br, 42.4; B, 1.9%; calculating phosphorus by difference = 9.2%, P:Cl:Br:B = 1.7:7.3:2.9:1.0).

3.1.3.xv. PCl_3Br_6

a. Prepared by direct reaction of Br_2 and PCl_3.

Br_2 (27.00 g., 0.169 mol.) was added to PCl_3 (35 g., 0.255 mol.). Two layers were produced. The lower layer was cooled to ca.-78°C. and solidified. The upper layer, supernatant liquid, was decanted and the remaining solid sublimed using a water condenser, as cold finger, and a water pump. After 3 days, a large amount of red crystalline solid had collected in the condenser leaving a small amount of yellow powder. The solid-state Raman spectrum of the yellow powder indicated the compound P_2Cl_9Br. (Found for red solid: P, 5.1; Cl, 17.3; Br, 75.9; as bromide, 27.0, as free bromine, 48.9; Calc for PCl_3Br_6: P, 5.0; Cl, 17.3; Br, 77.7%. Found for yellow powder: total halide expressed a mg. sample/1 ml. 0.1N $AgNO_3$, 4.64; Calc for P_2Cl_9Br: 4.61 $mg.ml^{-1}$).

b. Prepared by the addition of Br_2 and PCl_3 to liquid HCl.

Br_2 (2.43 g., 0.015 mol.) and PCl_3 (2.20 g., 0.016 mol.) were added to liquid HCl to give a clear solution. A further amount of Br_2 (2.43 g., 0.015 mol.) was added and the solvent evaporated. The resultant red solid was pumped for ca. 15 minutes. (Found:P, 5.1; Cl 17.3; Br, 75.9, as bromide, 27.0, as free bromine, 48.9; Calc for PCl_3Br_6: P, 5.0; Cl, 17.2; Br, 77.7%).

3.1.3.xvi. $\underline{PSbCl_7Br_3}$

The compound of stoichiometry $PSbCl_7Br_3$ was prepared according to the method of Duff (72).

PBr_3 (2.8 g., 0.010 mol.) in CH_2 Cl_2 was added to $SbCl_5$ (6.6 g., 0.022 mol.) in CH_2Cl_2. The resultant pale yellow precipitate was filtered and dried under vacuum. (Found: P, 5.0; Sb, 19.9; Cl, 39.0; Br, 36.0; Calc for $PSbCl_7Br_3$: P, 4.8; Sb, 19.0; Cl, 38.8, Br, 37.4%).

3.1.3.xvii. $\underline{Et_4N\ SbBr_6}$

To a CH_2Cl_2 solution of $SbBr_3$ (4.15 g., 0.012 mol.) and Br_2 (1.60 g., 0.010 mol.) was added Et_4N Br (2.07 g., 0.010 mol.) in CH_2Cl_2. A deep red solid remained after filtration and drying under vacuum. (Found: Br, 64.9; Calc. for Et_4N $SbBr_6$: Br, 65.6%).

3.1.3.xviii. $Bu_4N\ SbBr_6$ $(Bu = C_4H_9)$

$Bu_4N\ Br$ (2.04 g., 0.006 mol.) in CH_2Cl_2 was added to $SbBr_3$ (3.15 g., 0.009 mol.) and Br_2 (1.80 g., 0.011 mol.) in CH_2Cl_2. The resultant deep red precipitate was filtered and dried under vacuum. (Found: Br, 56.4; Calc for $Bu_4N\ SbBr_6$, 56.8%).

3.1.3.xviv. $Et_4N\ SbCl_5Br$

To $Et_4N\ Br$ (4.77 g., 0.023 mol.) in CH_2Cl_2 was added $SbCl_5$ (6.80 g., 0.023 mol.) also in CH_2Cl_2. A yellow solid precipitated out and was filtered and dried under vacuum. (Found: Sb, 23.8; Cl, 34.9; Br, 15.7; Calc for $Et_4N\ SbCl_5Br$: Sb, 23.9; Cl, 34.8; Br, 15.7%).

3.1.3.xx. $PSbCl_9Br$

Br_2 (4.65 g., 0.029 mol.), PCl_3 (3.93 g., 0.029 mol.) and $SbCl_5$ (8.65 g., 0.029 mol.) were added to liquid HCl. Evaporation of the solvent left a yellow solid. (Found: P, 5.4; Sb, 22.4; Cl, 57.6; Br, 14.8; Calc for $PSbCl_9Br$: P,5.6; Sb, 22.1; Cl, 57.8; Br, 14.5%).

3.1.3.xxi. $Et_4N\ SbCl_4Br_2$, $Et_4N\ SbCl_3Br_2$ and $Et_4N\ SbBr_5Cl$

The appropriate tetraethylammonium halide in CH_2Cl_2 was added to bromine and the appropriate antimony trihalide. The resulting solids were filtered and dried under vacuum. Results are summarised below:

$SbCl_3$ (2.50 g., 0.011 mol.) + Br_2 (2.0 g., 0.013 mol.) + Et_4N Cl (1.47 g., 0.009 mol.) — Et_4N $SbCl_4Br_2$ - a yellow/orange solid. (Found: Cl, 25.8; Br, 29.0; Calc. for Et_4N $SbCl_4Br_2$; Cl, 25.6; Br, 28.9%).

$SbCl_3$ (2.93 g., 0.013 mol.) + Br_2(2.07 g., 0.013 mol.) + Et_4N Br (2.68 g, 0.013 mol.) — Et_4N $SbCl_3Br_3$ - an orange solid. (Found: Cl, 17.7; Br, 40.2; Calc for Et_4N 8b Cl_3Br_3; Cl, 17.8; Br, 40.1%).

$SbBr_3$ (4.05 g., 0.011 mol.) + Br_2 (2.10, 0.013 mol.) + Et_4N Cl (1.42 g., 0.009 mol.) — Et_4N Sb Br_5Cl - brick red solid. (Found: Cl, 5.1; Br, 57.3; Calc for Et_4N $SbBr_5Cl$; Cl, 5.2; Br, 58.2%).

3.1.4. Handling

With very few exceptions, reagents used and compounds prepared in this work were hygroscopic. Consequently, the transfer of reagents and compounds and the preparation of samples for infrared and Raman spectroscopy and elemental analysis was carried out in a glove box under an atmosphere of dry nitrogen. Compounds prepared were transferred from reaction flasks to glass sample tubes with polythene caps, sealed with "parafilm" (Gallenkamp) and stored in sealed glass jars lined with $CaCl_2$ at ca. 4°C.

3.2. ELEMENTAL ANALYSIS

3.2.1. Chlorine and Bromine

Weighed samples (~100 mg.) were hydrolysed in dilute alkaline solution in stoppered flasks. Total halide(chloride and bromide) and chloride were determined by the Volhard method and bromide found by difference. Two samples were used for each determination.

Chloride was determined after the removal of bromide by oxidation to bromine (with KlO_3 in acid solution) and boiling, according to the method of Andrews (117). The sample, calculated to contain 10-50 mg. of chloride was hydrolysed (in 50 ml. 0.IN NaOH) in a 500 ml. long-necked (~15 cm.) flask. Initially, 6 ml. of 0.2N KlO_3 and 17 ml. of 2N HNO_3 were added. Then for each gram of bromine expected 75 ml. of iodate solution and 7.5 ml. of nitric acid were added. The volume was made up to 250 ml. with distilled water and boiled down to a volume of 90 ml. 100 ml. of distilled water were then added and the solution boiled down again to 90 ml. The process was repeated until no more bromine was detected by testing the vapour with starch-iodide paper. While the solution was still hot, 1.5 ml. of 25% phosphorous acid was added to remove excess iodate. The solution was then boiled to remove iodine, keeping the volume above 90 ml. It was then cooled and chloride determined.

For compounds containing antimony, samples were digested in 1N NaOH (~50 ml.) and refluxed for 2 hours, before determination of halide by the Volhard method. This was found necessary when determination of halide in standard compounds gave low answers indicating incomplete hydrolysis.

Free bromine (in PCl_3Br_6, Section 1.2.4.i.) was determined by the addition of KI in acid solution followed by titration of the iodine released against 0.1N throsulphate solution using starch as indicator.

3.2.2. Boron

Boron was determined acidimetrically as the boric acid mannitol complex. Samples were hydrolysed in a mixture of methanol and water (90 ml. MeOH/10 ml.H_2O). A trace of concentrated sulphuric acid was added and the methyl borate distilled into water. The solution was then titrate to a methyl-orange end point. Excess mannitol was then added, (which forms a boric acid-mannitol complex) followed by titration against 0.1N NaOH using phenolphthalein.

3.2.3. Fluoride

A fluoride electrode (Model 96-09, Orion Research Inc., U.S.A.) in conjunction with a specific ion meter (Model 401, Orion Research Inc.) was used for analysis of fluoride. Samples of the compound of stoichiometry PCl_4F ($\sim$400 mg.) were hydrolysed in 10 ml. 0.1N NaOH. This was then made up to 25 ml. 5 ml. samples of the above solution and two standard fluoride solutions

(0.01 M and 0.001 M KF) were diluted 10:1 with a 4 M buffered potassium acetate solution of pH 5 and fluoride ion concentration determined.

Phosphorus and antimony were determined at a commercial laboratory elsewhere (Alfred Bernhardt, Mikroanalytisches Laboratorium, West Germany).

3.3. SPECTRA

3.3.1. Solid-State Raman Spectra

Solid-state Raman spectra were recorded with the following four instruments:-

1) Cary 81 spectrometer with either a Spectra-Physics Model 125 He-Ne Laser with excitation at 6328 Å (red) or a Coherent Radiation Laboratories Model 52K mixed Kr-Ar Laser with excitation at 6471 Å (Kr^+) (red).
2) Spex 1401 spectrometer with excitation at 6471 Å (red) provided by a Coherent Radiation Laboratories Model 52 ionised Kr Laser.
3) Coderg PHO spectrometer with a Spectra-Physics Model Model 125 He-Ne Laser with excitation at 6328 Å (red).
4) Jarrell-Ash (25-500) Laser Raman Spectrometer with excitation at 5145 Å (green) and 4880 Å (blue).

Samples were made up in sealed melting-point tubes. For the Cary 81 instrument, melting-point tubes with one end flattened were used.

3.3.2. Solid-State Infrared Spectra

Solid-state infrared spectra in the region 1000 to 200 cm^{-1} were recorded, using a Perkin-Elmer Model 325 Grating Infrared Spectrometer. Spectra below 200 cm^{-1} were recorded with the aid of a Grubb-Parsons "Cube" Interferometer. Samples were prepared as Nujol mulls pressed between CsI plates for the region 1000-200 cm^{-1} and polythenes plate below 200 cm^{-1}.

3.4. DIFFERENTIAL SCANNING CALORIMETRY

Details concerning the operation and capabilities of differential scanning calorimetry have been reported extensively elsewhere (e.g. 118, 119). In this work, the output was displayed on a chart recorder and typical thermograms are shown in Figures 3 and 20. The areas of the peaks obtained for milligram quantities of sample are directly proportional to transition enthalpies for the sample Calibration using standard samples allowed the absolute magnitudes of these enthalpies to be determined.

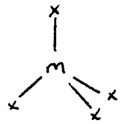
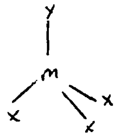
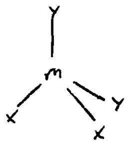
A Perkin-Elmer D.S.C. - 1B calorimeter with a Leeds and Northrup Speedomax w recorder was used. Peak areas were measured using a planimeter. Three readings were taken and averaged arithmetically. The instrument was calibrated using benzoic acid (British Chemical Standards, ΔH^{o}_{fus} ($C_6H_5CO_2H$, cryst.) = 17.19 kJ mole^{-1}, 120). The benzoic acid calibration was checked with another standard NH_4NO_3 (ΔH^{o}_{fus} (HN_4NO_3, cryst) = 6.39 kJ mole^{-1}, 121). Two separate determinations are detailed below:

Benzoic Acid Sample (mg)	ΔH^{o}_{fus} (NH_4NO_3, cryst) found (kJ mole^{-1})
1.00	6.45 ± 0.05
1.14	6.32 ± 0.12

Answers are correct to within 1% of the literature value (6.39 kJ mole^{-1}, 121).

Samples and standards were run under identical conditions; i.e. chart speed, sensitivity and rate of temperature increase. Samples were sealed in shallow aluminium pans under dry-box conditions and weights of samples determined by difference using a Cahn electrobalance ($\sim$50.00 - 1.00 mg.). Total weights (sample + pan) were determined after each run to check for loss of sample. Empty sample pans were used as references.

APPENDIX A. Vibrational Representation for Tetrahedral Species

Ion or Molecule	Geometry	Point Group	Number of Fundamental Frequencies	Number of Raman	Modes Active Infrared	Number of Coincidences	Examples
MX_4		Td	4	4 (a_1+e+2t_2)	2 $(2t_2)$	2	PCl_4^+, $SiCl_4$, PBr_4^+, $SiBr_4$.
MX_3Y		C_{3v}	6	6 $(3a_1 + 3e)$	6 $(3a_1 + 3e)$	6	PCl_3Br^+, $SiCl_3Br$, PBr_3Cl^+, $SiBr_3Cl$.
MX_2Y_2		C_{2v}	9	9 $(4a_1 + a_2 + 2b_1 + 2b_2)$	8 $(4a_1 + 2b_1 + 2b_2)$	8	$PCl_2Br_2^+$, $SiCl_2Br_2$.

APPENDIX B. Vibrational Representations for Some 6-Coordinate Species

Ion or Molecule	Point Group	Number of fundamental frequencies	Distribution of Modes						No.of I.R./ Raman Coin-Cidences
			(MX)	(MY)	Deformations	I.R.	Raman	Inactive	
MX_6	O_h	6	$a_{1g}+e_g+t_{1u}$	-	$t_{1u}+t_{2g}+t_{2u}$	$2(t_{1u})$	$3(a_{1g},e_g,t_{2g})$	$1(t_{2u})$	0
MX_5Y	C_{4v}	11	$2a_1+b_1+e$	a_1	$a_1+b_1+b_2+3e$	8 (a_1, e)	11 (a_1,b_1,b_2,e)	0	8
MX_4Y_2 (cis)	C_{2v}	15	$2a_1+b_1+b_2$	a_1+b_1	$3a_1+2a_2+2b_1+2b_2$	13 (a_1,b_1,b_2)	15 $(a_1,a_2,b_1.b_2)$	0	13
MX_4Y_2 (trans)	D_{4h}	11	$a_{1g}+b_{1g}+e_u$	$a_{1g}+a_{2u}$	$b_{2g}+e_g+a_{2u}+b_{2u}$ $+2e_u$	5 (e_u,a_{2u})	6 $(a_{1g},b_{1g},b_{2g},$ $b_{2u},e_g)$	0	0

APPENDIX C

NOTES

Preparation* :- The order of addition is indicated in the following way; eg.,. PCl_3 + BCl_3 + Br_2 the order of addition is 1) PCl_3, 2) BCl_3, 3) Br_2 also eg. (for reactions in dichloromethane only) PCl_3 + $\{BCl_3 + Br_2\}$ means that to a solution of PCl_3 in CH_2Cl_2, a solution of BCl_3 and Br_2 was added.

Analysis:- Analysis figures are in percentages and in atomic ratio eg. for PCl_3Br^+ BCl_4^- : P, 8.4; Cl, 67.1; Br, 21.6; B, 3.9%.

Raman Spectra* :- The terms "halide" and "polyatomic" refer to the bands assigned to the mixed chloro-bromo-phosphonium ions (PCl_3Br^+, $PCl_2Br_2^+$ and PBr_3Cl^+) in the Raman spectrum and whether they are characteristic of these ions in the presence of either (i) single halide ions or (ii) polyatomic anions. A convenient way of "describing" the Raman spectra is in terms of the relative intensities (on scale 0-10) of the totally symmetric (a_1) stretching bands (below):

Totally Symmetric (a_1) Stretching Bands (cm^{-1})

PCl_3 Br^+	PCl_2 Br_2^+	PBr_3 Cl^+	in the presence of
~375	~325	~280	(i) halide ions
~390	~345	~300	(ii) polyatomic anions

* reference numbers (eg. 104/100 and B3) refer to page numbers in notebook/roughbook and Raman spectrum file number.

APPENDIX C. (1) The Reaction of Phosphorus Trichloride, Bromine and Boron Trichloride in Dichloromethane

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(104/100) PCl_3 (4.60g., 0.034 mol.)	:Cl, 46.5; Br, 42.4; B, 1.9%. (P by	(B3) halide only
+ Br_2 (5.23g., 0.033 mol.)	difference, 9.2%)	373:327:280 = 7:10:7
+ BCl_3 (3.41 g., 0.033 mol.)	(P): Cl:Br:B = 1.7:7.3:2.9:1.0	
⟶ pale yellow precipitate		
(112/130) PCl_3(6.13g., 0.045 mol.)	:Cl, 45.9; Br, 47.7%	(B3) halide only
+ Br_2 (7.07 g., 0.044 mol.)	Cl : Br = 2.2 : 1.0	376:327:280 = 10:3:1
+ BCl_3 (5.63 g., 0.048 mol.)		
⟶ white solid		
(113/133) PCl_3(4.87g., 0.035 mol.)	in mg. sample/ 1 ml 0.1N	(M3) halide only
+ Br_2(5.49g., 0.034 mol.)	$AgNO_3$ = 5.50	374:328:280 = 9:10:6
+ BCl_3 (4.50 g., 0.038 mol.)		

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(115/142) BCl_3 (7.67 g., 0.065 mol.)	:P, 8.9; Cl, 47.7; Br, 41.6; B, 1.8%	(Q3) halide only
+ PCl_3 (7.35 g., 0.054 mol.)	P:Cl:Br:B = 1.7:7.9:3.0:1.0	376:324:279 = 10:1:0
+ Br_2 (5.47 g., 0.034 mol.)		
(116/146) Br_2(14.63 g., 0.091 mol.)	:Cl, 46.0; Br, 43.9%	(P3) halideonly
+ {BCl_3 (10.22g., 0.087 mol.)	Cl:Br = 2.4:1.0	375:328:280 = 10:10:5
+ PCl_3(10.61g., 0.077 mol.)}		
(117/148) BCl_3(4.07g., 0.035 mol.)	:Cl, 59.2; Br, 29.9%	(T3) predominantly polyatomic
+ PCl_3 (4.28 g., 0.031 mol.)	Cl:Br = 4.5:1	392:343:300 = 10:1:0
+ Br_2 (~0.5 g., 0.003 mol.)		
(121/155) PCl_3(7.59 g., 0.055 mol.)	:Cl, 47.6%;Br,43.9%	(W3) halide only
+ BCl_3 (7.53g., 0.064 mol.)	Cl:Br = 2.4:1.0	376:327:280 = 10:3:1
+ Br_2(4.31 g., 0.027 mol.)		

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(122/160) PCl_3(11.11 g., 0.081 mol.) + BCl_3(10.34 g., 0.088 mol.) + Br_2(4.89g., 0.031 mol.)	:Cl, 60.6; Br, 27.2% Cl:Br = 5.0 : 1.0	(V3) predominantly polyatomic 392:345:301 = 10:5:1
(123/161) PCl_3(8.21g., 0.060 mol.) + BCl_3(7.79 g., 0.066 mol.) + Br_2 (6.31 g., 0.039 mol.)	:Cl, 47.0; Br, 42.8% Cl:Br = 2.4 : 1.0	(Z3) halide only 375:324:280 = 10:1:0
(125/166) PCl_3(6.10 g., 0.044 mol.) + BCl_3(5.77 g., 0.049 mol.) + Br_2(5.87 g., 0.037 mol.) - reaction flask cooled in ice.	:Cl, 46.7 %; Br, 42.9% Cl:Br = 2.5 : 1.0	(C4) halide only 376:326:280 = 10:5:1
(126/168) PCl_3(6.39 g., 0.047 mol.) + BCl_3 (6.05 g., 0.052 mol.) + Br_2 (5.67 g., 0.036 mol.) reaction vessel cooled in ice.	:Cl, 49.4; Br, 40.2% Cl:Br = 2.8 : 1.0	(D4) halide only 376:329:280 = 10:10:4

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(129/173) PCl_3(6.40 g., 0.047 mol.) + BCl_3(5.77 g., 0.049 mol.) + Br_2 (5.24 g., 0.033 mol.)	:Cl, 49.8; Br, 40.3% Cl:Br = 2.8 : 1.0	(C4) halide only 376:328:280 = 10:7:3
(137/201) PCl_3(7.9g., 0.058 mol.) + {Br_2(8.00 g., 0.050 mol.) + BCl_3(11.7 g., 0.010 mol.)} reaction vessel cooled in ice.	:Cl, 46.0; Br, 42.4% Cl:Br = 2.4:1.0	(X4) halide only 375:327:279 = 10:10:4
(141/213) PCl_3(6.1 g., 0.044 mol.) + BCl_3(10.2 g., 0.087 mol.) + Br_2 (4.6 g., 0.029 mol.) reaction vessel below -10°C.	-	(D5) predominantly halide 376:325:280 = 10:6:3
(141/214) PCl_3(7.00g., 0.051 mol.) + BCl_3 (11.2 g., 0.095 mol.) + Br_2(5.5 g., 0.034 mol.)	:Cl, 52.5; Br, 34.1% Cl: Br = 3.5 : 1.0	(E5) predominantly halide 376:326:280 = 10:9:4

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(142/217) BCl_3 (12.1 g., 0.103 mol.)	:Cl, 47.1; Br, 33.4%	(F5) halide only
+ PCl_3(14.0 g., 0.102 mol.)	Cl:Br = 3.2 : 1.0	376:325:280 = 10:10:5
+ Br_2 (12.1 g., 0.076 mol.)		
(146/227) BCl_3(8.79 g., 0.075 mol.)	:P, 8.7; Cl, 46.9; Br, 41.8;	(P5) halide only
+ PCl_3 (9.19 g., 0.067 mol.)	B, 1.7%	375:324:280 = 10:1:0
+ Br_2 (7.12 g., 0.045 mol.)	P: Cl:Br:B = 1.8:8.4:3.3:1.0	
reaction vessel cooled to -50°C.		
and stirred using a glass stirrer.		
(151/8A) BCl_3(10.00 g., 0.085 mol.)	:Cl, 48.5; Br, 40.5%	(Z5) halide only
+ PCl_3 (10.15 g., 0.074 mol.)	Cl:Br = 2.7 : 1.0	376:328:282 = 10:3:1
+ Br_2(8.04 g., 0.050 mol.)		
reaction vessel cooled to -50°C.		
and reaction stirred using a glass stirrer.		

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(152/1B) BCl_3(10.11 g., 0.086 mol.)	:Cl, 47.3; Br, 43.2%	(A6) halide only
+ PCl_3 (9.98 g., 0.073 mol.)	Cl:Br = 2.5: 1.0	376:328:282 = 10:8:3
+ Br_2 (8.07 g., 0.050 mol.)		
as above (151/8A) but using a		
plastic stirrer.		

APPENDIX C. (2) The Reaction of Phosphorus Trichloride, Bromine and Boron Trichloride in Liquid Hydrogen Chloride

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(2/-) BCl_3(25.00 g., 0.213 mol.) + PCl_3 (20.00 g., 0.145 mol.) + Br_2 (24.00 g., 0.150 mol.) ⟶ yellow/red solid.	-	(K) predominantly halide 375:328:284 = 3:7:10
(2/-) above sublimed. - crushed and sublimed for 3 hours with cardice/acetone refrigerant.	-	sublimate predominantly polyatomic 391:346:301 = 10:10:6 residue halide only 374:328:282 = 7:10:9
(7/51) Br_2(3.09 g.,0.019 mol.) + PCl_3 (3.21 g.,0.023 mol.) + BCl_3 (15.00 g., 0.128 mol.) ⟶ a white solid.	P, 8.2; Cl, 65.1; Br, 20.9% P:Cl:Br = 1.0:7.0:1	(N) polyatomic only 394:347:301 = 10:1:0

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(95/71) Br_2 (9.96 g., 0.062 mol.) + PCl_3 (7.60 g., 0.055 mol.) + BCl_3 (6.50 g., 0.055 mol.)	expressed in mg. sample/1 ml. 0.1N $AgNO_3$ (Total Halide) = 4.96 (Calc.for $PBCl_7Br$, 4.62)	(K2) predominantly polyatomic 390:343:293 = 10;9:5
(96/84) PCl_3 (5.23 g., 0.038 mol.) + Br_2(6.35 g., 0.035 mol.) + BCl_3 (5.00 g., 0.042 mol.)	-	(Y2) polyatomic only 390:344:301 = 10:3:0
(109/116) PCl_3(3.42 g., 0.025 mol.) + Br_2(3.85 g., 0.024 mol.) + BCl_3(3.49 g., 0.030 mol.)	:Cl, 55.7; Br, 38.5% Cl:Br = 3.2:1	(F3) predominantly halide 374:329:282 = 4:10:8
(110/117) BCl_3(3.70 g., 0.032 mol.) + PCl_3 (3.89 g., 0.028 mol.) + Br_2(4.00 g., 0.025 mol.)	-	(G3) polyatomic only 391:346:300 = 10:1:0

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(114/138) PCl_3(6.50 g., 0.047 mol.)	expressing mg. sample/1 ml	(K3) polyatomic only
+ BCl_3(8.20 g., 0.053 mol.)	0.1 N $AgNO_3$ (Total Halide) = 467	392:345:300 = 10:1:0
+ BR_2(7.63 g., 0.47 mol.)	(calc.for $PBCl_7Br$, 4.62)	
(119/151) PCl_3(8.82 g., 0.064 mol.)	:Cl,65.0%; Br, 24.7%	(U3) polyatomic only
+ Br_2(10.37 g., 0.065 mol.)	Cl:Br = 5.8 : 1.0	392:346:302 = 10:3:0
+ BCl_3(8.72 g., 0.074 mol.)		
(127/170) PCl_3 (6.76 g., 0.049 mol.)	:Cl, 54.2; Br, 35.6%	(F4) polyatomic only
+ Br_2(7.47 g., 0.047 mol.)	Cl:Br = 3.4:1.0	388:342:297 = 8:10:8
pumped for 12 hours.		

APPENDIX C. (3) Reaction of Phosphorus Trichloride, Bromine and Boron Tribromide in Dichloromethane

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(75/20) PCl_3(4.83 g., 0.035 mol.)	: Cl, 11.3; Br, 80.7%	(J1) halide only
+ Br_2(5.72 g., 0.032 mol.)	Cl:Br = 1.0: 3.2	376:330:286 = 0:3:10
+ BBr_3(8.67 g., 0.035 mol.)		
→ a yellow solid		
(105/102) PCl_3(3.05 g., 0.022 mol.)	:Cl, 15.2; Br, 78.3%	(D3) predominantly halide
+ Br_2(3.68 g., 0.023 mol.)	Cl:Br = 1.0 : 2.3	376:328:284 = 0:4:10
+ BBr_3 (5.33 g., 0.021 mol.)		
→cooled to -78°C. → yellow precipitate.		
(113/136) PCl_3(5.25 g., 0.038 mol.)	:Cl, 13.7; Br, 79.4%	(I3) halide only
+ Br_2(5.95 g., 0.037 mol.)	Cl:Br = 1.0 : 2.6	375:330:285 = 0:4:10
+ BBr_3(10.17 g., 0.040 mol.)		
→ yellow solid		

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(138/206) PCl_3(4.70 g., 0.034 mol.)	-	(24) halide only
+ BBr_3 (8.2 g., 0.033 mol.)		376:330:285 = 0:3:10
+ Br_2(5.6 g., 0.035 mol.)		
⟶ yellow solid.		
(139/208) PCl_3(3.5 g., 0.026 mol.)	:Cl, 16.4; Br, 74.8%	(A5) polyatomic only
+ BBr_3(7.15 g., 0.029 mol.)	Cl:Br = 1.0:2.0	390:340:299 = 9:10:6
+ Br_2(2.7 g., 0.17 mol.)		Spectrum indicates BBr_4^-
⟶ white powder		anion (bands at 242, 118 cm^{-1})

APPENDIX C. (4) Reaction of Phosphorus Trichloride, Bromine, and Boron Tribromide in Liquid Hydrogen Chloride

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(120/15) Br_2(4.80 g., 0.030 mol.) + PCl_3(3.68 g., 0.027 mol.) + BBr_3(8.67 g., 0.035 mol.) ⟶ pumped for some time.	Pumped :P, 7.5; Cl, 51.5; Br, 38.7% P:Cl:Br = 1.0: 6.0:2.0	(P1) unpumped - predominantly halide. 374:329:280 = 9:10:8 (Q1) pumped for 24 hours.- predominantly polyatomic 390:348:302 = 10:10:4
(81/33) Br_2(7.64 g., 0.042 mol.) + PCl_3 (6.05 g., 0.044 mol.) + BBr_3(1114 g., 0.045 mol.) ⟶ inhomogenous solid pumped for 24 hours.	:Cl, 57.9; Br, 30.9% Cl:Br = 4.2:1.0	-
(107/107) Br_2(5.10 g., 0.032 mol.) + PCl_3 (4.39 g., 0.032 mol.) + BBr_3(10.00 g., 0.040 mol.)	:Cl, 48.2; Br, 42.1% Cl:Br = 2.6:1.0	(E3) unpumped - predominantly halide 375:329:286 = 1:4:10 pumped for 16 hours - predominantly polyatomic. 390:344:300 = 5:10:9

PREPARATION	ANALYSIS	SPECTRA (RAMAN)
(138/205) BBr_3(9.02 g., 0.036 mol.)	:Cl, 58.5; Br, 29.4%	(Y4) predominantly halide
+ PCl_3(4.4 g., 0.032 mol.)	Cl:Br = 4.5:1.0	379:328:282 = 10:4:1
+ Br_2(5.1 g., 0.032 mol.)		

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The Existence and Vibrational Characterisation of the Trichlorobromophosphonium Ion

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The Existence and Vibrational Characterisation of the Trichlorobromophosphonium Ion

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Summary The existence of the trichlorobromophosphonium ion $[PCl_3Br]^+$ has been confirmed in the solid complexes $PBCl_7Br$ and $P_2F_6Cl_3Br$ and a vibrational assignment is given.

Although the tetrahalogenophosphonium ions $[PX_4]^+$, (X = Cl or Br) are well known, evidence for the existence of the mixed species $[PX_nY_{4-n}]^+$, (X = Cl, Y = Br) is limited and characterisation is fragmentary. The existence of trichlorobromophosphonium tetrachloroborate (I), $[PCl_3Br][BCl_4]$ has been suggested by Salthouse and Waddington[1] and its presence in some other complex species postulated. We report a detailed vibrational characterisation of the

$[PCl_3Br]^+$ ion in (I) and in the new compound trichlorobromophosphonium hexafluorophosphate (II), $[PCl_3Br]$-$[PF_6]$.

Compound (I) was prepared by the addition of excess of boron trichloride to equimolar amounts of phosphorus trichloride and bromine in liquid hydrogen chloride at *ca.* −95°.[1] The precipitated white solid was pumped at ambient temperatures and subsequently manipulated under dry-box conditions. Variations in the order of addition of the three reactants were explored. The purest product, on the basis of analytical data and simplicity of Raman spectra, resulted from the following order of addition to the hydrogen chloride solvent: (i), boron trichloride (ii), phosphorus trichloride, (iii), bromine. The expected stoicheiometry of $PBCl_7Br$ is fully confirmed by analytical results.

I.r. and Raman spectra (cm^{-1}) *of the* PCl_3Br^+ *ion in* $PBCl_7Br$(I) *and* $P_2F_6Cl_3Br$(II)

$PBCl_7Br$ (I)		$P_2F_6Cl_3Br$ (II)		
I.r.	Raman	I.r.	Raman	Assignment
637(s)	647(vw)	647(s)	657(vw)	ν_4 (e)
597(m)		604(m)		
577(vs)	582(w)	588(m)	582(w)	ν_1 (a_1)
525(m)		522(m)		
493(vw)		490(w)		
390(m)	390(vs)	397(m)	399(vs)	ν_2 (a_1)
232(m)	233(s)	233(m)	235(s)	ν_5 (e)
213(m)	213(vs)	216(m)	217(s)	ν_3 (a_1)
155(w)	155(s)	[a]	159(s)	ν_6 (e)

[a] Not investigated.

Compound (II) was prepared‡ by the addition of equimolar amounts of phosphorus trichloride and bromine to liquid hydrogen chloride at *ca.* −95° followed by condensation of excess of phosphorus pentafluoride. Volatile residues were removed *in vacuo* and the white crystalline product was manipulated under anhydrous conditions. Analytical results confirm the expected stoicheiometry. Chlorine and bromine were measured by standard titrimetric procedures in this laboratory; phosphorus and fluorine were determined in a commercial laboratory.

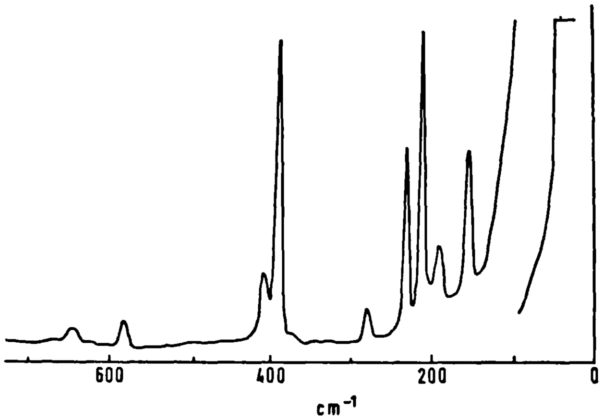

FIGURE. *Raman spectrum of crystalline* $PCl_3Br^+BCl^-_4$

Comparison of the spectra with those of authentic samples containing BCl_4^- and PF_6^- ions lead to the conclusions that (a) in (I), the Raman lines (Figure) at 411m, 280m, and 194m cm^{-1} together with a very strong broad i.r. absorption at 670—700 cm^{-1} confirm the presence of the BCl_4^- ion and, (b) in (II), Raman lines at 743s and 472w cm^{-1} with i.r. absorptions at 552s and 834s cm^{-1} confirm the presence of the PF_6^- ion. The remaining Raman lines and i.r. absorptions are common to both complexes and are assigned (Table) to PCl_3Br^+ on the basis of C_{3v} symmetry expected by analogy with the isoelectronic $SiCl_3Br$.[2]

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The Existence of Chlorobromoantimonates

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Recent reviews[1,2] have stated that chlorobromoantimonates, $SbCl_nBr_{6-n}^-$, do not apparently exist. Thus reaction of, for example, $SbCl_4^+$ and Br^- ions under appropriate conditions is said[3] to lead to mixtures of hexachloro- and hexabromoantimonates; X-ray powder studies on crystalline tetraethylammonium salts and ultraviolet spectra measurements on acetonitrile solutions are cited as evidence. This is surprising in view of the known existence[4] of the analogous phosphorus anion PCl_5Br^-, of antimony–fluorochloro compounds,[2] and of the halogenotrifluoromethyl antimonates[1] $Sb(CF_3)_3X_3^-$, X = Cl, Br. In this note we present evidence for the preparation of two compounds containing the pentachlorobromoantimonate anion, $SbCl_5Br^-$.

TABLE I
ANALYTICAL DATA FOR $(C_2H_5)_4NSbCl_5Br$ AND $PSbCl_9Br$

	% P		% Sb		% Cl		% Br	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$(C_2H_5)_4NSbCl_5Br$	...	...	23.9	23.8	34.8	34.9	15.7	15.7
$PSbCl_9Br$	5.6	5.4	22.1	22.4	57.8	57.6	14.5	14.8

Preparation and Characterization of the $SbCl_5Br^-$ Ion.—The two syntheses are summarized by the equations

$$PCl_3 + Br_2 + SbCl_5 \xrightarrow{\text{liquid HCl}} PSbCl_9Br\ (A) + HBr$$

$$(C_2H_5)_4NBr + SbCl_5 \xrightarrow{\text{dichloromethane}} (C_2H_5)_4NSbCl_5Br\ (B)$$

In each synthesis the mole ratio of reactants was unity. After precipitation of compound A, the HCl was removed by pumping at ambient temperatures for 2 hr, and the resultant yellow powder subsequently stored and manipulated under strictly anhydrous conditions. Compound B, a yellow solid, was filtered on a glass sinter before pumping and storing. Analytical results (Alfred Bernhardt, Munich, Germany) are summarized in Table I.

Raman Spectra.—Raman spectra of A and B in the solid state were recorded using a Cary 81 Raman spectrometer with 6328-Å helium–neon excitation; results are listed in Table II.

The presence of the PCl_4^+ ion in A is clearly shown by the position of bands at 660, 458, 251, and 182 cm^{-1}; these correspond to PCl_4^+ bands in the spectra of authentic samples of $[PCl_4][BCl_4]$ and also $[PCl_4][SbCl_6]$ prepared and run in this laboratory. Inspection of Table II shows that, apart from bands at 667 and 422 cm^{-1} in B, due to the tetraethylammonium ion, the spectra of A and B match extremely closely. Only two weak bands (396 and 363 cm^{-1} in A) are not common to both; the same anionic species is therefore inferred. Consideration of comparison spectra of compounds containing the ions $SbCl_6^-$, PCl_6^-, and PCl_3Br^+ eliminate the possibilities that A might be formulated as $[SbCl_3Br][PCl_6]$ or as $[PCl_3Br][SbCl_6]$. That $SbBr_6^-$ was not present was shown by the absence of a strong band at 194 cm^{-1} previously observed in the spectrum of a sample of $[(C_2H_5)_4N][SbBr_6]$ prepared in this laboratory. The remaining formulation, consistent with both analytical and Raman evidence, is $[PCl_4][SbCl_5Br]$, and B is hence established as $[(C_2H_5)_4N][SbCl_5Br]$. Infrared spectra, run as Nujol mulls, on both A and B are completely consistent with the above interpretation; a detailed presentation of the vibrational spectra will be given elsewhere.

TABLE II
RAMAN SHIFTS (CM^{-1}) FOR $PSbCl_9Br$ AND $(C_2H_5)_4NSbCl_5Br$[a]

$PSbCl_9Br$ (A)	$(C_2H_5)_4NSbCl_5Br$ (B)	Assignment
	677 w	Et_4N^+
660 w		PCl_4^+
458 s		PCl_4^+
	422 w	Et_4N^+
396 w		?
363 w, sh		?
332 vs	332 s	$SbCl_5Br^-$
310 m	308 m	$SbCl_5Br^-$
290 m	289 m	$SbCl_5Br^-$
251 s		PCl_4^+
222 s, br	223 s, br	$SbCl_5Br^-$
182 sh		PCl_4^+
175 s	173 m, br	$SbCl_5Br^-$
157 w	158 w	$SbCl_5Br^-$

[a] Abbreviations: Et, $(C_2H_5)_4$; vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

Differential Scanning Calorimetry.—To substantiate further that A was not a 5:1 (mole) mixture of $SbCl_6^-$ and $SbBr_6^-$ species, differential scanning calorimetric (dsc) measurements were made on $[(C_2H_5)_4N][SbCl_6]$ (a), on $[(C_2H_5)_4N][SbBr_6]$ (b), on a freshly prepared 5:1 molar mixture of a and b, and on B, using sealed pans, from ambient temperature to *ca.* 280°. The thermogram from the mixture exhibited features associated with the individual components, and, in particular, reversible endothermic phase changes near 60° (a) and 158° (b). The thermogram of B differed from that of the mixture; no evidence for the 158° endotherm was found, in contrast to the mixture.

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(2) L. Kolditz, *Halogen Chem.*, **2**, 133 (1967).
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Hence the conclusion that B was a compound is further indicated.

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