Mixed Halogen Complexes of Phosphorus. Part I. Preparation and Raman Spectra of the Chlorobromophosphonium Ions, $[PCl_nBr_{4-n}]^+$ $(0 \leqslant n \leqslant 4)$

By **Arthur Finch,* P. N. Gates,** and **F. J. Ryan,** Chemistry Department, Royal Holloway College, University of London, Englefield Green, Surrey
F. F. Bentley, Air Force Materials Laboratory (D.O.Y.), Wright Patterson Air Force Base, Dayton, Ohio, 45433

The preparation of some complexes and mixtures containing the PCl_3Br^+, $PCl_2Br_2^+$, and $PClBr_3^+$ ions is described. A vibrational assignment for each species has been made based on data from Raman spectra of the complexes in the solid state. Some characteristic shifts occur in the fundamental frequencies of the phosphonium ions where single halide or polyhalide anions are present in the crystal lattice. It is suggested that such vibrational frequencies can be used to infer (*a*) the structures of complexes involving phosphonium ions and (*b*) the presence or absence of single halide or trihalide ions in the lattice.

DESPITE considerable preparative studies concerning phosphorus mixed halogen systems the structures of most of the products remain obscure. Thus although the stoicheiometries of such species as P_2Cl_9Br,[1] $PBCl_7Br$,[2] PCl_3Br_6,[3] $PSbCl_7Br_3$,[4] *etc.*, are well established, and tentative suggestions of the presence of, *inter alia*, chlorobromophosphonium ions such as PCl_3Br^+ and $PClBr_3^+$ have been made,[2-4] no direct structural study has been reported.

We now present an assignment of vibrational frequencies for all members of the chlorobromophosphonium series, $PCl_nBr_{4-n}^+$ $(0 \leqslant n \leqslant 4)$. In conjunction with complementary techniques, especially solid-state ^{31}P n.m.r. spectra, these are shown to lead to reasonable formulations for the products of numerous reactions resulting in complex phosphorus chlorobromo-compounds. Further, some very characteristic frequency shifts occur for the phosphonium ions when a single halide (or trihalide) ion is present in the crystal lattice. Application of these results has enabled the identities of both single compounds and complex reaction mixtures to be established.

EXPERIMENTAL

Most of the reactants and products were moisture-sensitive and all manipulations were carried out under dry nitrogen in a dry-box.

Preparation of $PBr_4^+BBr_4^-$.—PBr_5 (14·0 g, 0·033 mol) in CH_2Cl_2 (50 ml) was added to BBr_3 (8·34 g, 0·033 mol) in CH_2Cl_2. The resultant yellow precipitate was filtered off and dried *in vacuo* (Found: Br, 93·0; Calc. for $PBBr_8$: Br, 94·0%).

Reactions between PCl_3, Br_2, *and* BCl_3 *in Liquid* HCl.—*Preparation of* $PCl_3Br^+BCl_4^-$. BCl_3 (3·70 g, 0·032 mol) was dissolved in liquid HCl at −95 °C and PCl_3 (3·89 g, 0·028 mol) followed by Br_2 (4·00 g, 0·025 mol) were added to form a white precipitate. Warming to room temperature followed by pumping left a white solid (Found: Cl, 65·1; Br, 20·9; P, 8·2. Calc. for $PBBrCl_7$: Cl, 67·1; Br, 21·6; P, 8·4%). Many variations in this preparative procedure were attempted but the above method gave

---

[1] L. Kolditz and A. Feltz, *Z. anorg. Chem.*, 1957, **293**, 286.

[2] J. A. Salthouse and T. C. Waddington, *J. Chem. Soc.*, 1967, 1096.

[3] A. I. Popov, D. H. Geske, and N. C. Baenziger, *J. Amer. Chem. Soc.*, 1956, **78**, 1793.

[4] J. K. Ruff, *Inorg. Chem.*, 1963, **2**, 813.

the purest product on the basis of analytical data and simplicity of the Raman spectrum. Under other conditions, mixtures involving PCl_3Br^+, $PCl_2Br_2^+$, and $PClBr_3^+$ were invariably produced.

Preparation of $PCl_3Br^+PF_6^-$. PCl_3 (2·37 g, 0·017 mol) and Br_2 (2·50 g, 0·016 mol) were added to liquid HCl at −95 °C followed by condensation of excess of PF_5. Volatile residues were removed by pumping to leave a white solid (Found: Cl, 28·5; Br, 22·9; P, 16·5; F, 30·3. Calc. for $P_2BrCl_3F_6$: Cl, 29·4; Br, 22·1; P, 17·1; F, 31·4%). A solid-state Raman spectrum indicated that the product was slightly contaminated with the corresponding $PCl_2Br_2^+$ and $PClBr_3^+$ complexes, consistent with the analytical data.

Attempts to prepare pure complexes containing $PCl_2Br_2^+$ *or* $PClBr_3^+$ *ions.* All such attempts (by variation of reaction conditions, *etc.*) were unsuccessful, resulting only in mixtures containing all three chlorobromophosphonium ions, as indicated by Raman spectroscopy.

Reactions between PCl_3, Br_2, *and* BCl_3 *in Dichloromethane.*—BCl_3 (3·91 g, 0·033 mol) in CH_2Cl_2 (50 ml) was added with stirring to a solution of PCl_3 (4·60 g, 0·034 mol) and Br_2 (5·23 g, 0·033 mol) in CH_2Cl_2 (50 ml). This pale yellow precipitate was filtered off and dried *in vacuo* (Found: B, 1·9; Cl, 46·5; Br, 42·4%). Solid-state ^{31}P n.m.r. and Raman spectra both indicate the presence of all three mixed chlorobromophosphonium ions.

Attempts to prepare pure complexes containing the chlorobromophosphonium ions. Many variations of the above procedure were carried out in an attempt to prepare a pure sample of a single complex. With one exception these resulted in similar mixtures, the relative amounts of the three chlorobromophosphonium ion varying with the preparation. However, with one set of conditions, solid-state ^{31}P n.m.r.[5] and Raman spectra indicated that an almost pure compound had been prepared: Br_2 (5·47 g, 0·034 mol) in CH_2Cl_2 (50 ml) was added with stirring to a solution of BCl_3 (7·67 g, 0·065 mol) and PCl_3 (7·35 g, 0·054 mol) in CH_2Cl_2 (50 ml) at −50 °C. The resultant white precipitate was filtered off and dried *in vacuo* (Found: Cl, 46·9; Br, 41·5; B, 1·7; P, 8·7%; total 98·8%). Raman and ^{31}P n.m.r. spectra indicated the presence of mainly the PCl_3Br^+ ion but with relatively very small amounts of $PCl_2Br_2^+$ and $PClBr_3^+$ ions.[5] Solid-state ^{11}B n.m.r. shows the presence of the BCl_4^+ ion. The analytical figures correspond to the ratio P : B : Cl : Br = 1·8 : 1·0 : 8·3 : 3·3 (Compound A).

Analytical Methods.—Halogen analyses were carried out by alkaline hydrolysis followed by standard Volhard titrimetry.

I.r. Spectra.—These were recorded on Nujol mulls between CsI plates in the range 200—1000 cm^{-1} on a Perkin-Elmer 325 spectrometer.

Raman Spectra.—These were recorded on powdered solid samples contained in glass capillary tubes with a Cary 81 Raman spectrometer, the 647·1 nm line of a mixed argon–krypton laser (Coherent Radiation Ltd.) being used for excitation.

^{31}P *N.m.r. Spectra.*—These were obtained as previously described[5,6] by Dr. K. B. Dillon at the University of Durham.

RESULTS AND DISCUSSION

The PCl_3Br^+ *Ion.*—The synthesis of pure compounds containing the mixed chlorobromophosphonium ions is extremely difficult. Initial preparations involving reaction of PCl_3 with Br_2 and BCl_3 in liquid HCl led to products which, exhibiting extremely complex Raman spectra, were obviously mixtures. The preparation in these Laboratories[7] of a pure sample of $PCl_3Br^+BCl_4^-$, and an assignment of the solid-state vibrational spectra, made possible the recognition of the PCl_3Br^+ cation in the mixture. A characteristic ^{31}P shift for this cation obtained from the solid-state n.m.r. spectra of both $PCl_3Br^+BCl_4^-$ and $PCl_3Br^+PF_6^-$ was used as further confirmation.

A further series of reactions with the same reactants, but with dichloromethane as solvent, yielded solid precipitates which also contained complex mixtures of products. One preparation, however, led to a product (compound A) with a relatively simple Raman spectrum showing mainly bands due to the PCl_3Br^+ ion, but with small contributions from $PCl_2Br_2^+$ and $PClBr_3^+$ ions; this was confirmed by solid-state ^{31}P data. A solid-state ^{11}B spectrum indicated the presence of the BCl_4^- ion [a shift of +11·7 p.p.m. relative to $B(OMe)_3$].[8] The fundamental frequencies of PCl_3Br^+ in this and in two other complexes are compared in Table 1 from which it is seen that some marked shifts occur. Thus it is clear, both from the spectra and the analytical data, that compound A and $PCl_3Br^+BCl_4^-$ are not identical. From the conclusions in the next paragraph concerning the significance of the frequency shifts in phosphonium ions it seems probable that a single-halide ion is present in the crystal lattice of compound A. A formulation which is consistent both with the analytical and spectral data is: $2PCl_3Br^+,BCl_4^-,Br^-$, the stoicheiometry of which ($P_2BCl_{10}Br_3$) corresponds to a total halogen analysis of 89·1% (Cl, 53·2; Br, 35·9%). The experimental value was 88·4% (Cl, 46·9%, Br 41·5%), hence the suggested formulation must be regarded as tentative.

TABLE 1

Fundamental frequencies/cm^{-1} of the PCl_3Br^+ ion in various complexes

Compd. A	$PCl_3Br^+BCl_4^-$ [a]	$PCl_3Br^+BBr_4^-$	$PCl_3Br^+PF_6^-$ [a]	Assignment
565w	582w	580w	582w	ν_1 (a_1)
376vs	390vs	390vs	399vs	ν_2 (a_1)
204vs	213vs	212vs	217s	ν_3 (a_1)
628w	647vw	645w	657vw	ν_4 (e)
230m	233s	230s	235s	ν_5 (e)
161w	155s	151s	159s	ν_6 (e)

s, Strong; m, medium; w, weak; v, very.

[a] See also ref. 7.

Frequency Shifts in Phosphonium Ions.—During the work frequency shifts analogous to those above were observed between PBr_5 (for which there is *X*-ray

---

[5] K. B. Dillon and P. N. Gates, *Chem. Comm.*, 1972, 348.

[6] K. B. Dillon and T. C. Waddington, *Spectrochim. Acta*, 1971, **27***A*, 1381.

[7] F. F. Bentley, Arthur Finch, P. N. Gates, and F. J. Ryan, *Chem. Comm.*, 1971, 860.

[8] K. B. Dillon, personal communication.

crystallographic evidence [9] for the $PBr_4^+Br^-$ structure) and $PBr_4^+BBr_4^-$. The literature revealed other examples, summarised in Table 2. In general, significant increases in frequency occur for the 229 cm^{-1} (a_1) and 476 cm^{-1} (t_2) modes of PBr_4^+ on passing from complexes where halide or polyhalide anions, *e.g.*, Br^-, Cl^-, Br_3^-, or $IClBr^-$ are present to those where a non-halide polyatomic anion (such as PF_6^-, BBr_4^-, or $TaBr_6^-$) occurs. Some similar frequency shifts of this type occur in PCl_4^+-containing complexes although the range of examples is more restricted. These are summarised in Table 3. The column listed ' Metastable PCl_5 ' deserves further comment. A metastable modification of PCl_5, for which the *X*-ray powder photograph differs from that of the normal tetragonal form, is known.[3] The solid-state Raman spectra of the two forms differ considerably.[10,11] The chief feature is a reversal of the relative intensities of the lines due to PCl_4^+ and PCl_6^- in the two systems Table 3 also shows clearly that some marked frequency shifts occur between the spectra of the two modifications in an analogous manner to that observed for the PBr_4^+ ion (above). The changes in the relative intensities of the Raman bands suggest that there may no longer be a 1 : 1 ratio between PCl_4^+ and PCl_6^- ions in the metastable form, with the former now predominating. If this is so, then in order to preserve (*a*) electrical neutrality and (*b*) the experimentally-determined stoicheiometry, the presence of Cl^- ions in the lattice must be presumed.

TABLE 2

Solid-state Raman spectra/cm^{-1} of PBr_4^+ ions in various complexes

Mode	$PBr_4^+Br^-$ [a]	$PBr_4^+Cl^-$ [b]	$PBr_4^+Br_3^-$ [a]	$PBr_4^+IClBr^-$ [c]	$PBr_4^+BBr_4^-$ [d]	$PBr_4^+TaBr_6^-$ [e]	$PBr_4^+PF_6^-$ [a]
ν_1 (a_1)	229	224	228	236	252	254	269
		231	231	238			
ν_2(e)	73	72	67	84	115	116	108
	85	74	69	87	104		
ν_3 (t_2)	470	471	479	479			
	476	473	480	480·5		496	508
	484	477	481	483·5	499	503	
		484		485			512
ν_4 (t_2)	139	140	147				
	141	143sh		133	149	148	153
	145	147	151				

[a] P. Dhamelincourt and M. Crunelle-Cras, *Compt. rend.*, 1971, **272**, *B*, 124, and references therein. [b] W. Gabes, K. Olie, and H. Gerding, *Rec. Trav. chim.*, 1972, **91**, 1367. [c] P. Dhamelincourt and M. Crunelle-Cras, *Compt. rend.*, 1971, **272**, *B*, 51. [d] This work. [e] M. Delhaye, P. Dhamelincourt, and J. C. Merlin, *Compt. rend.*, 1971, **272**, *B*, 370.

TABLE 3

Raman spectra/cm^{-1} of PCl_4^+ ions in various complexes [a]

Mode	$PCl_4^+ICl_2^-$	Metastable PCl_5	$PCl_4^+PF_6^-$	$PCl_4^+PCl_6^-$ [b]	$PCl_4^+SbCl_5Br^-$	$PCl_4^+BCl_4^-$
ν_1 (a_1)	449vs	441vs	462s	458s	458s	462s
ν_2 (e)	192w	187w	180mw	177m	179	182mw
ν_3 (t_2)	646w	639w	656w	658w	660w	656w
ν_4 (t_2)	245m	247m	254s	250s	249m	252m

[a] All frequencies are those obtained in the present work. [b] Normal PCl_5.

The available evidence thus suggests that (i) in species containing the PBr_4^+ ion some characteristic high-frequency shifts occur when various polyatomic anions are substituted for halide or trihalide anions, and (ii) in some species containing PCl_4^+ and PCl_3Br^+ ions (where the evidence is strong for the presence of single halide ions), a similar pattern of frequency-shift occurs. It is therefore suggested that such a pattern of shifts may be diagnostic for the presence of single halide (or trihalide) ions in these systems.

The $PCl_2Br_2^+$ *and* $PClBr_3^+$ *Ions.*—The Raman spectra of some of the mixtures resulting from reactions in liquid hydrogen chloride were extremely complex but bands associated with the PCl_3Br^+ ion could be clearly recognised, both at the frequencies associated with the presence of polyatomic anions (*e.g.*, at the same frequencies as in $PCl_3Br^+BCl_4^-$, $PCl_3Br^+PF_6^-$, *etc.*) and at those associated with species where the presence of single halide ions is postulated (above).

Preparations in dichloromethane, however, almost invariably yielded mixtures. In each of a large number of such preparations the same set of frequencies was observed, although the relative intensities of the bands varied considerably. A careful analysis of 25 such spectra showed that the intensities of the bands did not vary independently but could be grouped together, according to whether they increased or decreased relative to one another. Apart from the PCl_3Br^+ bands it was apparent that bands corresponding to *two* further

---

[9] M. van Driel and C. H. MacGillavray, *Rec. Trav. chim.*, 1943, **62**, 167.

[10] S. G. Shore and H. Knachel, personal communication.

[11] R. Baumgartner, W. Sawodny, and J. Goubeau, *Z. anorg. Chem.*, 1964, **333**, 171.

species were present; this is further confirmed by the presence of three appropriate[5] resonances in the solid-state ^{31}P n.m.r. spectrum. From reactions which produced mixtures, and in which it is known that PCl_3Br^+ ions are formed, it might reasonably be expected that these could be ascribed to the $PCl_2Br_2{}^+$ and $PClBr_3{}^+$ ions; this is strongly supported by the positions of the ^{31}P resonances.[5] Vibrational assignments for the species $PCl_2Br_2{}^+$ (C_{2v}) and $PClBr_3{}^+$ (C_{3v}) could then be made based on (*a*) a consistent set of frequency variations among the whole chlorobromophosphonium series and (*b*), as with the PCl_3Br^+ assignment, comparison with the fundamental frequencies of the isoelectronic silicon chlorobromide, $SiCl_nBr_{4-n}$, molecules for which good liquid-phase Raman data are available.[12] *All* bands in all the Raman spectra are accounted for with these assignments.

Frequency Shifts in the $PCl_2Br_2{}^+$ *and* $PClBr_3{}^+$ *Ions*.—Using the above assignments, we further examined the Raman spectra of products resulting from reactions in liquid HCl. Both Raman and analytical data indicated the presence of polyatomic anions (*i.e.*, $BCl_4{}^-$) in these complexes. The Raman spectra also show that the $PCl_2Br_2{}^+$ and $PClBr_3{}^+$ ions are present, but with certain of the fundamental frequencies shifted (relative to those complexes where single halide ions occur) in an analogous way to frequency shifts in $PCl_4{}^+$, $PBr_4{}^+$, and PCl_3Br^+ ions. Further reactions with BBr_3 instead of BCl_3 have produced compounds exhibiting similar spectroscopic patterns. Fundamental frequencies for the $PCl_2Br_2{}^+$ and $PClBr_3{}^+$ ions are summarised in Tables 4 and 5 respectively.

TABLE 4

Fundamental frequencies/cm^{-1} of the $PCl_2Br_2{}^+$ ion in various complexes [a]

$PCl_2Br_2{}^+$-Halide$^-$ species	$PCl_2Br_2{}^+BCl_4{}^-$	$PCl_2Br_2{}^+BBr_4{}^-$	Assignment
584w	600w	596w	ν_1 (a_1)
326vs	348vs	340vs	ν_2 (a_1)
191s	198s	192s	ν_3 (a_1)
132w	128w	Masked	ν_4 (a_1)
150w	155	151m	ν_5 (a_2)
616w	632w	633w	ν_6 (b_1)
201vs	207s	201s	ν_7 (b_1)
518w	522w	520w	ν_8 (b_2)
173s	179s	Masked	ν_9 (b_2)

[a] Anion bands omitted.

TABLE 5

Fundamental frequencies/cm^{-1} of the $PClBr_3{}^+$ ion in various complexes [a]

$PClBr_3{}^+$-Halide$^-$ species	$PClBr_3{}^+BCl_4{}^-$	$PClBr_3{}^-BBr_4{}^-$	Assignment
587w	583	Masked	ν_1 (a_1)
285vs	301vs	299vs	ν_2 (a_1)
149s	Masked	151s	ν_3 (a_1)
500m	503w	490vw	ν_4 (e)
172s	176s	Masked	ν_5 (e)
120w	126w	124m	ν_6 (e)

[a] Anion bands omitted.

The solid-state ^{31}P n.m.r. spectra of many of the products from the above reactions have been obtained and the shifts characteristic of the mixed-halide species inferred.[5] In all instances the ^{31}P and Raman data are mutually consistent. Thus the origins of all lines observed in the most complex Raman spectra of these mixtures are fully accountable although the exact nature of the complexes in which the presence of single halide ions has been inferred remains to be determined.

The assignments of the bands to particular modes for the $PCl_2Br_2{}^+$ and $PClBr_3{}^+$ species are included in Tables 4 and 5. Since the complex cations decompose in solution, Raman polarisation data were inaccessible; to this extent only, the assignments should be regarded as tentative. There is, however, little doubt that the *sets* of Raman bands assigned to each phosphonium species are correct and that some characteristic shifts occur if single halide (or trihalide) ions are present in the lattice. These data make it possible to infer the presence of such phosphonium ions in complexes of unknown structure and also to predict the presence or absence of single halide or trihalide ions in the lattice.

We thank Dr. K. B. Dillon, University of Durham, for provision of the solid-state ^{31}P and ^{11}B n.m.r. spectra and for discussions. The work was supported through the European Office of Aerospace Research, U.S.A.F.

[3/043 *Received*, 8*th January*, 1973]

---

[12] F. Höfler, *Z. Naturforsch.*, 1971, **26**, 547, and references therein.