

## The Existence and Vibrational Characterisation of the Trichlorobromophosphonium Ion

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*Summary* The existence of the trichlorobromophosphonium ion  $[\text{PCl}_3\text{Br}]^+$  has been confirmed in the solid complexes  $\text{PBrCl}_2$  and  $\text{P}_2\text{F}_6\text{Cl}_3\text{Br}$  and a vibrational assignment is given.

(X = Cl or Br) are well known, evidence for the existence of the mixed species  $[\text{PX}_n\text{Y}_{4-n}]^+$ , (X = Cl, Y = Br) is limited and characterisation is fragmentary. The existence of trichlorobromophosphonium tetrachloroborate (I),  $[\text{PCl}_3\text{Br}][\text{BCl}_4]$  has been suggested by Salthouse and Waddington<sup>1</sup> and its presence in some other complex species postulated.

ALTHOUGH the tetrahalogenophosphonium ions  $[\text{PX}_4]^+$ ,

We report a detailed vibrational characterisation of the

$[\text{PCl}_3\text{Br}]^+$  ion in (I) and in the new compound trichlorobromophosphonium hexafluorophosphate (II),  $[\text{PCl}_3\text{Br}]^+[\text{PF}_6]^-$ .

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.*  $-95^\circ$ .<sup>1</sup> 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 stoichiometry of  $\text{PBCl}_7\text{Br}$  is fully confirmed by analytical results.

*I.r. and Raman spectra ( $\text{cm}^{-1}$ ) of the  $\text{PCl}_3\text{Br}^+$  ion in  $\text{PBCl}_7\text{Br}$ (I) and  $\text{P}_2\text{F}_6\text{Cl}_3\text{Br}$ (II)*

$\text{PBCl}_7\text{Br}$ (I)		$\text{P}_2\text{F}_6\text{Cl}_3\text{Br}$ (II)		Assignment
I.r.	Raman	I.r.	Raman	
637(s)	647(vw)	647(s)	657(vw)	$\nu_4$ (e)
597(m)		604(m)		
577(vs)	582(w)	588(m)	582(w)	$\nu_1$ ( $a_1$ )
525(m)		522(m)		
493(vw)		490(w)		
390(m)	390(vs)	397(m)	399(vs)	$\nu_2$ ( $a_1$ )
232(m)	233(s)	233(m)	235(s)	$\nu_5$ (e)
213(m)	213(vs)	216(m)	217(s)	$\nu_3$ ( $a_1$ )
155(w)	155(s)	<sup>a</sup>	159(s)	$\nu_6$ (e)

<sup>a</sup> Not investigated.

Compound (II) was prepared<sup>†</sup> by the addition of equimolar amounts of phosphorus trichloride and bromine to liquid hydrogen chloride at *ca.*  $-95^\circ$  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 stoichiometry.

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<sup>‡</sup> We thank Professor T. C. Waddington for his suggestion of an alternative source of the  $[\text{PCl}_3\text{Br}]^+$  ion.

<sup>1</sup> J. A. Salthouse and T. C. Waddington, *Chem. Comm.*, 1967, 1096.

<sup>2</sup> M. L. Delwaille and F. Francois, *Compt. Rend.*, 1944, 219, 335; 1945, 220, 173.

Chlorine and bromine were measured by standard titrimetric procedures in this laboratory; phosphorus and fluorine were determined in a commercial laboratory.

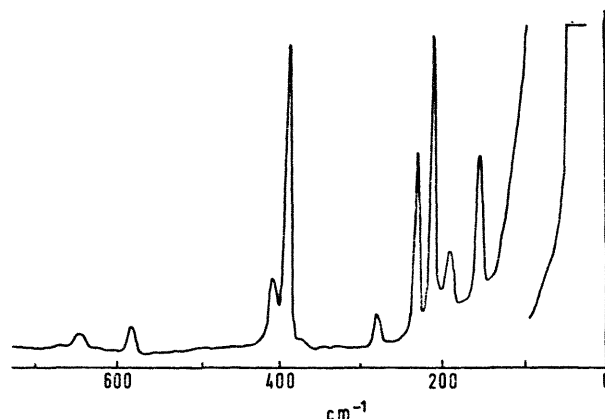


FIGURE. Raman spectrum of crystalline  $\text{PCl}_3\text{Br}^+\text{BCl}_4^-$

Comparison of the spectra with those of authentic samples containing  $\text{BCl}_4^-$  and  $\text{PF}_6^-$  ions lead to the conclusions that (a) in (I), the Raman lines (Figure) at 411m, 280m, and 194m  $\text{cm}^{-1}$  together with a very strong broad i.r. absorption at 670–700  $\text{cm}^{-1}$  confirm the presence of the  $\text{BCl}_4^-$  ion and, (b) in (II), Raman lines at 743s and 472w  $\text{cm}^{-1}$  with i.r. absorptions at 552s and 834s  $\text{cm}^{-1}$  confirm the presence of the  $\text{PF}_6^-$  ion. The remaining Raman lines and i.r. absorptions are common to both complexes and are assigned (Table) to  $\text{PCl}_3\text{Br}^+$  on the basis of  $C_{3v}$  symmetry expected by analogy with the isoelectronic  $\text{SiCl}_3\text{Br}$ .<sup>2</sup>

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