

57. The Phosphorus Pentachloride Addition Complexes of Group III Chlorides.

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The addition complexes $\text{PCl}_5\cdot\text{BCl}_3$, $\text{PCl}_5\cdot\text{AlCl}_3$, $\text{PCl}_5\cdot\text{GaCl}_3$, and $\text{PCl}_5\cdot\text{TlCl}_3$ have been prepared by relatively simple procedures, and their X-ray powder diffraction data and infrared spectra are reported. It is concluded that the compounds are ionic in the solid state and contain the PCl_4^+ cation as a species which is essentially independent of the anion.

THE known addition compounds of phosphorus pentachloride with Group III halides are $\text{PCl}_5\cdot\text{BCl}_3$,^{1,2} $\text{PCl}_5\cdot\text{AlCl}_3$,¹ $\text{PCl}_5\cdot\text{GaCl}_3$,² and $\text{PCl}_5\cdot\text{TlCl}_3$.¹ In general, synthetic procedures have involved conductometric titrations of the reactants in an ionizing solvent, followed by chemical analysis of the product. However, direct combination of reactants at elevated temperatures and direct combination of reactants in a non-ionizing liquid have been employed also, though less systematically. In ionizing solvents the complexes appear to be tetrachlorophosphonium salts, *i.e.*, $\text{PCl}_4^+\text{AlCl}_4^-$.³ With the exception of spectroscopic evidence for the existence of $\text{PCl}_4^+\text{BCl}_4^-$ ⁴ and $\text{PCl}_4^+\text{AlCl}_4^-$,⁵ descriptions of these compounds in the solid state have been restricted to statements of external appearance and melting point or dissociation temperature.

In the present investigation, we have prepared addition compounds of phosphorus pentachloride with Group III chlorides by relatively simple procedures which in general do not require a good ionizing solvent. We have shown, by X-ray powder diffraction techniques, that these compounds are unique crystalline species. We have also repeated and extended the spectroscopic observations of Waddington and Klanberg⁴ and Miller⁵ in the identification of these compounds as tetrachlorophosphonium salts.

EXPERIMENTAL

Materials.—Solids were purified by sublimation in an all-glass, vacuum sublimator. X-Ray powder diffraction photographs were taken of purified solids and were compared with data for the pure substances which are listed in the A.S.T.M. Index.⁶ Methylene chloride was dried over calcium hydride for two to three days, then fractionally distilled. Phosphorus oxychloride was fractionally distilled; boiling point was used as a criterion of purity. Gaseous boron trichloride was used as supplied by the Matheson Co.

Procedures.—(i) Phosphorus pentachloride adducts of aluminium trichloride and gallium trichloride were prepared as follows. Equimolar quantities of metal trichloride and phosphorus pentachloride were transferred to a dry 250-ml. round-bottom flask under an atmosphere of dry nitrogen. Anhydrous methylene chloride (100 ml.) was added to the flask, and the slurry was stirred for approximately 2 hr. at room temperature. The precipitate, a fine white powder, was filtered off on a medium porosity glass frit under a dry-nitrogen atmosphere and washed with methylene chloride (30 ml.). The solid was transferred to an ampoule and the remaining traces of solvent were removed by pumping on the solid for 24 hr. X-Ray powder diffraction patterns demonstrated that the individual crystalline components were absent from the reaction products [Found: Al, 8.1; Cl, 82.2; P, 9.1. Calc. for $\text{PCl}_5\cdot\text{AlCl}_3$: Al, 7.9; Cl, 83.0; P, 9.1%. Found: Cl, 73.2; Ga, 18.8 (diff.); P, 8.0. Calc. for $\text{PCl}_5\cdot\text{GaCl}_3$: Cl, 73.8; Ga, 18.1; P, 8.1%].

(ii) $\text{PCl}_5\cdot\text{BCl}_3$ was prepared as follows. Phosphorus pentachloride (~15 g.) was transferred to a dry 250-ml. round-bottom flask under an atmosphere of dry nitrogen. Anhydrous

¹ Groeneveld, *Rec. Trav. chim.*, 1952, **71**, 1152.

² Holmes, *J. Inorg. Nuclear Chem.*, 1960, **14**, 179.

³ Fialkov and Buryanov, *Doklady Akad. Nauk S.S.S.R.*, 1953, **92**, 585.

⁴ Waddington and Klanberg, *J.*, 1960, **2329**, 2339.

⁵ Miller, "International Symposium on Molecular Structure and Spectroscopy," Tokyo, 1962, Reprints A 311—1.

⁶ "Alphabetical Grouped Numerical Index of X-ray Diffraction Data," American Society for Testing Materials, Baltimore, 1960.

methylene chloride (100 ml.) was added, and the slurry was stirred for *ca.* $\frac{1}{2}$ hr. The undissolved phosphorus pentachloride was filtered off on a medium porosity glass frit under an atmosphere of dry nitrogen. The clear, saturated solution was collected in a gas bubbler and a two-fold excess of boron trichloride gas was passed through the solution at room temperature for *ca.* $\frac{1}{2}$ hr. A white, finely divided precipitate formed within the first minute of gas passage. The precipitate was filtered off and dried as for the phosphorus pentachloride adducts described above (Found: B, 3.3; Cl, 87.2; P, 9.5. Calc. for $\text{PCl}_5\cdot\text{BCl}_3$: B, 3.3; Cl, 87.1; P, 9.5%).

(iii) The preparation of $\text{PCl}_5\cdot\text{TlCl}_3$ required the use of an ionizing solvent; this compound was not formed in methylene chloride, and an X-ray powder examination of the reaction residue revealed the presence of unreacted starting materials. However, the adduct was formed when phosphorus oxychloride was used in a procedure similar to that described by Groeneveld¹ [Found: Cl, 54.7 (diff.); P, 5.9; Tl, 39.4. Calc. for $\text{PCl}_5\cdot\text{TlCl}_3$: Cl, 54.6; P, 5.9; Tl, 39.4%].

(iv) The addition compound $\text{PCl}_5\cdot\text{InCl}_3$ could not be prepared in methylene chloride, phosphorus oxychloride, or arsenic trichloride by the procedure described in (i) or the method of Groeneveld.¹ The resulting solid, in each case, was found by X-ray powder diffraction to contain the starting materials.

Analytical Procedures.—(i) Addition compounds were hydrolysed at 100° for 2–3 hr. in sealed tubes containing 5–7N-sodium hydroxide.

(ii) Phosphorus was determined by the method of Kassner and Ozier,⁷ boron by a modified Volhard procedure,⁸ boron by the method of Schafer and Sieverts,⁹ and aluminium by the method of Mellon.¹⁰ Thallium was determined by the procedure of Moeller and Cohen¹¹ on a sample which was hydrolysed in dilute sulphuric acid.

(iii) X-Ray powder diffraction photographs (CuK_α radiation) were taken of samples sealed in 0.3-mm. capillaries under an atmosphere of dry nitrogen. Exposures were of the order of 20 hr. at 32 kv and 15 mA. on a camera of 11.46 cm. effective diameter.

TABLE I.

Observed *d* spacings and intensities for phosphorus pentachloride addition complexes.

$\text{PCl}_4+\text{PCl}_6$ <i>d</i> (Å)	$\text{PCl}_5\cdot\text{BCl}_3$ <i>d</i> (Å)	$\text{PCl}_5\cdot\text{AlCl}_3$ <i>d</i> (Å)	$\text{PCl}_5\cdot\text{GaCl}_3$		$\text{PCl}_5\cdot\text{TlCl}_3$ <i>d</i> (Å)
			<i>d</i> (Å)	<i>d</i> (Å)	
6.66 vvw	6.28 vw	6.28 vw	7.08 vvw	3.38 w	6.92 vvw
5.83 vw	5.95 vw	5.31 vw	6.76 vvw	3.29 vvw	5.22 s
4.96 s	5.19 m	4.87 s	6.19 vw	3.13 vvw	4.95 s
4.65 s	4.75 s	4.67 m	5.64 vvw	3.06 w	3.85 vw
3.95 w	4.55 s	3.85 s	5.31 s	2.99 s	3.59 m
3.45 w	3.77 m	3.58 vw	5.10 vvw	2.88 w	3.14 m
2.95 m	3.48 w	3.27 vw	4.85 vs	2.79 w	3.10 m
2.86 w—m	3.21 vw	2.98 m	4.62 m	2.73 vvw	2.95 w
2.77 m—s	2.97 m	2.88 m	4.42 w	2.56 vvw	2.82 w
2.44 w	2.89 w	2.80 w—m	3.83 s	2.40 vvw	2.62 w
2.40 w	2.81 s		3.77 w	2.34 vw	2.47 w
2.33 w			3.62 m	2.26 vvw	2.24 m
			3.53 m	2.21 vw	2.20 m

(iii) Infrared spectra were obtained with a Perkin-Elmer 21 spectrophotometer. Sodium chloride optics were used in the range 4000–650 cm^{-1} , and potassium bromide optics in the range 800–400 cm^{-1} . Polystyrene and air were used to calibrate the instrument. Samples for infrared analysis were incorporated in potassium chloride pellets over which a stream of dry nitrogen was blown while the spectra were being taken.

RESULTS AND DISCUSSION

The X-ray powder diffraction photographs (Table I) demonstrate that the solids obtained from methylene chloride solution are not simple mixtures of phosphorus pentachloride with Group III halides, but are unique crystalline species. Corresponding powder

⁷ Kassner and Ozier, *Analyt. Chem.*, 1950, **22**, 194.

⁸ Swift, Arcand, Lutwack, and Meier, *Analyt. Chem.*, 1950, **22**, 306.

⁹ Schafer and Sieverts, *Z. analyt. Chem.*, 1941, **121**, 161.

¹⁰ Mellon, "Organic Reagents in Inorganic Analysis," Blakiston Co., Philadelphia, 1941, p. 239.

¹¹ Moeller and Cohen, *Analyt. Chem.*, 1950, **22**, 686.

TABLE 2.

Infrared bands (cm.^{-1}) of phosphorus pentachloride addition complexes.

PCl_5	$\text{PCl}_5, \text{BCl}_3$	$\text{PCl}_5, \text{AlCl}_3$	$\text{PCl}_5, \text{GaCl}_3$	$\text{PCl}_5, \text{TlCl}_3$
1300m sharp	1424w br	1642w	1289m—s	1290m sharp
700w br	1275w—m	1289m—s	1105vw	1107w br
650s br	1190vw	1106w	705w br	826w br
585s br	696s	833w br	669w	702m br
446s br	651s	704m	654s br	668m shoulder
	590m—s	668s shoulder	595s br	651s br
	485w br	653s br	492m br	588s br
		593s br		485vw
		499s br		463w br

patterns were obtained from samples which were prepared in phosphorus oxychloride. Furthermore, the adduct $\text{PCl}_5, \text{AlCl}_3$ which was prepared through the direct combination of the reactants at $450\text{--}500^\circ$ was identical with that prepared in solution. Thus, it is clear that the use of an ionizing solvent such as phosphorus oxychloride is not necessary, in general, for the synthesis of these addition compounds; the relative ease with which methylene chloride can be purified and handled makes it a far superior medium. The only compound which could be formed in phosphorus oxychloride but not in methylene chloride was $\text{PCl}_2, \text{TlCl}_3$. The indium trichloride adduct could not be formed under any of the conditions attempted in this investigation.

The observed infrared spectra (Table 2) have features in common with that reported by Waddington and Klanberg⁴ and Miller⁵ for PCl_4^+ in the solids phosphorus pentachloride, $\text{PCl}_5, \text{BCl}_3$, and $\text{PCl}_5, \text{AlCl}_3$. In particular, two strong bands, at 650 and 584 cm.^{-1} , have been attributed to this cation.⁴ There is little question that the band at *ca.* 650 cm.^{-1} is the fundamental mode ν_3 . Beattie and Webster¹² place this band at 649 cm.^{-1} from infrared spectroscopy. From Raman spectroscopy Miller⁵ places ν_3 at 658 cm.^{-1} and Taylor¹³ places it at 655 cm.^{-1} , in contrast to Gerding and Houtgraaf's¹⁴ assignment at 627 cm.^{-1} . The source of the band at 584 cm.^{-1} has been questioned.¹² Waddington and Klanberg⁴ attribute it to the combination band ($\nu_1 + \nu_4$) of PCl_4^+ . On the other hand, Beattie and Webster¹² point out that this value is about 100 cm.^{-1} lower than the calculated value for ($\nu_1 + \nu_4$). They believed the most likely source of this band, and a second band at about 1300 cm.^{-1} , to be phosphorus oxychloride, a possible hydrolysis product of PCl_4^+ salts. Our observations are in accord with Beattie and Webster's¹² in that the relative intensity of the band at 580 cm.^{-1} varies from sample to sample in relation to that of the fundamental at 650 cm.^{-1} . Since it is extremely difficult to eliminate the possibility of some hydrolysis of the sample during the process of taking the infrared spectrum of a mull or pellet, the hydrolysis product, phosphorus oxychloride, could contribute to the band at 580 cm.^{-1} . However, it has not been established conclusively by Beattie and Webster¹² that PCl_4^+ does not have an absorption band at this frequency.

We have found a band at *ca.* 650 cm.^{-1} , which can be attributed to ν_3 of PCl_4^+ , in the spectrum of each compound, as follows: phosphorus pentachloride, 650; $\text{PCl}_5, \text{BCl}_3$, 651; $\text{PCl}_5, \text{AlCl}_3$, 653; $\text{PCl}_5, \text{GaCl}_3$, 654; $\text{PCl}_5, \text{TlCl}_3$, 651. Since this absorption is essentially constant throughout the series, it is concluded that these compounds are ionic in the solid state and contain the PCl_4^+ cation as a species which is essentially independent of the anion.

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¹² Beattie and Webster, *J.*, 1963, 38.

¹³ Taylor, personal communication.

¹⁴ Gerding and Houtgraaf, *Rec. Trav. chim.*, 1955, 74, 5.