All of the ν_1 band parameters exhibit a sharp break—to lower frequency and intensity, and greater width—on adding more chloride to $TlCl_4^-$. The break in the stability sequence for the successive complexes is also pronounced. Most likely the product is octahedral $TlCl_6^{-3}$, in which the chlorides are, on the average, less tightly bound than in $TlCl_4^-$. Since addition of only one chloride would destabilize the $TlCl_4^-$ structure and the addition of one more would probably lead to a slight increase in stability, it is not surprising that $TlCl_5^{-2}$ does not appear to be an important species in aqueous solution.

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Pentacoordinated Molecules. V. The Preparation and Properties of $PClF_4$

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Phosphorus monochlorotetrafluoride, $PClF_4$, the only previously unknown member of the series PCl_xF_{5-x}, was successfully prepared by the controlled low-temperature fluorination of the molecular form of PCl_2F_3 using SbF_3 as the fluorinating agent. Its characterization and some of its physical properties are reported.

The phosphorus(V) chlorofluorides have been the subject of a number of recent investigations[1]; however, the over-all correlation of structural information on these substances was hampered to a degree for lack of one member of the series, $PClF_4$. We now wish to report the successful synthesis and characterization of this member. It was obtained by the low-temperature fluorination of PCl_2F_3 using SbF_3 as the fluorinating agent.

Experimental

Preparation.—The apparatus consisted of a 100-ml. reaction flask containing a Teflon-coated stirring magnet. Attached to the flask was a swivel-type addition tube for adding solid SbF_3 (Columbia Organic Chemical Co.) and a reflux condenser with a dewar head suitable for use at low temperatures. The entire assembly was attached to the vacuum line through the connection at the upper part of the reflux condenser. A quartz spiral Bourdon pressure gauge and fractionation train also were essential parts of the vacuum system. The stopcock grease used was Kel-F.

The molecular form of PCl_2F_3 (approximately 6 ml.) was prepared *in vacuo* according to a modification[2] of a previous procedure[3] and transferred to the 100-ml. flask. Reaction was initiated by adding a small amount of SbF_3 through the addition tube. The head temperature was maintained at −95° (the vapor pressure of PCl_2F_3 at −95° is near zero) by means of a toluene slush bath. The temperature of the reaction flask was controlled at −40 to −50°. Reaction proceeded with the continued addition of SbF_3 causing pressure buildup in the reaction zone due to the formation of volatile products. To prevent the desired product, $PClF_4$, from being fluorinated further, a low pressure (about 25 mm.) was kept in the reaction zone by continuously bleeding off the product gases. This procedure was effective in limiting the formation of PF_5 to 1% or less of the total product. The addition of SbF_3 was completed during the first hour but the reaction continued very slowly. The reaction usually was terminated after 6 hr. Vacuum fractionation of the product through traps cooled to −123, −136, and −196° yielded a tensiometrically homogeneous sample after three or four recyclings. The yield of pure material is estimated at 20%.

At the end of 6 hr. the product is being evolved at about the same rate as was observed initially. Hence further yield may be realized on lengthening the collection time. Some solid does appear on the walls of the flask during the reaction, presumably solid modifications of the mixed halides[3] resulting from prolonged contact at temperatures considerably above −78°, but this action may be limited by maintaining the entire reaction assembly at −30 to −40°.

Results

Infrared Spectrum.—The gas phase spectrum of $PClF_4$ was recorded in the range 2000–400 cm.$^{-1}$ with a Perkin-Elmer Model 337 Grating Infracord and in the range 2000–250 cm.$^{-1}$ with a Perkin-Elmer Model 421 spectrophotometer. The former was calibrated with polystyrene and the latter with polystyrene and H_2O vapor. A 10-cm. gas cell fitted with KBr or CsI windows was used. Argon was mixed with the $PClF_4$ for some of the runs to minimize cell reaction and window attack.

After thorough conditioning of the cell with the $PClF_4$, reproducible spectra were obtained in the pressure region from 2 to 500 mm. Table I lists all but the very weak bands and serves to characterize the compound.

The bands at 993 and 1415 cm.$^{-1}$ are easily recognizable as POF_3 impurity bands while the line at 1026 cm.$^{-1}$ is in the region of an intense SiF_4 fundamental.[4] The POF_3 lines grow with time while the

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[1] Previous paper: R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *Inorg. Chem.*, **3**, 1748 (1964), and references cited therein.

[2] R. R. Holmes and R. P. Carter, Jr., to be published.

[3] R. R. Holmes and W. P. Gallagher, *Inorg. Chem.*, **2**, 433 (1963).

[4] H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952).

TABLE I

INFRARED SPECTRUM OF $PClF_4$[a]

Cm.$^{-1}$	I	Cm.$^{-1}$	I	Cm.$^{-1}$	I
356	w	665	m	927	vs (sh)
427	mw	672	m	945	s
434	mw	692[b]	s	954	w
470	m	817[b]	w	993	vs
490[b]	s	859	m	1026	s
531	m	869	m	1063	w
541	s (sh)	895	vs	1415[b]	w
559[b]	vs	903	vs	1606	w
626	mw	921	vs		
633	mw				

[a] s, strong; m, medium; w, weak; sh, shoulder. [b] Band heads.

others do not. Little indication of the presence of the likely contaminants, PF_5 and PCl_2F_3, was revealed on comparison of their spectra[5] with that of $PClF_4$.

Molecular Weight.—The vapor phase molecular weight of $PClF_4$ was determined in the usual fashion by weighing a sample whose volume, pressure, and temperature had been established. The results gave a value of 142.2; calculated for $PClF_4$, 142.43.

Vapor Pressure.—The vapor pressure relationship was obtained in the range −123 to −54°. A new sample was used for each temperature. The temperature maintained to ±0.05° was measured with platinum resistance thermometer, the pressure (±0.1 mm.) with a sensitive quartz spiral Bourdon. Excellent linearity of the resulting log p (mm.) *vs.* $1/T$ plot was obtained. The equation governing the liquid–vapor equilibrium obtained by a least-squares fit is log p (mm.) $= -1126.893/T + 7.78633$. The standard deviation is 0.0100. The extrapolated boiling point is −43.4°. The heat of vaporization is 5.16 kcal./mole; Trouton's constant is 22.5. Table II contains representative vapor pressures. The melting point was recorded as −132 ± 3°.

TABLE II

VAPOR PRESSURES OF $PClF_4$

t, °C.	p, mm.	t, °C.	p, mm.
−122.98	1.9	−74.54	130.4
−119.37	2.9	−63.6	243.0
−95.37	27.7	−56.20	401.1
−83.88	69.5	−54.06	440.3
−78.42	101.6		

F^{19} Nuclear Magnetic Resonance Spectrum.—The F^{19} n.m.r. spectrum of an isopentane solution of $PClF_4$ (approximately 30% by volume), internally referenced with CCl_3F, was examined as a function of temperature in a Varian Associates HR-60 high resolution spectrometer operating at 56.4 Mc. The spectrum consisted of a simple doublet pattern (P–F coupling) 23.5 p.p.m. upfield from CCl_3F. The coupling constant was 1000 c.p.s. No shift with temperature was detected. However, the doublet began to broaden near −138°, and at −157°, the lowest temperature reached, the doublet was completely broadened. Presumably the molecule is exchanging intramolecularly at a rate intermediate between PF_5 and PCl_2F_3. In the latter molecule exchange was "stopped" at −143° and two fluorine environments are seen.[1] The averaged chemical shift, +23.5 p.p.m., for $PClF_4$ is intermediate between the averaged values for PF_5 and PCl_2F_3.[1] In the sample studied minor amounts of PF_5 (+66.5 p.p.m.) and PCl_2F_3 were detected as contaminants. At −157° the PF_5 doublet was not present, but the low-temperature pattern for PCl_2F_3[1] appeared at a barely detectable intensity. The lack of appearance of the PF_5 doublet at −157° is presumably a result of the compound precipitating out of solution and has nothing to do with slowing the suspected exchange process for this molecule since the very sharp doublet looses intensity continuously as the temperature is lowered and no change in line shape occurs.

Thermal Stability.—A sample of $PClF_4$ was stored in an ampoule in the gaseous state at room temperature. No solid formation was noticed for the first 4 days. After this time a white solid began to deposit on the walls of the ampoule. After 2 weeks the ampoule was opened and the volatile portion fractionated. Considerable PF_5 was detected as well as lesser amounts of PCl_2F_3 and unreacted $PClF_4$. Thus, as with the molecular forms of the other phosphorus(V) chlorofluorides,[1] molecular $PClF_4$ has a limited existence at room temperature.

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(5) J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964).