3.2; 50 (PF^+), 21.0; 45 (PN^+), 8.1; 31 (P^+), 3.2. The infrared and nmr spectra are considered in the Results and Discussion.

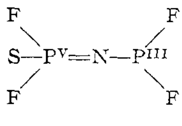
The compound was hydrolyzed by distilling 0.1731 g, 1.012 mmol, into a bulb with a Fischer-Porter valve containing excess 2 *N* NaOH. The solution was heated at 60° for 2 days. To analyze for nitrogen the ammonia produced was very carefully and slowly distilled out of the aqueous alkali and then redistilled twice through cold traps at −80 and −160°; the last held the ammonia. Both the pressure–volume–temperature relationship and the weight indicated 0.997 mmol of it corresponding to 98.5% recovery. The infrared spectrum of this ammonia at 50 mm indicated no impurities. The fluoride present in the hydrolysis solution was analyzed as triphenyltin fluoride.[3] The phosphorus was oxidized with concentrated nitric acid and measured by the titrimetric ammonium phosphomolybdate procedure.[4] The results are summarized. *Anal.* Calcd for F_5NP_2: F, 55.57; N, 8.24; P, 36.24. Found: F, 55.5; N, 8.12; P, 37.18.

Synthesis of PF_2Cl and $F_2P(S)SPF_2$.—Into the reactor were distilled PF_2NH_2 (0.365 mmol) and HCl (0.730 mmol). It was then allowed to warm to room temperature and its volatile contents distilled through traps cooled to −160 and −196°. That at −160° held the PF_2Cl (0.314 mmol, 83.2% yield based on eq 2) and the latter trap contained a small quantity of PF_3 and a trace of HCl. To prepare $F_2P(S)SPF_2$, PF_2NH_2 (0.608 mmol) and HPS_2F_2 (0.730 mmol) were condensed into the reactor and the reaction was allowed to progress in the same way indicated above. The volatile products were passed through traps maintained at −80 and −196°. The one at −80° retained the $PF_2SP(S)F_2$ (0.338 mmol, 92.2% yield) and the excess PF_2NH_2, and small quantities of PF_3 and an unidentified substance(s) were found in the −196° trap. The solids in the reactors were identified as the ammonium salts of the chloride and $PS_2F_2^-$ ions by their infrared spectra.

Results and Discussion

Fluorophosphorus compounds containing phosphorus in mixed valence states are rare. The only known examples were recently prepared by Cavell and coworkers[5,6] and DesMarteau,[7] and these are $F_2P(S)SPF_2$ and $F_2P(O)OPF_2$. Trifluoromethyl groups may be substituted for the fluorine atoms.[8] Also, the existence of F_3PPF has been speculated.[8] Trifluorophosphazodifluorophosphine, $F_3P{=}NPF_2$, is another example. However, in this case a nitrogen atom rather than an oxygen or sulfur atom separates the phosphorus atoms. The reaction between PF_2NH_2 and PF_3Cl_2 leads not only to $F_3P{=}NPF_2$ but also to PF_2Cl. These products may be explained by an initial reaction to give the phosphazo compound and hydrogen chloride. The hydrogen chloride would then react with PF_2NH_2 to give PF_2Cl according to eq 2. This second step must be rapid compared to the initial because HCl is rarely observed as a product. Equation 2 also provides a method for the synthesis of $F_2P(S)SPF_2$, recently prepared by a similar procedure employing a dialkylamidodifluorophosphine and HPS_2F_2.[6]

Spectroscopic analysis corroborates the proposed structural formulation given below for $F_3P{=}NPF_2$. The infrared spectrum of the compound has a complex, broad band having maxima at 1532 (m), 1460 (s), and 1416 cm^{-1} (ms) assigned to the P=N stretching frequency. The spectra of other trifluorophosphazo compounds also exhibit strong, broad, and complex absorptions in the same region.[9] A very strong-intensity absorption at 980 cm^{-1} having a shoulder at 964 cm^{-1} is associated with the PF_3 group P–F stretching vibration[9] while a broad peak at 816 cm^{-1} (m) is due to the PF_2 group stretching motion. Other PF_2-containing compounds display strong-intensity absorptions in this region, *e.g.*, PF_2Cl at 864 and 853, PF_2NH_2 at 875 and 804, and P_2F_4 at 842, 830, and 820 cm^{-1}.[10] Another unassigned band is centered at 675 cm^{-1} (wm). Further confirmation is obtained from the nmr spectra. The ^{19}F spectrum appears as a pair



of doublets of quadruplets centered at ϕ 45.72 ppm due to the PF_2 group and a doublet of triplets at ϕ 82.76 ppm for the PF_3 group fluorine atoms. The coupling constants are $J_{\mathrm{P^V-F}}$ = 1031 Hz, $J_{\mathrm{P^{III}-F'}}$ = 1279 Hz, $J_{\mathrm{F-F'}}$ = 7 Hz, and $J_{\mathrm{P^V-F'}}$ = 24.1 Hz. No coupling is observed between P^{III} and F. The ^{31}P spectrum shows a triplet at low field, −129 ppm (J = 1290 Hz), and a quadruplet at high field, 43.6 ppm (J = 1027 Hz). Both the chemical shift and the coupling constants of the $F_3P{=}N{-}$ moiety in the ^{19}F spectra of other trifluorophosphazo compounds are close to the values reported above, *viz.*, ϕ 86.7 ppm (J = 1090 Hz) in the spectrum of $F_3P{=}NSO_2F$ and ϕ 85.2 ppm (J = 1045 Hz) in that of $F_3P{=}NP(S)F_2$,[9] and the chemical shift and P—F coupling constant of the PF_2 group fluorine nuclei are in the expected range.[6,11]

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Mass Spectrometric Evidence of Dimers in Bismuth Pentafluoride and Antimony Pentafluoride

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The group V pentafluorides show a wide range in physical and chemical properties.[1] While PF_5 (bp −84.5°) and AsF_5 (bp −52.6°) are gases, SbF_5 (bp 149°) is a viscous liquid, and BiF_5 (mp 151°) is a sublimable solid. The BiF_5 is the strongest oxidative fluorinating agent,[2,3] but the irregular order of strengths

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as Lewis acids, $PF_5 < AsF_5 < BiF_5 < SbF_5$, has been suggested.[4] Viscosity,[5] surface tension,[6] and electrical conductivity studies[7] concluded that liquid SbF_5 was polymeric $(SbF_5)_n$ (where n = 7–8) rather than ionic and the ^{19}F nmr spectrum[8] has been interpreted[9] in terms of either dimeric octahedral SbF_5 groups joined by a double fluorine bridge or tetrameric cyclic octahedral SbF_5 groups joined by single F bridges. The tetragonal α-UF_5 structure of solid BiF_5 was ascribed[3] to an essentially ionic structure, but the high Trouton constant of liquid BiF_5 was taken[3] as indicative of SbF_5-type polymerization. In the present studies, the mass spectra of SbF_5, BiF_5, and also BiF_3 have been investigated, using a variable-temperature, direct-inlet probe and have given new information on the nature of these species in the gas phase.

Bismuth pentafluoride was sufficiently volatile under vacuum at ambient temperature to be readily observed mass spectrometrically. The parent molecule ion was not observed and the most intense peak was the parent less one F atom as is usually the case for highly fluorinated species, *i.e.*, BiF_4^+ at m/e 285 (Bi and F are both monoisotopic). All the ions with successive loss of fluorine down to Bi^+ are observed as are the doubly charged ions (typical of a heavy-metal species). In addition, a series of peaks is observed at m/e 589, 551, and 513 corresponding to the ions $Bi_2F_9^+$, $Bi_2F_7^+$, and $Bi_2F_5^+$, with faint peaks down to Bi_2^+. The indicated parent Bi_2F_{10} was not observed, but its presence is inferred by analogy with BiF_5. No evidence was observed of higher clusters such as $Bi_3F_{14}^+$. By comparison, BiF_3 had to be heated to about 350° before it began to volatilize measurably. In this case, the parent peak was observed, although the BiF_2^+ peak was the most intense peak, and no evidence of dimers was noted other than Bi_2^+. The mass spectrum of SbF_5 was essentially analogous to that of BiF_5 (with the exception that Sb is diisotopic). In addition to the monoantimony fluoride ions (SbF_4^+, etc.), the $Sb_2F_9^+$, $Sb_2F_7^+$, and $Sb_2F_5^+$ ions were also observed.

All the group V pentafluorides form well-known salts of the $M^+BF_6^-$ type (where B = P, As, Sb, or Bi).[10] In recent years, numerous salts of Sb have been reported which appear to contain anions of the type $Sb_2F_{11}^-$, $Sb_3F_{16}^-$, etc. The X-ray analyses indicate that these anions contain octahedral SbF_6 groups joined by single fluorine bridges.[11–13] The analogous $As_2F_{11}^-$ ion has also been reported[14] and salts of the $Bi_2F_{11}^-$ ion appear to form.[15] The present mass spectrometric studies have indicated that volatilization of SbF_5 and BiF_5 yields substantial amounts of the neutral dimers Sb_2F_{10} and Bi_2F_{10}, respectively, in addition to the simple pentafluorides. The absence of $(BiF_5)_{3-4}$ suggests that the dimers have the more stable double fluorine bridge form. The dimeric interpretation of the nmr results with liquid SbF_5 is favored. The form of solid BiF_5 remains of interest.

Experimental Section

Materials.—BiF_3, BiF_5, and SbF_5 were obtained from Ozark-Mahoning Co. and were handled in a dry-air glove box. *Anal.* Calcd for BiF_3: Bi, 78.6. Found: Bi, 78.5 (by titration of bismuth–thiourea complex with the disodium salt of ethylenediaminetetraacetic acid).[16] Calcd for BiF_5: Bi, 68.7; F, 31.3. Found: Bi,[17] 67.5; F, 29.4–30.7 (by the $Th(NO_3)_4$ method).[18]

Procedure.—Analyses were performed with an Atlas CH-4B mass spectrometer using the variable-temperature, direct-inlet probe with gold sample cup. A Teflon shroud was placed over the probe during transfer from the drybox to the spectrometer and a flow of dry helium was maintained through the spectrometer loading port during insertion of the probe in order to minimize contamination by moisture. Spectra were taken immediately after sample insertion and evacuation of the spectrometer and again after about 15-min pumping at ambient temperature (~30°). Stepwise, temperature increases were used with 3–4 min between successive spectra. The mass marker of the instrument was checked with perfluorokerosene. The mass numbers above 400 were also checked by using an expanded scale with calibration against the BiF_4^+ or SbF_4^+ peaks and are believed accurate within ±0.5 mass unit.

Bismuth Trifluoride.—A sample of BiF_3 was studied from 350° (where volatilization became significant) up to 520°. The 70-eV mass spectrum shown in Table I was recorded at 425 and 450°. At 500° the relative intensities of the BiF^+, Bi^+, and Bi_2^+ ions increased as did a weak BiF_2O^+ impurity peak (~1% of BiF_3^+ at 450°), suggestive of decomposition and wall reactions. A sample of BiF_3 from another supplier gave essentially the same cracking pattern but was contaiminated with unidentified organic matter.

Bismuth Pentafluoride.—Six BiF_5 samples were examined. The spectra at ambient temperature varied slightly between samples; *e.g.*, the intensity of the $Bi_2F_9^+$ peak varied from 10 to 20% of the BiF_4^+ peak. The intensity ratios of the monobismuth species also varied slightly between samples in a manner indicative of a small and variable amount of BiF_3, which showed a relative increase with prolonged pumping or upon heating.[19] A 70 eV mass spectrum at ambient temperature of the assumed Bi_2F_{10}–BiF_5 mixture is shown in Table I. The spectra also con-

TABLE I

MASS SPECTRAL CRACKING PATTERNS (70 eV)

m/e	Ion peak	BiF_3	BiF_5	m/e^a	Ion peak	SbF_5
589	$Bi_2F_9^+$		18.0	413	$Sb_2F_9^+$	0.2
551	$Bi_2F_7^+$		3.5	375	$Sb_2F_7^+$	0.05
513	$Bi_2F_5^+$		3.4	337	$Sb_2F_5^+$	0.05
494	$Bi_2F_4^+$		0.3			
475	Bi_2F_3		0.5			
456	$Bi_2F_2^+$		0.2			
437	Bi_2F^+		0.3			
418	Bi_2^+	1	0.3			
285	BiF_4^+		100.0	197	SbF_4^+	100.0
266	BiF_3^+	32	10.0	178	SbF_3^+	20.0
247	BiF_2^+	100	38.0	159	SbF_2^+	25.0
228	BiF^+	8	10.0	140	SbF^+	7.0
209	Bi^+	15	13.0	121	Sb^+	8.0
				98.5	SbF_4^{2+}	0.4
133	BiF_3^{2+}	1	1.3	89	SbF_3^{2+}	5.0
123.5	BiF_2^{2+}	5	3.0	79.5	SbF_2^{2+}	2.0
114	BiF^{2+}	23	7.0	70	SbF^{2+}	5.0
104.5	Bi^{2+}	6	6.0	60.5	Sb^{2+}	1.7

[a] Data for the ^{121}Sb ion; ^{123}Sb ions are omitted.

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[17] Air-hydrolyzed samples were warmed with dilute NaOH to complete hydrolysis of fluorobismuthate species, acidified, and treated with $NaHSO_3$ to reduce Bi(V) to Bi(III) before analysis.

[18] Samples hydrolyzed in dilute NaOH at −196 to +25°. Fluoride determined individually in the solution and solid residue.

[19] The residue of the heated sample underwent pronounced decomposition at 300° with evolution of BiF_5 (no Bi_2F_{10}). Essentially only BiF_3 was observed thereafter up to 500°, suggesting that a salt $BiF_2^+BiF_6^-$ had decomposed.

tained small peaks attributable to BiF_2O^+, BiF_3O^+, and $Bi_2F_8O^+$ ($\sim$0.1% of BiF_4^+ peak) and a variable amount of unidentified organic material which appeared to arise from reaction with residuals in the instrument since some of these peaks also resulted when other reactive solids such as NO_2ClO_4 were being analyzed. A series of spectra on one BiF_5 sample at nominal ionizing voltages of 15, 20, 25, and 30 eV and the use of CO_2^+ and SiF_3^+ peaks[20] as internal standards indicated that the BiF_4^+ and $Bi_2F_9^+$ ions both have appearance potentials of 14.5–15 eV while that of the BiF_3^+ ion was about 12 eV.

Antimony Pentafluoride.—A sample of SbF_5 was examined at 30, 80, 90, and 110°. The initial spectra were surprisingly complex and indicated the presence of mono- and diantimony species in which one or more F atoms were substituted by Cl or OH, such as SbF_3Cl^+ and $Sb_2F_5ClOH^+$. The diisotopic nature of both Sb and Cl and the overlap of mass peaks of different species prevented complete identification. These impurity peaks decreased substantially upon pumping and warming. The spectrum of SbF_5 as recorded at 90–110° and 70 eV is shown in Table I.

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Pressure Effects on the Absorbance of Cobaltous Chloride Solutions[1a]

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In 1923 Wick[2a] observed a marked pressure-induced change in the color of aqueous solutions of $CoCl_2$. Lüdemann and Franck[2b] made a detailed study of the pressure chromism of these aqueous solutions, with and without added salt, in the ranges 25–500° and 1–6000 atm. The color change was attributed to modification of the equilibrium between Co(II) species in octahedral (o) and tetrahedral (t) coordination[3]

$$CoS_6^{2+} + nCl^- \rightleftharpoons CoS_{4-n}Cl_n^{2-n} + (2 + n)S \qquad (1)$$

where S is the solvent and $0 \leq n \leq 4$, depending on the chloride ion concentration. Since the number of ions changes in this complex equilibrium, a strong pressure dependence of the equilibrium constant is anticipated due to ion–solvent interactions. The pressure parameter yields the volume change $\Delta V = -RT\mathrm{d}\ln K/\mathrm{d}P$ for the reaction. The objective of the present high-pressure spectrophotometric study is to ascertain the extent to which ion solvation and electrostriction are responsible for the observed pressure chromism of Co(II) solutions.

The high-pressure optical cell used for solid samples[4] was modified to accept liquids in plastic capsules. The cell and press fit into the sample compartment of a Cary Model 14 spectrophotometer. The pressure was calibrated by means of reversible phase transitions in chlorobenzene (4.6 kbars)[5] and bromobenzene (3.3 kbars)[6] and by comparison of the L_a absorption shift of anthracene in pentane (to 6 kbars) with the shift measured by Robertson, *et al.*[7] The advantage of this apparatus is its simplicity, although the error in absorbance measurements is greater than for conventional optical bombs designed for fluids.

The ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition of $Co(H_2O)_6^{2+}$, which is responsible for the pink color (λ 5120 Å) of aqueous solutions, is largely insensitive to pressure and temperature.[2b] The blue color (λ ~6600 Å) of aqueous solutions with excess halide is assigned to ${}^4A_2(F) \rightarrow {}^4T_1(P)$ of the tetrahedrally coordinated Co(II). While the extinction coefficient ϵ of tetrahedral species in crystalline Cs_2CoCl_4 decreases sharply at very high pressures,[8] the best guess for solutions at relatively low pressures is that the transition probability of $CoCl_3H_2O^-$ and $CoCl_2(H_2O)_2$ is independent of pressure.[2b] With this assumption the observed pressure decrease of the absorbance near 6600 Å can be related directly to the shift in equilibrium 1. Since $\epsilon_{6600} \approx 100\epsilon_{5120}$, experimental conditions can be easily achieved in which (o) > (t) and $\ln A_{6600} \approx \ln K$.[9,10] This approximation leads to $\Delta H = 10$ kcal/mol which is in essential agreement with earlier measurements.[9,10] The initial slope of the linear plot of $\ln A_{6600}$ *vs.* P gives reasonable ΔV values of 8 (0°), 16 (25°), and 24 cm³/mol (50°) for 0.5 *m* $CoCl_2$ and 4 *m* LiCl. The observed decrease in ΔV at higher pressures is greater than normally observed for chemical equilibria,[3] so that the results must be viewed with caution. Multiple equilibria and changes in ϵ with pressure can invalidate the equality $K(P) \approx A_{6600}(P)$. Until these effects are determined independently, the $\Delta V(P)$ behavior cannot be ascribed to an unusually high compressibility of the ions.

Effects of electrostriction make the largest contribution to the volume change of ionic equilibria[3]

$$\Delta V = -\sum_i (Q_i^2/2R_i)(\epsilon^{-2}\mathrm{d}\epsilon/\mathrm{d}P) \qquad (2)$$

where ϵ is the dielectric constant, Q is the total charge of the ion of radius R, and the summation refers to all ionic products and reactants (opposite sign). It is clear that the application of the Born formula depends critically on the value of n in eq 1. If we choose $n = 3$ in aqueous, concentrated salt solutions,[2b,11–13] eq 2 yields ΔV values of 10 (0°), 15 (25°), and 19 cm³/mol (50°), assuming the temperature dependence is entirely due to $\epsilon(T)$ and estimating R to be 2.2 Å for the octahedral species, 1.8 Å for Cl^-, and 2.3 Å for the tetrahedral species.[14] Thus the Born formula gives

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[1] (a) This work was supported by the Cancer Research Coordinating Committee (University of California) and the U. S. Office of Naval Research. (b) University of Chile–University of California Cooperative Program Fellow.

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