effected by immersing the sample in liquid nitrogen and allowing the tube to collapse by heating with a small tube oven.

The plastic sample tubes were inserted in standard 5-mm glass nmr tubes. The spectra were obtained on a Varian Associates A56-60A spectrometer equipped with a V-6040 variable-temperature controller. Neither an internal nor an external standard was employed; rather, a separate tube of CCl_3F was examined immediately before and after the samples. The post-sample standard spectra employed a variable-frequency oscillator with a counter to determine the position of the absorption peaks of the samples.

A sample of XeO_2F_2 in its Kel-F nmr tube was examined mass spectroscopically after it had been heated as high as 70° on several occasions during the nmr investigation. This sample showed only very slight decomposition to XeF_2 and the presence of low molecular weight fluorocarbons and CO_2, presumably from attacks on the Kel-F.

$XeOF_4$ containing ^{18}F was prepared by direct irradiation of $XeOF_4$ in a nickel container in the beam of a linear accelerator. A tungsten converter target was used; the preparation involves the reactions $^{19}F(\gamma,n)^{18}F$ and $^{19}F(n,2n)^{18}F$. Fluorine-18 is a positron emitter with a 110-min half-life. It is detected by means of the resulting 0.5-MeV annihilation γ radiation. The counting equipment used, a single-channel analyzer and scintillation crystal, has been described previously.[9]

The $XeOF_4$ containing ^{18}F was first purified to separate it from noncondensables by pumping on the tube at −80°. It was then distilled into a 0.25-in. Kel-F tube containing a known amount of XeO_2F_2. The tube was warmed to the exchange temperature and gently shaken to obtain a homogeneous solution. The tube was weighed to determine the amount of $XeOF_4$ distilled onto the XeO_2F_2 and kept at the exchange temperature for 1 hr. While maintaining the exchange temperature, the bulk of the $XeOF_4$ was rapidly distilled into a second 0.25-in. Kel-F tube and the remainder was pumped out of the exchange tube. The completeness of the removal of the $XeOF_4$ was ascertained by weighing both fractions. The two fractions were counted and weighed to determine specific activities. The $XeOF_4$ fraction was also examined mass spectrographically. No HF, which might have contributed to exchange, was found.

Results and Discussion

Strong, sharp nmr signals were observed for both the pure samples and the 1:1 solution. Each chemical species present produced only one main signal and a ^{129}Xe spin doublet. No significant broadening was observed for any line throughout the temperature range examined. Pure XeO_2F_2 and the 1:1 solution were examined from +16 to 70° while pure $XeOF_4$ was examined from −41 to +43°. The lower limits were imposed by the freezing points (XeO_2F_2, 30°; $XeOF_4$, −40°) while the upper ones were determined by the softening point of Kel-F. At 25° in the 1:1 solution the XeO_2F_2 line shifts upfield 0.53 ppm relative to pure XeO_2F_2 (−105.10 ppm; CCl_3F = 0). The $XeOF_4$ absorption shifts downfield 0.95 ppm relative to pure $XeOF_4$ (−100.27 ppm). The ^{129}Xe splittings for $XeOF_4$ and XeO_2F_2 are 1124 and 1178 Hz, respectively.

The difference in chemical shifts for the 1:1 solution as compared with the pure samples can be explained as being due to solution effects alone. Measurements of the bulk diamagnetic susceptibility were made according to a modification of the concentric-tube method of Li.[10] As could be expected from their chemical formula XeO_2F_2 and $XeOF_4$ differ only slightly ($-\chi_v$ = 0.86 and 0.82, respectively).

The results of the ^{18}F-exchange experiments at 29 and 0° are shown in Table I. Attempts to determine the extent of exchange at lower temperatures were inconclusive owing to experimental difficulties in obtaining complete dissolution of the solid XeO_2F_2 in the $XeOF_4$. Also, rapid separation of the two fractions after exchange was extremely difficult because of the low vapor pressure of $XeOF_4$ below 0°. Exchanges of less than 1-hr duration were not run because the time for separation would be too long a fraction of the exchange time to give meaningful results.

TABLE I

A 1-HR ^{18}F EXCHANGE IN THE SYSTEM $XeOF_4$–XeO_2F_2

Temp, °C	$XeOF_4$ mg	$XeOF_4$ mmol	$XeOF_4$ cpm (cor)	XeO_2F_2 mg	XeO_2F_2 mmol	XeO_2F_2 cpm (cor)	Fractional exchange
29	219.6	0.9834	145,000	130.1	0.6463	58,200	1.16
0	104.0	0.4657	174,000	113.3	0.5628	112,000	1.04

To ascertain that no exchange takes place between the $XeOF_4$ containing ^{18}F and the Kel-F counting tube, two samples of irradiated $XeOF_4$ (approximately 200 mg each containing about 10^6 cpm) were kept in the Kel-F counting tubes for 1.5 hr and then pumped out. Less than 0.1% of the activity remained in the tube.

Eight to ten half-times are required for the complete exchange observed at 0° in the ^{18}F experiments. Therefore it can be stated that $t_{1/2}$ for fluorine exchange in this system is less than 7 min at 0°. In order for exchange to be confirmed at 70° in the ^{19}F nmr experiments, a 2-Hz broadening of the lines would have to be observed. Since such broadening was not observed, it can be concluded that $t_{1/2}$ for the exchange is greater than 4 sec at 70°. The range of values of $t_{1/2}$ consistent with the observations is expected to become narrower when the difference in temperatures is taken into account. With this intermediate exchange rate and the experimental limitations already mentioned, a detailed kinetic study was not carried out. Therefore it is not possible to discriminate among the mechanisms proposed in the introduction.

CONTRIBUTION FROM THE EASTERN LABORATORY,
EXPLOSIVES DEPARTMENT,
E. I. DU PONT DE NEMOURS AND COMPANY,
GIBBSTOWN, NEW JERSEY 08027

The Reaction between Diphenylchlorophosphine and Hydrazine Hydrochloride

BY E. F. MORAN AND D. P. REIDER

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It has been reported[1] that the reaction between diphenylchlorophosphine and hydrazine monohydro-

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[9] I. Sheft, H. H. Hyman, R. M. Adams, and J. J. Katz, *J. Am. Chem. Soc.*, **83**, 291 (1961).

[10] N. C. Li, R. L. Scruggs, and E. D. Becker, *ibid.*, **84**, 4650 (1962).

[1] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

chloride yields a compound which was tentatively assigned the structure $(C_6H_5)_2P(Cl){=}NP({=}NH)(C_6H_5)_2$. Since this compound is end-capped with the elements of HCl, it was of interest to us as a polymer intermediate. Conceivably it could be homopolymerized under suitable conditions to yield long-chain linear polymers or polymerized with organic polymer intermediates, such as amino acids, to yield a polymer with an alternating phosphonitrilic, organic backbone. This communication reports the results of a more detailed study of the reaction between diphenylchlorophosphine and hydrazine monohydrochloride under a variety of conditions including those reported for the desired compound. A new compound, to which the structure $[H_2N(P(C_6H_5)_2{=}N)_2P(C_6H_5)_2NH_2]Cl$ has been assigned, was found to be a product of this reaction.

Experimental Section

Materials.—Diphenylchlorophosphine was obtained from the Victor Chemical Works. It was distilled and the fraction boiling between 178 and 180° (14 mm) was used. Hydrazine monohydrochloride was obtained from Columbia Organic Chemicals Co. Solvents used were dried over calcium hydride.

Analyses.—Elemental analyses were carried out by Micro-Analysis, Inc., Wilmington, Del. Molecular weights were obtained with a Mechrolab vapor pressure osmometer. Melting points were observed in a Thomas-Hoover capillary melting point apparatus and are uncorrected. The infrared spectra were obtained on a Perkin-Elmer 137 spectrophotometer as Nujol mulls. Phosphorus nmr measurements were made on a Varian HR-60 at a frequency of 24.3 Mc/sec using a capillary of 85% phosphoric acid as a reference.

Reaction of Diphenylchlorophosphine with Hydrazine Monohydrochloride in Tetrachloroethane.—This reaction was run a number of times and the pertinent data are outlined in Table I. Only the experiments run at 146° produced a reaction product. In the experiments conducted at 100 and 110° the hydrazine monohydrochloride was recovered quantitatively on filtration of the cooled reaction mixture. After removal of the solvent from the filtrate, on standing, the residue yielded diphenylphosphinic acid probably due to oxidative hydrolysis of the unreacted diphenylchlorophosphine. Only one run (the third of Table I) will be described in detail.

TABLE I

REACTION BETWEEN $(C_6H_5)_2PCl$ AND H_2NNH_2HCl IN TETRACHLOROETHANE

Mol of $(C_6H_5)_2PCl$/ mol of H_2NNH_2HCl	Temp, °C	Time, hr	% yield of $H_2N[(C_6H_5)_2P{=}N]_3H_2Cl^a$
0.5	146	13	11.0
1	146	24	9.2
1	146	45	34.6
1	100	7	0^b
1.5	110	24	0^b

[a] Based on $(C_6H_5)_2PCl$ used assuming 3 mol of $(C_6H_5)_2PCl$ yields 1 mol of product. [b] Recovered H_2NNH_2HCl quantitatively.

A suspension of 7.0 g (0.1 mol) of hydrazine monohydrochloride in 60 ml of *sym*-tetrachloroethane was heated at reflux in a flask to which a water separator trap was attached to remove any moisture that may be present in the hydrazine monohydrochloride. After 15 min the water trap was removed and 22.1 g (0.1 mol) of diphenylchlorophosphine in 50 ml of *sym*-tetrachloroethane was added dropwise with continuous stirring over a 30-min period. After heating at reflux for 45 hr the reaction mixture was cooled to 10°. On filtration 3.5 g of solid was obtained which after extracting twice with boiling benzene and twice with boiling acetonitrile yielded 3.2 g of unreacted hydrazine monohydrochloride, mp 84–88°. It was identified by a comparison of its infrared spectrum and X-ray diffraction pattern. The X-ray pattern also indicated the presence of some ammonium chloride.

The filtrate was reduced in volume under vacuum and poured into hot benzene, which on cooling and filtering yielded 7 g of a white solid. The solid was recrystallized twice from acetonitrile and identified as diphenylphosphonitrile trimer by its melting point of 230–235° and infrared spectrum.

The filtrate remaining after separation of diphenylphosphonitrile trimer was reduced in volume under vacuum almost to dryness and slurried with about 475 ml of acetone to yield, on filtration, 5 g of a white solid, compound I, mp 285°. Reduction in volume of the acetone filtrate yielded a second crop of 2.5 g of the white solid, mp 280°. After combining with the above 5 g and recrystallizing from acetonitrile a melting point of 285° was obtained.

Addition of petroleum ether (boiling range 30–60°) to the acetone filtrate yielded a white solid which after recrystallization from methanol was identified as diphenylphosphinic acid, $(C_6H_5)_2PO(OH)$, by its melting point, 193–196°, and elemental analysis. Complete evaporation of the filtrate yielded a straw-colored resinous material which did not yield to further separation attempts.

Identification of Compound I.—The elemental analysis, phosphorus nmr spectrum, and infrared spectrum are in agreement with that expected for the compound $[H_2N(P(C_6H_5)_2{=}N)_2P(C_6H_5)_2NH_2]Cl$. *Anal.* Calcd for $C_{36}H_{34}N_4P_3Cl$: C, 66.41; H, 5.26; N, 8.61; P, 14.27; Cl, 5.45. Found: C, 66.01; H, 5.16; N, 8.60; P, 13.80; Cl, 5.35. Molecular weights determined on a vapor pressure osmometer ranged from 396 in methanol to 730 in chloroform. The range could be explained as being due to ionization in the polar solvent. A more accurate estimation of the molecular weight was obtained by determination of the neutralization equivalent. A weighed sample was slurried in methanol solution with an excess of a strongly acidic cation-exchange resin (Rexyn AG-50H) in the hydrogen form. After filtration the filtrate was titrated with standard base. A neutralization equivalent of 650 was obtained (calcd, 651).

The phosphorus nmr spectrum as a solution in chloroform exhibited two peaks at −31.6 and −18.1 ppm in a 2:1 ratio. This spectrum is consistent with a linear $-P{=}NP{=}NP-$ chain structure, the center phosphorus atom being in a different chemical environment than the other two.

The infrared spectrum is shown in Figure 1. It resembles in all respects, except for the strong band at 1210 cm^{-1}, the spectrum of the next lower homolog $[H_2NP(C_6H_5)_2{=}NP(C_6H_5)_2NH_2]Cl$, first prepared by Bezman and Smalley[2] and described by Sisler.[1] The additional strong band at 1210 cm^{-1} is probably due to the vibration of the longer chain length $-P{=}N-$ backbone.

Pyrolysis of Compound I.—A 2.0-g sample of compound I was heated at 280–305° under 0.25–0.1 mm pressure for 2 hr to yield a white sublimate on the cooler parts of the tube. The sublimate was dissolved in acetone to give 0.04 g of insoluble solid, the infrared spectrum of which matched that for ammonium chloride. This solid sublimed between 320 and 330° in a melting point tube as is reported for NH_4Cl. Reduction in volume of the acetone solution yielded a white precipitate. On filtration, 1.5 g of diphenylphosphonitrile trimer, mp 230–232°, was obtained. The identity of this compound was confirmed by comparison of its infrared spectrum with that of an authentic sample.

Derivatives of Compound I.—In order to confirm further the identity of compound I, the perchlorate and picrate derivatives were prepared by metathesis with excess perchloric and picric acids in methanol solutions.

The perchlorate derivative melted at 236–238° and exhibited an

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[2] I. I. Bezman and J. H. Smalley, *Chem. Ind.* (London), 839 (1960).

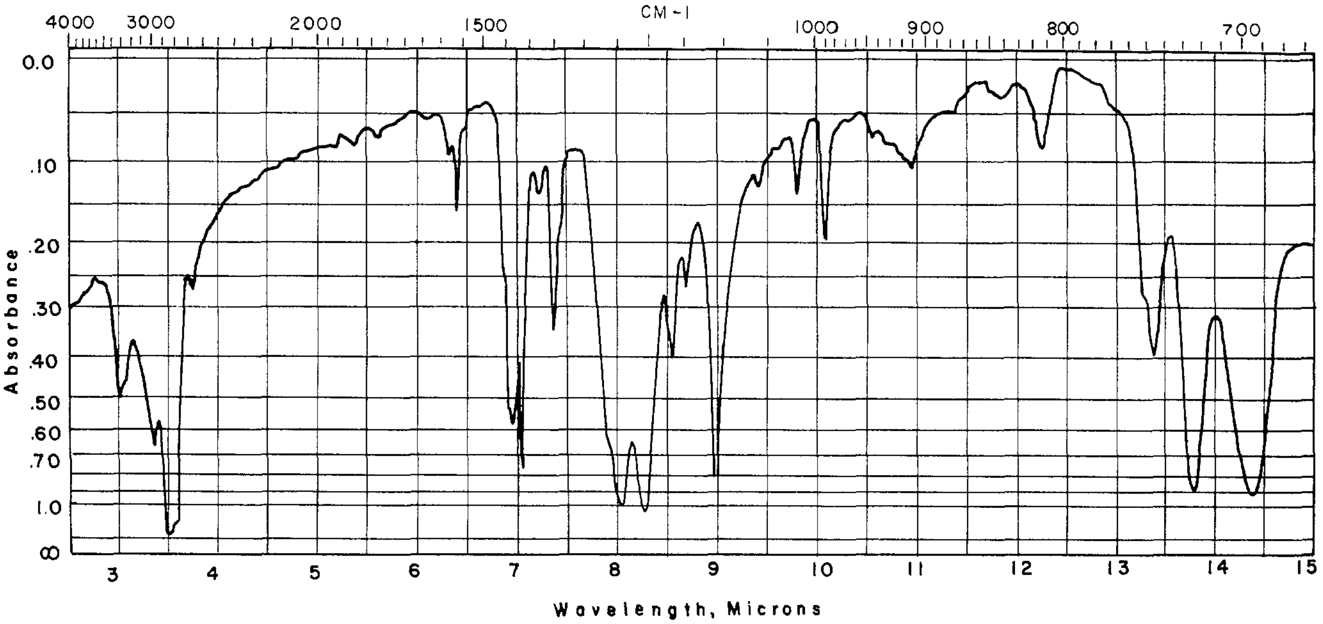

Figure 1.—Infrared spectrum of $[NH_2(P(C_6H_5)_2{=}N)_3H_2]Cl$ (Nujol mull).

infrared spectrum identical with that of the original compound except for a broad band at 1080 cm^{-1} due to the perchlorate ion.[3] The phosphorus nmr spectrum consisted of two peaks at -30.9 and -19.1 ppm in a 2:1 ratio. *Anal.* Calcd for $C_{36}H_{34}N_4P_3ClO_4$: C, 60.47; H, 4.79; N, 7.84; P, 12.99; Cl, 4.96. Found: C, 59.88; H, 4.54; N, 7.71; P, 12.91; Cl, 5.02.

The picrate salt melted at 200–202°. The infrared spectrum exhibited those bands found in the original compound along with weaker picrate ion bands. Two peaks at -31.0 and -17.5 ppm in a 2:1 ratio were found in the phosphorus nmr spectrum. *Anal.* Calcd for $C_{42}H_{36}N_7P_3O_7$: C, 59.79; H, 4.30; N, 11.62. Found: C, 59.95; H, 4.13; N, 11.19.

Reaction of Diphenylchlorophosphine with Hydrazine Monohydrochloride in Trichlorobenzene.—A mixture of 500 ml of 1,2,4-trichlorobenzene and 100 ml of *sym*-tetrachloroethane containing 34.3 g (0.5 mol) of hydrazine monohydrochloride was heated at reflux. As in the above reaction a water separator trap was employed and most of the tetrachloroethane was removed along with any moisture that may have been present. A 250-ml solution of 55.1 g (0.75 mol) of diphenylchlorophosphine in freshly distilled trichlorobenzene was added dropwise to the refluxing mixture over a 1-hr period. The mixture was refluxed at 200° for an additional 6.5 hr with the evolution of hydrogen chloride.

On cooling, solids were obtained which were separated by filtration. Extraction of the solids twice with hot acetone yielded 7.05 g of diphenylphosphonitrile tetramer, identified by its infrared spectrum and melting point of 328°. Evaporation of the acetone extracts yielded 46.7 g of a solid material which appeared from its infrared spectrum to be an aromatic amine hydrochloride probably resulting from reaction of the trichlorobenzene solvent with hydrazine monohydrochloride. Analysis indicated less than 0.4% phosphorus and this material was not examined further.

The trichlorobenzene solvent from the original filtration was removed under vacuum at 100–120°. The residue was extracted with a mixture of benzene and diethyl ether, which on reduction in volume yielded 21.5 g of diphenylphosphinic acid, $(C_6H_5)_2PO(OH)$, identified by its infrared spectrum and melting point of 189–192°. Further extraction of the remaining solid twice with hot benzene yielded an additional 10 g of diphenylphosphinic acid on reduction in volume of the solution. Complete evaporation of the combined filtrates gave 15.4 g of a resinous material that did not yield to further separation.

Recrystallization from chloroform of the solid remaining after the benzene–ether and benzene extractions above yielded 12.2 g of a white solid, mp 220–225°. The solid was identified as diphenylphosphonitrile trimer trihydrochloride. Extraction of a sample with water yielded an acidic chloride-containing solution and $[(C_6H_5)_2PN]_3$ identified by its melting point and infrared spectrum. The phosphorus nmr spectrum of the trihydrochloride in chloroform solution exhibited a single resonance at -21.2 ppm whereas the pure trimer gave a single peak at -13.8 ppm. The infrared spectrum of the trihydrochloride is essentially the same as that of the pure trimer except for a shift of the strong band at 1205 cm^{-1}, attributed to the P=N stretching vibration, to 1280 cm^{-1}. Also a strong band appeared at 952 cm^{-1}.

Anal.[4] Calcd for $C_{36}H_{33}P_3N_3Cl_3$: C, 61.16; H, 4.71; P, 13.14; N, 5.94; Cl, 15.05; mol wt, 707. Found: C, 62.90; H, 4.84; P, 12.69; N, 5.40; Cl, 13.94; mol wt, 752.

The formation of the trihydrochloride was verified by treating a sample of diphenylphosphonitrile trimer with excess concentrated hydrochloric acid in an evaporating dish and evaporating to dryness. A white solid was obtained which gave the same infrared spectrum as the material isolated from the reaction mixture.

Results and Discussion

The results reported above clearly establish the formation of the new compound 1-amido-1,1,3,3,5,5-hexaphenyl-6,6-dihydroketatriphosphonitrilium chloride, $[NH_2(P(C_6H_5)_2{=}N)_3H_2]Cl$, from the reaction between diphenylchlorophosphine and hydrazine monohydrochloride. This compound is the third member of the homologous series, $[NH_2(P(C_6H_5)_2{=}N)_nH_2]Cl$, the first being diphenyldiaminophosphonium chloride, $[(C_6H_5)_2P(NH_2)_2]Cl$, and the second 1-amido-1,1,3,3-tetraphenyl-4,4-dihydridoketadiphosphonitrilium chloride, $[NH_2(P(C_6H_5)_2{=}N)H_2]Cl$.[1,2]

The mechanism of formation of $[NH_2(P(C_6H_5)_2{=}N)_3H_2]Cl$ is not understood. Since hydrogen chloride is liberated during the reaction the first step could be the

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[3] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

[4] This analysis was done by Galbraith Laboratories, Inc., Knoxville, Tenn.

formation of $(C_6H_5)_2PNHNH_3Cl$. This could then be followed by an Arbuzov-type rearrangement, similar to that suggested by Winyall and Sisler[5] in the polymerization of 2,2-dimethylhydrazinodiphenylphosphine, to give $[(C_6H_5)_2P(NH_2)_2]Cl$. Intermolecular condensation of this intermediate with the elimination of NH_4Cl would be expected to yield $[NH_2(P(C_6H_5)_2{=}N)_nH_2]Cl$ and cyclic products $[(C_6H_5)_2P{=}N]_n$ as indicated by Sisler, *et al.*,[1] in the reaction of diphenylchlorophosphine with ammonia–chloramine mixtures. However, his mechanism is not entirely satisfactory since it does not explain why the reaction proceeds to a longer chain length moiety rather than stopping at the stable $[NH_2(P(C_6H_5)_2{=}N)_2H_2]Cl$.

The optimum conditions for the formation of $[NH_2(P(C_6H_5)_2{=}N)_3H_2]Cl$ appear to be long reaction times at moderate temperatures. In all experiments incomplete reaction was observed as evidenced by isolation of unreacted hydrazine hydrochloride and/or isolation of the oxidative hydrolysis product of diphenylchlorophosphine, namely, $(C_6H_5)_2POOH$. At temperatures below 145° no evidence of reaction was obtained, whereas at high temperature only cyclic polymers were isolated.

The linear compound $ClP(C_6H_5)_2{=}NP(C_6H_5)_2NH$ reported by Sisler, *et al.*,[1] was not detected in this work nor has a satisfactory mechanism for its formation been proposed. Furthermore, it would be expected that such a compound would hydrolyze readily owing to the presence of a labile chlorine atom. This compound would be analogous to $ClP(C_6H_5)_2{=}NP(C_6H_5)_2{=}O$ postulated as a product of the reaction between diphenylchlorophosphine and diphenylphosphenyl azide by Paciorek[6] which was isolated only as the hydrolysis product, $(C_6H_5)_2P(O)NHP(O)(C_6H_5)_2$. However, other evidence for this type of compound does exist. Bunting and Schmulbach[7] have reported the preparation of the next lower homolog, chlorodiphenylphosphinimine, $ClP(C_6H_5)_2NH$, which they found polymerizes to diphenylphosphonitrile tetramer on pyrolysis and hydrolyzes to diphenylphosphinic acid.

Pyrolysis of $[NH_2(P(C_6H_5)_2{=}N)_3H_2]Cl$ was found to yield diphenylphosphonitrile trimer. This is probably due to intramolecular condensation with the elimination of NH_4Cl, whereas in the case of the next lower homolog intermolecular condensation probably takes place yielding mainly the tetramer.[1] Likewise pyrolysis of $ClP(C_6H_5)_2{=}NP(C_6H_5)_2NH$ would be expected to yield the tetramer by intermolecular elimination of HCl rather than the trimer as reported for the compound tentatively assigned this structure.

Acknowledgments.—This work was supported in part by the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio (Contract No. AF-33(657)-10693).

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(5) M. Winyall and H. H. Sisler, *Inorg. Chem.*, **4**, 655 (1965).

(6) K. L. Paciorek, *ibid.*, **3**, 96 (1964).

(7) R. K. Bunting and C. D. Schmulbach, *ibid.*, **5**, 533 (1966).

Correspondence

Comments on the Article by R. A. Penneman

Sir:

Dr. Robert A. Penneman asked me to comment on his article "Molar Refractivity as a Diagnostic Tool for Determining Composition of Transition Element Fluoride Complexes," which is published on page 1379 of the present issue. An interesting correspondence developed which led to a mutual understanding of our somewhat different approaches to this kind of problem. The following remarks explain the situation.

The molar refractivity of the complexes is considered by Penneman to be additive according to the equation

$$R_{n\mathrm{AF}\cdot\mathrm{MF}_4} = nR_{(\mathrm{A}^+ + \mathrm{F}^-)} + R_{\mathrm{MF}_4}$$

Since the complexes as well as the MF_4 compounds are crystalline, additivity would imply that the values valid for gaseous ions are employed for R_{A^+} and R_{F^-}. However, the absolute values (in cm³) of the following differences Δ between, on the one hand, the average refractivities R_{cc} which the six fluorides have in the complexes according to Penneman's Table III and the values which their ions have (see footnote *a* to Penneman's Table III) in the aqueous or gaseous state are smaller (with the exception of NH_4F) for the aqueous ions.

TABLE I

DIFFERENCES BETWEEN THE REFRACTIVITIES (IN CM³) OF FLUORIDES IN THE COMPLEXES AND OF THEIR AQUEOUS OR GASEOUS IONS

Δ	LiF	NaF	KF	RbF	NH_4F	CsF
$R_{co} - R_{aq}$	+0.06	−0.10	+0.12	−0.03	−0.13	+0.03
$R_{co} - R_g$	−0.18	−0.22	+0.28	+0.13	+0.03	+0.19

The reason for distinguishing the values R_g and R_{aq} for Li^+, Na^+, and F^-, which have the largest energies of hydration, is as follows. According to a general principle,[1] cations (anions) tighten (loosen) the electronic system of neighboring anions (cations) and neutral molecules, *i.e.*, diminish (increase) their refractivity. For instance, the small Li^+ in aqueous solution decreases the refraction of the surrounding water by 0.40, while F^- increases it by 0.16. When 1 mol of gaseous Li^+ and F^- combines with $M^{4+}F^-{}_4$, a number of positive and negative effects occur and it is more or less accidental that the total effect (−0.18) comes close to that (−0.24)

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(1) K. Fajans and G. Joos, *Z. Phys.*, **23**, 1 (1924).