deductions of a 1:1 molar composition from the thermodynamic study of the *p*-xylene and *p*-dichlorobenzene Ni(4-mepy)$_4$(SCN)$_2$ by Hart and Smith.[3] Using our single crystal data, we were able to satisfactorily interpret the powder data given in their paper, as shown in Table II. There is no doubt that the clathrate lattice was the same in both investigations.

It was not possible to identify the powder data for the unclathrated complex on the basis of the tetragonal cell of the clathrates and this supports Hart and Smith's conclusion that the clathrated and unclathrated complexes have different crystal structures.

Contribution from the General Chemical Division,
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Dichlorofluoramine[1]

By Bernard Sukornick, Richard F. Stahl,
and Joseph Gordon

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The recent preparation of chlorodifluoramine[2] raised the question of the existence of its more highly chlorinated analog, dichlorofluoramine. We now wish to report the synthesis and characterization of this compound.

Experimental

In a 0.25-in. diameter copper U-tube surrounded by an ice bath was placed 15.0 g. (0.23 mole) of powdered sodium azide. Chlorine monofluoride, diluted with nitrogen, was passed over the solid for 8 hr. at the rate of 2.4 g. (0.044 mole) per hour. During the first 30 min. of reaction, chlorine azide formed almost exclusively. Thereafter, FNCl$_2$ appeared as the major product accompanied by small quantities of F$_2$NCl. The latter two gases were collected in a −80° trap. Subsequent distillation through an all-metal still equipped with a vapor-phase take-off provided 3.6 g. (20%) of FNCl$_2$, b.p. −2 to −3°. *Anal.* Calcd.: F, 18.28; Cl, 68.24; N, 13.48. Found: F, 18.13; Cl, 68.10; N, 13.47.[3]

The mass spectrum of dichlorofluoramine, obtained on a Consolidated Electrodynamics Model 21–103 mass spectrometer, is given in Table I. The cracking pattern provides strong corroborative evidence for the postulated structure. In particular, observation of the proper chlorine isotope effect for the parent peak confirms its identity.

The absence of any significant parent peak for NF$_2$Cl would indicate that the sample was relatively free of this compound.

One band was observed in the F^{19} n.m.r. spectrum of dichlorofluoramine. From the data given in Table II, it can be seen that this signal lies very close to the F^{19} chemical shifts for NF$_3$ and NF$_2$Cl. Therefore, it is quite likely that the N–F bonds in all three compounds are closely related electronically.

The infrared spectrum of dichlorofluoramine contains two strong bands at 12.0 and 12.2 μ. Both bands lie well within the N–F stretching region, although the one at 12.0 μ is probably best identified with the N–F stretch in FNCl$_2$.

Table I

Fragmentation Pattern of NFCl$_2$

m/e	Ion	Relative intensity
14	N$^+$	16.8
19	F$^+$	5.2
24.5	NCl^{+2}	0.80
25.5		0.28
33	NF$^+$	17.5
49	NCl$^+$	100
51		32.2
68	NClF$^+$	77.9
70		
84	NCl$_2$$^+$	1.6
86		1.1
88		0.19
103	NCl$_2$F$^+$	1.68
105		1.05
107		0.20

Table II

F^{19} N.m.r. and Infrared Spectra of Some N–F Compounds

Compound	F^{19} chem. shift, p.p.m.[a]	Principal N–F str. bands, μ
NF$_3$	−145 ± 1	9.7, 11.0
NF$_2$Cl[1]	−140.6	10.8, 11.7
NFCl$_2$	−128.7	12.0

[a] Measured relative to CFCl$_3$.

The compound absorbed at 2700 Å. in the ultraviolet. On exposure to a 360-watt high pressure mercury ultraviolet lamp, FNCl$_2$ partially decomposed to *cis*-difluorodiazine and, presumably, chlorine.

Small quantities of dichlorofluoramine also are formed by the reaction of chlorine azide and chlorine monofluoride. This fact, together with the initial formation of chlorine azide from sodium azide and chlorine monofluoride, suggests that ClN$_3$ is an intermediate in the formation of FNCl$_2$ *via* the NaN$_3$–ClF reaction

$$NaN_3 + ClF \longrightarrow ClN_3 + NaF$$
$$ClN_3 \longrightarrow [ClN<] + N_2$$
$$[ClN<] + ClF \longrightarrow FNCl_2$$

At present, however, there is no clear-cut evidence for the existence of the postulated chlorazene intermediate, ClN<.

Milligan[4] photolyzed samples of chlorine azide trapped in an argon matrix at 4.2°K. He attributed the appearance of infrared absorptions at 818 and 824 cm.$^{-1}$ on irradiation and the disappearance of these bands on warming to the formation and decomposition of chlorazene. Dimerization of ClN< also was suggested, but no dichlorodiazene, ClN=NCl, could be isolated.

Although no explosions have been encountered in handling gaseous FNCl$_2$, the liquid is extremely sensitive to friction and shock.

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(1) This work was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Research Missile Command, Redstone Arsenal, Huntsville, Alabama, under Contract No. DA-30-069-ORD-2638.

(2) R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

(3) Chlorine and fluorine analyses were obtained by reaction with sodium in liquid ammonia at 25° for 148 hr. Nitrogen was determined by a modified Dumas method.

(4) D. E. Milligan, *J. Chem. Phys.*, **35**, 372 (1961).

Contribution from the Department of Chemistry,
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A Silicon Metal Trap for the Safe Disposal of Chlorine Trifluoride

By Ralph G. Czerepinski and John L. Margrave

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The standard disposal method for chlorine trifluoride involves the use of a soda lime tower.[1,2] The chlorine oxides which result render the procedure hazardous and difficult to monitor.

In this Laboratory it has been found convenient to dispose of small (*e.g.*, 100 g.) quantities of chlorine trifluoride by passing the gas through a stainless steel trap filled with silicon metal. Low pressures of chlorine trifluoride react quite readily with silicon to form the very stable silicon tetrafluoride and chlorine. These can be collected in a liquid nitrogen trap and disposed of rather easily. A silicon trap also can be used for BrF_3 disposal.

The trap used in this Laboratory was designed for 1 mole of chlorine trifluoride and consisted of a 10-in. length of 1.5-in. (o.d.), $^1/_8$-in. walled stainless steel (Type N) tubing with a lid of 0.25-in. stainless steel plate. The trap was connected to the reaction system by a 0.25-in. stainless steel Swagelok[3] coupling with Teflon ferrules. The parts of the trap were silver soldered together and the lid was held on with six screws. A 60-mil Teflon gasket was machined to match the collar and several concentric grooves were cut in the lid and collar to help assure a vacuum-tight fit when the lid was in place. The trap was filled with crushed silicon, obtained by breaking silicon lumps with a hammer. It was found advisable to avoid loading the trap with silicon dust any finer than 100–150 mesh, as it tended to be blown through the lines and into the vacuum pump.

The main precaution to be observed when using this trap is to avoid passing ClF_3 into it too rapidly as the reaction is quite exothermic. When chlorine trifluoride at 1 atm. pressure was passed through the trap for 30 sec., the bottom three inches of the trap became orange hot (~750°). This could harm the silver-soldered connections if it continued very long.

This disposal system offers these advantages: (1) simply rattling the trap tells one how much silicon there is remaining, (2) the reaction products are safely collected in a cold trap and are conveniently released by letting the cold trap warm up slowly in a hood and bubbling the Cl_2 and SiF_4 vapors through aqueous base for hydrolysis, and (3) there is less danger of getting hazardous gases into the vacuum pump or into the room and no risk of explosions.

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(2) J. Gordon and F. L. Holloway, *Ind. Eng. Chem.*, **52**, 63A (1960).

(3) Crawford Fitting Company, Cleveland, Ohio.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Reaction of Silicon Tetrachloride with N,N-Dimethylhydrazine and Hydrazine

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The formation of compounds containing silicon–nitrogen bonds by the reaction of organohalosilanes with hydrazine and some of its alkyl-substituted derivatives has been given recent attention.[2-6] Compounds of the general types monotriorganosilyl-,[2,5] bis-(N,N′-triorganosilyl)-,[2,5] bis-(N,N-triorganosilyl)-,[2] and tris-(triorganosilyl)-hydrazine have been prepared in large number and their properties described. Tetrasilylhydrazine, $(H_3Si)_2NN(SiH_3)_2$, also has been prepared.[4] All of these compounds were prepared from a triorganohalosilane and the appropriate hydrazine. Reaction of hydrazines with diorganodihalosilanes[3,6] in dilute solution leads to the formation of six-membered ring compounds containing the $[-Si-N-N-]_2$ core with various alkyl or aryl groups as well as hydrogen atoms as substituents. However, the reaction of hydrazine, N_2H_4, and $(CH_3)_2SiCl_2$, which is of this type, led to the formation of a polymeric substance which analyzed for $[-Si(CH_3)_2-NHNH-]_x$ and possessed a molecular weight of about 3500.[2]

A general review of the field of silicon–nitrogen compounds was given recently by Fessenden and Fessenden.[7]

The purpose of the present investigation was to see if well defined compounds were formed in the reaction of even more highly halogenated silanes (in particular, $SiCl_4$) and various hydrazines. We hoped to prepare compounds containing four nitrogen atoms bonded to silicon in contrast to the known silicon–hydrazine compounds in which at most two nitrogen atoms per silicon had been obtained.

Under strictly anhydrous conditions and in the presence of an inert atmosphere, the reaction of a CCl_4 solution of silicon tetrachloride ($SiCl_4$) and an excess of N,N-dimethylhydrazine, $(CH_3)_2NNH_2$, proceeds smoothly with the formation of tetra-(N,N-dimethylhydrazino)-silane, $Si[-NHN(CH_3)_2]_4$, and the by-product N,N-dimethylhydrazine hydrochloride, $(CH_3)_2NNH_2 \cdot HCl$, according to the reaction

$$SiCl_4 + 8(CH_3)_2NNH_2 = Si[-NHN(CH_3)_2]_4 + 4(CH_3)_2NNH_2 \cdot HCl$$

The reaction is exothermic and proceeds by a mechanism[2,8] involving the elimination of HCl. The HCl so formed reacts with excess hydrazine to give the hydrochloride.

$Si[-NHN(CH_3)_2]_4$ is a white, crystalline solid, stable for several weeks in a sealed tube at room temperature, but is very sensitive to traces of moisture, hydrolyzing to give the hydrazine and, presumably, various silicic acids. It possesses a relatively low m.p. of 64°. The infrared and n.m.r. spectra of this material are consistent with the above formulation.

(1) (a) To whom requests for reprints should be sent. (b) Based, in part, on the research work undertaken by J. R. C., in partial fulfillment of the requirements for the Ph.D. Degree at the Illinois Institute of Technology.

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