Adducts of Silicon Tetrafluoride with Aminocyclophosphazenes: Synthesis and Characterization

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Stable solid adducts of SiF_4 with the following aminocyclophosphazenes have been synthesized: $N_3P_3(NHCH_2CH_2NH)(NMe_2)_4$, (1); $N_3P_3(NHCH_2CH_2NH)Cl_4$, (2); $N_3P_3(NMe_2)_4Cl_2$, (3); $N_3P_3(NHMe)_6$, (4); $N_3P_3(NMe_2)_6$, (5); $N_4P_4(NHMe)_8$, (6); $N_4P_4(NMe_2)_8$, (7); and $N_4P_4(NHBu^t)_8$, (8). They have been characterized by elemental analysis, i.r., and n.m.r. (^1H, ^{31}P, and ^{19}F) spectroscopy. The composition of the adducts varies depending on the ring size and also on the nature of the substituents on the phosphorus. The number of SiF_4 molecules accommodated by the ligands is larger when the ring size is large, while it is less when the ligands contain chlorine. Except in the cases of ligands (1) and (2), bonding is through the ring nitrogens. With (1), both exocyclic nitrogen and ring nitrogen atoms, and with (2) only exocyclic nitrogen atoms, participate in co-ordination. In these two cases the silicon is six-co-ordinated, while in the other cases it is five-co-ordinated.

Silicon tetrafluoride, a good Lewis acid, is known to form stable adducts with a variety of donor groups such as amines [1] and a few with oxygen donors.[2-4] There is not much information about adducts with ligands containing phosphorus and also with multidentate ligands containing more than two donor sites. The only relevant work is that of Beattie and Ozin [5] who obtained addition compounds, $SiF_4{\cdot}PMe_3$ and $SiF_4{\cdot}2PMe_3$, at low temperature. However, no adduct formation has been observed between silicon tetrafluoride and triphenylphosphine even when the reactants are cooled to −96 °C.[6] Therefore, it was of interest to see whether aminocyclophosphazenes, which behave as potential ligands towards suitable electron acceptors, having donor sites at ring nitrogen,[7] exocyclic nitrogen,[7] and phosphorus,[8] would bond with silicon tetrafluoride. Preliminary studies indicated reaction with the eight cyclophosphazenes studied.

Experimental

Materials.—The following ligands were prepared by standard methods: 4,4,6,6-tetrakis(dimethylamino)-2,2-spiro-(ethylenediamino)cyclotriphosphazene, $N_3P_3(NHCH_2CH_2NH)(NMe_2)_4$ (1);[9,10] 4,4,6,6-tetrachloro-2,2-spiro-(ethylenediamino)cyclotriphosphazene, $N_3P_3(NHCH_2CH_2NH)Cl_4$ (2);[11] 2-*cis*-4-dichloro-2,4,6,6-tetrakis(dimethylamino)cyclotriphosphazene, $N_3P_3(NMe_2)_4Cl_2$ (3);[12] hexakis-(methylamino)cyclotriphosphazene, $N_3P_3(NHMe)_6$ (4);[13] hexakis(dimethylamino)cyclotriphosphazene, $N_3P_3(NMe_2)_6$ (5);[12] octakis(methylamino)cyclotetraphosphazene, $N_4P_4(NHMe)_8$ (6);[14] octakis(dimethylamino)cyclotetraphosphazene, $N_4P_4(NMe_2)_8$ (7);[14] and octakis(t-butylamino)cyclotetraphosphazene, $N_4P_4(NHBu^t)_8$ (8).[15]

Silicon tetrafluoride was prepared by fluorination of silicon tetrachloride with lead fluoride in acetonitrile.[16] Its purity (99.8%) was checked by i.r. spectroscopy and chemical analysis. Diethyl ether was washed with cold water, dried over $CaCl_2$, and distilled over lithium aluminium hydride. Chloroform was washed with water, dried by refluxing over P_4O_{10}, and then distilled.

Preparation of the Adducts.—The reaction vessel consisted of a round-bottomed flask (250 cm³) fitted with standard joints and vacuum stopcocks. A known amount of the ligand was dissolved in a suitable solvent (100 cm³) and placed in the reaction vessel. The latter was connected to a glass globe containing a known amount of SiF_4. The solution was frozen in liquid nitrogen and the air was pumped out of the system. After bringing the contents of the flask to room temperature, a four-fold excess of SiF_4 was added by opening the interconnecting stopcocks. In all cases immediate formation of a precipitate was observed. The reaction mixture was stirred with a magnetic pellet for a few hours. The excess of unreacted SiF_4 remaining after the reaction was condensed back into the glass globe along with some vapours of the solvent. The flask was detached from the assembly and filled with dry nitrogen. The precipitate was filtered off under suction in a dry nitrogen atmosphere, washed with the solvent as quickly as possible, and dried under vacuum. The amount of unreacted SiF_4 was determined after dissolving the solvent vapours in benzene and freezing out the benzene at −80 °C.[16] By measuring the pressure and volume of SiF_4 at constant temperature before and after the experiment the stoicheiometry of the reaction could be determined.

The experimental procedure adopted for the synthesis of adducts of ligands (4) and (6) was slightly different. These ligands are not soluble in solvents such as diethyl ether and benzene, but slightly soluble in chloroform at room temperature, and completely soluble in boiling chloroform. Suspensions of these ligands were treated with SiF_4 for 12 h with continuous stirring at room temperature. The solids were then filtered off, washed with hot chloroform, and dried under vacuum. Details of the preparation of the individual adducts are given in Table 1.

Characterization of the Adducts.—The adducts were characterized by i.r., n.m.r., and analytical data. The i.r. spectra in the range 400—4 000 cm⁻¹ of the pure ligands and the adducts were recorded using Nujol mulls and a Perkin-Elmer 599 spectrophotometer. The important absorption bands are assigned in Table 2.

Proton n.m.r. spectra were recorded for $CDCl_3$ solutions with $SiMe_4$ as internal standard using a Varian T-60 spectrometer. Phosphorus-31 and ^{19}F n.m.r. spectra were recorded for CD_3CN solutions with 85% H_3PO_4 as external standard and $CFCl_3$ as internal standard respectively. Bruker WH 90, operating at 36.431 MHz, and WM250, operating at 233 MHz, instruments were used for recording ^{31}P and ^{19}F spectra respectively. The chemical shifts are expressed in terms of the δ scale, with upfield shifts negative (Table 3). The analytical data are given in Table 4.

Table 1. Preparation of adducts of silicon tetrafluoride with aminocyclophosphazenes

Ligand	Solvent	Reaction time (h)	Amount (mmol) Ligand	SiF_4	Reacted SiF_4	Combining ratio, ligand : SiF_4	Adduct	Solubility of adduct in $CHCl_3$ and CH_3CN	Nature of adduct
(1)	OEt_2	6	7.89	32.55	12.23	2 : 3	(1a)	Soluble	White, powdery hygroscopic solid
(2)	OEt_2	6	6.75	29.50	6.81	1 : 1	(2a)	Insoluble	Slightly yellowish hygroscopic sticky solid
(3)	OEt_2	6	3.45	16.24	3.39	1 : 1	(3a)	Soluble	White, powdery hygroscopic solid
(4)	$CHCl_3$	10	6.56	28.45	10.04	2 : 3	(4a)	Insoluble	White, powdery hygroscopic solid
(5)	OEt_2	6	2.95	13.35	4.57	2 : 3	(5a)	Soluble	White, powdery non-hygroscopic solid
(6)	$CHCl_3$	10	4.85	19.65	15.04	1 : 3	(6a)	Insoluble	Slight yellowish sticky, hygroscopic solid
(7)	OEt_2	6	3.47	16.24	10.59	1 : 3	(7a)	Soluble	White, powdery, non-hygroscopic solid
(8)	OEt_2	6	4.25	18.85	8.63	1 : 2	(8a)	Soluble	White, powdery non-hygroscopic solid

Table 2. Infrared spectral data (cm^{-1}) of aminocyclophosphazene adducts of silicon tetrafluoride and the free ligands

Compound	ν(N–H)	ν(P=N)	ν(Si–F)	ν(Si–F)/ + ν(P–N=P)	δ(Si–F)
(1)	3 360m, br 3 230m, br	1 200s			
(1a)	3 250m 3 180m	1 180s 1 260s	730s 750s 760s	900s	480m
(2)	3 430m, br 3 350m, br	1 205s			
(2a)	3 350m, br 3 250m, br 3 200m, br	1 220s 1 250s	730s 760(sh)	890w	470m
(3)		1 200s 1 230s			
(3a)		1 190s 1 230s 1 260s	750s	900m	480m
(4)	3 330m, br 3 200m, br	1 175s			
(4a)	3 290m, br 3 250m, br 3 160m, br	1 275s	730s 750s	900m	475m
(5)		1 200s			
(5a)		1 180s	770s	900s	470m
(6)	3 400m, br 3 270m, br	1 215s, br			
(6a)	3 350m 3 150m	1 300s, br	730s 760(sh)	900m	475w
(7)		1 265s			
(7a)		1 310s 1 340s	770s 790(sh)	900s	480m
(8)	3 430m 3 350m	1 230s, br			
(8a)	3 380m 3 320m 3 250s, br	1 200s 1 240s 1 320s	730s 750s	920s	480m

Results and Discussion

It is evident from the experimental results that SiF_4 forms stable adducts of various compositions depending on the nature of the aminocyclophosphazenes. The possible sites of co-ordination are (*i*) the endocyclic nitrogen, (*ii*) the exocyclic nitrogen, and (*iii*) the ring phosphorus.

In several studies reported on similar adducts, the effect of complex formation is reflected in the i.r. spectra of the complexes. The major effect of σ donation of a nitrogen lone pair of electrons will be on the in-plane bonding system.[17] In general, the i.r. spectra are more complex than those of the free ligands, and ν(P=N) undergoes a positive shift of 40—200 cm^{-1}.[18,19] The effect of co-ordination through the endocyclic nitrogen can also be seen in the ^1H n.m.r. spectrum of the substituents. The NH proton in $N_3P_3[NH(CH_2)_2CH_3]_6$ undergoes a downfield shift of about δ 1.4 upon adduct formation, while the CH_3 and CH_2 protons do not undergo any change in chemical shift.[20] It has also been observed that the ^{31}P n.m.r. chemical shifts of the adducts move upfield compared to those of the ligands.[18,21]

Silicon tetrafluoride forms five- and six-co-ordinated adducts (1 : 1 and 2 : 1, ligand: SiF_4) with unidentate ligands depending on the experimental conditions, the latter being more common than the former.[18] In six-co-ordinated SiF_4 adducts, which have octahedral structures, the ν(Si–F) frequency of SiF_4 at 1 031 cm^{-1} undergoes a negative shift of about 300 cm^{-1}.[3,22–24] The five-co-ordinate, 1 : 1 adducts of SiF_4 can have either a trigonal bipyramidal or tetragonal pyramidal structures. The ν(Si–F) in these cases [6] are found to lie in the region 900—1 000 cm^{-1}. The ^{19}F n.m.r. spectra are characteristic of five- or six-co-ordination in silicon fluorides; chemical shifts for the series SiF_4, SiF_5^-, and SiF_6^{2-} are δ 160.3, 136.0, and 128.2 respectively against CCl_3F as internal standard.[25] This was made use of in concluding that the silicon in $SiF_4 \cdot Pt(PPh_3)_2$ is five-co-ordinate, the ^{19}F spectrum at room temperature in acetone consisting of a singlet at δ 137.3.[6]

In the light of the above observations, the bonding in the present adducts will now be discussed.

Adducts with Ligands (1) *and* (2).—$2N_3P_3(NHCH_2CH_2NH)(NMe_2)_4 \cdot 3SiF_4$, (1a). The ν(P=N) absorption band has undergone a positive shift accompanied by splitting, Table 2, indicating that the ring nitrogens are involved in co-ordination. The ν(N–H) frequencies have suffered a negative shift and the n.m.r. resonances of the NH protons have shifted substantially downfield (δ 5.0), suggesting that the exocyclic nitrogens of the ethylenediamine group also participate in co-ordination. The strong band at 900 cm^{-1} in the i.r. spectrum could be assigned to a $P-\overset{+}{N}=P$ linkage,[20] or to a five-co-ordinated SiF_4 adduct. The ^{19}F n.m.r. spectrum shows a broad signal centred around δ −131, suggesting that the silicon is six-co-ordinate. Thus, the band at 900 cm^{-1} could be assigned to a ligand vibration and those at 700—800 cm^{-1} to ν(Si–F). Based on the above observations, adduct (1a) contains six-co-ordinated silicon and both exocyclic and endocyclic nitrogens participate in this co-ordination. This mode has been noted in a few other complexes of cyclophosphazenes.[26,27] The composition 2 : 3 suggests that the adduct is an equimolar mixture of 1 : 1 and 1 : 2 six-co-ordinated silicon adducts.

Table 3. N.m.r. data * for the adducts of silicon tetrafluoride and for the pure ligands

Compound	^1H	^{31}P	^{19}F
(1)	NH 2.2, NCH_3 2.6, NCH_2 3.34		
(1a)	NH 7.2, NCH_3 2.63, NCH_2 3.4		−131.42, −131.33 −131.29, −131.25
(3)	NCH_3 2.78		
(3a)	NCH_3 2.80		
(5)	NCH_3 2.55	24.6	
(5a)	NCH_3 2.70	19.58	−137.04
(7)	NCH_3 2.63	9.6	
(7a)	NCH_3 2.73	7.71	−137.0
(8)	NH 2.20, NBu^t 1.28	− 3.1	
(8a)	NH 3.63, NBu^t 1.40	−1.98	−136.87

* Chemical shifts are expressed in terms of the δ scale, with upfield shifts negative.

$N_3P_3(NHCH_2CH_2NH)Cl_4 \cdot SiF_4$, (2a). The non-participation of ring nitrogens can be seen in the moderate increase in the ν(P=N) frequency of about 30 cm^{-1} on adduct formation, compared to the other adducts. However, the ν(N–H) absorptions have undergone a substantial negative shift (100 cm^{-1}) indicating that the ethylenediamino-nitrogens are involved in co-ordination with SiF_4. The single strong band of ν(Si–F) at 730 cm^{-1} indicates that silicon is six-co-ordinate. The non-participation of the ring nitrogens could be due to the presence of four chlorine atoms in the ring which makes the endocyclic nitrogens more basic.

Adducts with Ligands (3)—(8).—$N_3P_3(NMe_2)_4Cl_2 \cdot SiF_4$, (3a), $2N_3P_3(NHMe)_6 \cdot 3SiF_4$, (4a), $2N_3P_3(NMe_2)_6 \cdot 3SiF_4$, (5a), $N_4P_4(NHMe)_8 \cdot 3SiF_4$, (6a), $N_4P_4(NMe_2)_8 \cdot 3SiF_4$, (7a), *and* $N_4P_4(NHBu^t)_8 \cdot 2SiF_4$, (8a). In the above six adducts a general pattern is observed. There is an increase in the ν(P=N) frequency accompanied by splitting in the i.r. spectrum indicating that only endocyclic nitrogens are involved in co-ordination. This is supported by the observation that the NCH_3 protons have undergone only a very small downfield shift of about δ 0.02 upon adduct formation, which indicates that the exocyclic nitrogens are not involved in bonding with SiF_4. The appearance of ν(Si–F) absorptions in the region 700—800 cm^{-1} and also at 900 cm^{-1} suggests that silicon is five-co-ordinated. This is supported by the ^{19}F n.m.r. spectra

Table 4. Analytical data for the adducts of silicon tetrafluoride with aminocyclophosphazenes

	Elemental analysis (%)						Composition of adduct	M.p. (°C)	
	Calc.			Found			ligand:		
Adduct	C	H	N	C	H	N	SiF_4	Pure ligand	Adduct
(1a)	22.85	5.70	24.0	23.05	6.3	23.85	2 : 3	138	149—152 (decomp.)
(2a)	5.45	1.35	15.95	5.60	1.65	15.45	1 : 1	198	225—230 (decomp.)
(3a)	19.75	4.95	20.15	19.75	5.35	20.20	1 : 1	104	145—150
(4a)	15.3	5.10	26.75	15.7	5.80	26.7	2 : 3	257	200 (decomp.)
(5a)	25.95	6.50	22.7	26.3	6.80	22.6	2 : 3	104	160—170 (sublim.)
(6a)	13.1	4.35	22.95	13.1	5.00	22.6	1 : 3	206	260—268 (charg.)
(7a)	22.75	5.70	19.9	23.35	6.35	20.45	1 : 3	230—237 (decomp.)	160
(8a)	40.15	8.30	17.55	40.55	8.80	17.55	1 : 2	180—200 (decomp.)	220—235 (decomp.)

which show a single sharp signal at δ −137 characteristic of five-co-ordinated silicon fluorides. The ^{31}P n.m.r. spectra also show an upfield shift which is characteristic of cyclophosphazene complexes, except in the case of (8a), having a composition 1 : 2, which shows a downfield shift on complexation.[18,21] A downfield shift on complexation occurs only in the case of adduct (8a).

The composition of the adducts, 2 : 3 or 1 : 3, indicates that they are equimolar mixtures of 1 : 1 and 1 : 2 and 1 : 2 and 1 : 4 adducts respectively. This has been observed with other SiF_4 adducts.[5,28–30] It seems that steric factors determine the co-ordination number of silicon, the bulky ligands favouring five-co-ordination.[31,32] Among the adducts (1a)—(8a) we see a regular trend in composition which can be attributed to steric as well as electronic factors. For instance, (*i*) the combining ratio (ligand : SiF_4) varies from 1 : 1 and 1 : 2 in the case of trimeric ligands to 1 : 2 and 1 : 4 in the case of tetrameric ligands. This can be explained on the basis of the ring size of the ligands. (*ii*) Even when the ring size is the same the composition varies. This can be attributed to the nature of the substituents present in the ligand molecules. Considering the adducts (1a)—(5a), the trimeric phosphazenes, it is clear that the ligands which do not contain any chlorine co-ordinate a larger number of SiF_4 molecules than those which contain chlorine. This might be due to electronic factors; chlorine being highly electronegative draws the electron density towards itself making the ring nitrogens less basic. It was observed in the present investigation that SiF_4 does not form any adduct with hexachlorocyclotriphosphazene ($N_3P_3Cl_6$). On the other hand, the variation in composition of adducts (6a)—(8a) of tetrameric phosphazenes can be explained on the basis of steric factors. Here the substituents on the phosphazene rings are of similar electronegativity and none of the ligands contains chlorine; t-butyl being more bulky than methyl, ligand (8) can accommodate fewer SiF_4 molecules than ligands (6) and (7).

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References

1 J. P. Guertin and M. Onyszchuk, *Can. J. Chem.*, 1969, **47**, 1275.
2 K. Issleib and G. Reinhold, *Z. Anorg. Chem.*, 1962, **314**, 113.
3 V. Gutman and K. Utvary, *Monatsh. Chem.*, 1959, **90**, 706.
4 T. S. Piper and E. G. Rochow, *J. Am. Chem. Soc.*, 1954, **76**, 4318.
5 I. R. Beattie and G. A. Ozin, *J. Chem. Soc. A*, 1969, 2267.
6 T. R. Durkin and E. P. Schram, *Inorg. Chem.*, 1972, **11**, 1048.
7 H. P. Calhown, N. L. Paddock, and J. N. Wingfield, *Can. J. Chem.*, 1975, **53**, 1765.
8 A. Schmidpeter, K. Blanck, H. Hess, and H. Riffel, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 650.
9 S. S. Krishnamurthy, K. Ramachandran, A. R. Vasudevamurthy, R. A. Shaw, and M. Woods, *Inorg. Nucl. Chem. Lett.*, 1977, **13**, 407.
10 K. Ramachandran, Ph.D. Thesis, Indian Institute of Science, Bangalore, 1978, p. 74.
11 S. S. Krishnamurthy, K. Ramachandran, A. R. Vasudeva Murthy, R. Keat, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1980, 840.
12 R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 3215.
13 S. K. Ray and R. A. Shaw, *J. Chem. Soc.* 1961, 872.
14 S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.* 1963, 3236; ref. 10, p. 120; A. C. Sau, Ph.D. Thesis, Indian Institute of Science, Bangalore, 1975, p. 102.
15 S. S. Krishnamurthy, A. C. Sau, A. R. V. Murthy, R. Keat, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1977, 1980.
16 D. K. Padma, B. S. Suresh, and A. R. Vasudeva Murthy, *J. Fluorine Chem.*, 1979, **14**, 327.
17 G. E. Coxan and D. D. Sowerby, *J. Chem. Soc. A*, 1969, 3012.
18 S. S. Krishnamurthy, A. C. Sau, and M. Woods, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 41.
19 M. F. Lappert and G. Srivastava, *J. Chem. Soc. A*, 1966, 210.
20 T. Moeller and S. J. Kokalis, *J. Inorg. Nucl. Chem.*, 1963, **25**, 275.
21 V. Chandrasekhar, S. S. Krishnamurthy, and M. Woods, *ACS Symp. Ser.*, 1981, **171**, 99, 481.
22 E. Schnell, *Monatsh. Chem.*, 1962, **93**, 1136.
23 W. C. Schumb and P. E. Cook, *J. Am. Chem. Soc.*, 1953, **75**, 5133.
24 E. Schnell, *Monatsh. Chem.*, 1962, **93**, 65.
25 P. Klanberg and E. L. Muetterties, *Inorg. Chem.*, 1968, **7**, 155.
26 H. P. Calhoun, N. L. Paddock, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1973, 2708.
27 V. Chandrasekar, Ph.D. Thesis, Indian Institute of Science, Bangalore, 1982, p. 148.
28 D. B. Miller and H. H. Sisler, *J. Am. Chem. Soc.*, 1955, **7**, 4998.
29 I. R. Beattie and G. A. Ozin, *J. Chem. Soc. A*, 1970, 370.
30 B. S. Ault, *Inorg. Chem.*, 1981, **20**, 2817.
31 E. L. Muetterties, *J. Am. Chem. Soc.*, 1960, **82**, 1082.
32 S. A. Andronati, A. V. Bogtskii, Yu. I. Vikhlyaev, A. I. Zhilina, V. N. Kats, T. A. Klygul, V. M. Khudykova, T. K. Chumechenko, and A. A. Ennan, *Zh. Obshch. Khim.*, 1970, **40**, 1881.

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