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Pentacoordinate fluorosilicate anions

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ABSTRACT. The literature data on the synthesis and properties of salts with pentacoordinate fluorosilicate anions have been classified and correlated. The geometric structural features of the pentafluorosilicate anion and its substituted derivatives are analysed, taking into account the hypervalent nature of the bonding in silicon(IV) complexes.
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I. Introduction

From the date of publication of Sommer's well-known monograph[1], which correlated the main results on the dynamic stereochemistry of organosilicon compounds, research workers have taken a greater interest in pentacoordinate fluorosilicate anions. Compounds of this type are potential intermediates in various reactions involving tetra- and hexa-coordinate silicon fluoro-complexes. In particular, the pentafluorosilicate anion and its substituted derivatives may be regarded as stable 'models' of S_N2 Si intermediates in nucleophilic substitution reactions involving the respective tetrahedral fluorosilanes.[1] The formation of pentacoordinate silicon fluoro-complexes as intermediates was postulated in a discussion of the probable mechanism of the dehydro-fluorination of octahedral complexes of silicon tetrafluoride with nitrogen- and oxygen-containing donor ligands giving organofluorosilicon compounds such as fluorosilylamines, fluorosilazanes, and alkoxysilanes with a valuable set of physicochemical properties.[2]

Two reviews[3,4] have been devoted to various aspects of the chemistry of pentacoordinate silicon fluoro-complexes, but a limited amount of correlation of the information on pentacoordinate fluorosilicate anions is only presented in one study.[3] Moreover, in recent years a considerable number of interesting studies in this field have been published, and evidently the time was ripe for a new review. The aim of the present review is to classify and correlate the information published during the last decade on the synthetic methods, geometric structure, dynamic stereochemistry and ligand exchange processes in solution, properties, and use of pentacoordinate anions of silicon fluoro-complexes in preparative synthesis.

II. Synthetic methods

The earliest information about the preparation of pentafluorosilicates—salts of the simplest pentacoordinate fluorosilicate anion—was published in 1967. Clark et al.[5] discovered that the reaction of *trans*-$[PtHCl(Et_3P)_2]$ with tetrafluoroethylene in a Pyrex tube gave *trans*-$[PtCl(CO)(Et_3P)_2]SiF_5$. In subsequent reports[6,7] a simple method for the synthesis of pentafluorosilicates was proposed, being based on the reaction of equimolar quantities of tetraalkylammonium chloride or bromide with silica in an aqueous methanol solution of HF. This method was used to obtain $(R_4N)SiF_5$, where R = Et, n-Pr, n-Bu. A similar method has been reported by Behrends and Kiel.[8] It is interesting that the product of the reaction between SiF_4 and $Pt(PPh_3)_3$, which was first identified[9] as the complex $SiF_4.Pt(PPh_3)_3$, according to later results[10] is hydrido-tris(triphenylphosphine)platinum pentafluorosilicate $[PtH(PPh_3)_3].SiF_5$. A similar reaction between BF_3 and $Pt(PPh_3)_3$ leads to the formation of tetrafluoroborate salts. Bird et al.[10] stressed the need to make a critical assessment of the results of a synthesis based on covalent fluorides and basic metal complexes when the reactions are carried out in a glass apparatus.

Dehydrofluorination of complexes of silicon tetrafluoride with alcohols and primary amines in the presence of tertiary amines were used[11,12] for the synthesis of a number of trialkylammonium pentafluorosilicates:

$$5SiF_4 + 4ROH + 4R_3N \rightarrow Si(OR)_4 + 4(R_3NH)SiF_5,$$
$$3SiF_4 + RNH_2 + 2R_3N \rightarrow 1/n\,(RNSiF_2)_n + 2(R_3NH)SiF_5.$$

Gel'mbol'dt et al.[13,14] proposed a method for the synthesis of dialkyl- and trialkyl-ammonium pentafluorosilicates based on dehydrofluorination in the system SiF_4–acetone–amine, where the enol form of acetone acts as a proton donor:

$$5SiF_4 + 4Me_2CO + 4R_nNH_{3-n} \rightarrow \left(CH_2{=}\overset{\displaystyle Me}{\overset{|}{C}}{-}O\right)_4 Si + 4(R_nNH_{4-n})SiF_5, \quad n = 2, 3.$$

This method was recently used to obtain *N*,*N*-dialkylanilinium pentafluorosilicates $(PhNHR_2)SiF_5$ (R = Et, n-Pr, n-Bu).[15]

As was demonstrated in two studies,[12,16] a fairly general method for the synthesis of trialkyl- and tetraalkyl-ammonium pentafluorosilicates consists of the treatment of the respective hexafluorosilicates or 'complex' fluorosilicates containing anions of the stoichiometric composition $Si_2F_{11}^{3-}$ and $Si_3F_{16}^{4-}$ with an excess of silicon tetrafluoride in a suitable solvent (benzene, acetonitrile, methylene chloride). Since fluorosilicates of the type $(R_3NH)_3Si_2F_{11}$

or $(R_3NH)_4Si_3F_{16}$ are the double salts $(R_3NH)_2SiF_6.n(R_3NH)SiF_5$ (n = 1, 2),[17-20] the chemical nature of the conversion of fluorosilicates higher in fluorine to pentafluorosilicates can be represented by the general scheme:

$$SiF_6^{2-} + SiF_4 \rightarrow 2SiF_5^-.$$

The use of this method in the preparative synthesis of pentafluorosilicates may only be limited by the poor solubility of the initial hexafluorosilicates or double fluorosilicates in aprotic solvents.

A general method for the synthesis of pentafluorosilicates and also mixed pentacoordinate tetraalkylammonium alkyl- and aryl-fluorosilicates has been proposed. It is based on the reaction between SiF_4 or R_nSiF_{4-n} (n = 1, 2) and R_4NF in methanol:[21]

$$R_nSiF_{4-n} + F^- \rightarrow [R_nSiF_{5-n}]^-.$$

Despite the complexity of obtaining a tetraalkylammonium fluoride that is free of impurities, the latter method has been widely applied. In particular, it has been used in the synthesis of virtually all samples of salts with pentacoordinate fluorosilicate anions for X-ray diffraction studies.

There has been a report on a similar method for obtaining mixed anions of the type $[XSiF_4]^-$ by reaction between silicon tetrafluoride and Me_4NX (X = CF_3COO^-, $MeCOO^-$, $HCOO^-$, NO_2^-, CN^-, etc.) in liquid sulphur dioxide or methylene chloride:[22]

$$SiF_4 + X^- \rightarrow [XSiF_4]^-.$$

An excess of silicon tetrafluoride reacted with acetate ion leads to the formation of a binuclear anion with a bridging fluorine atom and an equatorial configuration of the monodentate $MeCOO^-$ groups:

$$5SiF_4 + 4MeCOO^- \rightarrow 2[Si_2F_7(MeCOO)_2]^- + SiF_6^{2-}.$$

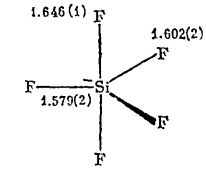
A proposed[21,22] route for the synthesis of pentacoordinate fluorosilicate anions was further developed by Ault and Tandoc,[23,24] who used the technique of low-temperature matrix isolation in order to obtain caesium salts with SiF_5^-, $[SiF_{5-n}Cl_n]^-$ (n = 1-4), and $[Me_nSiF_{5-n}]^-$ (n = 1, 2) anions. The compound $KSiF_5$ was also obtained. The synthetic method consisted of evaporating the respective metal fluoride (CsF, KF) followed by its cocondensation with samples of SiF_4, $SiF_{4-n}Cl_n$ (n = 1-4) or Me_nSiF_{4-n} (n = 1, 2) in an argon matrix at low temperatures.

In conclusion we should mention a simple method for synthesising tripropylammonium pentafluorosilicate by reaction of tripropylamine with a solution of fluorosilicic acid (molar ratio 1 : 3).[25] Unfortunately, this method is not a general one and when other tertiary amines are used, double trialkylammonium hexa- and penta-fluorosilicates are formed.

III. Electronic structure and stereochemistry

It was pointed out[2,3] that the specific nature of the structure and reactivity of fluoro-complexes of non-transition elements is most adequately expressed in terms of hypervalent bonds.[26] The elements of Subgroup IVB are not formally classified among the types of hypervalency as proposed by Musher for the electron-rich elements of Subgroups VB–VIIB. The scope of Musher's ideas[26] was extended by Voronkov et al.,[27-30] who modified the initial scheme for formation of a four-electron, three-centre bond [unshared electron pair (UEP) of the central atom and two unpaired electrons from ligands] for representing the mechanism of axial bonding in pentacoordinate silicon(IV) complexes such as silatranes, (aroyloxymethyl)trifluorosilanes, and related compounds. In the complexes $X-Si(OCH_2CH_2)_3N$ and $XC_6H_4COOCH_2SiF_3$ the coordination of the silicon polyhedron is a slightly distorted trigonal bipyramid. The formation of the hypervalent axial fragments X–Si ← N and F–Si ← O occurs as a result of intramolecular coordination using the UEP of the ligand (a nitrogen or oxygen atom). Out of the four valence atomic orbitals of silicon, three ($3s$, $3p_x$, $3p_y$) participate in equatorial bonding as sp^2 hybrids, forming three two-electron two-centre bonds. The bond in the linear X–Si ← N fragment and the slightly bent F–Si ← O fragment ($\angle$FSiO = 175–179°) arises from the $3p_z$ atomic orbital of silicon and the atomic orbitals of the axial ligands (one from each atom), in other words, it is a three-orbital three-central or hypervalent-II bond according to Musher.[26] This scheme for axial bonding has been extended to the pentafluorosilicate anion and its substituted derivatives.

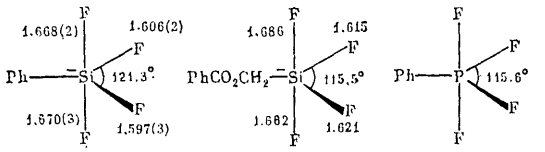
The first arguments in favour of a trigonal bipyramidal structure for the SiF_5^- anion were based on the results of spectroscopic studies.[7,21] In particular, according to the results of one study,[7] in the Raman spectrum of an acetonitrile solution of tetra-n-propylammonium pentafluorosilicate there was an intense polarised band at 708 cm^{-1} (A_1' mode), which was inactive in the IR spectrum; this was consistent with the SiF_5^- anion having D_{3h} symmetry. The marked similarities in the IR and Raman spectra of SiF_5^- and PF_5 (a trigonal bipyramidal configuration has been reliably established for the latter compound) support such a conclusion. An attempt to determine the structural parameters of the pentafluorosilicate anion in crystals of the salt $(Ph_4As)SiF_5$ proved unsuccessful because of the complex form of crystallographic randomisation.[31] More recently the results of an X-ray diffraction analysis of the complex salt $[IrH_2CO(PPh_3)_3]SiF_5$ were published.[10] The geometry of the SiF_5^- anion differed only slightly from the ideal trigonal bipyramidal form, but the accuracy in determining the structural parameters was limited by the intense vibrational movements of the anion and it amounted to 0.04 Å for the bond lengths and 4° for the bond angles. The lengths of the axial and equatorial Si–F bond coincided within the limits of experimental error and constituted 1.69 Å on average. A precise determination of the molecular structure of the SiF_5^- anion in the salt $(PhCH_2NMe_3)SiF_5$ was carried out only comparatively recently.[32] The pentafluorosilicate anion has a slightly distorted trigonal bipyramidal configuration with C_2 symmetry (the second-order axis passes through the silicon atom and one of the equatorial ligands), and in complete conformity with the model of Musher[26] the axial Si–F bonds are longer (weaker) than the equatorial bonds:



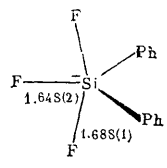
The axial F–Si–F fragment is virtually linear ($\angle F_aSiF_a$ = 179.4°). It is interesting that according to the results of an IR spectroscopic study, the pentafluorosilicate anion in matrix-isolated salts $MSiF_5$ (M = K^+ or Cs^+, which are comparable in size to the unsubstituted NH_4^+ cation) has an axially distorted geometry with C_{3v} symmetry.[23]

This observation can also have a natural explanation within the scope of the hypervalent bond model.[26] Since the scheme for three-centre bonding envisages a significant transfer of electron density within the axial F–Si–F group, the latter has high polarity and must have the maximum sensitivity towards the perturbing effect of small cations with high charge density and high polarising capacity.

The results of X-ray diffraction analysis of tetrapropylammonium phenyltetrafluorosilicate and 1,10-phenanthrolinium (benzoxymethyl)-tetrafluorosilicate are given in two reports.[33,34] The $[PhSiF_4]^-$ and $[PhCOOCH_2SiF_4]^-$ anions have a distorted trigonal bipyramidal structure with the phenyl or benzyloxymethyl group in an equatorial position:



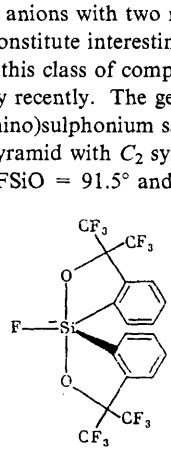
A similar structure was found for the isoelectronic phenyltetrafluorophosphorane.[35] The arrangement of electropositive ligands in the equatorial plane of the compounds and the nature of the angle deformations of the complexes when there is substitution are consistent with the concepts of hypervalency. The structure of the three-centre axial bonds is only stable in the case of highly electronegative ligands, whereby it follows from this model[26] that the axial and equatorial groups of bonds to a certain extent act independently in the transfer of electronic effects. It is logical to assume from this that the virtually identical angular distortion of the F_a-Si-F_a group in $[PhSiF_4]^-$ and the F_a-P-F_a group in $PhPF_4$ is due to the similar steric effect of the phenyl ligand in both complexes, whereas the differences in the equatorial angle deformations is caused by the steric and electronic effects acting in opposite directions. While the former compresses the angles in F_eSiF_e and F_ePF_e, the latter, on the other hand, increases them compared to the ideal angle for sp^2 hybrid atomic orbitals (120°) as a result of an increased *s* atomic orbital contribution in the Si–C and P–C bonds and a decreased *s* atomic orbital contribution in the Si–F and P–F bonds (Bent's rule[36]). For a complex of the more electropositive silicon ($EN_{Si} < EN_P$), the contribution of the 'electronic' component of the deformational forces proves to be greater than for the phosphorus derivative (the share of the *s* atomic orbital of Si in a Si–C bond is greater than the share of the *s* atomic orbital of P in a P–C bond), which, when the contribution of the steric effect from the phenyl group is deducted, results in the observed differences in the deformations of the equatorial angles ($\angle F_eSiF_e > \angle F_ePF_e$). An alternative interpretation of the nature of the angle deformations in the isoelectronic compounds $[PhSiF_4]^-$ and $PhPF_4$, based on the concepts of the Gillespie–Nyholm model,[37] is given by Schomburg.[33] According to the results of Schomburg and Krebs[32] a structural feature of the diphenyltrifluorosilicate anion in crystals of $(Me_4N)[Ph_2SiF_3]$ is the almost identical increase in length of the axial and equatorial Si–F bonds in comparision to the unsubstituted SiF_5^- anion. The angles of C_e-Si-C_e and F_a-Si-F_a are equal to 118.9 and 187.5° with ideal values of 120 and 180° respectively:



It should be noted that an equatorial configuration of the phenyl ligands in the trigonal bipyramidal structure of the $[Ph_2SiF_3]^-$ anion had previously been established in an analysis of the low-temperature ^{19}F NMR spectra of solutions of the salt $(Et_4N)[Ph_2SiF_3]$ in methylene chloride.[21] Similarly, the nature of the IR spectrum of the $[MeSiF_4]^-$ anion in the vibrational region for ν(SiF) (absorption bands at 712, 825, 837, and 862 cm^{-1}) and δ(SiF) (450 cm^{-1}) indicate that the anion has a symmetry which is of the type C_{2v} or lower, with the methyl group in the equatorial position.[24]

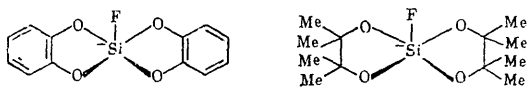
The structures of substituted anions of the type $[R_nSiF_{5-n}]^-$ (n = 1, 2) which have been examined above illustrate the validity of the well-known empirical rule of Muetterties,[38] which states that for a trigonal bipyramidal configuration of the complexes of non-transition elements, isomers with an axial orientation of the most electronegative substituents are stable. However, $SiF_4(L)$ complexes, L = Me_nNH_{3-n}, (n = 0–3) [39,40] or Py,[41] judging from the IR spectroscopy data, have a structure with the molecular ligands in the axial position, which is unexpected in relation to the models of Musher[26] and Gillespie.[37] This geometry, for the $SiF_4(NH_3)$ complex at least, has been accurately reproduced in *ab initio* calculations.[42,43] Out of the four alternative configurations of the coordination polyhedron of SiF_4N with C_{3v}, C_{2v}, C_{4v}, and C_s symmetry, the C_{3v} structure has the minimum energy, and according to the data of Mulliken population analysis the magnitude of the effective negative charge on the nitrogen atom (–1.15) is higher than the charges on the fluorine atoms [–0.49 (*a*), –0.48 (*e*)]. Subsequent to the study by Marsden,[42] if an attempt is made to correlate the electronegativities (Pauling) with the effective charges of the atoms (Mulliken), the axial position of the formally less electronegative nitrogen atom of the ammonia molecule in the trigonal bipyramidal structure of $SiF_4(NH_3)$ becomes clear. The results of quantum-chemical analysis show[44,45] (semiempirical MNDO method) that formation of the hypothetical anions $[XSiH_4]^-$ (X = H^-, F^-, Cl^-) and the molecular complex $FSiH_3(O=CH-OH)$ by the reaction $XSiH_3$ + Y (Y = H^-, O=CH–OH) is accompanied by a more substantial change (increase) in the interatomic distance of X_a-Si compared to the distance in H_e-Si. The latter is an indication of the *trans*-weakening effect on the axial bonds with a strengthening of coordination and is a logical consequence of the hypothetical models of Musher and Voronkov.[26,27] Frolov et al.[44,45] recorded significant contributions from the atomic orbitals of the equatorial ligands in the highest occupied molecular orbital (HOMO) representing the X_a-Si-H fragment in $[XSiH_4]^-$ anions. It was thus stressed that a complete hypervalent representation must take into account the atomic orbitals of the equatorial environment of the silicon atom.

Monofluorosilicate anions with two ring-forming *O*-donor ligands (λ^5-Si-spirosilicates) constitute interesting stereochemical compounds. The first examples of this class of compounds underwent structural analysis comparatively recently. The geometry of the anion (A) in the tris(dimethylamino)sulphonium salt is that of a slightly distorted trigonal bipyramid with C_2 symmetry: $\angle SiO$ = 176.6°, $\angle CSiC$ = 132.2°, $\angle FSiO$ = 91.5° and 91.9°, bond length of $Si-F_e$ 1.632(3) Å:[46]

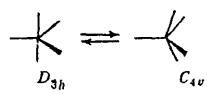


(A)

The structures of the spirobicyclic anions $[(OC_6H_4O)_2SiF]^-$ and $[(OCMe_2CMe_2O)_2SiF]^-$ have a different form of coordination polyhedron for silicon(IV):[47,48]

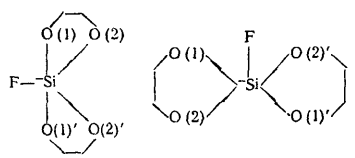


The immediate environment of the silicon atom in these complexes has a distorted tetragonal pyramidal (TP) structure. It was shown[49,50] that the structures of all known pentacoordinate complexes can be arranged in a series that exhibits a smooth transition from an ideal trigonal bipyramidal (TBP) geometry (D_{3h} symmetry) via an intermediate configuration with C_{2v} symmetry to a limiting TP geometry (C_{4v}). The observed deviations of the real structures of MX_5 complexes from the ideal D_{3h} and C_{4v} configurations corresponds to the C_{2v} coordinate in Berry pseudorotation:[51]

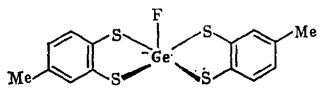


D_{3h} C_{4v}

By using the formal procedures suggested by Porai-Koshits and Aslanov,[52] it is possible to make a quantitative comparison between the real structure of the pentacoordinate complex with C_{2v} symmetry and the D_{3h} and C_{4v} limiting configurations. The TBP limit is built up by arranging the O(1) and O(1)′ atoms of the spirobicyclic anion in axial positions and the O(2) and O(2)′ atoms in equatorial positions, while the TP limit is developed with an axial orientation of the fluorine atom:



In the Berry process the fluorine atom is a pivotal ligand. According to the results of two studies,[47,48] each of the $[(OC_6H_4O)_2SiF]^-$ and $[(OCMe_2CMe_2O)_2SiF]^-$ anions in tetraalkylammonium salts forms two crystallographically independent forms, which are distorted towards the TP limit by 68.7 and 52.8% or 69.1 and 52.3% respectively. It is interesting that distortion of the structure of the isoelectronic anion $[(OC_6H_4O)_2SiF]^-$ towards the TP limit even reaches 81%,[53] while similar deformations in the structure of the phosphorus analogue $(OC_6H_4O)_2PF$ amount to 65%.[54] Evidently the degrees of distortion of the coordination polyhedra of silicon(IV) and phosphorus(V) are fairly similar, while for a complex of the most electropositive of the three elements, germanium(IV), the deformation towards the C_{4v} limit are the greatest. The features of the structural deformations in pentacoordinate complexes of *p*-elements have been discussed in a review,[55] which includes the ideas of Gillespie and Nyholm. According to the hypervalent bond model, the TP structure of spirobicyclic monofluorosilicate anions and their isoelectronic analogues can be represented in terms of two hypervalent O–Si–O groups involving the $3p_x$ and $3p_y$ atomic orbitals of silicon, forming the equatorial plane of the complexes, and the sp_z hybrid for the Si–F bond. The increased stability of the TP configuration in the $[(OC_6H_4O)_2GeF]^-$ anion compared to the corresponding silicon(IV) and phosphorus(V) derivatives is completely natural since it is for the most electropositive germanium that the maximum stabilisation of the hypervalent three-centre groups is achieved. The importance of the condition $EN_A \ll EN_L$ being fulfilled for ensuring the stability of hypervalent L–A–L bonds becomes evident when the structures of $[(OC_6H_4O)_2CHF]^-$ and $[(SC_7H_6S)_2GeF]^-$ anions are compared.[53] Despite the structural similarity of the chelate ligands in these complexes, the thio analogue



is distorted towards the ideal TP configuration by only 40%.

The similarity noted above between the quantitative characteristics of structural deformations in pentacoordinate isoelectronic fluoro-complexes of silicon(IV) and phosphorus(V) may be related to the ideas of Bartlett[5] on the characteristic separation energy of *ns* and *np* orbitals for non-transition elements of a given *n*th Period. His hypothesis[56] was based on the known fact that the bond angles have an approximately equal value in each of the series of isoelectronic compounds of *p*-elements in an incomplete valency state: $PF_3-SF_3^+$, $AsF_3-SeF_3^+$, $SbF_5^{2-}-TeF_5^-$, $IF-XeF_5^+$. Subsequently, Bartlett's ideas[56] were used to account for the similarity in the values of isomerisation constants of isoelectronic hexacoordinate tetrafluoro-complexes of *p*-elements of Groups IV–VI in the third to fifth Periods.[57] We can show that the automatic extension of Bartlett's ideas[56] to complexes with central atoms in higher oxidation states is not absolutely correct. While for TP complexes of the type AF_5E (E = UEP) the equatorial F–A–F bonds have a pure *p* character (hypervalent-I bonds in the terminology of Musher[26]), in TBP and TP structures of complexes of Group IV–V elements the axial and equatorial bonding based on three-centre L–A–L groups requires a given contribution from the *ns* atomic orbital of atom A (hypervalent-II bond). For symmetry considerations this contribution is usually neglected,[27] but it is very probable that the observed differences in the structural deformations of pentacoordinate silicon(IV) and phosphorus(V) fluoro-complexes are due to the varying degree of disproportionation of the hypervalent bonding system[58] of these elements with unequal contributions from the 3*s* atomic orbitals of the central atoms.

IV. Properties

Tetraalkylammonium pentafluorosilicates as solutions in nitromethane behave as 1 : 1 electrolytes.[7] In aqueous solution pentafluorosilicates are hydrolysed to a considerable degree.[7] According to the studies of Harris and Rudner[11] the hydrolysis of trimethylammonium pentafluorosilicate in moist air is given by the equation:

$$2SiF_5^- + 2H_2O \rightarrow SiF_6^{2-} + SiO_2 + 4HF.$$

Judging by the IR spectroscopic data, the SiF_5^- anion undergoes a similar conversion when the double salt $(Et_2NH_2)_2SiF_6(Et_2NH_2)SiF_5$ is dissolved in water.[13] The ^{19}F NMR spectra of a 19.1% aqueous solution of $(Pr_3NH)SiF_5$ indicate that a more complex equilibrium occurs:[59]

$$3SiF_5^- + 3H_2O \rightarrow SiF_6^{2-} + [SiF_5(H_2O)]^- + SiO_2 + 4HF.$$

Heating of an aqueous solution of $(Ph_4As)SiF_5$ leads to rapid and quantitative hydrolysis[8] in accordance with the equation:

$$SiF_5^- + 2H_2O \rightarrow F^- + SiO_2 + 4HF.$$

At the same time Kleboth[60] made a satisfactory interpretation of the IR and Raman spectra of an aqueous solution of tetraethylammonium

pentafluorosilicate by proposing C_{4v} symmetry for the coordination polyhedron of silicon, in other words, the formation of an aqueous pentafluoroaquo-complex is not accompanied by disproportionation of fluorine [sic] in solution:

$$SiF_5^- + H_2O \rightarrow [SiF_5(H_2O)]^-.$$

The stability of dialkyl-, trialkyl- and tetraalkyl-ammonium pentafluorosilicates regularly increases with the size of the cation,[7,12,13] which is due to the decrease in its polarising effect. For example, diisopropylethylamine forms a stable pentafluorosilicate. Triethylammonium pentafluorosilicate is stable in benzene and acetonitrile solutions but when the solvent is removed SiF_4 is lost and there is formation of the compound $(Et_3NH)_4Si_3F_{16}$, which is the double salt $(Et_3NH)_2SiF_6.2(Et_3NH)SiF_5$.[20] The salt $(Me_3NH)SiF_5$, with a smaller cation, is stable in acetonitrile but not in benzene solutions. However, all attempts to isolate trimethylammonium pentafluorosilicate by crystallisation at low temperatures have led to a product of composition $(Me_3NH)_3Si_2F_{11}$.[12] Similarly, diethyl- and dibutylammonium pentafluorosilicates are stable in a solvating acetone medium; removal of the solvent is accompanied by the formation of the double salt $(R_2NH_2)_2SiF_6.(R_2NH_2)SiF_5$.[13] According to Durkin and Schram,[9] the compound $(Pr_4N)SiF_5$ is stable on heating to 230 °C in a vacuum whereas tetramethylammonium pentafluorosilicate disproportionates at 100 °C according to the equation

$$2(Me_4N)SiF_5 \rightarrow SiF_4 + (Me_4N)_2SiF_6.$$

This was confirmed by the IR spectrum of the solid residue.[61] According to the results of thermogravimetric analysis,[25] tripropylammonium pentafluorosilicate dissociates over the temperature range 207–273 °C with the components passing complete into the gas phase:

$$(Pr_3NH)SiF_5 \rightarrow SiF_4 + HF + Pr_3N.$$

In two studies[13,62] it is proposed that the act of dissociation of pentafluorosilicates should be regarded as the vibrational movement of an anion of the type A_2'' smoothly converting the SiF_5^- complex of D_{3h} symmetry to an SiF_4 molecule (T_d). The intermediate distorted structures of the SiF_5^- anion, which link the initial geometry of the complex with the tetrahedral reaction product, should have C_{3v} symmetry:

$$SiF_5^-(D_{3h}) \rightleftarrows SiF_5^-(C_{3v}) \rightleftarrows SiF_4(T_d) + F^-.$$

According to the method of structural correlations,[63] the A_2'' route for the SiF_5^- anion may be reconstructed by analysing the geometric deformation of the anion in crystalline structures of pentafluorosilicates with cations of varying polarising effect. As was mentioned above, the geometry of the SiF_5^- anion in salts with large cations only slightly differs from an ideal TBP, while in $MSiF_5$ ($M = K^+$, Cs^+) salts that were isolated in a low-temperature matrix an axially distorted structure of the anion with C_{3v} symmetry was found as expected.

Having marked acceptor properties, tetraalkylammonium pentafluorosilicates react with ammonia[7,61,64] and methylamines[61] to form complex salts $(R_4N)[SiF_5(Me_nNH_{3-n})]$ ($n = 0$–3) which are isolated in a pure state. By using spectroscopic methods it was possible to study the donor-acceptor interaction between the SiF_5^- anion and a number of bases in non-aqueous media. Clark et al.[7] used IR spectroscopy to study complex formation in the system $SiF_5^- - L - MeCN$, having previously established that the process of dissolving pentafluorosilicate in acetonitrile is not accompanied by coordination of solvent molecules. An increase in concentration of the molecular ligand L produced a decrease in the intensity of the $\nu(Si-F)$ absorption band at ~ 874 cm^{-1} that is characteristic for the SiF_5^- anion. On the basis of this the following order of change in ligand donor capacity relative to SiF_5^- was established:

$$Et_2NH > Et_3N > n\text{-}Pr_3N > Py \sim Et_3P.$$

The basicity of these ligands decreases in the same series. According to the results of Gibson et al.,[65] introduction of ammonia or diethylamine into a solution of $(Pr_4N)SiF_5$ in methylene chloride results in the equilibrium

$$SiF_5^- + L \rightleftarrows [SiF_5(L)]^-,$$

which can be monitored by ^{19}F NMR spectroscopy. When the temperature is lowered, there is a shift in the equilibrium towards the formation of the pseudooctahedral anion.

It is interesting that by studying the interaction of $(Pr_4N)[PhSiF_4]$ and Pr_4NF in methylene chloride it was possible to resolve the problem concerning the structure of complex anions $[RSiF_5]^{2-}$ which had remained the subject of controversy for a considerable length of time. The opinion was held[21,66] that in the absence of structural data compounds with the empirical formula $M_2[RSiF_5]$ (M is an alkali metal, ammonium, or alkylammonium cation) should be regarded as double salts $M_2[RSiF_4]F$ containing pentacoordinate anions $[RSiF_4]^-$ rather than substituted derivatives of the corresponding hexafluorosilicates. However, Marat and Janzen[66] established that the $[PhSiF_4]^-$ anion accepts a fluoride ion to give a hexacoordinate complex $[PhSiF_5]^{2-}$, which has a structure that can be clearly demonstrated by low-temperature ^{19}F NMR spectroscopy.

The pentafluorosilicate anion may be regarded as the product of partial compensation of the acceptor capacity of silicon tetrafluoride by coordination of a single fluoride ion with the latter. Consequently the SiF_5^- anion should have a lower Lewis acidity than the initial SiF_4 molecule. This fairly obvious conclusion has been confirmed from quantitative data on the enthalpy of dissociation of the complexes $(R_4N)[SiF_4(L)]$ and $SiF_4(L)_2$:

$$(R_4N)[SiF_5(L)](s) \rightarrow (R_4N)SiF_5(s) + L(g),$$
$$SiF_4(L)_2(s) \rightarrow SiF_4(g) + 2L(g).$$

The determination was made using the results of tensiometric measurements (Table 1).

The noticeable difference in the values of the enthalpy of dissociation that were obtained by different research workers attracts attention. According to Wharf and Onyszchuk[64] the value $\Delta H = 7.9$ kcal mol^{-1} is not the true enthalpy of dissociation of the complex but is an average enthalpy for two processes—the adsorption of ammonia on the surface of solid pentafluorosilicate and the actual dissociation of the complex. It follows from the data of Table 1 that the enthalpies of dissociation of complexes $(R_4N)[SiF_5(NH_3)]$ depend on the size of the cation, increasing in the series $Et_4N^+ < Pr_4N^+ < Bu_4N^+ \sim Pent_4N^+$. The following thermodynamic cycle was examined in one report:[61]

$$\begin{array}{ccc} (R_4N)[SiF_5(NH_3)](s) & \xrightarrow{\Delta H_1} & NH_3(g) + (R_4N)SiF_5(s) \\ \downarrow & & \downarrow \\ R_4N^+(g) + [SiF_5(NH_3)]^-(g) & \xrightarrow{\Delta H_2} & NH_3(g) + R_4N^+(g) + SiF_5^-(g), \end{array}$$

From which

$$\Delta H_1 = \Delta H_2 + (U_1 - U_2).$$

It was proposed[61] that for complexes $(R_4N)SiF_5$ and $(R_4N)[SiF_5(NH_3)]$ with cations that are greater in size than the anions SiF_5^- and

$[SiF_5(NH_3)]^-$ the structure of the crystal lattice is mainly determined by the packing of the cation and the crystal lattice energies of the complexes are very similar. When this approximation is used ($U_1 = U_2$), the experimentally determined enthalpy of dissociation (ΔH_1) and the corresponding value (ΔH_2) for the process in the gas phase which is not dependent on the nature of the cation become equal. Wharf and Onyszchuk[61] assumed that the condition $U_1 = U_2$ was met for the tetrabutyl- and tetrapentyl-ammonium complexes and the slight difference in enthalpy of dissociation for these compounds could occur because the term $(U_1 - U_2)$ was the difference between two large quantities. A value of $\Delta H^0 = 16.8 \pm 0.6$ kcal mol^{-1} was taken by Wharf and Onyszchuk[61] to be the lower limit of the enthalpy of dissociation of the complex anion $[SiF_5(NH_3)]^-$ in the gas phase. If the crystal lattice energies of the complexes $(R_4N)[SiF_5(L)]$ and $SiF_4(L)_2$ are assumed to have similar values,[64] the thermochemical data given in Table 1 indicate that the SiF_5^- anion has a lower acceptor capacity than silicon tetrafluoride relative to this group of donors.

Table 1. Enthalpies of dissociation of silicon fluoro-complexes with nitrogen-donor ligands.

Complex	ΔH^0, kcal mol^{-1}	Refs.
$(Et_4N)[SiF_5(NH_3)]$	6.0±0.4	[61]
$(Pr_4N)[SiF_5(NH_3)]$	12.0±0.5	[61, 64]
»	7.9	[7]
$(Bu_4N)[SiF_5(NH_3)]$	16.8±0.6	[61]
$(Pent_4N)[SiF_5(NH_3)]$*	14.5±0.7	[61]
$(Pent_4N)[SiF_5(MeNH_2)]$	14.3±0.3	[61]
$(Pent_4N)[SiF_5(Me_2NH)]$	12.3±0.3	[61]
$(Pent_4N)[SiF_5(Me_3N)]$	12.4±0.7	[61]
$SiF_4(NH_3)_2$	52.7±1.9	[67]
»	54.6	[68]
$SiF_4(MeNH_2)_2$	58.1±1.9	[67]
$SiF_4(Me_2NH)_2$	55.2±0.7	[67]
$SiF_4(Me_3N)_2$	40.5±0.4	[67]
»	41.5	[69]

*Pent = C_5H_{11}.

V. Mechanisms of intra- and inter-molecular ligand exchange in solution

IR and Raman spectroscopic studies indicate[7] that the SiF_5^- anion in the solid state and in non-aqueous solution exists in the TBP configuration with non-equivalent axial and equatorial Si–F bonds. At the same time ^{19}F NMR spectra of pentafluorosilicates show that all the fluorine atoms are equivalent.[16,21,65] This apparent contradiction may be due to the difference in time-scale characteristics of these methods and to the rapid (on the time-scale of NMR) exchange of axial and equatorial fluorine atoms. It can be seen from the data given in Table 2 that spectroscopic equivalence of the fluorine atom is also exhibited in the monosubstituted anions $[RSiF_4]^-$ and $[XSiF_4]^-$ but the low-temperature ^{19}F NMR spectra of the disubstituted anions $[Ph_2SiF_3]^-$ and $[PhMeSiF_3]^-$ contain separate signals from the non-equivalent F_a and F_e.

The fact that $^{29}Si-^{19}F$ spin-spin coupling is preserved in the ^{19}F NMR spectra of solutions of pentafluorosilicates at temperatures below –60 °C has been related[21] to the intramolecular nature of ligand exchange, which most probably occurs by the pseudorotation mechanism proposed by Berry.[51] It may be recalled that exchange results in the transposition of two axial and two equatorial ligands in the TBP anion structure. The TP configuration acts as an intermediate state in this polytopic rearrangement.[71] The temperature dependence of the shape of the lines in the NMR spectra[46,70,72,73] is consistent with the pseudorotation mechanism of Berry for pentacoordinate fluorosilicate anions, although alternative mechanisms cannot be entirely excluded.[61,64] Damrauer and Danahey[70] calculated the activation parameters for intramolecular fluorine exchange in $[Ph_2SiF_3]^-$ and $[PhMeSiF_3]^-$ anions. The results obtained are given in Table 3 together with data for related pentacoordinate trifluorosilyl molecular complexes.

Table 2. ^{19}F NMR spectroscopic parameters of pentacoordinate fluorosilicate anions in non-aqueous solution.[21,22,70]

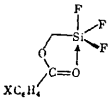
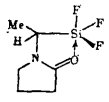
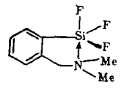
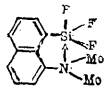
Compound	Solvent	^{19}F Chemical shift, rel. to $CFCl_3$, p.p.m.	$J(^{29}Si-^{19}F)$, Hz	t, °C
$(Pr_4N)SiF_5$	CH_2Cl_2	136.0	148±2	–66
$(Pr_4N)[MeSiF_4]$	CH_2Cl_2	110.9	218±1	–60
$(Bu_4N)[MeSiF_4]$	CH_2Cl_2	110.5	218	–60
$(Pr_4N)[BuSiF_4]$	CH_2Cl_2	116.6	223±2	–62
$(Me_4N)[PhSiF_4]$	Me_2SO	116.8	205	25
$(Pr_4N)[PhSiF_4]$	$CHCl_3$	119.2	206±2	35
$(Et_4N)[Ph_2SiF_3]$	CH_2Cl_2	98.0 (F_a); 134.0 (F_e)	254±4 212±2	–62
(18-crown-6.K)$[Ph_2SiF_3]$	acetone-d_6/vinyl chloride	100.5 (F_a); 133.9 (F_e)	252.7 204.6	–62
(18-crown-6.K)$[PhMeSiF_3]$	acetone-d_6/vinyl chloride	83.5 (F_a); 133.3 (F_e)	251 210	–62
$(Me_4N)[CF_3COOSiF_4]$	SO_2	124.9	92	–75
$(Me_4N)[MeCOOSiF_4]$	SO_2	120.8	155	–75
$(Me_4N)[PhSSiF_4]$	SO_2	125.5	—	–75
$(Me_4N)[ClO_3SiF_4]$	CH_2Cl_2	135.7	—	–75
$(Me_4N)[HCOOSiF_4]$	SO_2	117.8	—	–75
$(Me_4N)[NO_2SiF_4]$	CH_2Cl_2	136.5	150	–75
$(Me_4N)[NO_3SiF_4]$	CH_2Cl_2	142.3	—	–75
$(Me_4N)[N_3SiF_4]$	CH_2Cl_2	136.0	132	–75
$(Me_4N)[CNSiF_4]$	SO_2	130.1	105	–75
$(Me_4N)[SCNSiF_4]$	SO_2	148.7	—	–75

It is evident from the data of Table 3 that the energy barriers for intramolecular exchange of fluorine in pentacoordinate anionic and molecular SiF_3 derivative forms are very similar. It should be noted that the results from temperature-dependent ^{19}F NMR spectroscopic studies on 2-{(methyltrifluorosilylamino)methyl}pyridine[79] and 1-(trifluorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline [80] (energy barriers for fluorine exchange are 13.2 and 7.5 kcal mol^{-1} respectively) were interpreted by the authors of these studies in terms of an exchange model which incorporated the cleavage of an intramolecular Si ← N coordinate bond followed by rotation of the SiF_3 group in the tetrahedral intermediate. It was suggested[80] that this type of scheme for fluorine exchange is to be preferred to the alternative mechanisms for compounds with relatively weak intramolecular Si ← N coordinate bonds.

Wilhite and Spialter[81] carried out non-empirical calculations on the mechanism of the Berry pseudorotation for the hypothetical anions SiH_5^- and $[SiH_{5-n}X_n]^-$ (n = 1–5), where introduction of a more electronegative substituent X (EN_X = 2.9 on the Pauling scale) was formally effected by increasing the charge of the hydrogen atomic nucleus to +1.1. It was found that the pseudorotation barriers for SiH_5^- and SiX_5^- complexes were small (2.87 and

2.94 kcal mol^{-1} respectively) and that rearrangement took place almost freely whereas pseudorotation in the mixed anion $[SiH_2X_3]^-$ occurred via several alternative configurations and required a greater consumption of energy (about 7.03 kcal mol^{-1}). According to similar *ab initio* calculations on the rearrangements of PF_5 and PF_3H_2 molecules,[82,83] the change to trifluorophosphorane, as in the case of the substituted anion $[SiH_2X_3]^-$, is accompanied by an increase in the pseudorotation barrier and a greater complexity of rearrangement mechanism, the calculated values of the energy barriers being similar to the experimental values. If it is assumed that SiX_5^- and $[SiH_2X_3]^-$ complexes to a given approximation simulate the behaviour of the real anions SiF_5^-, $[Ph_2SiF_3]^-$, and $[PhMeSiF_3]^-$, the decrease in rate of axial-equatorial exchange of fluorine atoms on going from SiF_5^- to $[Ph_2SiF_3]^-$ and $[PhMeSiF_3]^-$ becomes clear.[21,70] Calculations[81-83] confirm the empirical rule of Muetterties and Schunn,[38] according to which isomers with an axial orientation of the electronegative substituents are the most stable for the TBP configuration of complexes of non-transition elements.

Table 3. Activation parameters for intramolecular exchange of fluorine in pentacoordinate trifluorosilyl complexes.

Compound	$\Delta G^{\neq}$, kcal mol^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, cal deg^{-1} mol	Refs.
$[Ph_2SiF_3]^-$	11.7	11.2	2.5	[70]
$[PhMeSiF_3]^-$	9.9	9.4	−4.4	[70]
	7.4—9.0	—	—	[75]
	9.5	—	—	[76]
	13.1	—	—	[77]
	12.0	—	—	[78]

A discussion of the probable mechanisms for intermolecular exchange of fluorine in pentacoordinate fluorosilicate anions first appeared in a study of Klanberg and Muetterties.[21] These authors proposed that the broadening of the ^{19}F NMR resonance signal from the SiF_5^- anion for a solution of tetrapropylammonium pentafluorosilicate in methylene chloride with a loss of the fine structure from $^{29}Si-^{19}F$ at temperatures above −60 °C could be due to either the dissociation:

$$SiF_5^- \rightleftarrows SiF_4 + F^-,$$

or association with formation of polymeric anions with fluoride bridges:

$$nSiF_5^- \rightleftarrows (nSiF_5)^-,$$

with both equilibria accompanied by cleavage of Si−F bonds. When the Lewis acidity of the pentafluorosilicate anion was taken into consideration, an associative mechanism was considered[21] to be the most favourable. On the other hand, alkyl- and aryl-substituted $[R_nSiF_{5-n}]^-$ anions have a much lower acceptor capacity than SiF_5^- and so dissociation is more probable for such compounds:

$$[Ph_2SiF_3]^- \rightleftarrows Ph_2SiF_2 + F^-.$$

This conclusion is indirectly confirmed by the results of a non-empirical calculation on the energy of the intermolecular ligand exchange in hypothetical $[SiH_{5-n}X_n]^-$ anions[81] (Table 4). However, the results of Damrauer and Danahey,[70] which demonstrate the absence of dissociative exchange of fluorine in solutions of $[Ph_2SiF_3]^-$ over a wide temperature range (^{19}F and ^{29}Si NMR data), should be noted. An important factor in this case is the relatively high dielectric constant of the solvent used[70] (acetone-d_6/vinyl chloride), which should favour this particular dissociative process involving the $[Ph_2SiF_3]^-$ anion.

Table 4. Calculated values of ΔH for intermolecular exchange in the hypothetical systems $[SiH_{5-n}X_n]^-$.

n	Reaction	ΔH, kcal mol^{-1}*
0	$SiH_4 + H^- \rightleftarrows SiH_5^-$	16.97 (16.97)
1	$SiH_4 + X^- \rightleftarrows [SiH_4X]^-$	12.59 (35.77)
2	$SiH_3X + X^- \rightleftarrows [SiH_3X_2]^-$	30.16 (55.08)
3	$SiH_2X_2 + X^- \rightleftarrows [SiH_2X_3]^-$	44.05 (70.72)
4	$SiHX_3 + X^- \rightleftarrows [SiHX_4]^-$	58.27 (86.73)
5	$SiX_4 + X^- \rightleftarrows SiX_5^-$	72.79

*Values in brackets refer to a reaction with hydride ion as the leaving group.

It cannot be ruled out that the occurrence of a given mechanism for fluorine exchange in the diphenyltrifluorosilicate anion—intermolecular dissociative exchange for a solution of $(Et_4N)[Ph_2SiF_3]$ in methylene chloride[21] and the intramolecular Berry process for a solution of (18-crown-6.K)$[Ph_2SiF_3]$ in an acetone-d_6/vinyl chloride mixture[70]—is due to the differences in polarising effects of the external cations. When the higher charge density on the Et_4N^+ cation compared to $(18\text{-crown-6.K})^+$ is taken into account, these difference in the mechanism for fluorine exchange in diphenyltrifluorosilicates then become completely consistent. In this connection there are some interesting results[84] which indicate that in non-aqueous solutions of trialkyl- and dialkyl-ammonium pentafluorosilicates dissociative intermolecular exchange of fluorine is occurring:

$$2SiF_5^- \rightleftarrows SiF_4 + SiF_6^{2-}.$$

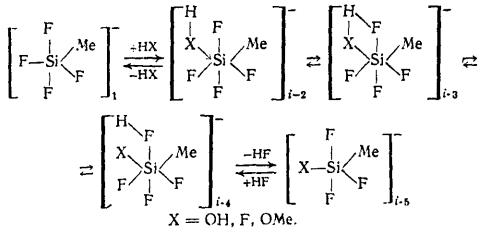
It was indicated[21] that intermolecular exchange processes with cleavage of Si–F bonds in pentacoordinate fluorosilicate anions may be caused by the presence of impurities in the samples studied. This question has been the subject of special studies.[65,85] The connection between exchange and hydrolysis processes is the most obvious. For example, the reversible loss of fine structure in ^{19}F NMR spectra of non-aqueous solutions of tetraalkylammonium pentafluorosilicate and methyltetrafluorosilicate when water is added to the samples followed by treatment with hexamethyldisilazane is consistent[65,85] with a hydrolysis mechanism of intermolecular fluorine exchange:

$$SiF_5^- + H_2O \rightleftarrows [SiF_4OH]^- + HF,$$
$$[MeSiF_4]^- + H_2O \rightleftarrows [MeSiF_3OH]^- + HF.$$

The action of $(Me_3Si)_2NH$ leads to HF, which is a fluorine carrier in the exchange process, being removed from the system by the reaction:

$$(Me_3Si)_2NH + 2HF \rightarrow 2Me_3SiF + NH_3.$$

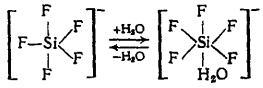
By using the concept of the change in coordination numbers of elements during the reaction, namely, Si(5) ⇆ Si(6), H(1) ⇆ H(2), F(1) ⇆ F(2), O(2) ⇆ O(3), Marat and Janzen[85] proposed the following generalised mechanism for intermolecular exchange of fluorine in the $[MeSiF_4]^-$ anion in the presence of H_2O, HF, or MeOH:



X = OH, F, OMe.

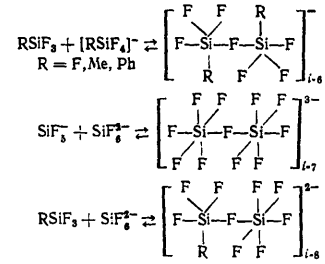
At the first stage the formation of the hexacoordinate intermediate *i*-2 is postulated, which is converted by a four-centre mechanism to *i*-3. The subsequent cleavage of the X–H bond and elimination of an HF molecule leads to the substitution product *i*-5.

It was demonstated[16,65] that the Lewis acid-base interaction in the system $SiF_5 - H_2O$ and the rapid exchange between penta- and hexacoordinate complexes can be taken as the basis for the mechanism of low-temperature intramolecular axial-equatorial ligand exchange in the SiF_5^- anion:



Exchange leads to 'averaging out' of the position of the fluorine atoms in the coordination polyhedron, but their bond with the silicon atom is preserved.

In conclusion, mention should be made of the results of the study by Marat and Janzen[16] on the intermolecular exchange of fluorine in the systems $SiF_4^- - SiF_5^-$, $MeSiF_3 - [MeSiF_4]^-$, $PhSiF_3 - [PhSiF_4]^-$, $SiF_5^- - SiF_6^{2-}$, $SiF_4 - SiF_6^{2-}$, and $MeSiF_3 - SiF_6^{2-}$ (external cation Pr_4N^+). The ^{19}F, ^1H, and ^{13}C NMR spectroscopic data obtained[16] were interpreted on the basis of the coordination model of the reaction mechanism[85] involving a change in coordination numbers Si(4) ⇆ Si(5), Si(5) ⇆ Si(6), Si(4) ⇆ Si(5) ⇆ Si(6), F(1) ⇆ F(2) in formation of the intermediates *i*-6, *i*-7, and *i*-8:



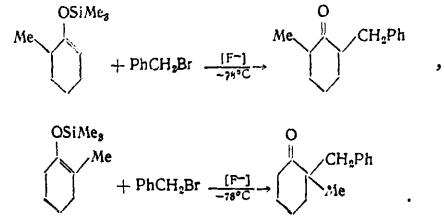
According to the results of this study[16] intermolecular exchange of fluorine is rapid (on the time-scale of NMR) if the fluoro-complexes participating in exchange have different coordination numbers. For example, introduction of excess ammonia into the system $SiF_5^- - SiF_6^{2-}$ inhibits exchange because of the formation of the hexacoordinate complex $[SiF_5(NH_3)]^-$. On the other hand, addition of diethylamine to a sample of $MeSiF_3$ is accompanied by a loss of fine structure from $^{19}F - Si - C - ^1H$ spin-spin coupling in its ^{19}F and ^1H NMR spectra since $MeSiF_3$ is involved in exchange with penta- and hexacoordinate products of donor-acceptor interaction.

VI. Use in preparative synthesis

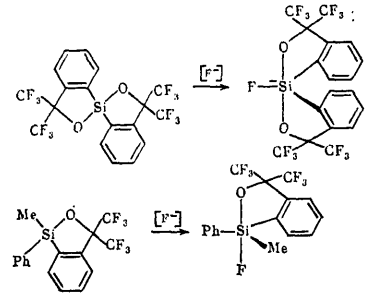
The known examples where salts of pentacoordinate fluorosilicate anions have been used in preparative synthesis are few in number but they serve as a good illustration of the synthetic possibilities of this class of compounds. Thus, tris(dialkylamino)sulphonium trimethyldifluorosilicates, which are fairly readily available and stable, serve as useful sources of the unhydrated fluoride ion:[86]

$$[(R_2N)_3S][Me_3SiF_2] \rightleftarrows (R_2N)_3S^+ + F^- + Me_3SiF.$$

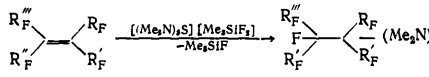
In the presence of $[(Et_2N)_3S][Me_3SiF_2]$, silyl enol ethers readily react under very mild conditions with primary alkyl bromides and alkyl iodides to form products from regiospecific *C*-monoalkylation (yield 60–95%):[87]



The analogous derivative, $[(Me_2N)_3S][Me_3SiF_2]$, was used in the synthesis of pentacoordinate monofluorosilicates:[46]



It was recently shown[88] that tris(dimethylamino)sulphonium trimethyldifluorosilicate reacts with perfluoroolefins in THF or acetonitrile to form stable fluorocarbanion salts:



Reactions of $(Me_2N)_3S^+CF_3(CF_2)_2C^-(CF_3)_2$ with a number of organic compounds have been reported, demonstrating the synthetic value of the salts obtained.

In two studies Gel'mbol'dt[89,90] has proposed a method for the synthesis of hexacoordinate silicon tetrafluoride complexes with molecular nitrogen-donor ligands by reaction of tripropylammonium pentafluorosilicate or the double fluorosilicates $(R_3NH)_2SiF_6.2(R_3NH)SiF_5$ (R = Et, Bu) with the respective bases in methylene chloride or acetonitrile, for example:

$$2SiF_5^- + \alpha,\alpha'\text{-Bipy} \rightarrow SiF_4(\alpha,\alpha'\text{-Bipy}) + SiF_6^{2-}.$$

This method of synthesis does not require operations involving gaseous silicon tetrafluoride; $SiF_4(L)$ complexes are virtually insoluble in the solvents used and are readily separated from a solution of trialkylammonium hexafluorosilicate. The use of alcohol solutions of silicon tetrafluoride[91] to obtain such compounds is unacceptable since even a base of medium strength such as aniline and especially highly basic amines bring about the alcoholysis of SiF_4.[92]

Finally, we should mention a simple and effective variant of the synthesis of graphite intercalation compounds by reaction of the readily available salt $C_{24}SiF_5$ [93,94] with strong Lewis acids such as PF_5, BF_3, or $C_6F_5PF_4$:

$$C_{24}SiF_5 + 2PF_5 \rightarrow C_{24}PF_6 \cdot PF_5 + SiF_4,$$
$$C_{24}PF_6 \cdot PF_5 \xrightarrow{20\ ^\circ C,\ \text{vacuum}} C_{24}PF_6 + PF_5,$$
$$C_{24}SiF_5 + C_6F_5PF_4 \rightarrow C_{24}C_6F_5PF_5 + SiF_4.$$

This method compares favourably with the traditional scheme for the synthesis of salts of graphite with fluorine-containing anions because of the possibility of using Lewis acids such as $C_6F_5PF_4$ which are unstable towards elemental fluorine.

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