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Matrix-Isolation Studies of Lewis Acid/Base Interactions. 2. 1/1 Adduct of SiF_4 with Methyl-Substituted Amines

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The matrix-isolation technique and twin-jet deposition have been employed to isolate and investigate the initial reaction products between SiF_4 and methylamines. The infrared spectra of these initial reaction products indicate the formation of an intermediate 1/1 adduct, while no indication of 1/2 adduct was obtained under these conditions. The major spectral features in the region 800–960 cm^{-1} were assigned to Si–F stretching modes in the complex, and a number of observations indicate a trigonal-bipyramidal structure for the complex. Spectroscopic and group-theoretical arguments suggest that the base occupies an axial position in the structure; for the $SiF_4 \cdot NH_3$ and $SiF_4 \cdot (CH_3)_3N$ complexes a C_3 axis is preserved. These Si–F stretching modes were observed to shift with a change in base, and these shifts have been correlated with the basicity and electron-donating power of the base. Complexes with $SiCl_4$ were formed as well, but with considerable difficulty, and less information about the complex could be extracted.

Introduction

Lewis acid/base adducts have been known for a number of years,[1-3] particularly for strong Lewis acids such as BF_3 and PF_5. Slightly weaker Lewis acids such as SiF_4 are of interest as well in that the opportunity for more than one stoichiometric combination is possible. Through the years, 1/2 adducts of SiF_4 with a variety of nitrogen-containing bases have been studied,[4-7] but very few 1/1 adducts are known.[6,7] Recently, the matrix-isolation technique has been used to study the 1/1 adduct of SiF_4 with NH_3; the 1/2 adduct had been known for years, but no mention had been made of a possible intermediate adduct. The codeposition of SiF_4 and NH_3 from separate vacuum lines, each diluted in argon, followed by rapid condensation into an inert matrix at 15 K led to the isolation of the 1/1 adduct.[8] A key structural finding of this study was that the NH_3 group occupies an axial position in the trigonal-bipyramidal structure about the central silicon. Further support for this conclusion might come from the spectra of 1/1 adducts of SiF_4 with substituted amines. An unsymmetrical base such as CH_3NH_2 or $(CH_3)_2NH$ may lower the symmetry of the SiF_4 skeleton, leading to a splitting of the degenerate equatorial stretching mode. Also, the effects of base strength upon band position for the Si–F stretching mode will be of interest, as will be a comparison of the reactivities of SiF_4 and $SiCl_4$. Consequently, a systematic investigation was conducted to isolate the 1/1 adducts of SiF_4 and $SiCl_4$ with several methylamines.

Experimental Section

A conventional matrix-isolation apparatus was used for all of the experiments in this study and has been described previously.[9] The two reactants for a given experiment were diluted with the matrix gas in separate vacuum lines to prevent equilibration and formation of the known 1/2 adducts. The samples were codeposited onto the 15 K cold surface; mixing occurred immediately in front of the cold window, followed by rapid condensation so that the initial reaction products might be trapped. So that the purest reactant samples possible might be obtained, each stainless steel vacuum line was flamed and conditioned with the reactant to be employed in that experiment. This conditioning proved to be particularly important for the experiments employing CH_3ND_2, where H/D isotope exchange is known to occur rapidly with hydrogen-containing impurities. CH_3NH_2 was found to contain slight amounts of NH_3 impurity; efforts were made to separate these by distillation, but the boiling points of CH_3NH_2 and NH_3 are quite similar, and some NH_3 remained at all times. However, the spectrum of the reaction product of NH_3 with SiF_4 could readily be accounted for in the final spectrum. $(CH_3)_2NH$ was found to contain both NH_3 and $(CH_3)NH_2$ impurities, which were, in part, removed by distillation from a dry ice/acetone bath. Some impurities remained but did not seriously hamper the $(CH_3)_2NH$ reaction studied. The remaining gases SiF_4 (Matheson), CH_3ND_2 (Merck), $(CH_3)_3N$ (Matheson), $(CD_3)_3N$ (Merck), and $SiCl_4$ (Alfa) were purified by repeated freeze/thaw cycles at 77 K and were found to be relatively pure. Argon and nitrogen were employed as matrix gases and were not subjected to any purification steps.

Samples were codeposited onto the 15 K cold window for 20–24 h, with flow rate of 2 mmol/h from each vacuum line. Infrared spectra, both survey and high resolution over the regions of interest, were recorded on a Beckman IR 12 infrared spectrophotometer.

Results

Prior to the investigation of the reaction of SiF_4 with substituted amines, blank experiments were conducted on each of the amines of interest, at dilutions comparable to those used throughout. The spectra became increasingly complex as the number of methyl substituents increased, and the spectra were in good agreement with literature spectra.[10-12]

SiF_4 + CH_3NH_2. These two reactants were codeposited in an initial experiment at a dilution of 1/1000 each in argon, so that the total dilution was about 1/1/2000. Under these conditions, extremely intense product bands were observed near 940 and 850 cm^{-1}, along with medium-intensity bands near 412, 424, and 469 cm^{-1}. The two higher energy bands were fully absorbing after 10–12 h of deposition and were also quite broad. A similar experiment was conducted with twice the dilution, 1/1/4000, and the same set of bands was observed. The two upper bands were still strongly absorbing, and moderately broad, although the band system near 940 cm^{-1} began to show some structure. At yet higher dilution, 1/1/8000, these two product bands were sufficiently less intense that accurate band positions and shapes could be determined. The uppermost band appeared as a distinct doublet, with nearly symmetrical components at 934 and 942 cm^{-1}, while the lower band appeared to be a single, sharp band at 845 cm^{-1}. At this very high dilution, the low-energy bands between 400 and 500 cm^{-1} were not observed. Figure 1 shows the infrared spectra of the reaction products of CH_3NH_2 with SiF_4 at several dilutions.

One experiment was conducted with nitrogen as the matrix gas, at a total dilution of 1/1/8000, and provided very clean, definitive spectra. A similar set of product bands was observed

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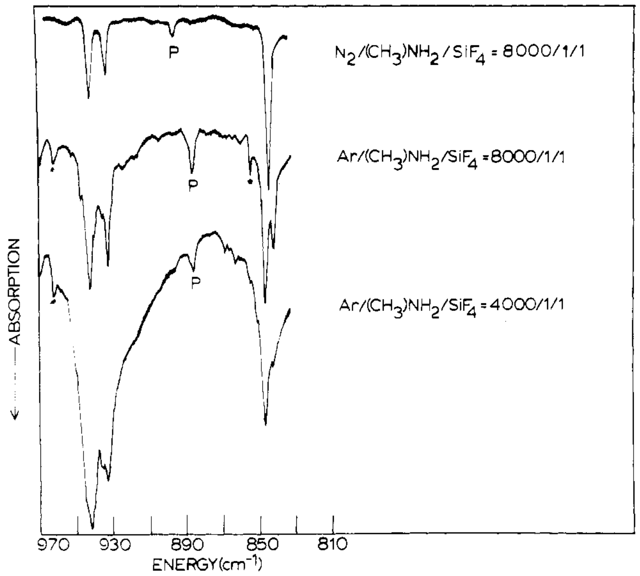

Figure 1. Infrared spectra, over selected regions, of the reaction product from the codeposition of SiF_4 and CH_3NH_2 into inert matrices. The top trace shows the nitrogen-matrix result at a dilution of 1/1/8000, while the middle trace shows the argon-matrix spectrum at the same dilution, and the lower trace shows the spectrum obtained at a dilution of 1/1/4000. Bands labeled P are due to parent CH_3NH_2, while bands labeled with an asterisk are due to either NH_3 impurity or the reaction product of NH_3 impurity with SiF_4.

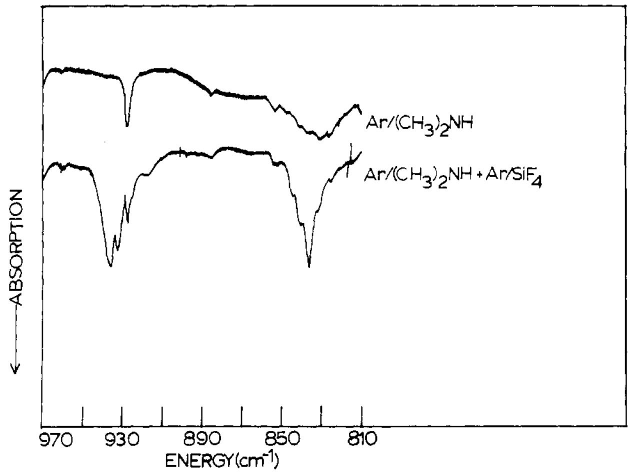

Figure 2. Infrared spectrum of the reaction product of the reaction of SiF_4 with $(CH_3)_2NH$ compared with that of a blank experiment of $(CH_3)_2NH$, both in argon matrices.

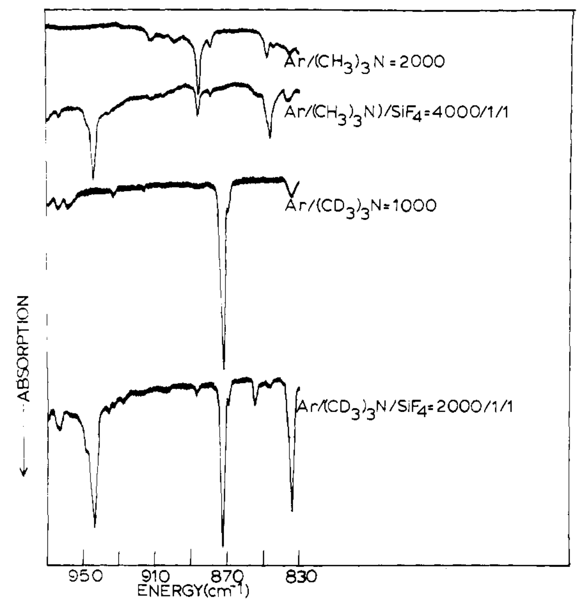

Figure 3. Infrared spectra of the reaction products from the codeposition of SiF_4 and either $(CH_3)_3N$ or $(CD_3)_3N$, contrasted with spectra from blank experiments of the amines in argon.

in the region 800–960 cm^{-1}, with only slight shifts from the argon-matrix positions. The upper band appeared as a distinct doublet with components at 931 and 940 cm^{-1}, while the lower band was located at 841 cm^{-1}, as shown in the top trace of Figure 1.

SiF_4 + CH_3ND_2. SiF_4 was codeposited with CH_3ND_2 in several experiments, and in each case it was apparent that some exchange had occurred, so that CH_3NHD and CH_3NH_2 were observed as well. In addition, product bands were observed near 845 and 942 cm^{-1}, when dilutions of 1/1/4000 were employed. The upper band appeared slightly split, but not distinctly, as the band width was about 12 cm^{-1}, probably due to the presence of three different isotopic species. No product bands were detected in the region between 400 and 500 cm^{-1}, which was not unexpected at these dilutions.

SiF_4 + $(CH_3)_2NH$. SiF_4 was codeposited with a sample of $(CH_3)_2NH$ in several experiments, with a total dilution of 1/1/4000 in argon. Intense product bands were observed at 836, 934, and 938 cm^{-1}, with the upper two bands appearing as a distinct doublet as can be seen in Figure 2. In addition, a weak product band was observed near 420 cm^{-1}.

SiF_4 + $(CH_3)_3N$. These two reactants were codeposited in several experiments, at dilutions of 1/1/2000 and 1/1/4000. In addition to parent bands, product bands were observed at 847 and 945 cm^{-1}, both being relatively sharp and distinct. In addition, a weak product band was detected at 418 cm^{-1}.

SiF_4 + $(CD_3)_3N$. SiF_4 was codeposited with a sample of Ar/$(CD_3)_3N$ in two experiments, with a total dilution of 1/1/2000. In this case, no hydrogen/deuterium isotope exchange occurred, and the only isotopic species observed was $(CD_3)_3N$. In addition to parent bands, product bands were observed quite near those observed for the normal hydrogen isotope, at 944 and 834 cm^{-1}, while no distinct product bands were observed in the low-frequency region. Figure 3 shows the infrared spectra of the reaction products of SiF_4 with $(CH_3)_3N$ and $(CD_3)_3N$.

$SiCl_4$ + $(CH_3)_2NH$. These two reactants were codeposited in two experiments, with dilutions of 1/1/500 and 1/1/2000. New product bands were observed, particularly in the 1/1/500 experiment, at 580, 566, 471, and 450 cm^{-1}. All four were relatively weak, suggesting that $SiCl_4$ reacts much more slowly under comparable conditions than does SiF_4.

$SiCl_4$ + $(CH_3)_3N$. $SiCl_4$ was codeposited with a sample of $(CH_3)_3N$ in two experiments, at total dilutions of 1/1/500 and 1/1/1000. In neither experiment could any bands be detected that could be assigned to a product species, supporting the indication above that $SiCl_4$ is substantially less reactive than SiF_4.

Discussion

Product Identification. The codeposition of SiF_4 with substituted amines diluted in argon gave rise to distinct, intense bands in the infrared spectrum that could not be attributed to parent species. These bands persisted in experiments up to dilution of 1/1/8000, in both argon and nitrogen matrices, making the formation of any species other than the 1/1 complex very unlikely. Moreover, the two most intense bands in each experiment fell within a few wavenumbers of the two most intense product bands for the recently[8] reported 1/1 adduct $SiF_4{\cdot}NH_3$. While the slight shifts are chemically significant, as will be discussed below, the relatively close agreement suggests that the isolated product is the 1/1 adduct of SiF_4 and the amine in question. In fact, most of the experiments that led to the $SiF_4{\cdot}NH_3$ complex were carried out at a total dilution of between 1/1/1000 and 1/1/2000, so that at the higher dilutions used here, the 1/1 adduct is even more likely. Finally, no product bands were observed in the region between 700 and 750 cm^{-1} where the intense Si–F stretching modes of the known 1/2 adducts absorb, further suggesting that only the 1:1 adduct is formed[4-7] under these conditions. Finally, since the 1/2 adducts of SiF_4 with amine bases are known at room temperature, the possibility of elimination reactions occurring under matrix-isolation conditions, so as to form $(CH_3)_2NSiF_3 + HF$, can be discounted. All of the evidence, then, points to the assignment of the product bands to a single isolated complex, the 1/1 adduct $SiF_4{\cdot}B$, for the bases mono-, di- and trimethylamine, as well as their deuterium counterparts.

Band Assignments. For each of the 1/1 complexes of SiF_4, the most intense product bands were observed in the region between 800 and 960 cm^{-1}. When deuterated amines were used, these intense bands showed little or no shift, indicating that they are vibrations of the SiF_4 skeleton rather than vibrations of the coordinated amine. Moreover, they lie close to the two bands of the $SiF_4{\cdot}NH_3$ adduct that were assigned to Si–F stretching modes. The region 800–960 cm^{-1} lies slightly below the 1025-cm^{-1} position of the triply degenerate Si–F stretching mode[13] of the parent SiF_4, and hence these bands are readily assigned to Si–F stretching vibrations in the 1/1 adduct. In several of the experiments with higher concentrations, product bands were also detected between 400 and 500 cm^{-1}. This, too, is quite similar to the case for the $SiF_4{\cdot}NH_3$ adduct, where two bands were observed in this region and assigned to Si–F deformation modes of the adduct. These low-energy bands, then, are assigned to Si–F deformation modes of the SiF_4 skeleton in the 1/1 complex.

No additional product bands were observed in these experiments that could be assigned to vibrations of the coordinated amine. This is contrary to the NH_3 results, where the symmetric deformation mode of NH_3 was observed to have shifted up several hundred wavenumbers from its position for free NH_3. However, coordinated methylamines do not have any particularly sensitive modes, as does NH_3, and only small shifts are expected. Since, under the high dilution conditions of these experiments, most of the parent material is trapped and isolated without an opportunity to react, intense parent bands are also observed in the spectra. Consequently, the observation of weak product bands, shifted only slightly from the intense parent bands, makes observation of these modes of the coordinated amine not feasible. This is not to suggest that they are not present, but the nature of the experiment precludes their observation.

In addition, six new vibrational modes are created, arising from the three rotational and three translational degrees of freedom that are lost upon complex formation. Several of these modes are low-frequency torsional modes that will escape detection, while modes such as the Si–N stretch and the amine rocking vibrations might be detected. The NH_3 rocking mode in the $SiF_4{\cdot}NH_3$ complex was observed near 700 cm^{-1}, but the increased mass of the substituted amines should shift this mode to lower frequency. Moreover, this was a very low intensity mode for the $SiF_4{\cdot}NH_3$ and should be even less intense here, due to a lower amplitude of vibration. Thus, it is understandable why this mode has escaped detection. The other mode that might have been observed is the Si–N stretching mode, which has been placed by other workers[5,14,15] anywhere from 200 to 900 cm^{-1}. This mode should have a relatively low dipole moment derivative and be quite weak. In addition, the relatively high mass of the amine will shift this mode to low energies. A combination of these factors must account for the fact that this mode was not observed, in agreement with the earlier $SiF_4{\cdot}NH_3$ studies.

Structure of the Complex. A C_{3v} structure was determined for the 1/1 adduct $SiF_4{\cdot}NH_3$, with a basic trigonal-bipyramidal structure about the central silicon and the NH_3 ligand in an axial position. This determination was made on the basis of a number of observed vibrational modes and a normal-coordinate calculation. By analogy and similarity of spectra, similar conclusions may be reached concerning the 1/1 adducts of the SiF_4 observed here. However, additional information is provided by the band system near 940 cm^{-1}, which was observed for each of the bases studied. This mode was assigned to the doubly degenerate equatorial Si–F stretching mode in the $SiF_4{\cdot}NH_3$ complex. If the NH_3 ligand is replaced by an amine that does not maintain a C_3 rotation axis such as CH_3NH_2 or $(CH_3)_2NH$, then the three equatorial fluorines are not longer equivalent, and the two components of this equatorial stretching mode can no longer be degenerate. Rather, this mode must split into two distinct bands, and the magnitude of this splitting will depend on the degree of nonequivalence of the fluorines. This is precisely the result observed for both unsymmetrical bases; a doublet at 942 and 934 cm^{-1} was observed for the $SiF_4{\cdot}CH_3NH_2$ adduct, and a doublet at 934 and 938 cm^{-1} was observed for the $SiF_4{\cdot}(CH_3)_2NH$ complex. The nitrogen-matrix experiment at a dilution of 1/1/8000 shows the doublet particularly clearly, as can be seen in the top trace of Figure 1. Moreover, this vibrational doublet should coalesce back into a single, relatively sharp line when a second C_{3v} base is used such as $(CH_3)_3N$ (with the methyl groups being treated as point masses). Precisely this behavior was observed, with a single line at 945 cm^{-1} observed for the $SiF_4{\cdot}(CH_3)_3N$ complex, as shown in Figure 3. The other likely structure, a C_{2v} structure with the base in an equatorial position, does not have any doubly degenerate vibrational modes so that such a splitting is not anticipated and could not readily be rationalized. In addition, the 1/1 adduct $SiF_4{\cdot}(CH_3)_3N$ has been synthesized at room temperature, and the infrared spectrum of this adduct also favored the C_{3v} axial structure.[6,7] The solution spectrum of this 1/1 adduct showed intense Si–F stretching at 794 and 936 cm^{-1}, shifted down somewhat from the argon-matrix positions observed here. Considering the differences in environment, these shifts are not particularly large. In addition, this room-temperature study included Raman spectra. The workers were able to observe the symmetric equatorial stretching mode at 702 cm^{-1} and were also unable to observe this mode in the infrared spectra. This argument of vibrational mode splitting by an unsymmetrical base strongly supports the previous conclusion that for these 1/1 adducts the amine ligand occupies an axial position in a trigonal-bipyramidal structure.

The second Si–F stretching mode, near 850 cm^{-1}, was assigned to the stretching mode of the axial fluorine, trans to the amine ligand, for the $SiF_4{\cdot}NH_3$ adduct. A similar assignment is preferred here and supported by the shift of 12 cm^{-1} upon substitution of $(CD_3)_3N$ for $(CH_3)_3N$. This mode must be vibrationally coupled to the coordinated amine ligand and will shift slightly with a change in mass of the ligand such as by isotopic substitution. While this effect may be small, a change of 9 mass units from $(CH_3)_3N$ to $(CD_3)_3N$ is apparently sufficient to shift this mode some 12 cm^{-1} to lower energy.

The observation of axial substitution of the amine ligand is contrary to the "Muetterties rule", which predicts that the less electronegative ligand will occupy an equatorial position.[16]

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Table I. Variation of Si-F Stretching Band Positions[a] with Amine Base Strength

amine	ν_{eq}	ν_{ax}	PA,[c] kcal/mol
NH_3	955[b]	854[b]	207
CH_3NH_2	942, 934	845	216
$(CH_3)_2NH$	938, 932	836	222
$(CH_3)_3N$	945	847	227

[a] Band positions in cm^{-1}. [b] Reference 8. [c] Reference 20.

It must be noted that the electronegativity of NH_3 is not known, and the difference between a covalent linkage such as in CH_3PF_4 and the coordinate linkage in $SiF_4{\cdot}NH_3$ may play a role. More importantly there have been no definitive stereochemical determinations of five-coordinate geometries for silicon compounds, in contrast with the very complete studies of Muetterties and co-workers on the pentacoordinate phosphorus compounds.[16,17] Magnetic resonance studies[18] have shown that in such phosphorus compounds the axial fluorines have a higher electron density than do the equatorial fluorines, in agreement with the "Muetterties rule". No definitive magnetic resonance studies have been performed on pentacoordinate silicon compounds; in fact, the ^{19}F NMR studies on SiF_5^- and $CH_3SiF_4^-$ both indicate dynamical equivalence[19] of the fluorines down to −60 °C. Hence little is known about the electron distribution in these compounds, and extension of the "Muetterties rule" to silicon complexes has no direct justification. Rather, the infrared spectra obtained here, and the studies[6,7] of previous workers on $SiF_4{\cdot}(CH_3)_3N$, support axial substitution for the amine ligand.

Base Strength Effects. Small but significant shifts were observed in the Si–F stretching modes as the base was changed through the methylamine family, as can be seen in Table I. While part of this effect, at least for the 850-cm^{-1} band system, might be rationalized in terms of increased mass, there is some indication that the basicity of the amine ligand plays a role as well. The basicity of the methylamines is known to increase as the number of methyl groups increases, with use of gas-phase proton affinities as a measure.[20] When SiF_4 is complexed to successively stronger bases, the SiF_4 skeleton will accept an increased amount of electron density, which enters an antibonding orbital.[21] This should have the effect of lowering the vibrational frequencies of the Si–F stretching modes, and this is the observed trend for NH_3, CH_3NH_2, and $(CH_3)_2NH$, from 955 to 938 and 936 cm^{-1}, with the center of the doublet being used for the two unsymmetrical amines. The singly degenerate mode near 850 cm^{-1} shows a similar trend, from 854 cm^{-1} with NH_3 to 845 and 836 cm^{-1} with CH_3NH_2 and $(CH_3)_2NH$, respectively. While this trend may also reflect an increased mass of the base for this vibrational mode, it is likely that basicity effects are present as well. However, $(CH_3)_3N$ is known to have a higher proton affinity than the other methylamines, yet the band positions of the $SiF_4{\cdot}(CH_3)_3N$ adduct at 945 and 847 cm^{-1} do not fit this trend. It has been noted that in solution the order of basicity is $NH_3 < CH_3NH_2 = (CH_3)_2NH > (CH_3)_3N$, as a consequence of solvation and/or steric effects.[22] This ordering fits very closely the observed band positions here, and these effects must also account for the band positions observed for the $SiF_4{\cdot}(CH_3)_3N$ adduct.

Complexes of $SiCl_4$. A number of reactions were studied in which $SiCl_4$ was codeposited with a substituted amine. Just as in the NH_3 study,[8] it was much more difficult to form $SiCl_4$ adducts, and much higher concentrations were necessary. The reaction of $SiCl_4$ with $(CH_3)_2NH$ at 1/1/500 dilution gave rise to several bands between 450 to 600 cm^{-1}, a region generally associated with Si–Cl stretches. The upper two, at 566 and 580 cm^{-1}, may be assigned as a doublet, due to the splitting of the equatorial Si–Cl stretching mode by an unsymmetrical base. The remaining bands can also be assigned as Si–Cl stretches, but little can be concluded about the structure of the adduct. When $(CH_3)_3N$ was codeposited with $SiCl_4$ under similar conditions, no product bands were observed, which supports the above argument that $(CH_3)_3N$ is substantially less reactive than the partially methylated amines.

Conclusions

The codeposition of samples of SiF_4 and methyl-substituted amines, each diluted in argon, has allowed for the formation and trapping of the intermediate 1/1 adducts. Only one of these adducts, $SiF_4{\cdot}(CH_3)_3N$, had been observed previously, and the spectra observed here are in good agreement, for those vibrational modes that were detected. These 1/1 adducts all appear to have a trigonal-bipyramidal structure about the central silicon, and spectroscopic arguments suggest that the amine ligand is in an axial position. A slight shift in Si–F stretching-band positions was observed with a change in base, which can be attributed to a change in the electron-donating capability of the base. Attempts were carried out to synthesize analogous complexes of $SiCl_4$ and were successful for the stronger bases but not for $(CH_3)_3N$. Even when the attempts were successful, much higher concentrations were required than for analogous SiF_4 reactions.

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Registry No. $SiF_4{\cdot}CH_3NH_2$, 80954-20-7; $SiF_4{\cdot}(CH_3)_2NH$, 80954-21-8; $SiF_4{\cdot}(CH_3)_3N$, 28478-86-6; SiF_4, 7783-61-1; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3N$, 75-50-3; $SiCl_4$, 10026-04-7.

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