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Matrix-Isolation Studies of Lewis Acid/Base Interactions. 3. Infrared Spectra of 1/1 Tetrafluorogermane/Amine Complexes

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The matrix-isolation technique has been applied to the study of the 1/1 adduct of GeF_4 with several amines, including NH_3 and mono- and trimethylamine. The adducts, formed by the codeposition from separate vacuum lines of the appropriate gases diluted in argon, gave rise to several absorptions in the Ge-F stretching region. For the $GeF_4 \cdot NH_3$ complex, the umbrella mode of the coordinated NH_3 group was detected as well, near 1245 cm^{-1}. Isotopic substitution data and group-theoretical arguments support a structure for the 1/1 adduct that is trigonal bipyramidal about the central germanium, with the NH_3 group in an axial position. For comparison, spectra of the 1/2 adducts were recorded as well, and all showed an intense, broad band near 600 cm^{-1}. Complexes of $GeCl_4$ with several of these bases were investigated as well, although the yields were lower and no definitive conclusion could be reached about the structure of these complexes.

Introduction

The structure and reactivity of adducts between strong Lewis acids and bases have been studied extensively in recent years,[1-3] particularly for the Lewis acids BF_3 and PF_5. In addition, many systems exist in which more than one stoichiometric ratio of the acid and base may give rise to stable products. In other cases such as the SiF_4/NH_3 system, only the 1/2 adduct[4] $SiF_4 \cdot 2NH_3$ had been observed until recently. Here, the codeposition of samples of Ar/SiF_4 with Ar/NH_3 samples under matrix-isolation conditions allowed an initial reaction to occur,[5] and the 1/1 adduct was trapped before equilibrium could be established and the 1/2 adduct formed. The matrix-isolation technique has been used previously for the study of acid-base complexes[6-8] and appears uniquely suited for the study of adducts of intermediate stoichiometry.

The acid/base chemistry of the germanium tetrahalides is considerably less well characterized than that of its group 4A counterparts.[9] In a few cases, a 1/2 adduct of GeF_4 with a nitrogen-containing base has been formed, and for two bases,[10,11] trimethylamine and acetonitrile, a 1/1 adduct has been reported.[12] However, it has also been postulated on the basis of melting points and conductivity that these 1/1 adducts are polymeric, with fluorine bridges to maintain an octahedral configuration around the germanium center.[9,13] The stability and structure of isolated 1/1 adducts of GeF_4 are not clear; the application of the matrix-isolation technique might provide direct answers to these questions. In addition, the relative acidities of GeF_4 and SiF_4 have been the subject of some debate, and comparison of adduct spectra may shed some light on this question.

Finally, it has been reported that GeF_4 is a stronger acid than $GeCl_4$; comparison of matrix spectra of similar complexes may provide information on this issue as well. For the resolution of the above questions, a thorough study was undertaken to investigate the 1/1 adducts of GeF_4 and $GeCl_4$ with amine bases in inert matrices.

Experimental Section

All experiments were carried out on a conventional matrix-isolation apparatus, which has been described previously.[14] So that equilibration and formation of the 1/2 complexes between GeF_4 (or $GeCl_4$) and the amine under study might be avoided, the two reactants were each diluted with the matrix gas in separate vacuum lines and codeposited onto the cold window. Mixing of the two reactants occurred immediately in front of the cold window, followed by rapid condensation and isolation of the initial reaction product. The gases employed in this study were GeF_4 (Ozark-Mahoning), NH_3 (Matheson), $^{15}NH_3$ (95% ^{15}N, Merck), CH_3NH_2 (Matheson), $(CH_3)_3N$ (Matheson), and $(CD_3)_3N$ (Merck, 99% D). Each gas was purified by a series of freeze/thaw cycles under vacuum before sample preparation. Argon and nitrogen were used as the matrix gases, with no further purification.

Matrix samples were deposited at a flow rate of approximately 1.5 mmol/h from each deposition line, for a total of 20-24 h. Both survey and high-resolution scans were recorded after deposition on a Beckman IR-12 infrared spectrophotometer.

The 1/2 complexes were generated in a glass sample tube by freezing premeasured amounts of both gases, with an excess of amine, into the tube at 77 K. The frozen mixture was allowed to warm to room temperature, and an immediate reaction occurred to form a white powder. The excess amine was pumped off and the sample tube opened to remove the white solid. Infrared spectra were run of these samples in Nujol mulls at room temperature.

Results

Before the reaction products of the germanium tetrahalides with a number of amines were studied, blank experiments were conducted on the germanium compounds. The spectrum of a sample of $Ar/GeF_4 = 1000$ showed a very intense band near 795 cm^{-1}, which was split by the five abundant isotopes of germanium. In addition, a moderately intense, sharp band was observed at 270 cm^{-1} and a broader, weak band was observed near 780 cm^{-1}. The former two bands are assigned to ν_3 and ν_4 of tetrahedral GeF_4, in agreement with literature spectra,[15] while the latter 780-cm^{-1} band is assigned to aggregated GeF_4 in the argon matrix. A blank experiment of $GeCl_4$ showed an intense fundamental at 464 cm^{-1}, with two weaker bands, possibly due to aggregate species near 420 and 310 cm^{-1}. Blank experiments of the amines of interest diluted in argon have been recorded previously in this laboratory.[5,16]

$GeF_4 + NH_3$. Samples of $Ar/GeF_4 = 1000$ were codeposited with samples of $Ar/NH_3 = 1000$ in several experiments, so that the total dilution was roughly 2000/1/1. After a full deposition period, three product bands were observed that could not be assigned to a parent species, at 718, 738, and 1245 cm^{-1}. All three were quite sharp, and the bands at 738 and 1245 cm^{-1} were relatively intense as well. Additional experiments were conducted at the total concentration ratios of 500/1/1 and 200/1/1. At these higher concentrations, all three product bands grew considerably in intensity and maintained a constant

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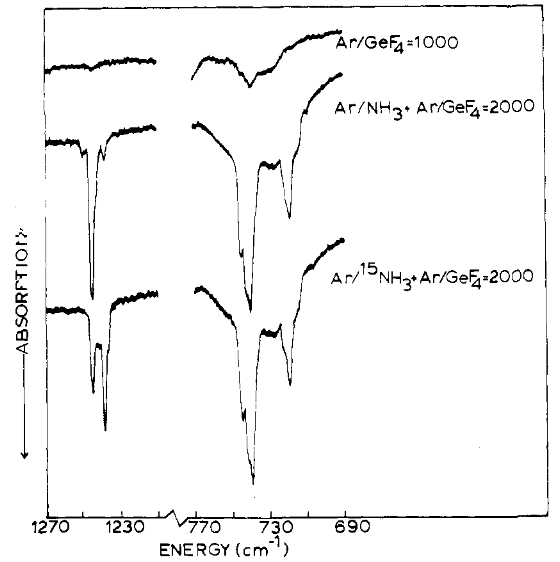

Figure 1. Infrared spectra of the reaction of products from the codeposition of samples of Ar/GeF$_4$ with samples of Ar/NH$_3$ and Ar/^{15}NH$_3$, over selected spectral regions.

intensity ratio to one another. No additional product bands were observed, although a decrease in transmission of the matrix as a whole was noted.

One experiment was conducted with nitrogen as the matrix material and a total dilution of 2000/1/1. Again, a set of three product bands was observed, shifted somewhat from the argon matrix values, at 702, 725, and 1288 cm^{-1}. The upper band was slightly split, but the relative intensities and band shapes matched the argon-matrix counterparts quite well.

GeF$_4$ + ^{15}NH$_3$. These two reactants were investigated in two experiments, each at a dilution of 2000/1/1 total. While the ^{15}NH$_3$ sample was supplied as 95% ^{15}N, exchange did occur with residual ^{14}NH$_3$ in the vacuum line, and the level of isotopic substitution in the matrix was roughly 65% ^{15}N. Consequently, the three product bands observed with the reaction of ^{14}NH$_3$ with GeF$_4$ were present. The two lower energy bands showed no measurable shift with ^{15}N substitution, while the upper band, at 1245 cm^{-1} with ^{14}N, shifted to 1238 cm^{-1}. Since both ^{14}NH$_3$ and ^{15}NH$_3$ were present, this region appeared as a distinct doublet at 1238 and 1245 cm^{-1}, with the expected intensity ratio. Figure 1 shows spectra of the reaction products of GeF$_4$ with NH$_3$ and ^{15}NH$_3$.

GeF$_4$ + CH$_3$NH$_2$. Samples of Ar/CH$_3$NH$_2$ were codeposited with samples of Ar/GeF$_4$, both at 1000/1, in three separate experiments. It was found, similar to previous work from this laboratory,[16] that the CH$_3$NH$_2$ contained some NH$_3$ impurity, which could not be completely removed, due to similarity in boiling points and strong intermolecular hydrogen bonding. Consequently, the product bands at 718, 738, and 1245 cm^{-1} due to the reaction of GeF$_4$ with NH$_3$ were observed in these experiments. In addition, three new product bands were observed in these experiments, presumably due to the reaction of GeF$_4$ with CH$_3$NH$_2$. These bands were located at 697, 712, and 727 cm^{-1} and were relatively sharp with the exception of the band at 727 cm^{-1}. This band was slightly broader and in several experiments appeared split into components at 725 and 728 cm^{-1}. These three bands showed a constant relative intensity in the three experiments, within the uncertainties in measurement of band intensities. Comparable experiments with (CH$_3$)$_2$NH were not undertaken, as previous experiments[16] with this compound have shown a very intense parent band that would obscure the primary spectral region of interest.

GeF$_4$ + (CH$_3$)$_3$N. These two reactants were studied in a total of three experiments, at concentrations of 2000/1/1 and 1000/1/1. In the first two experiments, at the higher dilution, two new product bands were observed, at 700 and 715 cm^{-1}, resembling the product bands observed with both NH$_3$ and CH$_3$NH$_2$ with slight shifts. At the higher concentration, these two bands remained, with constant relative intensities, but the band at 715 cm^{-1} appeared slightly split into two or possibly three components.

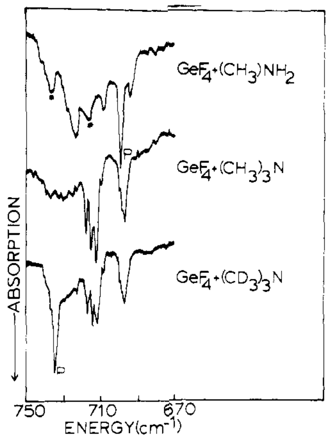

Figure 2. Infrared spectra of the reaction products produced by the codeposition of Ar/GeF$_4$ samples with CH$_3$NH$_2$ (top trace), (CH$_3$)$_3$N (middle trace), and (CD$_3$)$_3$N (lower trace) in the Ge–F stretching region. In the top trace, bands denoted by an asterisk are due to the reaction of GeF$_4$ with NH$_3$ impurity (see text).

GeF$_4$ + (CD$_3$)$_3$N. These two reactants were codeposited in a single experiment at a total dilution of 1000/1/1 to provide comparison to the above results. The two product bands remained nearly unchanged, shifting to 698 and 717 cm^{-1}, while maintaining while an intensity ratio similar to that observed in the experiments with (CH$_3$)$_3$N. No additional product bands were observed in the spectrum. Figure 2 shows spectra of the reaction products of GeF$_4$ with CH$_2$NH$_2$, (CH$_3$)$_3$N, and (CD$_3$)$_3$N.

GeCl$_4$ Reactions. Analogous experiments were conducted in which samples of Ar/GeCl$_4$ were codeposited with amine samples diluted in argon. When GeCl$_4$ was allowed to react with NH$_3$ and the initial reaction products were trapped, two new bands were detected in the low-energy region, at 264 and 344 cm^{-1}. These were observed in several experiments and maintained a constant intensity ratio. In addition a weak, split band was observed near 1210 cm^{-1} in all experiments. The substitution of (CH$_3$)$_3$N for NH$_3$ in these experiments led to nearly identical spectra in the low-energy region and the disappearance of the band near 1210 cm^{-1} in the upper region. The two low-energy bands shifted to 262 and 343 cm^{-1}, respectively. In addition, a sample of Ar/GeCl$_4$ was codeposited with an Ar/(CD$_3$)$_3$N sample in one experiment, with a total concentration of 1000/1/1, and product bands were observed, nearly unshifted, at 262 and 345 cm^{-1}. The infrared spectra of these GeCl$_4$ complexes are displayed in Figure 3.

Room-Temperature Solids. GeF$_4$ was mixed and allowed to react with excess NH$_3$ in a glass sample finger under conditions where the 1/2 adduct is known to form.[10] A white powder formed immediately, and the infrared spectrum of this material in Nujol showed a dominant absorption at 590 cm^{-1}. A similar reaction was carried out between GeF$_4$ and CH$_3$NH$_2$, and a white powder again formed. The spectrum of this solid, in Nujol, showed a similar characteristic intense band near 595 cm^{-1}.

Discussion

Identification of Product Species. The spectra in Figures 1 and 2 show clearly that a reaction does occur when a sample of Ar/GeF$_4$ is codeposited with an amine diluted in argon and that the reaction product is isolated. Similar results were

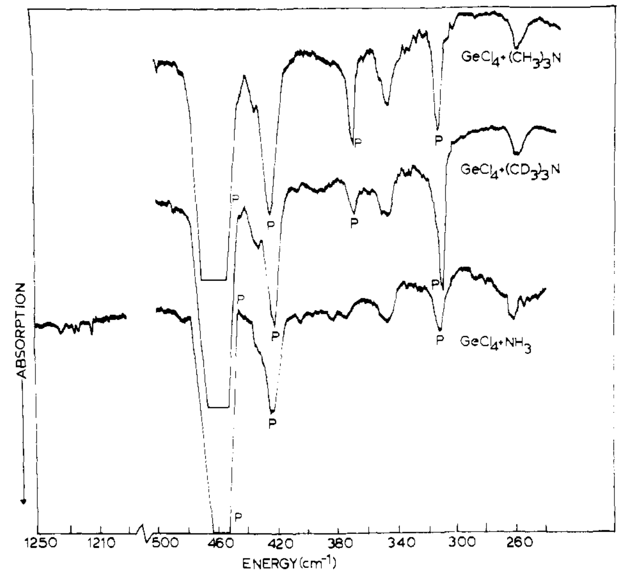

Figure 3. Infrared spectra, over selected spectral regions, of the reaction products of $GeCl_4$ with $(CH_3)_3N$, $(CD_3)_3N$ and NH_3 in argon matrices. Bands labeled P were present in the blank experiment of one of the parent species.

Table I. Infrared Band Positions (cm^{-1}) and Assignments for GeF_4·B Adducts

GeF_4·NH_3	GeF_4·CH_3NH_2	GeF_4·$(CH_3)_3N$	assignt[a]
1245			NH_3 sym def
738	712, 727	715	Ge-F eq str
718	697	700	Ge-F ax str

[a] Assignments assume a C_{3v} structure for the complex.

obtained with nitrogen matrices, the bands shifting only a few wavenumbers, indicating the lack of involvement of the matrix material in the reaction. A number of reaction products might be envisioned for such a system, including the formation of a 1/1 or 1/2 adduct or an elimination reaction to form GeF_3NH_2 + HF. The latter possibility can be ruled out by observing that no HF was detected in the final spectrum as well as by observing that the 1/2 adduct is well-known at room temperature and does not undergo elimination.[10] The 1/2 adducts GeF_4·$2NH_3$ and GeF_4·$2CH_3NH_2$ were synthesized as white powders at room temperature, and the spectra obtained were in good agreement with those obtained earlier[10,11] for 1/2 adducts of GeF_4. The spectra indicate that the Ge–F stretches for the 1/2 adduct should come near 600 cm^{-1}, where the GeF_6^{2-} anion is also known to absorb.[17,18] This region is clear in the current matrix experiments, suggesting that the 1/2 adduct is not formed. Moreover, at the very high dilutions employed here, 1/1/2000, formation of a 1/1 adduct seems to be much more likely. Indeed, if any 1/2 adduct did form, one would still expect to see considerable amounts of the 1/1 complex, as this must serve as the precursor to the 1/2 adduct. Finally the observation of a distinct doublet near 1240 cm^{-1} in the mixed ^{14}N–^{15}N experiment indicates the presence of just one nitrogen atom; if two were present, a triplet would be expected, unless they are totally vibrationally decoupled. All of these agruments support the assignment of the observed product bands to the 1/1 adduct GeF_4·B, for B = NH_3, CH_3NH_2 or $(CH_3)_3N$. It should also be noted that while the few known 1/1 adducts of GeF_4 and nitrogen-containing bases are postulated to be polymeric, the 1/1 adducts formed here must be the isolated 1/1 molecular complexes.

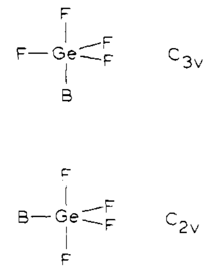

Figure 4. Possible structures for the 1/1 adduct of GeF_4 and an amine base, either C_{2v} or C_{3v} in a trigonal-bipyramidal arrangement.

Band Assignments. For the GeF_4·NH_3 complex, three product bands were observed, near 718, 738 and 1245 cm^{-1}. The former two showed no detectable shift upon substitution of ^{15}N, while the latter band showed a 7-cm^{-1} shift. The former two bands are both in the region associated with Ge–F stretches, shifted somewhat from the triply degenerate Ge–F stretching mode of GeF_4 near 795 cm^{-1}. In view of their nitrogen isotopic behavior and their location, they are readily assigned to two Ge–F stretching modes in the 1/1 adduct. The upper band at 1245 cm^{-1}, with its large ^{15}N shift, is suggestive of a vibration associated with the coordinated NH_3. The most intense mode of both free and coordinated NH_3 is the symmetric deformation, or umbrella mode, which is located at 970 cm^{-1} for free NH_3. The mode shifts to higher energy upon complex formation[19] and was located at 1253 cm^{-1} for the similar SiF_4·NH_3 complex.[5] Consequently, the 1245-cm^{-1} band is assigned to the symmetric deformation mode of the NH_3 group in the 1/1 adduct GeF_4·NH_3. The remaining modes of the coordinated NH_3 group have been shown in previous studies[19] to show very small shifts from free NH_3, and since the matrices in this study always contained a large excess of unreacted NH_3, observation of these modes was not feasible.

Product bands were observed in the experiments employing mono- and trimethylamine at 697, 712, and 727 cm^{-1} for CH_3NH_2 and at 700 and 715 cm^{-1} for $(CH_3)_3N$. In addition, these latter bands showed no shifts when $(CD_3)_3N$ was substituted, suggesting again vibrations of the GeF_4 skelton in the 1/1 adduct. These bands also lie very near the bands observed for the Ge–F stretches of the GeF_4·NH_3 complex and are consequently assigned to Ge–F stretching modes in the respective complexes GeF_4·CH_3NH_2 and GeF_4·$(CH_3)_3N$.

Many additional vibrational modes of the complex are anticipated from the coordinated amine group and may be detected in the matrix spectrum. However, previous workers have shown that these bands do not shift significantly from their positions in the free amine, and their presence is masked by the intense bands due to unreacted parent. In addition, most of the vibrational modes of the base (with the exception of the umbrella mode of NH_3) are not very intense (compared to the Ge–F stretching modes), and with the relatively low yield of product in these experiments, such modes will not be detected.

Structure of the Complex. The structure of the product complex is of some interest as well. The two Ge–F stretches that were observed for the GeF_4·NH_3 complex lie in a region associated with a trigonal-bipyramidal arrangement around the central germanium such as observed for the GeF_5^- anion.[20,21] Certainly, the Ge–F stretching modes do not lie as low as 600 cm^{-1}, the region usually associated with octahedral germanium complexes. Two possible structures might be

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envisioned for a trigonal-bipyramidal structure, either a C_{3v} structure with the NH_3 group axial or a C_{2v} structure with the NH_3 equatorial, as shown in Figure 4. In the former case, three distinct Ge–F stretches are infrared active (one doubly degenerate), although one should be very weak (the symmetric equatorial stretch). In the latter structure, four distinct Ge–F stretching modes are infrared active, and again one should be very weak (the symmetric axial stretch). Hence, for the C_{3v} structure, two Ge–F stretches are likely to be observed, while three are expected for the C_{2v} structure. The observation of two product bands in this region immediately suggests the C_{3v} axial structure. Moreover, this was the structure favored for the analogous $SiF_4{\cdot}NH_3$ complex, on the basis of both number of bands assigned and normal-coordinate calculations.[5] A final bit of evidence comes from the behavior upon substitution of an unsymmetrical amine, $(CH_3)NH_2$. Here, even in an axial configuration, the C_3 axis is no longer preserved, and the doubly degenerate equatorial mode should split into two bands, and three total bands should be detected. This is precisely the case and is in agreement with similar spectra recently obtained for the analogous SiF_4 complexes.[16] Finally, when the C_{3v} base $(CH_3)_3N$ was substituted (with treatment of the methyl groups as point masses), the three lines coalesced back into the two lines expected for a C_{3v} axial configuration. These arguments collectively indicate that the structure of the 1/1 adduct $GeF_4{\cdot}NH_3$ is of C_{3v} symmetry with the NH_3 group in an axial position in a trigonal-bipyramidal arrangement about the central germanium. A discussion as to why such a C_{3v} structure is observed, in disagreement with the "Muetterties rule", is presented in the preceding paper in this series.[16]

Acid/Base Strength Effects. Slight shifts were observed in the Ge–F stretching modes as the adduct base was changed from NH_3 to CH_3NH_2 to $(CH_3)_3N$. The shift, to lower energy, correlates directly with the increase in base strength of the amine as the number of methyl groups increases.[22] It is likely that as the base strength increases, more electron density is donated from the base to the acid, GeF_4. The additional electron density accepted by the GeF_4 skeleton enters an antibonding orbital[23] and should lower the Ge–F stretching frequencies. Since the difference in base strengths, as measured by gas-phase proton affinities, is small, these shifts to lower energies should be small as well, and the shifts observed here of a few wavenumbers are quite reasonable.

A second question concerns the relative acidities of SiF_4 and GeF_4 toward a standard base. The position of the umbrella mode and the magnitude of its shifts from the free NH_3 position have often been used as an empirical measure of adduct strength.[24] This mode was observed at 1253 cm^{-1} for the $SiF_4{\cdot}NH_3$ complex and at 1245 cm^{-1} for the $GeF_4{\cdot}NH_3$ complex, indicating that SiF_4 is a slightly stronger acid than GeF_4. This difference, however, is sufficiently small that very little distinction can, or should, be made concerning the ordering of acidities. Rather, the acidities of GeF_4 and SiF_4 appear equal, in agreement with results obtained by earlier workers.[9,25]

$GeCl_4$ Complexes. Several product bands were also detected when the reaction of $GeCl_4$ with several amine bases was investigated. In the reaction of $GeCl_4$ with NH_3, two product bands were observed in the region below 400 cm^{-1}, along with a weak band near 1210 cm^{-1}. This upper band is readily assigned to the umbrella mode of a coordinated NH_3 group, presumably in a 1/1 adduct with $GeCl_4$. This symmetric deformation mode shows a smaller shift up from free NH_3 at 970 cm^{-1} than did the analogous GeF_4 complex, suggesting that the interaction between $GeCl_4$ and NH_3 is weaker than for the fluoride analogue. This trend, although opposite that for the first-row Lewis acids such as BF_3, has been observed for a number of second- and third-row Lewis acids.[5,26] The lower energy bands, at 264 and 344 cm^{-1}, fall in a region generally associated with Ge–Cl stretches, below the fundamental of $GeCl_4$ near 465 cm^{-1}, and are so assigned. Also, two bands were observed in the $(CH_3)_3N$ and $(CD_3)_3N$ experiments, and these lay very close to the product bands in the NH_3 experiments.

These results are reminiscent of the GeF_4 results, where two germanium–fluorine stretching vibrations were observed. Hence, the assignment of a similar C_{3v} structure to this complex is suggested. It must be noted, however, that these $GeCl_4$ experiments were conducted at higher concentrations, and even so band intensities were quite low. Moreover, the spectra were recorded in a very difficult spectral region, due to interference from atmospheric water. Consequently, conclusions as to the structure of the $GeCl_4{\cdot}B$ complexes must be taken as somewhat less firmly established than for $GeF_4{\cdot}B$. Nonetheless, a trigonal-bipyramidal arrangement with the base in an axial position is the preferred structure.

Conclusions

The codeposition of GeF_4 or $GeCl_4$ with a variety of nitrogen-containing bases has led to the formation and isolation, for the first time, of the 1/1 adducts in inert matrices. For the $GeF_4{\cdot}NH_3$ complex, two Ge–F stretching modes were observed, shifted down from the position of free GeF_4 but above the region associated with octahedral germanium/fluorine complexes. The symmetric deformation mode of the coordinated NH_3, which is definitive evidence of complex formation, was observed at 1245 cm^{-1}, very close to the position observed for the similar $SiF_4{\cdot}NH_3$ complex. This supports earlier work that had concluded that GeF_4 and SiF_4 were quite similar in Lewis acid strength. Substitution of methylamine for NH_3 led to slight shifts in the Ge–F stretching-band positions, in accord with the changes in amine base strength. Several of the room-temperature solid 1/2 adducts were synthesized as well, for the characterization of the octahedral Ge–F stretching region. Finally, complexes of $GeCl_4$ with several bases were observed as well, but yields were lower and less could be concluded about the structure of the complex. Evidence was found, however, to suggest that $GeCl_4$ is a considerably weaker Lewis acid than GeF_4. A variety of studies is suggested by this work, and investigations into Lewis acid/base behavior are continuing in this laboratory.

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Registry No. $GeF_4{\cdot}NH_3$, 80954-22-9; $GeF_4{\cdot}CH_3NH_2$, 80954-23-0; $GeF_4{\cdot}(CH_3)_3N$, 32145-22-5; GeF_4, 7783-58-6; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $(CH_3)_3N$, 75-50-3; $GeCl_4$, 10038-98-9.

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