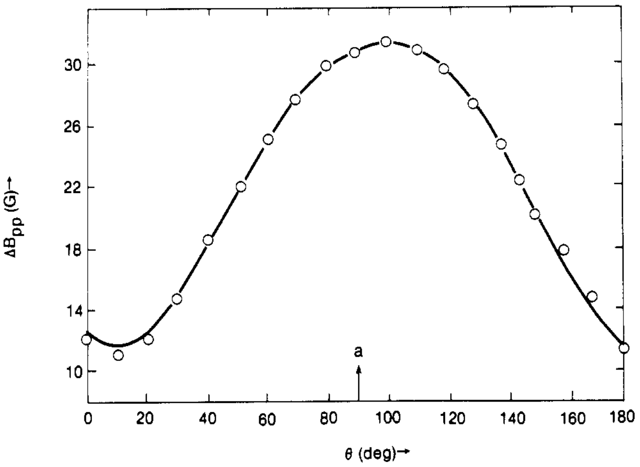

Figure 9. Experimental (solid line) and calculated (○) line widths in the *ac** plane. The calculated line widths are based on Blume–Hubbard $C_{BH}(t)$ with $\tilde{J}$ = 2100 G and with Fourier components $g(0) = 0.64 \times 10^{-3}$, $g(\omega) = 0.061 \times 10^{-3}$ G^{-1}, $f(0) = 2.79 \times 10^{-3}$ G^{-1}, $f(\omega) = 0.145 \times 10^{-3}$ G^{-1}, and $f(2\omega) = 0.006 \times 10^{-3}$ G^{-1} at ω = 9.47 GHz.

model are again given in Table VI.

Both models give almost the same values for nonsecular spin correlation functions. They also compare well with the experimental values. But secular spin correlations are not predicted correctly by these models. In the present system, $g(0)$ is overestimated and $f(0)$ is largely underestimated whereas in $[Cu(NH_3)_4][PtCl_4]$ both $g(0)$ and $f(0)$ are underestimated.[9] The Q-band (ω = 35 GHz) nonsecular Fourier components calculated by using the above models are negligibly small. This is to be anticipated as the Zeeman frequency is much larger than the exchange frequency.

However, one point is worth mentioning. The larger $f(0)$ clearly reflects the one-dimensional behavior as expected from the crystal structure. But, the smaller $g(0)$ is puzzling. The autocorrelation function $C(t)$ is usually normalized at $t = 0$, as in eq 14 and 17 for the two models. Now, the conditions $C(t) \leq 1$ lead to $f(0) < g(0)$ quite independently of any model, including those with diffusive tails. The opposite experimental conclusion could be due to (1) failure of the decoupling approximations (we are thankful to the reviewer for pointing this out), (2) not separating into intrachain and interchain dipolar second moments, or (3) the use, most probably, of six or seven equations for five unknowns. The observation of a Lorentzian line shape indicates sufficient interchain interaction, if not enough to mask the presence of two separate resonances for the two sites. This point may support the second reason cited above.

The exchange values obtained from these models ($J \simeq 1500$ G for the B–H model and $J \simeq 1200$ G for the A–W model) also agree reasonably well with that obtained from susceptibility measurements ($J \simeq 1250$ G). The calculated line width from the B–H model is compared with the experimental line widths in Figure 9 for the *ac** plane where both the sites are magnetically equivalent. The rather large value of $g(0)$ and $f(0)$ are surprising and may suggest one-dimensional exchange through $[NMP]^+$ ions between successive $[Cu(mnt)_2]^{2-}$ anions.

Conclusion

The salt $[(NMP)_2][Cu(mnt)_2]$ crystallizes in a mixed stack with a donor–acceptor sequence of the type DAD–DAD along the *a* axis. Since each anion is sandwiched between two cations, the exchange interaction within a chain is weak ($J \simeq 1200$ G) in spite of it having described as a linear Heisenberg chain. In addition, the prediction of the correct order to the exchange coupling through EPR line width in line with the susceptibility prediction has been found to be fairly successful by using the existing theories for weak exchange.

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Registry No. $[(NMP)_2][Cu(mnt)_2]$, 92241-56-0.

Supplementary Material Available: A listing of the structure factor amplitudes for $[(NMP)_2][Cu(mnt)_2]$ (9 pages). Ordering information is given on any current masthead page.

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Infrared Matrix Isolation Study of Intermediate Molecular Complexes: Complexes of GeF_4 with Oxygen-Containing Bases

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The codeposition of GeF_4 with a variety of oxygen-containing bases, through either the twin-jet or single-jet mode into argon matrices, has led to the formation of intermediate 1:1 complexes. The species of $H_2O{\cdot}GeF_4$, $CH_3(H)O{\cdot}GeF_4$, $(CH_3)_2O{\cdot}GeF_4$, $CD_2O{\cdot}GeF_4$, and $(CH_3)_2CO{\cdot}GeF_4$ were each identified and characterized spectroscopically. The infrared spectra indicate that all are bound through the oxygen to the germanium center. The observed spectral features could be divided into two categories, corresponding to perturbed acid and base subunit vibrations. These indicate that the structure is near a trigonal bipyramid, as was observed for the corresponding ammonia complex, although the lower symmetry of the base precludes a C_3 axis in the complex. The position of the antisymmetric Ge–F stretching mode of the "near-equatorial" fluorines was shown to correlate with the proton affinity of the base, as anticipated and as observed previously for the analogous SiF_4 complexes. In addition, with use of the degree of perturbation of the base subunit as a measure, the spectra indicate that GeF_4 forms substantially stronger complexes with these bases than does SiF_4.

Introduction

Lewis acid–base adducts and the nature of the coordinate bond have been of interest to chemists for a number of years, and many examples are known, particularly for strong acids and bases.[1] Within the past few years, the matrix isolation technique has been applied successfully to study less stable complexes, either those that are only weakly bound or those

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(1) Jensen, W. B. "The Lewis Acid-Base Concepts: An Overview"; Wiley–Interscience: New York, 1980, and references therein.

which are intermediates on the route to a more stable product.[2-4] Most recently, a number of 1:1 complexes of SiF_4 with oxygen-containing bases[5] were isolated and characterized in argon matrices and spectral features correlated with the intrinsic basicity (proton affinity) of the base. GeF_4 parallels, in many respects, the chemistry of SiF_4 and is thought to be a slightly stronger Lewis acid.[6] Many 1:2 complexes of GeF_4 with nitrogen-containing bases are known,[7-10] as well as a few 1:2 complexes with oxygen-containing bases.[11] However, very little has been reported to date on the likely intermediate 1:1 complexes of GeF_4, and nothing concerning 1:1 complexes with oxygen bases. Consequently, a study was undertaken to isolate and characterize a variety of 1:1 adducts of GeF_4 with small oxygen-containing bases in inert matrices, to provide further information on the Ge–O coordinate band, as well as comparison to the recently identified silicon analogues.

Experimental Section

The matrix isolation experiments performed in this study were carried out on an apparatus that has been described previously.[12] The majority of the spectra were recorded on a Beckman IR 12 infrared spectrophotometer, over the region 4000–200 cm^{-1}. More recent spectra were recorded on a Perkin-Elmer 983 infrared spectrometer with data station for spectral storage and handling. Resolution in either case was approximately 1 cm^{-1} at 1000 cm^{-1} and slightly greater in other spectral regions. H_2O, CH_3OH, and $(CH_3)_2CO$ were introduced into the system via a glass finger and subjected to two freeze–thaw cycles prior to sample preparation. $(CH_3)_2O$, $(CD_3)_2O$ (Merck, 98%), and GeF_4 (Ozark-Mahoning) were introduced into the vacuum line from lecture bottles and also subjected to at least one freeze–thaw cycle. CD_2O (Merck, 98% D) was sublimed into the vacuum system and deposition line from solid deuterated paraformaldehyde, after heating to approximately 65 °C. The matrix gases, argon and nitrogen, were used without further purification.

The majority of the matrix experiments were performed with use of twin-jet deposition, in which GeF_4 was diluted with the matrix gas in one vacuum line and the oxygen-containing base with the matrix gas in a separate vacuum line. These two samples mixed just briefly during the deposition process prior to condensation and isolation. For comparison, a few single-jet experiments were conducted, in which the base and GeF_4 were premixed in a single vacuum line and diluted with inert gas prior to deposition. Deposition was generally conducted for 20–24 h, at 2 mmol/h from each vacuum line employed, before final survey and high-resolution scans were recorded.

Results

Prior to the investigation of the reaction products of GeF_4 with oxygen-containing bases in inert matrices, blank experiments were conducted on all of the Lewis bases employed in this study, at representative concentrations. The spectra were in good agreement with literature spectra,[13-15] where available, as well as with spectra recorded previously in this laboratory.[5,16]

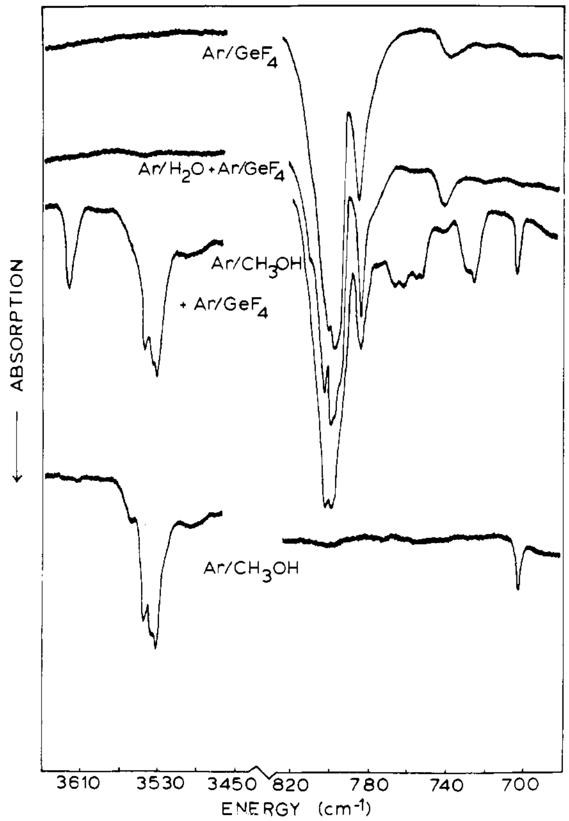

Figure 1. Infrared spectra of the products of codeposition of GeF_4 with H_2O and CH_3OH in argon matrices. The top trace shows the spectrum of a sample of $Ar/GeF_4 = 500$, with a slight amount of H_2O present as an impurity. The second trace shows a similar sample of Ar/GeF_4, codeposited with a sample of $Ar/H_2O = 2000$. The third trace shows the spectra obtained after codeposition of $Ar/GeF_4 = 500$ with a sample $Ar/CH_3OH = 500$, contrasted with the bottom trace, a blank experiment of $Ar/CH_3OH = 500$.

Several blank experiments of GeF_4 in both argon and nitrogen were recorded; however, water is always present as a minor impurity in these systems and these experiments effectively represented reaction runs with a very low level of H_2O. The most intense spectral feature in these experiments was the triply degenerate Ge–F stretching mode of GeF_4 near 800 cm^{-1}, which was split by the five isotopes of Ge that occur with a detectable percentage in natural abundance (^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge).[17]

GeF_4 + H_2O. In the above blank experiment, H_2O was present as an impurity at an estimated dilution of 10 000/1; in addition to the triply degenerate parent mode of GeF_4 near 800 cm^{-1}, two bands of moderate intensity (absorbance $\simeq$0.2) were observed, at 779 and 737 cm^{-1}, as shown in the top two traces of Figure 1. When a sample of $Ar/GeF_4 = 500$ was codeposited with a sample of $Ar/H_2O = 1000$ in a twin-jet experiment, the two bands mentioned above grew in intensity while maintaining a constant intensity ratio. Certainly, these new bands grew relative to the parent GeF_4 bands when H_2O was added. However, the vibrational regions of H_2O, near 1600 and 3700 cm^{-1}, were obscured by the parent H_2O absorption, and no new product bands were noted. Several additional experiments were conducted in which the concentrations of the Ar/H_2O and Ar/GeF_4 samples were varied, from 200/1 to 2000/1. In all of these experiments, the bands at 779 and 737 cm^{-1} showed a constant relative intensity ratio and grew whenever either the concentration of GeF_4 or the

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concentration of H_2O was increased.

Similar experiments were conducted in nitrogen matrices, at a GeF_4 dilution of 500/1, and varying H_2O levels. The parent GeF_4 absorption near 800 cm^{-1} shifted just slightly to lower energy and showed partially resolved Ge isotopic splitting. In addition, two moderately intense product bands were noted at 764 and 737 cm^{-1}, which matched the shape and intensity of the features observed in argon matrices. In addition, a new weak absorption was noted in these nitrogen matrix experiments at 781 cm^{-1}. Attempts were made to clarify the nature of this new absorption, by employing mixed matrices of argon and nitrogen. However, as soon as the level of N_2 decreased substantially and the level of argon was increased, the intensity of this band droppped effectively to zero.

GeF_4 + CH_3OH. These two reactants were codeposited into argon matrices under a variety of conditions and range of concentrations. When concentrations of 500/1 for each reactant were employed, two new absorptions were noted in the Ge–F stretching region, at 760 and 722 cm^{-1}. In addition, the product bands noted above for the GeF_4/H_2O system were weakly observed due to impurity water in the matrix. Two additional product bands were noted in the spectrum with considerable intensity, at 1002 and 3624 cm^{-1}. These reactants were also investigated at higher concentrations, and the same set of product bands were noted, with the same relative intensities, as shown in the lower traces of Figure 1. No additional product bands were detected at these higher concentrations.

To possibly improve product yield, one experiment was conducted in which GeF_4 and CH_3OH were premixed in a single vacuum line and diluted with argon to a level of 1000/1/1. The infrared spectrum of this sample showed only a weak GeF_4 parent absorption at 800 cm^{-1}, no absorptions due to parent CH_3OH, and no absorptions due to product species. This result suggests that reaction occurred in the sample container prior to deposition, leading to nonvolatile products; as a consequence, no further single-jet experiments were conducted on this system.

GeF_4 + $(CH_3)_2O$. The matrix reaction of GeF_4 with $(CH_3)_2O$ was also studied by both single- and twin-jet deposition techniques. When these two reactants, each at a dilution of 500/1 in argon, were deposited from separate vacuum lines, two new absorptions were noted in the Ge–F stretching region, at 759 and 718 cm^{-1}. These two bands were of moderate intensity, were somewhat broad, showed some indication of Ge isotopic splitting, and were comparable to the product bands in the CH_3OH and H_2O experiments. In addition, product absorptions were noted at 892 and 1047 cm^{-1}. When these two reactants were codeposited in a similar twin-jet experiment with concentrations of 250/1 each in argon, the same set of bands was observed, with similar intensity ratios, and no new product bands were noted in the spectrum.

GeF_4 and $(CH_3)_2O$ were also deposited in a single-jet experiment, after premixing the reactants with argon in one vacuum line. In this case, a room-temperature reaction did not occur; instead strong parent absorptions were noted for both parents, along with the set of product bands noted above. For a total dilution of 1000/1/1, the yield of product was not significantly increased when a single-jet mode was employed, relative to the twin-jet mode of deposition.

GeF_4 + $(CD_3)_2O$. Two twin-jet experiments were conducted with these two reactants, employing sample concentrations of 500/1 each in argon. In the Ge–F stretching region, two strong absorptions were noted at 759 and 717 cm^{-1}, virtually unshifted from the bands observed when GeF_4 and $(CH_3)_2O$ were studied. In addition, the product absorptions at 892 and 1047 cm^{-1} in the above experiments were no longer present, and a new absorption was observed at 1092 cm^{-1}. These experiments were conducted in a single-jet mode as well, and the results obtained were virtually identical with those of the twin-jet experiments, and for comparable concentrations, no increase in yield of product was noted. Infrared spectra of the codeposition products of GeF_4 with $(CH_3)_2O$ and $(CD_3)_2O$ are shown in Figure 2.

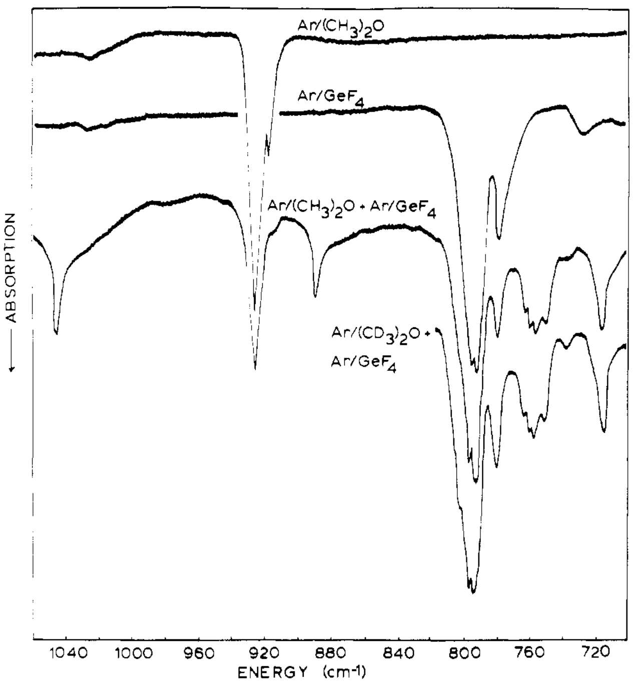

Figure 2. Infrared spectra of the reaction products formed through the codeposition of GeF_4 and $(CH_3)_2O$ and $(CD_3)_2O$ in argon matrices. The top trace shows a sample of $(CH_3)_2O$ in argon, while the second trace shows a blank experiment of Ar/GeF_4 = 500. The third trace shows the reaction products of $Ar/(CH_3)_2O$ with Ar/GeF_4, which is contrasted in the bottom trace with the spectrum of a sample of Ar/GeF_4 codeposited with $Ar/(CD_3)_2O$, in the Ge–F stretching region.

GeF_4 + $(CH_3)_2CO$. Acetone was codeposited in a twin-jet experiment with GeF_4 in argon on several occasions; when the individual concentrations were 500/1 each, two moderately intense product bands were detected in the Ge–F stretching region, at 747 and 715 cm^{-1}, in addition to the weak absorptions due to reaction of GeF_4 with H_2O (see above). Elsewhere in the spectrum, a very intense new absorption was noted in 1683 cm^{-1}, some 40 cm^{-1} below the carbonyl stretching mode of parent acetone, as shown in Figure 3. As in the previous experiments, these three product bands maintained a roughly constant intensity ratio when the initial reactant concentrations were altered. When a nitrogen matrix was employed, at a dilution of 500/1 each in a twin-jet experiment, three comparable product bands were observed, at 710, 745, and 1671 cm^{-1}. However, the yield of product appeared to decrease considerably in N_2 relative to argon, a conclusion that has been noted in a variety of similar studies.

GeF_4 + CD_2O. These two reactants were codeposited into an argon matrix, after CD_2O was sublimed from deuterated paraformaldehyde, with Ar/GeF_4 = 500. Two new weak product bands were detected, at 768 and 750 cm^{-1}, with optical densities of roughly 0.10. The higher energy band showed distinct Ge isotopic splitting, while the lower energy band was sufficiently broad that such isotopic resolution was not feasible. No additional product bands were detected in the spectrum.

Table I summarizes the product band positions reported above.

Discussion

Product Identification. The codeposition, from separate vacuum lines, of GeF_4 with a variety of oxygen-containing

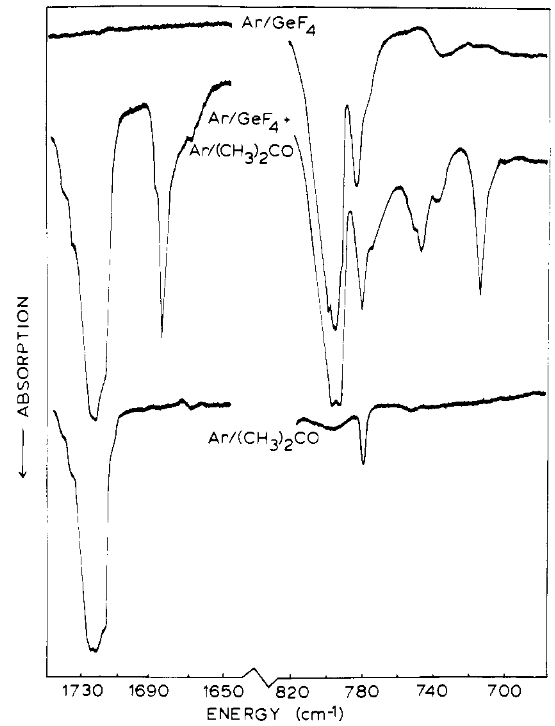

Figure 3. Infrared spectra of the $Ar/GeF_4/(CH_3)_2CO$ system, showing blank experiments of Ar/GeF_4 (top trace) and $Ar/(CH_3)_2CO$ (bottom trace) compared to the spectrum of a codeposited reaction mixture of GeF_4 and $(CH_3)_2CO$ in argon (twin jet).

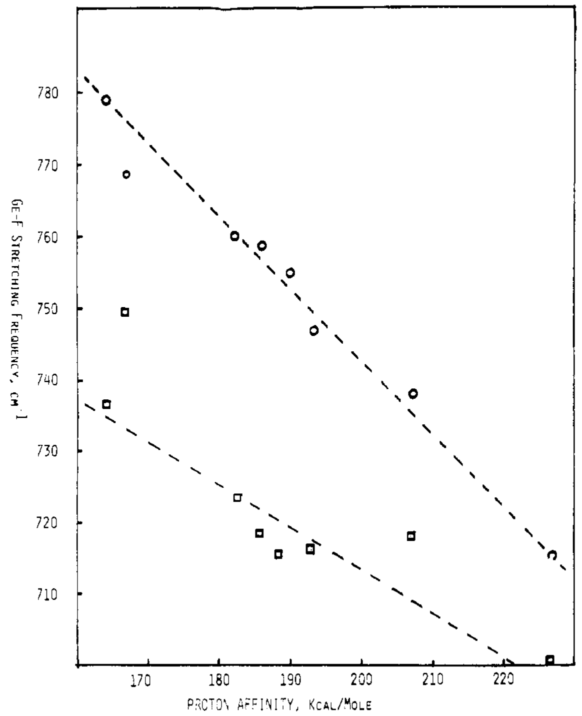

Figure 4. Plot of the axial (squares) and antisymmetric equatorial (circles) Ge–F stretching modes vs. the proton affinity of the coordinated base for a number of 1:1 complexes $GeF_4 \cdot B$, using the data from Table I.

Table I. Band Positions and Assignments for Argon Matrix Isolated 1:1 Complexes of GeF_4 with Oxygen-Containing Bases, Correlated with Base Proton Affinity

base	$\nu_{Ge-F(eq)}$,[a] cm^{-1}	$\nu_{Ge-F(ax)}$,[a] cm^{-1}	ν_B,[e] cm^{-1}	PA,[b] kcal/mol	ref
H_2O	779	737		164	*d*
CD_2O	768	750		166	*d*
CH_3OH	760	722	1002, 3624[c]	182	*d*
$(CH_3)_2O$	759	718	892, 1047[c]	186	*d*
$(CH_2)_3O$	755	714		190	23
$(CH_3)_2CO$	747	715	1683[c]	193	*d*
NH_3	738	718	1245[c]	207	16
$(CH_3)_3N$	715	700		227	16
F^-	730	696		373	24

[a] Approximate description; see text. [b] Proton affinities of the base, from ref 21. [c] See text for assignments. [d] This work. [e] Vibrational mode(s) of the complexed base.

bases diluted in argon gave rise to a number of new infrared absorptions that could not be attributed to either isolated parent species. Similar results were obtained when nitrogen matrices were employed, although product yields were somewhat less, as has been observed previously, and one additional band was noted, which will be discussed below. The most intense absorptions were generally in the region between 700 and 780 cm^{-1}, although product bands in other spectral regions were also noted. These results indicate formation of one or more product species, which is consistent with results obtained previously on similar systems. However, all of the product bands in a given system maintained a constant intensity ratio with respect to one another over a range of concentrations, generally from 200/1 to 1000/1. This suggests that only a single product is formed under these conditions, again in agreement with earlier work.[2,5]

Chemical reaction, probably leading to HF elimination and germanium oxide formation, is one possible mechanism for the formation of the product species. However, no HF was noted in the final spectrum, and while a variety of intermediate germanium oxides might be formed, no bands were noted in the Ge–O stretching region. In addition, the product bands in the 700–780-cm^{-1} region showed only slight changes (although in a systematic fashion, as will be discussed below) with the different bases employed. In addition, the product bands noted frequently in other spectral regions all fell near absorptions of the parent base. These observations suggest the acid (GeF_4) and base moieties are only slightly perturbed in the product species, rather than completely rearranged, as would be anticipated for a distinct chemical reaction. Hence, the spectra all indicate that complex formation has occurred, in agreement with the known chemistry of GeF_4.[6]

The only known complexes of GeF_4 with oxygen-containing bases to date are 2:1 complexes, of the form $GeF_4 \cdot 2B$, and only a few of these complexes are known, due to relatively low stability at room temperature.[11] The product observed here might be either an intermediate 1:1 complex or a 2:1 complex. However, it is difficult to envision how a 2:1 complex might be formed without an intermediate 1:1 complex. In addition, the few known 2:1 complexes all exhibit intense Ge–F stretching vibrations near 600 cm^{-1}, while the recently reported[16,24] five-coordinate GeF_4 complexes GeF_5^- and $GeF_4 \cdot NH_3$ show Ge–F stretching modes in the range 700–750 cm^{-1}, near the bands observed in the present study. Finally, all of the previous matrix isolation studies[2,3,5,16] of SiF_4 and GeF_4 complexes have shown that there is insufficient time during the twin-jet deposition process to form the 2:1 complex, until all of the matrix material is removed, and the pure reagents are being deposited. Even then, a mixture of 1:1 and 2:1 complexes is formed. All of these points, together, strongly support the identification of the product species formed in this study as the 1:1 complexes between GeF_4 and the oxygen-containing bases employed.

This conclusion represents the first evidence for the existence and stability of 1:1 complexes of GeF_4 with oxygen donors and suggests their possible intermediacy in chemical reactions of GeF_4. It is interesting to compare the results of the single- vs. twin-jet codeposition of GeF_4 with $(CH_3)_2O$ in argon; the yield of molecular complex was found to be nearly identical with the two different modes of deposition, suggesting that the gas-phase complex is not present in equilibrium at room temperature to any measurable degree. Instead, complex formation appears to occur on the surface of the matrix, where sufficient thermal energy has been removed from the reactants to stabilize the product complex. By comparison, the codeposition of CH_3OH with GeF_4 in single- and twin-jet modes led to very different results. In the twin-jet mode, product bands due to a molecular complex were readily identified, while in the single-jet mode, no product species were noted, and very little of one reactant (GeF_4) was present in the matrix, indicating that a reaction occurred in the gas phase in the sample can prior to deposition. The acidic hydrogen on CH_3OH must be sufficiently reactive at room temperature to give rise to a chemical reaction, while at low temperatures complex formation occurs and the complex is isolated before further reaction can occur.

Band Assignments. The product bands observed here can, in each case, be divided into two sets, the first of which appeared between 700 and 800 cm^{-1} and the second fell near certain of the vibrational modes of the base. The former bands were near, and on the low-energy side of, the triply degenerate Ge–F stretching mode[18] of parent GeF_4, in a region generally assigned to Ge–F stretches of five-coordinate germanium complexes. In addition, in several instances (see, for example, Figure 2) these bands showed partial germanium isotope structure, indicating assignment to a vibrational mode involving the central germanium atom. Finally, when the base subunit was deuterated ($(CD_3)_2O$), these bands showed less than 1-cm^{-1} shift, suggesting also a mode of the acid subunit. Hence, these bands (typified by the bands at 759 and 718 cm^{-1} for $(CH_3)_2O{\cdot}GeF_4$) are best assigned to Ge–F stretching modes of the GeF_4 subunit in the 1:1 complex.

The observation, generally, of two such bands for a given base supports a lowering of symmetry of the GeF_4 unit, from T_d to at least C_{3v} or lower. In the strictest sense, the symmetry of the acid subunit can be no higher than C_s due to the relatively low symmetry of the base.[18] However, if the coupling between the subunits is weak, the splitting of the E mode in C_{3v} into an A′ and A″ mode in C_s symmetry might not be observed. The Ge–F stretching mode of the axial fluorine in a nearly trigonal-bipyramidal structure should be quite intense, at slightly lower energies, while the symmetric equatorial stretching mode (A_1 symmetry in C_{3v} or A′ in C_s symmetry) should be at substantially lower energy and be very low in intensity. This mode has escaped detection in the previous study of similar complexes[16] and would likely do so here as well.

Two Ge–F stretching modes were observed in this region for the C_{3v} complex $GeF_4{\cdot}NH_3$, for which a trigonal-bipyramidal structure was deduced, with the NH_3 ligand in an axial position.[16] While such a structure is not (formally) possible here, these bands and their assignment may suggest tentative assignments for the bands observed in the present study. The higher energy band, by this analogy, is assigned to the antisymmetric equatorial Ge–F stretching mode of a nearly trigonal-bipyramidal complex (E symmetry in C_{3v} or A′ + A″ symmetry in C_s symmetry). The lower energy band is assigned to the stretching mode of the axial fluorine trans, or nearly so, to the coordinated base. In view of the lack of a complete spectrum and normal-coordinate calculation, these assignments must be taken as tentative but do fit with previous spectra (see also discussion of trends, below).

For three of the bases employed, additional infrared absorptions were noted near bands of the parent base. For $(CH_3)_2O$, these modes were located at 892 and 1047 cm^{-1}, while for CH_3OH, bands were noted at 1002 and 3264 cm^{-1}, and for $(CH_3)_2CO$, one band was detected at 1683 cm^{-1}. One would anticipate that all of the vibrations of the base subunit in a molecular complex would be perturbed by complex formation and shifted relative to those of the parent. In practice, however, only a few particularly sensitive modes have been observed to shift, usually those in closest proximity to the site of coordination (in this case, the oxygen atom). For the $(CH_3)_2O{\cdot}GeF_4$ complex, the bands at 892 and 1047 cm^{-1} are assigned to the symmetric and antisymmetric C–O–C stretching modes, shifted down from the parent positions[14] at 925 and 1098 cm^{-1}; these are precisely the vibrations anticipated to be affected most by coordination. For the CH_3OH complex, the product bands are assigned to the C–O stretch (1002 cm^{-1}) and the O–H stretch (3624 cm^{-1}), shifted from the parent positions of 1034 and 3673 cm^{-1}; again these are the two bonds closest to the coordination site and most sensitive to complexation.[13] Finally, in the acetone complex, $(CH_3)_2CO{\cdot}GeF_4$, only a single vibrational mode of the perturbed base was noted, at 1683 cm^{-1}, which certainly corresponds to the carbonyl stretching mode of the complexed base subunit. Apparently, the remaining modes of the base subunit in all of these complexes are not perturbed sufficiently to shift the product absorption a resolvable distance away from the intense parent bands.

One final absorption, observed only in the nitrogen matrix experiments, remains unassigned. This band, at 780 cm^{-1}, was observed in the GeF_4/N_2 blank experiment, the GeF_4/N_2 + H_2O/N_2 experiment, and the GeF_4/N_2 + $(CH_3)_2CO/N_2$ experiments. The intensity of this band remained roughly constant in all of these experiments and did not shift as the base was changed, nor was there an argon matrix counterpart. In addition, the intensity of this band decreased when mixed Ar/N_2 matrices were employed, and the nitrogen level was decreased. Moreover, the shift of this band from the parent GeF_4 position was the smallest shift observed in any system to date, suggesting a very weak interaction is responsible. In light of this, a tentative assignment to a complex of GeF_4 with N_2 can be made, similar to a number of dinitrogen complexes observed in recent years for transition metals.[19,20] With a very weak interaction, the N–N stretching mode is not activated, and consequently very little can be deduced concerning the nature of the complex. A second possible assignment would be to a 2:1 complex $GeF_4{\cdot}2N_2$, yielding an octahedral complex. If the two N_2 units were then trans to one another, the resulting D_{4h} complex would have only one infrared-active Ge–F stretching mode, in agreement with the observed spectrum. The spectra certainly do not allow for discrimination between these two possibilities. Nonetheless, the tentative observation of this complex is an interesting addition to the molecular complexes characterized here.

Chemical Bonding and Trends. In the previous studies of the complexes of SiF_4 with nitrogen and oxygen-containing bases, a correlation was made between the location of the most intense Si–F stretching mode (antisymmetric equatorial or near-equatorial stretch) and the intrinsic basicity of the base, as measured by gas-phase proton affinity.[21] A similar correlation can be made for the GeF_4 complexes with use of the data in Table I. As anticipated, this correlation is monotonic and nearly linear, suggesting a disruption of $p\pi$–$d\pi$ bonding between the filled p orbitals on fluorine and the empty d orbitals of germanium. A similar correlation can be made

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employing the positions of the second Ge–F stretching mode observed here (axial stretch), and again nearly linear behavior is observed, as shown in Figure 4.

Earlier workers[6] suggested the GeF_4 would form more strongly bound complexes with electron donors than SiF_4, as a consequence of the larger, more diffuse d orbitals on Ge as compared to those on Si, and consequently reduced $p\pi$–$d\pi$ bonding. While the present study does not provide a mechanism for the quantitative determination of ΔH values, some comparisons can be made. The degree of perturbation of the coordinated base qualitatively should measure the strength of interaction. For dimethyl ether complexes of SiF_4 and GeF_4, the symmetric C–O–C stretching mode shifted only 7 cm^{-1} in the SiF_4 complex, compared to 33 cm^{-1} for the GeF_4 complex. For comparison, in the quite strongly bound complex $BBr_3{\cdot}O(CH_3)_2$ a shift of 40 cm^{-1} was observed.[22] This, alone, suggests a substantially stronger interaction with GeF_4 than SiF_4. A second comparison can be made with the methanol complexes of each acid; for the SiF_4 complex no vibrational modes of the perturbed base were observed. This was rationalized in terms of a strength of interaction in $SiF_4{\cdot}CH_3OH$ that was comparable to that of $(CH_3OH)_2$, which is also known to be present. For the $GeF_4{\cdot}CH_3OH$ complex, the perturbed C–O and O–H stretching modes were both observed and showed shifts substantially greater than dimeric methanol. Finally, no perturbed carbonyl stretching mode was noted for the acetone complex[23] of SiF_4, while a shift of more than 40 cm^{-1} was noted for the $GeF_4{\cdot}(CH_3)_2CO$ complex. All of these data, together, indicate that GeF_4 does form substantially stronger complexes with a variety of electron donors than does SiF_4.

As noted above, the spectra do not allow a definitive determination of the structure of the complex, as was obtained for the $GeF_4{\cdot}NH_3$ complex. Nonetheless, the similarity of the spectra of the complexes reported here to that of the $GeF_4{\cdot}NH_3$ complex suggests a structure that is quite similar, particularly for acetone and the better electron donors. In any event, the sharpness of the vibrational modes of the perturbed bases suggests a well-defined specific interaction; one would anticipate similar sharpness for the Ge–F stretching modes were it not for the broadening due to the five naturally abundant germanium isotopes. Finally, the spectra and results presented here add to the rapidly growing body of knowledge concerning molecular complexes and perhaps will stimulate further experimental and theoretical work in this field.

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Resonance Raman Spectra of High Oxidation State Iron Porphyrin Dimers

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Resonance Raman spectra are reported and discussed for a series of single-atom-bridged iron porphyrin dimers, including $(FeTPP)_2C$ and $[(FeTPP)_2N]ClO_4$ (where TPP = 5,10,15,20-tetraphenylporphyrinato), with the use of B-band excitation (4067 Å). The symmetric Fe–X–Fe stretching frequency has been identified by using ^{54}Fe substitution. This band is at 440 and 465 cm^{-1}, respectively, for $(FeTPP)_2C$ and $[(FeTPP)_2N]ClO_4$ in methylene chloride. The Fe–X stretching force constants are estimated to be 4.62 and 5.42 mdyn/Å, respectively, with a stretch–stretch interaction constant of 1.75 mdyn/Å. The large size of these constants indicates substantial π bonding between the iron and the bridging carbon or nitrogen atoms. Using Badger's rule, we estimate that the Fe–N bond length in $(FeTPP)_2N^+$ is 0.05 Å shorter than that for Fe–C in $(FeTPP)_2C$. The core-size marker bands for these two complexes (1564 and 1568 cm^{-1}, respectively) indicate an expansion of 0.015 Å for the former, reflecting the increased nonbonding interaction caused by the shortened bond distances. The porphyrin C–N breathing mode increases for $(FeTPP)_2N^+$ compared to $(FeTPP)_2C$ (1370 vs. 1365 cm^{-1}); this may reflect increased π donation from the bridging carbon to the iron atom. Coordination of pyridine lowers the frequencies associated with the Fe–X–Fe stretch to 424 and 445 cm^{-1}, respectively, and decreases the Fe–X force constants. Pyridine coordination also lowers the core-size marker frequencies (by 8 and 2 cm^{-1} for $(FeTPP)_2$ and $[(FeTPP)_2N]ClO_4$, respectively), presumably as a result of nonbonding interactions between the pyridine and the porphyrin. The C–N breathing frequency of the porphyrin is also lowered (4 and 3 cm^{-1}, respectively), as expected from the decreased effective charge on the iron atom. Changes also occur in the resonant enhancement patterns and are discussed in terms of the electronic structure of these complexes.

Introduction

Iron porphyrin dimers bridged by oxygen, nitrogen, or carbon atoms have attracted recent attention from both experimental[1-8] and theoretical[9] perspectives. The common structural motif shared by these complexes is nearly parallel porphyrin rings connected by a nearly linear Fe–X–Fe bridge. The electron count is easily varied, however, which allows one to observe the effect of electronic structure on a variety of

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