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Matrix Isolation Spectroscopic Study of the 1/1 Complexes of Trimethylgallium with Group VI Alkyls

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The 1/1 molecular adducts of trimethylgallium with group VI dimethyl bases $(CH_3)_2X$ (X = O, S, Se) have been isolated and spectroscopically characterized for the first time in argon matrices. Perturbed vibrational modes of a number of the acid and base subunits were observed. Removal of degeneracy of the E modes of $(CH_3)_3Ga$ and activation of the GaC_3 stretching mode indicate a reduction in symmetry for the complex. The magnitudes of the shifts of the C–O–C stretching modes of $(CH_3)_2O$ were compared to those of previously studied complexes of dimethyl ether and used to qualitatively determine an order of acidity for a range of Lewis acids, including $(CH_3)_3Ga$.

Introduction

Trimethylgallium is a very important precursor in the metal organic chemical vapor deposition (MOCVD) of gallium-containing semiconductor materials. These thin films have proven to be very useful and versatile in the microelectronics industry.[1–4] The Lewis acidity of $(CH_3)_3Ga$ is well-known[5] and suggests that adduct formation with electron donors may be the first step in the reaction sequence leading to thin-film formation.[6] Adduct formation may or may not be advantageous in MOCVD, depending on the properties of the adduct, including volatility.[7–12] As a result, there is a need to more fully characterize adducts of $(CH_3)_3Ga$. In the 1950's, Coates and co-workers[13,14] identified a number of adducts of trimethylgallium with group VI bases, using only vapor pressure changes upon mixing to indicate complex formation. Very little further work has been carried out on these species, and no spectroscopic or structural data are currently available.

The matrix isolation technique[15,16] was developed for the study of unstable chemical intermediates and has been applied on a number of occasions to the study of weakly bound molecular complexes. Recently, complexes of $(CH_3)_3Ga$ and $(CH_3)_3In$ with group V hydrides were isolated and characterized for the first time in this laboratory.[17–19] Infrared spectral data provided insights into the structure of and bonding in these complexes. Because of the importance of $(CH_3)_3Ga$ and its complexes to MOCVD, a study was undertaken to isolate and spectroscopically characterize adducts of $(CH_3)_3Ga$ with $(CH_3)_2X$, (X = O, S, Se).

Experimental Section

The matrix isolation equipment used in this study has been described elsewhere.[20,21] $(CH_3)_3Ga$ (Morton International), $(CH_3)_2O$ (Matheson), and $(CD_3)_2O$ (Merck) were introduced into the vacuum line from lecture bottles and purified by freeze–pump–thaw cycles at 77 K. $(CH_3)_2S$ and $(CH_3)_2Se$ (both Aldrich) were introduced as the vapor above the room-temperature liquid and also purified by freeze–pump–thaw cycles. The reagents were then diluted with argon to the desired M/R (argon/reactant) ratio. For $Ar/(CH_3)_3Ga$, M/R ranged from 500/1 to 1000/1, while for the group VI compounds, M/R ranged from 500/1 to 500/3.

Samples were codeposited from separate manifolds via the merged jet mode onto a CsI cold window held between 14 and 16 K at a flow rate of approximately 2 mmol/h from each manifold. Final spectra were recorded after 20–24 h of deposition on a Mattson Cygnus Fourier transform infrared spectrometer at 1-cm^{-1} resolution over the range 400–4000 cm^{-1}.

Results

Prior to any codeposition experiments, blank experiments were conducted on each of the parent reagents at one or more dilutions in argon. In each case, the resultant spectra were in good agreement with literature spectra[22–24] and spectra previously recorded in the laboratory.

$(CH_3)_3Ga$ + $(CH_3)_2O$, $(CD_3)_2O$. In an initial experiment, a sample of $Ar/(CH_3)_3Ga$ = 500/1 was codeposited with a sample of $Ar/(CH_3)_2O$ = 500/1. The final spectrum of this matrix showed a number of new infrared absorptions, in addition to much reduced bands of unreacted parent. These include a weak absorption at 522 cm^{-1}, bands of medium intensity at 901, 1071, and 1157 cm^{-1}, intense bands at 721 and 1198 cm^{-1}, and two sets of quite intense multiplets located at 561 and 746 cm^{-1} (in high-dilution experiments, these multiplets resolved into distinct doublets). These new bands are listed in Table I and shown in Figure 1. A number of additional experiments were then conducted codepositing these reagents over a range of concen-

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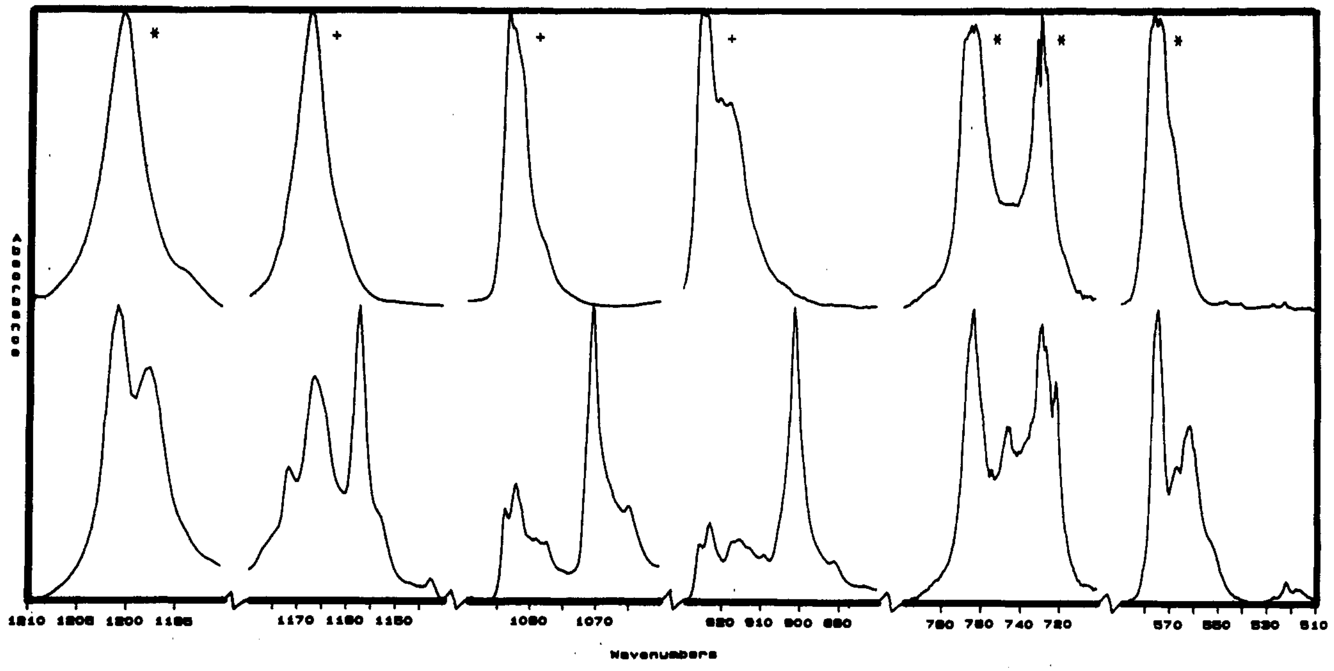

Figure 1. Infrared spectra of the products of the merged jet codeposition of a sample of $Ar/(CH_3)_2O = 500/1$ with a sample of $Ar/(CH_3)_3Ga = 1000/1$ over selected spectral regions (lower trace) compared to appropriate parent spectra (upper trace; bands marked with an "*" are due to parent $(CH_3)_3Ga$ and bands marked with a "+" are due to parent $(CH_3)_2O$). No absorptions (to 0.01 absorbance unit) were noted in the CO_2 regions (660–670 and 2330–2350 cm^{-1}). Details of experimental conditions are given in the Experimental Section.

Table I. Band Positions[a] and Assignments for the Adducts of $(CH_3)_3Ga$ with $(CH_3)_2O$ and $(CD_3)_2O$ in Argon Matrices

$(CH_3)_3Ga\cdot O(CH_3)_2$	$(CH_3)_3Ga\cdot O(CD_3)_2$	parent species	parent band	assgnt
	2228 m	$(CD_3)_2O$	2241	CD str
	2203 w	$(CD_3)_2O$	2189	CD_3 str
	2075 s	$(CD_3)_2O$	2056	CD_3 str
1198 s	1198 s	$(CH_3)_3Ga$	1201	CH_3 sym def
1157 m		$(CH_3)_2O$	1167	CH_3 rock
	1128 w	$(CD_3)_2O$	1152	C–O–C asym str
	1112 vs	$(CD_3)_2O$	1091	CD_3 sym def
1071 m		$(CH_3)_2O$	1098	C–O–C asym str
	929 w	$(CD_3)_2O$	933	CD_3 rock
901 m		$(CH_3)_2O$	925	C–O–C sym str
	810 m	$(CD_3)_2O$	830	C–O–C sym str
746[b] s	746[b] s	$(CH_3)_3Ga$	762	CH_3 rock
721 s	720 s	$(CH_3)_3Ga$	729	CH_3 rock
561[b] s	561[b] s	$(CH_3)_3Ga$	575	GaC_3 asym str
522 w	522 w	$(CH_3)_3Ga$	526[c]	GaC_3 sym str

[a] Band positions in cm^{-1}. [b] Center of doublet. [c] Infrared inactive for the parent molecule.

trations. In each experiment, the same set of bands was observed, and with constant relative intensities. In a few experiments, a broad weak shoulder was observed on the low-energy side of the weak product band at 522 cm^{-1}. No apparent correlation between the appearance of this shoulder and the sample concentration was observed. Finally, several experiments were conducted using N_2 as the matrix material. Product bands very similar to those in argon were observed, with comparable intensities.

Samples of $Ar/(CH_3)_3Ga$ were subsequently codeposited with samples of $Ar/(CD_3)_2O$ in a series of experiments, and new product bands were identified. Several of the above product absorptions (e.g. with $(CH_3)_2O$) were unshifted, including the absorptions at 522, 561, 720, 746, and 1198 cm^{-1}. As can be seen in Table I, a number of the bands observed for the $(CH_3)_3Ga/(CH_3)_2O$ pair were no longer present, and new absorptions were noted at 810, 929, 1112, 1128, 2075, 2203, and 2228 cm^{-1}. Parent bands were also greatly reduced. As precursor concentrations were systematically varied in further experiments, these product bands were always noted, and with constant relative intensities. No additional product bands were noted at other concentrations.

Table II. Band Positions[a] and Assignments for the $(CH_3)_3Ga\cdot S(CH_3)_2$ and $(CH_3)_3Ga\cdot Se(CH_3)_2$ Complexes in Argon Matrices

$(CH_3)_3Ga\cdot S(CH_3)_2$	$(CH_3)_3Ga\cdot Se(CH_3)_2$	parent species	parent band	assgnt
1197 vs	1195 vs	$(CH_3)_3Ga$	1201	CH_3 sym def
1036 m		$(CH_3)_2S$	1030	CH_3 rock
982 w		$(CH_3)_2S$	972	CH_3 rock
	968 m	$(CH_3)_2Se$	959	CH_3 rock
	922 m	$(CH_3)_2Se$	916	CH_3 rock
	818 w	$(CH_3)_2Se$	850	CH_3 rock
747[b] s	746[b] s	$(CH_3)_3Ga$	763	CH_3 rock
722 vs	721 vs	$(CH_3)_3Ga$	729	CH_3 rock
687 m		$(CH_3)_2S$	694	C–S–C sym str
	644	$(CH_3)_2Se$	652	C–Se–C sym str
561[b] s	561[b] s	$(CH_3)_3Ga$	575	GaC_3 asym str
517 w	516 m	$(CH_3)_3Ga$	526[c]	GaC_3 sym str

[a] Band positions in cm^{-1}. [b] Center of doublet. [c] Infrared inactive for the parent molecule.

$(CH_3)_3Ga$ + $(CH_3)_2S$. When a sample of $Ar/(CH_3)_3Ga = 1000/1$ was codeposited with a sample of $Ar/(CH_3)_2S = 500/1$ in an initial experiment, a number of new infrared absorptions were noted, as listed in Table II and shown in Figure 2. These included intense multiplets centered at 561 and 747 cm^{-1} (these multiplets resolved into doublets in the most dilute experiments), an intense absorption at 1197 cm^{-1}, bands of medium intensity at 687 and 1036 cm^{-1}, and weak bands at 517 and 982 cm^{-1}. In subsequent experiments over a range of sample concentrations, all of these absorptions were again present, and no new bands were observed. Intensity ratios were calculated for these bands; all of them maintained constant relative intensities over the range of concentrations employed.

$(CH_3)_3Ga$ + $(CH_3)_2Se$. These two reagents, each diluted in argon, were codeposited in a series of experiments. In an initial experiment, with M/R = 500/1 for both samples, two intense multiplets were observed, centered at 561 and 746 cm^{-1} (these multiplets also resolved into doublets in the best experiments). In addition, intense bands were noted at 721 and 1195 cm^{-1}, along with bands of medium intensity at 516, 818, 922, and 968 cm^{-1}. These are all listed in Table II. As the sample concen-

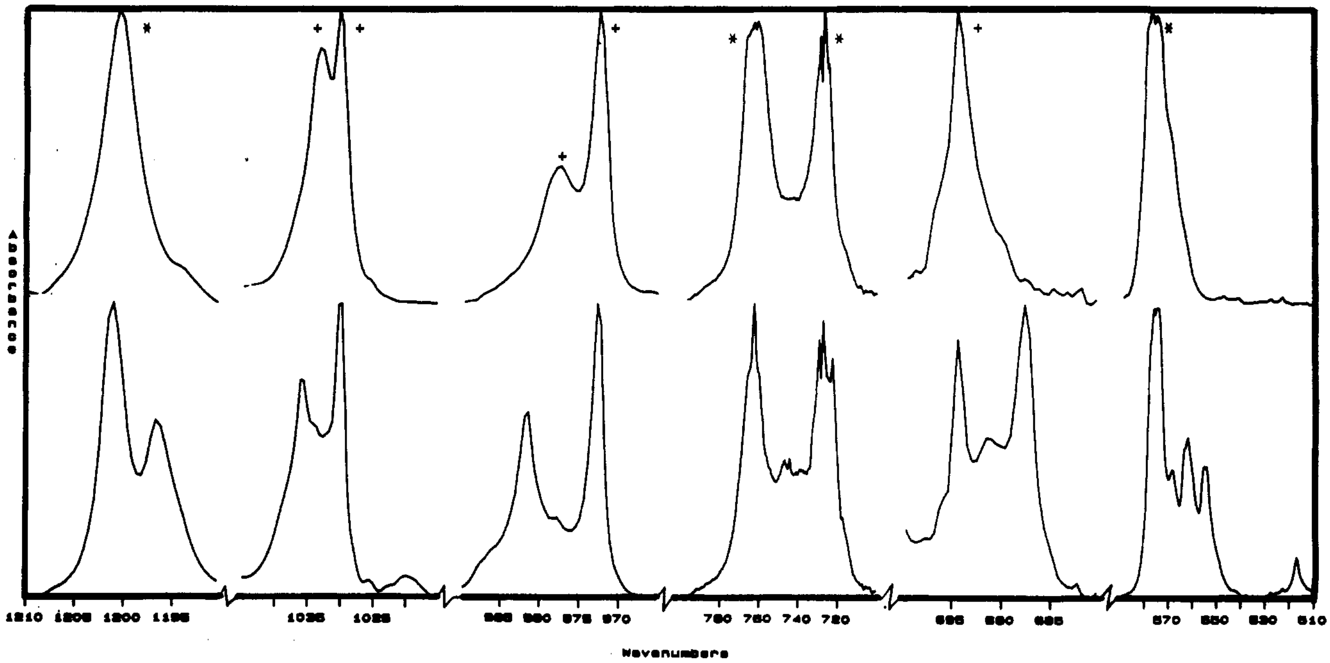

Figure 2. Infrared spectra of the products of the merged jet codeposition of a sample of Ar/$(CH_3)_2S$ = 500/1 with a sample of Ar/$(CH_3)_3Ga$ = 1000/1 over selected regions (lower trace) compared to appropriate parent spectra (upper trace; bands marked with an "*" are due to parent $(CH_3)_3Ga$ and bands marked with a "+" are due to parent $(CH_3)_2S$). No absorptions (to 0.01 absorbance unit) were noted in the CO_2 regions (660–670 and 2330–2350 cm^{-1}).

trations were varied in several additional experiments, these product bands were reproduced, and with constant relative intensities.

Discussion

Product Identification. The codeposition of trimethylgallium with each of the group VI alkyls resulted in numerous new infrared absorptions, as listed in Tables I and II. These bands maintained a constant intensity ratio over a range of experimental conditions, indicating formation of a single product absorber for each pair of reactants. It is noteworthy that each of the new absorptions came relatively close, within 3–30 cm^{-1} to higher or lower energy, to a parent band (with the apparent exception of the product band near 520 cm^{-1} in each system; see below). Those product absorptions lying near bands of parent $(CH_3)_2O$ in the $(CH_3)_3Ga/(CH_3)_2O$ experiments shifted strongly upon deuteration, while those product bands lying near bands of parent $(CH_3)_3Ga$ did not shift. These results are consistent with, and point to, the formation of a molecular complex or adduct between $(CH_3)_3Ga$ and each of the group VI alkyls. In a molecular complex, the two subunits are each perturbed but maintain their structural integrity.[21] As a consequence, certain sensitive vibrational modes are shifted relative to the parent band position, while other modes are less sensitive to complexation and do not shift out from under the parent band profile. In addition, the same set of bands was observed over a wide range of concentrations, to dilutions as high as 2000/1/2. Under these conditions, only the 1/1 complex is likely to form. Thus, the single new infrared absorber observed for each pair of reactants is identified as the matrix isolated 1/1 molecular complex. This conclusion is in agreement with the known Lewis acidity of $(CH_3)_3Ga$, as well as with the earlier detection of these complexes by vapor pressure lowering techniques.[13,14] *The results here represent the first direct observation of these complexes, as well as the first infrared spectroscopic characterization.* The shoulder on the low-energy side of the 522-cm^{-1} band could be taken as slight indication of the formation of a second complex, of higher stoichiometry. However, its very low intensity and lack of reproducibility make such an assertion very tenuous.

Band Assignments. All of the product absorptions lie relatively near a parent band, making band assignments relatively straightforward. Those absorptions that shifted upon substitution of $(CD_3)_2O$ for $(CH_3)_2O$ are readily assigned to vibrational modes of the complexed ether, while those bands that did not shift are assigned to modes of the $(CH_3)_3Ga$ subunit. Likewise, bands that shifted upon replacement of $(CH_3)_2S$ by $(CH_3)_2Se$ may be assigned to the group VI base, while those that did not shift must be due to the $(CH_3)_3Ga$ subunit.

Each complex studied here was characterized by a very intense doublet near 560 cm^{-1}, 15 cm^{-1} to the red of the parent GaC_3 antisymmetric stretching mode. For the parent species, this mode is doubly degenerate under effective D_{3h} symmetry. A shift of 5–30 cm^{-1} to the red has been observed for a series of complexes of $(CH_3)_3Ga$ with group V bases.[17–19] Assignment of the 560-cm^{-1} doublet to the GaC_3 antisymmetric stretch is quite appropriate. The doublet structure arises from the reduction in the symmetry of the complex, and hence the $(CH_3)_3Ga$ subunit, by the base. Loss of a C_3 axis in the complex must lead to a splitting of the degenerate mode into two components. It is probable that the relatively long Ga–O distance in the complex, as a result of the weak interaction, leads to a relatively small splitting of the two components and the closely spaced doublet that is observed.

A new peak was observed near 520 cm^{-1} for each new complex and is apparently not near any parent absorption. The symmetric GaC_3 stretching mode is infrared inactive for the parent and has been identified[24] in the Raman spectrum at 526 cm^{-1}. This mode should be activated in the 1/1 complex, although perhaps weakly so, and observable in the resultant spectrum. A similar new product band in this region was observed for complexes of $(CH_3)_3Ga$ with group V hydrides and assigned to the GaC_3 symmetric stretching mode. Thus, assignment of the band near 520 cm^{-1} for each complex to the GaC_3 symmetric stretch is made. Additional perturbed modes of the $(CH_3)_3Ga$ subunit include bands near 720, 745, and 1197 cm^{-1} for each complex. These are assigned by analogy to the parent to CH_3 rocking and deformation modes, as indicated in Tables I and II.

Vibrational modes of the base subunits likely to be perturbed upon complex formation include the skeletal C–X–C (X = O, S, and Se) symmetric and antisymmetric stretching modes. Earlier studies have shown that these modes generally shift to lower energy upon complex formation.[25-30] Bands were observed for the $(CH_3)_3Ga{\cdot}O(CH_3)_2$ complex at 901 and 1071 cm^{-1}, to the red of parent bands at 925 and 1098 cm^{-1}, which have been assigned to the symmetric and antisymmetric C–O–C stretching modes. Upon deuteration of the dimethyl ether subunit, these product bands shifted to 810 and 1128 cm^{-1}, while the parent absorptions shifted by a comparable amount. These observations make assignment of the 901- and 1071-cm^{-1} bands to the skeletal stretching modes of the $(CH_3)_2O$ subunit appropriate. For the complexes of $(CH_3)_3Ga$ with $(CH_3)_2S$ and $(CH_3)_2Se$, product bands were seen 7–8 cm^{-1} to the red of the parent symmetric skeletal stretching modes and are so assigned, as noted in Table II. Bands due to the perturbed antisymmetric stretch were not observed.

Additional product bands were seen for all three systems that are attributed to the base subunit. All of these are assigned by analogy to the parent spectra and are due to vibrations associated with the methyl groups. While the C–H stretching region for the $(CH_3)_3Ga{\cdot}O(CH_3)_2$ complex was very complicated due to methyl groups on both subunits, the C–D stretching region of the $(CH_3)_3Ga{\cdot}O(CD_3)_2$ complex was cleaner. Here, three new C–D stretching modes were detected. All of the band assignments are collected in Tables I and II.

Structural Considerations. With the spectra of the above complexes that are reported here for the first time, comparison to recently studied complexes[17-19] of $(CH_3)_3Ga$ can be made. The magnitudes of the shift of particularly sensitive vibrational modes of the acid and base subunits are often taken as a relative indicator of the strength of interaction. For $(CH_3)_3Ga$, the most sensitive and hence diagnostic mode is the GaC_3 antisymmetric stretch. This mode shifts to lower energy and, in the present study, splits into a doublet as a result of the lowering of symmetry in the complex. Using the center of the doublet for comparison, the shifts were nearly identical (14 cm^{-1}) for all of the complexes studied here. This is in marked contrast to earlier studies, where shifts from 5 to 30 cm^{-1} were observed. In those studies, an attempt was made to correlate shifts with proton affinities of the bases and, in a qualitative sense, a good correlation was observed. In the present study, the proton affinities of $(CH_3)_2O$ and $(CH_3)_2S$ are known[31] and are quite close to each other, while the proton affinity of $(CH_3)_2Se$ has not been reported. It is not surprising, then, that the shifts for the O and S compounds were nearly identical. This further suggests that the proton affinity of $(CH_3)_2Se$ is probably near 195 kcal/mol. All of the data fit nicely as well with the earlier study; the proton affinities[31] of PH_3 (189 kcal/mol) and NH_3 (204 kcal/mol) exactly bracket the bases studied here. For the PH_3 and NH_3 complexes of $(CH_3)_3Ga$, shifts of 14 and 16 cm^{-1} were observed, nearly identical to the 14-cm^{-1} shifts seen here.

Shifts in vibrational modes of the base often provide a good indication of the acid strength of the Lewis acid, by comparison to a series of acids. For $(CH_3)_2O$, the antisymmetric and symmetric C–O–C modes are particularly diagnostic; in the present study they were observed to shift 27 and 24 cm^{-1}, respectively. This compares to shifts ranging from 20 and 8 cm^{-1} for the $F_4Si{\cdot}O(CH_3)_2$ complex[25] to 73 and 51 cm^{-1} for the $SO_3{\cdot}O(CH_3)_2$ complex.[27] The fluoride ion affinity of a Lewis acid has often been taken as a measure of intrinsic acidity.[32,33] Table III lists the fluoride ion affinities that are known for related acids and shifts in the symmetric and antisymmetric C–O–C stretching modes. As can be seen in this table, somewhat different conclusions could be reached depending on whether the shift in the symmetric or the antisymmetric stretch is employed. If the *average* of the shifts is used, one can infer an order of acidity $BBr_3 > SO_3 > GeF_4 \approx (CH_3)_3Al > (CH_3)_3Ga > BCl_3 > ClF > SiF_4$. Determination of the F^- affinities of the trimethylmetal compounds would be of considerable interest and would provide further evidence as to the order of Lewis acidities. Finally, while the C–S–C and C–Se–C symmetric stretching modes were also perturbed, too few complexes of $(CH_3)_2S$ and $(CH_3)_2Se$ are known to permit useful comparisons.

Table III. Comparison of 1/1 Complexes of Lewis Acids with $(CH_3)_2O$

Lewis acid	$\Delta\nu_s$[a]	$\Delta\nu_a$[b]	$\Delta\nu_{av}$[d]	F^- affinity	ref
BBr_3	40	99	70		30
SO_3	51[c]	73	62	72[e]	27, 33
GeF_4	33	41	37		26
$(CH_3)_3Al$	30	43	37		29
$(CH_3)_3Ga$	24	27	26		[f]
BCl_3	22		22		30
ClF	20	21	21		28
SiF_4	8	20	14	68	25, 33
HCl	9	23	16	60	31, 37
HF	9	11	10	39	38, 39

[a] Shift of the C–O–C symmetric stretch. [b] Shift of the C–O–C antisymmetric stretch. [c] Shifts in cm^{-1}. [d] Average of shifts of the C–O–C symmetric and antisymmetric stretches. [e] In kcal/mol. [f] This work.

The Lewis acid complexes studied here and elsewhere may also be compared to hydrogen-bonded complexes of $(CH_3)_2O$; for example, the $(CH_3)_2O{\cdot}HCl$ complex has been studied by several groups.[34-36] For this complex, a shift of 9 cm^{-1} was observed for the C–O–C antisymmetric stretch, while a 23-cm^{-1} shift was observed for the C–O–C symmetric stretch. In terms of degree of perturbation to the base subunit, HCl is comparable to the weaker Lewis acids discussed above. These shifts are consistent with the F^- affinity of HCl,[37] 60 kcal/mol, which is somewhat less than those of many of the Lewis acids discussed above. The $(CH_3)_2O{\cdot}HF$ complex has also been observed, with shifts of 9 and 11 cm^{-1}, for the antisymmetric and symmetric C–O–C stretching modes,[38] respectively. This, too, is consistent with the yet lower F^- affinity of HF of 39 kcal/mol.[39] It could be argued that the variations in the shifts in these modes are due to steric effects. However, the hydrogen halides, particularly HF, are the least sterically hindered of the acids studied, yet they showed the smallest shifts. This indicates that electronic effects must be important. Also, the results are consistent with F^- affinities (where known), which must be due to electronic, not steric, effects.

On the basis of the infrared spectra, two observations as to the structure of the complexes can be made. First, the symmetric GaC_3 stretch was activated for all three complexes. This is due both to the loss of the C_3 axis in the complex and to distortion from planarity. While the former factor could account for all of the activation, in the group V hydride complexes, a C_3 axis was preserved and a similar degree of activation was seen. This can only arise from distortion from planarity, and hence this is likely to be a significant contributor to the activation in the present complexes. Also, as noted above, the GaC_3 antisymmetric stretch was split into a doublet (along with weak site splitting at higher sample concentrations). While the splitting was small, on the order of 2 cm^{-1}, this indicates that the $(CH_3)_3Ga$ subunit is sensitive to the presence and lower symmetry of the base and that distortion from planarity is not the only factor leading to changes in the infrared spectra.

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As a final point, it may be seen in Table I that the antisymmetric C–O–C stretch of $(CD_3)_2O$ falls at higher energy than the corresponding mode of $(CH_3)_2O$. This has been attributed[23] to Fermi resonance of the antisymmetric C–O–C stretch of $(CH_3)_2O$ with the CH_3 rocking mode at 1167 cm^{-1}. This resonance interaction lowers the energy of the antisymmetric stretch. When CD_3 replaces CH_3, the rocking mode shifts to much lower energy, eliminating the Fermi resonance. The antisymmetric stretch, then, shifts to its unperturbed position of 1152 cm^{-1}. Precisely the same effect was observed for the $(CH_3)_3Ga{\cdot}(CH_3)_2O$ and $(CH_3)_3Ga{\cdot}(CD_3)_2O$ complexes.

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