functions, which give sizeable contributions to the *g* value expressions in a strongly covalent system. In this case bonding parameters are difficult to extract from the *g* values, and they can be interpreted and reproduced only on the basis of a complete molecular orbital calculation.

Registry No. Nb($Et_2dtc)_4$, 12406-69-8; Ti($Et_2dtc)_4$, 12367-51-0; Ti($Et_2dsec)_4$, 80340-09-6; V($Et_2dtc)_4$, 12406-70-1; V($Et_2dsec)_4$, 80340-10-9.

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Spectra and Structure of Gallium Compounds. 4.[1a] Vibrational Studies of Ammonia–Trimethylgallane and Ammonia-d_3–Trimethylgallane

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Received October 21, 1981

The infrared (80–4000 cm^{-1}) and Raman (25–3500 cm^{-1}) spectra of $(CH_3)_3Ga{\cdot}NH_3$ and $(CH_3)_3Ga{\cdot}ND_3$ have been recorded for the solid state at 77 K. The spectra have been interpreted on the basis of C_{3v} molecular symmetry. None of the A_2 vibrations have been observed although a lower site symmetry in the solid state is indicated by the splitting of the bands assigned to the NH_3 and GaC_3 antisymmetric stretching modes. Additionally many of the symmetric modes (A_1) are split into two bands by the crystal field which indicates at least two molecules per primitive unit cell. The valence force field model has been utilized in calculating the frequencies and the potential energy distribution. The calculated potential constants for the adducts are compared to those previously reported for the Lewis acid and base moieties, and the differences are shown to be consistent with structural changes upon adduct formation. Only very minor coupling has been observed between the Ga–N stretch and several of the GaC_3 modes. The Ga–N force constant has been found to have a value of 1.08 mdyn/Å, which is much smaller than the value of the Ga–N force constant (2.43 mdyn/Å) in $(CH_3)_3N{\cdot}GaH_3$. The magnitudes of these force constants appear to adequately reflect the relative stabilities of the adducts.

Introduction

The relative donor strengths of nitrogen- and phosphorus-containing compounds toward a given acceptor have been a subject of continuing interest in coordination chemistry. We have recently studied[2,3] the spectra and structure of three coordination compounds of gallium: $(CH_3)_3P{\cdot}GaH_3$, $(CH_3)_3N{\cdot}GaH_3$, and $(CH_3)_3Ga{\cdot}PH_3$. In our studies of the first and second compounds we found that the Ga–P stretching force constant has a value of 2.0 mdyn/Å, which is much smaller than the value of the Ga–N force constant (2.43 mdyn/Å) in $(CH_3)_3N{\cdot}GaH_3$; however, this does not reflect the relative stabilities of these adducts as determined by other methods.[4] In an NMR study, Leib et al.[5] reported that the ammonia adduct of trimethylgallium was more stable than the corresponding adduct formed with trimethylphosphine but less stable than the adduct formed with trimethylamine. However, these authors[5] did not investigate the relative stability of the $(CH_3)_3Ga{\cdot}PH_3$ adduct since it has only recently been prepared.[3] In our investigation of $(CH_3)_3Ga{\cdot}PH_3$ we found this molecule to be relatively unstable at ambient temperature with the evolution of a noncondensable gas which is similar to the thermal decomposition of ammonia–trimethylgallane where a dimeric derivative containing three-center bonds is generated.[6]

Recently, we[2b] studied the microwave spectrum of $(CH_3)_3N{\cdot}GaH_3$ and obtained an r_s distance of 2.111 ± 0.002 Å for the Ga–N bond. This distance is considerably shorter than the Ga–N bond distance of 2.20 Å reported[7] for the $(CH_3)_3Ga{\cdot}N(CH_3)_3$ molecule. Since $(CH_3)_3Ga{\cdot}NH_3$ is isomeric with trimethylamine–gallane, we have investigated the low-temperature infrared and Raman spectra of ammonia–trimethylgallane in order to examine possible differences in the molecular structures of the two isomers and to determine the acid–base strengths of the donors and the acceptors involved in the Ga–N bonding. Additionally, it was hoped that we could obtain a microwave spectrum of $(CH_3)_3Ga{\cdot}NH_3$ from which the Ga–N bond distance could be ascertained. The results of these investigations are reported herein.

Experimental Section

The samples of $(CH_3)_3Ga{\cdot}NH_3$ and $(CH_3)_3Ga{\cdot}ND_3$ were prepared and handled with standard high-vacuum techniques in a system equipped with greaseless stopcocks. The synthesis was carried out in a Pyrex tube fitted with a greaseless stopcock by condensing into the tube approximately equimolar amounts of $(CH_3)_3Ga$, purchased from Alfa (electronic grade, 99.9+% pure) and used without further purification, and NH_3 or ND_3, prepared according to the literature[8] and purified by passage through two −78 °C traps into a −196 °C trap. The $(CH_3)_3Ga$ was used in slight excess to minimize multiple coordination. The reactants were allowed to warm to room temperature, the compound forming quickly as a clear–white semicrystalline solid. The tube was then cooled to −45 °C and the excess $(CH_3)_3$ Ga pumped out.

The Raman spectra (Figure 1) were recorded from 25 to 3500 cm^{-1} on a Cary Model 82 laser Raman spectrophotometer using a Spectra Physics Model 171 argon ion laser tuned to the 514.5-nm line at the excitation source. The amount of power measured at the sample was typically 1 W. Frequencies of the peaks were measured with a spectral band width of 2 or 3 cm^{-1}. The monochromator was calibrated against mercury emission lines, and frequencies for sharp resolvable lines are expected to be accurate to ±2 cm^{-1}. The sample was slowly deposited onto a blackened brass block, held at an angle of 75° from the normal and cooled by boiling liquid nitrogen, and annealed until no further change was observed in the spectrum.

The mid-infrared spectra from 200 to 4000 cm^{-1} (Figure 2) were recorded on a Perkin-Elmer Model 621 grating infrared spectrophotometer. The housing was purged with dry nitrogen, and the instrument was calibrated with standard gases in the high-frequency region and with water vapor in the low-frequency region. Sharp resolvable bands are expected to be measured accurately to ±2 cm^{-1}. The sample was condensed onto a cesium iodide substrate mounted

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(1) (a) For part 3, see *J. Mol Struct.* **1981**, *72*, 73. (b) Taken in part from the thesis of C. B. Bradley which will be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

(2) (a) Odom, J. D.; Chatterjee, K. K; Durig, J. R. *J. Phys. Chem.* **1980**, *84*, 1843. (b) Durig, J. R.; Chatterjee, K. K.; Li, Y. S.; Zozulin, A. J.; Odom, J. D. *J. Chem. Phys.* **1980**, *73*, 21.

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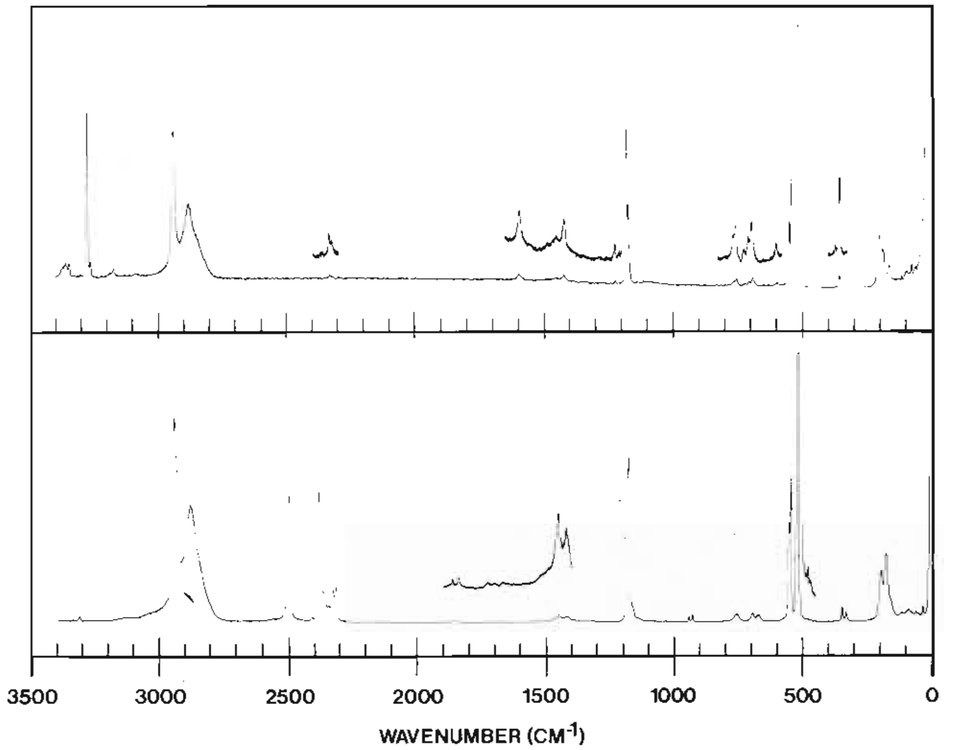

Figure 1. Raman spectra of polycrystalline $(CH_3)_3Ga{\cdot}NH_3$ (upper trace) and $(CH_3)_3Ga{\cdot}ND_3$ (lower trace) recorded at boiling-liquid-nitrogen temperature.

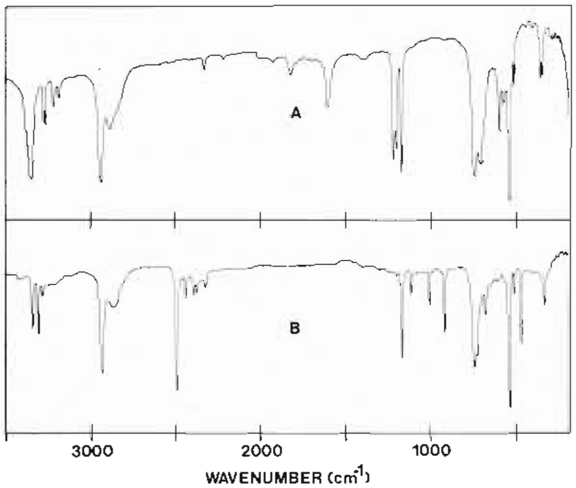

Figure 2. Mid-infrared spectra of polycrystalline (A) $(CH_3)_3Ga{\cdot}NH_3$ and (B) $(CH_3)_3Ga{\cdot}ND_3$ recorded at boiling-liquid-nitrogen temperature on CsI substrate.

in a brass holder, cooled by contact with a reservoir of liquid nitrogen, in an evacuated cell with cesium iodide windows, and annealed as for the Raman spectrum.

The far-infrared spectra (Figure 3) were obtained with a Digilab Model FTS-15B Fourier transform interferometer equipped with a 6.25 μm Mylar beam splitter. A total of 500 interferograms were coadded and transformed with a boxcar apodization function to give a spectrum having an effective resolution of 2 cm^{-1}. The cell was similar in design to the mid-infrared cell except that the substrate was a plate cut from a silicon crystal and the windows were polyethylene. The sample was deposited and annealed as for the Raman and mid-infrared spectra.

Assignment of Vibrational Fundamentals

The 45 vibrations of the C_{3v} molecule $(CH_3)_3Ga{\cdot}NH_3$ fall into the irreducible representations: $10\ A_1 + 5\ A_2 + 15\ E$. Of these the A_2 modes are neither Raman nor infrared active; the rest are active in both the infrared and the Raman effect. The inactive A_2 modes include all the vibrations which retain the symmetry element C_3 but which destroy the σ_v planes. These are the NH_3 torsion and the in-phase methyl motions which have no plane of symmetry. In addition to these five inactive modes, the out-of-plane methyl torsions (E) were not observed. Assignments are made according to characteristic group frequencies, comparison with related molecules,[9] and isotopic substitution data (see Tables I and II).

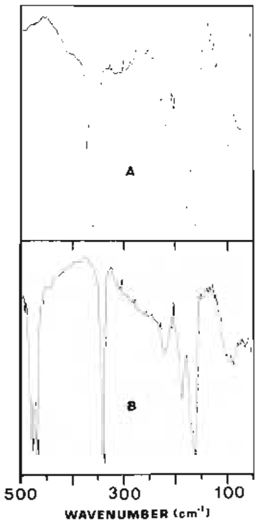

Figure 3. Far-infrared spectra of polycrystalline (A) $(CH_3)_3Ga{\cdot}NH_3$ and (B) $(CH_3)_3Ga{\cdot}ND_3$ recorded at boiling-liquid nitrogen-temperature on silicon substrate.

NH_3 Modes. Deuteration of the ammonia molecule causes the largest shifts in the frequencies of the NH_3 bands which allows an unambiguous assignment for these normal modes. The NH_3 stretches are the highest frequency fundamentals in the spectra of $(CH_3)_3Ga{\cdot}NH_3$. The two degenerate antisymmetric stretches give rise to the group of weak bands around 3360 cm^{-1} in the Raman spectrum and the intense band at 3350 cm^{-1} in the infrared spectrum. Since the sample was better annealed for the Raman spectrum, better splitting and

Table I. Observed[a] Raman and Infrared Frequencies and Assignment for Ammonia-Trimethylgallane

Raman $\Delta\nu$, cm^{-1}	rel intens	ν, cm^{-1}		assignt and approx descriptions
		IR	calcd	
3372	3			
3361	4			
3357	3	3350 s	3368	ν_{11} (E) antisym NH_3 str (100%)
3348	4			
3277	50	3277 m	3253	ν_1 (A_1) sym NH_3 str (100%)
3264	4	3267		
3175	2	3219 w 3187 w		$2 \times \delta_{asym}NH_3$
2944	44	2940 s	2963	ν_{12} (E), ν_2 (A_1) antisym CH_3 str (100%)
2884	22	2882 m	2847	ν_{13} (E), ν_3 (A_1) sym CH_3 str (100%)
		2832 sh		$2 \times \delta_{asym}CH_3$
2337	2	2331 w		$2 \times \delta_{sym}CH_3$
2326	<1			
		2216 vw		
		1928 vw		
		1827 w		
1599	2	1610 m	1594	ν_{14} (E) antisym NH_3 def (99%)
1456	<1		1424	ν_4 (A_1), ν_{15} (E) antisym CH_3 def (97%)
1425	2			
		1404 vw		
1225	<1	1224 s	1246	ν_5 (A_1) sym NH_3 def (98%)
		1207 s		
1182	48	1177 vs	1241	ν_{16} (E) sym CH_3 def (94%), antisym GaC str (5%); ν_6 (A_1) sym CH_3 def (95%), sym GaC_3 str (5%)
1175	24			
763	<1	750 vs	724	ν_7 (A_1) in-plane CH_3 rock (97%)
755	2			
721		723 s	715	ν_{17} (E) in-plane CH_3 rock (97%)
707	<1	709 s	683	ν_{18} (E) out-of-plane CH_3 rock (94%)
693	2	690 sh		
598	<1	604 m	594	ν_{19} (E) NH_3 rock (92%), antisym GaC_3 str (5%)
		581 m		
552	11	542 vs		ν_{20} (E) antisym GaC_3 str (86%), NH_3 rock (6%), sym CH_3 def (5%)
544	34			
		522 w	488	ν_8 (A_1) sym GaC_3 str (94%), sym CH_3 def (5%)
518	100	515 w		
372	<1	368 m	364	ν_9 (A_1) GaN str (95%)
357	3	357 m		
202	16	220 mw	205	ν_{21} (E) antisym GaC_3 def (96%)
188	12	180 m	137	ν_{10} (A_1) sym GaC_3 def (92%)
164	6	162 m	172	ν_{22} (E) GaC_3 rock (97%)
116				lattice modes
97		100 mw		
80		86 mw		
66				
62				
53				
49				
45				
37				

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; antisym, antisymmetric; sym, symmetric; str, stretch; def, deformation.

sharper bands are observed in the Raman spectrum as compared with the infrared spectrum. This is quite evident in the case of the NH_3 antisymmetric stretch: the Raman spectrum contains four bands, whereas the infrared spectrum contains a single, broad, intense band. In the spectra of the d_3 sample, these bands are shifted to 2497 cm^{-1}, giving a shift factor of 1.36. The symmetric stretch (A_1) is observed around 3277 cm^{-1} in the "light" compound and 2380 cm^{-1} in the "heavy" compound. This leads to a shift factor of 1.37.

The antisymmetric deformation occurs at 1599 cm^{-1} in the Raman spectrum of the light compound, the same frequency as was observed by Sawodny and Goubeau[9] in $(CH_3)_3B{\cdot}NH_3$. Upon deuteration it shifts to 1165 cm^{-1}, a shift factor of 1.37, where it is observed as a shoulder in the Raman spectrum and not seen in the infrared spectrum as a separate band, although it may be the cause of the asymmetry of the 1180-cm^{-1} band. The symmetric deformation gives rise to the bands near 1215 cm^{-1} in the infrared spectrum of the d_0 molecule and near 938 cm^{-1} in the d_3 molecule. This shift factor is 1.30. The final mode which shifts significantly with deuteration is the NH_3 rock. In the Raman spectra it shifts from 598 to 481 cm^{-1}, a factor of 1.24. Corresponding bands of moderate intensity appear in the infrared spectra at 604 and 482 cm^{-1}.

CH_3 Modes. The three methyl groups contribute 25 of the total of 45 vibrations of $(CH_3)_3Ga{\cdot}NH_3$, but the high symmetry reduces these to 5 A_1 + 4 A_2 + 8 E. The CH_3 stretches are not well resolved, however. Instead of (two) symmetric (A_1 + E) and (three) antisymmetric (A_1 + 2 E) bands, only two fairly broad bands are observed. In the Raman spectra, the antisymmetric and symmetric stretches are observed at 2944 and 2884 cm^{-1} for the light molecule and at 2943 and 2880 cm^{-1} for the heavy compound. The number and distribution of the CH_3 deformations which are possible correspond exactly to the stretches; however, these modes are somewhat better resolved. The antisymmetric deformations,

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(9) Sawodny, W.; Goubeau, J. *Z. Phys. Chem.* (*Wiesbaden*) **1965**, *44*, 227.

Table II. Observed[a] Raman and Infrared Frequencies and Assignment for Ammonia-d_3-Trimethylgallane

Raman $\Delta\nu$, cm^{-1}	rel intens	ν, cm^{-1} IR	ν, cm^{-1} calcd	assignt and approx descriptions
		3345 m		
3314	<1	3313 w		
		3289 w		
		3276 vw		
2943	52	2936 s	2960	ν_{12} (E), ν_2 (A_1) antisym CH_3 str (100%)
2880	30	2884 m	2844	ν_3 (A_1), ν_{13} (E) sym CH_3 str (100%)
2497	33	2497 vs	2510	ν_{11} (E) antisym ND_3 str (99%)
		2443 m		
2411	<1			
2394	sh	2394 w		
2381	33	2380 w	2351	ν_1 (A_1) sym ND_3 str (100%)
2366				
2329	8	2331 w		$2 \times \delta_{sym}CH_3$
2318	9	2319 w		
1865				$2 \times \delta_{sym}ND_3$
1841				
1452	1		1424	ν_4 (A_1), ν_{15} (E) antisym CH_3 def (97%)
1421	<1			
		1212 vw		
1182	40	1180 s	1241	ν_{16} (E) sym CH_3 def (94%) antisym GaC_3 str (5%); ν_6 (A_1) sym CH_3 def (95%) sym GaC_3 str (5%)
1176	41			
1165	sh		1158	ν_{14} (E) antisym ND_3 def (98%)
		1125 m		
		1018 m		
		958 vw		
945	1	945 vw	979	ν_5 (A_1) sym ND_3 def (95%), GaN str (4%)
931	2	931 s		
755	2	757 s	724	ν_7 (A_1) in-plane CH_3 rock (97%)
		741 s		
697	2	692 m	715	ν_{17} (E) in-plane CH_3 rock (98%)
679	1		683	ν_{18} (E) out-of-plane CH_3 rock (94%)
670	1			
575	<1			
556	19			
552	25	550 vs	554	ν_{20} (E) antisym GaC_3 str (89%), sym CH_3 def (5%)
548	38			
544	33			
521	100	524 w	487	ν_8 (A_1) sym GaC_3 str (94%), sym CH_3 def (5%)
518	100			
487	<1			
481		477 m	467	ν_{19} (E) ND_3 rock (95%)
466	1	466 m		
348	3	349 m	388	ν_9 (A_1) GaN str (92%), sym ND_3 def (4%), sym GaC_3 def (3%)
333	2	333 vw		
		219 vw		
197	13		201	ν_{21} (E) antisym GaC_3 def (96%)
180	18	185 w	157	ν_{10} (A_{11}) sym GaC_3 def (89%), GaN str
			168 sh	
160	sh	161 m	167	ν_{22} (E) GaC_3 rock (96%)
116				
91		98 vw		lattice modes
		86 vw		
77				
61				
36				

[a] For abbreviations used see Table I.

which are not found in the infrared spectra, are observed in the Raman spectra as very weak bands at 1456 and 1425 cm^{-1} (d_0) and at 1452 and 1421 cm^{-1} (d_3). The CH_3 symmetric deformations give rise to strong bands in both the infrared and Raman spectra. These are found at 1182 and 1175 cm^{-1} in the Raman spectrum of the light compound with a counterpart at 1177 cm^{-1} in the infrared spectrum. In the heavy compound the frequencies are 1182 and 1176 cm^{-1} (Raman) and 1180 cm^{-1} (infrared). The group of weak bands from 763 to 670 cm^{-1} in the Raman spectra of these compounds is assigned to the CH_3 rocking motions. The corresponding bands in the infrared spectra are fairly strong and broad.

Skeletal Modes. The vibrational modes remaining to be assigned belong to the heavy atom skeleton and include the GaC_3 stretches, deformations, and rocks, and the Ga–N stretching mode. The bands appearing near 550 cm^{-1} are assigned to the antisymmetric GaC_3 stretch and are stronger in the infrared than in the Raman spectra. The bands near 520 cm^{-1}, on the other hand, are very strong in the Raman effect, the strongest in the spectrum in fact, and weak in the infrared and are assigned to the GaC_3 symmetric stretching motion. The GaC_3 deformations give rise to two bands: the antisymmetric at 202 and 197 cm^{-1} in the Raman spectra of the d_0 and d_3 compounds, respectively, and the symmetric at 188 and 180 cm^{-1} in the Raman spectra, respectively. The GaC_3 rock is assigned to the band at 164 cm^{-1} in the light compound and to the bands near 160 cm^{-1} in the heavy compound.

The Ga–N stretch can be assigned to the remaining low-frequency bands, which occur at 372 (vvw) and 357 cm^{-1} in

Table III. Final Values of Force Constants for Ammonia-Trimethylgallane

force constant	description	value,[a] mdyn/Å
$K_{r'}$	N-H str	6.16 ± 0.05
K_R	Ga-N str	1.08 ± 0.12
K_r	Ga-C str	2.13 ± 0.10
K_s	C-H str	4.66 ± 0.02
H_α	H-N-H bend	0.57 ± 0.01
H_β	Ga-N-H bend	0.22 ± 0.01
H_γ	C-Ga-N bend	0.50 ± 0.07
H_δ	C-Ga-C bend	0.48 ± 0.06
$H_{\epsilon\parallel}$	Ga-C-H bend (in-plane of σ_v)	0.36 ± 0.02
$H_{\epsilon\perp}$	Ga-C-H bend (out-of-plane of σ_v)	0.31 ± 0.01
H_ζ	H-C-H bend	0.52 ± 0.01

[a] All bending coordinates are weighted by 1 Å.

the Raman spectrum of the light compound, corresponding to the infrared bands at 368 and 357 cm^{-1}. Deuteration causes these bands to shift to 348 and 333 cm^{-1}. The observed shift factor of 1.07 agrees satisfactorily with the value of 1.10, which is calculated on the basis of a mass change of 17 to 20. The intensity pattern of weak in the Raman effect and strong in the infrared spectrum is similar to the intensity pattern which was observed[2] for the corresponding mode in $(CH_3)_3N{\cdot}GaH_3$. It should be mentioned that the assignment of the Ga–N stretching mode for $(CH_3)_3Ga{\cdot}NH_3$ is considered to be unambiguous since no other normal mode is expected near this frequency region.

Normal-Coordinate Analysis

The normal coordinates of the observed fundamental vibrations were calculated according to Wilson's **F**–**G** matrix method[10] using programs written by Schachtschneider.[11] The **G** matrix was calculated with the following structural parameters: $r(GaC) = 1.998$ Å, $r(GaN) = 2.20$ Å, $r(CH) = 1.091$ Å, $r(NH) = 1.008$ Å, $\angle(CGaN) = 100.59°$. The GaC and GaN distances and CGaN angle were taken from the electron diffraction study of $(CH_3)_3N{\cdot}Ga(CH_3)_3$ by Golubinskaya et al.[7] The angles around the nitrogen and carbon atoms were assumed to be tetrahedral since no precise measurements were available.

Since the CH_3 torsion of E symmetry was not observed and the other torsional modes were of the inactive A_2 symmetry, no force constant was used to calculate frequencies for these motions. They were, however, included in the 50 internal coordinates used to form the 50 symmetry coordinates which are identical with those used in ref 2a.

The 11 force constants were adjusted individually to approximately fit the observed frequencies and were then individually reiterated to minimize the percentage error. Since these 11 force constants were able to fit the observed frequencies to within about 2% error, it was felt that inclusion of interaction constants would not significantly improve the understanding of the molecular force field. The final values are listed in Table III.

Results and Discussion

Examination of the spectra of ammonia–trimethylgallane and ammonia-d_3–trimethylgallane reveals that several of the bands ascribed to A_1 motions are split into two peaks, notably the NH_3 and GaC_3 symmetric stretches and especially the GaN stretch. Since a lower site symmetry will not account for this splitting, it is taken as an indication that there are at least two molecules per primitive unit cell. In several bands assigned to vibrations of E symmetry such as the NH_3 antisymmetric stretch and the GaC_3 antisymmetric stretch in the deuterated molecule, four peaks were observed. A site symmetry of C_s would account for two peaks being observed but not four. Again two or more molecules per primitive unit cell would lead to the observation of four peaks. It must be noted, however, that in the four frequencies recorded for the GaC_3 antisymmetric stretch referred to above, two of the frequencies are identical with those observed in the d_0 sample. It is certain that some hydrogen impurity is present in the d_3 sample, but the relative intensities of the bands and the foregoing argument preclude their assignment to an impurity.

While some information was gained about the crystal form, no microwave spectrum was obtained that would yield any information about the specific molecular structure. Evidently the compound decomposed immediately upon introduction into the waveguide since the observed spectrum consisted entirely of lines due to ammonia. This decomposition indicates a much weaker Ga–N bond and resulting lower stability than observed in the structural isomer $(CH_3)_3NGaH_3$. This relative stability is consistent with the relative magnitudes of the force constants for the Ga–N stretch, 2.43 vs. 1.08 mdyn/Å, and the assigned frequencies 508 vs. 357 cm^{-1}, for trimethylamine–gallane[2b] and ammonia–trimethylgallane, respectively. These force constant values are consistent with the relative base strengths of trimethylamine and ammonia.

There has been some controversy concerning the frequency of the Ga–N stretching mode in trimethylamine–gallane with it being assigned variously at 488 cm^{-1} in the gas[13,14] and 370 cm^{-1}[15,16] and 508 cm^{-1}[2] in the solid. The assignment of this mode in ammonia–trimethylgallane, however, is considered unambiguous since these bands are not obscured in any way by other modes in the spectral region 300–400 cm^{-1} and additionally because of the close agreement between experimental and calculated shift factors. On the basis of our recent work[2b] on $(CH_3)_3N{\cdot}GaH_3$, along with this study, it appears that the Ga–N stretch may be found over a rather large range of frequencies and that the observed frequency will probably depend on the relative value of the force constant for this normal mode.

It should also be mentioned that it is somewhat surprising that the Ga–N stretching mode is so weak in the Raman effect. The polarizability change with the stretching of the Ga–N bond must be relatively small but the relative intensity of this mode in the infrared spectrum indicates that there is an appreciable dipole change associated with this normal mode. It is probable that similar observations will be found for other gallium/nitrogen-containing compounds, as it has already been observed in $(CH_3)_3N{\cdot}GaH_3$.[2b]

As can be seen from the list of force constants in Table III, the in-plane and out-of-plane Ga–C–H bending force constants are separated, although they are more similar, at 0.36 and 0.31 mdyn/Å, respectively, than the corresponding ones of 0.39 and 0.28, respectively, reported for $(CH_3)_3Ga{\cdot}PH_3$.[3] According to the potential energy distribution among the symmetry coordinates, most of the vibrational modes are relatively pure. The major exceptions are the antisymmetric GaC_3 deformation and, in the deuterated molecule, the symmetric GaC_3 deformation. Additionally, there is some contribution made by the Ga–N stretch to several of the GaC_3 modes.

The N–H stretching force constant in ammonia has been reported[17] to have a value of 6.35 mdyn/Å. This value com-

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(10) Wilson, E. B.; Decius, J. C.; Cross, P. C. "Molecular Vibrations"; McGraw-Hill: New York, 1955.

(11) Schachtschneider, J. H. Technical Reports No. 231-64 and 57-65; Shell Development Co.: Emeryville, CA.

(12) In Table I of ref 1, the $S_{32} = \alpha_9 + \alpha_{10} + \alpha_{11} - \beta_9 - \beta_{10} - \beta_{11} - \alpha_{12} - \alpha_{13} - \alpha_{14} + \beta_{12} + \beta_{13} + \beta_{14}$ was omitted.

(13) Greenwood, N. N.; Storr, A.; Wallbridge, M. G. H. *Inorg. Chem.* **1963**, *2*, 1036.

(14) Greenwood, N. N; Storr, A.; Wallbridge, M. G. H. *Proc. Chem. Soc.* **1962**, 249.

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pares favorably with the value of 6.16 mdyn/Å calculated in this study for the similar motion in the adduct. The slightly smaller value for the adduct is expected on the basis of a slight elongation of the N–H bond with complex formation. Likewise the Ga–C stretching force constant of 2.14 mdyn/Å is very similar to the value of 2.15 mdyn/Å calculated for the corresponding force constant in the study of $(CH_3)_3Ga{\cdot}PH_3$.[3]

In support of the proposed assignment, Teller–Redlich product rule calculations were carried out. The A_1 symmetry block gave essential agreement between the theoretical and experimental values, while the E symmetry block contained an error of 1.91% between the calculated and observed ratios. The values for the calculated and observed ratios respectively are 1.976 and 1.995 for the A_1 species and 2.674 and 2.623 for the E symmetry block; a change of only one wavenumber in the values of the frequencies assigned to GaC_3 symmetric deformations reduces the observed ratio to 1.975 for the A_1 species. The excellent agreement between the experimental and theoretical values adds support to the assignment proposed herein.

Further studies on other gallium–nitrogen complexes should be carried out to check the range of the force constants associated with the Ga–N bond. With such studies it should be possible to ascertain whether there is a direct correlation of the bond strength with the force constant. Additionally it should also be possible to clearly define the frequency range expected for the Ga–N stretching motion.

Acknowledgment. We gratefully acknowledge the financial support of this study by the National Science Foundation by Grants CHE-79-20763 and CHE-80-13694.

Registry No. $(CH_3)_3Ga{\cdot}NH_3$, 15279-03-5; $(CH_3)_3Ga{\cdot}ND_3$, 80376-33-6.

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FT IR and Fluorometric Investigation of Rare-Earth and Metallic Ion Solvation. 1. Europium Perchlorate in Anhydrous Acetonitrile[1]

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Received June 10, 1981

The composition of the species in equilibrium in dilute and anhydrous solutions of $Eu(ClO_4)_3$ in acetonitrile is investigated by means of FT IR and fluorometric measurements. $Eu(ClO_4)_3$ is a 2:1 electrolyte in CH_3CN; fluorescence spectra and lifetimes reflect an inner-sphere interaction between ClO_4^- and Eu^{3+}. FT IR difference spectra show the simultaneous presence of ionic, monodentate, and bidentate perchlorates. A quantitative determination indicates that, in 0.05 M solutions, 71 ± 2% of the perchlorates are ionic; of the remaining 29%, two-thirds are monodentate and one-third are bidentate. A high-resolution analysis of the $^5D_0 \rightarrow {}^7F_0$ emission band reveals the presence of two main Eu-containing species. The concentration variations of the different perchlorate species vs. $[ClO_4^-]_t$ and various comparisons with methanolic solutions indicate that monodentate perchlorate, $ClO_4^-(m)$, is probably involved in inner-sphere association, whereas bidentate perchlorate, $ClO_4^-(b)$, is probably involved in outer-sphere interaction. One Eu–O vibration is observed at 217 cm^{-1}. Bonded acetonitrile molecules can also be evidenced; the Eu–N vibration occurs at 168 cm^{-1}. The average number of coordinated CH_3CN molecules per Eu^{3+} ion is 8.5 ± 0.3, as determined by quantitative measurements of the $\nu_3 + \nu_4$ absorption and by comparison with $Eu(NO_3)_3$ solutions. The average coordination number of the europium ion is therefore 9.1 ± 0.3. The reported data are consistent with the presence of two main nonacoordinated species in equilibrium in 0.05 M solutions of $Eu(ClO_4)_3$ in acetonitrile: $[(EuClO_4(m))(CH_3CN)_8]^{2+}$ (~60%) and $[Eu(CH_3CN)_9]^{3+}(ClO_4(b))^-$ (~30%). Silver perchlorate solutions contain ionic ClO_4^- only, whereas sodium perchlorate solutions also contain some nonionic ClO_4^- groups. Acetonitrile molecules bonded to these ions can be evidenced by FT IR.

Introduction

The coordinative properties of Ln(III) ions are different from those of d-transition ions because of the 4f electron shielding. The stabilization due to crystal field effects is only of the order of a few hundred cm^{-1}, and the bonding of Ln(III) ions to oxygen and nitrogen atoms remains essentially electrostatic. The number of ligands in the first coordination sphere and their geometrical arrangements will thus be largely determined by steric requirements. Large coordination numbers (N) are common, and their determination in solution is expected to be difficult since the following situations may occur: (i) equilibrium between species differing in constitution by one, or more, ligated solvent molecules[2,3] and (ii) equilibrium between species having the same N but different coordination polyhedra and thus different spectroscopic properties. Moreover, the solvated ion is surrounded by an outer-coordination sphere and rapid exchange usually takes place between the bulk and coordinated solvent molecules.

A number of estimates for N have been made by a wealth of different techniques, including absorption and emission spectra,[4] vibrational spectra,[5] NMR,[6] ultrasonic measurements,[7] and X-ray crystallography. Using this latter technique, Habenschuss and Spedding have unambiguously demonstrated a change in N across the rare-earth series: in concentrated aqueous chloride solutions, $N = 9$ for La^{3+}–Nd^{3+} [8] and $N = 8$ for Tb^{3+}–Lu^{3+},[9] whereas Sm^{3+}, Eu^{3+}, and Gd^{3+} are transitional, with N between 8 and 9.[10]

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