phase below room temperature, appears to be comparable in stability to $[(CH_3)_3N]_2GaCl_3$ and $[(CH_3)_3N]_2$-$GaBr_3$, which are reported to revert slowly to the corresponding 1:1 adducts under vacuum at $-48.7°$[19]; at this temperature $[(CH_3)_3N]_2GaH_3$ has a calculated dissociation pressure of 6.0 mm. The 2:1 compound is also comparable in stability to $[(CH_3)_3N]_2AlCl_3$, for which[19] $\log p_{mm} = 9.70 - 2280/T$; the heat of dissociation of the aluminum chloride complex is therefore 10.43 kcal./mole, which is close to the value of 10.35 kcal./mole in the gallane adduct.

The 1:1 complex $(CH_3)_3NGaH_3$ is considerably less stable than $(CH_3)_3NBH_3$ but is similar in stability to $(CH_3)_3NAlH_3$ although the two compounds decompose in rather different ways due to the fact that the $[(CH_3)_3N]_2AlH_3$ is much more stable than $[(CH_3)_2N]_2GaH_3$. The m.p. of the 1:1 alane, $76°$,[13] is also close to that of $(CH_3)_3NGaH_3$, $70.5°$. As expected, the 1:1 complexes of alane and gallane are considerably less stable than the corresponding complexes of aluminum and gallium trihalides and they are also less stable than the complexes of trimethylaluminum and trimethylgallium.[20]

The preparation of $(CH_3)_2SGaH_3$ from $(CH_3)_3$-$NGaH_3$ involves the replacement of a strong ligand by a weaker one. This type of reaction is frequently useful and deserves to be better known. The technique is to displace the desired acceptor by a stronger acceptor using the weaker ligand as solvent. In general, the strong ligand combines with the stronger acceptor leaving the weak ligand and weak acceptor to combine; separation then depends on the particular properties of the two new complexes formed.

$(CH_3)_2SGaH_3$ decomposes at lower temperatures than does $(CH_3)_2SGa(CH_3)_3$[21]; however, its properties suggest that it is more stable than the corresponding etherates and this point is being further investigated.

(19) R. E. Van Dyke and H. E. Crawford, *J. Am. Chem. Soc.*, **72**, 2829 (1950).

(20) G. E. Coates, "Organometallic Compounds," 2nd Ed., Methuen and Co., London, 1960.

(21) E. Wiberg, T. Johannsen, and O. Stecher, *Z. anorg. Chem.*, **251**, 114 (1943).

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Preparation and Characterization of Trimethylamine Gallane and Bistrimethylamine Gallane

BY D. F. SHRIVER AND R. W. PARRY

A new compound $(CH_3)_3NGaH_3$ (trimethylamine gallane) has been prepared and characterized. It is a volatile solid which decomposes upon standing at room temperature and is monomeric in dimethyl ether solution. Crystallographic evidence is presented which indicates the absence of a hydrogen bridge structure in the solid. It was found that trimethylamine gallane can take up a second mole of trimethylamine to form bistrimethylamine gallane. This latter compound is monomeric in trimethylamine solution and thus appears to contain a five-coordinated gallium atom. $\Delta H°$ and $\Delta S°$ for the reaction

$$((CH_3)_3N)_2GaH_3(s) = (CH_3)_3NGaH_3(s) + (CH_3)_3N(g)$$
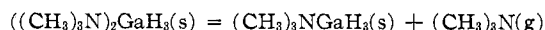
at $-31.05°$ are, respectively, 11.5 kcal./mole and 41.1 cal./mole-deg.

Amine adducts of BH_3 and AlH_3 have received considerable attention in the literature.[1-5] The alkyl amine addition compounds of BH_3 are typified by the monomeric compound $(CH_3)_3NBH_3$. By contrast, two points are of special interest with the amine–aluminum hydride derivatives. One is the partial dimerization of $(CH_3)_3NAlH_3$ and its related compounds in benzene solution.[2-4] There is some controversy over the nature of the interaction involved in this dimerization. Both

a hydrogen-bridged structure
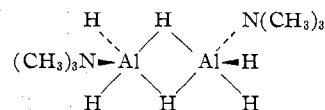
and dipole–dipole interactions have been proposed[2-5] to account for the dimer. Another item of interest is the addition of two moles of trimethylamine to AlH_3 to give a compound containing a five-coordinated aluminum atom.[4,6]

Since no data for the amine derivatives of GaH_3 were found in the literature, it was of interest to prepare and

(1) F. G. A. Stone, *Advan. Inorg. Chem. Radiochem.*, **2**, 279 (1960).

(2) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960).

(3) E. Wiberg, H. Graf, and R. Uson, *Z. anorg. allgem. Chem.*, **272**, 221 (1953).

(4) E. Wiberg and H. Noth, *Z. Naturforsch.*, **10b**, 273 (1955).

(5) G. Schomburg and E. G. Hoffman, *Z. Elektrochem.*, **61**, 1101, 1110 (1957).

(6) C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, **2**, 508 (1963).

characterize typical amine gallanes. The properties of the trimethylamine–gallane addition compounds are compared in this paper with the known properties of the corresponding alane and borane adducts.

Experimental

The Preparation of $(CH_3)_3NGaH_3$.—Trimethylamine gallane was prepared in a standard high vacuum system[7] by the reaction

$$Li[GaH_4] + [(CH_3)_3NH]Cl \xrightarrow[\quad]{(C_2H_5)_2O} (CH_3)_3NGaH_3 + LiCl\downarrow + H_2\uparrow$$
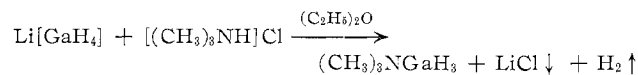
Similar reactions are common in the chemistry of LiAlH$_4$ and LiBH$_4$.[2,8–10]

Lithium gallium hydride used in the synthesis was prepared by the reaction of lithium hydride with gallium chloride as prescribed by Finholt, Bond, and Schlesinger.[11] For this purpose gallium trichloride was prepared by the reaction of HCl and Ga in a hot tube.[12]

Trimethylamine (Eastman anhydrous grade) was purified by shaking it with P$_2$O$_5$.[13] The resulting material was distilled from a trap held at $-78°$. The vapor pressure of the $(CH_3)_3N$ used was 682.5 mm. at $0°$; the literature value is 682 mm.[7] Diethyl ether and dimethyl ether were reagent grade materials which were dried over CaH$_2$ prior to use.

In a typical run a 2.06-g. portion of LiGaH$_4$ was stirred in the reaction tube of the vacuum filtration assembly[14a] with a mixture consisting of 12 ml. of dry $(C_2H_5)_2O$ and 2 ml. of liquid $(CH_3)_3$-N.[14b] The mixture was frozen with liquid N$_2$; the tube was flooded with dry N$_2$, opened, and a 2.18-g. sample of $(CH_3)_3$-NHCl was added. The system was reassembled and evacuated, and the reaction was initiated by allowing the system to warm slowly until gas evolution commenced. Excessive gas evolution was avoided by periodic cooling of the reaction tube. After the reaction subsided, the mixture was stirred for 2 hr. at $0°$. LiCl was filtered off[15] and solvent was removed under vacuum at temperatures ranging from -78 to $-45°$. The solid residue was sublimed from a trap at room temperature into a trap held at $-78°$. The 2.36-g. sample of $(CH_3)_3NGaH_3$ obtained represents a yield of 78% based on the LiGaH$_4$ used.

Characterization of $(CH_3)_3NGaH_3$.—The white sublimable solid obtained from the above process melts with slight decomposition in the range 68.9–69.8°, and decomposes slowly even at room temperature. It is soluble in $(C_2H_5)_2O$, $(CH_3)_2O$, Nujol, and $(CH_3)_3N$ and is vigorously hydrolyzed by water. Slow decomposition at room temperature precluded accurate vapor pressure determinations, but an approximate value of 2 mm. at $25°$ was obtained. The solid is best manipulated in a vacuum system and stored at $-78°$. To avoid contact with air and stopcock grease, samples of $(CH_3)_3NGaH_3$ for analysis or other precise manipulation were sublimed into the lower side of a diaphragm break-seal which was attached to the vacuum line by means of a ground glass joint. By means of the joint, the seal and its lead tube could be separated from the vacuum line and weighed before and after filling and sealing. The weight of the sample could thus be determined by difference. Since on the second weighing the sample tube section was evacuated, a buoyancy correction

(7) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, New York, N. Y., 1948.

(8) G. W. Schaeffer and E. R. Anderson, *J. Am. Chem. Soc.*, **71**, 2143 (1949).

(9) S. G. Shore and R. W. Parry, *ibid.*, **77**, 6084 (1955).

(10) J. M. Davidson and T. Wartik, *ibid.*, **82**, 5506 (1960).

(11) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

(12) W. C. Johnson and C. A. Haskew, *Inorg. Syn.*, **1**, 26 (1939).

(13) A. B. Burg, as quoted by J. R. Bright and W. C. Fernelius, *ibid.*, **2**, 159 (1946).

(14) (a) R. W. Parry, D. R. Schultz, and P. R. Girardot, *J. Am. Chem. Soc.*, **80**, 2 (1958); (b) $(CH_3)_3N$ in the ether made a small improvement in the yield but is not essential.

(15) Removal of LiCl by filtration is not essential, but it facilitates the subsequent sublimation of $(CH_3)_3NGaH_3$.

was applied in calculating the quantity of complex in the tube. Similar procedures are frequently used in vacuum line manipulation of reactive materials (ref. 7, p. 99).

Analyses.—Hydridic hydrogen was determined by distilling water onto a weighed sample in the vacuum line and measuring the volume of the hydrogen liberated. The identity of the H$_2$ was established by gas density and mass spectroscopic analysis. Gallium was determined by hydrolysis of a separate weighed sample in a Pyrex tube. Water was evaporated under an infrared lamp and the residue was dried to constant weight in a furnace at $350°$. The resulting Ga$_2$O$_3$ was weighed. Trimethylamine was determined by pyrolysis of $(CH_3)_3NGaH_3$ in a sealed tube at $150°$. The $(CH_3)_3N$ evolved was identified by vapor pressure, molecular weight, and infrared spectrum and measured as a gas in a calibrated volume on the vacuum line. *Anal.* Calcd. for $(CH_3)_3NGaH_3$: hydridic H, 2.29; $(CH_3)_3N$, 44.83; Ga, 52.88. Found: hydridic H, 2.30; $(CH_3)_3N$, 44.5; Ga, 52.76.

The molecular weight of $(CH_3)_3NGaH_3$ was determined by vapor pressure depression of $(CH_3)_2O$ solutions at $-31°$. Six separate measurements gave a value of 135 with a standard deviation of ± 5; theoretical for the monomer, 132.

X-Ray Diffraction and Density.—Sublimation of trimethylamine gallane into a capillary tube gave a finely divided crystalline mass. The resulting X-ray powder pattern is shown in Table I. In addition, a single crystal study was made on crystals

TABLE I

A Comparison of Observed and Calculated Interplanar Spacings for $(CH_3)_3NGaH_3$

Obsd. powder pattern		Calcd. for a rhombohedral lattice	
I/I_1	d exptl.,[a] Å.	d calcd.,[b] Å.	hkl
vvw[c]	5.21 K$_\beta$ [d]	5.22	100
	5.76	...	
s	5.21	5.22	100
vs	4.74	4.74	$10\bar{1}$
m	3.50	3.51	$11\bar{1}$
m	3.11	3.12	110
m	2.82	2.82	$20\bar{1}$
w	2.74	2.74	$11\bar{2}$
mw	2.60	2.61	200
w	2.37	2.37	$20\bar{2}$
w	2.28	2.28	$21\bar{1}$
w	2.24	2.25	111
mw	2.16	2.16	$21\bar{2}$
m	2.03	2.03	201
vvw	1.96	1.97	$11\bar{3}$
w	1.89	1.89	$30\bar{1}$
vw	1.82	1.82	$30\bar{2}$
vw	1.79	1.79	$21\bar{3}$
w	1.75	1.74	$22\bar{1}$

[a] Interplanar spacings calculated from the X-ray powder pattern; the copper Kα value of 1.5418 Å. was used for these calculations except as noted. [b] These interplanar spacings were calculated from unit cell parameters determined from single crystal X-ray patterns. [c] s, strong; m, medium; w, weak; v, very. [d] The two d-values presented here for the vvw line were calculated on the basis of Kβ and Kα radiation, respectively. Comparison with the next line in the table, s, shows that line one originated from incomplete elimination of the Kβ X-ray radiation.

grown in sealed capillaries. The single crystals were usually globular and twinned and most were not suited for study. The Buerger X-ray precession photographs of a selected crystal indicated a rhombohedral lattice with the following cell parameters: $a = 5.91$ Å. and $\alpha = 106°25'$. No systematic absences were observed in the reflections. One molecule per unit cell would be consistent with expected molecular dimensions and would give a calculated density of 1.254 g./cc.
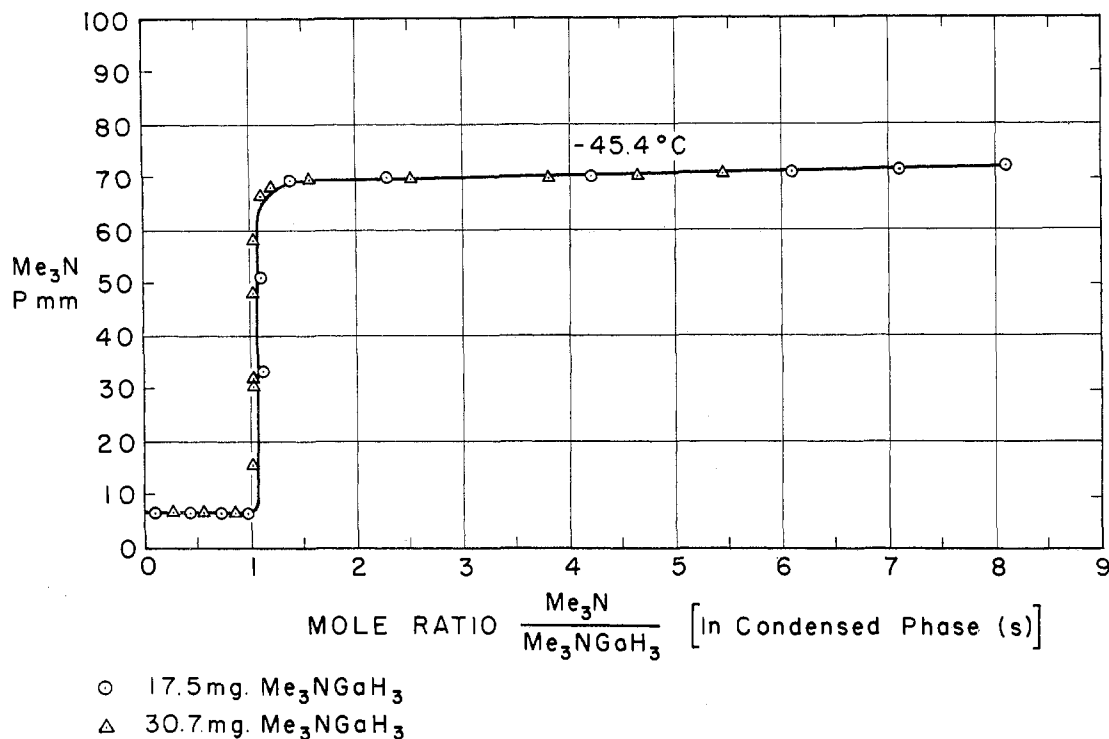
Figure 1.

For comparison, the density of trimethylamine gallane was determined experimentally. High reactivity and solubility of trimethylamine gallane precluded the use of methods which involve displacement of a liquid, so the volume of a weighed amount of solid was determined by displacement of purified nitrogen. An average density of 1.16 ± 0.10 g./cc. was found in five determinations. This experimental density is in reasonable agreement with the density calculated for one molecule per unit cell.

The rhombohedral cell constants obtained from the single crystal study were used to calculate interplanar spacings (d) in the crystal. The d-values from the X-ray powder investigation are in agreement with those calculated for a rhombohedral crystal.

The System $(CH_3)_3N-(CH_3)_3NGaH_3$. The Synthesis of $((CH_3)_3N)_2GaH_3$.—A study of the vapor pressure of excess trimethylamine above trimethylamine gallane revealed clearly the existence of the compound $((CH_3)_3N)_2GaH_3$ at temperatures of −45.4, −31.1, and −22.8°. Figure 1 shows a plot of trimethylamine pressure at −45.4° *vs.* the ratio: extra $(CH_3)_3N$/original $(CH_3)_3NGaH_3$. The vertical rise in the curve at the ratio 1 $(CH_3)_3N$ to 1 $(CH_3)_3NGaH_3$ and the constant pressure above the saturated trimethylamine solution at −45.4° indicate a compound $((CH_3)_3N)_2GaH_3$ which exists even in the amine solution. No evidence for higher amine adducts can be seen in the diagram (Fig. 1). The bistrimethylamine gallane is found also at −22.8°.

To obtain the data for Fig. 1 and related studies an evacuated sealed tube, equipped with a diaphragm break-seal and containing a weighed quantity of complex, was sealed to a mercury manometer equipped with a mercury inlet at the bottom of the U (ref. 7, p. 83). Before sealing, a stainless steel ball was placed in a side tube above the break-seal of the sample tube. The system was evacuated, the sample tube was cooled with liquid nitrogen, the break-seal was broken by manipulating the stainless steel ball with a magnet, and a measured quantity of $(CH_3)_3N$ was distilled in on top of the $(CH_3)_3NGaH_3$. Mercury was run into the U-tube manometer and the sample was warmed to −45.4° (chlorobenzene slush). The pressure was read at equilibrium. Constant volume in the sample bulb was achieved by manipulating the mercury level to a common fixed point on the sample side of the manometer. This volume of the tube was measured using dry nitrogen and the result was used to correct for $(CH_3)_3N$ in the

gas phase. Mercury in the manometer was kept free from stopcock grease by incorporating a coarse frit between the stopcock and the manometer (mercury passes through a coarse frit). The temperature of the slush bath during a run was −45.44 ± 0.05° as measured by an ammonia vapor pressure thermometer. In separate runs a bromobenzene slush was used to maintain a temperature of −31.05° and a carbon tetrachloride slush was used for a temperature of −22.76°. Both temperatures were measured with an SO_2 vapor pressure thermometer.

The apparent molecular weight of $(CH_3)_3NGaH_3$ in a large excess of $(CH_3)_3N$ was estimated by Raoult's law from vapor pressure depression of the solution. The vapor pressure of a sample of pure $(CH_3)_3N$ was measured by a tube dipped into the slush bath next to the sample container. This pressure was imposed on one side of the U manometer while that of the solution was imposed on the other and the desired ΔP value was read as the difference at −22°. The experimental value of 1.02 ± 0.03 g.-atoms of gallium associated with each mole of original $(CH_3)_3NGaH_3$ was obtained. This result taken in conjunction with the phase study indicates a monomer, $((CH_3)_3N)_2GaH_3$, in trimethylamine solution.

The vapor pressure of trimethylamine over $(CH_3)_3NGaH_3$ + $((CH_3)_3N)_2GaH_3$ was measured as a function of temperature. At least five determinations of the equilibrium pressure were made at each of three temperatures. Data are given in Table II. The standard enthalpy of this decomposition was found to be 11.54 ± 0.03 kcal./mole and the standard entropy of decomposition calculated at −31.05° was 41.1 ± 0.1 cal./mole-deg.

TABLE II

PRESSURE OF $(CH_3)_3N$ OVER $((CH_3)_3N)_2GaH_3$ + $(CH_3)_3NGaH_3$

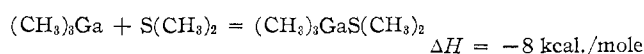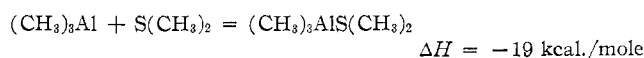| Pressure, mm.	Temperature, °C.
6.13 ± 0.09	−45.42 ± 0.05
28.49 ± 0.09	−31.05 ± 0.05
61.11 ± 0.09	−22.76 ± 0.05

Since the compound $((CH_3)_3N)_2GaH_3$ was visually observed to be a solid at −45 and at −22°, the equilibrium pressures of Table II represent the equilibrium constant for the reaction
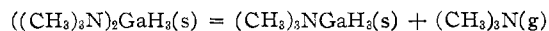
$$((CH_3)_3N)_2GaH_3(s) = (CH_3)_3NGaH_3(s) + (CH_3)_3N(g)$$

The standard enthalpy of this decomposition was found to be 11.54 ± 0.03 kcal./mole and the standard entropy of decomposition calculated at $-31.05°$ was 41.1 ± 0.1 cal./mole-deg. Values were obtained by using 17 P–T data points in a least squares computer program.

Discussion

The phase study indicated that a compound $((CH_3)_3\text{-}N)_2GaH_3$ is formed by the addition of $(CH_3)_3N$ to $(CH_3)_3NGaH_3$ at low temperatures. Comparison of this diadduct (dissociation pressure 6.1 mm. at $-45.4°$) with the similar aluminum diadduct, $((CH_3)_3N)_2AlH_3$, which can be sublimed at room temperature with only slight decomposition, clearly demonstrates the greater stability of the aluminum complex. A similar trend has been observed when comparing other gallium and aluminum addition compounds[16]

$(CH_3)_3Al + S(CH_3)_2 = (CH_3)_3AlS(CH_3)_2$
$$\Delta H = -19 \text{ kcal./mole}$$

$(CH_3)_3Ga + S(CH_3)_2 = (CH_3)_3GaS(CH_3)_2$
$$\Delta H = -8 \text{ kcal./mole}$$

From the monomeric nature of bistrimethylamine gallane in trimethylamine solution it is inferred that gallium in this compound is five-coordinated. While five-coordination is generally regarded as an oddity, a number of such compounds have recently been found in group three; examples include: "apex" boron atom(s) in B_5H_9 and $B_{10}H_{16}$[17] and aluminum in $((CH_3)_3\text{-}N)_2AlH_3$, $((CH_3)_3N)_2AlH_2X$, and $((CH_3)_3N)_2AlHX_2$ (X = Cl, Br, or I).[6,18]

Finally, $(CH_3)_3NGaH_3$ is much less stable than $(CH_3)_3\text{-}NBH_3$ and $(CH_3)_3NAlH_3$ with respect to decomposition into $(CH_3)_3N$, hydrogen, and the metal. This trend in stability is consistent with the general instability of hydrides of the heavier elements.

A comparison of the infrared and Raman absorption frequencies for $H_3BN(CH_3)_3$, $H_3AlN(CH_3)_3$, and $H_3\text{-}GaN(CH_3)_3$ has been reported elsewhere.[19] Stretching frequencies decrease in the order B–H, Ga–H, Al–H, but deformation frequencies increase in the order B–H, Al–H, Ga–H. A simple explanation for these trends is not apparent, but it is interesting that Ga–H stretching frequencies (1852 cm.$^{-1}$) fall much closer to those of

Al–H (1788 cm.$^{-1}$) than to those of B–H (2384 cm.$^{-1}$).

Interesting structural comparisons can also be made. In dimethyl ether the molecular weight of $(CH_3)_3\text{-}NGaH_3$ corresponds to a monomer; in this respect it is similar to $(CH_3)_3NAlH_3$, which is monomeric in diethyl ether solution.[3] It can be shown, however, that a hydrogen bridge structure like the one proposed for dimeric trimethylamine alane in benzene solution does not occur in solid trimethylamine gallane. The observed density and unit cell size for $(CH_3)_3NGaH_3$ indicate one molecule per unit cell. Thus, molecules must be related by translations; a condition which rules out structures such as[20]
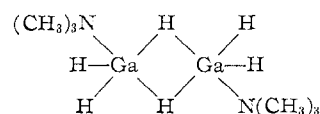
It is possible to visualize highly polymeric bridge structures in which $(CH_3)_3NGaH_3$ units are related by translations—for example
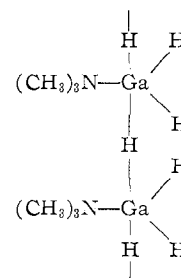
Such structures may be ruled out on one or more of the following grounds: (1) Unusually long Ga–H distances (2.96 Å. or larger) would be required. (2) Sterically improbable arrangements of the atoms would result. (3) Threefold symmetry would be lacking.

In keeping with the X-ray evidence, the Raman spectrum of solid trimethylamine gallane is interpretable in terms of C_{3v} point symmetry for the molecule.[19] From these considerations a crystal containing discrete molecular units in a "head to tail" arrangement is favored. A detailed X-ray structure determination is in progress.

(16) G. E. Coates, "Organo-Metallic Compounds," 2nd Ed., Methuen, London, 1960, p. 149.

(17) R. Grimes, F. F. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, **47**, 996 (1961).

(18) E. Wiberg, K. Moedritzer, and R. U. Lacal, *Rev. acad. cienc. exact. fis.-quim. nat. Zaragoza*, **9**, 91 (1954), as quoted in *Chem. Abstr.*, **52**, 3583i (1958).

(19) D. F. Shriver, R. Amster, and R. C. Taylor, *J. Am. Chem. Soc.*, **84**, 1321 (1962).

(20) This structure is also unlikely on other grounds. In the absence of a highly disordered structure the molecular unit should possess a threefold axis to conform with the point symmetry of the lattice.