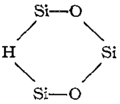
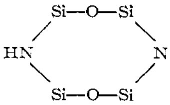
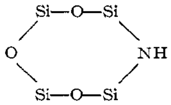
Table I

	[Si(CH₃)₂NH]₃		[Si(CH₃)₂]₃	[Si(CH₃)₂NH]₄			[Si(CH₃)₂O]₄
ν_{as} Si—O—Si, cm.$^{-1}$	...	1022	1022	...	1050	1065 1025	1078
Calcd. bond angle	...	124°	124°	...	132°	137° 125°	141.5°
Found bond angle	...	...	125 ± 5°	...	...	...	142.5 ± 5°
ν_{as} Si—N—Si, cm.$^{-1}$	928	978	...	938	938	928	...
Calcd. bond angle	118.5°	133.3°	...	121.3°	121.3°	118.8°	...
Found bond angle	117 ± 4°	...	...	123 ± 4°	...	...	...

larger cyclosiloxane rings, but has not been explained up to now.

The n.m.r. spectra of the substances prepared in this study are without any peculiarity. As is to be expected, I shows only one sharp signal at 4 c.p.s. ($\delta = 0.067$) because of the identical surrounding of the methyl groups, whereas compound III shows two equal signals at 3 c.p.s. ($\delta = 0.05$) and 5.1 c.p.s. ($\delta = 0.085$).

Comparison with the chemical shifts of compounds which contain only one kind of Si–X–Si bond allows an assignment. Hexamethylcyclotrisilazane absorbs at 3.2 c.p.s. (60 Mc.) ($\delta = 0.053$), whereas the corresponding tetramer shows absorption at 2.8 c.p.s. ($\delta = 0.047$). Hexamethylcyclotrisiloxane shows a shift of 7 c.p.s. ($\delta = 0.117$). The more downfield absorption of compound III is therefore due to the methyl groups in a pure siloxane neighborhood, whereas the higher frequency is due to the methyl groups near adjacent siloxane and silazane groups. Compound II surprisingly shows no splitting of its one signal at 6.2 c.p.s. ($\delta = 0.104$), but this signal is extraordinarily broadened. Probably this band should show splitting at higher resolution. Compounds I–III show an interesting behavior in broadline n.m.r. at different temperatures which will be reported elsewhere.

Infrared spectra were taken with a Perkin-Elmer Model 221 spectrograph, using either capillaries or CCl_4 solutions; n.m.r. spectra were taken in CCl_4 solution using tetramethylsilane as internal standard, with a Varian A-60 high resolution spectrometer.

Acknowledgment.—Financial support of this work by the Advanced Research Projects Administration by contract with Harvard University is gratefully acknowledged.

Notes

Joint Contribution from the Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois, and the Department of Chemistry, University of Michigan, Ann Arbor, Michigan

The Crystal Structure of Trimethylamine Gallane, $(CH_3)_3NGaH_3$

By D. F. Shriver and C. E. Nordman

Received February 28, 1963

Recently trimethylamine gallane was independently prepared in two different laboratories by the reaction of lithium gallium hydride with trimethylammonium chloride.[1,2]

$$LiGaH_4 + (CH_3)_3NHCl = LiCl + H_2 + (CH_3)_3NGaH_3$$

Raman spectra of the solid[3] and infrared spectra of the gas[4] were interpretable in terms of a *monomer* with C_{3v} symmetry analogous to the well known $(CH_3)_3NBH_3$. By contrast aluminum, the element between boron and gallium in the periodic table, is thought to form hydrogen-bridged dimers in benzene solutions of the compound $(CH_3)_3NAlH_3$.[5–8]

The present study was undertaken to confirm positively the monomeric nature of $(CH_3)_3NGaH_3$ and to obtain the molecular parameters which are of interest in the interpretation of Lewis salt formation.

Experimental

Crystals were prepared by sublimation of the compound into thin-walled Pyrex capillaries which subsequently were sealed under vacuum. The resulting multicrystalline mass was suitable for obtaining a Debye–Sherrer X-ray pattern, which has been reported elsewhere.[1] Single crystals were grown in the sealed capillary by slow sublimation in a small thermal gradient at room temperature. The resulting crystals were globular and usually imperfect. Out of a large number of such crystals only two

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[1] D. F. Shriver and R. W. Parry, *Inorg. Chem.*, **2**, 1039 (1963).

[2] N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *ibid.*, **2**, 1036 (1963).

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

[4] N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Proc. Chem. Soc.*, 249 (1962).

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

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

[7] E. Wiberg, H. Graf, M. Schmidt, and R. Uson, *Z. Naturforsch.*, **7b**, 278 (1952).

[8] G. Schomburg and E. G. Hoffmann, *Z. Elektrochem.*, **61**, 1101, 1110 (1957). These authors believe dimerization occurs through dipole-dipole interaction.

were suitable for X-ray investigation. The crystals were first characterized as monoclinic. However, after the last crystal had decomposed it was found that the four monoclinic cell parameters could, within experimental error, be accounted for in terms of a rhombohedral unit cell. A check of the distribution of diffracted intensities in reciprocal space unambiguously supported the threefold symmetry. Thus the lattice is rhombohedral. There is one molecule per unit cell for which $a = 5.91$ Å., $\alpha = 106°25'$, corresponding to a cell volume of 174.6 Å.^{3} and a calculated density of 1.254 g. cm.$^{-3}$. The most probable space group, R3m (C^5_{3v}), was confirmed by the subsequent structure analysis. A set of intensity data was first obtained by simple rotation technique with Cu Kα radiation. Another set was collected on a Buerger precession camera with Mo Kα radiation.

After about 1 week data collection was stopped due to decomposition of the crystal. In view of the difficulties of obtaining usable crystals it was decided to proceed with the structure determination using incomplete data.

Structure Determination

Intensities were determined visually by comparison with a standard scale of timed exposures. Overlapping reflections on the rotation photographs were not recorded. Lorentz and polarization corrections were performed, after which data from the various nets were put on a common scale. No absorption corrections were applied.

In the absence of extensive disorder and with the assumption of C_{3v} molecular symmetry, the structure should involve coincidence of the Ga–N molecular axis with the threefold unit cell axis. However, methyl groups in the trimethylamine part of the molecule may either point toward the edges or toward the faces of the rhombohedral unit cell. In view of the relatively rapid fall-off of intensities for successive orders of diffraction it was also possible that the methyl groups were disordered around the threefold symmetry axis. A more drastic disorder involving end-to-end randomness of the directions of the molecule axes was unlikely in view of the polar nature of the molecules. Also, such a disorder probably would have caused a more rapid fall-off in the intensities than was observed.

As a first approximation to the structure only the Ga atom was included, at the origin of the cell. Least squares refinement of its anisotropic thermal parameters led to a value of $R = 0.15$ and showed that the directions of greatest amplitude of thermal motion are perpendicular to the threefold axis. An end-to-end disorder in the orientation of the molecules would cause the mean gallium position to be spread out in the direction of the threefold (or molecular) axis. Thus the observed anisotropy contradicts such a disorder.

Next, a difference Fourier synthesis was computed with the Ga contributions subtracted from the observed structure factors. This function, which was necessarily centrosymmetric, revealed the gross features of the trimethylamine group on the threefold axis. It also suggested a partial disorder in the methyl positions corresponding to two possible orientations of the trimethylamine groups, somewhat unequally populated and 60° apart, about the threefold symmetry axis. The nitrogen and carbon atoms were now included, with isotropic thermal parameters, and two different models were further refined. In one model the carbons were assumed to be ordered, with the methyl groups pointing toward the faces of the unit cell. In the other model six half-carbons were assumed to occupy these positions and three additional positions, pointing toward the edges of the cell, and corresponding to a 60° rotation of the trimethylamine group. The first of these models refined to $R = 0.11$. The second gave $R = 0.12$, and widely different thermal parameters for the two half-carbons, showing that the methyl positions pointing toward the cell faces were significantly more occupied than the others. Since the experimental data did not seem to warrant a more detailed description, all subsequent calculations and the evaluation of molecular parameters were based on the ordered model. Methyl hydrogens in an assumed, doughnut-shaped arrangement about the molecular axis were included with high thermal parameters. Continued refinement of the Ga, N, and C parameters resulted in very minor shifts and a final R-factor of 0.105.

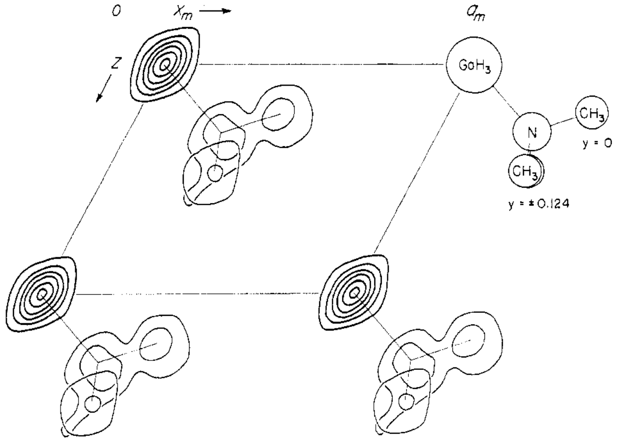

Fig. 1.—The crystal structure of $(CH_3)_3NGaH_3$ viewed perpendicular to a mirror plane, showing sections of the electron density function at $y_m = 0.000$ and 0.117. The Ga atom peaks are contoured at 5, 10 . . ., 30 electrons Å.$^{-3}$. The trimethylamine peaks, computed by a Fourier synthesis with the Ga contribution removed, are contoured at 1.25 and 2.5 electrons Å.$^{-3}$.

Atomic scattering factors for these calculations were those of Berghuis, *et al.*,[9] for carbon and nitrogen, while the scattering factor for gallium was taken from the compilation of Thomas and Umeda.[10] No corrections for anomalous dispersion were applied. The observed and final calculated structure factor magnitudes are listed in Table I.

Discussion

A composite electron density map is shown in Fig. 1, and atomic parameters are presented in Table II. In both the figure and table, atomic positions are alternatively referred to a monoclinic unit cell with two

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(9) J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta. Cryst.*, **8**, 478 (1955).

(10) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

Table I

Observed and Calculated Structure Amplitudes[a]

hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$
000	--	68.0	$31\bar{3}$	8.9	9.4	$4\bar{1}\bar{3}$	8.1	7.6
100	24.6	20.9	$3\bar{1}\bar{1}$	13.7	12.9	420	7.4	7.2
$10\bar{1}$	36.9	36.3	$3\bar{1}\bar{2}$	12.8	12.9	421	4.8	6.6
110	28.3	22.7	320	8.0	9.9	422	8.2	5.4
$11\bar{1}$	25.9	24.2	321	9.8	9.9	$42\bar{1}$	5.3	6.1
200	21.6	21.1	$32\bar{1}$	10.5	12.0	$42\bar{3}$	8.6	6.1
$20\bar{1}$	18.6	19.4	$32\bar{2}$	11.1	11.3	$4\bar{2}\bar{2}$	9.0	7.1
$20\bar{2}$	16.6	17.0	$3\bar{2}\bar{2}$	13.0	12.1	$4\bar{2}\bar{3}$	8.0	5.9
210	24.7	20.6	330	6.3	7.7	431	4.9	4.6
211	15.9	14.6	331	5.3	6.8	500	3.7	5.8
$21\bar{1}$	14.4	14.7	332	9.2	5.9	$50\bar{1}$	5.7	6.3
$21\bar{2}$	20.0	20.1	$33\bar{1}$	5.8	6.2	$50\bar{2}$	6.0	5.8
$2\bar{1}\bar{1}$	18.9	20.2	400	10.1	10.9	$50\bar{3}$	3.7	4.6
220	14.7	14.4	$40\bar{1}$	7.5	8.8	510	5.2	5.1
221	14.9	13.3	$40\bar{2}$	8.7	8.7	$51\bar{1}$	6.5	5.7
222	10.3	10.5	$40\bar{3}$	5.8	5.9	$51\bar{2}$	5.2	4.8
$22\bar{1}$	12.6	16.9	$40\bar{4}$	6.6	6.4	$51\bar{4}$	4.8	3.2
$22\bar{2}$	16.6	16.7	410	7.0	8.4	$5\bar{1}\bar{3}$	5.9	4.5
300	13.1	13.2	411	9.3	7.7	520	7.8	4.8
$30\bar{1}$	13.4	15.5	$41\bar{1}$	8.2	9.3	521	5.8	4.1
$30\bar{2}$	12.0	12.2	$41\bar{2}$	7.3	8.9	$52\bar{1}$	6.0	4.8
$30\bar{3}$	12.2	11.7	$41\bar{3}$	10.0	6.5	$52\bar{2}$	7.0	4.5
310	13.8	13.9	$41\bar{4}$	4.4	4.5	$5\bar{2}\bar{3}$	4.0	3.8
311	12.2	11.8	$4\bar{1}\bar{1}$	9.9	10.0	531	5.6	4.9
$31\bar{1}$	12.2	13.7	$4\bar{1}\bar{2}$	9.2	8.0	$61\bar{2}$	4.3	3.2
$31\bar{2}$	9.5	9.8						

[a] Rhombohedral indexing.

Table II

Atomic Parameters and Estimated Standard Deviations[a]

Rhombohedral cell

	x_r	y_r	z_r	β	
Ga	0	0	0	2.0 ± 0.4	∥ 3-fold axis
				6.1 ± 1.1	⊥ 3-fold axis
N	0.294 ± 0.015	0.294	0.294	10.9 ± 3.8	
C	0.462 ± 0.016	0.462	0.215 ± 0.013	10.1 ± 1.8	

Monoclinic cell: (0,0,0; $^1/_2$, $^1/_2$, 0) +

	x_m	y_m	z_m
Ga	0	0	0
N	0.294	0	0.294
C	.462	0	.215
2C′	.339	±0.124	.462

[a] Standard deviations are explicitly stated for the symmetrically independent parameters only.

molecules per unit cell and belonging to space group Cm(C_s^3), with

$$a_m = 7.08\ \text{Å.} = a_r + b_r$$

$$b_m = 9.46\ \text{Å.} = -a_r + b_r$$

$$c_m = 5.91\ \text{Å.} = c_r$$

$$\beta_m = 118°35'$$

The standard deviations given in Table II were estimated by dividing the set of 75 independent $F_o(hkl)$'s into three parts of 25 each, refining each part separately, and analyzing the spread of the resulting values of the parameters. The high values of the standard deviations reflect the loss of accuracy generally experienced in light-atom parameters in the presence of heavy atoms, as well as the quantitative and qualitative shortcomings of the available experimental data.

The gallium–gallium distance (5.91 Å.) and the fact that the structure contains only one Ga per lattice point preclude a hydrogen-bridge structure and thus confirm previous conclusions. The Ga–N distance 1.97 Å. with an estimated standard deviation of ±0.09 Å. is slightly larger than 1.94 Å. reported for this distance in gallium nitride.[11] Because of the large uncertainty in our Ga–N distance, firm conclusions cannot be drawn from this difference; however, it is noteworthy that the B–N distance in trimethylamine boron trifluoride (1.585 Å.)[12] is longer than in cubic boron nitride (1.565 Å.).[13] The compound $((CH_3)_3N)_2AlH_3$ has been investigated and found to have a linear N–Al–N skeleton with an Al–N bond distance of 2.18 Å.,[14] which is longer than that found for Ga–N in this study. This result is consistent with the similarity of gallium and aluminum covalent radii coupled with the unstable five-coordinated structure of bistrimethylamine alane.

Finally, the average N–C distance, 1.47 ± 0.06 Å., and C–N–C angle, 105 ± 10°, are, within their limits of accuracy, consistent with previous observations on the trimethylamine addition compound of boron trifluoride.

Acknowledgment.—Work performed at the University of Michigan was supported by the National Science Foundation, while that at Northwestern University was sponsored by the Advanced Research Projects Agency of the Department of Defense through the Northwestern Materials Research Center.

D. F. S. wishes to thank Dr. K. Nakatsu for frequent advice and S. Shriver for assistance with the calculations.

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(12) J. L. Hoard, S. Geller, and T. B. Owen, *Acta Cryst.*, **4**, 405 (1951).

(13) R. H. Wentorf, Jr., *J. Chem. Phys.*, **26**, 956 (1957).

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

Contribution from the Dow Chemical
Company, Midland, Michigan

Preparation of Nitryl Fluoride[1]

By Ralph A. Davis and Douglas A. Rausch

Received May 10, 1963

Since Moissan and Lebeau[2] first claimed to have prepared nitryl fluoride in 1905, many improved methods for the preparation of this compound have been developed and the literature pertaining to the various methods has been excellently reviewed.[3,4]

Although Ruff, Menzel, and Neumann[5] prepared

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(1) This work was supported by the Advanced Research Projects Agency under Contract AF 33(616)-6149, ARPA Order 24-61, Project Code 9100.

(2) H. Moissan and P. Lebeau, *Compt. rend.*, **140**, 1621 (1905).

(3) G. Hetherington and P. L. Robinson, "Recent Aspects of the Chemistry of Nitrogen," Special Publication No. 10, The Chemical Society, London, 1957, p. 23.

(4) C. J. Hoffman and R. G. Neville, *Chem. Rev.*, **62**, 1 (1962).

(5) O. Ruff, W. Menzel, and W. Neumann, *Z. anorg. allgem. Chem.*, **208**, 293 (1932).