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Notes

Hydrazide Derivatives of Gallium

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Introduction

Gallium nitride (GaN) continues to generate significant interest for applications in high luminosity light-emitting diodes and high speed, high power devices that are both radiation resistant and capable of operation at elevated temperatures.[1] In the context of metalorganic chemical vapor deposition (MOCVD) techniques, the most successful current approach to GaN involves the reaction of trimethylgallium or triethylgallium with ammonia at temperatures in excess of 900 °C.[2] Such elevated growth temperatures, however, result in thermal stresses in the cooling films as well as loss of stoichiometry due to nitrogen deficiency. Hydrazine[3] and dimethylhydrazine[4] have been proposed as alternative sources to ammonia for the lower temperature growth of GaN films. In order to explore further the utility of hydrazine as a nitrogen delivery source, we have synthesized a potential new class of single-source GaN precursor[5] that incorporates hydrazide moieties.

Results and Discussion

The colorless crystalline gallium hydrazides **1** and **2** were prepared in >60% yields *via* the reaction of the appropriate dialkylgallium chloride and lithium hydrazide as summarized:

$$\mathrm{Me_2GaCl + Me_2NNHLi \xrightarrow[-LiCl]{Et_2O,\ -78\ ^{\circ}C}}$$

$$\mathrm{{}^{1}/_{3}[Me_2Ga\text{-}\mu\text{-}N(H)NMe_2]_3}$$

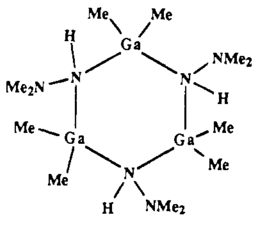
1

$$\mathrm{Et_2GaCl + Ph_2NNHLi \xrightarrow[-LiCl]{Et_2O,\ -78\ ^{\circ}C}}$$

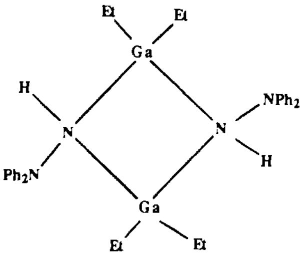
$$\mathrm{{}^{1}/_{2}[Et_2Ga\text{-}\mu\text{-}N(H)NPh_2]_2}$$

2

To our knowledge, **1** and **2** constitute the first examples of gallium hydrazides. However, aluminum hydrazides such as $[\mathrm{Me_2Al\text{-}\mu\text{-}N(H)NMe_2}]_2$ and $[\mathrm{Me_2Al\text{-}\mu\text{-}N(H)NMe_2}]_2$ are known, but not structurally authenticated.[6] Unfortunately, the crystals of **1** proved to be unsuitable for X-ray diffraction experiments. However, the trimeric nature of **1** was suggested by the CI mass spectrum which exhibits a parent peak at *m/z* 475, followed by fragmentation peaks that correspond to the loss of Me and $\mathrm{N(H)NMe_2}$ units. The identity of the M^+ peak for the trimer was confirmed by HRMS. The equivalence of the ^1H and $^{13}C\{^1H\}$ NMR resonances for both the $\mathrm{GaMe_2}$ and $\mathrm{N(H)NMe_2}$ moieties suggested the symmetrical cyclic structures:



1



2

Such a conclusion gains support from the fact that **2** was shown to possess a similar (albeit dimeric) structure by X-ray crystallography. The initial indication of a dimeric formulation for **2** stemmed from the observation of a sharp cut-off in the CI mass spectrum at *m/z* 622, followed by a series of fragmentations attributable to the loss of Et and $\mathrm{NPh_2}$ groups. The symmetrical nature of the proposed structure was indicated by the ^1H and $^{13}C\{^1H\}$ NMR spectral equivalence of the $\mathrm{GaEt_2}$ and $\mathrm{N(H)NPh_2}$ moieties. Confirmation of the dimeric structure was provided by X-ray crystallography (Figure 1 and Table 1). The $\mathrm{Ga_2N_2}$ ring is planar within experimental error (sum of bond angles = 360.0(3)°) and the average endocyclic angle at nitrogen (94.0(3)°) is larger than that at gallium (86.1(3)°). Such a trend in bond angles is, in fact, a structural feature of the $\mathrm{M_2E_2}$ cores of virtually all group 13/15 dimers or this general type.[7] Within experimental error the average Ga−N bond distance in the $\mathrm{Ga_2N_2}$ ring of **1** (2.054(7) Å) is identical to that in $[t\text{-}\mathrm{Bu_2Ga}(\mu\text{-}\mathrm{NHPh})]_2$ (2.060(9) Å)[8] but somewhat longer than those in

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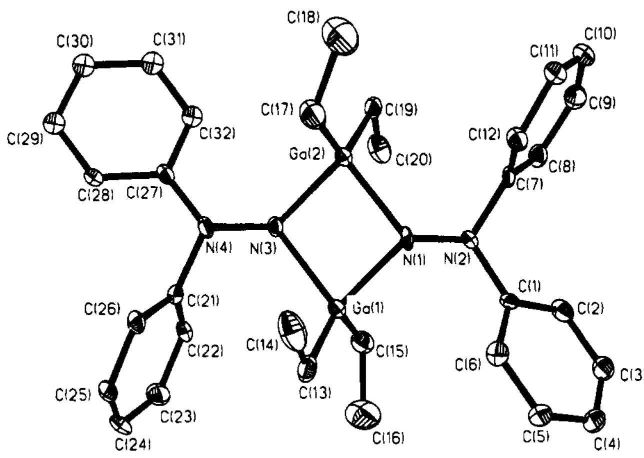

Figure 1. Structure of $[Et_2Ga\text{-}\mu\text{-}N(H)Ph_2]_2$ (**2**) in the crystal showing the atom numbering scheme; thermal ellipsoids are at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2**

Ga(1)−N(1)	2.046(7)	Ga(2)−N(3)	2.060(7)
Ga(1)−N(3)	2.070(7)	N(1)−N(2)	1.457(8)
Ga(2)−N(1)	2.042(7)	N(3)−N(4)	1.446(8)
N(1)−Ga(1)−N(3)	85.8(3)	N(1)−N(2)−C(7)	112.0(6)
Ga(1)−N(1)−Ga(2)	94.6(3)	C(1)−N(2)−C(7)	114.9(6)
N(1)−Ga(2)−N(3)	86.2(3)	N(3)−N(4)−C(21)	112.6(6)
Ga(2)−N(3)−Ga(1)	93.4(3)	N(3)−N(4)−C(27)	116.7(6)
N(1)−N(2)−C(1)	113.4(6)	C(21)−N(4)−C(27)	116.0(6)

other dimers such as $[(Me_2N)_2Ga(\mu\text{-}NMe_2)]_2$ (2.005(2) Å),[9] $[Me_2NGaH_2]_2$ (2.027(4) Å)[10] and $[t\text{-}Bu(H)NGa(\mu\text{-}N(H)\text{-}t\text{-}Bu)]_2$ (2.008(8) Å).[11] The hydrazide hydrogen atoms were located from difference Fourier maps and refined with fixed isotropic parameters. Nitrogen atoms N(2) and N(4) adopt somewhat flattened pyramidal geometries (sums of angles = 340.3(6) and 345.3(6)°, respectively), and these nitrogen lone pairs are arranged in a *trans* fashion with respect to the hydrogen atoms on N(1) and N(3). The average N−N bond distance is 1.453(8) Å.

Mass spectrometric monitoring of the pyrolysis of **1**[12] revealed that decomposition commences at 260 °C. Moreover, in the temperature range 260−500 °C, the signals corresponding to $[Me_2GaNH(NMe_2)]^+$ and $[NH(NMe_2)]^+$ decrease in intensity with increasing temperature while that of $[GaMe_2]^+$ increases, thus leading to the conclusion that the primary decomposition mode involves rupture of the Ga−N bonds. It is possible to deposit thin films (3−4 μm) of wurzitic gallium nitride from **1** at 580 °C (1×10^{-4} Torr) on gallium arsenide or sapphire substrates by means of chemical beam epitaxy.[12] However, examination of these films by scanning electron microscopy revealed particulate surfaces and poor surface morphologies. Moreover, the films diffracted X-rays weakly indicating their primarily amorphous nature.

Experimental Section

General Conditions. All manipulations were carried out under a purified argon atmosphere using standard Schlenk line or drybox techniques. Diethyl ether and hexane were distilled from sodium benzophenone ketyl before use. 1,1-Dimethylhydrazine was dried over CaH_2 and distilled before use.

Table 2. Crystal Data, Data Collection, and Refinement of the Structures of **2**

formula	$C_{32}H_{42}Ga_2N_4$
fw	622.14
cryst syst	monoclinic
cryst size, mm	0.09 × 0.28 × 0.52
space group	$P2_1/n$
a, Å	10.312(1)
b, Å	14.201(2)
c, Å	21.024(4)
β,deg	92.81(1)
V, Å^3	3075.1(8)
Z	4
d(calcd),g cm^{-3}	1.344
μ, cm^{-1}	17.79
index ranges	$-2 < h < 11$, $-5 < k < 16$, $-23 < l < 23$
scan range, deg	4.0 to 47.5
no. of indep. reflcns	4684
abs cor	SHELXA
min/max transm	0.25634/0.87605
params refined	353
R1/wR2,[a] %	6.44, 14.00
S	1.035

[a] $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. Weight $= 1/[\sigma^2(F_o^2) + (0.0400P)^2]$ where $P = (\mathrm{Max}\,(F_o^2, 0) + 2F_c^2)/3$.

Caution! The residues from the $Me_2NN(H)Li$ and $Ph_2NN(H)Li$ preparations discussed below are pyrophoric.

Physical Measurements. NMR spectra were recorded on a General Electric QE 300 spectrometer. The chemical shifts for ^1H (300.17 MHz) and ^{13}C (75.48 MHz) NMR spectra were referenced to solvent signals. Mass spectra were recorded on Bell and Howell CEC 24-491 and Finnigan MAT 4023 (70 eV, CI) instruments. Liquid and solid samples were loaded in capillary tubes and introduced *via* a direct insertion probe. IR spectra were obtained on a BioRad FTS-40 spectrometer. Melting points were determined in sealed capillary tubes with a Mel-Temp melting point apparatus and are uncorrected.

X-ray Crystallography. Selected bond length and angles for $[Et_2Ga\text{-}\mu\text{-}N(H)NPh_2]_2$ (**2**) are given in Table 1. Crystals of **2** were mounted on thin glass fibers under mineral oil. The data set was collected on a Siemens P4 diffractometer at −100 °C using Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods[13] and refined on F^2.[14] A summary of crystal data and structure refinement is presented in Table 2. Scattering factors are included in the software package.[14]

Synthesis of $[Me_2Ga\text{-}\mu\text{-}N(H)NMe_2]_3$ (1). A solution of *n*-BuLi (18.0 mL, 1.6 M hexane solution, 0.0288 mol) was added to a stirred solution of 1,1-dimethylhydrazine (1.70 g, 0.0283 mol) in Et_2O solution at −78 °C. The reaction mixture was allowed to warm to 25 °C and stirred for 6 h. The resulting $Me_2NN(H)Li$ solution was added dropwise to a stirred solution of Me_2GaCl in Et_2O solution at −78 °C. The reaction mixture was allowed to warm to 25 °C and was stirred overnight. Removal of the solvent resulted in a white precipitate which was extracted with pentane and filtered. Storage of the filtrate overnight at −20 °C afforded 1.53 g of colorless, microcrystalline **1**. Yield 69%, mp = 57−60 °C. ^1H NMR (300.15 MHz, C_6D_6): δ 2.76 (s, N*H*), 1.89 (s, 6H, N-C*H*$_3$), −0.21 (br s, 6H, Ga-C*H*$_3$), $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6): δ 49.5 (br s, N−*C*H$_3$), −6.6 (s, Ga−*C*H$_3$). HRMS (CI, M = $C_{12}H_{36}N_6{}^{69}Ga^{71}Ga_2$): 475.079574 (475.075128). MS (CI): *m/z* 475 (M), 461 (M − CH_3), 417 (M − $N(H)N(CH_3)_2$), 316 ($[(CH_3)_2GaN(H)N(CH_3)_2]_2$), 301 ($[(CH_3)_2GaN(H)N(CH_3)_2]_2 - CH_3$). IR (NaCl plates); 3247 (w), 3121 (w), 2955 (s, sh), 2921 (s), 2851 (s), 2814 (m, sh), 2766 (m), 1460 (s), 1378 (m), 1306 (w), 1260 (w), 1240 (w), 1202 (s), 1152 (w), 1093 (w), 1013 (m), 883 (m), 826 (m), 737 (m), 641 (w).

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Synthesis of [Et_2Ga-μ-N(H)NPh_2]$_2$ (2). A solution of *n*-BuLi (18.4 mL, 1.6 M hexane solution, 0.0368 mole,) was added to a stirred solution of 1,1-diphenylhydrazine hydrochloride (4.06 g, 0.0184 mol) in Et_2O solution at −78 °C. The reaction mixture was allowed to warm to 25 °C and was stirred for 6 h. The $Ph_2NN(H)Li$ solution was added dropwise to a stirred solution of Et_2GaCl (3.0 g, 0.0184 mol) in Et_2O solution at −78 °C. The stirred reaction mixture was allowed to warm to 25 °C overnight. Removal of the solvent resulted in a white precipitate which was extracted with pentane and filtered. Storage of the filtrate at −20 °C afforded 3.65 g of colorless, crystalline **2**. Yield: 64%; mp = 116−118 °C. ^1H NMR (C_6D_6): δ 7.08 (m, 6H, C*H*), 6.84 (m, 4H, C*H*), 3.51 (s, 2H, N*H*), 1.18 (t, 6H, CH_3), 0.60 (m, 4H, Ga-CH_2), $^{13}C\{^1H\}$ NMR (C_6D_6) δ 149.5 (s, N−*C*), 129.2 (s, *m*-*C*H), 122.3 (s, *p*-*C*H), 120.0 (s, *o*-*C*H), 10.8 (s, CH_3), 4.3 (s, CH_2). MS (CI, CH_4), M = [($Et_2GaN(H)NPh_2$)]$_2$: *m/z* 622 (M + 2H), 593 (M − C_2H_5 + 2H), 439 (M − $NNPh_2$ − H), 339 ($Et_2GaN(H)NPh_2$ + Et), 311 ($Et_2GaNNPh_2$). HRMS (CI-, CH_4, $C_{32}H_{41}N_4{}^{69}Ga^{71}Ga$) 621.186121 (621.183404). IR (KBr plates): 3343 (w), 3178 (w), 3061 (w), 3037 (w), 2936 (m), 2901 (m), 2864 (m), 2819 (w, sh), 2725 (w), 1588 (s), 1492 (s), 1452 (w, sh), 1311 (w), 1259 (m), 1184 (w), 1001 (w), 851 (w), 751 (m), 693 (m), 662 (w, sh), 560 (w), 509 (w).

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Supporting Information Available: Text giving experimental details for the synthesis of **1** and **2** and tables of crystallographic data, atomic coordinates, thermal parameters, bond distances, and bond angles for **2** (9 pages). Ordering information is given on any current masthead page.

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