1,1-Dimethylhydrazidogallane and a gallium hydrazide with two Ga_2N_2 rings bridged by two $NNMe_2$ ligands

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Volatile, thermally robust 1,1-dimethylhydrazidogallane, $[H_2GaN(H)NMe_2]_2$ 1 has been synthesized from the reaction of $H_3Ga(NMe_3)$ with H_2NNMe_2, whereas reaction of compound 1 with an excess of H_2NNMe_2 at elevated temperature afforded a gallium hydrazide derivative, $Ga_4[N(H)NMe_2]_8(NNMe_2)_2$ 2, which possessed a novel structure of two Ga_2N_2 rings bridged by $NNMe_2$ groups.

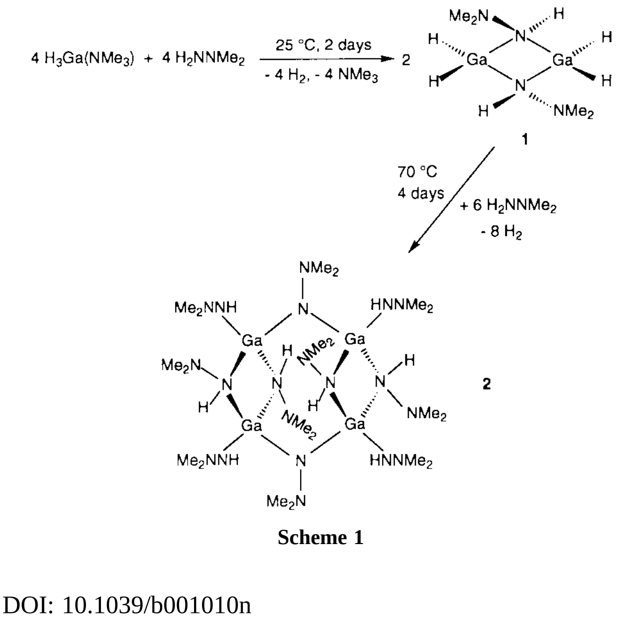
Gallium hydride derivatives with direct Ga–N bonds are attractive single-source precursors to gallium nitride. Two main advantages of these compounds over conventional precursors, such as trimethylgallium and triethylgallium, which are extensively used in MOCVD processes, are minimization of carbon contamination and reduction of deposition temperatures. We[1,2] and others[3,4] have reported that compounds with the above features, $(H_2GaNH_2)_3$ and $(H_2GaN_3)_n$, formed nanocrystalline GaN or GaN films at low temperatures. Related triazidogallium derivatives have also produced GaN nanoparticles.[5] Here, we report the syntheses and structures of a volatile, thermally robust dimeric 1,1-dimethylhydrazidogallane, $[H_2GaN(H)NMe_2]_2$ **1**, and a gallium hydrazide derivative with two Ga_2N_2 rings bridged by $NNMe_2$ groups, $Ga_4[N(H)NMe_2]_8(NNMe_2)_2$ **2**.

Hydrazine and 1,1-dimethylhydrazine have been used in conjunction with trialkyl-aluminum and -gallium compounds as alternative nitrogen sources replacing NH_3 for the preparation of AlN and GaN.[6–8] Several related group 13 hydrazide derivatives have been structurally characterized, including dimeric $[Me_2GaN(H)N(H)Ph]_2$,[9] $[Et_2GaN(H)NPh_2]_2$[10] and $[Me_2AlN(H)NMe_2]_2$,[11] a compound with a ladder-type structure, $Al_4[N(H)NMe_2]_6(NNMe_2)_4$,[12] and a compound with a Ga_4N_8 cage structure, $[MeGaN(H)NPh]_4$.[9]

Compound **1**[13] was obtained nearly quantitatively as a white crystalline solid after removal of the volatiles from the reaction of $H_3Ga(NMe_3)$ in excess H_2NNMe_2 at room temperature for 2 days (Scheme 1). Having an appreciable volatility (*ca.* 0.07 Torr) at room temperature, colorless crystals were obtained by sublimation at 55 °C under nitrogen (1 atm). Compound **1** melted at 62 °C and remained a stable liquid up to 90 °C. When heated at higher temperatures, compound **1** decomposed to gallium metal. These results suggested that compound **1** is potentially a clean precursor for deposition of gallium-containing films. The chemical ionization mass spectroscopic data of **1** were in good agreement with the formula of $[H_2GaN(H)NMe_2]_2$ ($[M + H]^+$, *m/z* 261.0, 100%). Two strong $\nu_{Ga–H}$ (KBr pellet) absorptions at 1897 and 1912 cm^{-1} and two $\nu_{N–H}$ absorptions at 3099 (broad) and 3145 (sharp) cm^{-1} were observed. Two singlets at δ 2.11 (sharp) and 2.35 (broad) in the ^1H NMR spectrum were assigned to N–H groups with the total integration of 2 H. The hydrides appeared as a broad resonance at δ 5.21. The presence of two N–H groups indicated the existence of a second isomer in solution. The ratio of the intensity of the δ 2.11 to the δ 2.35 resonances increased from 0.66 at 21 °C to 0.77 at 50 °C.

The molecular structure of **1**[14] (Fig. 1) was dimeric with a planar Ga_2N_2 core and a *trans* arrangement of the NMe_2 substituents. Along the *z* axis intermolecular hydrogen bonds were found between N(1) and N(2) of the neighboring molecule [N(1)···N(2) 3.238(7) Å, N(1)–H(1N)···N(2) 167(5)°]. The atoms N(3) and N(4) were not involved in hydrogen bonding. The hydrides were located on the difference Fourier map, and the only restraint applied in their refinement was to set similar the Ga–H bond lengths to the corresponding gallium atoms.

As also shown in Scheme 1, compound **2**[13] was obtained by refluxing the solution of compound **1** in H_2NNMe_2 for 4 days, followed by removal of volatiles and recrystallization from hexanes (63% yield based on gallium). The ^1H NMR spectrum of compound **2** was consistent with the solid state strtucture[14] (Fig. 2); the two unusual downfield shifts (δ 5.11 and 5.57) were assigned to two N–H bonds involved in hydrogen bonding (*vide infra*).



Scheme 1

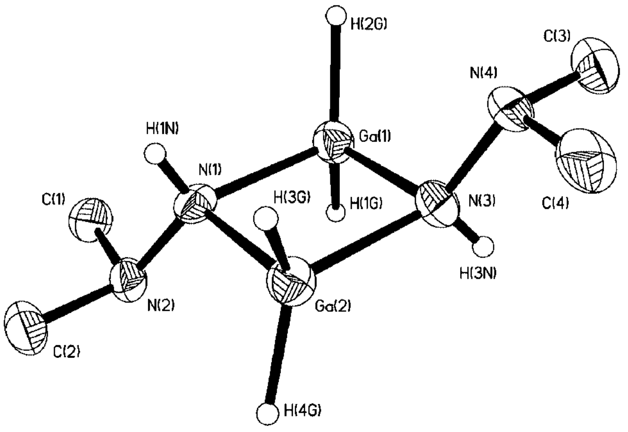


Fig. 1 Structure of **1** showing 50% thermal ellipsoids. Hydrogen atoms in the methyl groups are omitted for clarity. Selected bond distances (Å) and angles (°): Ga(1)–N(1) 1.991(5), Ga(1)–N(3) 2.017(5), Ga(1)–H(1G) 1.51(3), Ga(2)–N(1) 1.997(5), Ga(2)–N(3) 2.024(6), N(1)–N(2) 1.454(7), N(3)–N(4) 1.449(7); N(1)–Ga(1)–N(3) 87.3(2), N(1)–Ga(2)–N(3) 86.9(2), Ga(1)–N(1)–Ga(2) 93.6(2), Ga(1)–N(3)–Ga(2) 92.1(2).

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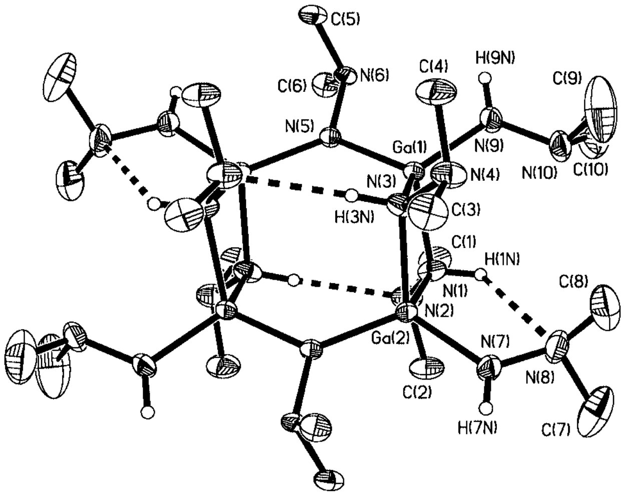

Fig. 2 Structure of **2** showing 30% thermal ellipsoids. Hydrogen atoms in the methyl groups are omitted for clarity. Selected bond distances (Å) and angles (°): Ga(1)–N(1) 1.989(3), Ga(1)–N(3) 2.029(3), Ga(1)–N(5) 1.847(3), Ga(1)–N(9) 1.833(3), Ga(2)–N(1) 1.990(3), Ga(2)–N(3) 2.034(3), Ga(2)–N(5A) 1.860(3), Ga(2)–N(7) 1.851(3), N(1)–N(2) 1.402(4), N(3)–N(4) 1.427(4), N(5)–N(6) 1.461(3), N(7)–N(8) 1.403(4), N(9)–N(10) 1.409(4); N(1)–Ga(1)–N(3) 84.30(11), N(1)–Ga(2)–N(3) 84.13(11), Ga(1)–N(1)–Ga(2) 96.53(12), Ga(1)–N(3)–Ga(2) 93.94(12), Ga(1)–N(5)–Ga(2A) 129.76(14), N(6)–N(5)–Ga(1) 108.5(2), N(6)–N(5)–Ga(2A) 121.7(2).

An inversion center correlated the two halves of the molecule **2**, which were connected by bridging $NNMe_2$ ligands and an intramolecular hydrogen bond between N(3) and N(2A). The distance N(3)···N(2A) was 3.214(5) Å and the angle N(3)–H(3N)···N(2A) was 174.8°. An additional intramolecular hydrogen bond was found between N(1) and N(8) [3.175(5) Å, 120.1°]. Each Ga_2N_2 ring adopted a sightly twisted shape with the gallium ends bending toward and the nitrogen ends away from the inversion center. The torsion angle N(3)–Ga(2)–N(1)–Ga(1) was 8.0(2)°. The four gallium atoms [Ga(1), Ga(2), Ga(1A) and Ga(2A)] and the two bridging nitrogen atoms [N(5) and N(5A)] were essentially on the same plane. The atom N(5) adopted a trigonal planar geometry with the sum of the angles being 360.0°. This suggested delocalization of the lone pair electrons of the nitrogen to the two adjacent gallium atoms, however, the bond lengths N(5)–Ga(1) [1.847(3) Å] and N(5)–Ga(2A) [1.860(3) Å] were not unusual for covalent Ga–N bonds.[15] With the exception of N(5)–N(6) [1.461(3) Å], the N–N bond lengths ranged from 1.402(4) to 1.427(4) Å, shorter than those in compound **1** [1.449(7) and 1.454(7) Å], $[Et_2GaN(H)NPh_2]_2$ [1.457(8) and 1.446(8) Å] and $[MeGaN(H)NPh]_4$ [1.489(3) Å].

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Notes and references

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13 Compound **1**: MS (CI, %): *m/z* 261.0 ($[M + H]^+$, 100), 188.0 ($[HGa[N(H)NMe_2]_2]^+$, 6), 131.0 ($[0.5M + H]^+$, 13), 74.1 ($[GaH_x]^+$, 23), δ_H(300 MHz, C_6D_6, 25 °C): 2.02 (12H, s, NMe_2), 2.11 (s) and 2.35 (br s) (total 2H, integration ratio: δ 2.35/δ 2.11 = 1.5, NH), 5.21 (2H, br s, GaH). Anal. Calc. for $C_4H_{18}N_4Ga_2$: C, 18.36; H, 6.93; N, 21.41. Found: C, 17.19; H, 6.67; N, 20.13%.

Compound **2**: decomp. at 130 °C without melting. δ_H(300 MHz, C_6D_6, 25 °C): δ 2.23 (4H, s, NH), 2.56 (12H, s, NMe_2), 2.61 (12H, s, NMe_2), 2.65 (12H, s, NMe_2), 2.67 (24H, s, NMe_2), 5.11 (2H, s, NH) and 5.57 (2H, s, NH). IR: ν_{NH}, 3054, 3087 and 3228 cm^{-1}.
14 *Crystal data*: for $C_4H_{18}Ga_2N_4$ **1**: M = 261.66, monoclinic, space group Cc (no. 9), a = 6.8583(5), b = 19.607(2), c = 8.0977(6) Å, β = 95.323(2)°, V = 1084.2(2) Å^3, T = 173 (2) K, Z = 4, μ(Mo-Kα) = 4.920 mm^{-1}, 3964 reflections collected, 1718 unique (R_{int} = 0.0378) which were used in all calculations, R_1 = 0.0294 and wR_2 = 0.0612 for 1554 reflections with $I > 2\sigma(I)$. A single crystal of compound **1** was mounted in inert oil and transferred to a cold N_2 gas stream of the diffractometer. The structure was solved using direct methods and refined by full-matrix least squares on F^2.

For $C_{20}H_{68}Ga_4N_{20}$ **2**: M = 867.82, monoclinic, space group $P2_1/c$ (no. 14), a = 9.8972(7), b = 22.489(2), c = 10.0230(7) Å, β = 112.824(1)°, V = 2056.2(3) Å^3, T = 173(2) K, Z = 2, μ(Mo-Kα) = 2.632 mm^{-1}, 12953 reflections collected, 4622 unique (R_{int} = 0.0372), R_1 = 0.0384 and wR_2 = 0.0887 for 3239 reflections with $I > 2\sigma(I)$. A single crystal of compound **2** was mounted in inert oil and transferred to a cold N_2 gas stream of the diffractometer. The structure was solved using direct methods and refined by full-matrix least squares on F^2. CCDC 182/1591. See http:/www.rsc.org/suppdata/cc/b0/b001010n/ for crystallographic files in .cif format.
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