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Synthesis and characterization of $[Me_2M\text{-}\mu\text{-}N(H)NMe_2]_2$ (M = Al, Ga). Crystal structure of *trans* $[Me_2Al\text{-}\mu\text{-}N(H)NMe_2]_2$

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Abstract

Reactions of MMe_3 (M = Al, Ga) with 1 equivalent of NH_2NMe_2 afford respective dimeric $[Me_2M\text{-}\mu\text{-}N(H)NMe_2]_2$ (M = Al (**1**), M = Ga (**2**)) complex as a mixture of *trans* and *cis* isomers. Purifications of **1** by sublimation and **2** by recrystallization give only *trans* isomers **1a** and **2a**, respectively. Variable-temperature ^1H NMR studies reveal that both **1** and **2** undergo fast *cis–trans* isomerization with free energy of activation ($\Delta G_c^{\ddagger}$), 9.3 kcal/mol for **1** and 15.6 kcal/mol for **2**. The *trans* isomer **1a** has been determined by a single-crystal X-ray diffraction study. The molecular geometry of **1a** consists of a centrosymmetric and dimeric unit with two bridging hydrazido groups and two terminal methyl groups bound to each aluminum atom. The two $N\text{–}NMe_2$ groups are trans to each other with respect to the $(Al\text{–}N)_2$ ring. The coordination geometry of both the aluminum and nitrogen atoms is distorted tetrahedral. © 1997 Elsevier Science S.A.

Keywords: 1,1-Dimethylhydrazine; Dimeric; Hydrazidoalane; Hydrazidogallane; Precursor

1. Introduction

In recent years there has been a renewed interest in the synthesis of hydrazido derivatives of group 13 elements (M), due to their potential application as single-source precursors for the preparation of group 13 nitride (MN) thin films, employing organometallic chemical vapor deposition (OMCVD) [1–5]. The most successful MN (M = Al, Ga) thin films have been grown at temperatures in excess of 900°C using MR_3 and ammonia [6–9]. The disadvantages associated with such high temperatures include introduction of thermal stresses as well as loss of stoichiometry due to nitrogen deficiency in the films. Thus, alternative nitrogen sources to ammonia such as hydrazine (N_2H_4) [10,11], 1,1-dimethylhydrazine (NH_2NMe_2) [12,13] and hydrogen azide (HN_3) [14–16] have been proposed to improve both disadvantages. The original work of Fetter et al. [12] for the synthesis of hydrazido compounds revealed that reactions of $AlMe_3$ with various methylhydrazines resulted in the formation of hydrazidoalanes, which were not fully characterized. Cowley and coworkers [13] recently reported the first structurally characterized example of dimeric gallium hydrazide, $[Et_2Ga\text{-}\mu\text{-}N(H)NPh_2]_2$. We herein report synthesis and characterization of single-source MN precursors of 1,1-dimethylhydrazine derivatives, dimeric $[Me_2M\text{-}\mu\text{-}N(H)NMe_2]_2$ (M = Al (**1**), M = Ga (**2**)) complexes, together with the crystal structure of the *trans* isomer of **1**.

2. Experimental section

2.1. General comments

All experiments were performed under argon either in a Vacuum Atmospheres drybox or with standard Schlenk techniques. Trimethylaluminum, trimethylgallium and 1,1-dimethylhydrazine were purchased from Strem Chemicals. Dichloromethane was refluxed over CaH_2 and then distilled under argon atmosphere. *n*-Pentane and *n*-heptane were distilled over sodium benzophenone under argon atmosphere.

The infrared spectra were obtained as KBr pellets with a Bomem MB-100 FT-IR spectrophotometer. The ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. The melting points were obtained in a sealed capillary under

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argon (1 atm) and were uncorrected. Mass spectra were recorded on a JEOL HX 100/HX 110 mass spectrometer. All m/z values were referenced to ^{27}Al and ^{69}Ga. Microanalytical data were provided by the analytical laboratory of the Korea Basic Science Institute.

2.2. Synthesis of $[Me_2Al\text{-}\mu\text{-}N(H)NMe_2]_2$ (1)

1,1-Dimethylhydrazine (0.526 g, 8.75 mmol) was added to a stirred solution of trimethylaluminum (0.607 g, 8.42 mmol) in dichloromethane (10 ml) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Gas evolution (presumably methane) was apparent from the observed frothing. Removal of the solvent and volatiles under reduced pressure resulted in a white solid. Upon sublimation, colorless crystals of the *trans* isomer **1a** (0.767 g, 6.60 mmol, 78%) were obtained: m.p. 78°C; ^1H NMR ($CDCl_3$, 20°C) δ −0.72 (s, Al–Me), 1.93 (br, N–H), 2.44 (s, N–Me); ^1H NMR (toluene-d_8, −90°C) δ −0.25 (s, Al–Me), 1.55 (br, N–H), 1.84 (s, N–Me); ^{13}C NMR ($CDCl_3$, 20°C) δ −10.32 (Al–Me), 52.74 (N–Me); MS (70 eV) m/z 232 (M^+); IR ν(NH) 3131 cm^{-1}. Anal. Calculated for $C_8H_{26}Al_2N_4$: C, 41.35; H, 11.30; N, 24.12. Found: C, 41.37; H, 11.45; N, 24.49.

Cis isomer **1b** (data obtained from an equilibrium mixture): ^1H NMR ($CDCl_3$, 20°C) δ −0.72 (s, Al–Me), 1.93 (br, N–H), 2.44 (s, N–Me); ^1H NMR (toluene-d_8, −90°C) δ −0.50 (s, Al–Me), −0.02 (s, Al–Me), 1.28 (br, N–H), 1.84 (s, N–Me); ^{13}C NMR ($CDCl_3$, 20°C) δ −10.32 (Al–Me), 52.74 (N–Me).

2.3. Synthesis of $[Me_2Ga\text{-}\mu\text{-}N(H)NMe_2]_2$ (2)

1,1-Dimethylhydrazine (0.158 g, 2.63 mmol) was added to a stirred solution of trimethylgallium (0.301 g, 2.62 mmol) in *n*-heptane (10 ml) at 0°C. The reaction mixture was stirred at 100°C for 3 h. The solvent and volatiles were removed in vacuo and the white residue was dissolved in *n*-pentane. Slow recrystallization of the *n*-pentane solution at −20°C gave the *trans* isomer **2a** (0.275 g, 1.73 mmol, 66%) as colorless crystals: m.p. 80°C; ^1H NMR ($CDCl_3$, −10°C) δ −0.31 (s, Ga–Me), 2.06 (br, N–H), 2.32 (s, N–Me); ^{13}C NMR ($CDCl_3$, −10°C) δ −7.24 (Ga–Me), 52.13 (N–Me); MS (70 eV) m/z 316 (M^+); IR ν(NH) 3136 cm^{-1}.

Cis isomer **2b** (data obtained from an equilibrium mixture): ^1H NMR ($CDCl_3$, −10°C) δ −0.46 (s, Ga–Me), −0.18 (s, Ga–Me), 1.91 (br, N–H), 2.32 (s, N–Me); ^{13}C NMR ($CDCl_3$, −10°C) δ −7.24 (Ga–Me), 52.13 (N–Me).

2.4. X-ray data collection and structure solution of 1a

A colorless crystal of **1a** obtained by slow sublimation was sealed in a thin walled glass capillary under argon and mounted on an Enraf-Nonius CAD4 diffractometer. The accurate cell parameters were obtained from 25 reflections in the range $11.57° < \theta < 13.91°$. Reflections were measured with the index range $-7 < h < 7$, $0 < k < 8$, $-9 < l < 8$ using a $\omega/2\theta$ scan mode, ω scan angle $= (0.8 + 0.35 \tan\theta)°$, $2\theta_{max} = 45°$. The intensities of three standard reflections monitored every 2 h showed no significant decay over the course of data collection. Lorentz and polarization corrections were applied to the intensity data. Details of crystallographic data are given in Table 1. All the calculations were carried out with the NRCVAX PC software package

Table 1
Crystallographic data for $[Me_2Al\text{-}\mu\text{-}N(H)NMe_2]_2$ (**1a**)

Formula	$Al_2N_4C_8H_{26}$
Formula weight	232.28
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	6.802 (2)
b (Å)	8.299 (3)
c (Å)	8.435 (1)
α (°)	115.30 (2)
β (°)	107.98 (2)
γ (°)	95.16 (2)
V (Å^3)	395.7 (2)
Z	2
T (K)	297
D_{calc} (g cm^{-3})	0.975
Crystal size (mm)	0.66×0.60×0.50
Radiation	graphite-monochromated Mo K α
λ (Å)	0.70930
μ (mm^{-1})	0.16
No. of unique data	990
No. of unique data with $I > 3\sigma(I)$	721
No. of variables	116
$R(F)$[a]	0.030
$R_w(F)$[b]	0.031
GOF[c]	1.33

[a] $R = \Sigma(F_o - F_c)/\Sigma(F_o)$.
[b] $R_w = \{\Sigma[(F_o - F_c)^2]/\Sigma[(F_o)^2]\}^{1/2}$.
[c] $GOF = \{\Sigma[(F_o - F_c)^2]/[N_{observns} - N_{params}]\}^{1/2}$.

Table 2
Positional and equivalent isotropic thermal parameters with Esd's for $[Me_2Al\text{-}\mu\text{-}N(H)NMe_2]_2$ (**1a**)

Atom	x	y	z	U_{eq} (Å^2)[a]
Al	0.0124 (2)	0.5828 (1)	0.1897 (1)	4.72 (5)
N1	0.1420 (4)	0.6509 (3)	0.0422 (3)	4.6 (2)
N2	0.1264 (4)	0.8234 (3)	0.0401 (4)	6.0 (2)
C1	0.239 (1)	0.560 (1)	0.3813 (9)	9.1 (4)
C2	−0.202 (1)	0.7147 (8)	0.246 (1)	8.6 (4)
C3	0.2535 (9)	0.9746 (6)	0.2301 (8)	8.7 (3)
C4	0.2131(9)	0.8354 (7)	−0.0941 (9)	8.6 (4)

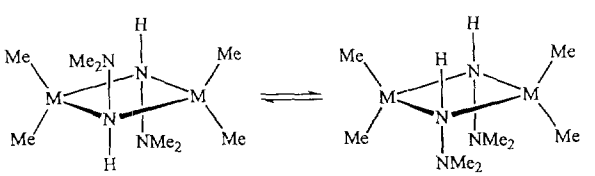
[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[17]. The structure was solved by direct and difference Fourier methods and refined by the full matrix least-squares methods employing unit weights. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically with a common thermal parameters. The final cycle of the refinement converged to the R factors listed in Table 1. The maximum shift to the sigma ratio was 0.043, and the highest and deepest peaks in the last difference map were 0.290 and -0.190 eÅ^{-3}, respectively. Final positional and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of 1a–2b

Reactions of MMe_3 (M = Al, Ga) with 1 equivalent of NH_2NMe_2 produce the dimeric hydrazidoalane $[Me_2Al\text{-}\mu\text{-}N(H)NMe_2]_2$ (**1**) and hydrazidogallane $[Me_2Ga\text{-}\mu\text{-}N(H)NMe_2]_2$ (**2**) complexes as a respective mixture of *cis* and *trans* isomers by methane elimination. The dimeric formulations of these complexes have been indicated by the observation of molecular ions for both **1** and **2** in the EI mass spectra. Purifications of **1** by sublimation and **2** by recrystallization afford colorless crystals of only *trans* isomers **1a** and **2a**, respectively. X-ray crystal structure determination of **1a** reveals the *trans* structure (vide infra), but in solution *trans* isomers **1a** and **2a** equilibrate with *cis* isomers **1b** and **2b**. IR spectra (KBr pellets) of **1a** and **2a** contain one strong ν(NH) stretch as expected for the *trans* isomer at 3131 and 3136 cm^{-1}, respectively. Two possible ν(NH) stretches for the corresponding *cis* isomer, however, could not be observed in the IR spectrum of each equilibrium mixture of **1** and **2**.



M = Al **1a** **1b**
M = Ga **2a** **2b**

The variable-temperature (VT) ^{1}H NMR spectra (263–333 K) of a *cis–trans* mixture of **2** in $CDCl_3$ are shown in Fig. 1. The limiting low temperature spectrum at 263 K shows a single peak for the Ga–Me groups of **2a** at δ -0.31 and two distinct resonances of equal intensity at δ -0.18 and -0.46 due to inequivalent Ga–Me groups of **2b**. Isomer **2b**, therefore, is assumed to be a *cis* isomer with the NMe_2 groups *cis* to the

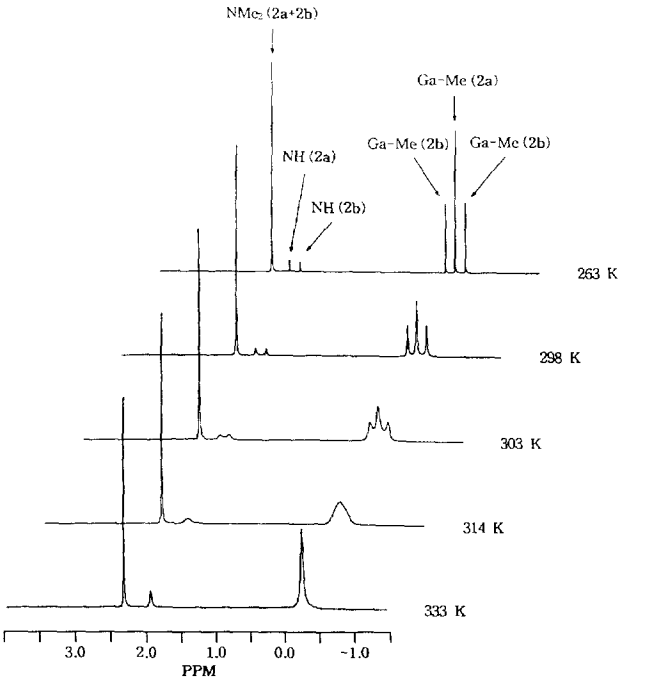


Fig. 1. VT ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **2**.

(Ga–N)$_2$ ring. As the temperature increases, both N–H (δ 2.06 for **2a** and 1.91 for **2b**) and Ga–Me resonances broaden and the N–H resonances coalesce to a single resonance at 314 K (300 MHz). The free energy of activation ($\Delta G_c^{\ddagger}$) of 15.6 kcal/mol for the *cis–trans* isomerization of **2** was derived from the coalescence temperature and peak separation of the N–H resonances using the Erying equation [18]. General features of VT ^{1}H NMR spectra of **1** in toluene-d_8 are essentially identical to those of **2** with T_c = 196 K and a similar line shape analysis gives $\Delta G_c^{\ddagger}$ 9.3 kcal/mol for the isomerization process of **1**. Both VT ^{1}H NMR spectra of **1** and **2** show reversible temperature behavior.

Compound **1** was previously reported by Fetter and coworkers [12], but not structurally authenticated. Cowley et al. [13] suggested the trimeric structure of **2** as $[Me_2Ga\text{-}\mu\text{-}N(H)NMe_2]_3$, which was isolated from the reaction of Me_2GaCl and Me_2NNHLi, although they reported the structural characterization of dimeric $[Et_2Ga\text{-}\mu\text{-}N(H)NPh_2]_2$. Our ^{1}H NMR studies, however, clearly indicate the dimeric nature of both **1** and **2**. If **2** were a trimer as was found for $[Me_2Al\text{-}\mu\text{-}N(H)Me]_3$ [19], the *cis* trimer would show two peaks of equal intensity corresponding to Ga–Me groups and the *trans* trimer would reveal four resonances in a 1:1:2:2 ratio. We previously reported the *cis–trans* isomerization of $[Me_2Ga\text{-}\mu\text{-}N(H)^tBu]_2$ (**3**) and proposed the isomerization pathways of **3** as an initial breaking of the Ga–N bond, followed by rotation about the nonbridged Ga–N bond and rebridging [20]. The ^{1}H NMR resonances due to *trans* and *cis* isomers of **3** were reported to remain

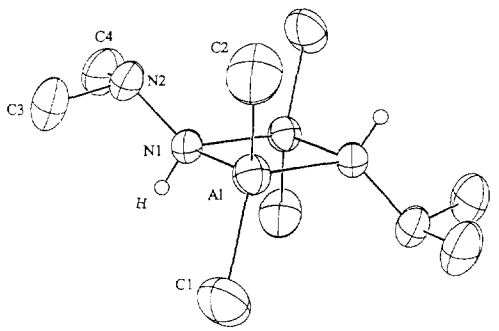


Fig. 2. Molecular geometry and atomic labeling for **1a**. Hydrogen atoms except for NH were omitted for clarity.

sharp even at 353 K, indicating that **3** undergoes much slower isomerization than **1** and **2**. In these complexes, the internal base NMe_2 group may facilitate the isomerization acting as an external base to neighbouring molecules. Similar acceleration of isomerization by external Lewis bases has been observed previously [20–22]. Furthermore, this study reveals that the aluminum analogue **1** undergoes a faster isomerization than the gallium analogue **2**. The Lewis acidities of species R_3M are known to increase for the lighter homologues of group 13 elements ($Me_3Al > Me_3Ga$), based on dissociation enthalpies for the adducts $R_3M{:}NMe_3$ [23]. The initial breaking of M–N bond in aluminum analogue **1**, therefore, is more facilitated by an attack of the internal base than that in gallium analogue **2**, which explains the faster isomerization of **1**.

3.2. Crystal structure of *1a*

The overall molecular geometry of **1a** with the atomic labeling scheme is shown in Fig. 2. Selected bond distances and angles are listed in Table 3. The molecule has a centrosymmetric and dimeric structure with aluminum atoms bridged by $N(H)NMe_2$. The coordination of the aluminum atoms is in a distorted-tetrahedral environment with interligand angles ranging from N1–Al–N1′ = 87.2 (1)° to C1–Al–C2 = 123.1 (4)°. The aluminum–methyl bond lengths, Al–C1 = 1.950 (5) Å and Al–C2 = 1.953 (5) Å suggest a covalent radius of 1.18 Å for aluminum (III) in this type of environment [1]. The $(Al–N)_2$ core structure is planar; the bond distances are Al–N1 = Al′–N1′ = 1.958 (3) and Al–N1′ = Al′–N1 = 1.953 (3) Å, which are close to those observed in other dimers [22,24,25]. The bridging $N(H)NMe_2$ groups take up a mutually trans arrangement with respect to the $(Al–N)_2$ ring as was observed for other known μ-amidoalanes [22,24,25]. The internal angle at nitrogen (92.8 (1)°) is larger than that at aluminum (87.2 (1)°), which is a general structural feature of the $(M–N)_2$ cores of virtually all group 13/15 dimers [20,22,24–28]. The N–H bond length of 0.83 (3) Å compares favorably with the value of 0.87 (3) Å in $[Me_2Al$-μ-N(H)(1-adamantyl)$]_2$ [24,25]. Nitrogen atoms N2 and N2′ adopt pyramidal geometries (ca. 109°) and their nitrogen lone pairs are arranged in a trans fashion with respect to the hydrogen atoms on N1 and N1′. All other features of the molecular geometry are within the expected range.

Table 3
Bond lengths (Å) and angles (°) with Esd's for $[Me_2Al$-μ-$N(H)NMe_2]_2$ (**1a**)

Bond lengths			
Al–N1	1.958 (3)	N2–C3	1.457 (5)
Al′–N1	1.953 (3)	N2–C4	1.462 (6)
Al–C1	1.950 (5)	Al · · · Al′	2.833 (2)
Al–C2	1.953 (5)	Al · · · H	2.34 (3)
N1–N2	1.452 (3)	Al′ · · · H	2.38 (3)
N1–H	0.83 (3)	N1 · · · N1′	2.696 (5)
Bond angles			
N1–Al–N1′	87.2 (1)	Al–N1–H	108 (2)
N1–Al–C1	107.7 (2)	Al′–N1–N2	119.6 (2)
N1–Al–C2	112.9 (2)	Al′–N1–H	111 (2)
N1′–Al–C1	113.6 (3)	N2–N1–H	107 (2)
N1′–Al–C2	106.6 (2)	N1–N2–C3	108.3 (3)
C1–Al–C2	123.1 (4)	N1–N2–C4	108.8 (3)
Al–N1–Al′	92.8 (1)	C3–N2–C4	109.4 (4)
Al–N1–N2	118.6 (2)		

3.3. Supplementary material

A full listing of positional and thermal parameters, complete lists of bond distances and angles and structure factor tables of complex **1a** are available from the authors.

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