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Synthesis and characterization of organogallium-antimony compounds

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Abstract

The simple Lewis acid–base adduct $Me_3Ga \leftarrow Sb(SiMe_3)_3$ (**1**) was prepared by the reaction of Me_3Ga and $Sb(SiMe_3)_3$. Dehalosilylation reaction between Me_2GaCl and $Sb(SiMe_3)_3$ in 1:1 mol ratio yields the trimeric $[Me_2GaSb(SiMe_3)_2]_3$ (**2**). **1** and **2** were fully characterized by mass and NMR spectroscopy. In addition, the solid state structure of compound **2** was determined by single crystal X-ray diffraction. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Gallium; Antimony; Single source precursor; Semiconductor

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1. Introduction

The chemistry of organogallium-Group 15 compounds has concentrated on phosphines $(R_2GaPR'_2)_x$ and arsines $(R_2GaAsR'_2)_x$. These compounds have attracted much attention due to their potential application in MOCVD processes (single source precursors) for the preparation of thin films of the corresponding materials GaP and GaAs, which play a key role in electronic and optoelectronic devices [1]. Numerous compounds have been synthesized mainly in the form of 1:1 Lewis acid–base adducts $R_3Ga \leftarrow ER'_3$ ($E = P$, As) [2] or dimers $(R_2GaER'_2)_2$ [3] and trimers $(R_2GaER'_2]_3$ [4] through general synthetic routes like lithium halide elimination or dehalosilylation reactions. Remarkably, only a handful of Ga–Sb compounds containing either dative bonds or sigma bonds have been synthesized and structurally characterized. Recently, Wells et al. reported the synthesis of $Et_3Ga \leftarrow Sb(SiMe_3)_3$ [5] and ${}^tBu_3Ga \leftarrow Sb(SiMe_3)_3$ [6] by reaction of $Sb(SiMe_3)_3$ with the corresponding gallium trialkyl in 1:1 mol ratio. The same group prepared $[{}^tBu_2GaSb(SiMe_3)_2]_2$, ${}^tBu_2GaSb(SiMe_3)_2Ga({}^tBu)_2Cl$, and $[(Me_3CCH_2)_2GaSb(SiMe_3)_2]_x$ by dehalosilylation reaction of the corresponding organogalliumchloride with $Sb(SiMe_3)_3$. In addition, Cowley et al. reported the synthesis of $[Cl_2GaSb{}^tBu_2]_3$ [7] by lithium salt elimination reaction and $[Me_2GaSb{}^tBu_2]_3$ [8] by dehalosilylation reaction.

In an attempt to expand the knowledge about these still inadequate investigated compounds we now report the synthesis of $Me_3Ga \leftarrow Sb(SiMe_3)_3$ (**1**) and $[Me_2GaSb(SiMe_3)_2]_3$ (**2**) by the reaction of $Sb(SiMe_3)_3$ and Me_3Ga, respectively, Me_2GaCl in 1:1 mol ratio and their full characterization by mass and NMR spectroscopy. In addition, the solid state structure of **2** was determined by single crystal X-ray diffraction.

2. Results and discussion

The simple Lewis acid–base adduct $Me_3Ga \leftarrow Sb(SiMe_3)_3$ (**1**) was prepared in quantitative yield by the reaction of Me_3Ga and $Sb(SiMe_3)_3$ in 1:1 mol ratio while the dehalosilylation reaction between Me_2GaCl and $Sb(SiMe_3)_3$ in 1:1 mol ratio affords the trimeric $[Me_2GaSb(SiMe_3)_2]_3$ (**2**). Both compounds have been characterized by mass and NMR spectroscopy. The solid state structure of **2** was determined by single crystal X-ray analysis.

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1 is the third example of a Lewis acid–base adduct containing Ga–Sb dative bonds. Preparation and X-ray analysis of $Et_3Ga \leftarrow Sb(SiMe_3)_3$ and $^tBu_3Ga \leftarrow Sb(SiMe_3)_3$, both prepared in solution, were described recently by Wells et al. We proved that compounds of this type can easily be obtained in quantitative yield simply by adding $Sb(SiMe_3)_3$ to the gallium trialkyl in the absence of solvent in the glovebox. Crystals of **1** were formed in pentane at −30°C, but the structure couldn't be determined due to the extreme sensitivity of **1** towards air and moisture.

^{1}H-NMR studies of **1** show two singlets at δ 0.12 and 0.36 ppm for the methyl, respectively the $SiMe_3$ groups. Compared with the $SiMe_3$ shift in $Et_3Ga \leftarrow Sb(SiMe_3)_3$ and $^tBu_3Ga \leftarrow Sb(SiMe_3)_3$ (δ 0.38 [4] and δ 0.41 ppm [5]) the resonance is shifted slightly highfield. The ^{13}C-NMR spectra show the GaMe resonance at 0.09 ppm and the $SiMe_3$ resonance at δ 5.61 ppm. Although **1** sublimes without decomposition, its molecular peak couldn't be observed in the mass spectra. Fragmentation occurs and signals for the resulting $GaMe_3^+$ at m/z 115 and $Sb(SiMe_3)_3^+$ at m/z 340 were detected.

The ^{1}H-NMR spectra of **2** show two singlets at δ 0.46 and 0.52 ppm for the methyl and $SiMe_3$ groups. In the mass spectra a peak in very low intensity was observed at m/z 634, indicating a four-membered Ga_2Sb_2 ring. However, a single crystal X-ray analysis proved **2** to be trimeric in the solid state forming a six-membered Ga_3Sb_3 ring, which adopts a slightly distorted envelope-type conformation.

Table 1
Crystallographic and data collection parameters for $[Me_2GaSb(SiMe_3)_2]_3$ (**2**)

Empirical formula	$C_{24}H_{72}Ga_3Sb_3Si_6$
Formula weight	1103.77
Temperature (K)	123(2)
Wavelength (Å)	Mo–K_α (0.71073)
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a (Å)	9.4929(2)
b (Å)	20.7073(4)
c (Å)	24.1236(4)
β (°)	95.950(1)
V (Å^3)	4716.5(2)
Z	4
$D_{calc.}$ (g cm^{-3})	1.554
μ (mm^{-1})	3.548
Crystal dimension (mm)	0.70 × 0.50 × 0.40
$2\theta_{max}$ (°)	56.5
Number of reflections recorded	24909
Number of non-equivalent reflections recorded	8253
R_{merg}	0.035
Number of parameters rfnd./restraints	332/114
R_1; wR^b	0.031; 0.082
Goodness of fit^c	1.034
Maximum shift/esd in final least-squares cycle	0.001
Final max, min $\Delta\rho$ (e Å^{-3})	1.111, −0.732

[a] $R_1 = \Sigma(\|F_o|-|F_c\|)/\Sigma|F_o|$ (for $I > 2\sigma(I)$).
[b] $wR = [\Sigma[w|F_o^2|^2]^{1/2}$.
[c] Goodness of fit $= \{\Sigma[w(|F_o^2|-|F_c^2|)^2]/(N_{observns}-N_{params})\}^{1/2}$.

This compares well with the structures of $[Cl_2GaSb^tBu_2]_3$ [6] and $[Me_2GaSb^tBu_2]_3$ [7], which also form six-membered rings. The ring size obviously depends on substituent group size; the small Cl and Me groups favor the formation of six-membered rings, while the large ^{t}Bu groups in $[^tBu_2GaSb(SiMe_3)_2]_2$ lead to the formation of a four-membered ring system. The average Ga–Sb bond distance in **2** of 269.07 pm is slightly longer than the sum of the covalent radii (266 pm) as well as the average bond distance in $[Cl_2GaSb^tBu_2]_3$ (266.1 ppm), but it is shorter than the Ga–Sb distances found in the dimeric compounds $[^tBu_2GaSb(SiMe_3)_2]_2$ (276.66 pm) and $^tBu_2GaSb(SiMe_3)_2Ga(^tBu)_2Cl$ (273.36 pm). The average bond angles are 123.55° for Ga–Sb–Ga and 105.22° for Sb–Ga–Sb. At Sb(1) both the average Ga–Sb distance of 267.97 pm as well as the GaSbGa bond angle of 118.325° represent minimum values while at Sb(3) the average distance of 270.75 pm and the Ga–Sb–Ga bond angle of 127.60° represent maximum values observed in this compound. A comparable wide range of both the bond lengths and angles was found in the related compound $[(Me_3Si)_2AlP(H)c\text{-}C_6H_{11}]_3$, which adopts also a six-membered ring conformation [9]. In contrast, the bond lengths and angles of the pnictinogallanes $[H_2GaE(SiMe_3)_2]_3$ (E = P, As) vary within a much smaller range [4].

3. Experimental section

3.1. General considerations

All manipulations were carried out in a glovebox under N_2-atmosphere or by standard Schlenk techniques. Pentane was carefully dried over sodium/potassium alloy under dry N_2. Me_3Ga was purchased from Aldrich and used as received, while Me_2GaCl was prepared in a standard ligand exchange reaction from $GaCl_3$ and $GaMe_3$. $Sb(SiMe_3)_3$ [10] was prepared by literature methods. Infrared spectra were recorded in Nujol between KBr plates with a Nicolet Magna 550 and are reported in reciprocal centimeters. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ^{1}H and $^{13}C\{^1H\}$ spectra were referenced to internal C_6D_5H (δ ^{1}H 7.154, δ ^{13}C 128.0). Mass spectra were recorded on a VG Masslab 12-250 spectrometer in the electron ionization mode at 20 eV. Melting points were observed in sealed capillaries and were not corrected.

Table 2
Selected structural parameters for **2**

Bond lengths			
Sb(1)–Ga(1)	268.22(5)	Ga(1)–C(19)	199.4(4)
Sb(1)–Ga(3)	267.73(5)	Ga(1)–C(20)	197.0(4)
Sb(2)–Ga(1)	268.96(5)	Ga(2)–C(21)	204.1(3)
Sb(2)–Ga(2)	267.99(5)	Ga(2)–C(22)	199.9(4)
Sb(3)–Ga(2)	270.05(5)	Ga(3)–C(23)	199.5(3)
Sb(3)–Ga(2)	271.44(5)	Ga(3)–C924)	198.5(3)
Sb(1)–Si(1)	255.81(11)	Sb(2)–Si(4)	256.17(11)
Sb(1)–Si(2)	254.43(11)	Sb(3)–Si(5)	256.70(10)
Sb(2)–Si(3)	256.48(11)	Sb(3)–Si(6)	256.69(11)
Bond angles (°)			
Ga(1)–Sb(1)–Ga(3)	118.325(15)	Sb(1)–Ga(1)–Sb(2)	104.697(15)
Ga(1)–Sb(2)–Ga(2)	124.720(15)	Sb(2)–Ga(2)–Sb(3)	107.333(17)
Ga(2)–Sb(3)–Ga(3)	127.595(15)	Sb(1)–Ga(3)–Sb(3)	103.649(15)
Si(1)–Sb(1)–Si(2)	102.34(4)	C(19)–Ga(1)–C(20)	120.4(2)
Si(3)–Sb(2)–Si(4)	100.53(4)	C(21)–Ga(2)–C(22)	113.40(16)
Si(5)–Sb(3)–Si(6)	102.08(3)	C(23)–Ga(3)–C(24)	120.42(16)
Si(1)–Sb(1)–Ga(1)	105.07(3)	C(19)–Ga(1)–Sb(1)	105.45(13)
Si(2)–Sb(1)–Ga(1)	116.09(3)	C(20)–Ga(1)–Sb(1)	109.45(13)
Si(1)–Sb(1)–Ga(3)	105.94(3)	C(19)–Ga(1)–Sb(2)	105.61(13)
Torsion angles (°)			
Si(2)–Sb(1)–Ga(3)	107.34(3)	C(20)–Ga(1)–Sb(2)	110.08(13)
Ga(3)–Sb(1)–Ga(1)–Sb(2)	−64.06(2)	Sb(1)–Ga(1)–Sb(2)–Ga(2)	24.46(2)
Ga(1)–Sb(2)–Ga(2)–Sb(3)	16.55(3)	Sb(2)–Ga(2)–Sb(3)–Ga(3)	−32.29(3)
Ga(1)–Sb(1)–Ga(3)–Sb(3)	51.03(2)	Ga(2)–Sb(3)–Ga(3)–Sb(1)	1.61(2)

3.2. Synthesis of $Me_3Ga \leftarrow Sb(SiMe_3)_3$ (1)

Me_3Ga (0.23 g, 2 mmol) was added in the glovebox to $Sb(SiMe_3)_3$ (0.68 g, 2 mmol). Immediately a light beige solid was formed. Yield: 0.91 g (100%). **1** can be purified either by recrystallization from pentane (5 ml) at low temperatures or by sublimation at 55°C at 10^{-2} mbar. Mp: 115–120°C. ^{1}H-NMR (300 MHz, C_6D_6, 25°C) δ 0.12 (s, 9H, GaMe), 0.36 (s, 27H, $SiMe_3$); ^{13}C-NMR (75 MHz, C_6D_6, 25°C) δ 0.09 (GaMe), 5.61 ($SiMe_3$); EI-MS (*m*/*z*, %) 340 ($Sb(SiMe_3)_3^+$, 20), 115 ($GaMe_3^+$, 15), 73 ($SiMe_3^+$, 100).

3.3. Synthesis of $[Me_2GaSb(SiMe_3)_2]_3$ (2)

To a stirred solution of Me_2GaCl (0.27 g, 2 mmol) in 50 ml pentane $Sb(SiMe_3)_3$ (0.68 g, 2 mmol) was added dropwise via syringe. After 2 h the solution had taken a light yellow color. After 4 h the volatiles were reduced in vacuo. Crystallization at −30°C for several days yielded 0.41 g (0.37 mmol, 56%) **2**. Mp: 194°C dec. IR (Nujol, cm^{-1}) $\nu = 1251$, 848, 716, 637. ^{1}H-NMR (300 MHz, C_6D_6, 25°C) δ 0.46 (s, 6H, GaMe), 0.52 (s, 18H, $SiMe_3$). ^{13}C-NMR (75 MHz, C_6D_6, 25°C) δ 2.95 (s, GaMe), 5.62 ($SiMe_3$). EI-MS (*m*/*z*, %) 634 (2/3M$^+$-

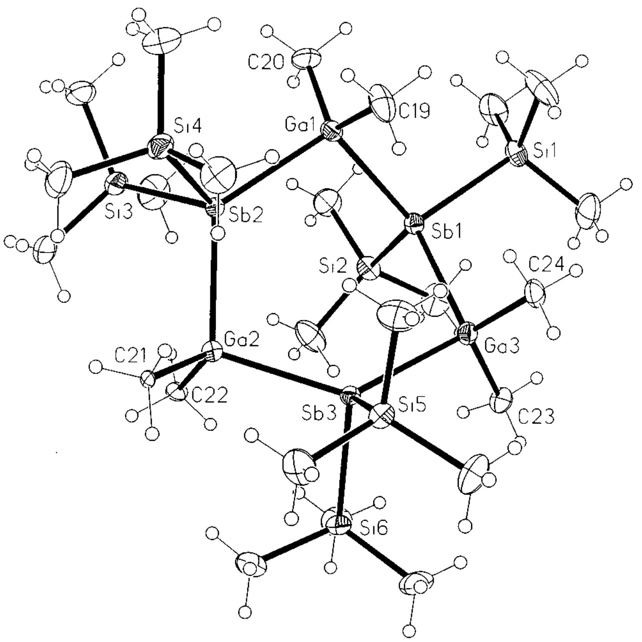

Fig. 1. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **2**.

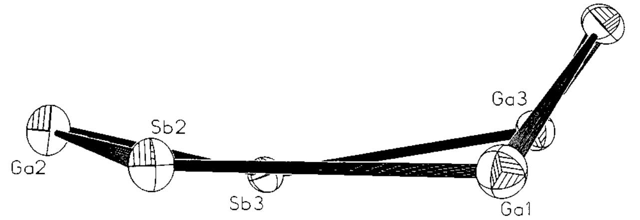

Fig. 2. ORTEP diagram (50% probability ellipsoids) showing the distorted envelope-type conformation of the six-membered Ga_3Sb_3 ring.

$GaMe_2$, 0.5), 620 (2/3M^+-$GaMe_2$-Me, 1), 536 (2/3M^+-2$GaMe_2$, 8), 368 (M^+/3, 6), 353 (M^+/3-Me, 10), 99 (Me_2Ga^+, 55), 73 ($SiMe_3^+$, 100).

3.4. Single-crystal X-ray diffraction analysis of **2**

Crystals of **2** were grown at −30°C in pentane. Crystallographic data are summarized in Table 1, and selected structural parameters in Table 2. Fig. 1 shows the ORTEP diagram of the solid state structure of **2**, and Fig. 2 the conformation of the six-membered Ga_3Sb_3 ring. Data were collected on a Nonius Kappa-CCD diffractometer. An extinction correction and an empirical absorption correction (minimum/maximum transmissions 0.4244/0.8187) were applied. The structure of **2** was solved by direct methods (SHELXS-90) [11] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97) [12].

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