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Synthesis and structural characterization of the first completely alkyl-substituted Ga–Sb Lewis acid–base adducts†

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The simple Lewis acid–base adducts $(n\text{-Bu})_3Ga(SbR_3)$ (R = Et **1**, *n*-Pr **2**, *i*-Pr **3**, *t*-Bu **4**) and $(t\text{-Bu})_3Ga(SbR_3)$ (R = Et **5**, *n*-Pr **6**, *i*-Pr **7**, *t*-Bu **8**) were prepared by combination of $n\text{-Bu}_3Ga$ or $t\text{-Bu}_3Ga$, respectively, with the corresponding trialkylstibanes in a 1 : 1 molar ratio. **1**–**8** were fully characterized by multinuclear NMR (^{1}H and ^{13}C) and mass spectroscopy. In addition, the solid state structures of **5** and **7** were determined by single crystal X-ray diffraction studies.

Introduction

The bulk of our recent research has focused on the preparation and structural characterization of compounds containing Group 13–Group 15 elements, which are of current interest due to their potential to serve as single source precursors for the preparation of the corresponding semiconducting materials by MOCVD technology. Primarily, we were interested in the synthesis of Group 13 antimonides. Our investigations have led to a simple synthetic route for the preparation of nanocrystalline GaSb material,[1] as well as to several metallo-organic AlSb[2] and GaSb[3] compounds, which were obtained as simple Lewis acid–base adducts or heterocycles containing σ-bonds between Al/Ga and Sb. The potential of $[R_2AlSb(SiMe_3)_2]_2$ (R = Et, *i*-Bu) to produce AlSb thin films by HV-MOCVD (high vacuum metal-organic chemical vapor deposition) at temperatures between 325–550 °C has previously been demonstrated.[4] However, films so-prepared showed a temperature-dependent incorporation of Si, obviously resulting from the silyl groups. Therefore, we became interested in the synthesis of precursor compounds containing only alkyl substituents.

We focused on the preparation of simple Lewis acid–base adducts of the type $R_3Ga(SbR'_3)$ (R, R′ = alkyl). While adducts of Al, Ga and In compounds with amines and phosphines are well known, investigations concerning the synthesis of Group 13–Sb adducts are rare and only a few examples have been structurally characterized: $X_3B[Sb(SiMe_3)_3]$,[5] $R_3Al[Sb(SiMe_3)_3]$,[2b] $R_2AlCl[Sb(SiMe_3)_3]$,[2b] $R_3Ga[Sb(SiMe_3)_3]$,[6] and $R_3In[Sb(SiMe_3)_3]$.[6a] Almost fifty years ago, Coates investigated the synthesis of $Me_3Ga(EMe_3)$ adducts (E = N, P, As, Sb, Bi) and found their stability to decrease from NMe_3 to $SbMe_3$, while $BiMe_3$ did not react.[7] To the best of our knowledge, no investigations concerning the structural characterization of all-alkyl-substituted Ga–Sb adducts were performed. Wells *et al.* have reported two structurally characterized Ga–Sb adducts, both containing silyl substituents bound to the Sb center.[6] The only example of completely alkyl-substituted Ga–Sb compound was described by Cowley *et al.* They prepared $[Me_2GaSb(t\text{-Bu})_2]_3$, a six-membered heterocycle, and demonstrated its potential to give GaSb films under MOCVD conditions.[8]

Herein, we report the synthesis and solid state structures of several Lewis acid–base adducts.

Results and discussion

The simple Lewis acid–base adducts $(n\text{-Bu})_3Ga(SbR_3)$ (R = Et **1**, *n*-Pr **2**, *i*-Pr **3**, *t*-Bu **4**) and $(t\text{-Bu})_3Ga(SbR_3)$ (R = Et **5**, *n*-Pr **6**, *i*-Pr **7**, *t*-Bu **8**) were prepared by reaction of $n\text{-Bu}_3Ga$ and $t\text{-Bu}_3Ga$ and the corresponding trialkylstibanes in a 1 : 1 molar ratio.

The ^{1}H NMR spectra show resonances due to the substituents bound to the Ga center shifted to lower field. Comparable results were observed in analogous adducts, *e.g.* $R_3Al(SbR'_3)$,[9] $Me_3Al(PR_3)$,[10] $R_3Ga(PR'_3)$ (R = Me, Et),[11] and $Me_3In(NR_3)$.[12] α-H and α-C shifts, as well as Δ(H), Δ(C), $\Delta_{H\text{–}H}$ and $\Delta_{C\text{–}C}$ values, for $n\text{-Bu}_3Ga$, $t\text{-Bu}_3Ga$ and the adducts **1**–**8** are summarized in Table 1.

The shifts to lower field of the α-H–Ga and α-C–Ga resonances observed for the adducts do not show a uniform development between the two adduct groups. While the resonances due to the $n\text{-Bu}_3Ga$ adducts (**1**–**4**) show the biggest lowfield shift (and therefore the biggest Δ(H) and Δ(C) values) with the electronically *strongest* base, $t\text{-Bu}_3Sb$, those due to the $t\text{-Bu}_3Ga$ adducts (**5**–**8**) show the biggest lowfield shift with the electronically *weakest* base, Et_3Sb. The spectra of **8** show resonances at exactly the same shift as was found for the starting materials, indicating this sterically overcrowded adduct to be fully dissociated in solution. Obviously, the absolute degree of shift extension of α-H–Ga or α-C–Ga related to the pure trialkyl is not useful for determination of the dative Ga–Sb bond strength. Comparable results were found for Al–P adducts.[10] In the case of the $t\text{-Bu}_3Ga$ adducts **5**–**8**, a comparison of the internal ^{13}C shift $[\Delta_{C\text{–}C} = \delta(\beta\text{-C})_{\text{trialkylgallium}} - \delta(\alpha\text{-C})_{\text{trialkylgallium}}]$ of the adduct and the pure trialkylgallium compound seems to be more useful for a qualitative determination of bond strength within Ga–Sb adducts. The largest value is observed for **5**, while **8** shows exactly the same value as $t\text{-Bu}_3Ga$. Electronically, **5** should be the weakest adduct due to the low basicity of the trialkylstibane (Et_3Sb) in this compound. However, with sterically hindered Lewis acids like $t\text{-Bu}_3Ga$, *steric repulsion* between the ligands becomes the dominating factor influencing the adduct strength. The melting points, which generally decrease within this group (**5**: 106; **6**: 56; **7**: 64; **8**: 37 °C), also agree with this expectation. The $\Delta_{C\text{–}C}$ values of **1**–**4** are higher than the $\Delta_{C\text{–}C}$ value of pure $n\text{-Bu}_3Ga$, but they are almost within the same range and are independent from the steric size of the antimony substituents.

Due to the extreme sensitivity of **1**–**8** in solution towards air and moisture, cryoscopic molecular weight measurements did

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† Electronic supplementary information (ESI) available: experimental data for adducts **2**–**4** and **6**–**8**. See http://www.rsc.org/suppdata/dt/a9/a908969a/

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Table 1 Selected ^{1}H and ^{13}C NMR shifts, Δ(H), Δ(C) values and internal shifts Δ_{H-H} and Δ_{C-C} of the pure trialkylgallium precursors and the Ga component within the adducts **1**–**8** in C_6D_6

Compound	δ^1H[a]	δ^{13}C[b]	Δ(H)[c]	Δ(C)[d]	Δ_{H-H}[e]	Δ_{C-C}[f]
n-Bu$_3$Ga	0.61	19.3	—	—	0.71	9.2
(*n*-Bu)$_3$Ga(SbEt$_3$) **1**	0.73	16.1	0.12	−3.2	0.77	12.7
(*n*-Bu)$_3$Ga[Sb(*n*-Pr)$_3$] **2**	0.66	16.9	0.05	−2.4	—	11.9
(*n*-Bu)$_3$Ga[Sb(*i*-Pr)$_3$] **3**	0.74	16.6	0.13	−2.7	0.76	12.3
(*n*-Bu)$_3$Ga[Sb(*t*-Bu)$_3$] **4**	0.80	16.4	0.19	−2.9	0.71	12.7
t-Bu$_3$Ga	1.16	31.5	—	—	—	0.4
(*t*-Bu)$_3$Ga(SbEt$_3$) **5**	1.32	26.9	0.16	−4.6	—	6.7
(*t*-Bu)$_3$Ga[Sb(*n*-Pr)$_3$] **6**	1.32	27.3	0.16	−4.2	—	6.3
(*t*-Bu)$_3$Ga[Sb(*i*-Pr)$_3$] **7**	1.23	30.0	0.07	−1.5	—	2.1
(*t*-Bu)$_3$Ga[Sb(*t*-Bu)$_3$] **8**	1.16	31.5	0	0	—	0.4

n-Bu$_3$Ga: [a] δ^1H(α-H); [b] δ^{13}C(α-C); [c] $\Delta(H) = \delta(\alpha\text{-H})_{adduct} - \delta(\alpha\text{-H})_{trialkylgallium}$; [d] $\Delta(C) = \delta(\alpha\text{-C})_{adduct} - \delta(\alpha\text{-C})_{trialkylgallium}$; [e] $\Delta_{H-H} = \delta(\beta\text{-H})_{trialkylgallium} - \delta(\alpha\text{-H})_{trialkylgallium}$; [f] $\Delta_{C-C} = \delta(\beta\text{-C})_{trialkylgallium} - \delta(\alpha\text{-C})_{trialkylgallium}$. *t*-Bu$_3$Ga: [a] δ^1H(β-H); [b] δ^{13}C(α-C); [c] $\Delta(H) = \delta(\beta\text{-H})_{adduct} - \delta(\beta\text{-H})_{trialkylgallium}$; [d] $\Delta(C) = \delta(\alpha\text{-C})_{adduct} - \delta(\alpha\text{-C})_{trialkylgallium}$; [f] $\Delta_{C-C} = \delta(\beta\text{-C})_{trialkylgallium} - \delta(\alpha\text{-C})_{trialkylgallium}$.

not give reliable values. Therefore, we were not able to determine in detail the degree of dissociation in solution, but we believe all the adducts to be extensively dissociated in solution. Beachley and Maloney investigated the adduct formation of several trialkylgallium compounds with phosphanes and found most of them to be extensively dissociated in solution.[13] Due to the weaker basicity of stibanes compared to phosphanes,[14] **1**–**8** should also dissociate in solution. However, in the absence of solvent, we believe **1**–**8** to be "real" adducts for the following reasons:

(1) The combination of the weak acid *t*-Bu$_3$Ga with the stibanes yields solids in each case, indicating adduct formation. The solid state structures of two such compounds were determined.

(2) *n*-Bu$_3$Ga is the stronger Lewis acid compared to the more sterically demanding *t*-Bu$_3$Ga and should give stronger adducts.

(3) *n*-Bu$_3$Ga forms a solid adduct with the most sterically demanding stibane *t*-Bu$_3$Sb.

Mass spectra of **1**–**8** show only the respective starting Ga and Sb trialkyls, indicating dissociation of the adducts in the gas phase. However, the solid adducts can be sublimed without decomposition at 60–80 °C at 10^{-2} mbar.

Single crystals of **5** and **7** suitable for X-ray crystallographic study were obtained from solutions in pentane at −30 °C. In **5** and **7**, the Ga and Sb centers reside in distorted tetrahedral environments with their ligands adopting a staggered conformation relative to one another. The mean Ga–C (**5**: 2.044; **7**: 2.042 Å) and Sb–C bond lengths (**5**: 2.151; **7**: 2.184 Å), as well as the mean C–Ga–C (**5**: 116.4; **7**: 115.9°) and C–Sb–C bond angles (**5**: 97.6; **7**: 100.2°), are within the expected range. The C–Ga–Sb angles range from 100.57(12) to 101.64(12)° in **5** and from 99.07(5) to 104.48(5)° in **7**. The C–Sb–Ga angles in **5** vary from 118.95(13) to 120.84(14)°, while **7** shows a much greater variation, from 111.26(4) to 122.51(4)°. Smaller ranges were observed in Et$_3$Ga[Sb(SiMe$_3$)$_3$] [Si–Sb–Ga 114.50(22)–116.10(24)°] and (*t*-Bu)$_3$Ga[Sb(SiMe$_3$)$_3$] [Si–Sb–Ga 114.68(7)–118.53(6)°]. However, the analogous Al–Sb adduct (*t*-Bu)$_3$Al[Sb(*i*-Pr)$_3$] shows comparable C–Sb–Al bond angles [112.20(4)–121.98(4)].[9] The Ga–Sb distances [**5**: 2.8479(5); **7**: 2.9618(2) Å] clearly display the influence of steric bulk on the bond lengths. *i*-Pr$_3$Sb is more sterically demanding than Et$_3$Sb, leading to an elongated Ga–Sb bond distance due to an increased steric repulsion between the ligands. The Ga–Sb bond distances determined in Et$_3$Ga[Sb(SiMe$_3$)$_3$] [2.846(5) Å] and (*t*-Bu)$_3$Ga[Sb(SiMe$_3$)$_3$] [3.027(2) Å] span a wide range of almost 18 pm. **5** and **7** fit into this "bond distance window" very well. Compared to Et$_3$Ga[Sb(SiMe$_3$)$_3$], the steric pressure within **5** is almost the same. The basicity of Et$_3$Sb should be greater than that of Sb(SiMe$_3$)$_3$ for the following reasons:

(1) The SiMe$_3$ group is a π-acceptor, which leads to reduced electron density at the Sb atom.

(2) Steric repulsion between the ligands, which should yield weaker adducts, is greater in Sb(SiMe$_3$)$_3$ compared to Et$_3$Sb.

Therefore, the Ga–Sb bond length in **5** should be shorter than that in Et$_3$Ga[Sb(SiMe$_3$)$_3$]. On the other hand, *t*-Bu$_3$Ga is less acidic than Et$_3$Ga, which should lead to an elongated Ga–Sb distance. Obviously, both effects compensate for each other, resulting in very similar bond lengths. Compared to (*t*-Bu)$_3$Ga[Sb(SiMe$_3$)$_3$], **5** and **7** are stronger adducts, due to less steric repulsion between the ligands, hence the shorter Ga–Sb bond lengths. On steric grounds **8** should show the longest Ga–Sb bond distance, but we were not able to obtain suitable crystals for a single crystal X-ray structure determination.

MOCVD studies are currently underway in our laboratories, using the *t*-Bu$_3$Ga adducts in an attempt to demonstrate their potential for producing GaSb thin films.[15]

Experimental

General considerations

All manipulations were performed in a glovebox under a N$_2$ atmosphere or by standard Schlenk techniques. Pentane was carefully dried over sodium–potassium alloy under dry N$_2$. *n*-Bu$_3$Ga and *t*-Bu$_3$Ga,[16] as well as Et$_3$Sb, *n*-Pr$_3$Sb and *i*-Pr$_3$Sb,[17] were prepared according to literature methods. *t*-Bu$_3$Sb was isolated from a standard salt elimination reaction between *t*-BuLi and SbCl$_3$ at −100 °C. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ^{1}H and ^{13}C{^{1}H} spectra were referenced to internal C$_6$D$_5$H (δ^1H 7.154, δ^{13}C 128.0). Mass spectra were recorded on a VG Masslab 12-250 spectrometer in electron ionization mode at 20 eV. Melting points were observed in sealed capillaries and were not corrected.

General synthesis of R$_3$Ga(SbR$_3$) adducts

Pure R$_3$Ga (2 mmol) and R$_3$Sb (2 mmol) were combined in the glovebox. **5**–**8** were obtained as white solids, the other adducts stayed liquid. At −30 °C **3** and **4** also solidified. **5**–**8** were crystallized in almost quantitative yield from pentane (5–10 mL) at −30 °C. Experimental data are given for one *n*-Bu$_3$Ga and one *t*-Bu$_3$Ga adduct only. Data for the other six adducts have been deposited as electronic supplementary information (ESI).

(*n*-Bu)$_3$Ga(SbEt$_3$) (1). Elemental analysis (C$_{18}$H$_{42}$GaSb, $M = 450.0$ g mol^{-1}), found (calc.): C, 47.82 (48.04); H, 9.32 (9.41). ^{1}H NMR (300 MHz, C$_6$D$_5$H, 25 °C): $\delta = 0.73$ (m, 2H, GaC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.02 (t, $^3J_{HH} = 7.2$ Hz, 3H, GaCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.10 (m, 3H, SbCH$_2$C*H*$_3$), 1.23 (m, 2H, SbC*H*$_2$CH$_3$), 1.50 (m, $^3J_{HH} = 7.1$ Hz, 2H, GaCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.67 (m, 2H, GaCH$_2$CH$_2$C*H*$_2$CH$_3$). ^{13}C{^{1}H} NMR (80 MHz, C$_6$D$_5$H, 25 °C): $\delta = 5.4$ (Sb*C*H$_2$CH$_3$), 11.4 (SbCH$_2$*C*H$_3$), 14.5 (GaCH$_2$-

Table 2 Crystallographic data for $(t\text{-Bu})_3\text{Ga}(\text{SbEt}_3)$ (**5**) and $(t\text{-Bu})_3\text{Ga}[\text{Sb}(i\text{-Pr})_3]$ (**7**)

	5	**7**
Chemical formula	$C_{18}H_{42}GaSb$	$C_{21}H_{48}GaSb$
Formula weight	449.99	492.06
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
Crystal dimensions/mm	0.35 × 0.25 × 0.20	0.60 × 0.55 × 0.50
a/Å	14.1615(3)	13.6128(2)
b/Å	9.5735(2)	9.0089(2)
c/Å	16.0291(4)	20.0307(2)
β/°	90.905(2)	91.750(1)
V/Å^3	2172.88(8)	2455.35(7)
Z	4	4
μ/mm^{-1}	2.477	2.198
Temperature/K	123(2)	123(2)
D_{calcd}/g cm^{-3}	1.376	1.331
Reflections collected	40096	31295
Non-equivalent reflections	5368	5802
R_{int}	0.052	0.039
$R1$,[a] $wR2$[b]	0.041, 0.114	0.020, 0.049

[a] For $I > 2\sigma(I)$. [b] For all data.

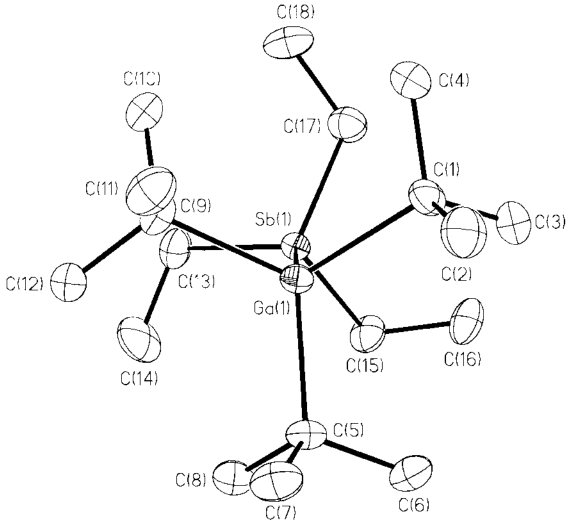

Fig. 1 ORTEP diagram (50% probability ellipsoids) showing the staggered conformation and atom-numbering scheme for **5**; selected bond lengths (Å) and angles (°): Ga(1)–Sb(1) 2.8479(5), Ga(1)–C(1) 2.058(4), Ga(1)–C(5) 2.035(4), Ga(1)–C(9) 2.039(4), Sb(1)–C(13) 2.156(4), Sb(1)–C(15) 2.150(4), Sb(1)–C(17) 2.148(5); C(1)–Ga(1)–C(5) 116.71(17), C(1)–Ga(1)–C(9) 115.88(17), C(5)–Ga(1)–C(9) 116.72(17), C(13)–Sb(1)–C(15) 97.32(18), C(13)–Sb(1)–C(17) 97.91(19), C(15)–Sb(1)–C(17) 97.55(19), C(1)–Ga(1)–Sb(1) 101.64(12), C(5)–Ga(1)–Sb(1) 100.83(12), C(9)–Ga(1)–Sb(1) 100.57(12), C(13)–Sb(1)–Ga(1) 120.84(14), C(15)–Sb(1)–Ga(1) 118.95(13), C(17)–Sb(1)–Ga(1) 119.26(13).

$CH_2CH_2CH_3$), 16.1 ($GaCH_2CH_2CH_2CH_3$), 28.8 ($GaCH_2CH_2CH_2CH_3$), 31.0 ($GaCH_2CH_2CH_2CH_3$). EI-MS (m/z, %): 240 (40) [n-Bu_3Ga^+], 208 (35) [Et_3Sb^+], 57 (100) [n-Bu^+].

$(t\text{-Bu})_3\text{Ga}(\text{SbEt}_3)$ (5). Elemental analysis ($C_{18}H_{42}GaSb$, $M = 450.0$ g mol^{-1}), found (calc.): C, 47.91 (48.04); H, 9.34 (9.41). Mp: 106 °C. ^1H NMR (300 MHz, C_6D_5H, 25 °C): $\delta = 1.06$ (m, 3H, $SbCH_2CH_3$), 1.28 (m, 2H, $SbCH_2CH_3$), 1.32 (s, 9H, t-Bu). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): $\delta = 5.9$ ($SbCH_2CH_3$), 11.1 ($SbCH_2CH_3$), 26.9 ($GaC(CH_3)_3$), 33.7 ($GaC(CH_3)_3$). EI-MS (m/z, %) 240 (55) [t-Bu_3Ga^+], 208 (25) [Et_3Sb^+], 57 (100) [t-Bu^+].

X-Ray structure solution and refinement

Crystallographic data are summarized in Table 2. Figs. 1 and 2 show ORTEP diagrams of the solid state structures of **5** and **7**, including selected bond lengths and angles. Data were collected on a Nonius Kappa-CCD diffractometer. Absorption corrections were applied. The structures were solved by direct methods (SHELXS-86)[18] 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).[19]

CCDC reference number 186/1817.

See http://www.rsc.org/suppdata/dt/a9/a908969a/ for crystallographic files in .cif format.

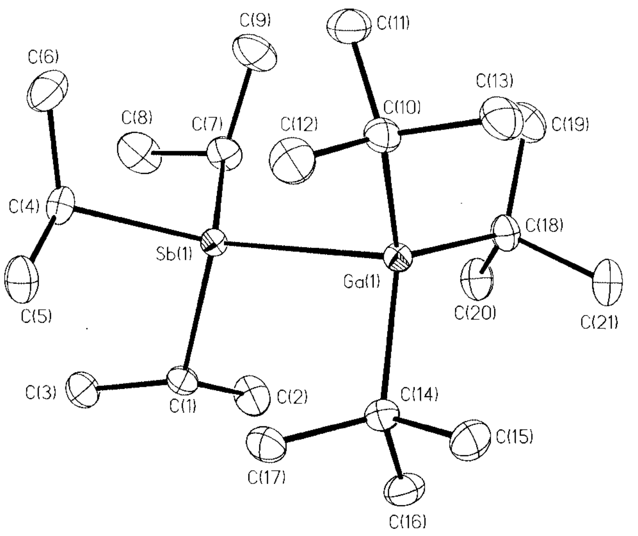

Fig. 2 ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **7**; selected bond lengths (Å) and angles (°): Ga(1)–Sb(1) 2.96178(19), Ga(1)–C(10) 2.0392(15), Ga(1)–C1(4) 2.0429(16), Ga(1)–C(18) 2.0450(16), Sb(1)–C(1) 2.1866(15), Sb(1)–C(4) 2.1805(15), Sb(1)–C(7) 2.1843(17); C(10)–Ga(1)–C(14) 115.74(7), C(10)–Ga(1)–C(18) 115.70(7), C(14)–Ga(1)–C(18) 116.20(7), C(1)–Sb(1)–C(4) 98.29(6), C(1)–Sb(1)–C(7) 100.96(6), C(4)–Sb(1)–C(7) 101.33(7), C(10)–Ga(1)–Sb(1) 104.48(5), C(14)–Ga(1)–Sb(1) 99.07(5), C(18)–Ga(1)–Sb(1) 102.05(5), C(1)–Sb(1)–Ga(1) 111.26(4), C(4)–Sb(1)–Ga(1) 122.51(4), C(7)–Sb(1)–Ga(1) 118.74(5).

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