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Lewis acid-base adduct Me₃Sb–Ga(*t*-Bu)₃

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Lewis acid-base adduct $\text{Me}_3\text{Sb}-\text{Ga}(t\text{-Bu})_3$

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The synthesis and single crystal X-ray analysis of the completely alkyl-substituted Lewis acid-base adduct $\text{Me}_3\text{Sb}-\text{Ga}(t\text{-Bu})_3$, which was obtained from the equimolar reaction of Me_3Sb and $\text{Ga}(t\text{-Bu})_3$, is described.

Lewis acid-base adduct Me₃Sb—Ga(*t*-Bu)₃

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Abstract The simple Lewis acid-base adduct Me₃Sb—Ga(*t*-Bu)₃ **1** was prepared by reaction of *t*-Bu₃Ga and SbMe₃ in 1:1 molar ratio. **1** was fully characterized by multinuclear NMR spectroscopy (¹H, ¹³C). In addition, its solid state structure was determined by single crystal X-ray diffraction studies. **1** is monoclinic, space group *P2₁/n* with *a* = 8.4895(2) Å, *b* = 12.9303(4) Å, *c* = 17.9976(5) Å, *β* = 97.472(2)° and *Z* = 4.

Keywords Lewis-base · Lewis acid · X-ray crystal structure

Short title: Lewis acid-base adduct

Introduction

Donor-acceptor interactions between Lewis-acidic group 13 complexes (R_3M ; $M = B - Tl$) and Lewis-basic group 15 complexes (R_3E ; $E = N - Bi$) have been intensely studied since the first report of $F_3B \cdot NH_3$ by Gay-Lussac more than two centuries ago [1] and the nature of the donor-acceptor interactions has been investigated in detail since then. Moreover, these type of complexes were found to play a key role both in organic and inorganic synthesis. More recently, their potential application to serve as *taylor-made* single-source precursors for the deposition of thin material films by MOCVD process forced the interest in such complexes. The role of the central metal atoms (M and E) and the organic substituents on the stability of these adducts, i.e. their dissociation energies, was of particular interest [2]. While borane, alane, and gallane adducts with amines and phosphines have been structurally characterized in large numbers [3], adducts of the heavier group 15 elements, stibines R_3Sb and bismuthines R_3Bi , were only scarcely investigated. Early studies on the reactions of $GaMe_3$ with trimethylpnictines EMe_3 ($E = N, P, As, Sb, Bi$) yielded the expected adducts $Me_3Ga-EMe_3$ except for $BiMe_3$, which did not form a stable compound [4]. In addition, $Me_3Ga-SbMe_3$ was unstable under these conditions so that the exact dissociation enthalpy could not be determined. These findings clearly correspond to the decreasing basicity of the trialkylpnictene R_3E with increasing atomic number of the central group 15 element due to the increased *s*-character of the *lone pair* of the heavier group 15 elements, which is now generally accepted.

Due to our interest in such complexes of the heaviest elements of group 15, Sb and Bi, we prepared several group 13-stibine adducts of the desired type in the last decade [5] as well as the first bismuthine [6], distibine [7] and dibismuthine adducts [8]. These adducts were typically formed with sterically hindered stibines and bismuthines contained bulky organic substituents such as *i*-Pr, *t*-Bu and $SiMe_3$ groups. Adducts containing the sterically less hindered group 15 bases such as $SbMe_3$ and $BiMe_3$ seem to be less stable, as was also found for analogous transition metal complexes of these bases [9]. Only a very few examples have been structurally characterized. Herein, we describe the first structurally characterized $SbMe_3$ adduct of a group 13 trialkyl.

Experiments

Manipulations were performed in a glove box under an Ar-atmosphere or with standard Schlenk techniques. Dry solvents were obtained from a solvent purification system (MBraun) and degassed prior to use. *t*- Bu_3Ga [10] and Me_3Sb [11] were prepared according to literature methods. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. 1H and $^{13}C\{^1H\}$ NMR spectra were referenced to internal C_6D_5H (1H : $\delta = 7.154$; ^{13}C : $\delta = 128.0$). Melting points were measured in

sealed capillaries and were not corrected. Elemental analyses were performed at the Elementaranalyse Labor of the University of Bonn.

Synthesis of $\text{Me}_3\text{Sb}-\text{Ga}(t\text{-Bu})_3$ **1**

$\text{Ga}(t\text{-Bu})_3$ (1 mmol, 0.24 g) and Me_3Sb (1 mmol, 0.17 g) were dissolved in *n*-pentane and stored at -30 °C. After 48 h, colorless crystals of **1** were obtained (0.35 g, 85 %. m.p. 98 °C). Elemental analysis $\text{C}_{15}\text{H}_{36}\text{GaSb}$ ($M = 407.91$ g/mol), Found (calc.): C 44.08 (44.2.); H 8.45 (8.9). Spectroscopic analysis: ^1H -NMR (300 MHz, C_6D_6 , 25 °C): $\delta = 0.62$ (s, 3H, SbCH_3), 1.28 (s, 9H, *t*-Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (80 MHz, $\text{C}_6\text{D}_5\text{H}$, 25 °C): $\delta = -5.1$ (SbCH_3), 25.8 ($\text{Ga}-\text{C}(\text{CH}_3)_3$), 31.8 ($\text{Ga}-\text{C}(\text{CH}_3)_3$).

The ^1H -NMR spectrum of **1** shows resonances due to the organic ligands bound to the metal centers, whose integration indicated the formation of a simple 1:1 Lewis acid-base adduct. The resonances of the substituents bound to the Ga atom are only slightly shifted to lower field compared to starting $\text{Ga}(t\text{-Bu})_3$, indicating **1** to be almost fully dissociated in solution at ambient temperature. Comparable results were observed in analogous $\text{R}_3\text{Sb}-\text{GaR}'_3$ adducts [5b].

Crystallization of **1**

A solution of 0.25 g **1** in 3 mL of *n*-pentane was stored at -30 °C. Single crystals suitable for a single crystal X-ray analysis were obtained after 72 h. Table 1 illustrates the crystal data and structure refinement of **1**.

((Table 1 here))

Crystal structure of **1**

Data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å) at $T = -150$ °C and the structure was solved by Direct Methods and refined by full-matrix least-squares on F^2 . A semi-empirical absorption correction was applied. All non-hydrogen atoms in **1** were refined anisotropically and hydrogen atoms were located from ΔF maps and refined at idealized positions using a riding model with C-H distances 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ [12]. CCDC-265625 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by contacting The Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk.

Results and Discussion

1 crystallizes in the monoclinic space group $P2_1/n$ (No. 14). Single crystals were obtained from solutions in pentane at $-30\text{ }^{\circ}\text{C}$. The metal atoms both adopt tetrahedral coordination spheres. The substituents bound to the Ga and Sb atom adopt a staggered conformation relative to one another as was previously observed for such complexes.

Figure 1 The solid-state structure and atom-numbering scheme for $\text{Me}_3\text{Sb-Ga}(t\text{-Bu})_3$ **1**. Displacement ellipsoids are drawn at the 50% probability level.

The mean Ga-C ($2.036(3)\text{ \AA}$) and Sb-C ($2.135(3)\text{ \AA}$) bond lengths in **1** are within the expected range but slightly shorter compared to those observed for $\text{R}_3\text{Sb-Ga}(t\text{-Bu})_3\text{Ga}$ [**5b**]. The Ga-Sb bond length in **1** ($2.8435(3)\text{ \AA}$) is also comparable to those in $\text{Et}_3\text{Sb-Ga}(t\text{-Bu})_3$ ($2.8479(5)\text{ \AA}$) whereas that observed for $i\text{-Pr}_3\text{Sb-Ga}(t\text{-Bu})_3$ is significantly elongated ($2.9618(2)\text{ \AA}$). These results clearly reflect the strong influence of the steric demand of the organic substituents on the structure parameters of such adducts. Comparable findings become obvious when comparing the sum of the bond angles observed at the metal centers. Those of the Me_3Sb (Ga: $350.6(2)^{\circ}$; Sb: $294.1(2)^{\circ}$) and Et_3Sb adducts (Ga: $349.2(2)^{\circ}$; Sb: $292.8(2)^{\circ}$) are comparable, whereas the $i\text{-Pr}_3\text{Sb}$ adduct shows smaller C-Ga-C and wider C-Sb-C bond angles (Ga: $347.7(1)^{\circ}$; Sb: $300.6(1)^{\circ}$) due to the sterically

more hindered *i*-Pr substituents, which lead to an increased steric repulsion between the ligands. Comparable trends have been previously reported for the corresponding Al-Sb adducts R₃Sb—Al(*t*-Bu₃) [5c].

((Table 2 here))

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Table 1 Crystal data and structure refinement of **1**

CCDC deposit no.	265625
Empirical formula	C ₁₅ H ₃₆ GaSb
Formular weight	407.91
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	$a = 8.4895(2)$ Å $b = 12.9303(4)$ Å $c = 17.9976(5)$ Å, $\beta = 97.472(2)^\circ$
Volume	1958.85(9) Å ³
Z	4
Density (calculated)	1.383 Mg m ⁻³
Absorption coefficient	2.739 mm ⁻¹
F(000)	832
Crystal size	0.30 x 0.25 x 0.20 mm
Theta range for data collection	25.00°
Index range	-10 ≤ h ≤ 10, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	15426
Independent reflections	3445; 2078 reflections with $I > 2_\sigma(I)$ ($R_{\text{int}} = 0.047$)
Completeness to theta = 56.60°	99.7%
Max. and min. transmission	0.58576 and 0.52498
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3445/0/154
goodness-of-fit on F^2	0.872
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.021$, $wR2 = 0.046$
R indices (all data)	$R1 = 0.045$, $wR2 = 0.051$
Largest diff. peak and hole	0.332 and -0.578 e Å ⁻³

Table 2 Selected geometric parameters (Å, °).

Sb1-C1	2.132(3)	Ga1-C4	2.035(2)
Sb1-C2	2.136(3)	Ga1-C8	2.036(2)
Sb1-C3	2.137(3)	Ga1-C12	2.037(2)
Sb1-Ga1	2.8435(3)		
C1-Sb1-C2	97.41(13)	C4-Ga1-C8	116.53(12)
C1-Sb1-C2	97.80(12)	C4-Ga1-C12	116.71(12)
C2-Sb1-C3	98.93(13)	C8-Ga1-C12	117.36(11)

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