

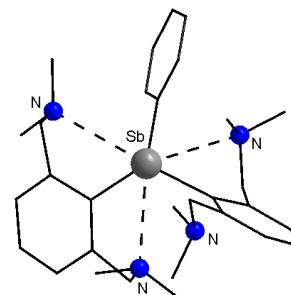
HYPERCOORDINATION IN TRIORGANOANTIMONY(III) COMPOUNDS. CASE STUDY OF HETEROLEPTIC [2,6-(Me₂NCH₂)₂C₆H₃]₂(Ph)Sb

Răzvan ȘUTEU, Cristian SILVESTRU and Anca SILVESTRU*

Supramolecular Organic and Organometallic Chemistry Centre (CCSOOM), Chemistry Department, Faculty of Chemistry and Chemical Engineering, “Babeș-Bolyai” University, RO-400028 Cluj-Napoca, Roumania

Received April 1, 2024

The triorganoantimony(III) compound [2,6-(Me₂NCH₂)₂C₆H₃]₂(Ph)Sb (**1**), containing three aryl groups, two of them with two pendant arms capable for N→Sb intramolecular interactions, was prepared and structurally investigated, both in solution and in solid state. The ¹H and the ¹³C NMR spectra suggested no intramolecular N→Sb interaction. The molecular structure was determined by single-crystal X-ray diffraction and revealed a *N,C,N*-tridentate coordination of one 2,6-(Me₂NCH₂)₂C₆H₃ group, while the other one displayed only a *C,N*-bidentate coordination behaviour towards antimony. The coordination environment about antimony is a highly distorted octahedron, and the compound can be described as a *14-Sb-6* hypercoordinate species.



INTRODUCTION

The chemistry of organoantimony compounds attracted a continuously growing interest during last years, mainly due to their importance in the technology of semiconducting materials for electronic devices,¹ as active catalysts in organic synthesis (*e.g.* the polymerization of oxirane (C₂H₄O) or substituted oxiranes,² oxidation of diaryl- α -ketoalcohols into the corresponding α -diketones,³ direct Mannich and cross-condensation reactions of amines, aldehydes and ketones⁴), or as biologically active agents.⁵ Organoantimony compounds were also found to successfully capture CO₂,⁶ or to catalyse the reaction of CO₂ with

various organic compounds,^{7–9} *e.g.* amines or epoxides.

In low oxidation states, organoantimony compounds can be stabilized by using either bulky organic groups, or ligands bearing organic groups with donor atoms capable of intramolecular coordination.^{5,10} Thus, various hypervalent organoantimony(III) compounds were synthesized using *C,E*-bidentate or *E,C,E*- and *C,E,C*-tridentate ligands (E = N, P, O, S, Se). It was pointed out that such organic groups not only confer stability to the antimony species, but also reduce the Lewis acidity of the metal centre. In this way, a balance between stability and reactivity of the organoantimony species can be finely tuned.^{11,12} The hypervalent

* Corresponding author: anca.silvestru@ubbcluj.ro

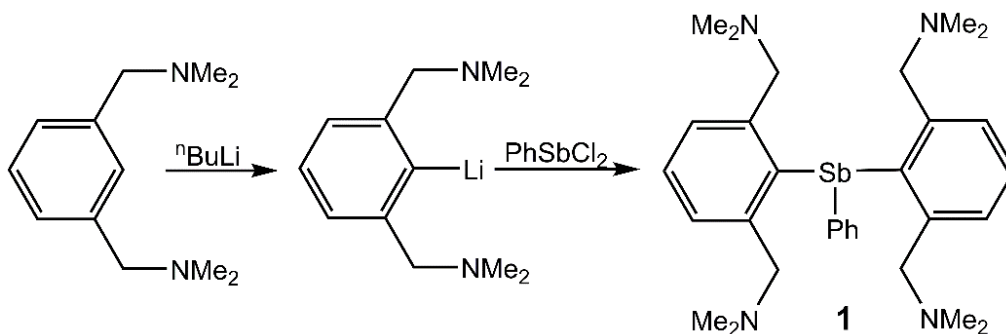
organoantimony(III) oxide cyclo-[2,6-(Me₂NCH₂)₂C₆H₃]₂Sb₂O₂ was reported to bind reversibly equimolar amounts of CO₂, thus resulting in the mononuclear carbonate [2,6-(Me₂NCH₂)₂C₆H₃]₂SbCO₃.⁶

We have reported previously organoantimony(III) compounds with organic groups bearing only one pendant arm capable for intramolecular N→Sb interaction, *e.g.* [2-(Me₂NCH₂)C₆H₄]_nSbX_{3-n} (X = Cl, Br, I, NCS; n = 1, 2),^{13,14} [2-(Me₂NCH₂)C₆H₄]₂SbONO₂,¹⁵ [2-(Me₂NCH₂)C₆H₄](R)SbF [R = 2-(Me₂NCH₂)C₆H₄, Ph],¹⁶ [2-(Me₂NCH₂)C₆H₄](Mes)₂Sb,¹⁷ [2-(Me₂NCH₂)C₆H₄](Ph)SbX, [2-(Me₂NCH₂)C₆H₄]₂(Ph)Sb,¹⁸ [2-(Me₂NCH₂)C₆H₄Sb]₄,¹⁹ or with two pendant arms, namely [2,6-{MeN(CH₂CH₂)₂C₆H₃}SbCl₂,²⁰ [2,6-(Me₂NCH₂)C₆H₃SbE]₂ (E = O, S, Se),²¹ and [2,6-(Me₂NCH₂)C₆H₃]₂Sb(OAr)₂ [Ar = C₆H₃ⁱPr₂-2,6, C₆H₃(OMe)₂-2,6].²² As a continuation of our work, we describe here the

synthesis and structural characterization of the compound [2,6-(Me₂NCH₂)₂C₆H₃]₂(Ph)Sb (**1**). To the best of our knowledge, this is the first example of a heteroleptic organoantimony(III) compound with two organic groups bearing two pendant arms capable for N→Sb intramolecular interactions.

RESULTS

The triorganoantimony(III) compound **1** was obtained by reacting the organolithium reagent [2,6-(Me₂NCH₂)₂C₆H₃]₂Li with PhSbCl₂ in a 2:1 molar ratio, as depicted in Scheme 1. The product was isolated as a beige powder, soluble in common organic solvents.



Scheme 1 – Synthesis of compound **1**.

Compound **1** was investigated by NMR spectroscopy (¹H, ¹³C, 2D experiments) in CDCl₃ solution, mass spectrometry, and by single-crystal X-ray diffraction. The molecular

structure of **1** with the atom numbering scheme is shown in Fig 1, while a selection of interatomic distances and bond angles are given in Table 1.

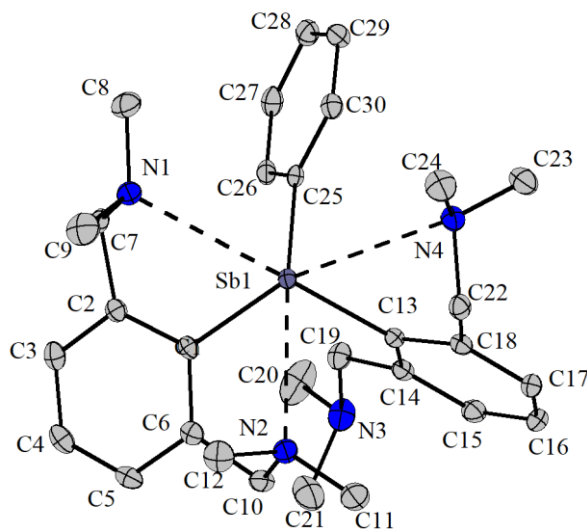


Fig. 1 – ORTEP-like representation of compound **1**, with thermal ellipsoids at 30% probability level. Hydrogen atoms were omitted for clarity.

Table 1

Interatomic distances (Å) and angles (°) for compound **1**

Sb1–C1	2.1936(12)	C1–Sb1–C13	100.97(5)
Sb1–C13	2.2247(13)	C13–Sb1–N1	159.174(46)
Sb1–C25	2.1765(13)	C13–Sb1–N2	73.728(43)
Sb1–N1	2.9683(14)	C13–Sb1–N4	67.526(42)
Sb1–N2	2.999(1)	N1–Sb1–N4	125.66
Sb1–N4	3.1816(14)	N1–Sb1–N2	114.94
		N2–Sb1–N4	100.20

DISCUSSION

Solution behaviour

The NMR spectra of compound **1** are in accordance with the desired composition and they suggest the equivalence of the two 2,6-(Me₂NCH₂)₂C₆H₃ groups in solution, as well as the equivalence of the two Me₂NCH₂ pendant arms in each 2,6-(Me₂NCH₂)₂C₆H₃ group. The aliphatic region of the ¹H NMR spectrum contains the expected resonances, namely a singlet resonance for the methyl protons in the CH₃ groups attached to nitrogen, while the resonance for the CH₂N protons appears as an AB spin system. In the aromatic region multiplet resonances corresponding to the non-equivalent protons in the phenyl group and the C₆H₃ rings were observed.

In the ¹³C NMR spectrum of compound **1** the expected resonances for the aliphatic and the aromatic carbons are present. In the aliphatic region two singlet signals were assigned to the equivalent methyl and methylene carbons in the pendant arms, while in the aromatic region, the resonances for the non-equivalent aromatic carbons could be assigned based on 2D correlation experiments.

Based on the NMR spectra we assume that in solution the pendant arms are not involved in any intramolecular N→Sb interaction.

The ESI+ mass spectrum contains the base peak characteristic for the ion [M-{(Me₂NCH₂)₂C₆H₃}]⁺ at the *m/z* value of 389.09692 (calcd. *m/z* 389.09722), resulted by fragmentation and removing one aromatic group with two pendant arms. Unfortunately, a peak corresponding to the molecular ion could not be observed.

Single-crystal X-ray diffraction studies

The two 2,6-(Me₂NCH₂)₂C₆H₃ groups behave differently towards antimony, namely one of them displays a *N,C,N*-tridentate coordination pattern, with both pendant arms intramolecularly coordinated to the metal, while the other has a bidentate *C,N*-coordination pattern, with only one of the two pendant arms interacting with antimony and the second nitrogen atom being pushed away from the metal atom, at a non-bonding distance (5.02 Å), much greater than the sum of the van der Waals radii of the two elements [$\Sigma r_{\text{vdw}}(\text{N,Sb}) = 4.13 \text{ \AA}^{23}$]. In this way, three NC₃Sb five-membered rings are formed, and they are not planar, but folded about the C⋯Sb imaginary axis (C7⋯Sb1, C10⋯Sb1, and C22⋯Sb1, respectively).

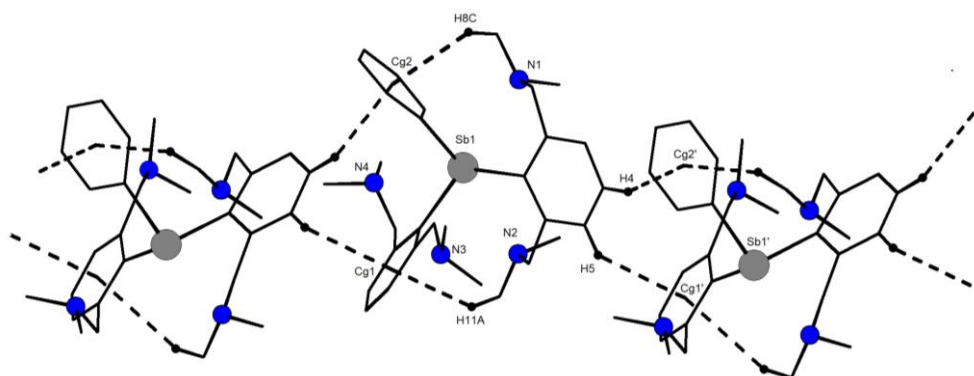


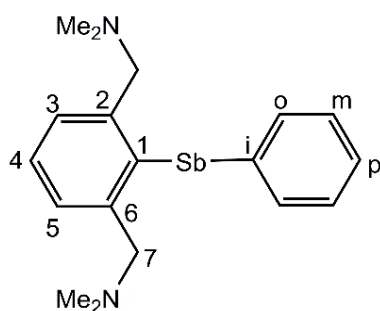
Fig. 2 – A chain in the crystal of **1**. Hydrogen atoms, except those involved in CH⋯π interactions were omitted for clarity.

Due to the induced planar chirality in each five-membered ring and the chirality of antimony, the compound can be described as a mixture of $C_{Sb}, pR_{N1}, pS_{N2}, pR_{N4}$ and $A_{Sb}, pS_{N1}, pR_{N2}, pS_{N4}$ isomers, where C and A refer to the chirality at the metal atom, while pR and pS refer to the planar chirality of each NC_3Sb five-membered ring.²⁴ The coordination sphere about antimony is completed by the phenyl group in a distorted octahedral environment and the compound can be described as a $14-Sb-6$ hypercoordinate species.²⁵

A close look at the crystal lattice revealed $CH\cdots\pi$ interactions, namely: $H4\cdots Cg(C25-C30)$ 2.673 Å, $H5\cdots Cg(C13-C18)$ 2.805 Å, $H8C\cdots Cg(C25-C30)$ 2.897 Å and $H11A\cdots Cg(C13-C18)$ 3.026 Å, thus resulting in a chain-like supramolecular association (Fig. 2).

EXPERIMENTAL

The starting materials $PhSbCl_2$,²⁶ and $2,6-(Me_2NCH_2)_2C_6H_3Li$,²⁷ were prepared by literature procedures. The other reactants were commercially available and used as received. The melting point was measured on an Electrothermal 9200 apparatus. Elemental analysis was performed on a Flash EA 1112 analyzer. The ESI+ mass spectrum was recorded on a Thermo Scientific LTQ-Orbitrap XL spectrometer equipped with a standard ESI/APCI source. The 1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a BRUKER Avance 400 instrument and the chemical shifts are reported in δ units (ppm) relative to the residual peak of the solvent ($CHCl_3$, 7.26 ppm) in the 1H NMR spectra and to the peak of the deuterated solvent ($CDCl_3$, 77.16 ppm) in the $^{13}C\{^1H\}$ NMR spectra. They are assigned according to the numbering way displayed in Scheme 2. The NMR and the mass spectra were processed using the MestReNova,²⁸ and the Thermo Xcalibur softwares,²⁹ respectively.



Scheme 2 – Numbering scheme for NMR assignments in compound **1**.

Synthesis of $[2,6-(Me_2NCH_2)_2C_6H_3]_2(Ph)Sb$ (**1**)

To a solution of $[2,6-(Me_2NCH_2)_2C_6H_3]Li$ (1 g; 5 mmol) in THF (20 ml) was gradually added $PhSbCl_2$ (0.680 g; 2.5 mmol) and the reaction mixture was left with stirring overnight. The solvent was removed in vacuum and the compound was extracted in CH_2Cl_2 , followed by evaporation of the solvent, when the desired product resulted as a beige

solid. Yield: 1.17 g (80%). M.p. 120 °C. Anal. calcd. for $C_{30}H_{43}N_4Sb$ ($M = 581.46$): C, 61.97; H, 7.45; N, 9.64%. Found C, 61.72; H, 7.27; N, 9.55%. 1H NMR ($CDCl_3$, 400.13 MHz): δ 1.90 (24H, s, CH_3), AB spin system with δ_A 3.18 and δ_B 3.48 (8H, H_7 , $^2J_{HH}$ 13.4 Hz), 7.10–7.15 (m, 9H, $H_{3-5} + H_{m+p}$), 7.70–7.74 (m, 2H, H_o). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ 44.59 (CH_3), 66.25 (C_7), 126.49 (C_i), 126.94 (C_m), 127.00 (C_4), 127.56 (C_{3+5}), 137.22 (s, C_o), 144.13 (C_p), 146.40 (C_{2+6}), 146.65 (C_i). HRMS (ESI+, MeOH): m/z (%) 389.09692 (100) $[M-\{2,6-(Me_2NCH_2)_2C_6H_3\}]^+$.

Crystal structure determination

Suitable crystals for single-crystal X-ray diffraction were obtained from a mixture of CH_2Cl_2 and n-hexane in a 1:4 ratio, v:v. Details of the crystal structure determination and refinement are given in Table 2. Data were collected on a Bruker D-8 Venture diffractometer, using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) from a I μ S 3.0 microfocus source with multilayer optics, at 110 K. The structure was refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the Bruker APEX3 Software Package was used.³⁰ Intermolecular secondary bonding interactions were found with PLATON.^{31,32} The drawings were created with the Diamond program.³³

Table 2

X-ray crystal data and structure refinement for compound $[2,6-(Me_2NCH_2)_2C_6H_3]_2(Ph)Sb$ (**1**)

Empirical formula	$C_{30}H_{43}N_4Sb$
Formula weight	581.43
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	
a (Å)	36.394(3)
b (Å)	10.4454(9)
c (Å)	16.7524(14)
α (°)	90
β (°)	111.515(2)
γ (°)	90
Volume (Å ³)	5924.7(9)
Z	8
D_c (g/cm ³)	1.304
Absorption coefficient (mm ⁻¹)	0.955
$F(000)$	2416.0
Crystal size, mm	0.43 x 0.12 x 0.19
θ range for data collections (°)	0.999 to 25.004
Reflections collected	5222
Independent reflections	5016 [R(int) = 0.0162]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3753 / 0 / 324
Goodness-of-fit on F^2	1.072
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1 = 0.0162$, $wR2 = 0.0342$
R indices (all data)	$R1 = 0.0239$, $wR2 = 0.0427$
Largest diff. peak and hole, eÅ ⁻³	0.877 and -0.540

CONCLUSIONS

The heteroleptic triorganoantimony(III) compound $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]_2(\text{Ph})\text{Sb}$ (**1**) resulted from the reaction between PhSbCl_2 and the lithiated derivative $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{Li}$, in a 1:2 molar ratio. The NMR spectra, recorded at room temperature, gave no clear evidence for a $\text{N}\rightarrow\text{Sb}$ intramolecular interaction in solution, but the single-crystal X-ray diffraction studies revealed the existence of three $\text{N}\rightarrow\text{Sb}$ intramolecular interactions, which determine a $14\text{-Sb-}6$ hypercoordinate species, with one of the two $2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3$ groups behaving as a tridentate N,C,N moiety, while the other displays only a N,C -bidentate coordination behaviour.

Acknowledgements. This work was supported by a grant from the Ministry of Research and Innovation, CNCS – UEFISCDI, project number PN-III-P4-ID-PCE-2020-2651. The support provided by the National Centre for X-ray Diffraction (Babeş-Bolyai University, Cluj-Napoca, Roumania) for XRD determination and refinement is highly acknowledged.

Supplementary material. CCDC 2339766 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

REFERENCES

- S. Schulz, *Coord. Chem. Rev.*, **2015**, 297-298, 49–76.
- R. Nomura, Y. Wada and H. Matsuda, *J. Polym. Sci. A Polym.*, **1988**, 26, 627–636.
- S. Yasuike, Y. Kishi, S. Kawara and J. Kurita, *Chem. Pharm. Bull.*, **2005**, 53, 425–427.
- J. Lei, L. Peng, R. Qiu, Y. Liu, Y. Chen, C.-T. Au and S.-F. Yin, *Dalton Trans.*, **2019**, 48, 8478–8487.
- C. I. Raț, C. Silvestru and H. J. Breunig, *Coord. Chem. Rev.*, **2013**, 257, 818–879.
- L. Dostál, R. Jambor, A. Růžička, M. Erben, R. Jirásko, E. Černošková and J. Holeček, *Organometallics*, **2009**, 28, 2633–2636.
- H. Matsuda, A. Ninagawa and H. Hasegawa, *Bull. Chem. Soc. Jpn.*, **1985**, 58, 2717–2718.
- R. Nomura, Y. Hasegawa, M. Ishimoto, T. Toyosaki and H. Matsuda, *J. Org. Chem.*, **1992**, 57, 7339–7342.
- Y. Chen, R. Qiu, X. Xu, C.T. Au and S. F. Yin, *RSC Adv.*, **2014**, 4, 11907–11918.
- K.-ya Akiba, “Chemistry of hypervalent compounds”, Wiley-VCH, Weinheim, 1999.
- K. Ohkata, M. Ohnishi and K.-ya Akiba, *Tetrahedron Lett.*, **1988**, 29, 5401–5404.
- J. Xia, R. Qiu, S. Yin, X. Zhang, S. Luo, C.-T. Au, K. Xia and W. Y. Wong, *J. Organomet. Chem.*, **2010**, 695, 1487–1492.
- L. M. Opris, A. Silvestru, C. Silvestru, H. J. Breunig and E. Lork, *Dalton Trans.*, **2003**, 4367–4374.
- A. Toma, C. I. Raț, A. Silvestru, T. Ruffer, H. Lang and M. Mehring, *J. Organomet. Chem.*, **2013**, 696, 2837–2844.
- R. Șuteu, C. I. Raț, C. Silvestru, A. Simion, N. Candu, V. I. Părvulescu and A. Silvestru, *Appl. Organomet. Chem.*, **2020**, 34, e5393.
- A. M. Preda, C. I. Raț, C. Silvestru and H. Lang, T. Ruffer, *RSC Adv.*, **2015**, 5, 99832–99840.
- D. Copolovici, F. Isaia, H. J. Breunig, C. I. Raț and C. Silvestru, *RSC Adv.*, **2014**, 4, 26569–26576.
- D. Copolovici, V. R. Bojan, C. I. Raț, A. Silvestru, H. J. Breunig and C. Silvestru, *Dalton Trans.*, **2010**, 39, 6410–6418.
- L. Opriș, A. Silvestru, C. Silvestru, H. J. Breunig and E. Lork, *Dalton Trans.*, **2004**, 3575–3585.
- G. Strîmb, A. Pöllnitz, C. I. Raț and C. Silvestru, *Dalton Trans.*, **2015**, 44, 9927–9942.
- G. Duneș, A. Soran and C. Silvestru, *Dalton Trans.*, **2022**, 51, 10406–10419.
- G. Duneș and C. Silvestru, *New J. Chem.*, **2024**, 68, 5523–5529.
- S. Alvarez, *Dalton Trans.*, **2013**, 42, 8617–8636.
- IUPAC Nomenclature of Organic Chemistry*, Pergamon Press, Oxford, **1979**.
- C. W. Perkins, J. C. Martin, A. J. Arduengo III, W. Lau, A. Alegria and K. Kochi, *J. Am. Chem. Soc.*, **1980**, 102, 7753–7759.
- M. Nunn, D. B. Sowerby and D. M. Wesolek, *J. Organomet. Chem.*, **1983**, 251, C45–C46.
- L. Balazs, H. J. Breunig, E. Lork, A. Soran and C. Silvestru, *Inorg. Chem.*, **2006**, 45, 2341–2346.
- MestReC and MestReNova, Mestrelab Research S.L., A Coruña, 15706 Santiago de Compostela, Spain.
- Qual Browser Thermo Xcalibur, version 2.1.0 SP1.1160, Thermo Fischer Scientific Inc., Waltham, MA, 02454, **2011**.
- G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, **2015**, 71, 3–8.
- A. L. Spek, *Acta Cryst.*, **2009**, D 65, 148;
- A. L. Spek, *Acta Cryst.*, **2015**, C71, 9–18.
- H. Putz and K. Brandenburg, DIAMOND – Crystal and Molecular Structure Visualization, Crystal Impact GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany, 2022.

