



## SYNTHESIS AND STRUCTURE OF $[\text{Sb}(\mu_2\text{-O})\text{Cl}(\text{DMSO-O})]_n$

Cite this: *INEOS OPEN*,  
2025, 8 (1–3), 52–53  
DOI: 10.32931/io2515a

I. V. Egorova,<sup>\*a</sup> I. N. Nesina,<sup>a</sup> V. V. Zhidkov,<sup>a</sup> N. A. Rodionova,<sup>a</sup>  
N. V. Kuratieva,<sup>b</sup> and N. V. Pervukhina<sup>b</sup>

<sup>a</sup> Blagoveshchensk State Pedagogical University,  
Blagoveshchensk, ul. Lenina 104, 675004 Russia

<sup>b</sup> Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy  
of Sciences, pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia

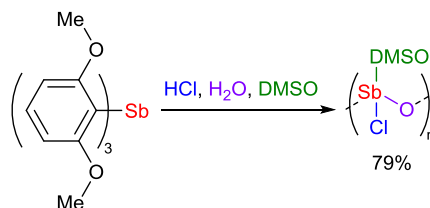
Received 18 October 2024,  
Accepted 17 January 2025

<http://ineosopen.org>

### Abstract

New complex  $[\text{Sb}(\mu_2\text{-O})\text{Cl}(\text{DMSO-O})]_n$  was obtained by the interaction of tris(2,6-dimethoxyphenyl)stibine with HCl in chloroform followed by the recrystallization of the product from DMSO. X-ray diffraction analysis revealed a distorted trigonal bipyramidal bisphenoidal environment of the antimony atoms, with the axial angles O–Sb–Cl of 163.8(3), 164.1(3)° and the interatomic distances  $\mu_2\text{-O-Sb}$  and  $\text{Sb-O}_{\text{ax}}$  of 1.948(9), 1.973(9) Å and 2.242(10), 2.194(11) Å, respectively.

**Key words:** triarylstibine, hydrochloric acid, dimethyl sulfoxide, Lewis acid, structure, synthesis.



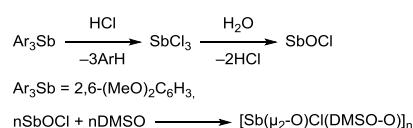
### Introduction

Recently, the possibility of using antimony(III,V) compounds as the reagents and catalysts in organic synthesis, as well as medicinal, antiseptic and antimicrobial drugs has been disclosed [1]. Antimony oxohalides can be used as electrodes for sodium and lithium-ion batteries and demonstrate excellent fire-retardant properties [2, 3]. The research into the reactions of triorganylstibines with HCl dates back to the twenties of the last century. However, this interaction was studied on a small number of organoantimony compounds. The reaction with hydrochloric acid is accompanied by the dearylation of triorganylstibine and/or its oxidation ( $\text{Sb(III)} \rightarrow \text{Sb(V)}$ ), which is dictated by the nature of the substituent that determines the strength of the Sb–C bond, acid concentration, solvent nature, and temperature [4]. Trialkylstibines ( $\text{Alk} = \text{Me, Et, Bn, Cy}$ ) are oxidized under the action of HCl to  $\text{Alk}_3\text{SbCl}_2$ . Tri- $\alpha$ -thienylstibine is completely dearylated with hydrochloric acid to form antimony trichloride and thienyl chloride. The formation of  $\text{Ar}_2\text{SbCl}$  and  $\text{ArH}$  occurs when a saturated alcohol solution of HCl is attacked with  $\text{Ar}_3\text{Sb}$  ( $\text{Ar} = \text{Ph, } p\text{-Tol, } 3\text{-NH}_2\text{C}_6\text{H}_4, 4\text{-MeC(O)NHC}_6\text{H}_4$ ). An increase in the acid concentration and heating duration leads to the more complete dearylation of triphenylstibine alone, while the use of concentrated aqueous acid in this reaction is accompanied by the formation of antimony trichloride. Triphenylstibine is oxidized by atmospheric oxygen in the presence of HCl to  $\text{Ph}_3\text{SbCl}_2$  [4]. Consequently, it is impossible to unambiguously predict the composition of the reaction products, which arouses interest to this problem. To date, the interaction of tris(2,6-dimethoxyphenyl)stibine with HCl has not been described.

### Results and discussion

The reaction of tris(2,6-dimethoxyphenyl)stibine with HCl

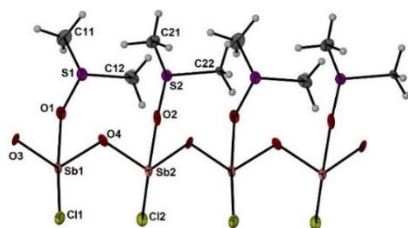
was performed in chloroform. The reaction product was antimony(III) oxochloride, which is insoluble in chloroform. Its identification was performed by the melting point ( $T_{\text{dec.}} = 170^\circ\text{C}$ , which corresponds to the literature data [5]) and IR spectrum ( $\nu(\text{SbO}) = 725\text{ cm}^{-1}$  [5]) (see Fig. S1 in the Electronic supplementary information (ESI)). Antimony(III) oxochloride is likely to result from the hydrolysis of antimony trichloride, preliminarily formed in HCl solution. The precipitate was recrystallized from DMSO to give  $[\text{Sb}(\mu_2\text{-O})\text{Cl}(\text{DMSO-O})]_n$  (Scheme 1).



**Scheme 1.** Synthesis of  $[\text{Sb}(\mu_2\text{-O})\text{Cl}(\text{DMSO-O})]_n$ .

The IR spectrum of  $[\text{Sb}(\mu_2\text{-O})\text{Cl}(\text{DMSO-O})]_n$  exhibits a broad band of  $\nu(\text{SO})$  stretches at 906, 922  $\text{cm}^{-1}$ , which are shifted to longer wavelengths compared to the spectrum of the free DMSO molecule, indicating the coordination of DMSO through the oxygen atom. By retaining a lone pair of electrons on the antimony atom, antimony oxochloride behaves like a Lewis acid towards the neutral O-donor ligand molecule. The antimony atoms in  $[\text{Sb}(\mu_2\text{-O})\text{Cl}(\text{DMSO-O})]_n$  have a distorted trigonal bipyramidal bisphenoidal coordination with the axially located oxygen atoms of the DMSO molecule and chlorine (Fig. 1). The selected interatomic distances are as follows:  $\text{Sb1-O1}$  2.242(10) Å,  $\text{Sb1-Cl1}$  2.646(3),  $\text{Sb2-O2}$  2.194(11),  $\text{Sb2-Cl2}$  2.655(4) Å.  $\text{Cl1-Sb1-O1}$  and  $\text{Cl2-Sb2-O2}$  bond angles are 163.8(3), 164.1(3)°. In the equatorial plane, there are bridging oxygen atoms and a lone electron pair of an antimony atom.

The oxygen atoms (O3, O4) perform only the  $\mu_2$ -bridging structural function, joining the adjacent molecule fragments  $\text{SbOCl}(\text{DMSO})$  into polymer chains in the complex (Fig. 1). The



**Figure 1.** Fragment of a polymer chain of  $[\text{Sb}(\mu_2\text{-O})\text{Cl}(\text{DMSO-O})]_n$ . Thermal ellipsoids are drawn at the 50% probability level.

selected interatomic distances are as follows: Sb1–O3 1.948(9), Sb1(Sb2)–O4(O3) 1.973(9) Å. Antimony(III) oxochlorides  $\text{SbOCl}$  [5, 6],  $\text{Sb}_2\text{OCl}_4$  [5],  $\text{Sb}_3\text{O}_4\text{Cl}$  [7],  $\text{Sb}_4\text{O}_5\text{Cl}_2$  [8], and  $\text{Sb}_8\text{O}_{11}\text{Cl}_2$  [9], derived from antimony(III) chloride or antimony(III) oxide, have a polymeric structure. The coordination polyhedra of an antimony atom are the distorted trigonal bipyramid  $[\text{SbO}_4\text{E}]$  [5–7, 9],  $[\text{SbO}_3\text{ClE}]$  [6, 7],  $\text{SbO}_2\text{Cl}_2\text{E}$ ,  $\text{SbOCl}_3\text{E}$  [5] or the distorted tetrahedron  $[\text{SbO}_2\text{ClE}]$  [6],  $[\text{SbO}_3\text{E}]$  [8, 9]. The Sb–O distances are determined by the coordination polyhedron of antimony atoms and the  $\mu_2$ –/ $\mu_3$ –bonding role of chlorine atoms. In tetrahedra, the Sb–O distances vary in a smaller range of values (1.898(0)–2.459(4) Å) compared to the trigonal bipyramid (1.947(6)–2.59(2) Å) [5–9]. The oxygen atom bonded to only two antimony atoms is always a short distance away.

## Experimental section

The IR spectra (KBr) were recorded on an FSM-2202 interference FT-IR spectrometer in the range of 400–4000  $\text{cm}^{-1}$ . The elemental analysis was performed on a Carlo Erba CHN analyzer (model 1106). The  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance III HD 500 spectrometer with an operating frequency of 500.13 MHz at room temperature. The X-ray diffraction analysis was performed on a Bruker Nonius X8Apex diffractometer with a 4K CCD detector using  $\phi$ - and  $\omega$ -scanning. The corrections for absorption were introduced with the aid of the SADABS program [10]. The structures were solved by the direct method and refined by the full-matrix F2 MNC method in the anisotropic approximation for non-hydrogen atoms using the SHELXT-2014/5 software package [11]. CCDC 2389596 contains the supplementary crystallographic data for the compound explored (<http://www.ccdc.cam.ac.uk/>).

**Synthesis of  $[\text{Sb}(\mu_2\text{-O})\text{Cl}(\text{DMSO-O})]_n$ .** A solution of hydrochloric acid (32%, 1.1 mL, 11.25 mmol) was added to a stirred solution of tris(2,6-dimethoxyphenyl)stibine (2.00 g, 3.75 mmol) in 50 mL of  $\text{CHCl}_3$ . The reaction mixture was heated at ~ 50 °C for 2 h. The resulting precipitate was filtered off and washed with  $\text{CHCl}_3$  (2×10 mL). The solvent was evaporated. The IR and NMR spectra of *m*-dimethoxybenzene, obtained after evaporation of chloroform, are identical to those of the known compound. IR ( $\text{v}/\text{cm}^{-1}$ ):  $\nu_{\text{as,s}}(\text{C}_{\text{Ar}}\text{--O--C}_{\text{Me}})$  1210, 1050,  $\nu_{\text{as,s}}(\text{C}_{\text{Ar}}\text{--C}_{\text{Ar}})$  1600, 1494,  $\nu_{\text{as,s}}(\text{C}_{\text{Me}}\text{--H})$  2959, 2836 (see Fig. S2 in the ESI).  $^1\text{H}$  NMR:  $\delta$  3.84 (6H, 1,3- $\text{CH}_3\text{--O}$ ), 6.58 (H, 2-Ph), 6.57 (2H, 4,6-Ph), 6.53 (H, 5-Ph), 7.24 (H,  $\text{CDCl}_3$ ), 1.72 (H,  $\text{H}_2\text{O}$ ) ppm. The product ( $\text{SbOCl}$ ) was dissolved in 5 mL of DMSO. The crystals were obtained by the slow evaporation of DMSO at ambient temperature (5 days). Yield: 0.75 g (79%).

Mp: 225 °C. IR ( $\text{v}/\text{cm}^{-1}$ ):  $\nu_{\text{as}}(\text{CH}_3)$  3008, 2988,  $\nu_{\text{s}}(\text{CH}_3)$  2910,  $\nu(\text{SO})$  906, 922,  $\nu(\text{SbO})$  725,  $\nu(\text{CS})$  611 (see Fig. S3 in the ESI). Anal. Calcd. for  $\text{C}_2\text{H}_6\text{ClO}_2\text{SSb}$ : C, 9.56; H, 2.41. Found: C 9.37; H 2.65%. As a result of the analysis carried out on a JXA-8100 microprobe, the single-phase nature of the target product was established (Sb, Cl, S wt/at % 38.40–42.18/71.83–74.06, 13.95–14.63/25.61–27.44, and 9.80–12.11/21.20–25.82, respectively).

## Conclusions

The interaction of tris(2,6-dimethoxyphenyl)stibine with hydrochloric acid (in a 1:3 molar ratio) upon heating leads to the complete dearylation of the organoantimony compound. The complex of antimony(III) with dimethyl sulfoxide was synthesized and studied. According to the results of X-ray diffraction analysis, the antimony atoms have distorted trigonal bipyramidal bisphenoidal coordination.

## Corresponding author

\* E-mail: bgpu.chim.egorova@mail.ru. Tel: +7(416)299-1516 (I. V. Egorova).

## Electronic supplementary information

Electronic supplementary information (ESI) available online: the IR spectra. For ESI, see DOI: 10.32931/io2515a.

## References

1. V. V. Sharutin, A. I. Poddel'sky, O. K. Sharutina, *Russ. J. Coord. Chem.*, **2020**, 46, 663–728. DOI: 10.1134/S1070328420100012
2. K. P. Lakshmi, K. J. Janas, M. M. Shaijumon, *Carbon*, **2018**, 131, 86–93. DOI: 10.1016/j.carbon.2018.01.095
3. L. Costa, G. Paganetto, G. Bertelli, G. Camino, *J. Therm. Anal.*, **1990**, 36, 1141–1153. DOI: 10.1007/BF01904648
4. K. A. Kocheshkov, A. P. Skoldinov, N. N. Zemlyanskii, *Methods of Organoelement Chemistry. Antimony, Bismuth*, Nauka, Moscow, **1976** (in Russian).
5. C. Hu, D. Chu, X. Hou, F. Zhang, J. Han, *Inorg. Chem. Front.*, **2024**, 11, 3367–3376. DOI: 10.1039/D4QI00564C
6. M. Edstrand, *Arkiv Kemi*, **1953**, 6, 89–112.
7. H. Katze, Y. Oka, Y. Kanke, K. Kato, T. Yao, *Z. Kristallogr. Cryst. Mater.*, **1999**, 214, 284–289. DOI: 10.1524/zkri.1999.214.5.284
8. C. Särnstrand, *Acta Cryst., Sect. B*, **1978**, 34, 2402–2407. DOI: 10.1107/S056774087800833X
9. Z. Mayerová, M. Johnsson, S. Lidin, *Solid State Sci.*, **2006**, 8, 849–854. DOI: 10.1016/j.solidstatesciences.2006.04.010
10. Bruker AXS Inc., APEX2 (Version 1.08), SAINT (Version 7.03), and SADABS (Version 2.11). Bruker Advanced Xray Solutions, Madison, Wisconsin, USA, **2004**.
11. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, **2015**, 71, 3–8. DOI: 10.1107/S2053229614024218

This article is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License.

