DOI: 10.1002/ejic.200601083

Synthesis and Characterization of the First Silver Complexes with Antimony Anions

Dieter Fenske,*[a] Alexander Rothenberger,[a,b] and Stephan Wieber[b]

Dedicated to Joachim Strähle on the occasion of his 70th birthday

Keywords: Silver / Antimony / Clusters

The synthesis and characterization of the silver antimony complexes $[Ag_{12}\{Sb(SiMe_3)\}_6(PiPr_3)_6]$ (**1**), $[Ag_4(Sb_4Ph_4)_2(PiPr_3)_4]$ (**2**) and $[Ag_4(Sb_6Ph_6)_2(PnBu_3)_4]$ (3) is reported.

Introduction

In 1989 Cowley et al. had synthesized the first copper complex containing an antimony anion by the metathesis reaction of a Cu^I salt with lithium dimesitylantimonide.[1] More recent developments in the area of complexes containing antimony anions represent the discovery of a new class of compounds with unstoichiometric mixtures of Cu and Sb atoms and a range of novel group 13 metal complexes.[2,3] The synthesis of complexes e.g., $[Cu_{40}Sb_{12}(PMe_3)_{20}]$ and $[Cu_{45}Sb_{16}(PEt_2Me)_{16}]$, was achieved by reactions of silylated stibanes with phosphane complexes of Cu^I salts. For the heavier coinage metals, only very few complexes with stibanes as ligands are known and a common feature of them is the interaction of the coinage metal (Ag or Au) with the lone pair of a neutral trisubstituted stibane.[4]

In contrast to antimony, several examples for arsenic anions bridging silver or gold centres are known.[5] The silver arsinidene cluster $[Ag_{14}(AsPh)_6Cl_2(PEt_3)_8]$ or the isostructural complexes $[Ag_4(As_4Ph_4)_2(PEt_3)_4]$ and $[Au_4(As_4Ph_4)_2(PnPr_3)_4]$ can be obtained by the reaction of coinage metal salts with $PhAs(SiMe_3)_2$ in the presence of tertiary phosphanes.[6] This prompted us to attempt the synthesis of silver and gold complexes containing antimony anions. In the following first results of mixed-metal Ag/Sb complexes are described.

Results and Discussion

The reactions of silver nitrate with stibanes produced the silver antimony compounds $[Ag_{12}\{Sb(SiMe_3)\}_6(PiPr_3)_6]$ (**1**), $[Ag_4(Sb_4Ph_4)_2(PiPr_3)_4]$ (**2**) and $[Ag_4(Sb_6Ph_6)_2(PnBu_3)_4]$ (**3**) (Scheme 1).

$$AgNO_3 + Sb(SiMe_3)_3 \xrightarrow{PiPr_3} [Ag_{12}(SbSiMe_3)_6(PiPr_3)_6]\ (\mathbf{1})$$

$$AgNO_3 + PhSb(SiMe_3)_2 \xrightarrow{PiPr_3} [Ag_4(Sb_4Ph_4)_2(PiPr_3)_4]\ (\mathbf{2})$$

$$AgNO_3 + PhSb(SiMe_3)_2 \xrightarrow{PnBu_3} [Ag_4(Sb_6Ph_6)_2(PnBu_3)_4]\ (\mathbf{3})$$

Scheme 1. Synthesis of the Ag/Sb complexes **1**, **2** and **3**.

The complex **1** crystallizes from diethyl ether as orange blocks in the trigonal space group $P\bar{3}$ with three molecules in the unit cell. It can be described by a distorted triangular antiprism of antimony atoms in which every edge is capped by a silver atom (Ag1) (Figure 1). The other six silver atoms (Ag2) are coordinated by phosphane ligands.

On each Sb atom a trimethylsilyl group is retained. The Sb–Si bond length of 2.527(1) Å is in the range of commonly observed Sb–Si bond lengths.[2] The Sb–Ag distances in **1** are also similar to reported average Ag–Sb distances of 2.72 Å in 75 compounds with most of them of the general type $[R_3Sb–AgX]$ (R = organic group, X = anion).[7,8] The stability of the cluster compounds increased when $PhSb(SiMe_3)_2$ was used as antimony source. By the reaction of $AgNO_3$ with $PhSb(SiMe_3)_2$ and four equivalents of $PiPr_3$ in diethyl ether the cluster compound $[Ag_4(Sb_4Ph_4)_2(PiPr_3)_4]$ (**2**) is obtained as red crystals together with colourless blocks of the silver phosphane complex $[Ag(NO_3)(PiPr_3)_2]$ (Table 1) and $[PhSb]_6$.[9] **2** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the unit cell and

---

[a] Institut für Anorganische Chemie, Universität Karlsruhe, Geb. 30.45,
Engesserstr. 15a, 76131 Karlsruhe
E-mail: dieter.fenske@chemie.uni-karlsruhe.de
[b] Institut für Nanotechnologie, Forschungszentrum Karlsruhe GmbH,
P. O. Box 3640, 76021 Karlsruhe, Germany

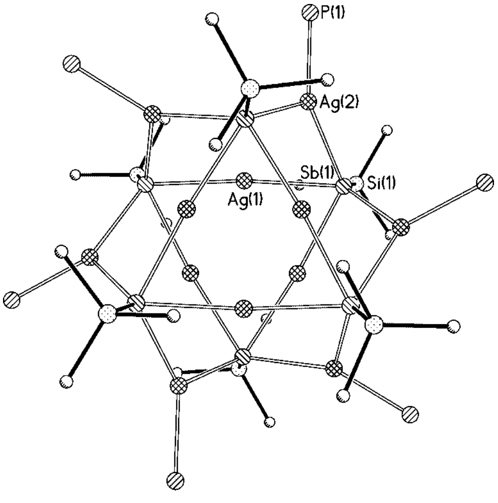

Figure 1. Molecular structure of **1** in the crystal (without C atoms of phosphane ligands and disordered components). Selected bond lengths [Å] and angles [°]: Sb(1)–Ag(1) 2.7183(6), Sb(1)–Ag(2) 2.754(1), Si(1)–Sb(1) 2.527(1), Ag(1)···Ag(2) 2.902(1), Ag(2)–P(1) 2.446(2), Si(1)–Sb(1)–Ag(1) 104.53(4), Si(1)–Sb(1)–Ag(2) 119.56(4), Ag(1)–Sb(1)–Ag(2) 64.04(3), Sb–Ag(1)–Sb 171.86(2), P(1)–Ag(2)–Sb(1) 133.90(5).

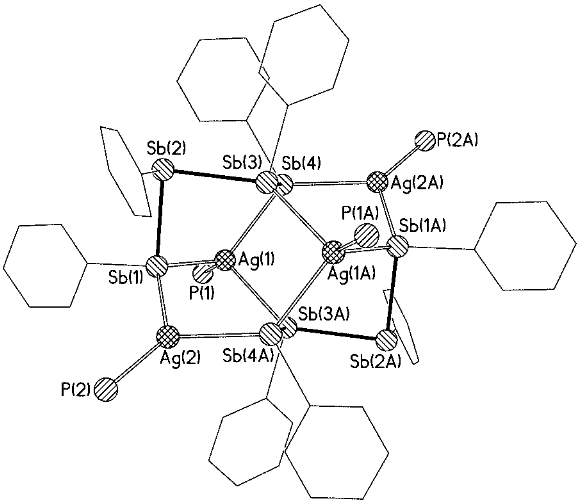

Figure 2. Molecular structure of **2** in the crystal (without C atoms of phosphane ligands). Final label letter A denotes the symmetry operation –*x*, –*y*, –*z* + 1. Selected bond lengths [Å] and angles [°]: Sb(1)–Ag(2) 2.7220(10), Sb(1)–Ag(1) 2.7452(12), Sb(1)–Sb(2) 2.7987(11), Sb(2)–Sb(3) 2.8301(11), Sb(3)–Sb(4) 2.8031(12), Sb(3)–Ag(1A) 2.8567(12), Sb(4)–Ag(2A) 2.7144(11), Sb(4)–Ag(1) 2.7463(10), Ag(1)–P(1) 2.454(2), Ag(2)–P(2) 2.430(2), Ag(2)–Sb(1)–Ag(1) 118.18(3), Ag(2)–Sb(1)–Sb(2) 112.04(3), Ag(1)–Sb(4)–Sb(3) 92.09(3), Ag(1)–Sb(1)–Sb(2) 98.29(3), Sb(1)–Sb(2)–Sb(3) 89.24(3), Sb(4)–Sb(3)–Sb(2) 95.32(3), P(1)–Ag(1)–Sb(1) 119.41(6), P(1)–Ag(1)–Sb(4) 116.69(6), Sb(1)–Ag(1)–Sb(4) 109.63(4), P(1)–Ag(1)–Sb(3A) 118.84(7), Sb(1)–Ag(1)–Sb(3A) 92.43(3), Sb(4)–Ag(1)–Sb(3A) 95.03(3), P(2)–Ag(2)–Sb(4A) 128.74(7), P(2)–Ag(2)–Sb(1) 133.03(7), Sb(4A)–Ag(2)–Sb(1) 98.15(3).

two lattice-bound ether molecules (Figure 2). The molecular structure of **2** is isostructural to the structure of $[Ag_4(As_4Ph_4)_2(PEt_3)_4]$ in the solid state.[6]

The structure of **2** can be described as a centrosymmetric dimer of a $[(PhSb)_4]^{2-}$ anion and two Ag-phosphane units. Each $[(PhSb)_4]^{2-}$ anion chelates Ag(1,1A) by terminal Sb atoms. Ag(2) is coordinated by Sb atoms of different anions. The longest Ag–Sb bond in **2**, which is observed between Sb(3) and Ag(1A), corresponds to distances commonly observed between neutral stibanes and Ag^I centres.[4a,4b] These interactions are slightly longer than bonds between silver and terminal antimony atoms. The coordination sphere of the four silver atoms is completed by additional P*i*Pr$_3$ ligands. The formation of the $[(PhSb)_4]^{2-}$ anion in **2** is intriguing, and it is currently assumed that **2** represents an intermediate of the Ag^I-induced oxidation of $PhSb(SiMe_3)_2$ to *cyclo*-$[PhSb]_6$. The Sb–Sb distances are in the range of reported Sb–Sb bond lengths of about 2.8 Å.[9]

Table 1. Details of the X-ray data collection and refinements.

Compound	**1**	**2**	**3**	$[Ag(NO_3)(PiPr_3)_2]$
Formula	$C_{72}H_{180}Ag_{12}P_6Sb_6Si_6$	$C_{92}H_{144}Ag_4O_2P_4Sb_8$	$C_{120}H_{168}Ag_4P_4Sb_{12}$	$C_{18}H_{42}AgNO_3P_2$
Formula weight	3425.46	2811.43	3626.90	490.34
T [K]	100(2)	110(2)	150(2)	150(2)
Crystal system	trigonal	triclinic	triclinic	triclinic
Space group	$R\text{-}3$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	18.589(3)	13.176(4)	15.980(2)	8.3773(5)
b [Å]	18.589(3)	14.823(3)	16.758(3)	10.0485(7)
c [Å]	31.487(6)	15.128(4)	24.559(4)	14.485(1)
α [°]	90	65.508(19)	90.793(12)	95.259(6)
β [°]	90	77.09(2)	90.689(12)	95.940(6)
γ [°]	120	86.72(2)	90.960(12)	98.329(6)
V [Å^3]	9423(3)	2618.7(12)	6574.7(17)	1192.93(14)
Z	3	1	2	1
μ [mm^{-1}]	3.251	2.858	3.091	0.994
$F(000)$	4968	1368	3496	516
Reflections collected	22270	15930	43872	9274
Unique data	4122	9536	26763	5197
R_{int}	0.0499	0.0631	0.0454	0.0518
Parameters	159	509	673	238
wR_2 (all data)	0.0950	0.0992	0.1499	0.1160
R_1 [$I > 2\sigma(I)$]	0.0364	0.0450	0.0570	0.0333

The use of the phosphane PnBu$_3$ instead of PiPr$_3$ leads to the cluster compound [Ag$_4$(Sb$_6$Ph$_6$)$_2$(PnBu$_3$)$_4$] (**3**). Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell (Figure 3).

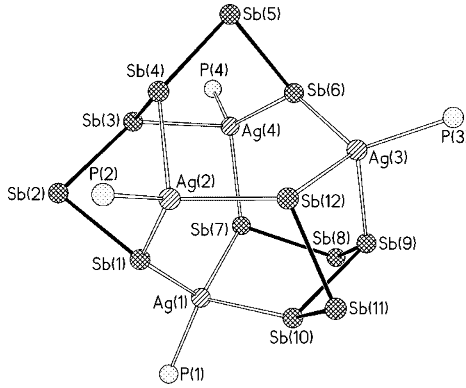

Figure 3. Molecular structure of **3** in the crystal (without organic substituents). Selected bond lengths [Å] and angles [°]: Sb(1)–Ag(2) 2.7462(11), Sb(1)–Ag(1) 2.7635(10), Sb(3)–Ag(4) 2.9944(10), Sb(4)–Ag(2) 2.9331(12), Sb(6)–Ag(4) 2.7433(10), Sb(6)–Ag(3) 2.7853(11), Sb(7)–Ag(1) 2.7248(11), Sb(7)–Ag(4) 2.7620(12), Sb(1)–Sb(2) 2.8012(10), Sb(2)–Sb(3) 2.8234(10), Sb(3)–Sb(4) 2.8446(10), Sb(4)–Sb(5) 2.8197(10), Sb(5)–Sb(6) 2.7868(10), Sb(7)–Sb(8) 2.7946(9), Sb(8)–Sb(9) 2.8161(10), Sb(9)–Sb(10) 2.8359(11), Sb(9)–Ag(3) 2.9445(11), Sb(10)–Sb(11) 2.8354(10), Sb(10)–Ag(1) 2.9237(11), Sb(11)–Sb(12) 2.8035(11), Sb(12)–Ag(2) 2.7631(10), Sb(12)–Ag(3) 2.7666(11), Ag–P 2.459(3)–2.481(3), Sb–Sb–Sb 88.06(3)–92.95(3).

The molecular structure of **3** consists like **2** of two *oligo*-[(PhSb)$_6$]$^{2-}$ anions and four Ag atoms. Compound **3**, however, represents, in comparison to **2**, an intermediate where the [PhSb]$_6$ chain is preformed at metal centres and "ready to cyclize" to *cyclo*-[PhSb]$_6$, which is formed in all the investigated reactions between Ag^I salts and PhSb(SiMe$_3$)$_2$. The almost tetrahedral arrangement of the four Ag atoms in **3** is favoured by the sterically demanding anions over the centrosymmetric arrangement in the solid-state structure of **2** or other possibilities. Each of the [(PhSb)$_6$]$^{2-}$ anions in **3** chelates two Ag atoms forming five-membered rings as observed in **2** and all Ag atoms are coordinated by Sb atoms of both dianions. Bond lengths between silver atoms and inner antimony atoms in **3** are ca. 0.2 Å longer than distances Ag–Sb(terminal).

Conclusions

In this contribution the first examples of silver complexes containing antimony anions are reported. A common feature of the compounds is their thermal instability and rather difficult syntheses. Currently, attempts are made to optimise the reactions towards a selective formation of a particular complex in high yield in order to allow subsequent investigations of physical properties.

Experimental Section

General Remarks: All operations were carried out under purified nitrogen. Hexane and diethyl ether were dried with LiAlH$_4$ and freshly distilled. AgNO$_3$ and PnBu$_3$ were purchased from Sigma–Aldrich. PnBu$_3$ was distilled prior use. PiPr$_3$, PhSb(SiMe$_3$)$_2$ and Sb(SiMe$_3$)$_3$ were prepared according to published procedures.[10]

1: AgNO$_3$ (0.18 g, 1.06 mmol) was dissolved in Et$_2$O (15 mL) and PiPr$_3$ (0.79 mL, 4.2 mmol) by briefly heating to reflux. The clear, colourless solution was cooled to –78 °C and Sb(SiMe$_3$)$_3$ (1.467 mL, 0.66 mmol, 0.45 mol/L in hexane) was added. The brown reaction mixture was stored at –78 °C for four days. Sensitive red crystals of **1** could be isolated for crystallographic measurements.

2: AgNO$_3$ (0.18 g, 1.06 mmol) was dissolved in Et$_2$O (15 mL) and PiPr$_3$ (0.79 mL, 4.2 mmol) by briefly heating to reflux. The clear, colorless solution was cooled to –78 °C and PhSb(SiMe$_3$)$_2$ (0.27 mL) was added. The brown reaction mixture was stored at –78 °C for one day. Then it was warmed up to –40 °C. After one week red crystals of **2** besides colourless crystals of the silver phosphane complex could be isolated for crystallographic measurements.

3: AgNO$_3$ (0.18 g, 1.06 mmol) was dissolved in Et$_2$O (15 mL) and PiPr$_3$ (0.79 mL, 4.2 mmol) by briefly heating to reflux. The clear, colorless solution was cooled to –78 °C and PhSb(SiMe$_3$)$_2$ (0.27 mL) was added. The brown reaction mixture was stored at –78 °C for one day. Then it was warmed up to –8 °C. After three weeks red crystals of **3** could be isolated for crystallographic measurements.

Due to thermal instability of **1**–**3** (slow decomposition even at –80 °C) characterization was restricted to X-ray crystallography.

X-ray Crystallographic Study: Data were collected with a STOE IPDS II diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the SHELXTL programme package (Table 1).[11] Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters. Disordered components were refined with isotropic thermal parameters.

CCDC-627012 to -627014 and CCDC-627632 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We gratefully acknowledge the DFG Center for Functional Nanostructures, the Forschungszentrum Karlsruhe and the Fonds der Chemischen Industrie for financial support.

---

[1] A. H. Cowley, R. A. Jones, C. M. Nunn, D. L. Westmoreland, *Angew. Chem.* **1989**, *101*, 1089–1090; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1018–1019.

[2] R. Ahlrichs, D. Fenske, M. McPartlin, A. Rothenberger, C. Schrodt, S. Wieber, *Angew. Chem.* **2005**, *117*, 4002–4005; *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 3932–3936.

[3] S. Schulz, F. Thomas, M. Nieger, *Chem. Commun.* **2006**, 1860–1861.

[4] a) A. M. Hill, W. Levason, M. Webster, *Inorg. Chem.* **1996**, *35*, 3428–3430; b) A. Cingolani, E. Effendy, J. V. Hanna, M. Pellei, C. Pettinari, C. Santini, B. W. Skelton, A. H. White, *Inorg. Chem.* **2003**, *42*, 4938–4948; c) Au–Sb: J. Vicente, A. Arcas, P. G. Jones, J. Lautner, *J. Chem. Soc., Dalton Trans.* **1990**, 451–456.

[5] a) P. Sevillano, O. Fuhr, M. Kattannek, P. Nava, O. Hampe, S. Lebedkin, R. Ahlrichs, D. Fenske, M. Kappes, *Angew. Chem.*

2006, *118*, 3785–3791; *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 3702–3708; b) D. Fenske, W. Holstein, *Angew. Chem.* **1994**, *106*, 1311–1312; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1290–1292; c) J. Besinger, D. Fenske, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1487–1494.

[6] D. Fenske, F. Simon, *Z. Anorg. Allg. Chem.* **1996**, *622*, 45–52.

[7] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380–388.

[8] I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallogr., Sect. B* **2002**, *58*, 389–397.

[9] H. J. Breunig, K. H. Ebert, S. Gülec, J. Probst, *Chem. Ber.* **1995**, *128*, 599–603.

[10] a) W. C. Davies, *J. Chem. Soc.* **1933**, 1043–1044; b) M. Ates, H. J. Breunig, S. Gülec, *Phosphorus Sulfur Silicon Relat. Elem.* **1989**, *44*, 129–133; c) G. Becker, H. Freudenblum, O. Mundt, M. Reti, M. Sachs, in: *Synthetic Methods of Organometallic and Inorganic Chemistry* (Eds.: Herrmann, Brauer), vol. 3 (Ed.: H. H. Karsch), Thieme, Stuttgart, **1996**, p. 193–198.

[11] G. M. Sheldrick, SHELXTL-97, University of Göttingen, **1997**.

Received: November 19, 2006