

SYNTHESIS AND STRUCTURE OF IODOTRIS(TRIPHENYLSTIBINE)SILVER [(Ph₃Sb)₃AgI]

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Interaction of silver iodide with triphenylstibine in dimethyl sulfoxide has led to the neutral complex iodotris(triphenylstibine)silver (1), whose structure has been established by X-ray diffraction analysis. The silver atom has distorted tetrahedral coordination. The angles SbAgSb and SbAgI equal 106.501(13)°, 109.644(13)°, 111.099(13)° и 103.063(13)°, 111.594(14)°, 114.337(14)°, the bond lengths Ag–Sb and Ag–I equal 2.7291(4), 2.7326(4), 2.8087(4) и 2.7600(4) Å.

Keywords: iodotris(triphenylstibine)silver, synthesis, structure, X-ray diffraction analysis.

Introduction

Synthesis and structure of molecular complexes of silver that contain the bonds Sb–Ag and Ag–Hal, obtained from silver halide and triphenylstibine in water-alcohol solution, are described in the literature [1–2]. In the present paper the interaction of silver iodide with triphenylstibine in dimethyl sulfoxide has been studied; the characteristic structural features of the obtained Sb-, I-containing silver complex have been investigated.

Experimental

Synthesis of iodotris(triphenylstibine)silver (1). The mixture of 0.529 g (1.50 mmol) triphenylstibine, 0.117 g (0.5 mmol) silver iodide and 10 mL dimethyl sulfoxide was stirred for 1 h at room temperature, the volume was reduced to 0.5 mL, then the mixture was cooled. The yield was 0.520 g (80%) of colorless crystals 1 with decomposition temperature 118 °C. Found, %: C 49.87; H 3.55. Calculated for C₅₄H₄₅Sb₃AgI, %: C 50.08; H 3.48.

X-ray diffraction analysis of the crystal **1** was performed on the Bruker D8 QUEST automatic four-circle diffractometer (Mo K_α-emission, λ = 0.71073 Å, graphite monochromator). The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the SMART and SAINT-Plus programs [3]. All calculations for structure determination and refinement were performed using the SHELXL/PC programs [4,5]. The structure **1** was determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The position of hydrogen atoms was refined according to the riding model (*U*_{iso}(H) = 1.2*U*_{eq}(C)). The main crystallographic data and refinement results for structure **1** are listed in Table 1, the geometric characteristics of the antimony atom coordination tetrahedron are given in Table 2.

Table 1
Crystallographic data and the experimental and structure refinement parameters for compound 1

Parameter	Value
Empirical formula	C ₅₄ H ₄₅ Sb ₃ AgI
Formula weight	1293.92
<i>T</i> , K	296(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	17.7497(6)

Table 1 (end)

Parameter	Value
b , Å	14.4787(4)
c , Å	19.6167(7)
α , deg	90.00
β , deg	98.2820(10)
γ , deg	90.00
V , Å ³	4988.8(3)
Z	4
ρ (calcd.), g/cm ³	1.723
μ , mm ⁻¹	2.646
$F(000)$	2488
Crystal size, mm	0.52 × 0.28 × 0.19
2 θ Range of data collection, deg	3.449 – 27.189
Range of refraction indices	$-22 \leq h \leq 22$, $-18 \leq k \leq 18$, $-25 \leq l \leq 25$
Measured reflections	82314
Independent reflections	11060 ($R_{int} = 0.0294$)
Refinement variables	533
$GOOF$	1.100
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0321$, $wR_1 = 0.0648$
R factors for all reflections	$R_1 = 0.0436$, $wR_1 = 0.0725$
Residual electron density (min/max), e/Å ³	0.824/–0.673

Table 2

Selected bond lengths and bond angles in the structure of compound 1

Bond	d , Å	Angle	ω , deg.
Sb(1)–C(1)	2.132(4)	C(1)Sb(1)C(11)	101.16(15)
Sb(1)–C(11)	2.131(4)	C(1)Sb(1)C(21)	97.96(16)
Sb(1)–C(21)	2.126(4)	C(11)Sb(1)C(21)	101.78(17)
Sb(2)–C(31)	2.128(4)	C(1)Sb(1)Ag(1)	122.48(10)
Sb(2)–C(41)	2.129(4)	C(11)Sb(1)Ag(1)	117.10(11)
Sb(2)–C(51)	1.140(4)	C(21)Sb(1)Ag(1)	112.92(12)
Sb(3)–C(61)	2.137(4)	Sb(1)Ag(1)I(1)	111.594(14)
Sb(3)–C(71)	2.143(4)	Sb(2)Ag(1)I(1)	114.337(14)
Sb(3)–C(81)	1.125(4)	Sb(3)Ag(1)I(1)	103.063(13)
Ag(1)–Sb(1)	2.7291(4)	Sb(1)Ag(1)Sb(2)	111.099(13)
Ag(1)–Sb(2)	2.7326(4)	Sb(1)Ag(1)Sb(3)	106.501(13)
Ag(1)–Sb(3)	2.8087(4)	Sb(2)Ag(1)Sb(3)	109.644(13)
Ag(1)–I(1)	2.7600(4)	C(31)Sb(2)Ag(1)	114.86(11)

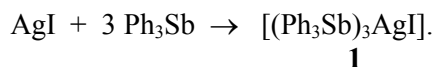
The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1440827; deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

Results and Discussion

It is known that mixing aqueous solutions of silver halides with the methanol solution of triphenylstibine (1:3 mol) leads to formation of colorless crystals of addition complexes with the general formula $[(Ph_3Sb)_3AgHal]$ (Hal = Cl, Br, I) [1]. The interaction of silver iodide with triphenylstibine in dimethyl sulfoxide, a strong n-donor solvent, has not been studied previously. The choice of the solvent is due to the fact that in the presence of two n-donor ligands in the reaction mixture, containing silver iodide, competition between them arises together with the possibility of complex formation, in which the coordination sphere of the metal atom would include one of them or both at once.

Химия элементоорганических соединений

We have established that at mixing silver iodide with triphenylstibine in dimethyl sulfoxide the solven molecules are not coordinated with the metal atom, so the sole product of the reaction is the molecular complex **1**:



The structure **1** is proven by the X-ray diffraction method. The silver atom in **1** has distorted tetrahedral coordination (Fig. 1).

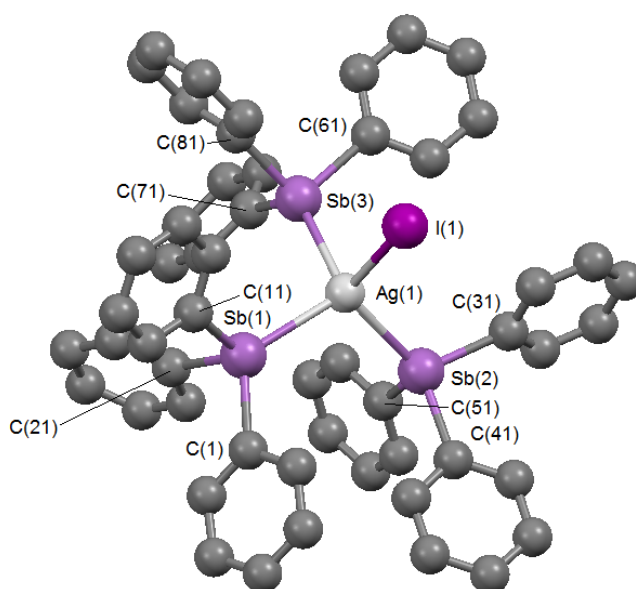


Fig. 1. The structure of compound **1**

The angles SbAgSb and SbAgI equal $106.501(13)^\circ$, $109.644(13)^\circ$, $111.099(13)^\circ$ and $103.063(13)^\circ$, $111.594(14)^\circ$, $114.337(14)^\circ$. The bond lengths Ag–Sb and Ag–I equal 2.7291(4), 2.7326(4), 2.8087(4) and 2.7600(4) Å, which exceed the sums of the covalent radii of atoms Ag, Sb (2.67 Å [6]) and Ag, I (2.58 Å [6]). Note that in a similar chlorine-containing complex $(\text{Ph}_3\text{Sb})_3\text{AgCl}$ the bond lengths Ag–Sb are smaller (2.720, 2.722, 2.764(4) Å) [1]. In the complex of silver iodide with morpholine $[\text{AgI}\cdot\text{C}_4\text{H}_9\text{NO}]$, in which the coordination sphere is formed by nitrogen and three iodine atoms, the lengths Ag...I equal 2.824(6), 2.845(6) and 2.908(6) Å [7].

The atoms Sb(1,2,3) are tetracoordinated, at that the angles CSb(1)C ($97.96(16)^\circ$ – $101.78(17)^\circ$), CSb(2)C ($98.20(16)^\circ$ – $102.28(16)^\circ$), CSb(3)C ($97.22(16)^\circ$ – $99.70(15)^\circ$) are less than the ideal values, while CSb(1)Ag ($112.92(12)^\circ$ – $122.48(10)^\circ$), CSb(2)Ag ($114.18(11)^\circ$ – $124.41(12)^\circ$), CSb(3)Ag ($111.91(11)^\circ$ – $128.03(11)^\circ$) are greater than them. The lengths Sb–C (2.125(4)–2.143(4) Å) are smaller than in the molecule of free triphenylstibine (2.140(4)–2.168(4) Å) [8].

It is notable that the molecular and crystal structure of complex **1** was discussed previously in [1], but the experiment was carried out imperfectly.

Conclusions

Hence, the interaction of silver iodide with triphenylstibine in dimethyl sulfoxide solution leads to formation of iodotris(triphenylstibine)silver; dimethyl sulfoxide does not exhibit the properties of a ligand capable of coordination with the silver cation.

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Received 12 December 2015

УДК 546.865+547.53.024+547.563.4+548.312.5

DOI: 10.14529/chem160107

СИНТЕЗ И СТРОЕНИЕ ИОДОТРИС(ТРИФЕНИЛСТИБИН)СЕРЕБРА $[(Ph_3Sb)_3AgI]$

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Взаимодействием иодида серебра с трифенилстибином в диметилсульфоксиде синтезирован нейтральный комплекс иодотрис(трифенилстибин)серебро (1), строение которого установлено методом РСА. Атом Ag имеет искаженную тетрагональную координацию. Углы SbAgSb и SbAgI составляют 106,501(13)°, 109,644(13)°, 111,099(13)° и 103,063(13)°, 111,594(14)°, 114,337(14)°, длины связей Ag–Sb и Ag–I равны 2,7291(4); 2,7326(4); 2,8087(4) и 2,7600(4) Å.

Ключевые слова: иодотрис(трифенилстибин)серебро, синтез, строение, рентгеноструктурный анализ.

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Поступила в редакцию 12 декабря 2015 г.

ОБРАЗЕЦ ЦИТИРОВАНИЯ

Synthesis and structure of iodotris-(triphenylstibine)silver [(Ph₃Sb)₃AgI] / V.V. Sharutin, O.K. Sharutina, V.S. Senchurin et al. // *Вестник ЮУрГУ. Серия «Химия».* – 2016. – Т. 8, № 1. – С. 46–50. DOI: 10.14529/chem160107

FOR CITATION

Sharutin V.V., Sharutina O.K., Senchurin V.S., Neudachina A.N., Andreev P.V. Synthesis and structure of iodotris(triphenylstibine)silver [(Ph₃Sb)₃AgI]. *Bulletin of the South Ural State University. Ser. Chemistry.* 2016, vol. 8, no. 1, pp. 46–50. DOI: 10.14529/chem160107