

New Silver Complexes with Triarylstibine Ligands: Specific Features of the Structure

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Abstract—The reactions of silver nitrate with triphenyl-, tri(*para*-tolyl)-, and tris(2-methoxy-5-bromophenyl)stibine in polar solvents afford complexes $[(\text{Ph}_3\text{Sb})_3\text{AgNO}_3]$, $[(p\text{-Tol}_3\text{Sb})_4\text{Ag}][\text{NO}_3]$ (**I**), and $[(2\text{-MeO-5-Br-C}_6\text{H}_3)_3\text{SbAg}(\mu_2\text{-NO}_3)(\text{Me}_3\text{CN})]_2 \cdot 2[(2\text{-MeO-5-Br-C}_6\text{H}_3)_3\text{SbAgNO}_3(\text{Me}_3\text{CN})]$ (**II**). Complex $[(\text{Ph}_3\text{Sb})_3\text{AgNO}_3]$ reacts with chloroacetic and ferrocenecarboxylic acids in the presence of triethylamine to form the corresponding carboxylates $[(\text{Ph}_3\text{Sb})_3\text{AgOC}(\text{O})\text{CH}_2\text{Cl}]$ (**III**) and $[(\text{Ph}_3\text{Sb})_3\text{AgOC}(\text{O})\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5]$ (**V**). Solvate $[(\text{Ph}_3\text{Sb})_3\text{AgOC}(\text{O})\text{CH}_2\text{Cl}] \cdot 1/2\text{C}_4\text{H}_8\text{O}_2$ is formed after the recrystallization of complex **III** from dioxane. The silver and antimony atoms in all complexes are found by X-ray diffraction to be tetracoordinate (CIF files CCDC nos. 1985086, 2019358, 1984428, 1992301, and 1973285 for compounds **I–V**, respectively).

Keywords: triarylstibine, silver nitrate, carboxylic acid, addition complexes, substitution reaction, structure, X-ray diffraction

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INTRODUCTION

Binary organic compounds of group 15 elements R_3E ($\text{E} = \text{P}, \text{As}, \text{Sb}$) have significant donor properties due to a lone electron pair on the E atom and, hence, they are popular ligands in coordination chemistry. The strength of E–M bonds in transition metal complexes decreases in the order $\text{R}_3\text{P} > \text{R}_3\text{As} > \text{R}_3\text{Sb} \gg \text{R}_3\text{Bi}$, which explains the most frequent use of phosphine ligands (arsine ligands are met less frequently likely because of their toxicity). Many complexes of the $(\text{Ph}_3\text{E})\text{M}_n\{\text{X}\}$ type ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$; $\text{E} = \text{P}, \text{As}$; $n = 1\text{--}4$) were structurally characterized [1–4]. The donor abilities of triphenylstibine are much weaker, and its coordination compounds are stable only under certain conditions. The silver complexes containing four, three, two, or one Ag–Sb bond are known. For example, the $[(\text{Ph}_3\text{Sb})_4\text{Ag}]\{\text{X}\}$ complexes are stable in the presence of counteranions with low nucleophilic properties ($\text{X} = \text{ClO}_4^-, \text{NO}_3^-$ [5], $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ [6], $[\text{BF}_4]^-$ [7], $[\text{BrO}_3]^-$ [8]). The fourth site in the coordination sphere of silver of the complexes with three Ph_3Sb fragments is occupied by halogen (Cl, Br, I), pseudo-halogen (SCN, NCS, CN) [9], oxime residue [10], large ligand [11, 12], or bidentate ligand enhancing the coordination number of silver to five [13]. Two Ph_3Sb molecules at the silver atom are observed in the binuclear structures bearing bridging ligands, for example, $[(\text{Ph}_3\text{Sb})_2\text{Ag}\{\text{C}_2\text{B}_9\text{H}_{12}\}]_2$ [14], $[(\text{Ph}_3\text{Sb})_2\text{Ag}(\mu\text{-X})_2\text{Ag}$

$(\text{SbPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [15], and polymeric structures of the $-\text{Ag}(\text{SbPh}_3)_2-\text{CN}-\text{Ag}(\text{SbPh}_3)_2-\text{CN}-$ type [16]. In the complexes with one Ag–Sb bond, the coordination sphere of silver is saturated by the addition of mono- or bidentate ligands performing various structural functions [13, 17]. The complexes with the Ag–Sb bonds were synthesized using diverse silver salts in polar solvents with varied molar ratios of the reagents.

Note that interest in the heterometallic compounds with Ag–Sb bonds is due to diverse design of the structures and their biological activity [11, 12].

An analysis of publications suggests that the literature data concern the studies of the silver complexes containing triphenylstibine as ligands. The exception is the study in which the phenyl group was replaced by the heteroaromatic group (2- $\text{C}_4\text{H}_3\text{X}$), where $\text{X} = \text{S}, \text{O}$, or NMe [18]. There are two examples of the complexes in which the nitro group is replaced by the carboxyl group [12].

The synthesis and structural features of the following new complexes with the Ag–Sb bond are described in this work: $[(p\text{-Tol}_3\text{Sb})_4\text{Ag}][\text{NO}_3]$ (**I**), $[(2\text{-MeO-5-Br-C}_6\text{H}_3)_3\text{SbAg}(\mu_2\text{-NO}_3)(\text{Me}_3\text{CN})]_2 \cdot 2[(2\text{-MeO-5-Br-C}_6\text{H}_3)_3\text{SbAgNO}_3(\text{Me}_3\text{CN})]$ (**II**), $[(\text{Ph}_3\text{Sb})_3\text{AgOC}(\text{O})\text{-CH}_2\text{Cl}]$ (**III**), and $[(\text{Ph}_3\text{Sb})_3\text{AgOC}(\text{O})\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5]$ (**V**).

EXPERIMENTAL

Synthesis of [(*p*-Tol₃Sb)₄Ag][NO₃] (I). A solution of silver nitrate (54 mg, 0.3 mmol) in a methanol–acetonitrile (1 : 1 vol/vol) mixture (3 mL) was poured to a solution of tri(*para*-tolyl)antimony (500 mg, 1.2 mmol) in the same mixture of solvents (7 mL). The reaction mixture was stirred and left to stay for 24 h in the dark. The yield of the silvery crystals of complex I was 434 mg (78%). $T_m = 174^\circ\text{C}$.

IR (ν, cm⁻¹): 3061, 3037, 3022, 3008, 2949, 2918, 2862, 1905, 1805, 1743, 1651, 1591, 1490, 1442, 1390, 1340, 1309, 1280, 1211, 1186, 1114, 1062, 1037, 1014, 854, 844, 831, 794, 702, 634, 574, 484, 480, 432.

For C₈₄H₈₄NO₃Sb₄Ag

Anal. calcd., %	C, 57.59	H, 4.80
Found, %	C, 57.50	H, 4.85

Synthesis of [(2-MeO-5-Br-C₆H₃)₃SbAg(μ₂-NO₃)-(Me₃CN)]₂·2[(2-MeO-5-Br-C₆H₃)₃SbAgNO₃(Me₃CN)] (II). A solution of silver nitrate (42 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) was poured to a solution of tris(2-methoxy-5-bromophenyl)stibine (510 mg, 0.75 mmol) in THF (4 mL). The mixture was left to stay at room temperature in the dark for 24 h. The formed powder was recrystallized from acetonitrile. The yield of silvery crystals of compound II was 167 mg (76%). $T_m = 196^\circ\text{C}$.

IR (ν, cm⁻¹): 3080, 3051, 3008, 2987, 2931, 2835, 2260, 1897, 1759, 1629, 1566, 1460, 1435, 1425, 1373, 1303, 1282, 1263, 1240, 1176, 1141, 1085, 1043, 1014, 887, 806, 738, 713, 665, 615, 536, 518, 437.

For C₄₆H₄₂N₄O₁₂Br₆Ag₂Sb₂

Anal. calcd., %	C, 30.98	H, 2.36
Found, %	C, 30.94	H, 2.43

Synthesis of [(Ph₃Sb)₃AgOC(O)CH₂Cl] (III). A solution of monochloroacetic acid (15 mg, 0.16 mmol) in a methanol–acetonitrile (1 : 1, vol/vol) mixture (3 mL) was poured to nitratotris(triphenylstibine)silver(I) (200 mg, 0.16 mmol) synthesized using a known procedure [12] and dissolved in the same mixture (3 mL) of solvents. Then triethylamine (0.5 mL, 3.5 mmol) was added. The mixture was left to stay for 24 h in the dark. The yield of colorless crystals of III·1/2CH₃OH was 178 mg (87%). $T_m = 148^\circ\text{C}$.

IR (ν, cm⁻¹): 2939, 2676, 2493, 1478, 1431, 1396, 1384, 1067, 996, 731, 692, 454.

For C₁₁₃H₉₈O₅Cl₂Ag₂Sb₆

Anal. calcd., %	C, 53.11	H, 3.84
Found, %	C, 52.89	H, 3.91

Solvate [(Ph₃Sb)₃AgOC(O)CH₂Cl] (IV)·1/2C₄H₈O₂ was obtained after the recrystallization of compound III from dioxane.

A similar procedure was applied to synthesize [(Ph₃Sb)₃AgOC(O)C₅H₄FeC₅H₅] (V). The yield was 75%. $T_{\text{decomp}} = 192^\circ\text{C}$.

IR (ν, cm⁻¹): 3062, 3043, 2987, 1961, 1894, 1815, 1764, 1658, 1575, 1550, 1477, 1465, 1431, 1406, 1382, 1354, 1340, 1301, 1265, 1180, 1157, 1107, 1066, 1035, 1018, 997, 918, 856, 835, 819, 800, 786, 731, 694, 655, 617, 599, 542, 505, 486, 453, 416.

For C₆₅H₅₄O₂FeAgSb₃

Anal. calcd., %	C, 55.87	H, 3.87
Found, %	C, 55.82	H, 3.92

The IR spectra of compounds I–V were recorded on a Shimadzu IR Affinity-1S FT-IR spectrometer. The samples were prepared by pelleting with KBr (absorption range 4000–400 cm⁻¹).

X-ray diffraction (XRA) of the crystals of compounds I–V was carried out on a D8 QUEST diffractometer (Bruker) (MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator). Data were collected and edited, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [19]. All calculations on structure determination and refinement were performed using the SHELXL/PC [20] and OLEX2 programs [21]. The structures were determined by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. Selected crystallographic data and structure refinement results are given in Table 1.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1985086, 2019358, 1984428, 1992301, 1973285 for the structures of compounds I–V, respectively; deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

As follows from published data, compounds with Ag–Sb bonds are synthesized from various silver salts and triphenylstibine in diverse solvents with the variation of reagent molar ratios causing the formation of complexes of certain stoichiometry.

We found that the reaction of tri(*para*-tolyl)antimony with silver nitrate in a molar ratio of 3 : 1 in a methanol–acetonitrile (1 : 1, vol/vol) mixture afforded complex [(*p*-Tol₃Sb)₄Ag][NO₃] (I) instead of the complex of the expected stoichiometry. Complex I was also isolated when the reaction was carried out with a reagent ratio of 4 : 1.

According to the XRD data, complex I is ionic. In the centrosymmetric cation the coordination of the

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds I–V

Parameter	Value				
	I	II	III	IV	V
<i>FW</i>	1750.39	1781.53	2553.05	2609.11	1396.05
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	13.717(14)	9.360(5)	13.131(12)	13.173(5)	13.892(8)
<i>b</i> , Å	28.68(2)	17.532(13)	13.750(17)	14.898(6)	14.112(7)
<i>c</i> , Å	19.504(14)	18.020(11)	14.861(16)	27.467(6)	14.913(8)
α , deg	90.00	97.18(4)	93.43(5)	93.01(2)	84.593(18)
β , deg	95.62(2)	92.836(19)	90.61(5)	103.083(16)	88.53(3)
γ , deg	90.00	99.21(2)	103.34(5)	90.897(14)	76.50(2)
<i>V</i> , Å ³	7636(11)	2889(3)	2605(5)	5241(4)	2830(3)
<i>Z</i>	4	2	1	2	2
ρ_{calc} , g/cm ³	1.523	2.048	1.627	1.653	1.638
μ , mm ⁻¹	1.696	5.801	2.001	1.991	2.046
<i>F</i> (000)	3480.0	1696.0	1250.0	2560.0	1372.0
Crystal size, mm	0.65 × 0.11 × 0.11	0.18 × 0.18 × 0.11	0.23 × 0.14 × 0.06	0.28 × 0.16 × 0.07	0.26 × 0.24 × 0.21
Range of data collection over θ , deg	5.56–57.74	6.128–49.542	5.75–56.998	5.602–57.00	6.04–54.34
Ranges of reflection indices	–18 ≤ <i>h</i> ≤ 18, –38 ≤ <i>k</i> ≤ 38, –26 ≤ <i>l</i> ≤ 22	–11 ≤ <i>h</i> ≤ 10, –20 ≤ <i>k</i> ≤ 20, –21 ≤ <i>l</i> ≤ 21	–17 ≤ <i>h</i> ≤ 17, –18 ≤ <i>k</i> ≤ 18, –19 ≤ <i>l</i> ≤ 19	–17 ≤ <i>h</i> ≤ 17, –20 ≤ <i>k</i> ≤ 20, –36 ≤ <i>l</i> ≤ 36	–17 ≤ <i>h</i> ≤ 17, –18 ≤ <i>k</i> ≤ 18, –19 ≤ <i>l</i> ≤ 19
Measured reflections	96994	54901	99054	289768	73491
Independent reflections (<i>R</i> _{int})	9971 (0.0688)	9847 (0.0426)	13 189 (0.0526)	26 492 (0.0750)	12 505 (0.0245)
Reflections with <i>I</i> > 2σ(<i>I</i>)	7033	7747	9048	16 533	10 690
Refinement parameters	427	667	568	1190	649
GOOF	1.005	1.016	1.076	1.066	1.064
<i>R</i> factors for <i>F</i> ² > 2σ(<i>F</i> ²)	<i>R</i> ₁ = 0.0332, <i>wR</i> ₂ = 0.0575	<i>R</i> ₁ = 0.0344, <i>wR</i> ₂ = 0.0772	<i>R</i> ₁ = 0.0381, <i>wR</i> ₂ = 0.0868	<i>R</i> ₁ = 0.0478, <i>wR</i> ₂ = 0.0964	<i>R</i> ₁ = 0.0365, <i>wR</i> ₂ = 0.0860
<i>R</i> factors for all reflections	<i>R</i> ₁ = 0.0665, <i>wR</i> ₂ = 0.0669	<i>R</i> ₁ = 0.0503, <i>wR</i> ₂ = 0.0842	<i>R</i> ₁ = 0.0712, <i>wR</i> ₂ = 0.1046	<i>R</i> ₁ = 0.0980, <i>wR</i> ₂ = 0.1164	<i>R</i> ₁ = 0.0451, <i>wR</i> ₂ = 0.0946
Residual electron density (max/min), e/Å ³	0.46/–0.57	0.88/–0.97	0.79/–0.90	0.74/–1.21	1.38/–1.25

silver and antimony atoms is tetrahedral (Fig. 1). The SbAgSb angles vary in a range of 102.30(7)°–116.13(3)°. The angles CSb(1)C, CSb(2)C, CSb(1)Ag, and CSb(2)Ag vary in ranges of 97.17(12)°–101.44(12)°, 97.90(12)°–100.27(12)°, 116.26(8)°–120.36(9)°, and 113.51(8)°–123.26(8)°, respectively. The Ag–Sb(1) and Ag–Sb(2) distances are 2.7283(14) and 2.7339(18) Å. The Sb(1)–C and Sb(2)–C bonds are 2.119(3)–2.130(3) and 2.112(3)–2.129(3) Å. Note that in the symmetric tri(*para*-tolyl)antimony molecule the CSbC angles are 97.31(5)° and the Sb–C

bonds (2.141(3) Å) are somewhat longer than those in compound I [22].

The nitrate anion is nearly planar, but the ONO angles differ from the theoretical value equal to 120°: one of the angles is 109.6(8)°, and two others are 125.2(4)°. One of the N(1)–O(1) bonds (1.131(6) Å) is somewhat shorter than two other bonds (1.161(4) Å).

Each anion is bound to three cations by intermolecular hydrogen bonds: the N–O⋯H–C_{Ar} distances are 2.46–2.59 Å.

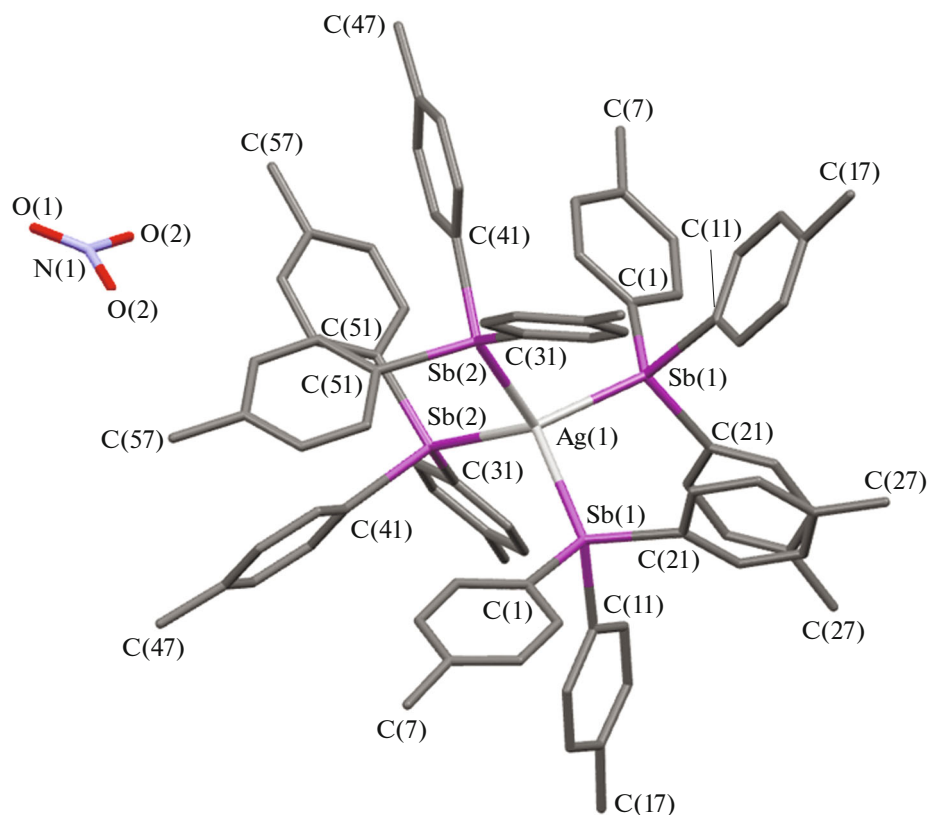


Fig. 1. General view of complex I.

Mixing of homogeneous solutions of tris(5-bromo-2-methoxyphenyl)stibine and silver nitrate in a molar ratio of 3 : 1 affords a product the recrystallization of which from acetonitrile gave crystals representing, according to the XRD data, adduct $[(2\text{-MeO-5-Br-C}_6\text{H}_3)_3\text{SbAg}(\mu_2\text{-NO}_3)(\text{Me}_3\text{CN})]_2 \cdot 2[(2\text{-MeO-5-Br-C}_6\text{H}_3)_3\text{SbAgNO}_3(\text{Me}_3\text{CN})]$ (**II**). It has recently been found that the reaction in the ratio 1 : 1 (mixture of dioxane, methanol, and acetonitrile as the solvent) afforded the product: solvate of the complex with dioxane $[(2\text{-MeO-5-Br-C}_6\text{H}_3)_3\text{SbAg}(\text{NO}_3)(\text{MeCN})] \cdot (\text{C}_4\text{H}_8\text{O}_2)$ [23] in which the nitrate group is bidentate.

The crystal cell of complex **II** contains molecules of two types: monomeric and dimeric. In these molecules the nitrate ligand performs different structural functions: in the monomeric molecule the nitrate group exhibits the bidentate properties by coordinating via two oxygen atoms with one silver atom, whereas in the dimeric molecule this group is bridging and links two silver atoms (Fig. 2). The coordination sphere of the silver atom Ag(2) in the monomeric molecule includes tris(5-bromo-2-methoxyphenyl)stibine, the acetonitrile molecule, which coordinates to the metal atom via the nitrogen atom, and the chelate nitrate group. The bond angles at the Ag(2) atom vary in a range of $51.50(17)^\circ$ – $126.28(18)^\circ$, and the $\text{O}(11)\text{Ag}(2)\text{Sb}(2)$, $\text{N}(4)\text{Ag}(1)\text{O}(11)$, and $\text{N}(4)\text{Ag}(1)$ –

$\text{O}(10)$ angles are close to a theoretical value of 109° ($114.69(13)^\circ$, $107.0(2)^\circ$, $109.2(3)^\circ$). As should be expected, the $\text{O}(10)\text{Ag}(2)\text{O}(11)$ angle is minimal ($51.50(17)^\circ$). The $\text{Ag}(2)\text{–Sb}(2)$ and $\text{Ag}(2)\text{–N}(4)$ distances are 2.6253(13) and 2.244(7) Å, respectively. The $\text{Ag}(2)\text{–O}(10,11)$ bond lengths are 2.398(5) and 2.493(5) Å, indicating the anisobidentate mode of ligand binding. The $\text{O}(10)\text{N}(3)\text{O}(11)$ angle is smaller than the theoretical value ($118.3(6)^\circ$), and two other angles at the N(3) atoms are equal to $120.6(7)^\circ$ and $121.2(6)^\circ$. The $\text{N}(3)\text{–O}(10,11,12)$ bonds are 1.242(7), 1.236(7), and 1.240(7) Å, respectively, and coincide within the experimental error. The Sb(2) atom is tetracoordinate, and the bond angles vary from $95.84(19)^\circ$ to $118.82(14)^\circ$. The $\text{Sb}(2)\text{–C}$ distances are 2.123(5), 2.128(5), and 2.133(5) Å, being shorter than similar bonds in the $(2\text{-MeO-5-Br-C}_6\text{H}_3)_3\text{Sb}$ molecule (2.1569(16), 2.1603(15), and 2.1631(15) Å [24]).

The dimeric molecule is centrosymmetric. The central fragment represents the eight-membered cycle $[\text{Ag}_2\text{O}_4\text{N}_2]$. The environment of the Ag(1) atom consists of the stibine ligand, acetonitrile molecule, and two oxygen atoms of two nitrate groups. The bond angles at the Ag(1) atom change in a range of $83.6(3)^\circ$ – $136.1(3)^\circ$. The $\text{Ag}(1)\text{–Sb}(1)$ bond (2.6493(15) Å) is somewhat longer than the analogous

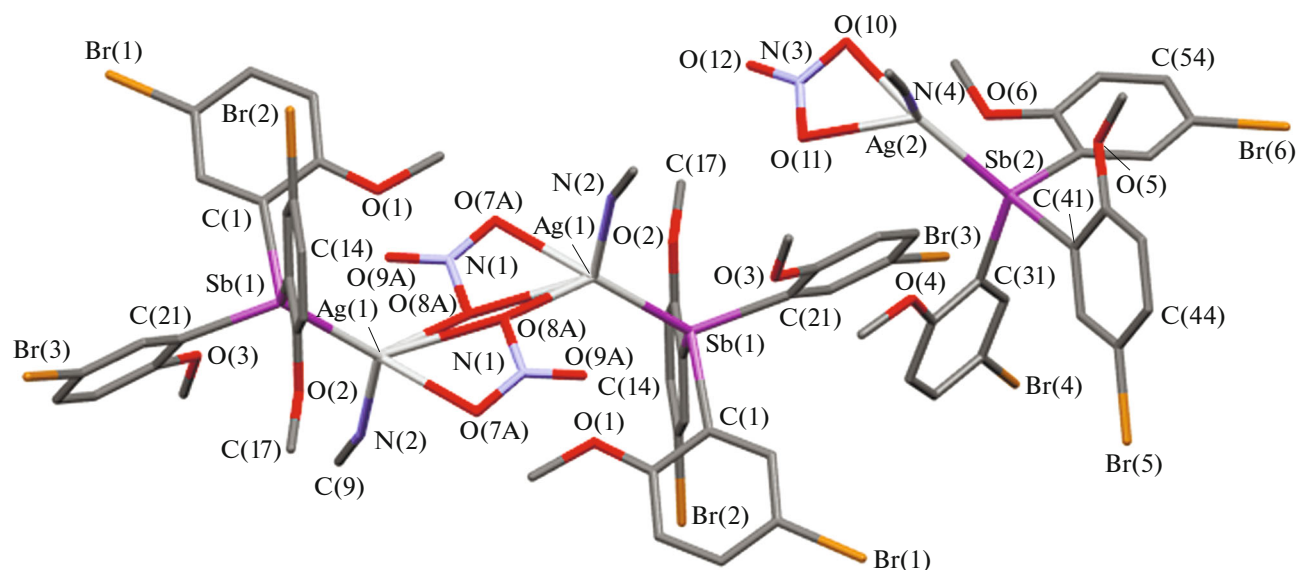


Fig. 2. General view of complex II.

bond in the monomeric molecule. The bridging nitrate ligand nearly symmetrically coordinates to the adjacent silver atoms, since the Ag(1)–O(7A) and Ag(1)–O(8A) distances are close (2.528(14) and 2.507(11) Å) and exceed the Ag(2)–O(10,11) bond lengths. As should be expected, the N(1)–O bonds in the nitrate group are different: the shortest of them (1.189(9) Å) corresponds to the uncoordinated O(9A) oxygen atom, and two other bonds (1.236(7) and 1.242(7) Å) are much longer. The Ag(1)–N(2) distance is equal to 2.326(7) Å.

The angles at the Sb(1) atom range from 96.23(19)° to 124.23(13)°. The Sb(1)–C distances are 2.131(5), 2.136(5), and 2.138(5) Å.

The three-dimensional crystal structure of complex II is formed by numerous intermolecular hydrogen bonds involving the electronegative O and Br atoms.

The synthesis of the complexes bearing Ag–Sb bonds with salicylate and acetylsalicylate anions (Ph₃Sb)₃Ag(SalH) and (Ph₃Sb)₃Ag(Asp) was described [12], and the attempt to replace the nitrate anion by the carboxylate anion met difficulties.

The reaction of nitratotris(triphenylstibine)silver(I) (synthesized using a described procedure [12]) with monochloroacetic and ferrocenecarboxylic acids in the presence of a triethylamine excess in a methanol solution afforded complex [(Ph₃Sb)₃AgOC(O)CH₂Cl]·1/2CH₃OH (III), which was isolated as solvate [(Ph₃Sb)₃AgOC(O)CH₂Cl]·1/2C₄H₈O₂ (IV) after recrystallization from dioxane, and complex [(Ph₃Sb)₃AgOC(O)C₅H₄FeC₅H₅] (V).

According to the XRD data, the silver atoms have a distorted tetrahedral coordination in solvates III and IV (whose geometric parameters differ slightly and, hence, will not be discussed specially) and in complex V (Figs. 3, 4). The bond angles at Ag(1) in III vary from 92.59(15)° to 122.25(13)°, the Sb(1)Ag(1)Sb(3), Sb(1)Ag(1)Sb(2), and Sb(2)Ag(1)Sb(3) angles are 112.09(6)°, 110.56(8)°, and 112.18(7)°, and the O(1)Ag(1)Sb(1), O(1)Ag(1)Sb(3), and O(1)Ag(1)Sb(2) angles are 122.25(13)°, 92.59(15)°, and 105.98(14)°, respectively. The coordination of the silver atom in V differs substantially from an ideal one, since the range of changing angles is rather large: 88.40(9)°–137.33(11)°. The angles Sb(1)Ag(1)Sb(3), Sb(1)Ag(1)Sb(2), and Sb(2)Ag(1)Sb(3) are 109.89(4)°, 111.92(4)°, and 109.48(3)°. The angles O(1)Ag(1)Sb(1), O(1)Ag(1)Sb(2), and O(1)Ag(1)Sb(3) are 97.58(11)°, 88.40(9)°, and 137.33(11)°. The Ag–Sb bond lengths are 2.700(3), 2.716(2), and 2.750(3) Å in III and 2.7406(13), 2.7076(16), and 2.7742(13) Å in V. The angles at the antimony atoms lie in the ranges 98.3(2)°–125.06(18)° (III) and 96.93(17)°–125.84(12)° (V). The Sb–C distances vary in ranges of 2.107(6)–2.142(6) and 2.119(4)–2.144(5) Å in compounds III and V, respectively.

The Ag(1)–O(1) distances are 2.307(4) and 2.308(4) Å in compounds III and V, respectively, and do not differ from a similar distance found in the (Ph₃Sb)₃Ag(SalH) complex [12]. It should be mentioned that in V the carboxylate ligand demonstrates a tendency to the bidentate binding mode, since the Ag(1)–O(2) distance is 2.813(5) Å, whereas the similar distance in III is much longer (3.188(5) Å). Note that in the tetraphenylantimony ferrocenecarboxylate

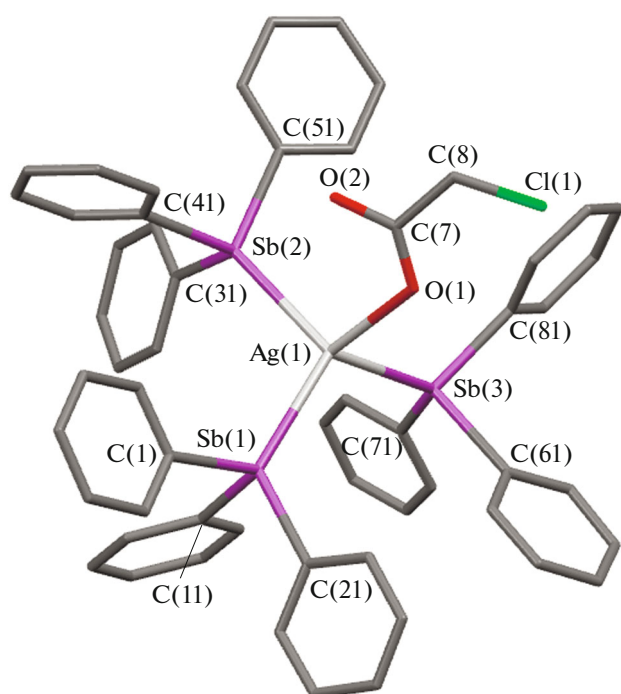


Fig. 3. General view of complex III.

molecule the ligand is bidentate and symmetrically coordinates to the antimony atom by two oxygen atoms (Sb–O 2.333 and 2.338 Å) [25]. In the carboxylate ligands of complexes III and V, the C–O ordi-

nary bonds (1.231(9) and 1.241(5) Å) are longer than the double bonds (1.214(8) and 1.222(5) Å), and the OCO angles are 128.6(7)° and 124.2(4)°.

In the ferrocenyl fragment and the parallel cyclopentadienyl rings exist in the eclipsed conformation, and the angle between the ring and carboxyl group planes is 20.52°.

The crystal structures of compounds III and V are formed due to intermolecular hydrogen bonds of the C–H···O type.

To conclude, the compositions of the complexes with Ag–Sb bonds are not determined only by the molar ratio of silver nitrate and triarylstibine in the reaction mixture. The reaction of tri(*para*-tolyl)antimony with silver nitrate gives the 4 : 1 ionic complex in the cation of which silver is bound to four stibine ligands. On the contrary, silver nitrate with tris(5-bromo-2-methoxyphenyl)stibine forms the 1 : 1 complex regardless of the reagent ratio, and the coordination sphere of this complex is saturated due to the *p*-donor solvent and bidentate nitrate group capable of performing various structural functions. The nitrate group in nitratotris(triphenylstibine)silver(I) in the presence of a triethylamine excess can be substituted by carboxylic acid residues that form Ag–O covalent bonds.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

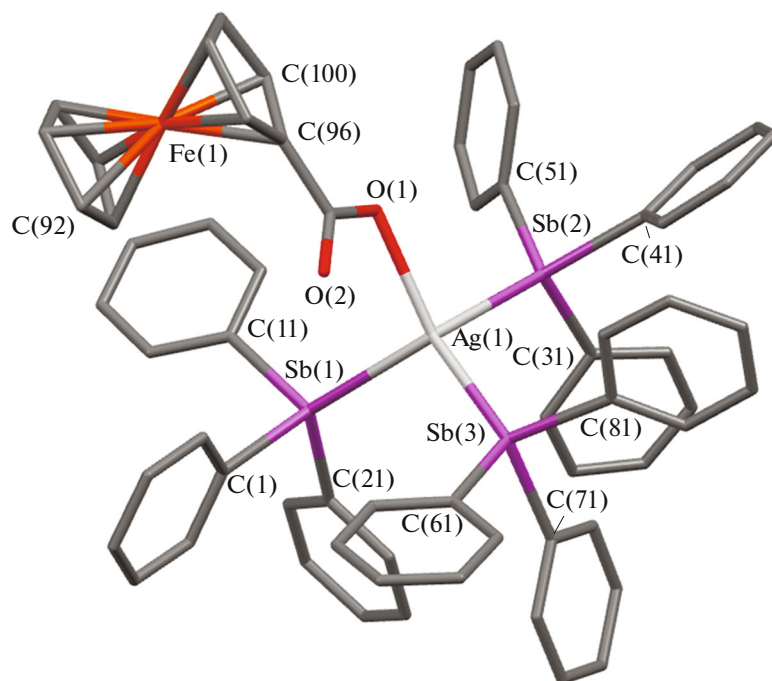


Fig. 4. General view of complex V.

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